μ-Peroxo-bis[*trans*-chloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III)] bis(tetraphenylborate) diacetone solvate

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The title complex, $[Co_2Cl_2(\mu-O_2)(cyclam)_2](C_{24}H_{20}B)_2 \cdot 2Me_2CO$, was obtained when $[Co(cyclam)Cl_2](BPh_4)_2$ was crystallized from acetone in air; cyclam is 1,4,8,11-tetraazacyclotetradecane, $C_{10}H_{24}N_4$. The peroxo O–O moiety straddles a crystallographic centre of inversion (the two octahedral Co atoms are symmetrically bridged by the O_2 moiety), hence only half of the complex cation is in the asymmetric unit. A comparison of the O—O [1.483 (3) Å], Co—Cl [2.2647 (8) Å] and Co—O [1.894 (2) Å] bond lengths with similar bonds in previously determined structures indicates the oxidation of Co^{II} to Co^{III} during the crystallization process. In the crystal lattice, cation dimers are encapsulated by six $[BPh_4]^-$ anions, with C—H$\cdots\pi$ hydrogen bonds between the cyclam methylene groups and the phenyl rings of the anion.

Comment

Whilst tetraaza macrocyclic ligands have been extensively studied for several decades, their complexes still attract significant attention. This continued interest is due to the wide range of physical and chemical properties exhibited by these materials, one relevant example being the ability to bind dioxygen to Co^{II} or Fe^{II} centres (Busch & Alcock, 1994). An extensive series of saturated and unsaturated macrocycles is known, with one of the more widely used ligands being 1,4,8,11-tetraazacyclotetradecane, also known as cyclam (McAuley & Subramanian, 2000; Melson, 1979; Donnelly & Zimmer, 1999). As an 'innocent' ligand, cyclam is often used to coordinatively saturate the four equatorial sites of an octahedral centre, without influencing the nature of the metal centre. Thus, whilst investigating a series of complexes with axial hydrogen-bonding functionality, the complex [Co(cyclam)Cl$_2$](BPh$_4$)$_2$ was crystallized in air, yielding the oxygenated title compound, [Cl(cyclam)Co(μ-O$_2$)Co(cyclam)Cl](BPh$_4$)$_2\cdot$2Me$_2$CO, (I). A search of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) revealed 34 structures containing analogous Co–(μ-O$_2$)–Co moieties.

However, whilst 21 of these structures contain polydentate aminoalkane ligands (for example, ethylenetriamine or ethylenediamine), no saturated macrocyclic complexes have been reported.

(I)
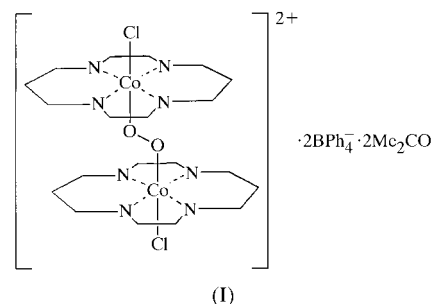
The molecular structure of the cobalt complex cation of (I) comprises two octahedral {Co(cyclam)Cl} moieties bridged by a dioxygen molecule (Fig. 1). The O—O bond straddles a crystallographic centre of inversion, hence only half of the cation, one anion and one solvent molecule are observed in the asymmetric unit.

With redox-active ligands (in this instance O$_2$) bridging two Co atoms, there is some difficulty in assigning formal oxidation states to the metal centres. Thus, the analogous structures in the CSD were examined to aid in the characterization of (I). Of the 21 structures, 12 are assigned Co^{II}–Co^{II}, three Co^{III}–Co^{III}, three Co^{II}–Co^{III}, while three are denoted Co^{II}–Co^{I}. In the structure of (I), either the Co atoms are both in the +3 oxidation state and bridged by a peroxide O_2^{2-} molecule, or there exists a mixed-valence Co^{II}–Co^{III} system, with the atoms bridged by superoxide O_2^-. However, the complex is characterized as comprising two peroxo-bridged octahedral Co^{III} atoms, due to two main features of the molecular structure supporting this assignation. Firstly, the O—O distance of (I) is 1.483 (3) Å, indicating a doubly bridging peroxo species,
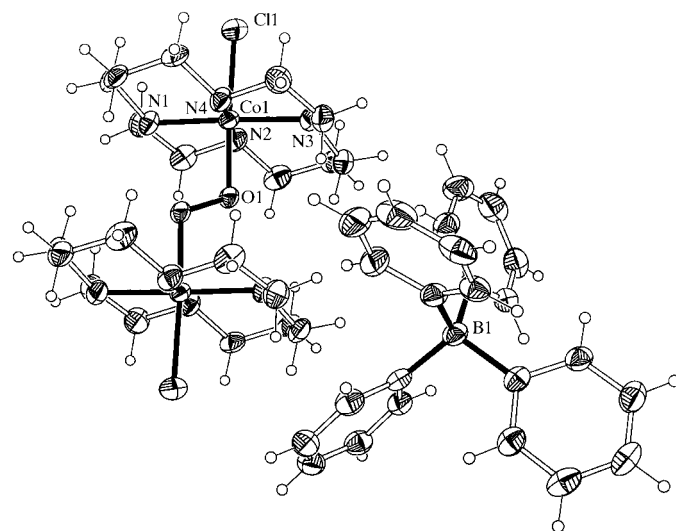

