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Tetrakis(2,2′-bipyridine)tetra-μ_3-hydroxo-di-μ-trifluoroacetato-tetracobalt(II) diiodide diacetonitrile monohydrate: a compound containing a tetranuclear 'cubane'-type cobalt(II) core

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A new compound, $[Co_4(C_2F_3O_2)_2(OH)_4(C_{10}H_8N_2)_4]I_2\cdot 2C_2H_3N\cdot H_2O$, containing a tetranuclear cobalt(II)–hydroxo core with a cube-like structural geometry is reported. The four Co^{II} coordination polyhedra are irregular octahedra and the Co^{II} atoms are linked by three hydroxo and trifluoroacetate ions resulting in a Co_4O_4 core with approximate tetrahedral symmetry. The coordination polyhedra share edges with short Co···Co distances. A bond valence analysis shows that a cube-like arrangement of atoms in a tetranuclear cluster is ideal for the clusters $[M_4(OR)_4]^{4+}$ (R is a strongly binding group) and $[M_4O_4]^{8+}$ when the metal ions are in oxidation states of +2 and +4, respectively.

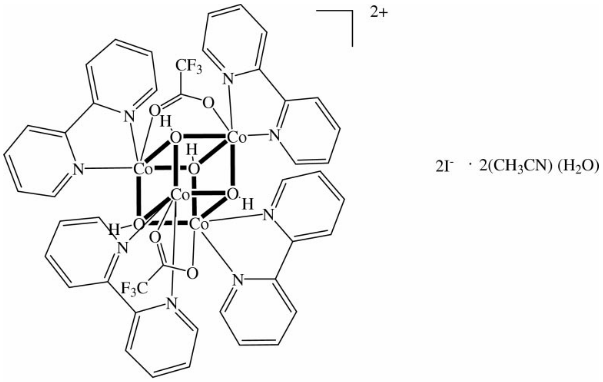
Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.058
wR factor = 0.139
Data-to-parameter ratio = 16.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Many polynuclear oxo-bridged metal complexes having a cubane-type structural geometry have been characterized. In a cube-like cluster, the coordination polyhedra share edges and the distances between cationic metal centers are short, thereby decreasing the stability of the compound (Pauling, 1927). However, a bond-valence analysis (Brown, 2002) shows that a cube-like arrangement is ideal for all $[M_4O_4]$ clusters when the metal ions are in oxidation states of +4 and +2, respectively. In this arrangement, each O atom forms three analogous bonds to the metal ions and the valence sums of the M—O bonds at each O atom are −2 and −1 for oxidation states of +4 and +2, respectively. In an M^{2+} cluster, the O atom needs to form one more strong bond. In known coordination compounds with organic ligands, the O atom binds to a proton or to a C atom of an alkyl group (Brechin *et al.*, 1996; Chiang *et al.*, 2001; Gubina *et al.*, 2002; He & Lippard, 2000, Wang *et al.*, 2001; Kessler *et al.*, 2001; Simonov *et al.*, 1982). Other groups, such as SiO_4, PO_4 and BO_3 anions, can be envisaged with one O atom forming the corner of the cube. Cubane-type fragments occur in



(I)

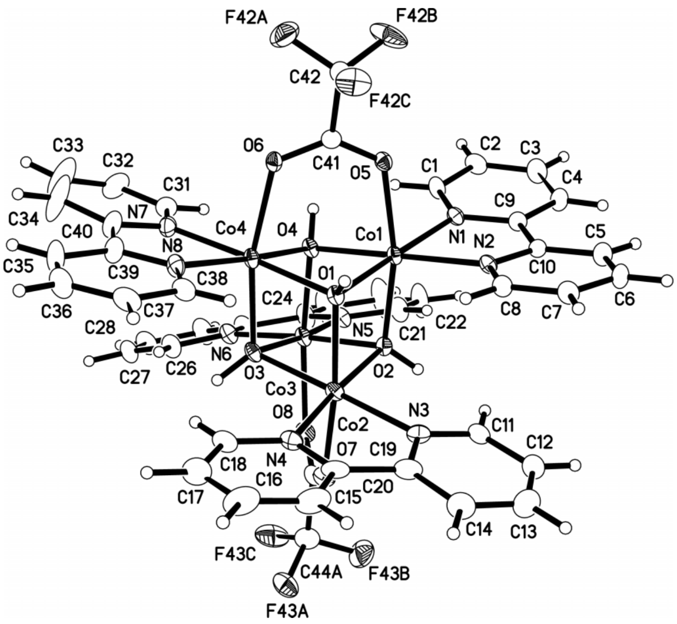


Figure 1
A displacement ellipsoid plot of the molecular structure of the cationic complex of (I). Only one component of the disordered CF_3 group is shown for clarity. Non-H atoms are represented by 30% probability ellipsoids and H atoms are shown as circles with an arbitrary radius.

