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Structure of Bis(1-thia-4,7-diazacyclononane)cobalt(III) Perchlorate

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Abstract. $[Co(C_6H_{14}N_2S)_2](ClO_4)_3$, $M_r = 649{\cdot}8$, orthorhombic, *Pmnn*, $a = 8{\cdot}838$ (2), $b = 10{\cdot}652$ (2), $c = 12{\cdot}606$ (2) Å, $V = 1186{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}818$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 12{\cdot}35$ cm^{-1}, $F(000) = 668$, $T = 294$ K, final $R = 0{\cdot}055$ for 945 reflections. The tridentate macrocyclic ligands coordinate in an arrangement having *trans* S atoms with Co—S 2·238 (1) Å and Co—N 1·984 (3) Å. The geometry about Co is approximately octahedral. The C atoms of the nine-membered ring show disorder.

Introduction. The stereochemistries, electron-transfer and spectral properties of thioether complexes, particularly those of multidentate ligands, have been the subject of recent and extensive studies. The complex $[Co(daes)_2]Cl_3.2H_2O$ [daes = di(aminoethyl) sulfide] has been structurally characterized (Hammershoi, Larsen & Larsen, 1978) and adopts a geometry with the S atoms in *cis* positions. All attempts to prepare an isomer with *trans* S atoms proved unsuccessful (Searle & Larsen, 1976). Preparation and spectral analysis of the complex $[Co(tasn)_2]^{3+}$ (tasn = 1-thia-4,7-diazacyclononane) gave equivocal results; the absorption spectrum was similar to that of $[Co(daes)_2]^{3+}$, suggesting that the *cis* isomer was again the one formed, while the ^{13}C NMR spectrum indicated the presence of more than one isomer (Gahan, Lawrence & Sargeson, 1982). However, chromatographic techniques which are normally successful at separating such isomers failed to achieve any separation in this case.

In order to establish the geometry adopted by the title complex we have determined its structure and report it here.

Experimental. Complex prepared as described previously (Gahan *et al.*, 1982); crystals obtained by ethanol vapour diffusion into a water solution of the perchlorate salt. Data collected using Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated Mo $K\alpha$ radiation, space group *Pmnn*;* 25 independent reflections with $19° \leq 2\theta \leq 25°$ used for least-squares determination of cell constants; intensities of three standard reflections monitored, less than 1% decomposition. Structure solved by heavy-atom method with *SHELX*76 (Sheldrick, 1976); H atoms included at calculated sites (C—H and N—H, 0·97 Å). Co, N, S and Cl atoms anisotropic, all others isotropic. Full-matrix least-squares refinement based on F values converged with shifts $< 0{\cdot}05\sigma$ in positional parameters of non-H atoms. Maximum excursions in a final difference map, $\pm 0{\cdot}7$ e Å^{-3}. All calculations performed with *SHELX*76 (Sheldrick, 1976). Scattering factors (neutral Co for Co^{III}) and anomalous-dispersion terms taken from *International Tables for X-ray Crystallography* (1974). Data-collection and refinement parameters are given in Table 1. Final positional parameters are listed in Table

* Non-standard setting of *Pnnm*. Equivalent positions: $\pm(x, y, z;\ x, -y, -z;\ \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z;\ \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z)$.

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2,* and interatomic distances and angles in Table 3. A view of the complex cation is shown in Fig. 1, drawn with *ORTEP* (Johnson, 1965).

Discussion. The structure consists of the complex cation and two perchlorate anions; all moieties lie on symmetry sites and are disordered. One perchlorate lies at a site of $2/m$ symmetry and the other on a twofold axis giving a total of six perchlorate anions per unit cell. There are weak H bonds between the latter perchlorate and the amine H atom.

The complex cation lies at a site of $2/m$ symmetry giving the expected 3:1 stoichiometry. The chelate rings of the complex are disordered with all rings adopting each of the two possible skew conformations with equal probability. This is not unexpected since the conformation usually adopted by the cyclononane ring does not conform to m symmetry. Refinement was also attempted in space group $P2nn$ but was hampered by large correlations and did not lead to disappearance of the disorder.

Cobalt to donor-atom bond distances are similar to those observed for $[Co(daes)_2]Cl_3.2H_2O$ (Hammershoi *et al.*, 1978) as is the N—Co—S angle in the chelate ring. The precision of all other distances and angles is limited by the disorder and they are not discussed further.

