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Physical Chemical Studies on Inorganic Coordination Compounds. I. Metallic Complexes of Dimethylsulfoxide. II. Preparation and Spectral Studies of Vanadyl Complexes.

Lawrence Henry Holmes Jr
Louisiana State University and Agricultural & Mechanical College

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I. METALLIC COMPLEXES OF DIMETHYLSULFOXIDE

II. PREPARATION AND SPECTRAL STUDIES OF VANADYL COMPLEXES

A DISSERTATION

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Lawrence Henry Holmes, Jr.
B.S., Southeastern Louisiana College, 1957
August, 1961
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Abstract

The compound dimethylsulfoxide (DMSO), (CH₃)₂SO, has recently been found to be a good solvent for inorganic compounds and therefore it was of interest to study its donor properties toward metal ions. Twenty-four new DMSO-metal complexes were prepared and partially characterized by their infrared spectra and other properties. It was found, unexpectedly, that DMSO is an excellent coordinating agent, competing favorably with water in all the compounds prepared and equally with chloride in several of them. The shift of S=O stretching frequency on coordination (relative to free DMSO) was used to determine the relative degree to which the DMSO coordinates with various metal ions. The infrared spectra also allowed a determination of whether the DMSO was coordinated through the oxygen or through the sulfur. It was found that with palladium(II) and platinum(II) the coordinate bond is through the sulfur and with the other metals studied, Zn, Al, Hg(II), Ni, VO(IV), Mn(II), Co(II), Cr(III), Cd, Ga, In, Fe(II), Fe(III), Cu(II) and Pb(II), it is through the oxygen.

A series of new complexes of the vanadyl ion, VO⁺⁺, were also prepared. It was found, as expected from previous work, that vanadyl can have a coordination number of five or six. In the five-coordinate case the position opposite the vanadyl oxygen is open. Conductivities, infrared, visible, and ultraviolet spectra were obtained for many of these compounds in order to help characterize their structure and bonding. Conductivities were used to indicate if ionic ligands present were coordinated. Since the V=O bond has an infrared stretching
frequency, the shift in this frequency can be used to determine the relative effects of the remaining ligands on the vanadium. This allows the establishment of a ligand series which bears some similarity to the spectrochemical or Fajans-Tsuchida series of ligands. Using Badger's Rule the $V=O$ bond distances for the compounds prepared were calculated from the $V=O$ stretching frequency on the assumption of a Hookian oscillator.

The visible and ultraviolet spectra were found to qualitatively fit some preliminary calculations on energy levels within the vanadyl entity. However, complete explanation of the visible and ultraviolet spectra of these compounds must await more detailed calculations which are being prepared at present.
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Introduction

The compound dimethylsulfoxide (DMSO), \((\text{CH}_3)_2\text{SO}\), has recently become available commercially. It apparently is a very good solvent for many inorganic compounds as well as organic compounds. Therefore it is of some interest to study its donor properties toward metal ions, particularly in view of the fact that it possesses the possibility of coordination either through the sulfur or the oxygen. A survey of the literature shows that little had been done in regard to the donor properties of DMSO until 1959, when this investigation began. Since that time at least ten publications \(^1\text{--}^{10}\) from several different investigating groups have appeared in the literature, reporting the preparation of complex compounds of DMSO and studies of their properties.

Although most of the studies of the donor properties of DMSO seem to have been made within the past several years, the fact that it could act as an electron donor was suggested as early as 1907 by some work of Hoffmann and Ott\(^11\). They found that from a reaction mixture containing toluene, thionyl chloride and ferric chloride, a crystalline compound could be isolated which had the formula \((\text{CH}_3\text{C}_6\text{H}_4)_2\text{SO}\cdot\text{FeCl}_3\). Hydrolysis of the compound yielded tolylsulfoxide. Similar reactions were found to occur for benzylsulfoxide and phenylsulfoxide. In 1956, Addison and Sheldon\(^12\) found that by the oxidation of alkyl sulfides to sulfoxides with \(\text{N}_2\text{O}_4\), addition compounds of the sulfoxide and \(\text{N}_2\text{O}_4\) may be obtained. With DMSO, for example, a 1:1 compound was obtained, \((\text{DMSO}\cdot\text{N}_2\text{O}_4\)). Since no addition compounds of the corresponding sulfones were obtained, the authors assumed that coordination of the sulfoxides to \(\text{N}_2\text{O}_4\) occurred through the electron pair on the sulfur, an electron pair which is not
available in sulfones. Their line of reasoning and their postulation of sulfur coordination is not conclusive in the light of present knowledge. It is now known that sulfones show slight, if any, coordinating tendency toward metals to which sulfoxides bond readily through the oxygen. Therefore it would seem that the fact that sulfones do not coordinate in a particular case is no guarantee that coordination of the corresponding sulfoxide must be through the sulfur and not through the oxygen.

The hydrogen bonding properties of some sulfoxides were studied by Barnard, et. al.,\textsuperscript{13} who found that the characteristic S-O bond stretching frequencies of sulfones and sulfoxides are lowered by hydrogen bonding in the solvents methanol and chloroform. From their studies of the infrared spectra and calculated stretching force constants, they concluded that the S-O bond in sulfoxides and sulfones is nearly completely a covalent double bond with only a small amount of contribution from the hybrid form $R_2S^+ - O^-$ (or $R_2S\equiv O^+$). The structure could be considered as a resonance involving the canonical forms
\[
\begin{align*}
R_2S^+ & - O^- & \rightarrow & R_2S = O & \rightarrow & R_2S\equiv O^+ \\
I & & II & & III
\end{align*}
\]
with form (II) predominating. Both theoretical\textsuperscript{11} and experimental studies\textsuperscript{15,16} have indicated that this view is essentially correct, i.e., that there is at least some double-bond character in the S-O bond of both sulfones and sulfoxides. Barnard and co-workers\textsuperscript{13} say that the hybrid $R_2S^+ - O^-$ contributes more (relatively) in sulfoxides than in sulfones.

Since 1959, the study of compounds of DMSO with metals has greatly
intensified. Some carbonyl compounds of the type $\text{Mo}(\text{CO})_3(\text{DMSO})_3$ and $\left[\text{Fe}(\text{DMSO})_6\right] \left[\text{Fe}_4(\text{CO})_{13}\right]$ have been reported. Also some molecular addition compounds of the type $\text{SbCl}_5\cdot\text{DMSO}$ and $\text{MF}_4\cdot2\text{DMSO}$ (where $M = \text{Ti}$, $\text{Zr}$, $\text{Si}$, $\text{Ge}$, $\text{Sn}$, and $\text{Me}$) have been prepared and the bonding is suggested to be occurring through the oxygen.

In the work by Muetterties, in which he prepared DMSO complexes of the type $\text{MF}_4\cdot2\text{DMSO}$, a whole series of metal tetrafluorides with other organic donors was also studied. He reached the conclusion that the compounds have an octahedral structure and that the organic donor molecules occupy cis positions of the octahedron.

In addition to the above compounds, several researchers have recently reported complexes of DMSO with metal halides, perchlorates, nitrates and sulfates. Various methods have been applied to aid in the elucidation of the structures and properties of the various complexes. The work to be described here represents part of these investigations.

Both S-alkyl and O-alkyl sulfoxonium salts have been prepared. The S-alkyl compound was prepared first by Kuhn and Trischman, but Smith and Weinstein showed that the O-alkyl isomers, although metastable, do usually exist. They isolated a number of both S-alkyl and O-alkyl sulfoxonium salts of DMSO. These compounds are of the type $\left[(\text{CH}_3)_3\text{SO}\right]^+$, where the third methyl group is attached either to the sulfur (S-alkyl) or to the oxygen (O-alkyl).

Recently, Lindqvist and coworkers have reported results concerned with the relative donor strengths of several oxo compounds and the inductive effects of substituents on the donor strength of oxo compounds such as sulfoxides, phosphine oxides, arsine oxides, selenoxides, etc. Thermochemical methods were used to obtain the relative
donor strengths of the oxo compounds, separating the donors into three classes. There is a considerable difference in donor strength among the classes, but within each class the differences are much smaller. They substituted alkoxy groups on the oxo compounds in order to study the inductive effect of the substituents.

In order to thoroughly understand the infrared spectra of DMSO and its complexes, Cotton and Horrocks\textsuperscript{10} have made a complete normal coordinate analysis of DMSO and DMSO-d\textsubscript{6}, the fully deuterated compound. Using this theoretical treatment, they have assigned the bands of the infrared and Raman spectra of the two compounds.

The purpose of this investigation was the preparation and characterization of crystalline compounds of DMSO with various metal salts. Twenty-eight complexes of DMSO representing fifteen metals were prepared and their infrared spectra used as a method of investigating their structure and bonding. The melting points (or explosion or decomposition points, as the case may be) were determined and in a few cases conductivity data were obtained as an aid in deciding between alternative structures.
Experimental

A. Preparation of Compounds

All chemicals used were of at least reagent grade quality and except for the DMSO, which was vacuum distilled, they were used without further purification.

Co(ClO₄)₂·6DMSO and Zn(ClO₄)₂·₄DMSO

The appropriate salt was dissolved in a minimum amount of acetone and a slight excess of DMSO added. On cooling, crystals were obtained which were recrystallized from acetone.

Analysis for Co(ClO₄)₂·6DMSO: Found: ClO₄, 27.30; Co, 7.87;
Calc'd: ClO₄, 27.38; Co, 8.13

Analysis for Zn(ClO₄)₂·₄DMSO: Found: ClO₄, 34.70; Zn, 11.00;
Calc'd: ClO₄, 34.55; Zn, 11.33

Fe(ClO₄)₃·6DMSO and Ga(ClO₄)₃·6DMSO

The appropriate hydrated salt was dissolved in acetone and DMSO added. The solid complex precipitated immediately and is quite insoluble in acetone. The complex was purified by washing it thoroughly several times with hot acetone which removed any excess salt or DMSO.

Analysis for Fe(ClO₄)₃·6DMSO: Found: ClO₄, 36.00; Calc'd: ClO₄, 36.38
Analysis for Ga(ClO₄)₃·6DMSO: Found: ClO₄, 35.40; Calc'd: ClO₄, 35.80

Mn(ClO₄)₂·6DMSO

The hydrated manganese salt was dissolved in acetone and DMSO added.
On cooling in ice, crystals were obtained. Better crystals were obtained if the salt were present in slight excess instead of the DMSO as in other preparations. The complex was recrystallized from acetone containing a small amount of ether to reduce its solubility.

Analysis for $\text{Mn(ClO}_4\text{)}_2 \cdot 6\text{DMSO}$: Found: ClO$_4$, 27.30; Calc'd: ClO$_4$, 27.60

Cu(ClO$_4$)$_2 \cdot 4\text{DMSO}$ and Ni(ClO$_4$)$_2 \cdot 6\text{DMSO}$

The appropriate hydrated salt was dissolved in ethanol, an equal volume of ether added and then DMSO. Crystals were obtained immediately or upon cooling in ice. Both complexes can be recrystallized from acetone.

Analysis for Cu(ClO$_4$)$_2 \cdot 4\text{DMSO}$: Found: ClO$_4$, 31.20; Cu, 10.40; Calc'd: ClO$_4$, 31.62; Cu, 11.05

Analysis for Ni(ClO$_4$)$_2 \cdot 6\text{DMSO}$: Found: ClO$_4$, 27.50; Ni, 8.15; Calc'd: ClO$_4$, 27.40; Ni, 8.32

Pb(ClO$_4$)$_2 \cdot 3\text{DMSO}$

The hydrated lead salt was dissolved in ethanol, an equal volume of ether added, then DMSO. On cooling in ice, crystals were obtained. A slight excess of the salt should be used; the complex apparently solvates readily so an excess of DMSO is undesirable. The product can be recrystallized from acetone.

Analysis for Pb(ClO$_4$)$_2 \cdot 3\text{DMSO}$: Found: ClO$_4$, 31.00; Pb, 31.80; Calc'd: ClO$_4$, 30.86; Pb, 32.10
Fe(ClO₄)₂·6DMSO

The hydrated iron salt was dissolved in acetone and DMSO added. The solution became cloudy at once and upon cooling light green crystals were deposited. On heating the product in acetone, a yellow solid was left undissolved, presumably some iron(III) compound, and the filtered solution yielded very light green crystals on cooling. The product decomposes slowly on standing to a brown colored material, even in the absence of light, moisture and oxygen.

Analysis for Fe(ClO₄)₂·6DMSO:  Found: ClO₄, 30.50; Calc'd: 27.50

The reason for this poor analysis may be related to the instability of the compound.

CoCl₂·3DMSO

(a) The hexahydrated cobalt salt was dissolved in acetone and a slight excess of DMSO added. On cooling blue crystals were obtained which can be recrystallized from acetone.

(b) The hydrated salt was dissolved in hot DMSO and cooling produced blue crystals.

Method (b) was that used by Dr. W.E. Bull (see reference 3)

Analysis for CoCl₂·3DMSO:  Found: Cl, 19.20; Co, 15.90; DMSO, 64.20; C, 19.81; H, 5.31; Calc'd: Cl, 19.50; Co, 16.20; DMSO, 64.30; C, 19.78; H, 4.98

NiCl₂·3DMSO

The hydrated nickel salt was heated in air (over a flame) until a uniform yellow-colored product was obtained. This "dried" NiCl₂ was
added to pure DMSO. The solution undergoes the following color changes: yellow to green to blue. The DMSO solution was heated to boiling and undissolved NiCl₂ removed by filtration. Cooling of the filtrate resulted in formation of blue crystals of the complex. Care is necessary to prevent exposure of the compound to the atmosphere because of its strong hygroscopic tendencies. The product was washed with benzene and dried in vacuo.

This compound was prepared by Dr. W.E. Bull (see reference 3). Analysis for NiCl₂·3DMSO: Found: Cl, 18.00; DMSO, 63.60; C, 18.73; H, 5.30; Calc'd: Cl, 19.50; DMSO, 61.40; C, 19.80; H, 5.90

CuCl₂·2DMSO

(a) Anhydrous CuCl₂ was dissolved in DMSO with the evolution of heat; crystals were obtained upon cooling, filtered and washed with ether, and dried in air.

(b) DMSO was added to a saturated solution of anhydrous CuCl₂ in absolute ethanol, a green solution resulting. A small volume of water was added to this solution and then ether, which caused crystallization of a green product. The crystals were washed with ether after filtration.

Method (b) was that used by Dr. W.E. Bull (see reference 3). Analysis for CuCl₂·2DMSO: Found: Cu, 21.84; Cl, 24.30; DMSO, 53.30; C, 16.42; H, 4.39; Calc'd: Cu, 21.85; Cl, 24.40; DMSO, 53.70; C, 16.52; H, 4.16
**CuCl₂·DMSO**

DMSO was added to a saturated solution of anhydrous CuCl₂ in absolute ethanol, producing a green solution. An excess of 1:1 DMSO should not be used. Addition of ether resulted in the formation of a bright orange crystalline solid. It was isolated by filtration in a dry atmosphere. The orange complex is very hygroscopic, in contrast to the previous complex which is quite stable in air.

This compound was prepared by Dr. W.E. Bull (see reference 3).

Analysis for CuCl₂·DMSO: Found: Cu, 29.5; Cl, 33.6; DMSO, 37.20; C, 11.90; H, 3.15; Calc'd: Cu, 29.9; Cl, 33.40; DMSO, 36.7; C, 11.30; H, 2.85

**CuBr₂·2DMSO**

Addition of DMSO to anhydrous CuBr₂ dissolved in absolute ethanol yielded orange crystals of the complex. These were collected by filtration and washed with absolute ethanol.

This compound was prepared by Dr. W.E. Bull (see reference 3).

Analysis for CuBr₂·2DMSO: Found: Cu, 16.70; Br, 43.50; DMSO, 38.2; Calc'd: Cu, 16.7; Br, 42.2; DMSO, 41.20

The DMSO analysis here includes a correction for oxidation of bromide to bromine as well as oxidation of the DMSO. (See analytical procedures below.)

**HgCl₂·DMSO**

(a) HgCl₂ was dissolved in DMSO at about 60-70°C; cooling produced white crystals which were twice recrystallized from acetone.
(b) A saturated ethereal solution of HgCl₂ was treated with DMSO, white crystals forming immediately. These were washed with ether and air-dried.

Method (b) was that used by Dr. W.E. Bull (see reference 3).

Analysis for HgCl₂·DMSO:  Found: Cl, 19.9; DMSO, 21.20; Calc'd: Cl, 20.3; DMSO, 22.3

FeCl₃·2DMSO

(a) Anhydrous FeCl₃ was dissolved in ether and some solid filtered off. DMSO was then added; the oil obtained could not be solidified by ether or benzene. It was placed in a vacuum for 10 hours, whereupon a yellow solid was obtained which, after crushing, was easily recrystallized from acetone, washed with ether and vacuum-dried.

(b) The hexahydrated chloride was dissolved in hot DMSO. Cooling the solution yielded yellow crystals of the complex; recrystallization can be effected from ethanol. No water bands were observed in the infrared spectrum of this compound.

Method (b) was that used by Dr. W.E. Bull (see reference 3).

Analysis for FeCl₃·2DMSO:  Found: Cl, 35.5; DMSO, 46.7; C, 14.57; H, 3.77; Calc'd: Cl, 35.5; DMSO, 49.1; C, 15.05; H, 3.80

AlCl₃·6DMSO

Anhydrous aluminum chloride dissolved in ether solution was treated dropwise with DMSO. The white complex precipitated immediately and was washed with ether. It is very hygroscopic.

This compound was prepared by Dr. W.E. Bull (see reference 3).
Analysis for $\text{AlCl}_3\cdot6\text{DMSO}$: Found: Cl, 17.7; DMSO, 75.1; Calc'd: Cl, 17.7; DMSO, 77.8

$\text{PdCl}_2\cdot2\text{DMSO}$

Palladium chloride was dissolved in DMSO at an elevated temperature, the excess being filtered off while hot if necessary, and upon cooling, yellow crystals were obtained which are insoluble in acetone, ether and ethanol. Purification was accomplished by refluxing the solid in a 3:1 acetone/ethanol mixture.

Analysis for $\text{PdCl}_2\cdot2\text{DMSO}$: Found: Pd, 31.75; Calc'd: Pd, 31.90

$\text{CdCl}_2\cdot\text{DMSO}$

The dihydrate was dissolved in hot DMSO and the solution cooled. Addition of ether promoted crystallization. The product was filtered and washed with ether.

Analysis for $\text{CdCl}_2\cdot\text{DMSO}$: Found: Cl, 27.4, 26.8; DMSO, 29.8; Calc'd: Cl, 27.2; DMSO, 29.9

$\text{CdBr}_2\cdot\text{DMSO}$

An ethereal solution of $\text{CdBr}_2$ was treated with DMSO. White crystals of the complex formed immediately and were filtered and then washed with ether.

This compound was prepared by Dr. W.E. Bull (see reference 3).

Analysis for $\text{CdBr}_2\cdot\text{DMSO}$: Found: Br, 44.8, 45.3; C, 6.98; H, 2.01; Calc'd: Br, 45.7; C, 6.86; H, 1.73
PbCl$_2$·DMSO and PbBr$_2$·DMSO

The lead halide was dissolved in DMSO at an elevated temperature and the solution was then cooled until crystallization occurred. The filtered crystals were washed with hot acetone and dried in a vacuum.

Analysis for PbCl$_2$·DMSO: Found: Cl, 19.4; Calc'd: Cl, 19.9
Analysis for PbBr$_2$·DMSO: Found: Br, 37.8; Calc'd: Br, 38.6

Cr(NO$_3$)$_3$·6DMSO

Cr(NO$_3$)$_3$·9H$_2$O was dissolved in a minimum amount of water and a large excess of DMSO added. The resulting solution was heated on a hot plate for some time. After a large volume decrease, green crystals began to appear, at which time the solution was cooled and the precipitate filtered, washed with acetone and ether and dried in vacuo.

Analysis for Cr(NO$_3$)$_3$·6DMSO: Found: C, 21.0, 20.90; H, 5.67, 5.60; N, 5.93, 5.71; Calc'd: C, 20.40; H, 5.10; N, 5.95

In(ClO$_4$)$_3$·6DMSO

The hydrated indium perchlorate was dissolved in acetone and DMSO added, yielding a white crystalline precipitate which was cooled in ice, filtered, washed with ether and vacuum dried.

Analysis for In(ClO$_4$)$_3$·6DMSO: Found: C, 17.19, 17.02; H, 4.18, 4.37; Calc'd: C, 18.40; H, 4.60

VO(DMSO)$_5$ (ClO$_4$)$_2$

An aqueous solution of vanadyl perchlorate is added to pure DMSO; the solution becomes hot and subsequently a blue crystalline precipitate
is obtained. The vanadyl perchlorate must be added to the DMSO; addition of DMSO to a vanadyl perchlorate solution did not yield a crystalline product. The crystals are washed well with ether and dried in vacuo.

Analysis for \( \text{VO(DMSO)}_2 (\text{ClO}_4)_2 \):
- Found: \( \text{ClO}_4, 31.0; \ C, 18.55, 18.49; \ H, 4.63, 4.65 \)
- Calc'd: \( \text{ClO}_4, 30.6; \ C, 18.65; \ H, 4.57 \)

\[ \text{VO(DMSO)}_2 \text{SO}_4 \]

Vanadyl sulfate pentahydrate and DMSO are heated to dissolution, then cooled, giving blue crystals. These are washed with acetone and ether, then vacuum dried.

Analysis for \( \text{VO(DMSO)}_3 \text{SO}_4 \):
- Found: \( \text{SO}_4, 25.4; \ C, 18.41, 18.38; \ H, 4.88, 4.78 \)
- Calc'd: \( \text{SO}_4, 25.2; \ C, 18.15; \ H, 4.54 \)

\[ \text{VO(DMSO)}_3 \text{Cl}_2 \]

Syrauy vanadyl chloride is dissolved in DMSO with the liberation of heat; on cooling the solution becomes syrauy and does not yield a precipitate. It is heated to drive off some of the DMSO, then dissolved in alcohol. Acetone is added to this solution at its boiling point and the mixture cooled in ice. A light blue powder is obtained, which can be recrystallized from an alcohol-acetone mixture (50%), filtered, washed with ether and vacuum-dried.

