Diaquatetramethanolcobalt(II) sulfate

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In the title compound, $[Co(CH_3OH)_4(H_2O)_2]SO_4$, the Co^{II} atom and S atom lie on special positions on a twofold rotation axis. The Co^{II} ion is six-coordinated by four O atoms of methanol molecules and two water molecules in a distorted octahedral geometry. The cations and anions are linked by hydrogen bonds into a three-dimensional supramolecular network.

Comment

The study of metal–oxime complexes is currently subject to extensive research owing to their increasingly recognized biochemical activities and unusual electronic properties (Chaudhuri, 2003). Terephthalaldoxime is a potential multidentate bridging agent formed by condensing terephthalaldehyde with hydroxylamine. However, there are no reports of any metal derivative. Recently, we used it as ligand to react with $CoSO_4 \cdot 6H_2O$ in a mixed solution of MeOH (10 ml) and DMF (2 ml), but we obtained a new cobalt complex by accident, namely, $[Co(CH_3OH)_4(H_2O)_2]SO_4$, (I), whose crystal structure is reported here.

(I)
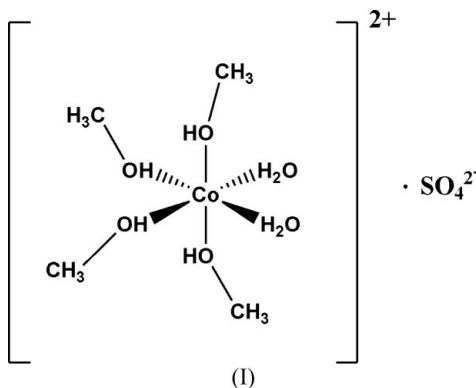
The structure of (I) comprises a tetramethanolcobalt(II) cation and a sulfate anion (Fig. 1). The Co^{II} atom and S atom lie on special positions on a twofold rotation axis. The Co center has a slightly distorted octahedral coordination geometry defined by four O atoms from methanol molecules and two water molecules. Atoms O1, O1^i, O1W and O1W^i form the equatorial plane of the octahedron, with an average atomic displacement of 0.04 (4) Å, while the Co^{II} ion is coplanar with the equatorial plane. The two hydroxyl atoms, O2 and O2^i, are located in the axial positions, with an O—Co—O angle of 178.79 (8)° [symmetry code: (i) $x - y + \frac{1}{3}$, $-y + \frac{2}{3}$, $-z + \frac{1}{6}$].

The ions are linked by O—H···O hydrogen bonds involving the water molecules, the methanol molecules and the O atoms
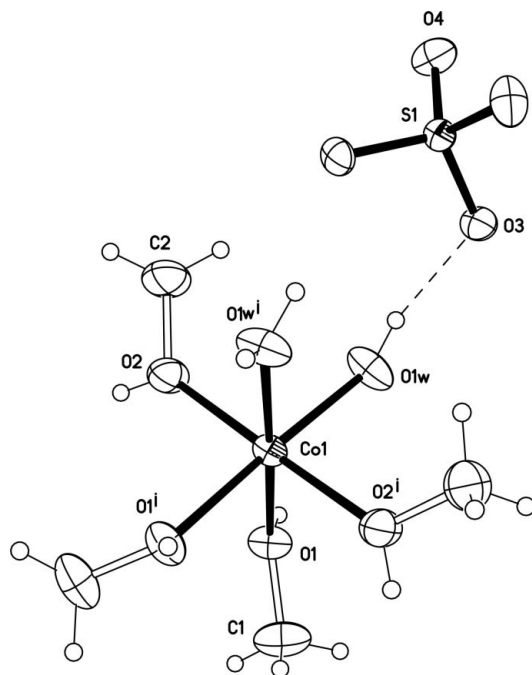
Figure 1
The structure of the cation and anion of (I), showing 30% probability displacement ellipsoids. The dashed line indicates an intermolecular hydrogen bond. [Symmetry code: (i) $x - y + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{6}$.]
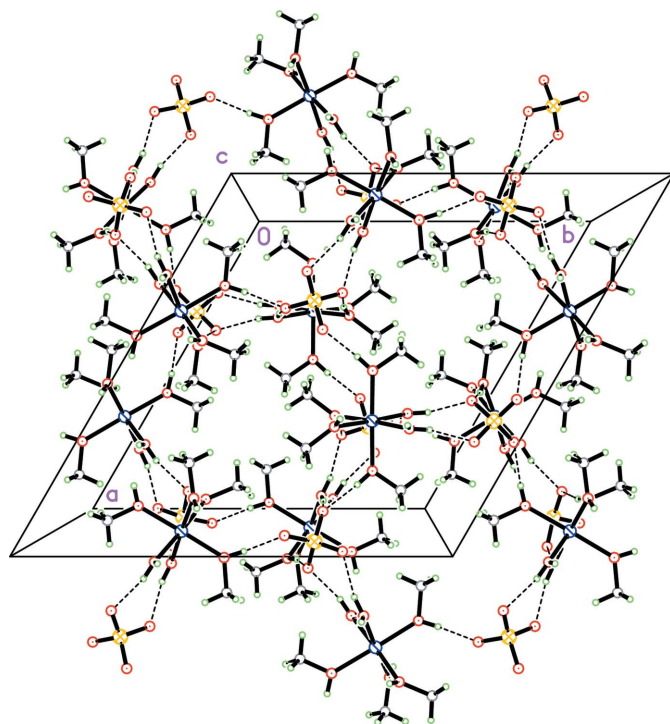

