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.

References

Abraham, R. J., Medforth, C. J., Mansfield, K. E., Simpson, D. J. & Smith, K. M. (1988). *J. Chem. Soc. Perkin Trans.* 2, pp. 1365–1370.

Abraham, R. J. & Rowan, A. E. (1991). *Chlorophylls*, edited by H. Scheer, pp. 797–834. Boca Raton: CRC Press.

Färber, G., Keller, W., Kratky, C., Jaun, B., Pflatz, A., Spinner, C., Kobelt, A. & Eschenmoser, A. (1991). *Helv. Chim. Acta*, **74**, 697–716.

Henrick, K., Owston, P. G., Peters, R., Tasker, P. A. & Dell, A. (1980). *Inorg. Chim. Acta*, **45**, L161–L163.

Hope, H. (1994). *Prog. Inorg. Chem.* **41**, 1–13.

Parkin, S. R., Moezzi, B. & Hope, H. (1995). *J. Appl. Cryst.* **28**, 53–56.

Pelter, A., Ballantine, J. A., Murray-Rust, P., Ferrito, V. & Psaila, A. F. (1978). *Tetrahedron Lett.* **21**, 1881–1884.

Renner, M. W., Furenlid, L. R., Barkigia, K. M., Forman, A., Shim, H.-K., Simpson, D. J., Smith, K. M. & Fajer, J. (1991). *J. Am. Chem. Soc.* **113**, 6891–6898.

Scheidt, W. R. & Lee, Y.-J. (1987). *Struct. Bonding (Berlin)*, **64**, 1–70.

Senge, M. O. & Kurreck, H. (1997). In preparation.

Senge, M. O. & Smith, K. M. (1994). *J. Chem. Soc. Chem. Commun.* pp. 923–924.

Sheldrick, G. M. (1995). *SHELXTL-Plus*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991). *P3/P4-PC Diffractometer Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Smith, K. M. & Simpson, D. J. (1987). *J. Am. Chem. Soc.* **109**, 6326–6333.

Staab, H. A., Krieger, C., Anders, C. & Rückemann, A. (1994). *Chem. Ber.* **127**, 231–236.

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

Siân C. James, Nicholas C. Norman, A. Guy Orpen and Michael J. Quayle

School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, England. E-mail: guy.orpen@bris.ac.uk

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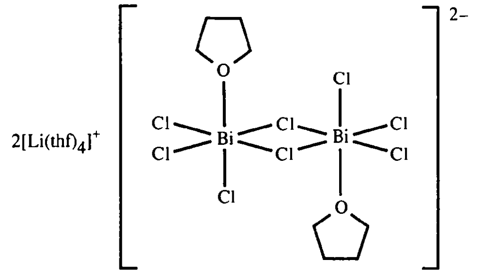
Abstract

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.

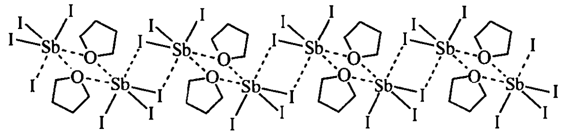
Comment

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

$[Bi_4I_{14}(thf)_2]^{2-}$ (Krautscheid, 1994*a*), $[Bi_4I_{14}(thf)_4]^{2-}$ and $[Bi_2I_8(thf)_2]^{2-}$ (Krautscheid, 1994*b*). In no case is there any significant stereochemical activity associated with the Bi^{III} lone pair.