Analysis for \( \text{VO(DMSO)}_3 \text{Cl}_2 \):
- Found: \( \text{Cl}, 19.39; \ C, 19.48, 19.60; \ H, 5.34, 5.44 \)
- Calc'd: \( \text{Cl}, 19.20; \ C, 19.35; \ H, 4.88 \)
(a) Aqueous vanadyl bromide and DMSO are mixed in acetone and ether is used to precipitate a green-blue solid. This can be recrystallized from absolute alcohol, washed with ether and dried in vacuo.

(b) Aqueous vanadyl bromide is dissolved in DMSO and after cooling to melting ice temperature, blue crystals are precipitated. They can be recrystallized from absolute alcohol, washed with ether and vacuum-dried.

Analysis for VO(DMSO)$_2$Br$_2$: Found: Br, 26.50, 26.03; C, 19.21, 19.24; H, 1.80, 5.11; Calc'd: Br, 25.93; C, 19.49; H, 1.87

Co(CIO$_4$)$_2$·6DPSO and Fe(CIO$_4$)$_3$·6DPSO

The appropriate hydrated salt was dissolved in acetone and an acetone solution of DPSO was added. Crystals were obtained immediately or upon cooling in ice. They were washed in ether and vacuum dried.

Analysis for Co(CIO$_4$)$_2$·6DPSO: Found: CIO$_4$, 13.7; Calc'd: CIO$_4$, 13.5?
Analysis for Fe(CIO$_4$)$_3$·6DPSO: Found: CIO$_4$, 20.35; Calc'd: CIO$_4$, 19.1?

It is interesting to note the high molecular weights of these compounds, 1471.4 for the cobalt one and 1567.76 for the iron one.

Complexes of DPSO were also obtained with Mn(II), Zn and Ni(II), but these were not analyzed. Presumably many more could have been obtained but, interestingly, no product was formed with Pd(II) (vide infra).

The stoichiometries of the compounds obtained in this investigation were independent of the absolute amounts of starting materials used.

All the complexes were stored in a dessicator to prevent their
absorbing moisture.

B. Analytical Procedures

Perchlorate analyses were obtained by precipitation with nitron. Halogen analyses were obtained by standard titrimetric procedures using either mercuric nitrate or silver nitrate as titrant. DMSO was determined by dissolving the complex in water and following the procedure of Douglas. An excess of standard KMnO₄ is added which oxidizes the DMSO to the sulfone (in the absence of other reductants). Standard ferrous sulfate is added and the excess ferrous ion titrated with permanganate.

Metal determinations were made by specific gravimetric procedures found in standard texts. Carbon, hydrogen, and nitrogen were determined by a commercial analytical laboratory.

C. Infrared Spectra

Infrared spectra in the 2-15 μ region were obtained with a Perkin-Elmer Model 21 Recording Spectrometer employing NaCl optics. The pure DMSO was run as a film on a NaCl window. Most of the compounds were run as Nujol mulls since KBr pellets generally gave poorer spectrum, presumably owing to partial decomposition of the complex under the conditions of pellet preparation.
Results and Discussion

With DMSO, the possibility exists for coordination to a metal ion through either the oxygen or the sulfur atom. It is of interest then with any complexes formed with metals to determine their structure with regard to which atom is directly attached to the metal atom.

In determining the structure of coordination compounds, several tools may in general be employed. The ultimate and incontestable tool is, of course, X-ray diffraction. Particularly interesting in regard to this type of study would be an investigation of the iron, cobalt and nickel complex halides. Their stoichiometries, which at first glance indicate possible five coordination for these metals, while not impossible, are certainly quite unusual and apparently anomalous. In fact, however, evidence indicates that they are bi-nuclear, i.e., dimeric (see later discussion).

One may also build scale models of the compounds in question and determine steric requirements. Certain configurations or structures may be found to be sterically improbable. However, this is good only for relatively simple, uncomplicated molecules due to the difficulties involved in building good scale models of large molecules. This is especially true if the interatomic distances and bond angles are not known with accuracy.

For transition metal compounds the visible spectra and (in some cases) the magnetic properties may be used to indicate structure. The visible spectra of transition metals is governed by the symmetry and strength of the electrostatic field generated by the ligands, the
so-called crystal field. In the case of DMSO, the crystal field of the oxygen would be expected to be different than that of sulfur. Thus if the spectra of DMSO compounds were compared with similar compounds containing sulfur and oxygen donors, some indication of which atom is coordinated might be gained. However there are few, if any, compounds available for comparison except the aqua ones, so that a useful comparison of this type cannot be made at the present time.

While magnetic measurements usually are of little, if any, help in determining which atom is directly attached to the metal (except in $d^4$-$d^7$ systems when the crystal fields are very different, i.e., one atom has a strong and the other a weak field), the measurements can be helpful sometimes in the determination of structure. Cotton and Francis used this method to advantage in indicating the bi-nuclear structure of the nickel and cobalt complex halides. Magnetic measurements might also be of help in a similar manner for the ferric chloride-DMSO complex.

Another useful tool is the infrared spectra, which is the one used primarily in this investigation. The effect of coordination on the stretching frequency of a particular bond in the ligand can often be used to indicate structure. The vibrational frequency can also be used as a criterion for the type of bonding occurring between the metal and the ligand. For example, the stretching frequency of the S-O bond in complexes of DMSO can be used to indicate which atom (sulfur or oxygen) is coordinating and also the relative electron accepting ability of the metals for the DMSO to which they bond. It is generally agreed$^{14,15,16}$ that the S-O bond in sulfoxides and sulfones possesses at least partial double-bond character, which is presumably due to the
pπ - dπ bonding from the oxygen to the sulfur superimposed upon the ordinary S-O sigma bond. If, then, electrons are drained from oxygen by some process (such as coordination) this pπ - dπ back donation would be decreased, the double-bond character of the S-O bond would be decreased and its stretching frequency would be expected to decrease. If, however, electrons are drained from sulfur (as by coordination) the amount of pπ - dπ back donation would be increased since the sulfur would become relatively more positive; this would increase the double-bond character and shift the S-O stretching vibration to higher frequencies. Thus the direction of the shift of the S-O stretching frequency (relative to free DMSO) can be used as a criterion to differentiate sulfur coordination from oxygen coordination in DMSO. Also, if only the metals are considered to which DMSO bonds through oxygen or sulfur, then the greater the shift the greater the donation of the electrons by DMSO to the metal. Therefore the direction of the shift of the S-O stretching frequency can be used to determine which atom is coordinating and for a given direction the size of the shift is a measure of the electron accepting ability of the metal. All of these shifts are relative to the S-O stretching frequency of free DMSO.

That the foregoing conclusions are borne out experimentally was shown by Cotton and Horrocks. They considered the IR spectra of S-alkyl and O-alkyl sulfoxonium salts (see references 17 and 18 for preparations), using [(CH₃)₃SO]⁺I⁻ as an example of an S-alkyl sulfoxonium and [(CH₃)₃SO]⁺NO₃⁻ as the O-alkyl sulfoxonium salt. The S-alkyl compound had the S-O stretch at 1233 cm⁻¹, which is a considerable increase in frequency over free DMSO (see Table I), a result which agrees
with the above reasoning. The O-alkyl compound has a series of broad bands in the 1050 - 925 cm\(^{-1}\) region, one of which is the S-O stretch; this is also in agreement with the above theory since it is a decrease in frequency relative to free DMSO.

The assignments of the S-O and C-S stretching frequencies for the complexes prepared are given in Table I. The assignments in Table I for the S=O frequency are different from those quoted by Cotton and Horrocks,\(^1\) but are in agreement with those of Drago and coworkers.\(^1\) Since there is some question as to which assignments are correct, Drago and Meek\(^2\) further investigated the problem and reached the conclusion that their assignments are valid. Since their approach seems to be in the main correct, the assignments in Table I are assumed to be correct. The assignment of the C-S stretching frequency was the same in all three investigations.

The assignments of the very strong and broad 1053 cm\(^{-1}\) band in the spectra of pure liquid DMSO (run as a liquid film between NaCl windows) is made on the basis of the literature summary on sulfur-oxygen frequencies by Bellamy.\(^2\) This is in good agreement with Cotton and Horrocks\(^1\) who give the S-O frequency as 1055 cm\(^{-1}\) in chloroform and carbon disulfide solvents and with Drago, et. al.,\(^1\) who finds the S-O frequency to be 1045 cm\(^{-1}\) in nitromethane. The moderately strong band at 697 cm\(^{-1}\) is assigned to the C-S stretching vibration on the basis of the same literature survey as for the S-O.

In the compounds reported here, it is observed (see Table I) that the S-O stretching frequency in the complexes is decreased relative to free DMSO in every case except those of Pd(II) and of Pt(II), where an increase was noted. On the basis of the considerations given
Table I

Infrared Bands of DMSO Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>M.P. °C</th>
<th>S=0(cm⁻¹) max.ₐ</th>
<th>C-S(cm⁻¹) max.ₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. DMSO</td>
<td>clear</td>
<td>---</td>
<td>1053</td>
<td>697</td>
</tr>
<tr>
<td>2. Zn(ClO₄)₂·4DMSO</td>
<td>white</td>
<td>73</td>
<td>1018</td>
<td>717</td>
</tr>
<tr>
<td>3. AlCl₃·6DMSO</td>
<td>white</td>
<td>---</td>
<td>(1009)</td>
<td>(727)</td>
</tr>
<tr>
<td>4. HgCl₂·DMSO</td>
<td>white</td>
<td>125-126</td>
<td>1005(1030)</td>
<td>711(709)</td>
</tr>
<tr>
<td>5. NiCl₂·3DMSO</td>
<td>blue</td>
<td>67</td>
<td>1004(999)</td>
<td>716(714)</td>
</tr>
<tr>
<td>6. VOBr₂·5DMSO</td>
<td>blue</td>
<td>106-168</td>
<td>1003</td>
<td>723</td>
</tr>
<tr>
<td>7. Ni(ClO₄)₂·6DMSO</td>
<td>lt. green</td>
<td>expl.</td>
<td>1002</td>
<td>716</td>
</tr>
<tr>
<td>8. Mn(ClO₄)₂·6DMSO</td>
<td>lt. rose</td>
<td>211-212</td>
<td>1001</td>
<td>716</td>
</tr>
<tr>
<td>9. Co(ClO₄)₂·6DMSO</td>
<td>pink</td>
<td>212-244</td>
<td>1000</td>
<td>717</td>
</tr>
<tr>
<td>10. CoCl₂·3DMSO</td>
<td>blue</td>
<td>97-99</td>
<td>999(1000)</td>
<td>717(713)</td>
</tr>
<tr>
<td>11. Cr(NO₃)₃·6DMSO</td>
<td>green</td>
<td>dec.215-220</td>
<td>997</td>
<td>724</td>
</tr>
<tr>
<td>12. CdBr₂·DMSO</td>
<td>white</td>
<td>173</td>
<td>(996)</td>
<td>(709)</td>
</tr>
<tr>
<td>13. VOCl₂·3DMSO</td>
<td>blue</td>
<td>120-129</td>
<td>1013, 995, 989sh</td>
<td>722</td>
</tr>
<tr>
<td>Compound</td>
<td>Color</td>
<td>M.P. °C</td>
<td>$S=O\text{ (cm}^{-1}\text{)}_{\text{max.}}^a$</td>
<td>$C-S\text{ (cm}^{-1}\text{)}_{\text{max.}}^a$</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-----------------</td>
<td>---------</td>
<td>---------------------------------------------</td>
<td>---------------------------------------------</td>
</tr>
<tr>
<td>Ga(ClO$_4$)$_3$·6DMSO</td>
<td>white</td>
<td>expl.</td>
<td>991 (993)</td>
<td>727 (720)</td>
</tr>
<tr>
<td>CdCl$_2$·DMSO</td>
<td>white</td>
<td>dec.</td>
<td>991 (993)</td>
<td>716 (716)</td>
</tr>
<tr>
<td>VO(ClO$_4$)$_2$·5DMSO</td>
<td>blue</td>
<td>expl. viol. 185</td>
<td>991 (993)</td>
<td>723 (723)</td>
</tr>
<tr>
<td>In(ClO$_4$)$_3$·6DMSO</td>
<td>white</td>
<td>expl. 257</td>
<td>991 (993)</td>
<td>724 (724)</td>
</tr>
<tr>
<td>Fe(ClO$_4$)$_2$·6DMSO</td>
<td>lt. green</td>
<td>expl.</td>
<td>989 (989)</td>
<td>723 (723)</td>
</tr>
<tr>
<td>CuBr$_2$·2DMSO$^b$</td>
<td>orange</td>
<td>dec. 115</td>
<td>(989) (989)</td>
<td>(723) (723)</td>
</tr>
<tr>
<td>Fe(ClO$_4$)$_3$·6DMSO</td>
<td>chartreuse</td>
<td>expl.</td>
<td>988 (988)</td>
<td>723 (723)</td>
</tr>
<tr>
<td>FeCl$_3$·2DMSO</td>
<td>yellow</td>
<td>106-108</td>
<td>988 (981)</td>
<td>722 (720)</td>
</tr>
<tr>
<td>PbCl$_2$·DMSO</td>
<td>white</td>
<td>---</td>
<td>987 (987)</td>
<td>726 (726)</td>
</tr>
<tr>
<td>CuCl$_2$·DMSO</td>
<td>orange</td>
<td>dec. 125</td>
<td>(987) (987)</td>
<td>(726) (726)</td>
</tr>
<tr>
<td>Pb(ClO$_4$)$_2$·3DMSO</td>
<td>white</td>
<td>124-127</td>
<td>986 (986)</td>
<td>710 (710)</td>
</tr>
<tr>
<td>Cu(ClO$_4$)$_2$·4DMSO</td>
<td>aqua</td>
<td>expl.</td>
<td>986 (986)</td>
<td>722 (722)</td>
</tr>
<tr>
<td>CuCl$_2$·2DMSO</td>
<td>emerald green</td>
<td>153-155</td>
<td>980 (987)</td>
<td>728 (726)</td>
</tr>
<tr>
<td>Compound</td>
<td>Color</td>
<td>M.P. °C</td>
<td>S=0(cm⁻¹) (_{\text{max.}}^a)</td>
<td>C-S(cm⁻¹) (_{\text{max.}}^a)</td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
<td>----------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>27. PbBr₂·DMSO</td>
<td>white</td>
<td>---</td>
<td>978</td>
<td>714</td>
</tr>
<tr>
<td>28. PdCl₂·2DMSO</td>
<td>yellow</td>
<td>202-203</td>
<td>1118</td>
<td>732</td>
</tr>
<tr>
<td>29. PtCl₂xDMSO⁵</td>
<td>impure</td>
<td>---</td>
<td>1110(1030-1040)</td>
<td>737(724)</td>
</tr>
</tbody>
</table>

a. The values in parentheses are for KBr pellets, the others are for nujol mulls.
b. These compounds were prepared by Dr. William E. Bull (see reference 3).
c. Not obtained in pure form.
above, it can be concluded that DMSO is bonding through the sulfur to Pd(II) and Pt(II) and through the oxygen in the remainder of the compounds studied.

The C-S stretching frequency for all complexes is shifted toward higher frequencies indicating a strengthening of this bond. The shifts range from 12 to 35 cm\(^{-1}\) in magnitude, the latter being the shift for the Pd(II) compound. This direction of shift is expected since coordination through either oxygen or sulfur would cause a drift of electrons from carbon toward sulfur, thus strengthening this bond. Also coordination through sulfur would be expected to effect the largest shift due to its proximity to the C-S bond.

Of the twenty-eight compounds prepared there are thirteen different stoichiometric types of compounds. These are shown in Table II along with the molecular formulas suggested for them. The first four formulas suggested are certainly reasonable since perchlorate does not coordinate when other ligands are present and nitrate is a weak coordinating agent or at least in all likelihood weaker than DMSO. The vanadyl compounds are all reasonable since they have a total of six groups coordinated to the vanadium(IV) species. The formula for number 12 is substantiated by conductivity data (see Table III). The infrared spectra of the two compounds of number 11 are almost identical; thus the formula for the bromide was suggested as shown, since the perchlorate almost certainly has this molecular formula. A more complete discussion of the vanadyl compounds will be made in Part II.

Formula 5 of Table II is unusual in that it postulates three coordination for lead(II); however, appearances could be deceiving as is discussed later for compounds of stoichiometric type ten.
### Table II

**Suggested Formulas for DMSO Complexes**

<table>
<thead>
<tr>
<th>Stoichiometry</th>
<th>Suggested Formula</th>
<th>Metal*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. M(CIO₄)₃·6DMSO</td>
<td>( \frac{M(DMSO)₆}{(CIO₄)₃} )</td>
<td>Ga &lt; In &lt; Fe(III)</td>
</tr>
<tr>
<td>2. M(NO₃)₃·6DMSO</td>
<td>( \frac{M(DMSO)₆}{(NO₃)₃} )</td>
<td>Cr(III)</td>
</tr>
<tr>
<td>3. M(CIO₄)₂·6DMSO</td>
<td>( \frac{M(DMSO)₆}{(CIO₄)₂} )</td>
<td>Ni &lt; Mn &lt; Co &lt; Fe(II)</td>
</tr>
<tr>
<td>4. M(CIO₄)₂·4DMSO</td>
<td>( \frac{M(DMSO)₄}{(CIO₄)₂} )</td>
<td>Zn</td>
</tr>
<tr>
<td>5. M(CIO₄)₂·3DMSO</td>
<td>( \frac{M(DMSO)₃}{(CIO₄)₂} )</td>
<td>Pb</td>
</tr>
<tr>
<td>6. MCl₃·6DMSO</td>
<td>( \frac{M(DMSO)₆}{Cl₃} )</td>
<td>Al</td>
</tr>
<tr>
<td>7. MCl₃·2DMSO</td>
<td>( \frac{M(DMSO)₄Cl₂}{[FeCl₄]} )</td>
<td>Fe(III)</td>
</tr>
<tr>
<td>8. MCl₂·3DMSO</td>
<td>( \frac{M(DMSO)₆}{MCl₄} )</td>
<td>Ni &lt; Co</td>
</tr>
<tr>
<td>9. MX₂·2DMSO</td>
<td>a. ( \frac{M(DMSO)₂X₂}{MX₄l} )</td>
<td>Pd</td>
</tr>
<tr>
<td>10. MX₂·DMSO</td>
<td>b. ( \frac{M(DMSO)₆}{MX₄l} )</td>
<td>b. ( \frac{M(DMSO)₄Cl₂}{[FeCl₄]} )</td>
</tr>
<tr>
<td>11. VOX₂·5DMSO</td>
<td>( \frac{VO(DMSO)₅}{X₂} )</td>
<td>VO(X=Br) &lt; VO(X=Cl)</td>
</tr>
<tr>
<td>12. VOCl₂·3DMSO</td>
<td>( \frac{VO(DMSO)₃Cl₂}{V(IV)} )</td>
<td>V(IV)</td>
</tr>
<tr>
<td>13. VOSO₄·3DMSO</td>
<td>( \frac{VO(DMSO)₃SO₄}{V(IV)} )</td>
<td>V(IV)</td>
</tr>
</tbody>
</table>

*The order given is that of decreasing S=O stretching frequency, which has tentatively been assumed proportional to the increase in metal-oxygen bond strength.*
The aluminum compound represented by formula 6 is white and salt-like; thus aluminum chloride does not act in this case like a molecular Lewis acid in which case one would expect to obtain a compound of type $\text{AlCl}_3\cdot\text{DMSO}$. It has been found that aluminum nitrate$^{2a}$ reacts similarly. This phenomenon is not completely unexpected since it is known that aluminum prefers oxygen donors in preference to chloride ions, and also that, as stated above, nitrate does not coordinate strongly.

Table III

Conductivities of Some DMSO Complexes in Nitrobenzene

\begin{tabular}{ll}
1. Pd(DMSO)$_2$Cl$_2$ & 0 \\
2. $[\text{Cu(DMSO)}_4][\text{CuCl}_4]$ & 18.5 \\
3. VO(DMSO)$_3$Cl$_2$ & 0 \\
\end{tabular}

A most unusual formula is the one for the ferric chloride-DMSO adduct. The formula suggested in Table II is strong in imagination and weak in facts. However, since nickel and cobalt chlorides (and other Ni(II) and Co(II) salts; see reference 2b) form tetrachloro anions it is not unreasonable that iron might also do so. In fact, the tetra-chloroferrate(III) ion, $\text{FeCl}_4^-$, is well characterized. In addition, a binuclear structure as shown or some polymeric structure is more reasonable than five-coordinated iron. Further investigation is needed for this compound as well as for the compounds mentioned next.
These investigations are apparently going to be carried out in the near future.\textsuperscript{1,2,3,4,5} Conductivity data, visible spectra and magnetic properties would be of much help in elucidating the structure of the ferric chloride complex and other of the complexes given here. X-ray diffraction data would also be of extreme value and interest.

The formulas suggested for compound 8 in Table II are supported by their color and by their infrared spectra. Further evidence is also available to help substantiate the formulas suggested in Table II, principally visible spectral data and magnetic data\textsuperscript{2,5} and also some chemical evidence.\textsuperscript{1} Both of the compounds have the characteristic deep color of the tetrahedrally coordinated anion \([\text{MCl}_4]^2^-(\text{M=Co or Ni})\) rather than the weak pink or light green color of hexacoordinated cobalt(II) or nickel(II). That the cation \([\text{M(DMSO)}_6]^{2^+}\) actually exists for each compound is given credence by the fact that the infrared spectra of these compounds and those of the corresponding hexacoordinated metal perchlorate-DMSO complexes are nearly identical. The color of the cation would, of course, be hidden by the deep color of the tetracoordinated anion.