Figure 1
Displacement ellipsoid plot showing the atomic numbering scheme of (I) with atoms represented at the 50% probability level. The acetone molecules have been omitted for clarity.

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[doubly bridging peroxo complexes typically have O—O separations in the range 1.44–1.49 Å, compared with analogous superoxo values in the range 1.26–1.36 Å (Greenwood & Earnshaw, 1984)]. Secondly, the Co—Cl bond length of 2.2647 (8) Å supports the presence of Co^{III} over Co^{II} (Orpen *et al.*, 1989). The Co—O distance of 1.894 (2) Å does not assist this characterization, as the comparable structures in the CSD all have Co—O bond lengths in the range 1.742–1.947 Å. Of these, only one outlying structure {the Co^{II}–Co^{I} species [Co$_2$(en)$_4$(μ-OH)(μ-O$_2$)]I$_3$·H$_2$O; CSD refcode BATTAR (Bigoli *et al.*, 1981)} has a Co—O length below 1.842 Å. Thus, there is no significant correlation between assigned cobalt oxidation states and Co—O bond length.

Interestingly, the O—O—Co angle of 110.2 (2)° in (I) is lower than the value of 120° expected for an sp^2-hybridized O atom binding *via* a lone pair. The reason for this contraction is not readily apparent, especially as the cyclam ligands are well separated (the Co—N$_4$ mean planes are *ca* 4.30 Å apart). However, the geometry of the peroxide coordination here is consistent with the related structures in the CSD, which have
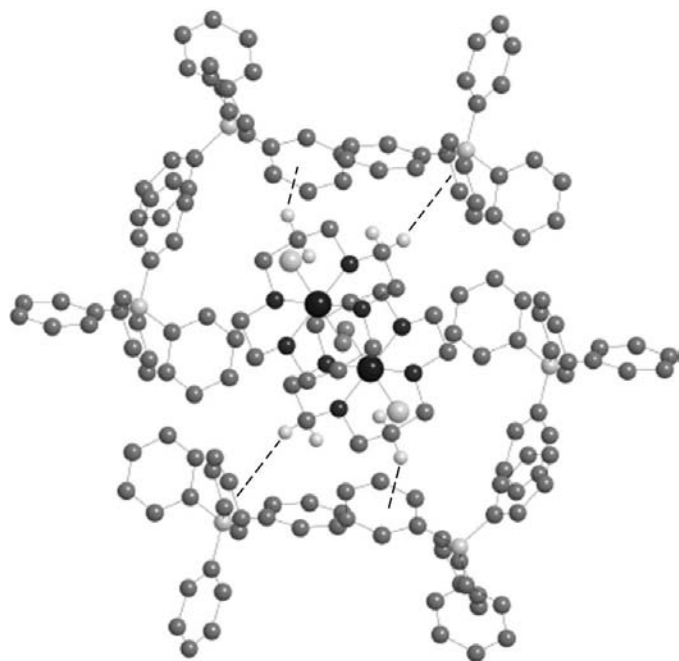

Figure 2
The cobalt dimer forms four interionic C—H···π contacts (shown as dashed lines) to closely packing anions.

O—O—Co values ranging from 109.8° in [Co$_2$(μ-O$_2$)L$_2$](ClO$_4$)$_4$ [L is N,N′,N″-tris(2-aminoethyl)ethane-1,2-diamine; CSD refcode VIRCAA (Gatehouse *et al.*, 1991)] to 120.6° in [Co$_2$(μ-O$_2$)L$_2${OC(NMe)$_2$}$_2$] [L is N,N′-ethylenebis(salicylideneiminate); CSD refcode DOESCF10 (Calligaris *et al.*, 1970)]. Evidently, the nature of this coordination is flexible, with small variations in local geometry permitted.

The Co—N distances of (I) are in the range 1.961 (2)–1.978 (2) Å, with the angles about the cobalt centre close to ideal octahedral values. All intramolecular bond lengths and angles for the tetraphenylborate anion and acetone solvent molecules are as expected.