The geometry adopted in the present structure has *trans* S donor atoms in contrast to the

* Lists of structure factors, anisotropic thermal parameters, positional and thermal parameters of H atoms, and close intermolecular contact distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43053 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Summary of data-collection and processing parameters*

Crystal dimensions	0·25 × 0·18 × 0·18 mm
Data-collection range	$2 < 2\theta < 50°$
Scan width	$(1·00 + 0·35\tan\theta)°$
Horizontal counter aperture	$(2·40 + 0·50\tan\theta)$ mm
Scan type	ω–1·33θ
Absorption correction	
number of sampling points	256
max. correction	2·052
min. correction	1·128
Range of *hkl*	0→10, 0→12, −15→15
Total data collected	2374
Unique data after merging	1086
R_{int}	0·044
Data with $I > 2·5\sigma(I)$	945
Total variables	108
R	0·055
wR	0·079
Weighting constants $[w = g/(\sigma^2F_o + kF_o^2)]$	$g = 5·0$, $k = 0·00060$

Table 2. *Positional* (× 10[4]) *and equivalent isotropic thermal parameters*

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	B_{eq}(Å^2)	Occupancy
Co(1)	0	0	0	1·99	1·0
S(2)	0	0·1734 (1)	−0·1003 (1)	3·12	1·0
N(3)	−0·1520 (4)	0·0837 (3)	0·0918 (2)	2·77	1·0
C(4)	−0·1704 (12)	0·2403 (9)	−0·0620 (8)	3·56	0·5
C(5)	−0·2063 (13)	0·2088 (11)	0·0543 (8)	4·20	0·5
C(6)	−0·0848 (11)	0·0953 (10)	0·1997 (8)	3·54	0·5
C(4′)	−0·1471 (11)	0·2649 (9)	−0·0257 (9)	3·36	0·5
C(5′)	−0·2495 (11)	0·1732 (9)	0·0324 (7)	3·02	0·5
C(6′)	0·0763 (13)	0·1436 (12)	0·1854 (8)	4·50	0·5
Cl(7)	0	0	0·5000	4·85	1·0
O(8)	0	0·1290 (11)	0·4433 (9)	5·10	1·0 (1)
O(9)	0	0·0898 (22)	0·5831 (16)	5·10	0·46 (1)
O(10)	−0·1382 (22)	0·0093 (15)	0·5592 (16)	5·10	0·25 (1)
O(11)	−0·0883 (45)	0·0541 (34)	0·5946 (27)	5·10	0·26 (1)
O(12)	0·1705 (49)	0	0·5000	5·10	0·07 (1)
O(13)	0·0678 (73)	0·0470 (62)	0·4220 (44)	5·10	0·07 (1)
Cl(14)	0	0·5155 (2)	−0·2672 (2)	4·33	1·0
O(15)	0	0·3930 (20)	−0·3102 (28)	5·10	0·30 (2)
O(16)	0	0·5104 (20)	−0·1446 (17)	5·10	0·30 (2)
O(17)	−0·1410 (11)	0·5839 (9)	−0·2855 (14)	5·10	0·50 (2)
O(19)	−0·0898 (31)	0·5866 (22)	−0·3342 (23)	5·10	0·20 (1)
O(20)	−0·1411 (21)	0·5645 (20)	−0·2397 (25)	5·10	0·25 (2)
O(21)	−0·0593 (50)	0·5312 (26)	−0·1589 (22)	5·10	0·16 (2)
O(22)	−0·0324 (18)	0·3839 (13)	−0·2709 (16)	5·10	0·32 (2)
O(23)	−0·0392 (25)	0·5166 (19)	−0·3960 (17)	5·10	0·16 (1)

Table 3. *Interatomic distances* (Å) *and angles* (°)

S(2)—Co(1)	2·238 (1)	N(3)—Co(1)	1·984 (3)
C(4)—S(2)	1·73 (1)	C(4′)—S(2)	1·88 (1)
C(5)—N(3)	1·49 (1)	C(6)—N(3)	1·49 (1)
C(6′)—N(3^{i})	1·50 (1)	C(5′)—N(3)	1·49 (1)
C(5)—C(4)	1·54 (2)	C(6′)—C(6)	1·52 (1)
C(5′)—C(4′)	1·52 (1)	O(8)—Cl(7)	1·55 (1)
O(9)—Cl(7)	1·42 (2)	O(10)—Cl(7)	1·43 (2)
O(11)—Cl(7)	1·54 (3)	O(12)—Cl(7)	1·51 (4)
O(13)—Cl(7)	1·26 (6)	O(15)—Cl(14)	1·41 (2)
O(16)—Cl(14)	1·54 (2)	O(17)—Cl(14)	1·462 (9)
O(19)—Cl(14)	1·38 (2)	O(20)—Cl(14)	1·40 (2)
O(21)—Cl(14)	1·47 (3)	O(22)—Cl(14)	1·43 (2)
O(23)—Cl(14)	1·66 (2)		
N(3)—Co(1)—S(2)	87·6 (1)	N(3)—Co(1)—N(3^{ii})	94·8 (2)
N(3)—Co(1)—N(3^{i})	85·2 (2)	C(4)—S(2)—Co(1)	100·5 (3)
C(4′)—S(2)—Co(1)	98·4 (3)	C(5)—N(3^{i})—Co(1)	115·7 (4)
C(6)—N(3)—Co(1)	107·5 (4)	C(6′)—N(3)—Co(1)	110·4 (4)
C(5′)—N(3)—Co(1)	112·7 (4)	C(5′)—N(3)—C(6′)	112·5 (7)
C(5)—C(4)—S(2)	110·8 (7)	C(4)—S(2)—C(4′^{i})	104·1 (8)
C(5′)—C(4′)—S(2)	108·7 (6)	C(4′)—C(5′)—N(3)	108·0 (7)
C(6)—N(3)—C(5)	110·0 (6)	C(6′)—C(6)—N(3)	107·0 (7)
C(4)—C(5)—N(3)	115·4 (7)		

Symmetry code: (i) $-x, y, z$; (ii) $x, -y, -z$.