Since Pd(II) is almost invariably four-coordinate, the formula given in 9(a) is reasonable. The conductivity of this compound (see Table III) substantiates the molecular formula given as the correct one. The analogous copper(II) compound (9b), however, is an electrolyte in nitrobenzene and thus its formula is as given in Table III. This result is in agreement with the data of Drago, et. al.\textsuperscript{1}

Three-coordinate structures are suggested in number 10 for Hg(II), Cd, Pb(II), and Cu(II). More data is needed for these compounds before any definite conclusions can be reached. It is quite possible
that the appearance of the unusual coordination number three is misleading and that in the solid state the actual coordination number is greater than three. A case in point is \( \text{NH}_4 \text{CdCl}_3 \), which was shown by Pauling and Brasseur\(^{25} \) to have a coordination number in the solid state of six. This might also apply to the lead(II) perchlorate-DMSO compound, which according to stoichiometry alone appears to be three-coordinate.

The most unusual feature exhibited by all the compounds prepared in this investigation is that they contain no water, either coordinated or un-coordinated. This is quite striking in view of the fact that almost all of the complexes were prepared using hydrated salts as starting materials. Especially interesting are the iron(III), aluminum and chromium(III) compounds since all three of these species usually exhibit a quite high affinity for water. It appears then that when present in excess, DMSO can compete very favorably with water for coordination sites on many metals. Another striking complex formed is the one with tin(IV) chloride.\(^{2a,8} \) This complex has great stability; it will precipitate from aqueous solutions in preference to hydrolysis of stannic chloride and also it can be sublimed without decomposition at 180°.

It is interesting to note that, except for the aluminum chloride complex, in no case is the chloride ion completely displaced from the coordination sphere of the metal. Apparently chloride can compete equally or possibly better than DMSO for coordination sites, since DMSO is usually present in great excess in the preparation of these compounds. Apparently bromide and iodide do not compete as well because they can be displaced by DMSO.\(^{2b,1} \) The displacement of chloride in the
aluminum chloride compound can be explained by the previously stated fact that aluminum prefers oxygen donors to chloride ions.

The fact that the DMSO complexes can be obtained without water might be of practical significance; if some method could be devised which would remove the DMSO from the metal without decomposing the salt, then these complexes might provide a route to anhydrous metal salts. Oxidation of the sulfoxide to the weakly coordinating sulfone might be a possibility and should certainly be tried with metal complexes in which the metal cannot be easily oxidized.

If one assumes that the decrease in the strength (or double-bond character) of the S-O bond is proportional to the increase in the metal oxygen bond, then the following series for the relative strengths of the metal-oxygen bonds can be deduced.

(a) for divalent chlorides
   \[ \text{Hg} < \text{Ni} < \text{Co} < \text{Cd} < \text{Pb} < \text{Cu} \]

(b) for divalent perchlorates
   \[ \text{Ni} < \text{Mn} < \text{Co} < \text{Fe} < \text{Pb} < \text{Cu} \]

(c) for trivalent ions
   \[ \text{Al} < \text{Ga} < \text{In} < \text{Fe} \]
Diphenylsulfoxide Complexes

Preliminary attempts were made to prepare compounds of diphenyl-
sulfoxide (DPSO), \((\text{C}_6\text{H}_5\text{SO})_2\), analogous to the ones of DMSO. Compounds
with Co(II) and Fe(III) were obtained which gave agreement in analytical
data. Solids were obtained with several other metals but the analyses
were not good or not carried out. However, with some perseverance it
is almost certain that a series of compounds containing DPSO which
are analogous to the DMSO ones could be prepared.

Since the phenyl group is more electron withdrawing than the
methyl group, some differences might be noted in the properties of the
complexes formed. For instance, it is possible that DPSO would be
unable to displace bromide or iodide from the coordination sphere and
thus would not give complexes of the type \(\text{MX}_2\cdot6\text{DPSO (X=Br,I)}\) as does
DMSO.\(^1,2\) Also the steric requirements of DPSO are different than
those of DMSO due to difference in size of the phenyl and methyl
groups; this might affect its coordinating ability.

It was found in the attempt to prepare DPSO compounds that Pd(II)
would not form a complex, while the one with DMSO formed quite easily.
Pd(II) coordinates to DMSO through the sulfur and should act the same
with DPSO. Since no complex was obtained it is possible that the
bulkyl phenyl groups are preventing the formation of a complex. They
can do this in two ways: due to their larger size they probably
hinder coordination to sulfur strictly on steric considerations, and
also since they are more electron withdrawing, the sulfur probably has
a smaller tendency to donate electrons in DPSO than in DMSO. The applications of both these effects apparently prevents the formation of a Pd(II)-DPSO complex.

The IR spectra of some of the solids obtained were run but were fairly complicated. The S=O frequency is not easily identified and so was not recorded.
Introduction

Vanadium is element number twenty-three. It thus has an argon core outside of which it possesses (in the zero oxidation state) three 3d electrons and two hs electrons. Like the other transition metals it would be expected to exhibit multiple oxidation states. It exists commonly as V(II), V(III), V(IV), and V(V), each oxidation state (or hydrated ion) having its own particular color in solution: violet for V(II), green for V(III), blue for V(IV) and yellow for V(V) (in vanadates). Recently a new complex has been reported which apparently has vanadium in the -1 oxidation state. The compound is K$_5$[V(CN)$_5$NO]$_2$·H$_2$O, and it is bright orange and quite deliquescent. The V(0) and V(I) states are also known in a few compounds.

Vanadium in the +1 oxidation state is believed to exist in solution as the cation VO$^{++}$ (vide infra) and compounds of V(IV) containing this cation are called vanadyl or oxovanadium(IV) compounds. In the vanadyl ion, vanadium has one 3d electron in its valency level. Its color is very much like the color of Cu(II) and since Cu(II) has nine 3d electrons with a "positive hole", one might draw an analogy between the electronic transitions of the "positive hole" of Cu(II) and the "negative hole" (electron) of the vanadyl ion.

The vanadyl ion and Cu(II) ion both seem to have tetragonally distorted crystal fields although the signs of the tetragonality are opposite (see below) and also VO$^{++}$ and Cu$^{++}$ are "isoelectronic" (see page 54), so there may be some justification for this analogy.
In solution the vanadyl ion is certain to be solvated and since no work has been reported in nonaqueous media, this solvation will be hydration (solvation by water) in all cases discussed.

Potentiometric studies have shown that the cation present in \( V(IV) \) solutions has a +2 charge rather than a +4 charge as might have been expected. This fact raises a question as to the form of \( V(IV) \) in aqueous solutions. Two obvious forms can be given immediately: the \( V(IV) \) has two hydroxy groups attached or one oxo group attached; either leads to the required +2 charge.

Now the equilibrium

\[
\text{VO}^2+ + \text{H}_2\text{O} \rightleftharpoons 2\text{OH}^-
\]

lies very far to the right and one would not expect that the ion in vanadyl solutions would be the oxovanadium cation, \( \text{VO}^{++} \). Hydrolysis to \( V(\text{OH})_2^+ \) would be expected. This does happen to many metal ions and ions which have in the past been written as oxo ions are not really oxo ions; e.g., \( \text{CrO}_4^{2-} \) is undoubtedly \( \text{Cr}(\text{OH})_4^-(\text{H}_2\text{O})_2^- \) or a polymer. However, the dioxo ions of the +5 and +6 actinides seem to retain their linear oxo form in aqueous solution and the conclusion is that oxygen can be held so tightly that affinity for a proton disappears. This tight bonding is due probably to \( \pi \)-bonding of oxygen to the metal, which should be easy with vanadium since it has several empty 3d orbitals to accept the electrons. One other piece of evidence might be given. An instantaneous equilibrium has been found between \( V(IV) \) and \( V(V) \) in solution, which might suggest that \( V(V) \) exist in acid solution as \( V(\text{OH})_3^+ \). The initial species of vanadyl might be \( V(\text{H}_2\text{O})_4^{+4} \) (after acquiring protons from the acidic medium). However it is difficult to see why the species is
so acidic for the first two protons while the third has a $pK$ between 6 and 5 after which oxide formation soon follows.\textsuperscript{30,31,32} This is a moot point whether the V(IV) ever exists as the above species or not since in any case it will be hydrated.

It has been proposed by Jorgensen that the vanadyl ion in aqueous solution can have one of three possible configurations:\textsuperscript{29}

1. tetrahedral, containing either two hydroxyl or one oxo group
2. trigonal bipyramid, containing either two hydroxyl or one oxo group
3. distorted octahedral (tetragonal), containing two hydroxyl or one oxo group.

(The remaining positions would be occupied by water molecules.)

Jorgensen has concluded on the basis of absorption spectra that the vanadyl ion has a tetragonal field in its complexes. With a tetragonal field there are two possibilities:

1. The field along two of the cartesian axes is stronger than along the third. This happens in the Cu(II) complexes where square planar bonding is observed, the weak field being along the axis perpendicular to the plane containing the copper and the ligands.

2. The field along one cartesian axis is stronger than along the other two. This is the situation believed to be true for the vanadyl complexes since Jorgensen claims that their behavior is opposite to that of Cu(II).

A stronger field along one axis is evidence for the formulation of vanadyl as VO$^{++}$. Oxygen alone might give such a strong field but it would not be expected from two hydroxyl ions. Oxygen can $\pi$-bond rather well in some circumstances\textsuperscript{33} and this could explain the existence of oxo complexes with mainly linear ligand field at the beginning of the transition groups (VO$^{++}$, MoO$_2^{++}$, UO$_2^{++}$) as well.
as the preference for oxygen donors of the light members of a given transition period. Oxygen would \( \pi \)-bond better to those metals which had the necessary empty \( d \) orbitals, i.e., the early members in a transition series.

Jorgensen\(^{29}\) states that the general tendency to prefer oxygen in the beginning of a transition series and nitrogen in the end may have some connection with the number of \( d \) electrons, which are destabilized because they are in antibonding orbitals.

(In the molecular orbital treatment of ligand fields, the \( e_g \) orbitals are antibonding orbitals. Thus if they contain electrons, the metal may form more stable bonds with ligands to which it can "donate" these electrons, thus lowering their energy some if not taking them out of antibonding orbitals completely.)

Evidence for the vanadium-oxygen bond in vanadyl being a double covalent bond in crystals of vanadyl sulfate pentahydrate has been obtained through the use of paramagnetic resonance, polarized light absorption, and x-ray studies.\(^{31h}\) In an attempt to explain paramagnetic data, a crystal field calculation was made assuming the central atom was \( V^{4+} \) surrounded by six equivalent oxygens; an ionic \( V-O \) bond was assumed. This did not agree with the data, which is not greatly surprising in view of the evidence given above supporting the fact that one of the oxygens is very tightly bound to the vanadium and thus would affect it more than the others. On assumption of a central ion of \( VO^{2+} \) containing an oxygen-vanadium double covalent bond, the data was apparently more explainable.
The unit cell for VOSO$_4 \cdot 5$H$_2$O was determined by X-ray diffraction and it was found that each monoclinic cell contained four molecules of the pentahydrate. The spatial group was given as $P2_1/2(C_{2h})$. The structure of the compound is one in which the V(IV) is surrounded by six oxygens: four from water molecules, one from the sulfate, and the vanadyl oxygen. This disagrees with the configuration given by Lundgren, who assigns the five water oxygens to the five other positions.

The V=O distance in VOSO$_4 \cdot 5$H$_2$O is given by reference 34 as 1.67Å. This oxygen is closer than any other so that apparently the vanadyl groups maintain its identity even in the solid state (see also the structure of VO(acac)$_2$, page 50). The sum of the ionic radii of vanadium and oxygen is 2.03Å and the sum of the atomic radii is 1.91Å; 1.67Å is much less than either and is additional evidence for the V-O bond being a multiple one.

Although it seems certain that vanadyl exists as VO$^{++}$ in aqueous solution, it will still associate with water and its hydrolytic properties are therefore of interest. The hydrolysis equation may be written as follows:

$$\text{VO}^{++} + \text{H}_2\text{O} = \text{VOOH}^+ + \text{H}^+$$

Potentiometric and absorptiometric studies indicate that the species present is VO$^{++}$ in acidic solutions where $2.95 \text{M} \geq \text{H}^+ > 0.002 \text{M}$. For $\text{H}^+ < 0.002$, the potentiometric data can be explained by assuming that only two complexes are formed, VOOR$^+$ and (VO)$_2$(OH)$_2$$^{++}$. No evidence of higher polymeric forms were found. It was calculated that only 0.2% of the total vanadium present is in the form VOOR when the average number of hydroxyl ions per vanadyl group,
It is difficult to say what the structures of the hydroxo complexes are in solution. Rossotti\textsuperscript{30} says that they could be of the form \([\text{V(OH)}_3 \cdot n\text{H}_2\text{O}]^+\) and \([\text{V}_2(\text{OH})_6 \cdot n'\text{H}_2\text{O}]^+\) where \(n\) and \(n'\) are + or - integers such that \(n \geq -1\) and \(n' \geq -3\). Thus several complexes of various values of \(n\) and \(n'\) could exist and isomers are possible. The approximate solubility product of vanadyl hydroxide was calculated to be \(10^{-23}\).

Martell and coworkers\textsuperscript{36} have studied the hydrolytic properties of some vanadyl chelates. They have found that vanadyl does not form 1:1 complexes with simple diamines which are stable in aqueous solutions at intermediate and high pH. The analogy between vanadyl and Cu(II) breaks down here in the difference of their behavior toward diamines.

The most stable of the complexes studied were the EDTA and the HEDTA(N-hydroxyethylethlenediaminetriacetic acid) ones.\textsuperscript{36} With ligands containing fewer donor groups such as HEDDA(N,N'-dihydroxyethylethlenediaminetriacetic acid) and HLMDA(N-hydroxyethyliminodiacetic acid), there seemed to be two hydrolysis steps rather close together.\textsuperscript{36} The hydroxo complexes thus formed may contain a hydroxyl ion bound directly to the metal or may contain alkoxide linkages derived from the hydroxyethyl groups of the ligand.

With ligands having only oxygen donors, vanadyl ion forms stable complexes in which protons are dissociated from all groups attached directly to the metal.\textsuperscript{36} This is true of the vanadyl complexes of PDS(disodium pyrocatechol-3,5-disulfonate), DNS(1,8-dihydroxynaphthalene-3,6-disodium sulfonate) and 5-SSA(5-sulfosalicylic acid). Equilibrium constants for these chelates in solution have been determined.\textsuperscript{36}
Riveng\textsuperscript{37} titrated a solution of vanadyl with KCN solution, following the titration potentiometrically. However, he apparently did not take into account hydrolysis. At two cyanides per vanadyl he got an endpoint and a gray precipitate which he called vanadyl cyanide and which dissolved in a large excess of cyanide. He also titrated this solution in the reverse direction using sulfuric acid and interpreted the data as meaning that the species in solution varies from $K_1 \left[ VO(CN)_6 \right]$ to $K_2 \left[ VO(CN)_4 \right]$ to insoluble $VO(CN)_2$, followed by dissolution of the vanadyl cyanide by excess sulfuric acid. He analyzed the precipitate for vanadyl by the permanganate method (see experimental section) and got a molecular weight equal to that of vanadyl cyanide.

Ducret\textsuperscript{32} does not agree with Riveng, and from studies on the titration of vanadyl perchlorate solutions with KOH, Ducret concludes that the precipitate is vanadyl hydroxide and not vanadyl cyanide. This seems reasonable since vanadyl hydroxide is fairly insoluble (\textit{vide supra}) and KCN produces a basic solution.

Ducret\textsuperscript{32} studied the titration of pure vanadyl perchlorate solution with KOH and the titration of vanadyl perchlorate solutions containing varying amounts of HCN. The neutralization curves were the same in both cases. With ten cyanide molecules per molecule of vanadyl, the precipitate occurred only 0.05 pH units lower than with the pure vanadyl perchlorate solution. On the basis of these results Ducret concludes that there are no stable cyanide complexes in acid solution; this is not unreasonable since HCN is only slightly dissociated in aqueous solution.
One thing is not explained by Ducret; that is the molecular weight obtained by Riveng. However, this could be explained if the precipitate were \( VO(OH)_2 \cdot H_2O \) since this would have the same molecular weight as \( VO(CN)_2 \).

It is strange that nothing was done by either of these investigators to try to show whether the precipitated compound contained cyanide. It seems that this would be the most conclusive and convincing experiment that could be performed. More work will have to be done before this question is completely settled.

It has been found\(^{38} \) that if sodium hydroxide is added rapidly to a vanadyl solution, the vanadyl hydroxide formed dissolves in excess base to give a red solution. On standing this solution deposits a black crystalline sodium vanadite, \( Na_2O \cdot 2V_2O_4 \cdot xH_2O \). This illustrates the amphoteric character of vanadyl hydroxide.

Vanadites had been prepared much earlier than this, however\(^{39} \) the compounds \( M_2V_4O_9 \) and \( M'V_4O_9 \), where \( M \) is sodium or ammonium and \( M' \) is barium, were reported in 1903.

A rose-colored compound of formula \( V_2O_4 \cdot 2H_2O \) has been reported\(^{40} \). It will apparently undergo an isomeric change to an olive green compound of the same formula in the absence of water vapor. On heating, both lose a molecule of water around \( 140-150^\circ C \), giving a blue-black material of formula \( V_2O_4 \cdot H_2O \). This can be made to lose the other water molecule in a current of hydrogen at \( 250-300^\circ C \), yielding a black compound of formula \( V_2O_4 \), which is insoluble in water and is only slightly soluble in acids.

On dissolution in sulfuric acid, the rose-colored compound gives an azure blue solution and the green one a green solution. From the
differences in their heats of solution in sulfuric acid and heats of
neutralization by KOH in sulfuric acid (yielding the same end
product), the energy of the transition from rose to green colored
compound was calculated to be about 1.6 kcal per mole.\textsuperscript{40}

Later work was done on the rose-colored compound to determine its
structure and the infrared spectrum was used (Table IV).\textsuperscript{41} It was
concluded from the IR spectrum and the comparison of the spectrum with
that of Cu(OH)\textsubscript{2} that the formula of the rose colored compound is
VO(OH)\textsubscript{2} and not V\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O. The 955 cm\textsuperscript{-1} band was attributed to
vanadium-oxygen stretching vibration, the ones at 3529 cm\textsuperscript{-1} and
3566 cm\textsuperscript{-1} to free OH stretch (symmetrical and antisymmetrical), and
the one at 3276 cm\textsuperscript{-1} was assigned to a hydrogen-bonded OH stretch.

| Infrared Bands of VO(OH)\textsubscript{2} (in cm\textsuperscript{-1}) |
|-----------------|-----------------|-----------------|
| 400m            | 860m            | 3529s           |
| 460s            | 955s            | 3566s           |
| 532m            | 1620w           |                 |
| 607m            | 1675w           |                 |
| 792m            | 3276s           |                 |

It is possible to get to V(IV) either by oxidation of the +2 and/or
+3 states or by reduction of the +5 state. The usual method is to
reduce the +5 state (as V\textsubscript{2}O\textsubscript{5}) in an acid solution of the anion desired,
probably because vanadium pentoxide is readily available and easily
stored and handled; it is not affected by air. An acid solution is
necessary since vanadyl precipitates as the hydroxide if the pH is above about 6.

The methods used to reduce vanadium pentoxide to vanadyl vary depending on the resultant vanadyl compound that is sought. For the bromide, chloride, and sulfate, the simplest and most convenient method is to reduce the vanadium pentoxide with ethyl alcohol in a strong acid solution of the appropriate anion. The excess ethyl alcohol and acetaldehyde (and any acetic acid formed) can be distilled away after reaction, leaving a solution of a pure product (if the vanadium pentoxide is pure). The sulfate can also be prepared using sulfur dioxide as reductant, and the excess sulfur dioxide can be readily removed.

A novel way of preparing pure vanadyl chloride solution is the use of mercury to reduce the vanadium pentoxide in HCl solution, giving vanadyl and Hg(I). The precipitate of Hg₂Cl₂ and excess mercury can be filtered off, leaving a pure vanadyl chloride solution. Cadmium will also reduce vanadium pentoxide to vanadyl in HCl, but this will not give a pure solution due to cadmium contamination. This mercury reduction method has not been tried using HBr but a priori there seems to be no reason why it should not work.

The use of mercury is not necessary when HI is used because the iodide itself will reduce the vanadium pentoxide to vanadyl liberating free iodine. The first investigation of this reaction yielded a nearly black crystalline solid which on air-drying had the formula \( V_2O_3\cdot I_2\cdot 3HI\cdot 10H_2O \) and after vacuum-drying, \( V_2O_3\cdot I_2\cdot HI\cdot H_2O (2VOL_2\cdot 9H_2O) \). It appears that the vanadium is present in the +4\(_I\) state.

It was found that the reduction of vanadium pentoxide by iodide
goes through the intermediate production of V(III), which reacts quickly with V(V). In the presence of air, fixation of oxygen on V(III) causes a greater than expected liberation of iodine.

The reaction of HI with V$_2$O$_5$ is sluggish and the iodine is produced slowly, causing slow dissolution of the V$_2$O$_5$. The reaction rate is approximately proportional to the strength of the acid. On evaporation of the reaction mixture, the iodine apparently will sublime and at dryness, a maroon solid is obtained which was believed to be vanadyl iodide. In attempting to duplicate this work during the course of this investigation, carbon tetrachloride was used to extract the iodine instead of evaporation. After extraction a blue solution is obtained which will decompose on sitting at room temperature for a day or two. The decomposition is slower at ice temperatures. If this solution is evaporated, it turns brown and yields a solid that is apparently the same as the solid formulated as vanadyl iodide. Its color leaves doubt as to its being vanadyl iodide, however, especially since vanadyl iodide appears unstable in solution. Since hydriodic acid apparently will give a V(III) in solution (see above) then it should not be at all surprising that vanadyl iodide is unstable. Since the reduction by HI is slow, one might use mercury reduction if it would work, even though it is not necessary. This would eliminate the great amount of iodine which must be removed. The compound vanadyl iodide deserves more study.

