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H···Br hydrogen bonding in *trans*-bis(acetonitrile-*N*)tetraaqua-cobalt(II) dibromide

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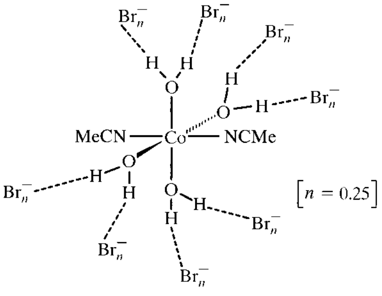
In the title complex, $[Co(CH_3CN)_2(H_2O)_4]Br_2$, the Co^{II} atom lies on an inversion centre and is octahedrally coordinated by two *trans* acetonitrile molecules and four water molecules. Hydrogen bonding between the water molecules and lattice bromide ions yields a three-dimensional structure.

Comment

Despite there being numerous acetonitrile- and aqua-metal complexes reported in the literature, *trans*-bis(acetonitrile-*N*)tetraaquacobalt(II) dibromide, (I), is the first reported structure of a metal complex where the ligands are exclusively coordinated water and acetonitrile molecules. The cobalt(II) atom lies on a centre of symmetry and is coordinated to two *trans* acetonitrile molecules and to four water molecules (Fig. 1). The metal coordination is close to octahedral (Table 1), with the maximum deviation ($X—Co—Y$) from 90° being 3.7 (2)°. The mean Co—O length, 2.063 Å, is consistent with reported $Co—OH_2$ distances of tetraaqua complexes (2.060–2.124 Å) (Abrahams *et al.*, 1996; de Meester & Skapski, 1973; Salas *et al.*, 1992). Variations in the two Co—O bond lengths [0.15 (7) Å], although here barely significant, have been observed previously in tetraaquacobalt(II) complexes; for example, *trans*-tetraaquabis(adenine)cobalt(II) has Co—O bond lengths of 2.073 (4) and 2.114 (5) Å, which the authors attributed to different constraints imposed by hydrogen-bonding linkages (de Meester & Skapski, 1973).



(I)

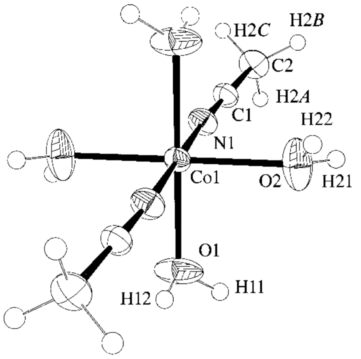


Figure 1
ORTEP-3 (Farrugia, 1997) diagram of $[Co(CH_3CN)_2(H_2O)_4]^{2+}$ with displacement ellipsoids drawn at the 50% probability level and H atoms of arbitrary size. Unlabelled atoms are related to labelled atoms by the inversion centre at Co1.

All the coordinated water H atoms form hydrogen bonds to adjacent bromide ions, creating a three-dimensional network (Fig. 2 and Table 2). Each bromide ion forms four hydrogen bonds in a distorted tetrahedral arrangement to different $[Co(CH_3CN)_2(H_2O)_4]^{2+}$ cations with H···Br distances consistent with the reported distances of 2.30–2.68 Å (Mikenda, 1986; Tegenfeldt *et al.*, 1979; Sieron & Bukowska-Strzyzewska, 1997). Three of the O—H···Br angles are close to the most probable angle of 160° for a two-centre hydrogen bond (Jeffrey *et al.*, 1985) while the fourth makes a smaller angle at the H atom, 135 (10)°, but with the Br···O contact the smallest at 3.283 (6) Å. The Br···O distances range from 3.283 (6) to 3.315 (6) Å compared with previously observed values between 3.195 (6) and 3.421 (3) Å (Kepert *et al.*, 1996; Sieron & Bukowska-Strzyzewska, 1997; Cunningham *et al.*, 1991).