The crystal lattice of (I) comprises a body-centred array of cations, with the long axis of the dimers aligned parallel to the z axis of the unit cell. The tetraphenylborate anions and acetone solvent molecules pack closely around the cobalt dimers, with no significant anion–anion interactions, and solvent molecules fill small pockets between the anions. Each cation is encapsulated by six nearest-neighbour [BPh$_4$]$^-$ anions, three surrounding each cyclam moiety of the dimer. This close packing results in two C—H···π contacts per cyclam ring from methylene H atoms to the phenyl rings of the anions (Fig. 2). Tetraphenylborate anions have been shown to be better aromatic hydrogen-bond acceptors than phenyl rings in neutral compounds (Steiner *et al.*, 2001), with aromatic hydrogen bonds having typical X···Ph$_{centroid}$ separations in the range 3.2–3.6 Å (where X is the donor atom). The donor groups from the cyclam ring are C7—H7A and C9—H9B, with C···Ph$_{centroid}$ separations of 3.427 (3) and 3.471 (3) Å, respectively. The C—H···Ph$_{centroid}$ angles are near linear, with H···Ph$_{centroid}$ distances of 2.614 (3) (for H7A) and 2.669 (3) Å (for H9B).

Experimental

Cyclam was prepared according to published methods (Barefield *et al.*, 1976). CoCl$_2$ and NaBPh$_4$ were purchased from Aldrich and used as received. Under a nitrogen atmosphere, a solution of cyclam (75 mg, 0.37 mmol) in EtOH (5 ml) was added to a blue solution of CoCl$_2$ (50 mg, 0.37 mmol) in EtOH (20 ml). Addition of a solution of NaBPh$_4$ (253 mg, 0.74 mmol) in EtOH (10 ml) gave an immediate brown precipitate, which analysed as [Co(cyclam)Cl$_2$](BPh$_4$)$_2$ (found: C 72.5, H 6.4, N 6.0%; calculated: C 72.2, H 6.3, N 5.8%), and was collected by filtration, washed with EtOH and Et$_2$O, and dried. Orange–brown crystals suitable for X-ray analysis were grown by allowing diethyl ether vapour to diffuse into a concentrated acetone solution (in air) over a period of 3 d.

Crystal data

[Co$_2$Cl$_2$(O$_2$)(C$_{10}$H$_{24}$N$_4$)$_2$]-(C$_{24}$H$_{20}$B)$_2$·2C$_3$H$_6$O	D_x = 1.299 Mg m^{-3}
M_r = 1367.94	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2759 reflections
a = 15.293 (2) Å	θ = 2.4–26.2°
b = 12.5644 (13) Å	μ = 0.61 mm^{-1}
c = 18.225 (2) Å	T = 150 (2) K
β = 92.610 (2)°	Cube, orange–brown
V = 3498.2 (6) Å^3	0.24 × 0.22 × 0.16 mm
Z = 2	

Data collection

Bruker SMART1000 CCD area-detector diffractometer	8132 independent reflections
ω scans	5620 reflections with >2$\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	R_{int} = 0.041
T_{min} = 0.895, T_{max} = 1.000	θ_{max} = 28.6°
24 509 measured reflections	h = −19 → 19
	k = −16 → 16
	l = −23 → 15

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0590P)^2 + 3.2407P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.047	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.134	$(\Delta/\sigma)_{max}$ = 0.002
S = 1.01	$\Delta\rho_{max}$ = 0.76 e Å^{-3}
8132 reflections	$\Delta\rho_{min}$ = −0.42 e Å^{-3}
417 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Co1—O1	1.8943 (18)	Co1—N4	1.975 (2)
Co1—N1	1.978 (2)	Co1—Cl1	2.2647 (8)
Co1—N2	1.967 (2)	O1—O1^i	1.483 (3)
Co1—N3	1.961 (2)		
O1—Co1—N3	89.66 (8)	N2—Co1—Cl1	93.57 (7)
O1—Co1—N2	90.57 (8)	N4—Co1—Cl1	87.52 (7)
O1—Co1—N4	88.36 (9)	N1—Co1—Cl1	88.45 (7)
O1—Co1—N1	88.52 (9)	O1^i—O1—Co1	110.17 (16)
N3—Co1—Cl1	93.44 (7)		

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

All H atoms were placed in idealized positions and were refined using a riding model (C—H = 0.95–0.99 Å). The anisotropic displacement parameters of the solvent O2 atom are large, suggesting that the atom is disordered over two sites. However, as attempts to model the disorder required severe constraints to yield very little improvement in the structure, this minor artefact was discounted. A view of the body-centred array of cation dimers has been deposited.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* and *SHELXTL* (Sheldrick, 1997a); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997b); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997b); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1072). Services for accessing these data are described at the back of the journal.

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