(1)



(2)

The compound $[Li(thf)_4]_2[Bi_2Cl_6(thf)_2(\mu\text{-}Cl)_2]$, (1), comprises separated ions with no short interionic contacts. The dianion (Fig. 1) has a crystallographically centrosymmetric edge-shared bi-octahedral structure in which the thf ligands occupy terminal sites perpendicular to the $Bi_2(\mu\text{-}Cl)_2$ plane, the Bi—O distance [2.588 (7) Å] being comparable with those in $[BiCl_3(thf)_3]$ [2.63 (2)–2.67 (2) Å; Eveland & Whitmire, 1996] and $[BiCl_3(thf)_2]$ [2.551 (4)–2.622 (12) Å; Carmalt *et al.*, 1996]. Of the Bi—Cl distances, the one to the terminal Cl atom (Cl1) *trans* to the thf ligand is the shortest [2.558 (3) Å]. The other two terminal Bi—Cl bonds are slightly longer [Bi1—Cl3 2.565 (3) and Bi1—Cl4 2.576 (3) Å], both being *trans* to bridging Cl atoms, the Bi—Cl distances for which are significantly longer than the terminal bonds as expected [Bi1—Cl2 2.896 (3) and Bi1—Cl2^{i} 2.924 (3) Å; see Table 1 for symmetry code], although not very different from each other, resulting in a fairly symmetrical $Bi_2(\mu\text{-}Cl)_2$ unit. None of the interbond angles deviate significantly (>10°) from idealized octahedral angles. The $[Li(thf)_4]^+$ cation has an orthodox geometry (Krautscheid, 1994*a*).

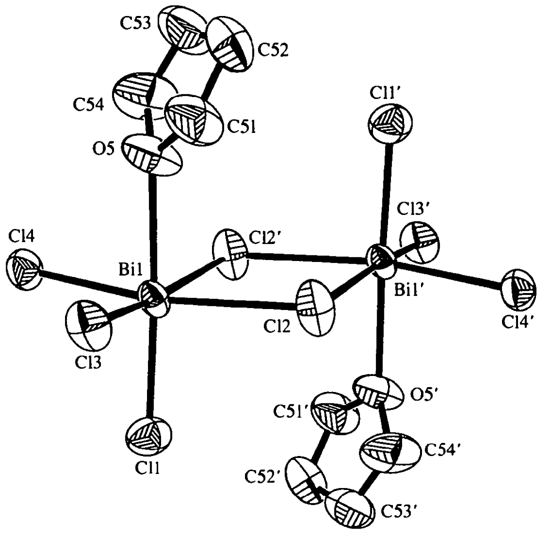


Fig. 1. A view of the $[Bi_2Cl_6(thf)_2(\mu\text{-}Cl)_2]^{2-}$ dianion in $[Li(thf)_4]_2[Bi_2Cl_6(thf)_2(\mu\text{-}Cl)_2]$ showing the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

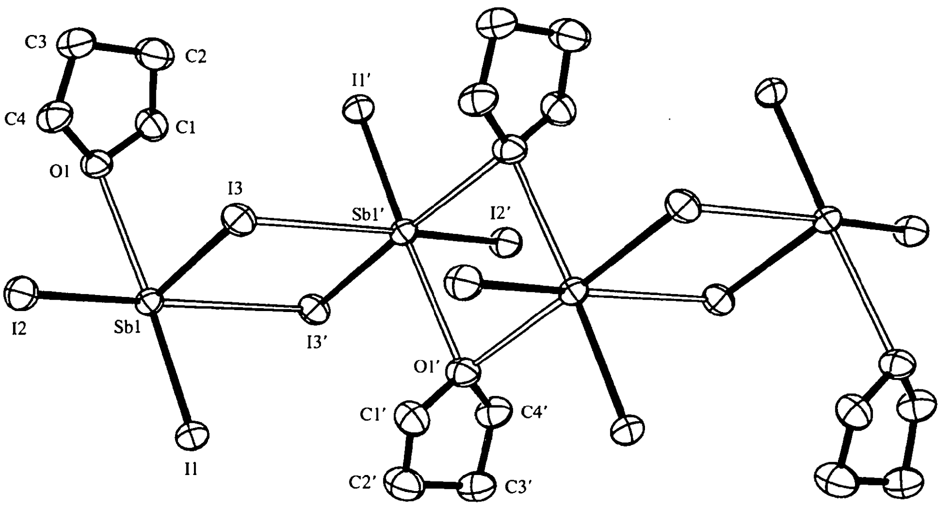


Fig. 2. A view of part of the polymeric structure of $SbI_3(thf)$ showing the atom-numbering scheme. Ellipsoids are drawn at the 50% probability level.