inorganic crystals, notably the orthosilicates, $M_2(SiO_4)$. This structural arrangement is overlooked in these crystals because of the extended networks of other bonds. A cubane motif occurs in most redox-active proteins, as it is an arrangement in which several metal atoms in a variety of oxidation states can exist in close proximity and therefore be involved in directed electron transfer.

The asymmetric unit of this compound consists of the cobalt complex, $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CCF_3)_2(C_{10}H_8N_2)_4]^{2+}$ containing a distorted 'cubane' $[Co_4(OH)_4]^{4+}$ cluster bridged by two trifluoroacetate ions (Fig. 1), two iodide ions, two acetonitrile molecules and a water molecule of crystallization. The complex has no imposed crystallographic symmetry, but the $[Co_4(OH)_4]^{4+}$ cluster has approximate T_d ($\overline{4}3m$) symmetry with the Co and O atoms occupying the corners of two irregular tetrahedra. Deviation of this cluster from a regular cube is a consequence of the different sizes of Co and O atoms and may be thought of as occurring by displacements of the Co atoms from the centroid of the cluster along the body diagonals of the cube. Each Co^{II} ion is coordinated by four μ_3-hydroxide moieties, a bipyridine molecule and an O atom of a trifluoroacetate ion with irregular octahedral coordination geometry. Each hydroxo O atom links three Co^{II} atoms, resulting in the edges of the three polyhedra being shared with short Co$\cdots$Co separations [3.003 (1)–3.242 (1) Å]. The trifluoroacetate ions bridge the pairs of atoms Co1/Co4 and Co2/Co3. The distances Co1$\cdots$Co4 [3.028 (1) Å] and Co2$\cdots$Co3 [3.004 (1) Å] are therefore shorter than the distances Co2$\cdots$Co4 [3.242 (1) Å] and Co3$\cdots$Co4 [3.186 (1) Å]. The corresponding Co—O(hydroxo)—Co bond angles involving pairs of Co atoms bridged by carboxylate groups are nearly right angles [91.9 (1)–92.9 (1)°], while those that are not bridged are much larger [99.5 (1)–101.8 (1)°]. This effect is a consequence of the rigidity of the carboxylate bond angles, which brings the Co atoms closer to each other. The Co—O bond distances are in the range 2.073 (2)–2.155 (3) Å and are typical for Co^{II} ions.

The valence sums for all Co and O atoms (without hydrogen bonds) are close to +2.0 and −2.0, respectively, and this confirms that the cube-like arrangement is stable for a $[Co_4(OH)_4]^{2+}$ cluster. The valence sums also indicate that the H atoms will have no tendency to form further strong bonds. According to Pauling's electroneutrality principle (Pauling, 1960), the overall positive charge of the complex is likely to be distributed over the H atoms of the hydroxo groups and the bipyridine ligands. The iodide counter-ions, due to their large size, are ideal for forming weak hydrogen bonds. Two of the four hydroxo H atoms donate hydrogen bonds to iodide counter-ions (O1—H1O$\cdots$I1*A* and O2—H2O$\cdots$I2), while the others donate bonds to the acetonitrile and water molecules of crystallization (O3—H3O$\cdots$N1*SA* and O4—H4O$\cdots$O1*S*). Although water was not used in the preparation of this compound, an O atom belonging to a water molecule of crystallization was located during the refinement. The low residual electron density and the presence of suitable hydrogen-bond donors and acceptors for this water molecule confirmed that this assignment was correct. The proportion of water in the crystal structure is small and this water may have come from one of the reagents (probably 2,2′-bipyridine).