Figure 2
The three-dimensional supramolecular network of (I), with hydrogen bonds indicated by dashed lines.

of the SO_4^{2-} into a three-dimensional hydrogen-bonded framework. These hydrogen bonds appear to complement the Coulombic interaction and help to further stabilize the structure (Fig. 2 and Table 2).

Experimental

The title complex was prepared by the addition of $CoSO_4\cdot6H_2O$ (0.263 g, 1 mmol) and terephthalaldoxime (0.164 g, 1 mmol) to a mixed solvent of MeOH (10 ml) and DMF (2 ml). The mixture was stirred for 0.5 h at room temperature and then filtered. Orange crystals separated from the filtered solution after several days. Analysis calculated for $C_4H_{20}CoO_{10}S$: C 15.05, H 6.32%; found: C 15.09, H 6.34%.

Crystal data

$[Co(CH_4O)_4(H_2O)_2]SO_4$	$D_x = 1.542$ Mg m^{-3}
$M_r = 319.19$	Mo $K\alpha$ radiation
Trigonal, $R\bar{3}c$	$\mu = 1.43$ mm^{-1}
$a = 15.656$ (2) Å	$T = 295$ (2) K
$c = 29.144$ (6) Å	Prism, orange
$V = 6186.8$ (17) Å^3	$0.32 \times 0.25 \times 0.18$ mm
$Z = 18$	

Data collection

Rigaku R-AXIS RAPID diffractometer	18840 measured reflections
ω scans	1583 independent reflections
Absorption correction: multi-scan ($ABSCOR$; Higashi, 1995)	1383 reflections with $I > 2\sigma(I)$
$T_{min} = 0.657$, $T_{max} = 0.783$	$R_{int} = 0.020$
	$\theta_{max} = 27.5°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0486P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$+ 4.4049P]$
$wR(F^2) = 0.079$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
1583 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
88 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Co1—O1	2.0940 (12)	Co1—O1W	2.0584 (13)
Co1—O2	2.0703 (15)		
O1—Co1—O1^i	88.16 (7)	O1W—Co1—O1	91.42 (5)
O2—Co1—O1	87.62 (6)	O1W^i—Co1—O1	177.48 (6)
O2^i—Co1—O1	93.25 (6)	O1W—Co1—O2	89.21 (7)
O2^i—Co1—O2	178.79 (8)	O1W^i—Co1—O2	89.93 (6)

Symmetry code: (i) $x - y + \frac{1}{3}, -y + \frac{2}{3}, -z + \frac{1}{6}$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1W1$\cdots$O4^{ii}	0.839 (13)	1.847 (9)	2.6839 (18)	176 (3)
O1W—H1W2$\cdots$O3	0.84 (3)	1.89 (3)	2.7117 (17)	170 (3)
O1—H1$\cdots$O3^{ii}	0.84 (3)	1.85 (3)	2.6770 (16)	168 (2)
O2—H2$\cdots$O4^{iii}	0.83 (3)	1.83 (3)	2.629 (2)	174 (3)

Symmetry codes: (ii) $y, -x + y, -z$; (iii) $-x + y, -x, z$.

The H atoms on carbon were placed in calculated positions, with C—H = 0.96 Å and U_{iso}(H) = $1.5U_{eq}$(C), in the riding-model approximation. O-bound H atoms were located in difference Fourier

maps and refined with an O—H distance restraint of 0.85 (1) Å and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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