The compound $[SbI_3(thf)]$, (2), is the first structurally characterized example of a thf adduct of an antimony halide and is quite different from any previously described neutral bismuth halide thf adducts. The structure (Fig. 2) 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 such that each Sb atom has an octahedral coordination geometry. With regard to the antimony–iodine bonds, there are three short bonds [Sb1—I1 2.7610 (5), Sb1—I2 2.7574 (5) and Sb1—I3 2.7974 (5) Å] which have a mutually *fac* arrangement, and a fourth much longer bond [Sb1—I3^{ii} 3.6842 (5) Å; see Table 2 for symmetry code] which lies *trans* to I2. The I3 atoms are bridging and, as can be seen from the Sb—I distances, the bridging interaction is highly asymmetric, although its effect on the Sb1—I3 bond is apparent in that this bond is slightly longer than the Sb1—I1 and Sb1—I2 bonds. The thf ligands bridge the antimony centres more symmetrically [Sb1—O1 2.854 (4) and Sb1—O1^{i} 3.020 (4) Å; see Table 2 for symmetry code], although with Sb—O bonds which are quite long (*cf.* a terminal Sb—O distance of 2.236 Å in $[SbCl(thf)\{Cr(CO)_5\}_2]$; Sigwarth, Weber, Zsolnai & Huttner, 1985). Furthermore, this compound is unusual in having bridging thf ligands, since such a bridging role is very rare, the only other example of which we are aware being $[Ti_2F_4(C_5H_4Me)_2(\mu\text{-}F)_2(\mu\text{-}thf)]$ (Herzog *et al.*, 1994). The *M*—O—*M* angle in (2) is notably larger [95.2 (2)°] than in the titanium complex [Ti—O—Ti 80.3 (6)°]. None of the interbond angles at antimony deviate significantly (>10°) from idealized octahedral angles indicating little stereochemical activity of the Sb^{III} lone pair in (2). A similar conclusion holds for (1).

Experimental

Reactions were carried out using standard Schlenk and dry box techniques under an atmosphere of nitrogen or argon gas. Compound (1) was obtained as a side product from the reaction between $BiCl_3$ (0.500 g, 1.59 mmol) in THF, and lithium 2,6-dichlorophenoxide prepared from 2,6-dichlorophenol (0.772 g, 0.00476 mol) and ^{n}BuLi (3 ml of 1.6 *M* solution in *n*-hexanes) in Et_2O. After filtration, crystallization yielded white needle-like crystals. Orange crystals of (2) were obtained as a side product of the co-crystallization of SbI_3 (0.392 g) and TCNE (tetracyanoethene) (0.1 g) in a minimum of THF layered with hexane. Crystals coated with a hydrocarbon oil were mounted on a glass fibre with silicone grease under an argon atmosphere.

Compound (1)

Crystal data

$[Li(C_4H_8O)_4]_2[Bi_2Cl_8(C_4H_8O)_2]$
$M_r = 718.24$
Monoclinic
$P2_1/n$
$a = 10.598\ (2)$ Å
$b = 24.577\ (3)$ Å
$c = 11.378\ (4)$ Å
$\beta = 104.24\ (2)°$
$V = 2872.7\ (12)$ Å^3
$Z = 4$
$D_x = 1.661$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 72 reflections
$\theta = 5–50°$
$\mu = 6.535$ mm^{-1}
$T = 173\ (2)$ K
Block
0.3 × 0.3 × 0.2 mm
Clear

Data collection

Siemens SMART area detector diffractometer
ω rotation with narrow frame scans
Absorption correction: *SADABS* (Sheldrick, 1996)
$T_{min} = 0.044$, $T_{max} = 0.096$
13 321 measured reflections