Experimental

$[Co(O_2CCF_3)_2(C_{10}H_8N_2)_2]$ was prepared by stirring a mixture of cobalt(II) dichloride (1.5 mmol), 2,2′-bipyridine (1.5 mmol), and NaO_2CCF_3 (4.5 mmol) in tetrahydrofuran (30 ml) for 24 h at room temperature. Crystals were obtained by slowly diffusing the resulting pink solution into hexane. Compound (I) was prepared by stirring a mixture of $[Co(O_2CCF_3)_2(C_{10}H_8N_2)_2]$ (0.25 mmol) and cobalt(II) diodide (0.25 mmol) in tetrahydrofuran (20 ml) for 12 h at room temperature. The solid product was collected by filtration, washed and re-dissolved in acetonitrile (10 ml). Diffraction quality crystals were obtained from the filtrate after several days.

Crystal data

$[Co_4(C_2F_3O_2)_2(OH)_4(C_{10}H_8N_2)_4]$-
$I_2\cdot 2C_2H_3N\cdot H_2O$
M_r = 1508.45
Orthorhombic, *Pbca*
a = 20.027 (1) Å
b = 18.774 (1) Å
c = 29.771 (2) Å
V = 11194 (1) $Å^3$
Z = 8

D_x = 1.790 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 5517 reflections
θ = 2.5–27.3°
μ = 2.35 mm^{-1}
T = 110 (2) K
Prism, brown
0.29 × 0.25 × 0.11 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
T_{min} = 0.549, T_{max} = 0.782
72 201 measured reflections

12 523 independent reflections
8819 reflections with $I > 2\sigma(I)$
R_{int} = 0.068
θ_{max} = 27.5°
$h = -25 \rightarrow 23$
$k = -24 \rightarrow 24$
$l = -38 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.139$
$S = 1.04$
12 523 reflections
775 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2 + 25.7334P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.028$
$\Delta\rho_{\max} = 1.67$ e Å^{-3}
$\Delta\rho_{\min} = -1.00$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O2	2.083 (3)	Co2—Co3	3.0034 (7)
Co1—O1	2.091 (2)	Co2—Co4	3.2419 (8)
Co1—O4	2.095 (3)	O2—Co3	2.092 (3)
Co1—N1	2.122 (3)	Co3—O3	2.073 (2)
Co1—O5	2.129 (3)	Co3—O4	2.101 (3)
Co1—N2	2.134 (3)	Co3—N5	2.113 (3)
Co1—Co4	3.0283 (7)	Co3—N6	2.133 (3)
O1—Co2	2.086 (3)	Co3—O8	2.154 (3)
O1—Co4	2.088 (3)	Co3—Co4	3.1864 (7)
Co2—O2	2.087 (2)	O3—Co4	2.089 (3)
Co2—O3	2.104 (3)	Co4—O4	2.085 (2)
Co2—N4	2.118 (3)	Co4—N8	2.129 (3)
Co2—N3	2.120 (4)	Co4—N7	2.134 (3)
Co2—O7	2.138 (3)		
O2—Co1—O1	80.29 (9)	O3—Co3—O4	80.21 (9)
O2—Co1—O4	78.6 (1)	O2—Co3—O4	78.3 (1)
O1—Co1—O4	84.42 (9)	Co2—Co3—Co4	63.09 (2)
O2—Co1—N1	101.6 (1)	Co3—O3—Co4	99.9 (1)
O4—Co1—N1	99.5 (1)	Co3—O3—Co2	92.0 (1)
O1—Co1—O5	89.37 (9)	Co4—O3—Co2	101.29 (11)
N1—Co1—O5	89.2 (1)	O4—Co4—O1	84.73 (9)
N1—Co1—N2	76.7 (1)	O4—Co4—O3	80.20 (9)
O5—Co1—N2	89.7 (1)	O1—Co4—O3	78.5 (1)
Co2—O1—Co4	101.9 (1)	O1—Co4—N8	103.2 (1)
Co2—O1—Co1	99.3 (1)	O3—Co4—N8	100.4 (1)
Co4—O1—Co1	92.85 (9)	O4—Co4—O6	92.8 (1)
O1—Co2—O2	80.32 (9)	O1—Co4—O6	89.6 (1)
O1—Co2—O3	78.2 (1)	O3—Co4—O6	166.7 (1)
O2—Co2—O3	85.05 (9)	Co1—Co4—Co3	62.80 (2)
O1—Co2—N4	98.1 (1)	Co1—Co4—Co2	60.90 (2)
O3—Co2—N4	101.0 (1)	Co3—Co4—Co2	55.79 (2)
O1—Co2—N3	101.9 (1)	Co4—O4—Co1	92.85 (9)
O2—Co2—Co4	81.77 (7)	Co4—O4—Co3	99.1 (1)
Co3—Co2—Co4	61.21 (2)	Co1—O4—Co3	101.2 (1)
Co1—O2—Co2	99.5 (1)	O6—C41—O5	131.1 (4)
Co1—O2—Co3	101.8 (1)	O6—C41—C42	115.3 (3)
Co2—O2—Co3	91.88 (9)	O5—C41—C42	113.5 (3)
O3—Co3—O2	85.7 (1)	O8—C43—O7	131.4 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···I1*A*	0.95 (2)	2.78 (2)	3.672 (2)	157 (3)
O2—H2O···I2	0.967 (9)	2.67 (1)	3.641 (2)	176 (2)
O3—H3O···N1*SA*	0.966 (9)	2.04 (1)	2.944 (7)	155 (2)
O4—H4O···O1*S*	0.96 (2)	2.08 (2)	2.954 (5)	150 (3)
O1*S*—H1*SB*···I1*A*$^{\text{i}}$	0.99 (2)	2.49 (3)	3.471 (4)	171 (3)
O1*S*—H1*SA*···N2*SA*	0.98 (2)	1.86 (2)	2.79 (1)	159 (3)