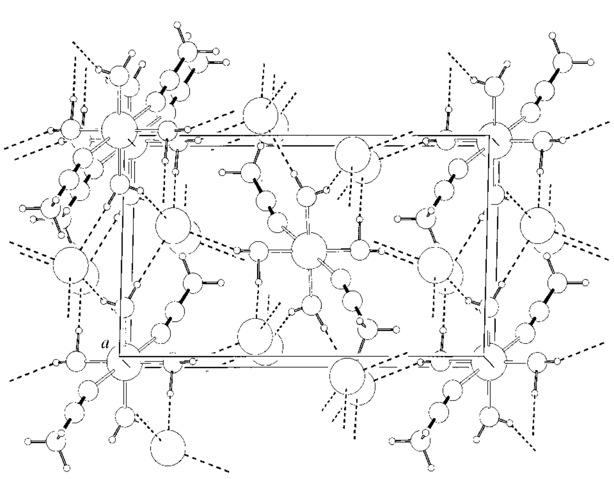


Figure 2
The three-dimensional network of O—H···Br bonds in the structure of $[Co(CH_3CN)_2(H_2O)_4]Br_2$ viewed down the *a* axis, with the *b* axis to the right. Some link atoms have been omitted for clarity.

As expected, the acetonitrile molecule is linear [N1—C1—C2 = 179.0 (6)°], but with bent coordination to the cobalt(II) [Co—N1—C1 = 165.0 (4)°]. Such coordination has been observed in polymeric $Co(O_2PF_2)_2(CH_3CN)_2$ [164.4°; Begley *et al.*, 1985]. Metal–acetonitrile bent coordination is indeed quite common with angles from 145.2 to 176.9°, and an average of 167°, having been reported (Agterberg *et al.*, 1998; Begley *et al.*, 1985; Chisholm *et al.*, 1996; Holligan *et al.*, 1992; Libby *et al.*, 1993). This average is somewhat lowered by the two extremely low values for nickel(II) (Holligan *et al.*, 1992) (145.2°) and manganese(III) (Libby *et al.*, 1993) (149.1°) complexes, which have been attributed to hydrogen bonding and steric effects, respectively.

Experimental

Crystals of $[Co(CH_3CN)_2(H_2O)_4]Br_2$ were obtained after unintentional co-extraction of excess $CoBr_2$ with CH_2Cl_2 from the reaction of excess $CoBr_2$ with hexakis(2-pyridyloxy)cyclotriphosphazene (prior to extraction with CH_2Cl_2, CH_3CN solvent was evaporated from the reaction mixture).

Crystal data

$[Co(CH_3CN)_2(H_2O)_4]Br_2$
$M_r = 372.92$
Monoclinic, $P2_1/c$
$a = 6.843$ (4) Å
$b = 12.553$ (7) Å
$c = 8.076$ (5) Å
$\beta = 111.370$ (8)°
$V = 646.0$ (6) Å^3

$Z = 2$
$D_x = 1.917$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 7.502$ mm^{-1}
$T = 158$ (2) K
Block, pale brown
0.44 × 0.22 × 0.16 mm

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan [*SAINT* (Siemens, 1994) and *SADABS* (Sheldrick, 1996)]
$T_{min} = 0.151$, $T_{max} = 0.301$
4724 measured reflections

1313 independent reflections
925 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 26.4°$
$h = -8 \rightarrow 7$
$k = -6 \rightarrow 15$
$l = -9 \rightarrow 10$

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.087$
$S = 0.904$
1313 reflections
78 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 1.050$ e Å^{-3}
$\Delta\rho_{min} = -0.523$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O2	2.056 (5)	N1—C1	1.125 (6)
Co1—O1	2.071 (5)	C1—C2	1.454 (7)
Co1—N1	2.112 (4)		
O2—Co1—O1	90.3 (2)	O1^i—Co1—N1	89.13 (19)
O2—Co1—N1	86.34 (18)	C1—N1—Co1	164.9 (4)
O1—Co1—N1	90.87 (19)	N1—C1—C2	179.2 (6)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H11···Br1	0.98 (7)	2.38 (6)	3.315 (6)	161 (5)
O1—H12···Br1^i	0.64 (7)	2.65 (7)	3.295 (6)	175 (7)
O2—H21···Br1^{ii}	0.88 (7)	2.42 (7)	3.289 (5)	169 (7)
O2—H22···Br1^{iii}	0.76 (10)	2.70 (11)	3.283 (6)	135 (10)

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The H atoms bound to O1 and O2 were located from a difference Fourier synthesis and refined unrestrained; methyl-H atoms are in calculated positions. The residual electron-density maximum is 0.97 Å from Br1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1994) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *WINGX* (Farrugia, 1998), *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1257). Services for accessing these data are described at the back of the journal.

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