The compound vanadyl fluoride, VOF$_2$, was first reported in 1889. A blue solid designated as VOF$_2$$\cdot$H$_2$O was obtained on evaporation of an HF solution of vanadyl (see also a later discussion of fluoride
complexes). Anhydrous vanadyl fluoride has been prepared\textsuperscript{49} by heating anhydrous vanadyl bromide (whose preparation is also given in reference \textsuperscript{49}) at red heat in a stream of HF. A yellow product is obtained which is insoluble in water, alcohol and ether but somewhat soluble in acetone. Ethyl alcohol in HF solution will not reduce vanadium pentoxide to vanadyl. Whether mercury will or not is unknown, but it should be tried.

The methods above using ethyl alcohol and/or mercury reduction will not work in perchlorate solutions. Ethyl alcohol gives a slight reaction, but a lower temperature has to be used here to prevent reaction between the perchloric acid and the alcohol. Vanadyl perchlorate has been prepared in solution\textsuperscript{50,29} but until now has not been obtained in the solid state. In this investigation three methods were used to get vanadyl perchlorate solutions and from these two methods were devised to get the solid, one method giving an impure solid. These methods are described in the experimental section. Vanadyl perchlorate is unstable at elevated temperatures for periods of several hours, being oxidized to vanadium pentoxide.

Vanadyl nitrate is quite unstable in anything but low concentrations and these decompose with time.\textsuperscript{51,52} It can be prepared by treating a dilute solution of vanadyl chloride quantitatively with silver nitrate.

One method can be used in obtaining almost all of the compounds mentioned above; this is electrolytic reduction of the vanadium pentoxide at constant potential in an acid solution of the desired anion. This is practical for laboratory preparations when the anion concerned
is more difficult to reduce than is vanadium pentoxide. This method was applied to the preparation of solutions of vanadyl perchlorate and vanadyl fluoride and will be discussed in the experimental section.

Aqueous solutions of all the vanadyl halides can be prepared and all except iodide have been obtained in solid form. However only for fluoride and chloride have higher complex vanadyl halides been reported.\textsuperscript{48,53}

With fluoride, compounds containing the ions $\text{VOF}_{4}^{\text{---}}$ and $\text{VOF}_{5}^{\text{---}}$ were prepared quite some time ago. In 1889, the compounds whose stoichiometries are shown in Table V were reported.

| Table V |
| Complex Vanadyl Fluorides |

1. $\text{VOF}_{2} \cdot 3\text{NH}_{4} \text{F}$
2. $\text{VOF}_{2} \cdot 2\text{NH}_{4} \text{F} \cdot n\text{H}_{2} \text{O}$ ($n = 0$ or 1)
3. $\text{VOF}_{2} \cdot 2\text{KF}$
4. $3\text{VOF}_{2} \cdot 7\text{KF}$
5. $4\text{VOF}_{2} \cdot 7\text{NH}_{4} \text{F} \cdot 5\text{H}_{2} \text{O}$
6. $3\text{VOF}_{2} \cdot 8\text{NaF} \cdot 2\text{H}_{2} \text{O}$

The methods of preparation for the compounds listed in Table V are given in reference \textsuperscript{48}. The interesting thing is that these fluoride compounds were in some cases obtained from aqueous solutions in anhydrous form. Compound number one in Table V is moderately soluble
in water and can be recrystallized from water.

Complex vanadyl chlorides have not been obtained from aqueous solutions. Spectral studies of vanadyl perchlorate solutions with varying concentrations of chloride ion indicate that there is little formation of chloro complexes in aqueous solutions. However some complex vanadyl chlorides have been reported of the form $\text{VOCl}_2 \cdot 2\text{RCl} \cdot x\text{H}_2\text{O}$ and $\text{VOCl}_2 \cdot y\text{RCl} \cdot x\text{H}_2\text{O}$, where $R$ is pyridine or chinoline and $x$ is 2, 2.5, 3, and 4.5. These were obtained using $\text{VCl}_4$ in non-aqueous media or very syrupy $\text{VOCl}_2 \cdot x\text{H}_2\text{O}$ in non-aqueous solutions. The compound containing two pyridinium groups is very hygroscopic.

Some complexes of vanadyl chloride with methyl alcohol and pyridine have been prepared in none of them is the chloride displaced completely from the coordination sphere. The compounds reported are listed in Table VI.

<table>
<thead>
<tr>
<th>Compounds of VOCl₂ with Methanol and Pyridine</th>
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<tbody>
<tr>
<td>1. VOCl₂ \cdot 3\text{MeOH}</td>
</tr>
<tr>
<td>2. VOCl₂ \cdot 2\text{C}_5\text{H}_5\text{N} \cdot \text{MeOH}</td>
</tr>
<tr>
<td>3. VOCl₂ \cdot 3\text{C}_5\text{H}_5\text{N} \cdot \text{Et}_2\text{O}</td>
</tr>
<tr>
<td>4. VOCl₂ \cdot 2\text{C}_5\text{H}_5\text{N}</td>
</tr>
<tr>
<td>5. VOCl₂ \cdot 3\text{C}_5\text{H}_5\text{N}</td>
</tr>
</tbody>
</table>
Some oxalate complexes of vanadyl have been prepared\textsuperscript{39} and the stoichiometries of these are given in Table VII along with two thiocyanate complexes prepared by the same investigators. These investigators were not able to obtain solid vanadyl oxalate but they showed that an aqueous solution of oxalic acid and vanadium pentoxide react to give V(IV) and carbon dioxide when heated. They showed that the solution so obtained when an excess of vanadium pentoxide is used is a solution of vanadyl oxalate.

Sulfate complexes of the form $M_2\text{VO(SO}_4)_2$ have been reported\textsuperscript{55} where $M$ is sodium or potassium. Complexes of the form $M_2(\text{VO})_2(SO_4)_3$ have also been prepared\textsuperscript{55} where $M$ is ammonium or potassium. If the ratio of sulfuric acid to vanadyl is greater than 1.5 (mole ratio), then the species present is $H_2(\text{VO})_2(SO_4)_3$ and if it less than 1.5 (mole ratio), then ordinary vanadyl sulfate, $\text{VOSO}_4$, is present.

Table VII

Oxalate Complexes\textsuperscript{39}

1. $2\text{VO}_\text{ox}(\text{NH}_4)_2\text{ox} \cdot 6\text{H}_2\text{O}$
2. $\text{VO}_\text{ox}(\text{NH}_4)_2\text{ox} \cdot 2\text{H}_2\text{O}$
3. $2\text{VO}_\text{ox} \cdot K_2\text{ox} \cdot 4\text{H}_2\text{O}$
4. $2\text{VO}_\text{ox} \cdot \text{Na}_2\text{ox} \cdot 8\cdot 5\text{H}_2\text{O}$

Thiocyanate Complexes\textsuperscript{39}

1. $\text{VO(CNS)}_2 \cdot 2\text{NH}_4\text{NCS} \cdot 5\text{H}_2\text{O}$
2. $\text{VO(NCS)}_2 \cdot 2\text{KNCS} \cdot 5\text{H}_2\text{O}$
Some interesting compounds of vanadyl chloride with diazotized amines have been reported. These are of the form $(RN_2Cl)_2VOCl_2\cdot H_2O$ where $R$ is the phenyl group or the para-methoxy phenyl group. The phenyl diazonium adduct can be obtained anhydrous and is greenish, turning bluish on addition of a molecule of water. It decomposes at $72-79^\circ$. The $p$-methoxyphenyl diazonium adduct is stable at steam bath temperatures but is hygroscopic, changing from green-blue to blue-gray on addition of water.

Some vanadyl chloride compounds were obtained from reactions of VOCl$_3$ with some organic molecules. Vanadium oxytrichloride is quite reactive and it was found that it could react in two ways:

1. Oxidation of the organic molecule followed by addition.
2. Simple addition of the organic molecule.

The mode of reaction depended on the conditions. Alcohols, phenols, diacetylidioxime, and acetylacetone undergo addition while diacetylidoxime and acetylacetone also undergo oxidation in some cases, giving vanadyl compounds. With naphthols, pyrocatechol, and salicylic acid, oxidation-reduction occurs, giving the appropriate vanadyl compounds. Vanadyl complexes with chelating agents have been prepared in the solid form with a number of chelating agents: tartrates, citrates, oxalates, $\beta$-diketones, bis-salicylaldehyde-ethylenediamine, tetraphenylporphines, a variety of Shiff bases and salicylaldimino acids. In nearly all of these compounds one finds a central VO group and four ligand groups attached to it.

Some of the earliest and best characterized of these chelates are the $\beta$-diketones, especially the acetylacetonates. Vanadyl acetylacetionate was first prepared by Morgan and Moss, and later by
Rosenheim and Mong \textsuperscript{55} who prepared other vanadyl chelate compounds also. The latter workers reported it as a monohydrate, but later work\textsuperscript{60} using their preparatory procedure gave an anhydrous compound which, according to molecular weight determinations in benzene, is monomeric.

The reactions of several \( \beta \)-diketone complexes toward addition basic groups has been studied.\textsuperscript{55,60,64} Rosenheim and Mong\textsuperscript{55} obtained ammonia and pyridine adducts of VO(acac)\textsubscript{2} in their studies; this work was extended by Jones\textsuperscript{60}. He found that the oxygen and sulfur in the ether and the thioether linkages, respectively, would not add. Both basicity (electron-pair donating ability) and steric considerations apparently affect the addition reaction. The nitrogen in quinoline, isoquinoline and acridine are about equally basic, but acridine, in which the nitrogen is shielded on both sides by aromatic systems, does not add; quinoline and isoquinoline readily form adducts. Triethylamine and 2,5-dimethylpyridine do not add presumably due to steric factors, while tris(hexamylarsine and tris(phenylphosphine also do not add, probably due to both low basicity and the fact that P and As both derive much of their coordinating tendencies from their ability to accept \( \pi \)-bonding electrons from metals. The vanadyl ion has no such electrons to "back donate".

The thermodynamics of the addition of several bases has also been determined.\textsuperscript{65} Using vapor pressure measurements, the enthalpies, entropies, and free energies of coordination of the bases to the sixth, open position of vanadyl acetylacetonate were determined. The bases used were ammonia, methylamine, ethylamine, isopropylamine, and \textit{t}-butylamine.
Vanadyl acetylacetonate may have one of two structures. It may be polymeric or an example of five-coordinated vanadium(IV). Since, as discussed above, it is monomeric, it must represent a five-coordinated vanadium(IV).

If it is five-coordinate, then the geometrical arrangements most likely are square pyramidal or trigonal bipyramidal. If the trigonal bipyramidal structure is the correct one, then a molecular rearrangement must take place in order to add the sixth group as described above. This is possible but due to the ease of addition and the small change in the properties of the vanadyl acetylacetonate upon addition, Jones believes that the structure is square pyramidal. This structure is also more probable if one allows for the requirement of a stereochemical position for the lone d electron.

In postulating this structure, Jones objected to a four or six-coordinated vanadium as follows: if the vanadium is four-coordinate, then the oxygen of the VO group is not coordinated; this is unreasonable since the oxygen is held more firmly than any of the other groups (in the solid or in solution). For a six-coordinate vanadium, it must be assumed that the vanadyl oxygen is coordinated twice to the vanadium, i.e., it occupies two corners in an octahedral structure. This type of structure would not only be hard to visualize, but it would violate all that is known about structure and bonding between two atoms.

Thus the square pyramidal structure, in which the vanadium and oxygen of the VO group lie on an axis of two-fold symmetry and the oxygen at the apex of the pyramid, is postulated. The other four oxygens of the two acetylacetonates would form a plane perpendicular
to the VO axis. This structure can be described in terms of $d^2sp^2$ or $d^2p^3$ hybridization.

This five coordinate structure for vanadyl acetylacetonate has been substantiated by X-ray diffraction studies. It was found that the molecule has $C_{2v}$ symmetry and that the structure is as shown in Figure 1. The values for the interatomic angles and distances are averages obtained from several runs on all the similar bonds in the molecule. No bond length deviates more than twice the standard deviation so that the molecule has $C_{2v}$ symmetry within the error of the determination. There are no close approaches between molecules. The nearest approach is approximately 3.50Å. The nearest V-V distance is 5.71Å, second nearest 6.96Å; the nearest non-bonding V-O distance is 6.27Å, second nearest 6.72Å.

The preparation of a chelate compound between vanadyl and 8-hydroxyquinoline (oxine) has been reported. Two compounds were obtained from a mixture of vanadyl sulfate and oxine in water; they are shown in Figure 2. The expected inner salt (I) was obtained and the other was assigned the structure shown in (II). I is dark brown (will become green brown on grinding to fine powder) and II is green. Compound II is especially interesting since as shown it contains three-coordinated vanadium. It is likely that the sulfate groups may be coordinated, giving vanadium a coordination number of six. Compound II dissolves in water producing an acid solution. Also prepared was the pyridine adduct of vanadyl oxine, and it was prepared in water solution.

An hydroxy oxine chelate of vanadium(V) was also prepared which was found to exist in isomeric cis and trans forms. Both of
Fig. 1 The Structure of Vanadyl Acetylacetonate
Fig. 2 Proposed Structures for Some Vanadium-Oxine Chelates
\[(\text{HSO}_4)_2\text{H}_2\text{SO}_4\]
these isomers, when reduced in methanol solution, gave the same end product, which was presumably I. The V(V) compound is shown as (III) in Figure 2.

Studies of vanadyl chelate complexes in solution have been made by several investigators. The chelates studied included citrate, oxalate, tartrate, malonate, salicylaldehyde, oxine, acetylacetone, and 1,10-phenanthroline. Compounds with some of these ligands have been obtained in solid form also. The form of the complexes in solution have been determined and range from the two oxalate complexes having formulas $\text{VO(C}_2\text{O}_4)_2^{-}$ and $\text{VO(HC}_2\text{O}_4)_2$, to a complex containing a bridging ligand group (a malonate ion) of formula $[(\text{VO})_2(\text{mal})]^{2+}$. In some cases equilibrium constants for the dissociation of the complexes were obtained. The pH of the solution was used in several cases to determine which complex is present.

The position of the vanadyl ion in the Irving-Williams series has been determined from a study of the relative stabilities of vanadyl and other metal chelates of acetylacetone, salicylaldehyde, and oxalate. It was found that the relative order was independent of the ligand and in the order $\text{VO}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{3+} > \text{Fe}^{3+} > \text{Mn}^{2+}$. This series was obtained using chelates having oxygen donors, however. If other donor atoms were used it is likely that vanadyl would not occupy its extreme position among the other metals investigated here. The position of vanadyl was explained by saying that vanadyl is isoelectron-ic with Cu(II). These authors say that vanadyl ion has 27 electrons as does Cu(II). However, if one counts the electrons in vanadyl, one obtains 29; V(0) has 23 electrons and an oxygen atom has 8, giving 31.
If two are removed to give VO$^{++}$, this leaves 29. It is possible that the two 1g electrons of vanadium were not considered in reference 73, which would give 27; however, if this were done for vanadium(IV) it should also be done for Cu(II). Some resemblance can be drawn between vanadyl and Cu(II) if the 3d electron of V(IV) and the eight electrons of oxygen are considered. This gives a total of nine "valence" electrons for vanadyl which is "isoelectronic" with Cu(II) which has nine 3d electrons. However the use of the 1s electrons of oxygen here is certainly highly questionable. It is more correct to state that VO$^{2+}$ is a d$^9$ "hole" system and Cu(II) is a d$^9$ electron system.

Not much work has been done on infrared studies of vanadyl compounds, probably partly because there has not been a wide variety obtained in the solid form. The IR spectra of some vanadyl tetraphenylporphines (para-substituted) have been reported$^{74}$ as well as those of vanadyl bis-salicylaldehydeethylenediamines$^{75}$ and an EDTA solid complex.$^{76}$ Probably the most significant study to date is the recent one by Barraclough, Lewis and Nyholm.$^{77}$ They examined the stretching frequencies in the infrared of several metal-oxygen multiple bond structures such as TiO$^{++}$, VO$^{++}$, MoO$^{3+}$, CrO$_2$$^{++}$. It was discovered that the metal-oxygen double bond stretching frequency is to be found generally between 900 cm$^{-1}$ and 1100 cm$^{-1}$. This work, together with the data of this investigation, indicate that the assignment of the V-O stretching frequency in references 74-76 are not correct. The V-O frequency is quoted in these references as being greater than 1100 cm$^{-1}$.

Recently, in a study of metal acetylacetonates, the spectra of
vanadyl acetylacetonate was reported from 4000 cm\(^{-1}\) to approximately 300 cm\(^{-1}\). However, the vanadyl spectra was not discussed in any detail.

Visible and ultraviolet absorption spectra of vanadyl complexes have not received a great amount of attention. Use has been made of these spectra in studies of complexes in solution using Job's method, and the absorption spectra of several chelates have been reported along with their preparation.\(^79\),\(^7\)\(_\text{u}\),\(^7\)\(_\text{v}\) Ueno and Martell\(^7\)\(_\text{u}\),\(^7\)\(_\text{v}\) prepared a tetraphenylporphine and several para-substituted derivative chelates of vanadyl, reporting both the IR and the visible spectra. The absorption bands are given in Table VIII.

### Table VIII

Absorption Spectra of Some Vanadyl TPP Chelates

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Molarity</th>
<th>(\lambda_{\text{max}}(\text{m}\mu\text{)})</th>
<th>(\epsilon\left(\times 10^{-3}\right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. TPP(^a)</td>
<td>0.140</td>
<td>548</td>
<td>23.6</td>
</tr>
<tr>
<td></td>
<td>2.8 x 10(^{-4})</td>
<td>424</td>
<td>509</td>
</tr>
<tr>
<td>2. p-methyl TPP</td>
<td>0.099</td>
<td>548</td>
<td>23.3</td>
</tr>
<tr>
<td></td>
<td>1.98 x 10(^{-4})</td>
<td>425</td>
<td>530</td>
</tr>
<tr>
<td>3. p-methoxy TPP</td>
<td>0.117</td>
<td>548</td>
<td>21.5</td>
</tr>
<tr>
<td></td>
<td>1.17 x 10(^{-4})</td>
<td>429</td>
<td>564</td>
</tr>
<tr>
<td>4. p-chloro TPP</td>
<td>0.086</td>
<td>548</td>
<td>26.2</td>
</tr>
<tr>
<td></td>
<td>1.72 x 10(^{-4})</td>
<td>425</td>
<td>564</td>
</tr>
</tbody>
</table>

\(^a\) TPP = tetraphenylporphine

\(^b\) Additional bands at: 590 m\(\mu\) \((\epsilon = 4.6 \times 10^3)\), 512 m\(\mu\) \((\epsilon = 3.6 \times 10^3)\), 481 m\(\mu\) \((\epsilon = 6.3 \times 10^3)\)

The preparation and the visible and ultraviolet spectra of chelates
of vanadyl with bis-salicyaldehyde-ethylenediamine and the corresponding propylenediamine chelate have been reported. The absorption bands of these are given in Table IX along with the bands of one of the chelating agents.

It can be seen from Tables VIII and IX that all of these complexes have charge transfer (very intense) bands in the visible which account for the intense colors of these compounds. These bands also probably obscure any d-d transitions which are expected to occur and so these compounds are of no value in the investigation of the splitting of the d orbitals of vanadyl.

Several investigators have begun discussions of the visible spectra of vanadyl. Jorgensen discusses the spectra of hydrated vanadyl perchlorate and several other complexes; he concludes from these that the splitting of the d levels of the vanadium is due to a tetragonal crystal field with the axis of the strongest field strength along the V-O bond (see page 33). In some cases the splitting may be rhombic due to the lower symmetry of the complexes. In this case there would be four absorption bands in contrast to three as predicted for tetragonal splitting. Other investigators made some preliminary calculations on vanadyl assuming a double covalent bond and a tetragonal distortion of an octahedral configuration; their calculations were used to explain the paramagnetic resonance absorption and polarized light absorption of vanadyl sulfate pentahydrate. Furlani used a different model for his calculations (see discussion on visible spectra) and obtained the result that the number of bands in the visible depends on the symmetry of the complex. This work and that of Jorgensen will be discussed further in the next section.
### Table IX

Absorption Spectra of Vanadyl Diimine Chelates

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. bis-salicylaldehyde-ethylenediimine</td>
<td>methanol</td>
<td>238</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td></td>
<td>277</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>361</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>572</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>chloroform</td>
<td>247</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>281</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>370</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>594</td>
<td>0.14</td>
</tr>
<tr>
<td>2. bis-salicylaldehyde-propylenediimine</td>
<td>methanol</td>
<td>240</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>277</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>360</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>567</td>
<td>0.27</td>
</tr>
<tr>
<td>3. bis-salicylaldehyde-ethylenediimine</td>
<td>methanol</td>
<td>258</td>
<td>48</td>
</tr>
<tr>
<td>(pure)</td>
<td></td>
<td>317</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>405</td>
<td>3</td>
</tr>
</tbody>
</table>

**Structural Formula of Chelating Agents**

![Structural Formula](image)
The purpose of this investigation was to prepare and characterize complexes of vanadyl with several coordinating agents. The infrared, visible and ultraviolet spectra along with conductivity data were used to attempt to elucidate the properties of the compounds prepared. It was also anticipated that certain properties of ligands could be determined from their effect after coordination on the properties of the oxycation species. Although the technique of utilizing the properties of an oxycation as a probe to learn more about the properties of ligands was suggested and initiated by McGlynn and co-workers (utilizing uranyl, $\text{UO}_2^{2+}$), it was felt necessary to extend the ideas to a first transition series metal. Furthermore it was felt that the vanadyl species with a single metal oxygen bond, might prove simpler than the uranyl species which has two metal oxygen bonds.
Experimental

The IR spectra reported here were obtained using a Perkin Elmer Model 21 recording spectrophotometer employing NaCl optics throughout. Samples were generally run as Nujol mulls as these gave better spectra than the KBr pellet technique. The visible and ultraviolet spectra were obtained using a Beckman Model DK-1 spectrophotometer with recorder attachment. Solvents used included acetonitrile and water. Acetonitrile was used as solvent for all the compounds except VO(ClO$_4$)$_2$, VOSO$_4$, Cs$_3$VO(CN)$_5$, and (NH$_4$)$_3$VOF$_5$. The Cs$_3$VO(CN)$_5$ and (NH$_4$)$_3$VOF$_5$ were run in aqueous solutions of KCN and KF, respectively, to reduce hydrolysis. Analyses for carbon, hydrogen and nitrogen were performed by a commercial laboratory; analyses for other elements or groups reported were carried out by methods most convenient to the compounds analyzed. Vanadyl was determined by titration with potassium permanganate in an acid solution. This was not applicable to compounds containing oxidizable groups such as, for example, DMSO. Chloride, bromide, thiocyanate, and cyanide were determined using the Vollhard method and sulfate was analyzed for by the standard gravimetric procedure employing barium ion. Perchlorate was determined gravimetrically by a nitron precipitation.

