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Complex of cobalt(II) bromide with hexamethylphosphoric triamide

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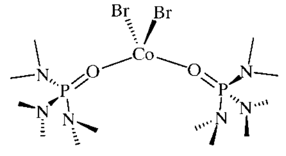
The title compound, dibromobis[tris(dimethylamino)phosphine oxide]cobalt(II), [CoBr$_2$(C$_6$H$_{18}$N$_3$OP)$_2$], displays tetrahedral coordination about cobalt. The molecule has twofold crystallographic site symmetry. The short P—N bonds and the planarity of the dimethylamino groups indicate the importance of *dπ–pπ* interactions. One of the NMe$_2$ groups has an irregular conformation about the P—N bond and deviates from planarity. It is ascribed to the steric hindrance induced by coordination at the O atom of hexamethylphosphoric triamide.

Comment

Hexamethylphosphoric triamide (HMPA) is an important solvent with very high nucleophilicity (the donor number D_N = 38.8) (Normant, 1967; Gutmann, 1978). Its bulky mushroom-like molecular shape leads to a tendency to form tetrahedral complexes with first-row bivalent metal ions, except for Mn^{II} (Wayland & Drago, 1965; Ozutsumi *et al.*, 1994). Steric interactions between coordinated HMPA molecules control the formation thermodynamics of halogeno complexes in this solvent (Abe *et al.*, 1989, 1992; Abe & Ishiguro, 1991). To obtain detailed structural information on HMPA in a tetrahedral coordination environment, we have performed an X-ray diffraction study of the title complex, (I).



(I)

The structure (Fig. 1) displays tetrahedral geometry and twofold crystallographic site symmetry, in which two Br atoms and two crystallographically equivalent HMPA molecules coordinate. The coordination bond length of HMPA [Co—O = 1.957 (4) Å] is similar to those in [Co(HMPA)$_4$]$^{2+}$ [1.94 (1) Å] and [CoCl(HMPA)$_3$]$^+$ [1.95 (1) Å] in solution determined by the fluorescent EXAFS method (Ozutsumi *et al.*, 1994). The coordination bond angle [Co—O—P = 145.3 (3)°] is at the lower end of the wide range of metal—O—P angles (144–173°) found in octahedral HMPA complexes (Carpentier *et al.*, 1972; Viossat *et al.*, 1977).

The intramolecular bond lengths and angles of HMPA are consistent with the reported values for this molecule. The P—N bonds [1.618 (5)–1.641 (5) Å] are much shorter than the typical single-bond length (1.77 Å), indicating partial double-bond character (Radonovich & Glick, 1973). This is further supported by the flattened dimethylamino groups; the NMe$_2$ groups are approximately planar, with the P—N—C and C—N—C angles close to 120°, which points to *sp*^{2} hybridization and strong *dπ–pπ* interactions.

The geometry around phosphorus is nearly tetrahedral; however, the molecule shows marked deviations from threefold rotational symmetry around the P═O bond. One of the dimethylamino groups (N1, C1 and C2) is clearly distinguished from the other two by the conformation around the P—N bond. This is manifested in its O—P—N—C torsion angles [54.1 (6) and −91.8 (6)°] compared with the corresponding values for the N2 [39.4 (6) and −153.8 (7)°] and N3 [35.9 (7) and −160.4 (6)°] moieties. Thus, the molecule adopts a propeller conformation, in which one of the wings is nearly perpendicular to the others.

A closer look reveals that the geometry of the N1 group is also markedly distorted from planarity towards pyramidal geometry. The planarity of these groups has been checked by defining a least-squares plane with the PCC atoms of a particular group. The N1 atom is 0.257 (7) Å from the plane defined by P, C1 and C2, whereas the N2 atom is 0.093 (8) Å from the P—C3—C4 plane and N3 is 0.120 (8) Å from the P—C5—C6 plane. It is also noted that the P—N1 bond is slightly longer than the other two. This is consistent with the observation that the dimethylamino group tends to depart from planarity towards pyramidal geometry as the P—N bond becomes longer (Hussain *et al.*, 1970).

The conformational and geometrical deviation of one dimethylamino group from the other two has commonly been observed in HMPA complexes and adducts, so that one might consider it as a fundamental structural feature of the molecule. There is an important exception, however, in which all three NMe$_2$ groups of HMPA adopt a similar conformation and planarity (Brown *et al.*, 1981). In the crystal structure of the adduct of AsMePh$_2$S and HMPA, the O—P—N—C torsion angles are all similar [42.8 (9)–46.7 (9) and −139.5 (10)–151.3 (9)°] and the NMe$_2$ groups are all planar. An unusual feature of this structure is that there is no interaction between HMPA and the sulfide other than van der Waals forces.

