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

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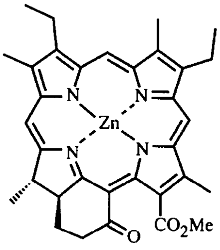
Abstract

The title compound, bis[(methyl 8,13-diethyl-2,2^1,2^2,2^3-tetrahydro-3,7,12,17-tetramethyl-2^3-oxo-3*H*-benzo[*at*]-porphyrin-18-carboxylato-κ^4N)zinc(II)], $[Zn(C_{33}H_{34}N_4O_3)]_2$, has similar structural characteristics to the naturally occurring factor F430 and forms dimers that are held together by axial interactions between the zinc(II) center and the cyclohexanone carbonyl O atom of a neighboring macrocycle [Zn—O3 2.204 (3) Å]. These dimers form infinite stacks in the crystal stabilized by π–π interactions between the aromatic ring systems.

Comment

The structure of the cofactor F430 of methyl coenzyme M reductase involved in methanogenesis has been determined unambiguously as a nickel hydrocorphin (Färber *et al.*, 1991). The structure is characterized by a high degree of saturation of the basic porphyrin system and the presence of a fused cyclohexanone ring. The latter structural feature is also found in derivatives of the anhydro-*meso*-porphyrin-XV series, which can be chemically synthesized from chlorophyll derivatives (Smith & Simpson, 1987).

The zinc(II) complex of anhydro-*meso*-rhodochlorin methyl ester, (I), shows the same *trans* arrangement of the H atoms at C17 and C18 as found in cofactor F430, with a C17—C18 single bond of 1.451 (7) Å. 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_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_4 ruffling (Renner *et al.*, 1991).



(I)

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.

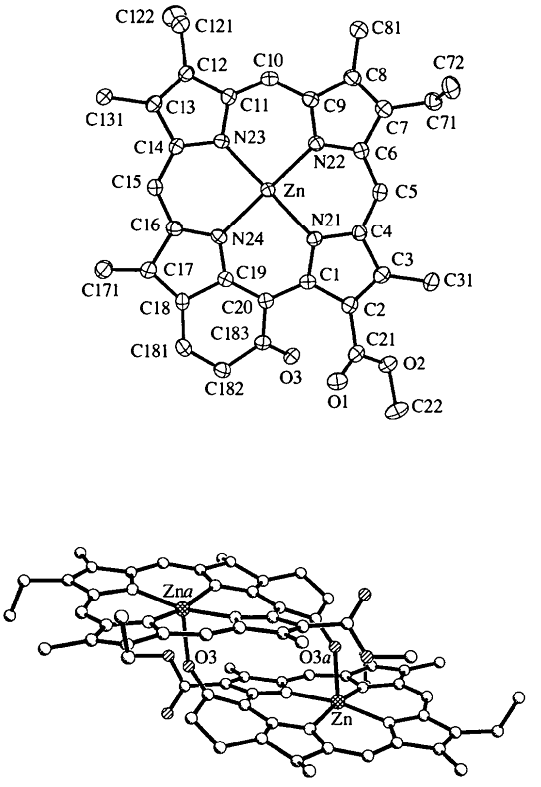


Fig. 1. The molecular structure and numbering scheme for the macrocycle in the asymmetric unit (top) and a view of the dimers formed *via* axial Zn—O interactions (bottom). H atoms have been omitted for clarity and ellipsoids are drawn at the 50% probability level.

Much stronger intermolecular π–π 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 (Pelter, 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_2Cl_2/*n*-hexane and mounted according to Hope (1994).

Crystal data

$[Zn(C_{33}H_{34}N_4O_3)]_2$
$M_r = 1200.02$
Triclinic
$P\overline{1}$
$a = 9.838\ (5)$ Å
$b = 12.524\ (5)$ Å
$c = 12.842\ (6)$ Å
$\alpha = 69.12\ (3)°$
$\beta = 68.00\ (4)°$
$\gamma = 82.42\ (4)°$
$V = 1370.7\ (11)$ Å^3
$Z = 1$
$D_x = 1.454$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 34 reflections
$\theta = 10.0$–$12.5°$
$\mu = 0.939$ mm^{-1}
$T = 126\ (2)$ K
Plate
0.6 × 0.5 × 0.2 mm
Blue

Data collection

Siemens *R*3*m*/*V* diffractometer
ω scans
Absorption correction: empirical (*XABS*2; Parkin, Moezzi & Hope, 1995)
$T_{min} = 0.57$, $T_{max} = 0.83$
6703 measured reflections
6332 independent reflections