The vanadyl sulfate used was the pentahydrate, obtained from E.H. Sargent Co. It was used without further purification. Vanadium pentoxide was of reagent grade quality, obtained from J.T. Baker Chemical Co. Vanadyl acetylacetonate was also obtained as a
commercial product from K and K Laboratories. All other chemicals used were of reagent grade quality or better.

The methods of preparation of the compounds studied follows.

**Vanadyl perchlorate**

(a) Vanadyl sulfate is treated with sodium hydroxide and the precipitated vanadyl hydroxide is filtered and washed until free of sodium sulfate. (An excess of sodium hydroxide should be avoided due to the amphotericism exhibited by vanadyl.) The vanadyl hydroxide is then dissolved in perchloric acid to give a solution of vanadyl perchlorate. It is stable over long periods of time at room temperature or below.

(b) Vanadium pentoxide and perchloric acid are placed in a beaker and electrolyzed at a constant potential of 0.55V (vs Ag-AgCl electrode). The complete dissolution may take some time; after this occurs the solution is filtered, yielding a solution of vanadyl perchlorate.

(c) Perchloric acid is added to a solution of vanadyl chloride (see below for preparation of vanadyl chloride) and heated on the steam bath to drive off HCl. The oxidation of vanadyl by perchlorate can be reversed by keeping ethanol in the solution; as long as ethanol and chloride are there, any pentoxide formed is reduced (see below). A blue solution is finally obtained which gives a negative test for chloride with silver nitrate. Filtration improves the purity.

The procedures (a), (b), and (c) above give vanadyl perchlorate in solution; to obtain solid vanadyl perchlorate, two methods can be used:

(1) The solution can be placed under vacuum and evaporated slowly. This procedure gives beautiful crystals of blue vanadyl
perchlorate which should have high purity (no analysis was made since vanadyl perchlorate is very hygroscopic and picks up water on weighing, dissolving itself). Using a liquid nitrogen trap for the water evaporated by the vacuum shortens the time of evaporation.

(2) The solution can be evaporated on a steam bath until solid begins to form and subsequently cooled to get a solid after filtration. If heating continues for more than several hours or overnight, a considerable amount of oxidation to vanadium pentoxide takes place; however if the evaporation process is accelerated, as e.g., by passing a stream of air over the liquid surface, a solid vanadyl perchlorate can be obtained. It is not pure since the blue solid has dark areas and also it cannot be obtained without water adhering to it due to its highly hygroscopic nature. This procedure can give an impure vanadyl perchlorate quickly while the preceding procedure gives a pure product but takes a longer time.

Vanadyl chloride, vanadyl bromide, vanadyl sulfate (in aqueous solution)

These compounds are prepared in aqueous solution by heating a mixture of vanadium pentoxide, ethyl alcohol, water and the appropriate acid until all the vanadium pentoxide has reacted. The general procedure followed is that given for vanadyl sulfate in Inorganic Syntheses, Vol. V, p. 111, in the preparation of vanadyl acetylacetonate. Vanadyl sulfate will precipitate from solution on evaporation; vanadyl chloride gives a syrupy green liquid which cannot be heated to a solid due to hydrolysis. Vanadyl bromide solution, if evaporated to syrupy consistency gets darker and darker as if it is decomposing.

Vanadyl iodide solution

Vanadyl hydroxide is obtained from vanadyl sulfate using ammonia,
excess ammonia being washed from the filtered product. The vanadyl hydroxide is treated with HI and heated on the steam bath for approximately one hour. The iodine produced is removed by extraction with carbon disulfide. When the carbon disulfide layer is no longer colored by shaking, the aqueous layer is a bluish green. It appears to be stable overnight if kept in ice but on standing at room temperature it appears to decompose. If the bluish green solution is heated to dryness on the steam bath, a maroon solid is obtained, apparently a decomposition product and iodine (however, see reference 17 for another opinion).

**Vanadyl fluoride (hydrated)**

(a) Vanadium pentoxide and HF are electrolyzed at constant potential and any excess vanadium pentoxide is filtered off, giving a vanadyl fluoride solution. If this solution is evaporated a blue solid can be obtained which is probably VOF$_2$$\cdot$H$_2$O (see reference 18).

(b) A solution of vanadyl chloride is treated with a solution of AgF in HF (prepared from silver oxide $+$ HF) and the silver chloride removed by filtration. This solution can then be treated as in procedure (a).

$$\left[(C_2H_5)_4N\right]_3\text{VO(CN)}_5$$

**Vanadyl sulfate** is dissolved in a concentrated aqueous solution of sodium cyanide; the initial precipitate of hydroxide dissolves with stirring. The solution, which is dark green, is cooled in ice and filtered to remove any precipitate (such as sodium sulfate). The resulting clear green solution is mixed with an aqueous solution of tetraethylammonium bromide and the mixture is evaporated at room
temperature in a stream of air. After several hours, green crystals separate, which can be filtered, washed with ether, and dried in vacuo. Acetone cannot be used here since it seems to cause the complex to decompose. The compound is insoluble in organic solvents and dissolves with decomposition in water.

Analysis for $\left[(\text{C}_2\text{H}_5)_4\text{N}\right]_3\text{VO(CN)}_5$: Found: VO, 12.25; CN, 22.20; Calc'd: VO, 11.41; CN, 22.20

The analysis for vanadyl was made by precipitating the cyanide with silver nitrate and titrating with permanganate after filtration. This perhaps might explain the high analysis for VO since some AgCN would dissolve as Ag(CN)$_2^-$ and permanganate would oxidize cyanide even in Ag(CN)$_2^-$. 

Vanadyl sulfate is dissolved in concentrated aqueous sodium cyanide solution and a hot solution of tetramethylammonium iodide in water is added. A precipitate forms immediately which is cooled in ice, filtered, washed with alcohol and ether, and vacuum-dried. It is a light green powder.

Analysis for $\left[(\text{CH}_3)_4\text{N}\right]_3\text{VO(CN)}_5$: Found: VO, 16.80; CN, 32.20; Calc'd: VO, 16.00; CN, 31.25

Analysis for vanadyl was made in the same manner as for the previous compound. The high value for VO might be explained in a manner similar to that for the previous compound.

Vanadyl sulfate is dissolved in concentrated aqueous sodium
cyanide as described previously and a solution of cesium chloride is added. An aqua colored precipitate is obtained which is cooled in ice and filtered. It is then washed with a moderately concentrated solution of sodium cyanide to remove any sodium sulfate that may have coprecipitated. The cyanide solution is used for washing because these cyanide complexes are unstable in water but are stable in cyanide solution. The precipitate is then filtered, washed with alcohol and ether and dried in air.

Analysis for Cs$_3$VO(CN)$_5$: Found: VO, 20.70; CN, 21.07; Calc'd: VO, 20.36; CN, 21.80

Vanadyl analysis was done as on the previous two compounds.

Vanadyl sulfate is dissolved in a concentrated aqueous solution of ammonium thiocyanate. An aqueous solution of tetraethylammonium bromide is added, yielding an immediate precipitate. The solution is heated and the precipitate dissolves; on cooling slowly to ice temperatures blue needles are obtained. They are recrystallized from absolute alcohol, filtered, washed with alcohol and ether and vacuum-dried.

Analysis for $[\text{C}_2\text{H}_5\text{N}]_3\text{VO(NCS)}_5$: Found: NCS, 40.70; C, 42.39, 42.01; H, 7.25, 7.27; N, 11.48, 11.50; Calc'd: NCS, 38.90; C, 46.50; H, 8.08; N, 16.05

\[
\begin{align*}
\text{C}/\text{H (found)} &= 5.68 & \text{C}/\text{N (found)} &= 2.92 \\
\text{C}/\text{H (calc'd)} &= 5.75 & \text{C}/\text{N (calc'd)} &= 2.90
\end{align*}
\]

Apparently this compound was not fully decomposed in the analysis for carbon and hydrogen and nitrogen, as the ratios would indicate.
The crystals are well formed and recrystallized nicely. They appear to be quite pure and the analysis for thiocyanate run in this laboratory is satisfactory. There is also a possibility that bromide is present; it would lower C, H, and N percentages but raise the thiocyanate percentage.

\[
\left(\text{CH}_3\right)_4\text{N}_3\text{VO(NCS)}_5
\]

Vanadyl sulfate is dissolved in a concentrated aqueous solution of ammonium thiocyanate and hot solution of tetramethylammonium iodide is added. On cooling a precipitate of light-weight sparkling blue crystals are obtained. These can be filtered, recrystallized from absolute alcohol, washed with alcohol and ether and air-dried. A hot solution of tetraethylammonium iodide is used here as previously because of the lesser solubility of this compound at lower temperatures.

Analysis for \( \left(\text{CH}_3\right)_4\text{N}_3\text{VO(NCS)}_5 \): Found: NCS, 49.50; C, 33.20, 33.53; H, 6.51, 6.66; N, 19.00, 19.21; Calc'd: NCS, 50.01, C, 33.61, H, 6.26; N, 20.50

\( \text{VO(dipy)SO}_4 \)

Vanadyl sulfate is dissolved in warm dimethylformamide (DMF) and then added to a solution of \( \alpha, \alpha'-\text{dipyridyl} \) in DMF. A green solution is obtained at first and upon further addition of vanadyl sulfate, a green precipitate is obtained. The green powder is refluxed in absolute alcohol, filtered, washed with ether and dried in vacuo.

Analysis for \( \text{VO(dipy)SO}_4 \): Found: VO, 21.40; SO_4, 31.00; Calc'd: VO, 21.00; SO_4, 30.10
Vanadyl sulfate is dissolved in DMF and added to o-phenanthroline in DMF. A yellow solid forms immediately which on further addition of vanadyl sulfate dissolves to give a green solution. This solution is heated and near the boiling point of DMF, a greenish (chartreuse) powder is precipitated. It is refluxed in absolute alcohol, filtered, washed with ether, and dried in vacuo. It may be possible to use solvents other than DMF for this preparation and the previous preparation but this was not investigated.

Analysis for VO(o-phen)SO₄: Found: VO, 19.35; SO₄, 28.70; Calc'd: VO, 19.50; SO₄, 28.00

Vanadyl sulfate is dissolved in ethanol (containing enough water to cause dissolution) and added to o-phenanthroline in ethanol; the quantities of each are such that there is a two to one mole ratio of o-phenanthroline to vanadyl sulfate. On mixing the solutions, a gummy precipitate is obtained which dissolves if the solution is heated. Upon cooling, a yellow-brown powder is deposited which is not very soluble in ethanol after drying. It is washed with acetone and ether and dried in vacuo.

Analysis for VO(o-phen)₂SO₄: Found: VO, 11.20; SO₄, 18.20; Calc'd: VO, 12.50; SO₄, 18.35

\[
\left[\left(CH_3\right)_4N\right]_2\left[VOCl_4(C_2H_5OH)\right]
\]

Syrupy vanadyl chloride is mixed with a very concentrated solution
of tetramethylammonium chloride and alcohol is added. On addition of acetone and ether to this solution a blue oil separates. This oil is washed with successive portions of absolute alcohol-acetone mixtures (enough acetone to prevent great solubility of the oil) and then dissolved in a little absolute alcohol. Acetone addition to this gives a greenish blue gummy solid which is washed with several portions of acetone. It can then be recrystallized from absolute alcohol by dissolving it and then evaporation of some of the solvent, followed by cooling. An aqua colored powder is obtained, which is ether-washed and dried in vacuo.

Analysis for \[
\left[\left(\text{CH}_3\right)_4\text{N}\right]_2\text{VOCl}_4\left(C_2\text{H}_5\text{OH}\right)
\] Found: VO, 16.42; Cl, 35.00; Calc'd: VO, 16.62; Cl, 35.25

\[
\left[\text{VO(dipy)}_2\right]\left(\text{ClO}_4\right)_2
\]

Vanadyl perchlorate (aqueous or solid) is dissolved in acetone and then added to \(\alpha',\alpha''\)-dipyridyl in acetone. A greenish-brown solution results which is evaporated to dryness in a vacuum. The solid obtained is washed several times with a 1:1 mixture of acetone-ether and again evaporated to dryness under vacuum at room temperature. When washing the solid with acetone-ether mixtures, an oil may be obtained. The final compound is a greenish-brown powder and is washed with ether and dried in vacuo.

Analysis for \[
\left[\text{VO(dipy)}_2\right]\left(\text{ClO}_4\right)_2
\] Found: VO, 11.24; C, 42.51, H2.46; H, 3.39, 3.38; N, 9.60, 9.45; Calc'd: VO, 11.58; C, 41.60; H, 2.80; N, 9.69
Vanadyl perchlorate in acetone is added to o-phenanthroline in acetone. After stirring for some minutes a green precipitate begins to appear and precipitation is complete after cooling in ice. It is filtered, washed well with ether, then vacuum-dried.

Analysis for $\left[\text{VO(o-phen)}_2\right]\left(\text{ClO}_4\right)_2$: Found: VO, 10.75; C, 1.76, 1.92; H, 2.98, 2.99; N, 8.45, 8.35; Calc'd: VO, 10.70; C, 1.60, 2.58; N, 8.96

Aqueous vanadyl bromide in acetone is added dropwise with stirring to o-phenanthroline in acetone. A chartreuse precipitate appears at once and increases in amount as vanadyl bromide is added. The solution is nearly colorless above the precipitate as long as excess o-phenanthroline is present; if excess vanadyl bromide is added it becomes greenish. The addition is stopped before excess of vanadyl bromide is added. The precipitate is refluxed for some minutes in a 1:1 alcohol-acetone mixture and filtered, washed with ether, and vacuum-dried.

Analysis for $\left[\text{VO(o-phen)}_2\text{Br}\right]\text{Br}\cdot\text{H}_2\text{O}$: Found: Br, 26.40; C, 16.14, 16.16; H, 2.93, 2.93, 2.96; N, 9.10, 8.91; Calc'd: Br, 26.40; C, 18.00; H, 3.00; N, 9.33

A solution of hydrated vanadyl bromide in acetone is added dropwise with stirring to a solution of $\alpha,\alpha'$-dipyridyl in acetone. A green precipitate separates at once, increasing in quantity as vanadyl
bromide is added. The solution remains colorless if an excess of dipyridyl is present, greenish, if not. The precipitate is filtered from the mother liquor and dissolved in a 1:1 alcohol-acetone mixture. On cooling for several hours in ice a dark green powder is obtained, which is washed with ether and vacuum dried.

Analysis for $\left[\text{VO(dipy)_2Br}\right]\cdot\text{H}_2\text{O}$: Found: Br, 28.20; C, 42.38; H, 3.66, 3.56; N, 10.18, 9.98; Calc'd: Br, 28.70; C, 43.20; H, 3.24; N, 10.09

Syrupy vanadyl chloride in acetone is added dropwise with stirring to o-phenanthroline in acetone. A light greenish-yellow precipitate forms at first which is quite fluffy. On further addition of vanadyl chloride the precipitate becomes green and heavier, settling easily to the bottom. When the solution above the precipitate becomes green the addition is stopped and the solution heated at boiling for several minutes. It is refluxed in fresh hot acetone for several minutes, filtered, washed with ether and vacuum-dried. It is a green powder.

Analysis of $\left[\text{VO(o-phen)_2Cl}\right]\cdot\text{Cl}$: Found: VO, 13.98; Cl, 14.08; Calc'd: VO, 13.42; Cl, 14.24

The vanadyl analysis was done with permanganate following precipitation and filtration of silver chloride.

Syrupy vanadyl chloride in acetone is added dropwise with stirring to $\alpha,\alpha'$-dipyridyl in acetone. A green precipitate is obtained
immediately and vanadyl chloride addition is stopped when the solution turns green. The mixture is boiled for several minutes, the solid filtered and refluxed in fresh acetone for several more minutes, then washed with ether and dried in vacuo.

Analysis for $\text{[VO(dipy)$_2$Cl]}$: Found: VO, 15.01, Cl, 11.51; Calc'd: VO, 11.12; Cl, 11.95

$\text{VOC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$

Aqueous vanadyl chloride is mixed with excess oxalic acid and the solution is heated on the steam bath for several hours, water being added as it evaporates. Finally the mixture is evaporated to dryness, leaving a blue solid. This solid is broken up and heated with 95% ethanol. It is filtered hot, yielding a blue powder, which was repeatedly washed with hot 95% ethanol until a negative test for chloride was obtained when dissolved in water. The blue powder was filtered, ether washed and dried in vacuo.

Analysis for $\text{VOC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$: Found: VO, 22.20; C$_2$O$_4$, 58.40; C, 16.28, 16.24; H, 2.05, 1.95; Calc'd: VO, 22.38; C$_2$O$_4$, 58.90; C, 16.05; H, 2.67

The vanadyl and oxalate were analyzed for as follows: A sample was titrated with permanganate and the percent vanadyl calculated using 1/5 the volume of permanganate used and the oxalate percent calculated using 4/5 the volume used.

$\text{VO(dipy)C}_2\text{O}_4$

$\text{VOC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ is dissolved in ethanol (containing enough
water to cause dissolution) and added dropwise with stirring to α, α'-dipyridyl in alcohol. The solution turns yellow immediately, then darkens to green. After addition of several drops with stirring, a green precipitate appears. The vanadyl solution is added until there is about a 2:1 ratio present. It is then heated at the boiling point for several minutes, cooled, washed with ether and acetone and air-dried.

Analysis for VO(dicy)C₂O₄: Found: VO, 20.65; C₂O₄, 27.10; C, 13.98, H, 3.18, 3.15; N, 8.45, 8.51; Calc'd: VO, 21.60; C₂O₄, 28.30 C, 16.10; H, 2.58; N, 9.00

C/N (found) = 5.20
C/N (calc'd) = 5.17

VO(o-phen)C₂O₄

VOC₂O₄·H₂C₂O₄·3H₂O is dissolved in warm DMF and added dropwise with stirring to o-phenanthroline in ethanol. Immediate precipitation of a yellow-green solid occurred and the addition was stopped when the ratio was near 2:1. The mixture was then heated at boiling for several minutes, cooled in ice, washed in acetone and dried in vacuo.

Analysis for VO(o-phen)C₂O₄: Found: VO, 19.10; C₂O₄, 26.40; C, 17.29, 17.13; H, 3.22, 3.33; N, 9.61, 9.19; Calc'd: VO, 20.00; C₂O₄, 26.25; C, 50.20; H, 2.39; N, 8.38

VO(o-phen)F₂

An aqueous solution of vanadyl fluoride (or solid vanadyl fluoride) is dissolved in an ethanol-water mixture (approx. 1:1) and then added dropwise with stirring to o-phenanthroline in ethanol. A green powder
is obtained which, after boiling in the mother liquor for a few minutes, is washed with several portions of 95% alcohol, acetone washed and vacuum-dried.

Analysis for VO(o-phen)F$_2$ : Found: VO, 23.50; C, 61.87; H1.82; H, 3.85; N, 7.3; Calc'd: VO, 23.45; C, 50.60; H, 2.91; N, 10.01

C/N (found) = 5.71
C/N (calc'd) = 5.01

The reasons for the poor agreement on the C, H, and N are not known; the compound appears to be pure and our own analysis for vanadyl is good.

VO(dipy)F$_2$

A solution of vanadyl fluoride in a 1:1 mixture of water and alcohol is added dropwise with stirring to O', O'-dipyridyl in alcohol. The vanadyl fluoride is added until a green solution is obtained, then the green precipitate is filtered after heating to boiling in the mother liquor. It is refluxed in acetone for several minutes, washed with ether and vacuum-dried.

Analysis for VO(dipy)F$_2$ : Found: VO, 26.18; C, 55.21; H5.35; H, 3.63; N, 10.82, 10.71; Calc'd: VO, 25.63; C, 56.00; H, 3.07; N, 10.72

VO(o-phen)$_1$O(NCS)$_2$

This compound was prepared by using a solution of vanadyl thio-
cyanate in alcohol prepared as follows: Syrupy vanadyl chloride is dissolved in absolute alcohol and treated with about three moles of ammonium thio cyanate to each mole of vanadyl chloride. The solution is heated on a hot plate for some time and then cooled for several
hours in ice. The precipitated ammonium chloride is filtered off, leaving vanadyl thiocyanate (and some ammonium thiocyanate) in solution. This is added droewise with stirring to a solution of o-phenanthroline in alcohol. A greenish-yellow, chartreuse precipitate separates immediately and the mixture is heated for several minutes at the boiling point. After cooling in ice, it is filtered, washed with acetone, and dried in vacuo.

Analysis for VO(o-phen)$_{1.5}$(NCS)$_2$: Found: C, 52.24, 52.30; H, 2.73, 2.97; N, 11.68, 11.60; Calc’d: C, 53.00; H, 2.65; N, 11.45

VO(dipy)$_{1.5}$(NCS)$_2$

The solution of vanadyl thiocyanate in alcohol (see previous preparation) is added to α,α'-dipyridyl in alcohol. A light fluffy green precipitate is obtained immediately and when precipitation is complete, the solution is boiled for several minutes. The precipitate becomes heavier and powdery, settling easily to the bottom. It is refluxed in acetone for several minutes, washed with ether and air-dried.