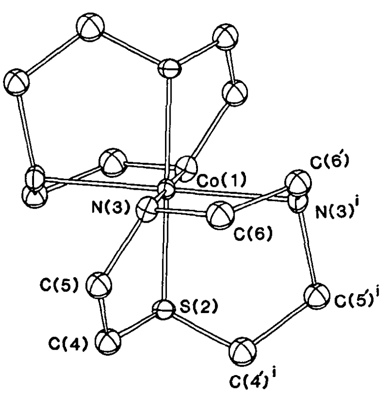

Fig. 1. View of $[Co(tasn)_2]^{3+}$ with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. One contributor to the disordered C-atom sites is omitted for clarity. Symmetry code as in Table 3.

$[Co(daes)_2]Cl_3.2H_2O$ structure (Hammershoi *et al.*, 1978). A similar result has been observed for the analogous Ni complexes, $[Ni(daes)_2](ClO_4)_2$ (Hart, Boeyens & Hancock, 1983) and $[Ni(tasn)_2](NO_3)_2$ (Hart, Boeyens, Michael & Hancock, 1983), which adopt *cis* and *trans* S geometries respectively. The ^{13}C NMR spectrum of $[Co(tasn)_2]^{3+}$ has eight resonances, and is inconsistent with the presence of only the *trans* isomer for which only three resonances are expected. Thus, we must conclude that the chromatographic methods have failed in this case to achieve a separation of the isomers. This result must cast a slight doubt on the report that only one isomer of $[Co(daes)_2]^{3+}$ exists, although the ^{13}C NMR spectrum in that case does support that assertion (Searle & Larsen, 1976).

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[(+)-(*R*)-2,2′-Bis(diphenylphosphino)-6,6′-dimethylbiphenyl](8,9,10-trinorborna-2,5-diene)rhodium(I) Tetrafluoroborate

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Abstract. $[Rh(C_7H_8)(C_{38}H_{32}P_2)]BF_4$, $M_r = 832·48$, orthorhombic, $P2_12_12_1$, $a = 12·292\ (2)$, $b = 16·766\ (6)$, $c = 18·167\ (7)$ Å, $V = 3744\ (2)$ Å^3, $Z = 4$, $D_x = 1·476\ (1)$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 0·587$ mm^{-1}, $F(000) = 1704$, $T = 210$ K, final $R = 0·036$ for 2247 reflections. The rhodium atom has a distorted square-planar coordination involving the two phosphorus atoms and the two double bonds in norbornadiene. The norbornadiene molecule is tilted 13·7 (1)° compared with the P(1)—Rh—P(2) plane. The diphosphine ligand coordinates to the Rh^I and forms a seven-membered chelate ring with a λ skew(v) conformation. The helical chirality of both phosphorus atoms is assigned as *P* (right-handed). The coordination of the diphosphine ligand causes the dihedral angle between the least-squares planes through the two phenyl rings in the biphenyl unit to be 71·8 (3)°. The absolute conformation of the diphosphine ligand has been assigned as *R*.

Introduction. Optical yields approaching 100% have been obtained by the use of chiral rhodium(I) diphosphine complexes (Knowles, Vineyard, Sabacky & Stults, 1979; Chan, Pluth & Halpern, 1979*a*). An interesting new type of chiral diphosphine ligand, (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, subsequently abbreviated binap, was recently published (Miyashita, Yasuda, Takaya, Toriumi, Ito, Souchi & Noyori, 1980) and the structure of its rhodium(I) norbornadiene complex was determined by X-ray crystallography (Toriumi, Ito, Takaya, Souchi & Noyori, 1982). In order to obtain a catalyst system which would be easier to modify, both enantiomers of the ligand bis(diphenylphosphino)-6,6′-dimethylbiphenyl have been prepared (Hansen & Schmid, 1984; Frejd, 1986). The ligand is abbreviated dimep below. Here we report an X-ray study of the tetrafluoroborate salt of the Rh^I complex with ligands dimep and norbornadiene.

Experimental. Dark red crystals of [Rh(norbornadiene)-{(+)-dimep}]BF_4 were grown from a $(C_2H_5)_2O/CHCl_3$ solution; approximate dimensions 0·10 ×

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