4690 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 27.56°$
$h = -11 \rightarrow 12$
$k = -14 \rightarrow 16$
$l = 0 \rightarrow 16$
2 standard reflections every 198 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.163$
$S = 1.029$
6330 reflections
370 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 3.2049P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.934$ e Å^{-3}
$\Delta\rho_{min} = -0.825$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Zn—N23	2.039 (4)	C7—C8	1.369 (6)
Zn—N22	2.050 (4)	C8—C9	1.437 (6)
Zn—N21	2.077 (4)	C9—C10	1.403 (6)
Zn—N24	2.078 (4)	C10—C11	1.371 (6)
Zn—O3'	2.204 (3)	C11—C12	1.460 (6)
N21—C1	1.349 (5)	C12—C13	1.354 (6)
N21—C4	1.387 (5)	C13—C14	1.454 (6)
N22—C9	1.367 (5)	C14—C15	1.403 (6)
N22—C6	1.379 (5)	C15—C16	1.369 (6)
N23—C14	1.358 (5)	C16—C17	1.499 (6)
N23—C11	1.383 (5)	C17—C171	1.447 (7)
N24—C19	1.344 (5)	C17—C18	1.451 (7)
N24—C16	1.366 (5)	C18—C181	1.415 (7)
C1—C20	1.429 (6)	C18—C19	1.508 (6)
C1—C2	1.453 (6)	C181—C182	1.475 (7)
C2—C3	1.360 (6)	C182—C183	1.504 (6)
C3—C4	1.443 (6)	C183—O3	1.248 (5)
C4—C5	1.384 (6)	C183—C20	1.459 (6)
C5—C6	1.390 (6)	C19—C20	1.400 (6)
C6—C7	1.445 (6)		
N23—Zn—N22	89.47 (15)	N24—C16—C17	110.2 (4)
N23—Zn—N21	168.04 (14)	C15—C16—C17	124.4 (4)
N22—Zn—N21	89.76 (14)	C18—C17—C16	104.0 (4)
N23—Zn—N24	89.90 (14)	C181—C18—C17	130.2 (5)
N22—Zn—N24	167.99 (14)	C181—C18—C19	114.0 (4)
N21—Zn—N24	88.37 (14)	C17—C18—C19	104.3 (4)
N23—Zn—O3'	100.13 (13)	C18—C181—C182	117.0 (5)

N22—Zn—O3^{i}	103.24 (13)	C181—C182—C183	115.1 (4)
N21—Zn—O3^{i}	91.66 (13)	O3—C183—C20	121.1 (4)
N24—Zn—O3^{i}	88.67 (13)	O3—C183—C182	118.4 (4)
C1—N21—Zn	127.0 (3)	C20—C183—C182	120.5 (4)
C4—N21—Zn	125.4 (3)	N24—C19—C20	127.4 (4)
C9—N22—Zn	125.7 (3)	N24—C19—C18	110.3 (4)
C6—N22—Zn	127.6 (3)	C20—C19—C18	122.2 (4)
C14—N23—Zn	126.8 (3)	C19—C20—C1	124.7 (4)
C11—N23—Zn	126.3 (3)	C19—C20—C183	114.6 (4)
C19—N24—C16	109.3 (3)	C1—C20—C183	120.3 (4)
C19—N24—Zn	124.1 (3)	C21—O2—C22	115.0 (4)
C16—N24—Zn	125.2 (3)	C183—O3—Zn^{i}	124.3 (3)
N24—C16—C15	125.4 (4)		

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

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

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL-Plus* (Sheldrick, 1995). Program(s) used to solve structure: *XS93* in *SHELXTL-Plus*. Program(s) used to refine structure: *XL93* in *SHELXTL-Plus*. Molecular graphics: *XP* in *SHELXTL-Plus*. Software used to prepare material for publication: *XCIF* in *SHELXTL-Plus*.

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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.

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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)], $[Li(C_4H_8O)_4]_2[Bi_2Cl_8(C_4H_8O)_2]$, contains centrosymmetric edge-shared bi-octahedral dianions with the formula $[Bi_2Cl_6(thf)_2(\mu\text{-}Cl)_2]^{2-}$ in which the thf ligands occupy terminal sites at 90° to the $Bi_2(\mu\text{-}Cl)_2$ plane; the cations are $[Li(thf)_4]^+$. The latter structure, triiodo(tetrahydrofuran-*O*)antimony(III), $[SbI_3(C_4H_8O)]$, comprises a polymeric arrangement of $SbI_3(thf)$ 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*-$[BiCl_3(thf)_3]$ (Eveland & Whitmire, 1996), *fac*-$[BiBr_3(thf)_3]$ and $[BiCl_3(thf)_2]$ (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 $[BiCl_3(thf)_2]$ 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 dianions