Analysis for VO(dipy)$_{1.5}$(NCS)$_2$: Found: C, 48.61, 48.94; H, 2.70, 2.98; N, 17.18, 17.00; Calc’d: C, 48.99; H, 2.16; N, 16.79

VO(C$_9$H$_6$ON)$_2$, vanadyl oxinate

This compound was prepared by the method given in reference 31. Vanadyl sulfate and oxine are heated in water for an hour or so on a steam bath. The brown vanadyl oxinate separates as a solid and can be filtered off, washed with hot water and dried in vacuo. It is anhydrous.
This compound was prepared by the method of reference 8. Ammonium bifluoride is added to an aqueous solution of vanadyl fluoride and a light blue powder precipitates. It is recrystallized from water and air-dried. It is anhydrous. The same compound can be obtained using vanadyl sulfate in HF to which ammonium bifluoride is added.

Analysis for \((\text{NH}_4)_3\text{VOF}_5\): Found: VO, 30.90, 31.00; Calc'd: VO, 31.00

\(\text{VO(phthalocyanine)}\)

This compound was prepared from \(\text{V}_2\text{O}_5\) and phthalonitrite using the method given in reference 81.

\((\text{NH}_4)_2(\text{VO})_2(\text{SO}_4)_3\)

\(\text{VOSO}_4\cdot 5\text{H}_2\text{O}\) and \((\text{NH}_4)_2\text{SO}_4\) were dissolved in concentrated \(\text{H}_2\text{SO}_4\) containing just enough water to bring about an appreciable dissolution of both chemicals. The solution was filtered and then heated on a hot plate to drive off water. The solution if heated long enough will turn green but if water is added it will return to blue. Upon cooling the green solution to ice temperatures a blue anhydrous powder was obtained. Crystals can also be obtained from the blue solution. These crystals were washed with alcohol and ether and vacuum-dried.

Analysis for \((\text{NH}_4)_2(\text{VO})_2(\text{SO}_4)_3\): Found: VO, 28.58; Calc'd: VO, 26.65

The preparatory procedures for the vanadyl dimethylsulfoxide complexes are given in Part I.
Results and Discussion

1. Conductivity Data

In the preceding section the preparatory procedures and chemical analyses for a series of vanadyl compounds are reported. The infrared spectra of all of these new compounds as well as some previously known ones were obtained; also for many of them the visible and ultraviolet spectra and conductivity data were obtained. The conductivities were obtained in order to ascertain which groups were present within the coordination sphere of the vanadyl ion. To explain, using a specific example, analysis is capable of establishing the stoichiometry of an orthophenanthroline complex as VO(o-phen)\(_2\)Cl\(_2\), but it cannot determine whether one of the chlorides occupies the sixth coordination position or if this position is open and both chlorides are ionic. Conductivity data can differentiate between these two possibilities since in one case there will be a total of three ions and in the other, two ions. Conductivities were obtained in nitrobenzene and are given in Table X.

According to previous data for the conductivities of complexes in nitrobenzene,\(^{82,83,84}\) the range for equivalent conductivities in ohm\(^{-1}\) cm\(^2\) are as follows: for four ions, 70-90; for three ions, 40-60; for two ions, 20-30. The following conclusions can then be drawn from the data of Table X. Compounds VOC(DMSO)\(_2\)(ClO\(_4\))\(_2\), VO(o-phen)\(_2\)(ClO\(_4\))\(_2\), and VO(dipy)\(_2\)(ClO\(_4\))\(_2\), have a total of three ions. This is not unexpected since the perchlorate ion does not usually coordinate. The compounds VO(o-phen)\(_2\)Br\(_2\)*H\(_2\)O, VO(dipy)\(_2\)Br\(_2\)*H\(_2\)O,
Table X.
Equivalent Conductivities of Vanadyl Complexes in Nitrobenzene

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. (Moles/liter x 10^4)</th>
<th>Equiv. Cond. (ohm⁻¹ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. VO(DMSO)₅(ClO₄)₂</td>
<td>10</td>
<td>4.85</td>
</tr>
<tr>
<td>2. VO(DMSO)₃Cl₂</td>
<td>8.6</td>
<td>0</td>
</tr>
<tr>
<td>3. VO(o-phen)₂Br₂·H₂O</td>
<td>2.9</td>
<td>26.2</td>
</tr>
<tr>
<td>4. VO(dipy)₂Br₂·H₂O</td>
<td>3.9</td>
<td>25.2</td>
</tr>
<tr>
<td>5. VO(o-phen)₂Cl₂</td>
<td>3.2</td>
<td>23.7</td>
</tr>
<tr>
<td>6. VO(dipy)₂Cl₂</td>
<td>4.5</td>
<td>18.2</td>
</tr>
<tr>
<td>7. VO(o-phen)₂(ClO₄)₂</td>
<td>2.7</td>
<td>56.5</td>
</tr>
<tr>
<td>8. VO(dipy)₂(ClO₄)₂</td>
<td>3.3</td>
<td>56</td>
</tr>
<tr>
<td>9. VO(o-phen)₁.₅(NCS)₂</td>
<td>2.3ᵃ</td>
<td>10</td>
</tr>
<tr>
<td>10. VO(dipy)₁.₅(NCS)₂</td>
<td>2.5ᵃ</td>
<td>10</td>
</tr>
<tr>
<td>11. VO(oxine)₂</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>12. [C₂H₅N]₃VO(NCS)₅</td>
<td>7.8</td>
<td>69.1</td>
</tr>
<tr>
<td>13. VO(DMSO)₅Br₂</td>
<td>5</td>
<td>18.4</td>
</tr>
<tr>
<td>14. [(CH₃)₄N]₃VO(NCS)₅</td>
<td>8.5</td>
<td>86</td>
</tr>
<tr>
<td>15. VO(o-phen)₂SO₄</td>
<td>2.9</td>
<td>7.6</td>
</tr>
</tbody>
</table>

ᵃ. The concentration here was calculated using the molecular weight of the compounds with the formulas listed.
VO(o-phen)$_2$Cl$_2$, and VO(dipy)$_2$Cl$_2$ are univalent electrolytes, i.e., one uni-positive and one uni-negative ion each. This fact indicates that one of the halides in each case is coordinated to the vanadium and occupies the sixth coordination position. Compounds $\left[(\text{C}_2\text{H}_5)_4\text{N}\right]_3\text{VO}($NCS$)_5$ and $\left[(\text{CH}_3)_4\text{N}\right]_3\text{VO}($NCS$)_5$ have a total of four ions as expected. Vanadyl oxinate and VO(DMSO)$_3$Cl$_2$ are non-electrolytes, not unexpected with either compound. Compound VO(o-phen)$_2$SO$_4$ has a conductivity which is too low for an electrolyte with a total of two ions of its type and yet is not zero as it should be for a non-electrolyte. The explanation for this is not known. However, it could possibly be due to partial ionization of the complex or to strong ion-pair formation, which is not unknown with sulfate ions. Since AC current with a frequency of 1000 cps was used for all conductivity determinations it is unlikely that the anomaly is due to capacitance effects, since the molecules of the complex could not possibly align and realign themselves this rapidly. The conductivity of the compound VO(DMSO)$_5$Br$_2$ is not in agreement with the structure which is expected from its stoichiometry. The conductivity indicates a total of two ions when it is expected to have three. It is possible that in nitrobenzene solution (and perhaps in the solid state) one bromide is coordinated, but then there is apparently no reason only one bromide is coordinated and not the other also. The infrared spectra of this compound is similar to that of VO(DMSO)$_5$(ClO$_4$)$_2$, but the region of V-O stretch is not well defined and the assignment for the bromide compound is not completely certain. (see IR data). Its visible spectra is different than that of the perchlorate compound in that the first visible band
of VO(DMSO)$_5$Br$_2$ occurs at higher frequencies than that of the former compound (see absorption spectra data). Further study is indicated for this compound as well as for compounds VO(o-phen)$_{1.5}$(NCS)$_2$ and VO(dipy)$_{1.5}$(NCS)$_2$. The analytical data for these last compounds are good for the stoichiometries presented in Table X. However, the molecular structure of these compounds is a complete mystery on the basis of data now available. The compounds could be equimolar mixtures of VO(AA)$_2$(NCS)$_2$ and VO(AA)(NCS)$_2$ (where AA represents o-phenanthroline or o',o''-dipyridyl) or they could have a dimeric (or polymeric) structure. The conductivity data can be reconciled with either the mixture hypothesis or with a dimeric structure. Certainly if an equimolar mixture is present, the conductivity would be expected to lie about midway between the value of zero for a non-electrolyte and the value for a uni-univalent electrolyte (assuming one thiocyanate is coordinated in VO(AA)$_2$(NCS)$_2$). However, why one should obtain an equimolar mixture is not clear; a mixture is not unreasonable but an equimolar one, especially in the case of both compounds, seems improbable.

If the molecular formulas were dimeric with stoichiometries (VO)$_2$(AA)$_3$(NCS)$_4$, and the structure such that it was a uni-univalent electrolyte, then the conductivity data would also be satisfied. A formulation that would fit these requirements is \[ \text{VO(AA)$_2$NCS$\cdot$VO(AA)(NCS)$_3$.} \] This formula, while purely speculative, is not unreasonable since the starting material was in the form of VO(NCS)$_5$; the chelating agent undoubtedly adds stepwise and the anion postulated above probably exists in the solution. Further study is thus indicated for these two compounds.
The conductivities of the remainder of the compounds reported in the experimental section (those not shown in Table X) were not determined, for the most part due to their almost complete insolubility in nitrobenzene (and other suitable solvents) and also because their stoichiometries usually indicated their structure. The conductivity of VOSO$_4$·5H$_2$O would be of value and interest, to determine if the sulfate is coordinated, but it is totally insoluble in solvents suitable for conductivity measurements, i.e., nitrobenzene, nitromethane, nitroethane, acetonitrile, etc.

2. Infrared Data

Vanadium(IV) has been shown to exist as the VO$^{4+}$ ion both in solution and the solid state (see introduction). Furthermore, it has been suggested that the stretching frequency of the V-O bond lies in the infrared between 1100 and 900 cm$^{-1}$, depending on its environment.$^{77}$ The V-O bond is presumed to be a double covalent bond$^{29,31}$ consisting of pπ-dπ donation of electrons by the oxygen to the vanadium superimposed upon the sigma bond between the vanadium and oxygen. The amount of pπ-dπ donation depends both on the tendency of oxygen to donate and the tendency of vanadium to accept electrons. Coordination of ligands to vanadium should not greatly affect the donating tendency of oxygen but should change the acceptor properties of the vanadium. This change will affect the degree of double bonding between the oxygen and the vanadium. The degree of double bonding will affect the strength of the vanadium-oxygen bond which will be reflected in the stretching frequency for this bond. Thus any change in the acceptor properties of vanadium
should be detectable in the change of the vanadium-oxygen frequency. Since coordination involves donation of electrons from the ligand to the d orbitals of the metal atom, it will tend to increase the electron density around the vanadium. Increasing this electron density should act to decrease the amount of p→d donation from the oxygen to vanadium, decreasing the amount of double bond character in the V-O bond and thus, by the above reasoning, lead to a decrease in the stretching frequency of the V-O bond. The greater the donation of electrons to vanadium, the greater the decrease expected in the V-O stretching frequency. The V-O stretching frequency can then be used to determine the relative electron donating tendencies (coordinating abilities) of ligands toward vanadyl. This discussion has considered only sigma-bond formation as the mode of bond formation from ligand to metal; if any π-bond formation occurs, the effect on the V-O frequency should be more pronounced than for pure sigma-bonded ligands. That oxygen can π-bond is shown by the existence of the vanadyl ion. Another π-bonding ligand which until recently was believed not to be capable of π-bond formation is fluoride. The π-bonding of oxygen and fluoride may be attributed to the high electron density around these atoms and the stabilizing effect of decreasing this electron density by delocalization of electrons away from them, i.e., π-bonding. Cyanide can also form π-bonds due to the electrons available in the carbon-nitrogen triple bond. It is possible also to have metal to ligand π-bonding but this should not have much significance here since vanadium(IV) has only one d electron outside a closed-shell.

An analogous infrared study has already been made on complexes of
the uranyl ion, \( \text{UO}_2^{++} \), in which case it was found\(^{85,86}\) that the symmetric and antisymmetric infrared stretching frequencies of the uranyl entity could be used as a criterion to set up a ligand series which shows a striking parallelism to the spectrochemical series.

The vanadyl compounds prepared in this investigation (plus a few obtained from the literature cited) are given with their V-O stretching frequencies in Table XI. From this table it can be seen that there are a variety of compound types obtained with vanadyl. For example, V\(_2\)O\(_7\), V\(_2\)O\(_4\)b\(_2\), V\(_2\)O\(_3\)b\(_2\), V\(_2\)(AA)\(_3\), V\(_2\)(AA)\(_2\), V\(_2\)(AA)(BB), V\(_2\)(AB)\(_2\), V\(_2\)(ABBA), V\(_2\)(AAAA) (where a and b are unidentate ligands and AA, BB, etc., are polydentate symmetrical or unsymmetrical ligands) are all represented by at least one compound. Interpretation under these circumstances is more difficult than for uranyl\(^{85,86}\) for which uniformity of complex type was obtained for at least six compounds. However, a few of the compound types have several members so that some conclusions can be reached concerning the relative effects of ligands on the vanadium-oxygen vibration. If compounds fourteen, seventeen and eighteen (o-phen complexes) are compared with compounds twenty-two, thirty-four and thirty-five (the analogous dipy complexes), it is observed that in each case the V-O vibration for the dipyridyl compounds occurs at a lower frequency than for o-phenanthroline complexes. This indicates more effective coordination (electron donation) by dipyridyl than by o-phenanthroline. Dipyridyl differs from o-phenanthroline in that it has much greater freedom of movement than o-phenanthroline in the direction of the arrows shown in Figure 3. It also has other directions in which it has greater freedom of motion than o-phenanthroline, e.g., dipyridyl could have the planes of the pyridyl rings at right angles
### Table XI

Infrared Stretching Frequencies for the V-O Bond in Vanadyl Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>V=O stretch (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. VOSO(_4) \cdot 5H(_2)O</td>
<td>1017s, 1003s, 976(sh)</td>
</tr>
<tr>
<td>2. VO(p-OCH(_3)-TPP)</td>
<td>(1020, 1003, 987)(^{a, f})</td>
</tr>
<tr>
<td>3. VO(phthal)</td>
<td>(1015)(^{b})</td>
</tr>
<tr>
<td>4. VO(p-cl-TPP)</td>
<td>1004s</td>
</tr>
<tr>
<td>5. VO(TPP)</td>
<td>(1002)(^{b})</td>
</tr>
<tr>
<td>6. VO(p-CH(_3)-TPP)</td>
<td>(1001)(^{b})</td>
</tr>
<tr>
<td>7. ([\text{C}_2\text{H}_5\text{N}]_3\text{VO(NCS)}_5)</td>
<td>997s, 979w-m</td>
</tr>
<tr>
<td>8. VO(acac)(_2)</td>
<td>996s, (995)(^{a}) (1000)(^{e})</td>
</tr>
<tr>
<td>9. VOBr(_2) \cdot xH(_2)O</td>
<td>996s</td>
</tr>
<tr>
<td>10. VO(ClO(_4))(_2) \cdot xH(_2)O</td>
<td>995s</td>
</tr>
<tr>
<td>11. VOCl(_2) \cdot xH(_2)O</td>
<td>990s</td>
</tr>
<tr>
<td>12. ([\text{VO(o-phen)}(\text{ox})])</td>
<td>989s</td>
</tr>
<tr>
<td>13. ([\text{CH}_3\text{N}]_3\text{VO(NCS)}_5)</td>
<td>987s, 979s</td>
</tr>
<tr>
<td>14. ([\text{VO(o-phen)}_2])(\text{ClO}_4)_2</td>
<td>987s</td>
</tr>
<tr>
<td>15. VOCl(_2) \cdot xH(_2)O</td>
<td>98ls</td>
</tr>
<tr>
<td>16. ([\text{CH}_3\text{N}]_2[\text{VOCl}_4(\text{C}_2\text{H}_5\text{OH})])</td>
<td>982s, 969s, 958s(sh)</td>
</tr>
<tr>
<td>17. ([\text{VO(o-phen)}_2\text{Br}]\text{Br\cdot H}_2\text{O})</td>
<td>98ls(sh), 981s</td>
</tr>
<tr>
<td>18. ([\text{VO(o-phen)}_2\text{Cl}]\text{Cl})</td>
<td>982s, 960m</td>
</tr>
<tr>
<td>19. VO(en-bis-sal)</td>
<td>(980)(^{c})</td>
</tr>
<tr>
<td>20. VO(oxine)_2</td>
<td>980s</td>
</tr>
<tr>
<td>21. ([\text{VO(dipy)SO}_4])</td>
<td>979s</td>
</tr>
<tr>
<td>Compound</td>
<td>V=O stretch (cm(^{-1}))</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>22. ([\text{VO(dipy)}_2]_2(\text{ClO}_4)_2)</td>
<td>979s</td>
</tr>
<tr>
<td>23. ([\text{VO(dipy)}(\text{ox})])</td>
<td>979s</td>
</tr>
<tr>
<td>24. ([\text{VO(o-phen)}\text{SO}_4])</td>
<td>978s</td>
</tr>
<tr>
<td>25. ([\text{VO(dipy)}_1.5(\text{NCS})_2])</td>
<td>977s, 967s</td>
</tr>
<tr>
<td>26. ((\text{NH}_4)_2\text{VO(mal)}_2\cdot 4\text{H}_2\text{O})</td>
<td>(977, 967)(^a)</td>
</tr>
<tr>
<td>27. ((\text{NH}_4)_2\text{VO(ox)}_2\cdot 2\text{H}_2\text{O})</td>
<td>(876)(^a)</td>
</tr>
<tr>
<td>28. ([\text{VO(o-phen)}_1.5(\text{NCS})_2])</td>
<td>973s, 961m (sh)</td>
</tr>
<tr>
<td>29. ([\text{VO}_2\text{C}_2\text{O}_4\cdot H_2\text{C}_2\text{O}_4\cdot 3\text{H}_2\text{O}]</td>
<td>973vs, 987s (sh)</td>
</tr>
<tr>
<td>30. ([\text{VO(o-phen)}_2\text{SO}_4])</td>
<td>972s, 960m (sh)</td>
</tr>
<tr>
<td>31. ([\text{Na}_2\text{VO(EDTA)}\cdot 5\text{H}_2\text{O}]</td>
<td>(970)(^d)</td>
</tr>
<tr>
<td>32. ([\text{VO(o-phen)}\text{F}_2])</td>
<td>968s, 964s</td>
</tr>
<tr>
<td>33. ([\text{VO(dipy)}\text{F}_2])</td>
<td>968m-s</td>
</tr>
<tr>
<td>34. ([\text{VO(dipy)}_2\text{Cl}]_2\text{Cl})</td>
<td>965s, 973m (sh)</td>
</tr>
<tr>
<td>35. ([\text{VO(dipy)}_2\text{Br}]_2\text{Br}\cdot 2\text{H}_2\text{O}]</td>
<td>958s, 971m (sh)</td>
</tr>
<tr>
<td>36. ([\text{C}_2\text{H}_5\text{ NH}]_3\text{VO(CN)}_5]</td>
<td>956s, 965s (sh)</td>
</tr>
<tr>
<td>37. ([\text{VO(DMSO)}_2]_2(\text{ClO}_4)_2)</td>
<td>955s, 962m (sh, ill defined)</td>
</tr>
<tr>
<td>38. ([\text{VO(OH)}_2])</td>
<td>(955)(^g)</td>
</tr>
<tr>
<td>39. ([\text{VO(DMSO)}_3\text{SO}_4])</td>
<td>964s (sh), 95hs</td>
</tr>
<tr>
<td>40. ([\text{VO(DMSO)}_3\text{Br}_2])</td>
<td>950 (sh, ill defined)</td>
</tr>
<tr>
<td>41. ([\text{CH}_3\text{NH}]_3\text{VO(CN)}_5)</td>
<td>952s</td>
</tr>
<tr>
<td>42. ([\text{Cs}_3\text{VO(CN)}_5])</td>
<td>953s, 968s (sh)</td>
</tr>
<tr>
<td>43. ([\text{VO(DMSO)}_3\text{Cl}_2])</td>
<td>962s (sh), 948vs, 936vs (sh)</td>
</tr>
<tr>
<td>44. ([\text{NH}_4)_3\text{VOF}_5)</td>
<td>947s, 937s</td>
</tr>
</tbody>
</table>
Table XI (cont)

<table>
<thead>
<tr>
<th>Compound</th>
<th>V=O stretch (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>h5. ((\text{NH}_4)_2(\text{VO})_2(\text{SO}_4)_3)</td>
<td>991s</td>
</tr>
</tbody>
</table>

a. Taken from reference 50
b. Taken from reference 47
c. Taken from reference 55
d. Taken from reference 49
e. Taken from reference 52
f. The vanadyl sulfate used for this investigation was anhydrous.
g. Taken from reference 41

Abbreviations used: TPP = tetraphenylporphine; phthal = phthalocyanine; acac = acetylacetonate ion; o-phen = orthophenanthroline; dipy = \(\alpha, \alpha'-\text{dipyridyl}\); en-bis-sal = ethylenediamine-bis-salicylaldehyde; ox = oxalate; mal = malonate; oxine = oxinate(8-hydroxyquinolinate) ion; EDTA = ethylenediaminetetraacetate; DMSO = dimethylsulfoxide; s = strong; vs = very strong; m = medium; sh = shoulder.