5039 independent reflections
2685 reflections with $I > 2\sigma(I)$
$R_{int} = 0.129$
$\theta_{max} = 25.02°$
$h = -12 \rightarrow 11$
$k = -19 \rightarrow 29$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.086$
$S = 0.854$
5039 reflections
280 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.021P)^2]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$

$(\Delta/\sigma)_{max} = -0.015$
$\Delta\rho_{max} = 1.79$ e Å^{-3} (0.91 Å from Bi1)
$\Delta\rho_{min} = -2.07$ e Å^{-3} (0.36 Å from Bi1)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Bi1—Cl1	2.558 (3)	Bi1—Cl2^{i}	2.924 (3)
Bi1—Cl3	2.565 (3)	Li1—O3	1.90 (2)
Bi1—Cl4	2.576 (3)	Li1—O4	1.93 (2)
Bi1—O5	2.588 (7)	Li1—O2	1.91 (2)
Bi1—Cl2	2.896 (3)	Li1—O1	1.94 (2)
Cl1—Bi1—Cl3	91.67 (9)	Cl4—Bi1—Cl2	170.08 (8)
Cl1—Bi1—Cl4	94.52 (9)	O5—Bi1—Cl2	87.6 (2)
Cl3—Bi1—Cl4	92.51 (9)	Cl1—Bi1—Cl2^{i}	96.42 (9)
Cl1—Bi1—O5	175.7 (2)	Cl3—Bi1—Cl2^{i}	170.29 (9)
Cl3—Bi1—O5	84.2 (2)	Cl4—Bi1—Cl2^{i}	92.20 (8)
Cl4—Bi1—O5	84.7 (2)	O5—Bi1—Cl2^{i}	87.8 (2)
Cl1—Bi1—Cl2	93.59 (9)	Cl2—Bi1—Cl2^{i}	81.22 (9)
Cl3—Bi1—Cl2	92.96 (9)	Bi1—Cl2—Bi1^{i}	98.78 (9)

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

Compound (2)

Crystal data

$[SbI_3(C_4H_8O)]$
$M_r = 574.55$
Monoclinic
$P2_1/n$
$a = 7.92871\ (11)$ Å
$b = 12.663\ (2)$ Å
$c = 11.447\ (3)$ Å
$\beta = 94.116\ (3)°$
$V = 1146.40\ (3)$ Å^3
$Z = 4$
$D_x = 3.329$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 197 reflections
$\theta = 5–50°$
$\mu = 10.430$ mm^{-1}
$T = 293\ (2)$ K
Block
0.4 × 0.3 × 0.2 mm
Orange

Data collection

Siemens SMART area detector diffractometer
ω rotation with narrow frame scans
Absorption correction: *SADABS* (Sheldrick, 1996)
$T_{\min} = 0.019$, $T_{\max} = 0.064$
7156 measured reflections
2606 independent reflections
2134 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 27.46°$
$h = -10 \rightarrow 9$
$k = -16 \rightarrow 15$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.057$
$S = 0.818$
2606 reflections
82 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 3.591P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

Sb1—I2	2.7574 (5)	Sb1—O1$^{\rm i}$	2.854 (4)
Sb1—I1	2.7610 (5)	Sb1—O1	3.020 (4)
Sb1—I3	2.7974 (5)	Sb1—I3$^{\rm ii}$	3.6842 (5)
I2—Sb1—I1	94.64 (2)	I3—Sb1—O1	84.37 (8)
I2—Sb1—I3	93.49 (2)	O1$^{\rm i}$—Sb1—O1	95.22 (11)
I1—Sb1—I3	96.65 (2)	I2—Sb1—I3$^{\rm ii}$	174.02 (2)
I2—Sb1—O1$^{\rm i}$	82.66 (8)	I1—Sb1—I3$^{\rm ii}$	83.385 (14)
I1—Sb1—O1$^{\rm i}$	83.58 (8)	I3—Sb1—I3$^{\rm ii}$	81.156 (14)
I3—Sb1—O1$^{\rm i}$	176.15 (8)	O1$^{\rm i}$—Sb1—I3$^{\rm ii}$	102.68 (8)
I2—Sb1—O1	82.45 (8)	O1—Sb1—I3$^{\rm ii}$	99.58 (7)
I1—Sb1—O1	176.99 (8)		

Symmetry codes: (i) $-x, 2-y, 2-z$; (ii) $1-x, 2-y, 2-z$.

