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**Bis[(anhydro-meso-rhodochlorinato-XV methyl ester)zinc(II)]**

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The structural characteristics of the macrocycle system are typical for chlorins (Scheidt & Lee, 1987). The ring system shows a moderate degree of ruffling, i.e. a non-planar macrocycle distortion with tilting of the pyrrole rings against the mean plane (Scheidt & Lee, 1987). The average deviation of the 24 atoms comprising the tetrapyrrole system from their least-squares plane is 0.132 Å. The largest deviations from planarity are observed for some C\text{b} positions and the meso-C atoms, the latter being displaced alternately above and below the mean plane by 0.2-0.3 Å. The structure of the corresponding nickel(II) isobacteriochlorin [(anhydro-meso-rhodoisobacteriochlorinato)nickel(II)] shows a significantly higher degree of S\text{4} ruffling (Renner et al., 1991).

Interestingly, the presence of the fused cyclohexanone ring leads to the formation of a bischlorin structure, consisting of two macrocycles, related to each other by an inversion center and held together using the carbonyl O atom of the cyclohexanone ring of one macrocycle as an axial ligand to the zinc center of another (Fig. 1). Thus, the core geometry is similar to that of pentacoordinate zinc(II) porphyrins, with the zinc center located 0.22 Å above the mean plane of the molecule and a Zn---O bond length of 2.204 (3) Å.

This bond length is comparable to that found in monomeric pentacoordinate zinc(II) porphyrins with water or alcohols as axial ligands (Scheidt & Lee, 1987), but is shorter than those found in the polymeric (2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetranitroporphyrinato)zinc(II), where a nitro O atom serves as an axial ligand [Zn---O 2.485 (5) Å; Senge & Smith, 1994], and in a cyclophane-type zinc(II) porphyrin benzoquinone, which has a quinone O atom as an axial ligand [Zn---O 2.532 (3) Å; Staab, Krieger, Anders & Rückemann, 1994]. Axial coordination of carbonyl O atoms to metal centers of neighboring macrocycles is often found in chlorophyll aggregates (Abraham & Rowan, 1991) and in the solid-state structures of covalently linked zinc(II) porphyrin quinones (Staab, Krieger, Anders & Rückemann, 1994; Senge & Kurreck, 1997).

The bischlorin is further characterized by weak π-π interactions. The interplanar separation (i.e. the distance between the centers of the planes defined by the four N atoms) of the ring systems in a given dimer is 3.95 (1) Å.
Much stronger intermolecular $\pi-\pi$ aggregation of individual dimers is observed, which leads to the formation of infinite stacks within the crystal. These intermolecular aggregates exhibit an interplanar separation of 3.46 (1) Å and show more overlap of neighboring macrocycles [lateral shift of the ring centers = 3.24 (1) Å, as defined by Scheidt & Lee (1987)] than the intramolecular aggregates [lateral shift = 5.59 (1) Å]. Related structure determinations include the chlorin anhydrobonellin methyl ester (Pelten, Ballantine, Murray-Rust, Ferrito & Psaila, 1978) and a porphyrin with a fused benzocyclohexenone ring (Henrick, Owston, Peters, Tasker & Dell, 1980).

**Experimental**

The title compound was prepared as described by Abraham, Medforth, Mansfield, Simpson & Smith (1988). Crystals were grown from CH$_2$Cl$_2$/n-hexane and mounted according to Hope (1994).

**Crystal data**

\[
\text{[Zn(C$_{13}$H$_{34}$N$_4$O$_3$)$_2$]} \quad \text{Mo } K\alpha \text{ radiation} \\
M_r = 1200.02 \\
\lambda = 0.71073 \text{ } \AA
\]

**Table 1. Selected geometric parameters (Å, °)**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bond Lengths (Å)</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C13--C14</td>
<td>1.403 (6)</td>
<td>C16--C17--C18</td>
</tr>
<tr>
<td>C14--C15</td>
<td>1.403 (6)</td>
<td>C19--C20--C182</td>
</tr>
<tr>
<td>C15--C16</td>
<td>1.360 (6)</td>
<td>C183--C184--C185</td>
</tr>
<tr>
<td>C16--C17</td>
<td>1.344 (5)</td>
<td>C186--C187--C188</td>
</tr>
<tr>
<td>C17--C18</td>
<td>1.344 (5)</td>
<td>C189--C190--C191</td>
</tr>
<tr>
<td>C18--C19</td>
<td>1.344 (5)</td>
<td>C192--C193--C194</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 1.** The molecular structure and numbering scheme for the macrocycle in the asymmetric unit (top) and a view of the dimers formed via axial Zn—O interactions (bottom). H atoms have been omitted for clarity and ellipsoids are drawn at the 50% probability level.


H atoms were placed in calculated positions and refined using a riding model. 


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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1192). Services for accessing these data are described at the back of the journal.

References


Tetrahydrofuran Adducts of a Chlorobismuthate(III) Anion and Antimony Triiodide

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Abstract

Tetrahydrofuran (thf) adducts of a chlorobismuthate(III) anion and of antimony triiodide have been prepared and characterized by X-ray crystallography. The former compound, bis[tetrakis(tetrahydrofuran-O)-lithium(I)] di-μ-chloro-bis[trichloro(tetrahydrofuran-O) bismuthate(III)], [Li(C4H9O)2][Bi2Cl6(C4H9O)2], contains centrosymmetric edge-shared bi-octahedral di-anions with the formula [Bi2Cl6(thf)2(μ-Cl)2]2− in which the thf ligands occupy terminal sites at 90° to the Bi2(μ-Cl)2 plane; the cations are [Li(thf)4]+. The latter structure, triiodo(tetrahydrofuran-O)antimony(III), [SbI3(C4H9O)], comprises a polymeric arrangement of SbI3(thf) units, the antimony centres being bridged alternately by pairs of I atoms and pairs of thf ligands.

Comment

Antimony and bismuth trihalides have an extensive coordination chemistry as a result of the Lewis acidity of the group 15 element centre, and a number of complexes are known, mostly for bismuth, in which the number of coordinated ligands ranges from one to three per element centre (Carmalt et al., 1996, and references therein). One particular class of element trihalide complexes has thf as the ligand. Previously characterized examples in this class are fac-[BiCl3(thf)3] (Eveland & Whitmire, 1996), fac-[BiBr3(thf)] and [BiCl3(thf)2] (Carmalt et al., 1996). The first two complexes are mononuclear with octahedrally coordinated bismuth centres around which the thf ligands and halides both adopt fac configurations. The compound [BiCl3(thf)2] has a polymeric structure in the solid state in which each bismuth centre resides in a seven-coordinate pentagonal bipyramidal coordination environment with one axial and one equatorial thf, one axial Cl atom which is terminal, and four equatorial bridging Cl atoms, two with short Bi—Cl bonds and two with rather longer Bi— Cl distances. A related group of compounds consists of iodobismuthate(III) anions to which thf ligands are coordinated, examples of which include the diatomic