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

The solvent molecules of crystallization and one iodide ion refined with values of U_{eq} that were larger than the non-solvent atoms and with prolate ellipsoids. These atoms were split into two discrete positions and refined isotropically with their displacement parameters constrained to be equal to each other. This approach gave an improved electron-density model that included one position for each solvent molecule with anisotropic displacement ellipsoids. However, the U_{iso} values for these atoms were large and it is likely that the crystal lost some solvent during the analysis. The populations of each component of the disordered atoms were refined with the combined occupancy of each atom fixed at unity. A CF_3 group was disordered by rotation about its C—C bond axis and was modeled using three components. The site-occupancy factors [0.437 (4), 0.275 (4) and 0.288 (4)] for each component were refined with the restraint that the sum of their occupancies equals one. These F atoms were refined anisotropically with prolate ellipsoids representing the diffuse electron density. Several C atoms belonging to one of the bipyridine ligands refined with prolate ellipsoids. For example C23 and C24 refined with values for U_{11} and U_{12} in the ranges 0.094 (4)–0.068 (3) and 0.027 (2)–0.024 (2) Å^2, but bonds and intermolecular contacts involving these atoms made chemical sense so they were not split. The disorder in this crystal accounts for the larger than usual *R* factors. All the H atoms belonging to the hydroxo groups could be located in difference electron-density maps. Further evidence of their presence is that all of them are in suitable positions for donating hydrogen bonds to either iodide counter-ions or solvent molecules of crystallization. These H atoms were refined with restraints on the O—H distances [O—H = 0.952(18)—0.967(19) Å]. Phenyl and methyl H atoms were placed in geometrically optimized positions (C—H = 0.95 and 0.98 Å) and the bond distances and angles were idealized during refinement with the H-atom U_{iso} values set at 1.2 and 1.5 times the equivalent isotropic U_{eq} of the C atoms to which they were attached. After refinement of the $[Co_4(\mu_3\text{-}OH)_4(\mu\text{-}O_2CCF_3)_2(C_{10}H_8N_2)_4]^{2+}$ complex, the two iodide ions and the two acetonitrile molecules, a large peak (5.8 e Å^{-3}) was present in the difference map. This peak was in an ideal position for accepting a hydrogen bond from H4O. This peak was used to add an O atom of a water molecule. H atoms belonging to the water molecule were placed in positions for donating hydrogen bonds to atoms I1*A* and N2*SA* and refined with the O—H and H···H distances restrained [O—H = 0.977 (16) and 0.988 (16) Å, and H···H = 1.59 (3) Å]. The highest residual peak is located 0.32 Å from atom H1*SB* and the deepest hole is located 0.25 Å from atom C1*SA*.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *X-SEED* (Barbour, 2001) and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *SHELXTL* (Bruker, 2000).

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