For both data sets, unit-cell dimensions were determined from reflections taken from three sets of 30 frames (at 0.3° steps in ω) each at 30 s exposure for (1) and 20 s for (2). A full hemisphere of reciprocal space was scanned by 0.3° ω steps at φ = 0, 88 and 180° with the area detector held at $2\theta = -27°$. The crystal-to-detector distance was 4.974 cm. Crystal decay was monitored by repeating the initial 50 frames at the end of data collection and analysing the duplicate reflections. No decay was observed in either data set. H atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the $U_{\rm iso}$ value of their attached C atom for aromatics and 1.5 times $U_{\rm iso}$ for all others.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1995); program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1150). Services for accessing these data are described at the back of the journal.

References

Carmalt, C. J., Clegg, W., Elsegood, M. R. J., Errington, R. J., Havelock, J., Lightfoot, P., Norman, N. C. & Scott, A. J. (1996). *Inorg. Chem.* **35**, 3709–3712.

Eveland, J. R. & Whitmire, K. H. (1996). *Inorg. Chim. Acta*, **249**, 41–46.

Herzog, A., Feng-Quan, L., Roesky, H. W., Demsar, A., Keller, K., Noltemeyer, M. & Pauer, F. (1994). *Organometallics*, **13**, 1251–1256.

Krautscheid, V. H. (1994*a*). *Z. Anorg. Allg. Chem.* **620**, 1559–1564.

Krautscheid, V. H. (1994*b*). Personal communication.

Sheldrick, G. M. (1995). *SHELXTL-Plus*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1996). *SADABS. Program for Absorption Correction.* University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT. Area-Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sigwarth, B., Weber, U., Zsolnai, L. & Huttner, G. (1985). *Chem. Ber.* **118**, 3114–3126.

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Bis(pyridine-*N*)(7,8,17,18-tetracyano-5,10,15,20-tetraphenylporphyrinato)nickel(II) Dimethanol Solvate

HUGUES DUVAL, VÉRONIQUE BULACH, JEAN FISCHER AND RAYMOND WEISS

Laboratoire de Cristallochimie et Chimie Structurale, UA 424, Université Louis Pasteur, Institut Lebel, 4, rue Blaise Pascal, 67070 Strasbourg CEDEX, France. E-mail: fischer@chimie.u-strasbg.fr

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Abstract

The title compound, $[\mathrm{Ni(C_{48}H_{24}N_8)(C_5H_5N)_2].2CH_4O}$, is a high-spin bis(pyridine)–Ni$^{\rm II}$ derivative of an antipodally β-pyrrole–tetracyano-substituted *meso*-tetraphenylporphyrin. The [Ni(py)$_2${tpp(CN)$_4$}] molecule [py is pyridine and tpp(CN)$_4$ is 7,8,17,18-tetracyano-5,10,15,20-tetraphenylporphyrinato] lies on a crystallographic centre of symmetry, but its non-crystallographic symmetry is close to D_{2h}. The core of the tpp(CN)$_4$ porphyrin dianion is essentially planar. The high-spin state of the Ni$^{\rm II}$ cation leads to a lengthening of the Ni—N(pyrrole) bond distances relative to those present in the low-spin [Ni$^{\rm II}$tpp] derivative. Moreover, the electron-withdrawing β-pyrrole cyano substituents, which lie in the antipodal pyrrolic rings, cause an increase in the C7—C8 and the antipodal C7′—C8′ bond distances as well as an opening of the C6—N2—C9 and the antipodal C6′—N2′—C9′ bond angles.

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