This suggests that coordination at the O atom may induce the conformational and geometrical change of one NMe$_2$ group in the HMPA complex. The torsion angle Co—O—P—N1 of 9.3 (6)° indicates that the N1 moiety is particularly close to the Co atom. Therefore, we have examined possible steric hindrance by assuming a hypothetical structure of the complex, in which the N1 group is rotated about the P—N1 bond to make the ‘unusual’ conformation, *i.e.* all the NMe_2 groups similar. In the resulting structure, the Co$\cdots$C1 distance is estimated to be 3.2–3.5 Å. This is appreciably smaller than the closest distance [Co$\cdots$C1 = 3.840 (8) Å] observed in the real structure. The steric repulsion may go beyond tolerance in the hypothetical conformation, leading to the rotation of one NMe_2 group and the actual conformation.

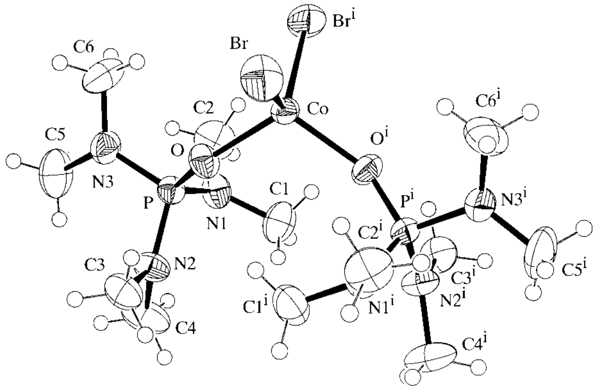


Figure 1
A molecular diagram of (I) showing the labelling of the non-H atoms [symmetry (i): $-x + 1, y, -z + \frac{3}{2}$]. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

Experimental

The title complex was prepared according to the literature (Bolster & Groeneveld, 1971). The single crystal was grown from a solution of the complex in nitromethane, and sealed in a capillary tube in a glove box over P_2O_5.

Crystal data

$[CoBr_2(C_6H_{18}N_3OP)_2]$
$M_r = 577.16$
Monoclinic, $C2/c$
$a = 23.525$ (7) Å
$b = 8.2344$ (8) Å
$c = 15.841$ (5) Å
$\beta = 127.996$ (14)°
$V = 2418.2$ (11) Å^3
$Z = 4$

$D_x = 1.585$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 13–15°$
$\mu = 4.16$ mm^{-1}
$T = 296$ (2) K
Prism, blue
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.434$, $T_{max} = 0.435$
5914 measured reflections
2921 independent reflections
2027 reflections with $I > 2\sigma(I)$

$R_{int} = 0.115$
$\theta_{max} = 28.3°$
$h = -31 \rightarrow 30$
$k = -10 \rightarrow 10$
$l = -20 \rightarrow 16$
3 standard reflections frequency: 60 min intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.212$
$S = 1.26$
2921 reflections
120 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0907P)^2 + 4.3903P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.08$ e Å^{-3}
$\Delta\rho_{min} = -1.04$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—Br	2.4041 (10)	P—N1	1.641 (5)
Co—O	1.957 (4)	P—N2	1.618 (5)
O—P	1.493 (4)	P—N3	1.633 (6)
Br—Co—Br^i	117.97 (6)	O—P—N2	110.1 (3)
Br—Co—O	104.99 (12)	O—P—N3	108.3 (3)
Br—Co—O^i	109.11 (12)	N1—P—N2	104.8 (3)
O^i—Co—O	110.7 (3)	N1—P—N3	108.2 (3)
Co—O—P	145.3 (3)	N2—P—N3	110.2 (3)
O—P—N1	115.2 (3)		
Co—O—P—N1	9.3 (6)	O—P—N2—C3	39.4 (6)
Co—O—P—N2	127.5 (5)	O—P—N2—C4	−153.8 (7)
Co—O—P—N3	−112.0 (5)	O—P—N3—C5	−160.4 (6)
O—P—N1—C1	54.1 (6)	O—P—N3—C6	35.9 (7)
O—P—N1—C2	−91.8 (6)		

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Methyl H atoms were placed at idealized tetrahedral positions with a fixed C—H distance and H—C—H angle, and refined using a riding-rotating model *via SHELXL*97. The displacement parameters were set at 1.5 times the equivalent isotropic displacement parameter of the methyl C atom.

Data collection, cell refinement and data reduction: AFC-5*S* software; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1472). Services for accessing these data are described at the back of the journal.

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