The values listed for compounds numbered 2, 4, 5, 6, 19, 26, and 31 were taken from the literature cited; in no case did the authors assign the value quoted here to the V=O stretching vibration. However, in light of the data given here, it seems likely that the values quoted above are due to the V=O vibration and not the previously given values.
Fig. 3 Structures of o-phenanthroline and \( \alpha',\alpha'' \)-dipyridyl

Fig. 4 Structures of Phthalocyanine and Tetraphenylporphines
o-phenanthroline (rigid planar molecule)  
\[ \alpha,\alpha'-\text{dipyridyl} \] (free rotation allowed)

phthalocyanine

\[ \text{p-substituted tetraphenylporphines} \]
\[ X = H, \text{CH}_3, \text{OCH}_3, \text{Cl} \]
to each other. Thus sterically it is possible that dioyridyl can get both nitrogens into closer proximity to the vanadium atom than o-phenanthroline, an arrangement which could lead to more effective chelation and electron donation.

It is observed from compounds 8, 14, 22, and 24 that the V=O frequency decreases in the order acac > o-phen > dipy > oxinate; since coordinating ability is apparently inversely related to this, its order is dipy ≈ oxinate > o-phen > acac. The fact that oxine is more effective than o-phenanthroline is not surprising since it has one oxygen donor as one of its two donor atoms and oxygen could give a certain amount of $\pi$-bonding, thus affecting the V=O frequency to a greater extent than would a nitrogen donor. The position of acetylacetonate in the sequence seems anomalous, however. It has two oxygen donors and thus might be expected to give stronger coordination than the other ligands. Water is also observed to be anomalous as a ligand (see below).

From a comparison of compounds two through six, it can be concluded that substitution on the aromatic rings of porphine-type compounds has very little effect on the V=O stretching frequency. This is not unexpected since the ligands are large and the positions on which substitution occurs is relatively distant from the vanadium and should effect only small, if any changes. The structure of phthalocyanine is closely related to that of TPP (Figure 4) so that its V=O frequency is in the expected position.

Consideration now will be given to compounds number 1, 7, 10, 13, 36, 37, 40, 41, and 43. These all are presumed to be representatives of vanadium in the configuration VOa (except possibly number one; see introduction page 35). Again, if the decrease in the V=O stretching
frequency is used as an inverse measure of the increase in the coordinating ability, then the following series is obtained: $F > CN > DMSO > NCS > H_2O$. The positions of fluoride and cyanide are as expected; both can $\pi$-bond and thus would be expected to give the largest shifts.

The position of DMSO is not unreasonable for this series based on vanadyl compounds since it is an oxygen donor, and also from previous experience (see discussion on DMSO complexes) it has been found to be quite an excellent coordinating agent for many metals. Water might have been expected to give a larger shift since it is an oxygen donor but its position seems substantiated by compounds nine, ten and eleven. With some reservations, compound sixteen might be used to introduce chloride into this series. The replacement of ethanol by a chloride in compound sixteen probably would not effect a shift enough different to make the total shift less than that for thiocyanate or greater than that for DMSO; thus chloride may be tentatively placed in the series giving: $F > CN > DMSO > Cl > NCS > H_2O$.

If compounds fourteen, seventeen and eighteen are compared, it is seen that if chloride or bromide is coordinated in the sixth position, a greater shift is observed than if this position is open, an expected result. The same conclusion is reached from compounds twenty-two, thirty-four and thirty-five. Also if seventeen is compared with eighteen and thirty-four with thirty-five it is observed that chloride and bromide have about equal effect on the $V=O$ frequency.

In Figure 5 is shown a plot of the $V=O$ stretching frequency versus the visible absorption band for the o-phenanthroline and dipyridyl complexes. It is seen that for the o-phenanthroline compounds that the thiocyanate, chloride, bromide and perchlorate exhibit a certain degree
Fig. 5  Plot of V=O Stretching Frequency versus the First Visible Absorption Frequency
First visible absorption frequency (cm$^{-1} \times 10^4$)
of linearity. The sulfate compound does not fit the curve, but its position may be explained as follows: The sulfate is supposedly coordinated and thus occupies the sixth coordination position. It is a doubly charged ion, however, and would probably have a larger effect on the splitting of the d levels of vanadium than would the singly charged ions; it would then not be improbable that its visible band would occur at a higher frequency than the others of the series placing it in the position it occupies on the plot of Figure 5. The fact that the thiocyanate compound of the o-phenanthroline series fits the linearity is explainable in terms of the tentative dimeric structure given on page , since this structure has a cation with the same structure as the other compounds of this series. The same sort of graph is shown for the dipyridyl compounds in Figure 5, and the same sort of linearity is obtained as for the o-phenanthroline compounds, except that the thiocyanate compound is out of line. This cannot be explained at the present since the structure of the thiocyanate compounds are not known; it may not be possible to include them in these series. There is no a priori reason to expect linearity in these plots; the fact that it is obtained seems to indicate that the two pieces of data are measuring to some degree the same phenomena.

From Table XI it can be seen that when the vanadium(IV) has a coordination number of six, two IR bands appear which have only a small separation; one usually appears as a shoulder on the other. When the coordination number is five, though, only one IR band is observed. Since it is assumed that when vanadyl has four groups attached they are attached in a plane perpendicular to the V-O axis, then when no group is
in the sixth position no splitting occurs and when a group is present
two bands are produced. The reason for this is not known; it may be that
a coupling effect between the V=O bond and the V-ligand bond directly
below is the cause. However, one deterrent to taking this point of view
is that in most linear triatomic molecules the difference between the
two bands (symmetrical and unsymmetrical stretching) is one to two
hundred wave numbers\(^87\) whereas the splitting observed here is usually
under forty wave numbers. The splitting in uranyl compounds is less
than this, but is still much larger than that observed here for vanadyl.

It is sometimes possible to calculate bond lengths from infrared
data. A relationship often used is known as Badger's Rule,\(^88\) which
relates the interatomic distance to the force constant of the bond,
using two parameters:

\[ r_{A-B} = \beta k_{A-B}^{1/3} + d \] (1)

In equation (1), \( r_{A-B} \) is the interatomic distance, \( k_{A-B} \) is the stretch­
ing force constant for the bond between atom A and atom B, and \( \beta \)
and \( d \) are parameters. \( \beta \) and \( d \) were considered by Badger\(^88\) to vary for
bonds between elements of different periods of the periodic table but
they are assumed constant for elements from two given periods. Thus \( \beta \)
and \( d \) for vanadyl and titanyl would be the same and would be different
from those for uranyl because vanadium and titanium are from a different
period than uranium. Badger gave values of \( \beta \) and \( d \) for combinations
of elements from various periods but in most cases these values do not
give satisfactory agreement with experiment. The usual procedure is to
determine \( \beta \) and \( d \) empirically and then use them for other calculations.
The value of \( k_{A-B} \) is obtained usually from an independent source (for
instance, IR data) and the values of $\beta$ and $d$ are adjusted until the calculated $r_{A-B}$ values agree with experimental ones, usually determined by X-ray diffraction. Since two parameters are involved, two experimental values of $k_{A-B}$ and $r_{A-B}$ are needed to fix $\beta$ and $d$, unless a value is assumed for $\beta$ and a $d$ value calculated (or vice versa). The equation may then be checked by comparing the experimental bond distance for an independent compound with the one obtained from equation (1) using the appropriate $\beta$ and $d$.

The procedure outlined above has been utilized for uranyl complexes by Jones and co-workers. They assumed a value for $\beta$ and calculated a value for $d$ from experimental data on a uranyl complex and obtained good agreement. On this basis they used the equation so obtained to predict U-O bond distances in other uranyl complexes. It is their contention that the value $\beta = 1.08$ will suffice for all pairs of elements in which at least one element has an atomic number greater than 18. However, they do not say how this has been determined, and this value does not give good agreement with vanadyl compounds.

The calculation of $k_{A-B}$ from infrared data can be involved since in complex molecules there are interactions between bonds. For instance in uranyl, $UO_2^{2+}$ complexes there is interaction between the two U-O bonds and also interaction of the U-O bonds with the U-ligand bonds. Jones has decided that the interaction of the U-ligand bonds with the U-O bond can be neglected with the introduction of only about 3% error. He thus calculates a force constant for the U-O bonds taking into account only the U-O and U-O' interaction. This is the force constant used in Badger's Rule to get the bond distances.
For vanadyl compounds at least two V-O distances have been determined experimentally: VO(acac)$_2$ and VO$_3$($\text{H}_2$)$_2$; one V-O distance for a V(V) compound has been determined, VOCl$_3$. If values for $k_{\text{V-O}}$ can be calculated, then two of the above compounds may be used to calculate $\beta$ and $d$ which can be checked by comparison of the calculated and experimental $r_{\text{V-O}}$ values for the third. Since Jones neglected the interaction between the metal-ligand and metal-oxygen bonds in uranyl with apparent success, the same procedure will be followed here. There is no second metal-oxygen bond so that a simple Hookian oscillator will be assumed and the force constant will be calculated using the equation

$$k_{\text{V-O}} = \frac{1}{\hbar} \frac{\pi^2 c^2 \mu \nu_{\text{V-O}}^2}{2}$$

(2)

where $c$ is the speed of light, $\mu$ the reduced mass, $m_A m_B / (m_A + m_B)$ (of the VO group in this case), and $\nu_{\text{V-O}}$ is the V-O stretching frequency. If the values for $c$, $\mu$ and $\nu$ are put into (2) one obtains the equation:

$$k_{\text{V-O}} = 0.711 \nu_{\text{V-O}}^2$$

(3)

where $k_{\text{V-O}}$ is in dynes/cm and $\nu$ is in cm$^{-1}$. To obtain $k_{\text{V-O}}$ in milidynes/Angstrom, equation (3) must be multiplied by $10^{-5}$, giving

$$k_{\text{V-O}} = 7.111 \times 10^{-6} \nu_{\text{V-O}}^2$$

(4)

Equation (4) will be used to calculate V-O stretching force constants from the IR data given in Table XI. If equation (4) is put into equation (1), one obtains

$$r_{\text{V-O}} = \beta_{\text{V-O}} \left[ 7.111 \times 10^{-6} \nu_{\text{V-O}}^2 \right]^{-1/3} + d_{\text{V-O}}$$

(5)
Equation (5) can be used to evaluate the values of $\beta$ and $d$ using the IR stretching frequency and experimental $r_{V-O}$'s. If VOCl$_3$ and VO(acac)$_2$ are chosen as the reference compounds the equations which define $\beta$ and $d$ are

$$1.59 = \beta_{V-O} \left[ 7.141 \times 10^{-6} (1000)^2 \right]^{-1/3} + d_{V-O}$$

$$1.56 = \beta_{V-O} \left[ 7.141 \times 10^{-6} (1035)^2 \right]^{-1/3} + d_{V-O}$$

Exact solution of these simultaneous equations gives $\beta = 2.56$ and $d = 0.26$. However, using the 976 cm$^{-1}$ band of vanadyl sulfate these do not give good agreement with the experimental values of $r_{V-O}$. If values of $\beta = 2.60$ and $d = 0.26$ are used the experimental and calculated values of $r_{V-O}$ agree much better. Thus the equation

$$r_{V-O} = 2.60 \left[ 7.141 \times 10^{-6} \frac{2}{V_{V-O}} \right]^{-1/3} + 0.26$$

can be used to calculate approximate V-O distances from IR stretching frequencies. The values so obtained for the vanadyl compounds prepared in this investigation are shown in Table XII.

The use of equation (7) might be questioned on the basis that data for a vanadium(V) compound, VOCl$_3$, was used to obtain it and that a change of valence might possibly affect the constants. This argument has some merit since there surely should be some repulsion between the electrons of the V-O bond and the single $d$ electron of V(IV). Thus an equation to be used to calculate vanadyl V-O distances possibly should be derived using only vanadyl compounds as references. This can be done using VOSO$_4$·5H$_2$O and VO(acac)$_2$ in an exactly similar fashion as was used to obtain equation (7) above. This gives
### Table XII

**Calculated V=O Bond Distances**

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR band used (cm⁻¹)</th>
<th>k_v=O (mdynes/Å)</th>
<th>r_v=O (Å) (eq. 7)</th>
<th>r_v=O (Å) (eq. 8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. VOSO₄·5H₂O</td>
<td>976</td>
<td>6.80</td>
<td>1.63</td>
<td>1.67</td>
</tr>
<tr>
<td>2. VO(acac)_2</td>
<td>1000</td>
<td>7.11</td>
<td>1.61</td>
<td>1.59</td>
</tr>
<tr>
<td>3. VOCl₃ᵃᵇ</td>
<td>1035</td>
<td>7.60</td>
<td>1.58</td>
<td>1.48</td>
</tr>
<tr>
<td>4. VO(p-Cl-TPP)</td>
<td>1002</td>
<td>7.16</td>
<td>1.60</td>
<td>1.58</td>
</tr>
<tr>
<td>5. VO(TPP)</td>
<td>1001</td>
<td>7.15</td>
<td>1.60</td>
<td>1.59</td>
</tr>
<tr>
<td>6. VO(p-CH₃-TPP)</td>
<td>1001</td>
<td>7.15</td>
<td>1.60</td>
<td>1.59</td>
</tr>
<tr>
<td>7. [(C₂H₅)₄N]₃VO(NCS)₅</td>
<td>997</td>
<td>7.09</td>
<td>1.61</td>
<td>1.60</td>
</tr>
<tr>
<td>8. VO(p-OCH₃-TPP)</td>
<td>1015</td>
<td>7.36</td>
<td>1.59</td>
<td>1.57</td>
</tr>
<tr>
<td>9. VO(phthal)</td>
<td>1004</td>
<td>7.19</td>
<td>1.60</td>
<td>1.58</td>
</tr>
<tr>
<td>10. [(CH₃)₄N]₃VO(NCS)₅</td>
<td>987</td>
<td>6.95</td>
<td>1.62</td>
<td>1.63</td>
</tr>
<tr>
<td>11. VO(o-phen)_2(ClO₄)_2</td>
<td>987</td>
<td>6.95</td>
<td>1.62</td>
<td>1.63</td>
</tr>
<tr>
<td>12. [(C₂H₅)₄N]₂[VOCl₄·C₂H₅OH]</td>
<td>969</td>
<td>6.70</td>
<td>1.63</td>
<td>1.69</td>
</tr>
<tr>
<td>13. VO(o-phen)_2Br₂·H₂O</td>
<td>981</td>
<td>6.87</td>
<td>1.62</td>
<td>1.65</td>
</tr>
<tr>
<td>14. VO(o-phen)_2Cl₂</td>
<td>982</td>
<td>6.88</td>
<td>1.62</td>
<td>1.65</td>
</tr>
<tr>
<td>15. VO(dipy)SO₄</td>
<td>979</td>
<td>6.81</td>
<td>1.62</td>
<td>1.66</td>
</tr>
<tr>
<td>16. VO(dipy)_2ClO₄</td>
<td>979</td>
<td>6.81</td>
<td>1.62</td>
<td>1.66</td>
</tr>
<tr>
<td>17. VO(en-bis-sal)</td>
<td>980</td>
<td>6.85</td>
<td>1.62</td>
<td>1.65</td>
</tr>
<tr>
<td>18. VO(dipy)ox</td>
<td>979</td>
<td>6.81</td>
<td>1.62</td>
<td>1.66</td>
</tr>
<tr>
<td>19. VO(o-phen)SO₄</td>
<td>978</td>
<td>6.83</td>
<td>1.63</td>
<td>1.66</td>
</tr>
<tr>
<td>20. VO(oxine)</td>
<td>980</td>
<td>6.85</td>
<td>1.62</td>
<td>1.65</td>
</tr>
<tr>
<td>21. VO(dipy)_1,5(NCS)₂</td>
<td>977</td>
<td>6.81</td>
<td>1.63</td>
<td>1.67</td>
</tr>
</tbody>
</table>
Table XII (cont'd)

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR band used (cm⁻¹)</th>
<th>kν₋₀ (mdynes/A) (eq.7)</th>
<th>γν₋₀(Å) (eq.7)</th>
<th>γν₋₀(Å) (eq.8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22. (NH₄)₂VO(mal)₂·4H₂O</td>
<td>977</td>
<td>6.816</td>
<td>1.63₁</td>
<td>1.67₀</td>
</tr>
<tr>
<td>23. (NH₄)₂VO(ox)₂·2H₂O</td>
<td>976</td>
<td>6.801</td>
<td>1.63₂</td>
<td>1.67₃</td>
</tr>
<tr>
<td>24. VO(o-phen)₁.₅(NCS)₂</td>
<td>973</td>
<td>6.760</td>
<td>1.63₅</td>
<td>1.68₉</td>
</tr>
<tr>
<td>25. VO₃O₄·H₂C₂O₄·3H₂O</td>
<td>973</td>
<td>6.760</td>
<td>1.63₅</td>
<td>1.68₉</td>
</tr>
<tr>
<td>26. VO(o-phen)ox</td>
<td>989</td>
<td>6.98₁</td>
<td>1.62₀</td>
<td>1.63₀</td>
</tr>
<tr>
<td>27. VO(o-phen)₂S₀₄</td>
<td>972</td>
<td>6.747</td>
<td>1.63₆</td>
<td>1.68₆</td>
</tr>
<tr>
<td>28. Na₂VO(EDTA)·5H₂O</td>
<td>970</td>
<td>6.719</td>
<td>1.6₃₇</td>
<td>1.6₉₃</td>
</tr>
<tr>
<td>29. VO(o-phen)F₂</td>
<td>968</td>
<td>6.69₁</td>
<td>1.6₃₉</td>
<td>1.7₀₀</td>
</tr>
<tr>
<td>30. VO(dipy)F₂</td>
<td>968</td>
<td>6.69₁</td>
<td>1.6₃₉</td>
<td>1.7₀₀</td>
</tr>
<tr>
<td>31. VO(dipy)₂Cl₂</td>
<td>965</td>
<td>6.6₃₆</td>
<td>1.6₄₃</td>
<td>1.7₁₄</td>
</tr>
<tr>
<td>32. VO(dipy)₂Br₂·H₂O</td>
<td>958</td>
<td>6.₅₅₃</td>
<td>1.₆₄₉</td>
<td>1.₇₃₅</td>
</tr>
<tr>
<td>33. [(C₂H₅)₄N]₃VO(CN)₅</td>
<td>956</td>
<td>6.₅₂₆</td>
<td>1.₆₅₁</td>
<td>1.₇₁₁</td>
</tr>
<tr>
<td>34. VO(DMSO)₂ClO₄</td>
<td>955</td>
<td>6.₅₁₂</td>
<td>1.₆₅₂</td>
<td>1.₇₁₅</td>
</tr>
<tr>
<td>35. VO(DMSO)₃S₀₄</td>
<td>9₅₅</td>
<td>6.₄₉₉</td>
<td>1.₆₅₃</td>
<td>1.₇₄₉</td>
</tr>
<tr>
<td>36. [(CH₃)₄N]₃VO(CN)₅</td>
<td>9₅₂</td>
<td>6.₁₇₂</td>
<td>1.₆₅₅</td>
<td>1.₇₅₅</td>
</tr>
<tr>
<td>37. Cs₃VO(CN)₅</td>
<td>9₅₂</td>
<td>6.₁₇₂</td>
<td>1.₆₅₅</td>
<td>1.₇₅₅</td>
</tr>
<tr>
<td>38. VO(DMSO)₃Cl₂</td>
<td>9₄₈</td>
<td>6.₁₁₈</td>
<td>1.₆₅₉</td>
<td>1.₇₆₉</td>
</tr>
<tr>
<td>39. (NH₄)₃VOF₅</td>
<td>9₃₇</td>
<td>6.₂₆₉</td>
<td>1.₆₆₉</td>
<td>1.₈₀₈</td>
</tr>
<tr>
<td>40. VOBr²⁺</td>
<td>10₂₅</td>
<td>7.₉₉₈</td>
<td>1.₄₈₆</td>
<td>1.₅₁₆</td>
</tr>
</tbody>
</table>

Values of \( r_{\text{V-O}} \) calculated from equation (8) are also shown in Table XII. They are in general higher than those obtained from equation (7) and the range from shortest to longest is greater using equation (8). The cause of this is probably the large value of \( \beta \) in equation (8).

Equation (7) gives a slightly low value for \( r_{\text{V-O}} \) in \( \text{VOSO}_4 \cdot 5\text{H}_2\text{O} \) and the values for the other vanadyl compounds might be slightly low. Because of this and the fact that it was obtained using two vanadyl compounds, equation (8) may give the more correct values. This point may be checked in the future when more V-O distances are determined directly for other vanadyl compounds.

3. Visible and Ultraviolet Spectra

The visible and ultraviolet spectra of inorganic complexes are determined primarily by the arrangement of the ligands around the metal (its symmetry) and by the strength of the electrostatic field presented by these ligands (in the purely electrostatic crystal field model). The presence of \( \pi \)-bonding and strong covalent bonding is also very important but much more difficult to treat and interpret. The symmetry of the complex determines the number of bands that will be observed and the crystal field strength of the ligands determines the relative positions of the absorption bands observed. The splitting of the \( d \) orbitals which determine the inter-\( d \) level transitions is given in Figure 6 for various arrangements of ligands \(^9\) (i.e., for fields of various symmetries). The splittings are not drawn to scale since the energy differences depend on the ligands present in the
Fig. 6 Crystal Field Splittings of the d Orbitals of a Central Ion in Regular Complexes of Various Symmetries
tetrahedral free ion octahedral tetragonal or square square pyramid planar
coordination sphere, as well as the number of \( d \) electrons. A discussion of these splittings and of crystal field theory is given in reference 91.

The crystal field strengths produced by various ligands can be determined from the absorption spectra of symmetrical (octahedral or tetrahedral) complexes of the ligands. For octahedral or tetrahedral complexes only one band is observed (see Figure 6) whose energy (frequency) is proportional to the effect of the ligand on the \( d \) orbitals of the metal; as the effect decreases, the frequency decreases, which means a lower electrostatic field is being presented by the ligands. Several ligands have been placed in a series, their position determined by the relative values of the frequency of the visible absorption bands for a number of different central metal ions. This is the so-called spectrochemical or Fajans-Tsuchida series.\(^{92}\) It is as follows in increasing effect on the absorption band: \( I^- < Br^- < SCN^- < Cl^- < NO_3^- < F^- < urea < OH^- < NO_2^- < HCOO^- < ox^- < H_2O < mal^- < SCN^- < gly^- < edta < py < NH_3 < en < dien < tren < dipy < o-phen < NO_2^- < CN^- .\(^{93}\) If this series is compared to the one obtained on page 89 from IR data, it can be seen that there is some similarity. Fluoride does not show as great an effect here but this is explainable in terms of fluoride exerting a larger than expected effect on the IR frequency of vanadyl due to \( \pi \)-bonding.

The energy difference between the split \( d \) levels of octahedral and tetrahedral complexes has been given several symbols, \( 10Dq \) and \( \Delta \) being the most common. Thus if the position of the band is known, the empirical parameter \( Dq \) can be calculated. (Ideally this is the case only for \( d^4 \) systems.) This quantity can be used as above to give a spectrochemical series of ligands or it might be used to set up a
series of metals in terms of the decrease in Dq as the metal is varied and ligand is held constant. The Dq values for the divalent transition metal hydrates are given in Table XIII in terms of decreasing Dq. The value for vanadyl was obtained using an aqueous solution of vanadyl sulfate and is quite close to the value 1310 cm\(^{-1}\) obtained by Jorgenson\(^2\) for vanadyl perchlorate in 1M perchloric acid. Vanadyl can be inserted in this series only with reservations since it does not form symmetrical octahedral complexes. However there is some similarity between the series in Table XIII and the one obtained by Trujillo\(^7\) which strengthens the significance of the series of Trujillo since he obtained his through a thermodynamic argument involving stability constants. Alternatively, his series helps to bolster the placing of vanadyl in the series with symmetrical octahedral complexes.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Dq (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. VO(IV)</td>
<td>1320 (first visible band)</td>
</tr>
<tr>
<td>2. Cr(II)</td>
<td>1260</td>
</tr>
<tr>
<td>3. Cu(II)</td>
<td>1250</td>
</tr>
<tr>
<td>4. V(II)</td>
<td>1220</td>
</tr>
<tr>
<td>5. Fe(II)</td>
<td>1050</td>
</tr>
<tr>
<td>6. Co(II)</td>
<td>970</td>
</tr>
<tr>
<td>7. Ni(II)</td>
<td>850</td>
</tr>
<tr>
<td>8. Mn(II)</td>
<td>780</td>
</tr>
</tbody>
</table>

In considering theoretical calculations for a group such as the
complexed VO$^{++}$, there are at least two basic approaches available. One method is to consider the VO$^{++}$ group as an independent entity first and calculate the effect of the oxygen on the $d$ orbitals of vanadium and use this as a starting point. The effects of the ligands are then considered as perturbations of the vanadyl group rather than of the vanadium(IV). This is the approach taken by Furlani. He says that the VO$^{++}$ group (free ion) has two energy levels (see Figure 7a) each of which may be split into two further sublevels by coordination. His conclusion is that for coordinated molecules of VO$^{++}$ with $C_{4v}$ symmetry only the lower level is split, leading to two $d$-$d$ transition bands (Figure 7b); for molecules with $C_{2v}$ symmetry both levels are split and three $d$-$d$ transitions are expected (Figure 7c). The second method is to consider the coordinated vanadyl ion (VO$^{++}$ plus ligands) as a distorted octahedron with a tetragonal field. This is the view taken by Jorgensen and apparently leads to four $d$ levels for a tetragonal splitting (see Figure 6). On the basis of this view it appears that four levels are obtained here irrespective of the symmetry of the molecule. At the present time this is at odds with the approach of Furlani discussed above; there is no a priori reason why both methods should not give the same results if applied properly. Some further work is indicated on this problem in order to resolve this apparent paradox. McGlynn is treating the problem by a combination of crystal field and molecular orbital theories (ligand field theory).

The visible and ultraviolet bands for vanadyl compounds are given in Table XIV along with the corresponding extinction coefficients. It can be seen that qualitatively this data fits the predictions of the
Fig. 7 Energy Levels of Vanadyl Ions of Various Symmetries
$C_{\infty v}$

$VO^{++}$ (free ion)

$C_{\infty v}$

$VO_6$ species

$C_{\infty v} \rightarrow C_{4v}$

$C_{\infty v}$

$VO(AA)_2$ species

$C_{\infty v} \rightarrow C_{2v}$
Table XIV

Visible and Ultraviolet Spectral Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\bar{\nu}$ (cm$^{-1}$)</th>
<th>$\lambda$ (m$\mu$)</th>
<th>$\epsilon$ (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. VO(o-phen)$_{1.5}$(NCS)$_2$</td>
<td>13,700</td>
<td>730</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>19,000</td>
<td>525</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>23,800</td>
<td>420</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>30,500</td>
<td>343</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>31,700</td>
<td>288</td>
<td>---</td>
</tr>
<tr>
<td>2. VO(o-phen)$_2$Cl$_2$</td>
<td>14,500</td>
<td>690</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>17,900</td>
<td>560</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>25,300</td>
<td>395</td>
<td>326</td>
</tr>
<tr>
<td></td>
<td>26,800</td>
<td>318</td>
<td>1685</td>
</tr>
<tr>
<td></td>
<td>30,800</td>
<td>325</td>
<td>2115</td>
</tr>
<tr>
<td></td>
<td>34,300</td>
<td>294</td>
<td>111,300</td>
</tr>
<tr>
<td>3. VO(o-phen)$_2$Br$_2$*H$_2$O</td>
<td>14,600</td>
<td>685</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>band not resolved</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25,300</td>
<td>395</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td>28,800</td>
<td>317</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>34,300</td>
<td>294</td>
<td>111,900</td>
</tr>
<tr>
<td>4. VO(o-phen)$_2$(ClO$_4$)$_2$</td>
<td>14,100</td>
<td>650</td>
<td>417</td>
</tr>
<tr>
<td></td>
<td>28,900</td>
<td>316</td>
<td>417</td>
</tr>
<tr>
<td></td>
<td>30,600</td>
<td>327</td>
<td>4320</td>
</tr>
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<td>33,800</td>
<td>296</td>
<td>25300</td>
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<tr>
<td>Compound</td>
<td>$\bar{\nu}$ (cm$^{-1}$)</td>
<td>$\lambda$ (m$\mu$)</td>
<td>$\varepsilon$ (molar)</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------</td>
<td>----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>5. VO(o-phen)$_2$SO$_4$</td>
<td>16,000</td>
<td>625</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>23,600</td>
<td>434</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>28,900</td>
<td>336</td>
<td>---</td>
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<tr>
<td></td>
<td>30,800</td>
<td>325</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>35,000</td>
<td>286</td>
<td>---</td>
</tr>
<tr>
<td>6. VO(dipy)$_{1.5}$(NCS)$_2$</td>
<td>13,700</td>
<td>730</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>18,300</td>
<td>515</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>32,000</td>
<td>313</td>
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<tr>
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<td>32,500</td>
<td>308</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>33,900</td>
<td>295</td>
<td>---</td>
</tr>
<tr>
<td>7. VO(dipy)$_2$Br$_2$H$_2$O</td>
<td>11,300</td>
<td>700</td>
<td>58</td>
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<tr>
<td></td>
<td>16,000</td>
<td>660</td>
<td>50</td>
</tr>
<tr>
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<td>27,000</td>
<td>367</td>
<td>634</td>
</tr>
<tr>
<td></td>
<td>31,900</td>
<td>315</td>
<td>5760</td>
</tr>
<tr>
<td></td>
<td>33,400</td>
<td>300</td>
<td>8520</td>
</tr>
<tr>
<td>8. VO(dipy)$_2$Cl$_2$</td>
<td>11,600</td>
<td>685</td>
<td>50</td>
</tr>
<tr>
<td>band not resolved</td>
<td></td>
<td></td>
<td>50</td>
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<td>373</td>
<td>699</td>
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<td>313</td>
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<td>32,500</td>
<td>308</td>
<td>8610</td>
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<td>Compound</td>
<td>$\bar{\nu}$, (cm$^{-1}$)</td>
<td>$\lambda$, (m$\mu$)</td>
<td>$\varepsilon$, (molar)</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------------------------</td>
<td>---------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>9. VO(dipy)$_2$(ClO$_4$)$_2$</td>
<td>15,400</td>
<td>650</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
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<td>317</td>
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<tr>
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<td>33,300</td>
<td>292</td>
<td>15,400</td>
</tr>
<tr>
<td>10. VO(DMSO)$_5$(ClO$_4$)$_2$</td>
<td>12,800</td>
<td>780</td>
<td>28</td>
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<tr>
<td></td>
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<td>675</td>
<td>18</td>
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<tr>
<td></td>
<td>39,200</td>
<td>255</td>
<td>14,90</td>
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<td></td>
<td>40,200</td>
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<td>14,00</td>
</tr>
<tr>
<td>11. VO(DMSO)$_5$Br$_2$</td>
<td>14,000</td>
<td>715</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>25,700</td>
<td>388</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>39,100</td>
<td>254</td>
<td>19,900</td>
</tr>
<tr>
<td></td>
<td>40,300</td>
<td>248</td>
<td>11,900</td>
</tr>
<tr>
<td>12. VO(ClO$_4$)$_2$ (in 1M HClO$_4$)$^a$</td>
<td>13,100</td>
<td>765</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>16,000</td>
<td>625</td>
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</tr>
<tr>
<td></td>
<td>11,700</td>
<td>210</td>
<td>240</td>
</tr>
<tr>
<td>13. VO$\text{SO}_4$·5H$_2$O (in H$_2$O)</td>
<td>13,200</td>
<td>755</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>17,000</td>
<td>590</td>
<td>19</td>
</tr>
<tr>
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<td>12,000</td>
<td>328</td>
<td>305</td>
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Table XIV (cont'd)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\lambda$ (m$\mu$)</th>
<th>$\varepsilon$ (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14. $(Me_4N)_3VO(NCS)_5$</td>
<td>13,500</td>
<td>740</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>17,200</td>
<td>580</td>
<td>34</td>
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<tr>
<td></td>
<td>23,900</td>
<td>419</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>31,820</td>
<td>315</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>37,900</td>
<td>264</td>
<td>3370</td>
</tr>
<tr>
<td>15. $(Et_4N)_3VO(NCS)_5$</td>
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<td>735</td>
<td>114</td>
</tr>
<tr>
<td></td>
<td>17,200</td>
<td>580</td>
<td>49</td>
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<td>422</td>
<td>9</td>
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<tr>
<td></td>
<td>31,800</td>
<td>315</td>
<td>5570</td>
</tr>
<tr>
<td></td>
<td>38,500</td>
<td>260</td>
<td>10,100</td>
</tr>
<tr>
<td>16. $(NH_4)_3VOF_5$ (in aqueous HF)</td>
<td>15,800</td>
<td>630</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>143,000</td>
<td>233</td>
<td>534</td>
</tr>
<tr>
<td>17. $Cs_3VO(CN)_5$</td>
<td>11,700</td>
<td>674</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>24,300</td>
<td>412</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>UV not determined</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18. VO(acac)$_2$</td>
<td>11,200</td>
<td>705</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>16,800</td>
<td>595</td>
<td>31</td>
</tr>
<tr>
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<td>25,800</td>
<td>388</td>
<td>86</td>
</tr>
<tr>
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<td>33,400</td>
<td>299</td>
<td>11,900</td>
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<tr>
<td></td>
<td>45,200</td>
<td>221</td>
<td>7680</td>
</tr>
<tr>
<td>Compound</td>
<td>$\bar{\nu}$(cm$^{-1}$)</td>
<td>$\lambda$(m$\mu$)</td>
<td>$\epsilon$(molar)</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------------------------</td>
<td>-------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>19. VO(oxine)$_2$</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>21,300</td>
<td>470</td>
<td>683</td>
</tr>
<tr>
<td></td>
<td>26,700</td>
<td>375</td>
<td>4920</td>
</tr>
<tr>
<td></td>
<td>30,000</td>
<td>333</td>
<td>4430</td>
</tr>
<tr>
<td></td>
<td>31,400</td>
<td>318</td>
<td>4230</td>
</tr>
<tr>
<td>20. VO(DMSO)$_3$Cl$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>14,400</td>
<td>695</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>25,300</td>
<td>395</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>34,000</td>
<td>294</td>
<td>690</td>
</tr>
<tr>
<td></td>
<td>39,200</td>
<td>255</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>40,200</td>
<td>248</td>
<td>625</td>
</tr>
<tr>
<td>21. (Me$_4$N)$_2$[VOCl$_4$.C$_2$H$_2$.OH]</td>
<td>13,900</td>
<td>720</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>25,250</td>
<td>396</td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>34,240</td>
<td>292</td>
<td>1180</td>
</tr>
<tr>
<td></td>
<td>38,450</td>
<td>260</td>
<td>not well</td>
</tr>
<tr>
<td></td>
<td>39,400</td>
<td>254</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td>40,500</td>
<td>247</td>
<td>resolved</td>
</tr>
</tbody>
</table>

a. Data taken from reference 29
theory of Furlani. With two exceptions, it is observed that all of the complexes of the species VO_{a^5} exhibit two absorption bands in the visible region. Since these compounds should have C_{4v} symmetry this is what is expected from Figure 7b. The exceptions here are the fluoride and thiocyanate complex. The thiocyanate compound gives three bands in the visible; the reasons for this are unknown. Possibly the symmetry is lower than C_{4v}, which could lead to more bands. The fluoride complex exhibits only one band in the visible which can be a d-d transition. Now fluoride can π-bond and it is possible that the fluorides have as great an effect on the d levels of the vanadium as the oxygen. Thus the vanadium would be surrounded by an approximately octahedral field even though the field is caused by different ligands. If this is true then only one band would be expected on the basis of the octahedral splitting (see Figure 6).

From Table XIV it can be seen that compounds 1, 2, 3, 6, 7, 8, and 18, which presumably have C_{2v} symmetry, all show two bands in the visible region which are undoubtedly d-d transitions and a third band at higher frequencies which could be a d-d transition, but in several of the compounds it has an extinction coefficient larger than expected for a forbidden d-d transition. There is one very slim piece of evidence indicating that this third band is a d-d transition. Since the charge transfer bands for the electron transfer from oxygen to vanadium involve the transfer of an electron from an oxygen orbital to the same d orbitals that the d-d transitions are concerned with, the difference in the first two d-d transitions should be equal to the difference in the second and third charge transfer bands (see Figure 8). For compound number 2, VO(o-phen)_{2}Cl_{2}, it can be seen
Fig. 8 Relation of Charge Transfer and $d-d$ Transitions
charge transfer bands

\[ \text{d orbitals of vanadium} \]

\[ \text{oxygen level} \]
from Table XIV that the difference in the fifth and sixth absorption bands is 3500 cm$^{-1}$ and that the difference in the first and second absorption bands is 3400 cm$^{-1}$. This indicates that band number three is not a charge transfer band. This is a very meager piece of evidence, however, and no similar correlation can be obtained with other compounds; however, no other complexes of known structure exhibit six bands as does the one considered here. Compounds 4 and 9 exhibit only one band in the visible; no reason for this is known. It would be expected that they should also have three d-d transitions since their symmetry is probably $C_{3v}$.

It has been found by McGlynn$^{94}$ that for small changes in the interatomic distance, the intensity of a charge transfer band between two atoms should increase as the square of the interatomic distance. Table XV shows that again the data obtained are qualitatively explained on this basis for several compounds. This table gives the interatomic distance from Table XII, the absorption band and extinction coefficient for that band from Table XIV. It is seen that qualitatively as the V=O distance increases, more intense bands are observed. Table XV presents some evidence that the third band discussed above is a charge transfer band, so that its true nature is not known at present.

One further observation and comment can be made about the first visible band of these compounds. The aquo, fluoro, and DMSO complexes would be expected to show the smallest deviations from octahedral symmetry of the crystal field around the vanadium and thus would be expected to exhibit the greatest amount of "forbiddenness" (i.e., lowest $\varepsilon$ values) in the first visible band. This is exactly what is observed and as expected the fluoride has the lowest value since it is presumably almost octahedral as discussed above.
Table XV

V=O Bond Distances and Molar Extinction Coefficients

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r_{V=O}$</th>
<th>$\epsilon$ (cm$^{-1}$)</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. VO(o-phen)$_2$Br$_2$$\cdot$H$_2$O</td>
<td>1.657</td>
<td>25,300</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28,800</td>
<td>2000</td>
</tr>
<tr>
<td>2. VO(o-phen)$_2$Cl$_2$</td>
<td>1.653</td>
<td>25,300</td>
<td>326</td>
</tr>
<tr>
<td></td>
<td></td>
<td>28,800</td>
<td>1685</td>
</tr>
<tr>
<td>3. VO(o-phen)$_2$ClO$_4$$\cdot$H$_2$O</td>
<td>1.636</td>
<td>28,900</td>
<td>2580</td>
</tr>
<tr>
<td>4. VO(dipy)$_2$Br$_2$$\cdot$H$_2$O</td>
<td>1.735</td>
<td>27,200</td>
<td>634</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31,900</td>
<td>5760</td>
</tr>
<tr>
<td>5. VO(dipy)$_2$Cl$_2$</td>
<td>1.714</td>
<td>26,800</td>
<td>699</td>
</tr>
<tr>
<td>6. VO(dipy)$_2$(ClO$_4$)$_2$</td>
<td>1.663</td>
<td>31,600</td>
<td>11,100</td>
</tr>
</tbody>
</table>

h. Dipole Moment Studies of Vanadyl Acetylacetonate

The dipole moments of a few vanadium compounds containing a vanadium oxygen double bond have been determined by Cartan. He found that the dipole moment of VOCl$_3$ was approximately 0.35 Debye. From this value it was concluded that the vanadium oxygen bond moment is low.

The dipole moment of VO(acac)$_2$ has been measured in this investigation in both benzene and dioxane. In dioxane the value obtained was $\mu = 4.250.3$ Debyes and in benzene approximately the same value was obtained. This is interesting in that it indicates no appreciable interaction between the dioxane and the Vu(acac)$_2$. This should not
be completely surprising since the VO(acac)$_2$ can be obtained anhydrous from aqueous solutions and water would be expected to have a better chance of attaching itself in the sixth position than would dioxane. The surprising feature is that small, if any, interaction is indicated in solution; it seems that with an excess of dioxane some interaction should occur.

The value for the dipole moment obtained is quite large and rather unexpected. From the structure of VO(acac)$_2$ (see Figure 1) it can be seen that the four vanadium to acetylacetonate oxygen bonds should give a resultant dipole moment opposite in direction to the V=O dipole moment. Also the lone d electron presumably will be opposite the vanadyl oxygen and should contribute to the opposition of the V=O dipole. Thus the value obtained for $\mu$ is larger than would be expected if the V=O bond moment is small as indicated by the measurements of Cartan. It may well be the case that in approximately tetrahedral vanadium oxytrichloride the resultant moment of the three V-Cl bonds is larger than the resultant of the V-O bonds in VO(acac)$_2$. Even though the V-Cl bonds make larger angles with the plane perpendicular to the vanadyl bond direction this does not seem likely since oxygen is more electronegative than chlorine. Some further dipole moment studies on other vanadyl compounds such as vanadyl oxinate would be of great value and interest.
Appendix

Representative Infrared and Visible Spectra
WAVE NUMBER (cm$^{-1}$)

VO(dipyr)SO$_4$

Cs$_2$VOICN$_6$

[CH$_3$N]$_3$VOINC$_3$
TRANSMITTANCE

A. PHENANTHROLINE in CH₃CN
B. ACETYLACETONE in CH₃CN
C. β-QUINOLINOL (OXIME) in CH₃CN

WAVE NUMBER (x 10⁵)

A. V10NH₃⁺/CHBr₃ in CH₃CN
B. a₆'-DIPYRIDYL in CH₃CN

A. B. C.
Selected Bibliography


23. Drago, Russel, and Meek, Devon, in press.


11. Cabannes-Ott, Christiane, "Infrared Study, Between 300 and 4000 cm\(^{-1}\), of Copper and Vanadyl Hydroxides," Compt. rend., 212, 2825 (1956).


51. Santini, Rafael, J.R., Hazel, J.F., and McNabb, W.M., "Spectro-
trophotometric Determination of Vanadium Based on the

52. Walchli, H.E., and Morgan, H.W., "Magnetic Shielding Effects in


Vanadinoxochlorid mit organischen Verbindungen," Z. anorg.

55. Rosenheim, A., and Mong, H.Y., "Uber Salze und Komplexverbin-
dungen des vierwertigen Vanadiums," Z. anorg. Chem., 118,
25(1925).


57. Funk, H., Weiss, W., and Zeising, M., "Die Umsetzungen von
Vanadinoxochlorid mit organischen Substanzen," Z. anorg.

58. Bielig, Hans-Joachim, and Bayer, Ernst, "Uber Innerkomplexe des
5-, 4-, und 3-wertigen Vanadiums mit 8-oxychinolin and deren

12B, 595(1957).


63. Morgan, G.T., and Moss, H.W., "Coordination Compounds of Vanadium,

64. Parisi, E., "Ricerche sul vanadio tetravalente - Nota II. Sul
numero di coordinazione del vanadio nei sali complessi di


Vita

Lawrence Henry Holmes, Jr. was born April 24, 1935, in Robert, Louisiana. He graduated from Hammond High School in 1953, entering Southeastern Louisiana College in Hammond the same year. He received a B.S. in chemistry from that institution in June, 1957, and entered the Graduate School of Louisiana State University in the fall of 1957.

On May 31, 1958, he married the former Patricia Sticker.

He is now a candidate for the degree Doctor of Philosophy.
Candidate: Lawrence H. Holmes, Jr.

Major Field: Chemistry

Title of Thesis: Physical Chemical Studies on Inorganic Coordination Compounds
I. Metallic Complexes of Dimethylsulfoxide
II. Preparation and Spectral Studies of Vanadyl Complexes

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination: July 18, 1961