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Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.029
wR factor = 0.087
Data-to-parameter ratio = 14.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Tetrahyronium hexaaquacobalt(II) bis{[propane-1,3-diyldiamine-*N,N,N',N'*-tetraacetato]cobaltate(III)} octamolybdate hexahydrate

The title compound, $(\text{H}_3\text{O})_4[\text{Co}(\text{H}_2\text{O})_6][\text{Co}(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_8)]_2[\text{Mo}_8\text{O}_{26}] \cdot 6\text{H}_2\text{O}$, features two anionic cobalt complexes and an octamolybdate ion (site symmetry $\bar{1}$), three cationic hydroxonium and one hexaaquacobalt(II) ions (site symmetry $\bar{1}$), and six isolated water molecules, forming an inorganic–organic hybrid. These cationic and anionic components together with isolated water molecules are linked together to form a three-dimensional framework connected by various hydrogen bonds.

Comment

Polyoxometalates, because of their diverse electronic, magnetic, photochemical and catalytic properties, are widely regarded as important molecular building units for inorganic–organic coordination polymers (Coronado & Gomez-Garcia, 1998; Hill, 1998). Recently, an important advance in polyoxomolybdate chemistry has been the modification of polyoxomolybdates with various organic ligands and transition metal complexes or fragments. The introduction of transition metal ligand units can not only enrich the framework of polyoxomolybdates but also improve their electronic and magnetic properties. Based on this approach, a large variety of organic–inorganic hybrid materials have been isolated (An *et al.*, 2005; Bar-Nahum *et al.*, 2005). In these compounds, the secondary transition metal complex often acts as cation.

In this paper we report a mixed anionic cobalt complex and cobalt-ion-based octamolybdate by the introduction of the diaminopropanetetraacetate (dpta) ligand. The asymmetric unit consists of half an $[\text{Mo}_8\text{O}_{26}]^{4-}$ complex, an anionic $[\text{Co}^{\text{III}}(\text{dpta})]^-$ complex, half a $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ cation, and three neutral and two protonated water molecules, as shown in Fig. 1. The centrosymmetric $[\text{Mo}_8\text{O}_{26}]^{4-}$ anion consists of eight MoO_6 units, assembled as two equivalent connected $[\text{Mo}_4\text{O}_{13}]^{2-}$ units. All Mo atoms within the $[\text{Mo}_8\text{O}_{26}]^{4-}$ clusters have distorted octahedral environments. The O atoms can be divided into four sets according to their bonding features, namely, terminal, bi-bridging, tri-bridging and penta-bridging O atoms. All Mo–O bond distances are within the expected ranges. Bond valence sum (BVS) calculations (Brown & Altermatt, 1985) show that the oxidation state of all the Mo atoms is located in the range 5.929–6.061, which agrees with the expected value of 6 for Mo atoms. In the $[\text{Co}^{\text{III}}(\text{dpta})]^-$ anion, the central Co ion is coordinated by four O atoms of the carboxylate groups and two N atoms. BVS calculations (3.123) demonstrate the +3 oxidation state of this Co atom, which indicates that the Co^{II} was oxidized to Co^{III} in the reaction. Interestingly, the Co atom of the hexaaqua cation is in the +2 oxidation state and each $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is surrounded by four $[\text{Co}^{\text{III}}(\text{dpta})]^-$ units linked by hydrogen bonds with $\text{O} \cdots \text{O}$

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distances in the range 2.702 (5)–3.208 (5) Å. These linked units extend along the *a* axis to form an infinite chain, with octamolybdate anions located between the chains, as depicted in Fig. 2. Moreover, the title compound further forms a three-dimensional network by various hydrogen bonds between hydronium ions, water molecules, polyanions, and anionic complexes. The detailed hydrogen bonding parameters are summarized in Table 1.

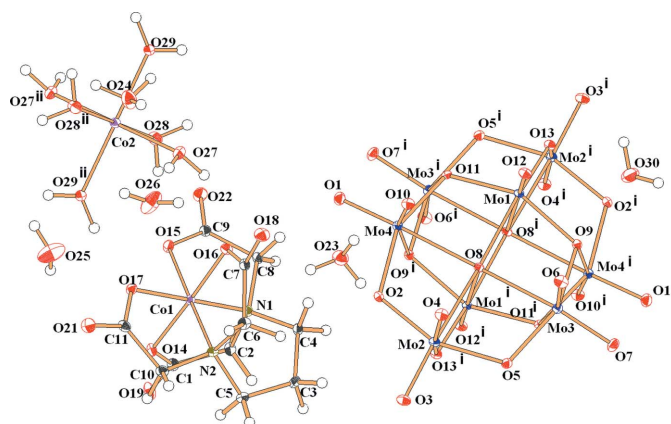
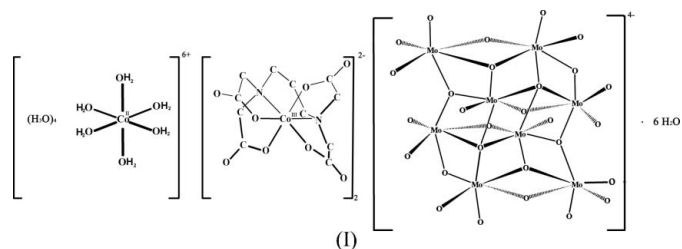


Figure 1

The contents of the asymmetric unit, together with symmetry-generated atoms to complete all the structural components. Displacement ellipsoids are drawn at the 30% probability level [symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, 1 - y, -z$].

Experimental

All the analytically pure reagents and solvents were purchased from Siping Chemical Reagent Company and used without further purification. H_2MoO_4 (1 g) was dissolved in 0.2 M NaOH solution (25 ml) with stirring. H_4dpta (0.12 g) and $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.5 g) were added to the transparent solution and the pH was adjusted to about 2.4 by adding 4 M HCl. The mixture was stirred at 353 K for about 2 h and then cooled to room temperature; the solution was filtered into a 50 ml beaker. Slow evaporation of the solvent at room temperature led, after several days, to violet crystals of the title compound suitable for X-ray diffraction.

Crystal data

$(\text{H}_3\text{O})_4[\text{Co}(\text{H}_2\text{O})_6] \cdot$	$\gamma = 78.4996 (8)^\circ$
$[\text{Co}(\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_8)]_2 \cdot$	$V = 1546.76 (14) \text{ \AA}^3$
$[\text{Mo}_8\text{O}_{26}] \cdot 6\text{H}_2\text{O}$	$Z = 1$
$M_r = 2257.08$	$D_x = 2.423 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.3925 (4) \text{ \AA}$	$\mu = 2.48 \text{ mm}^{-1}$
$b = 10.7997 (6) \text{ \AA}$	$T = 296 (2) \text{ K}$
$c = 17.4788 (10) \text{ \AA}$	Block, violet
$\alpha = 89.8891 (8)^\circ$	$0.27 \times 0.24 \times 0.22 \text{ mm}$
$\beta = 85.1910 (7)^\circ$	

Data collection

Bruker SMART APEX-II diffractometer	8404 measured reflections
ω scans	6031 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	5022 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.520, T_{\max} = 0.590$	$R_{\text{int}} = 0.019$
	$\theta_{\text{max}} = 26.1^\circ$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.029$	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$
$wR(F^2) = 0.087$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{\text{max}} < 0.001$
6031 reflections	$\Delta\rho_{\text{max}} = 0.73 \text{ e \AA}^{-3}$
430 parameters	$\Delta\rho_{\text{min}} = -0.96 \text{ e \AA}^{-3}$

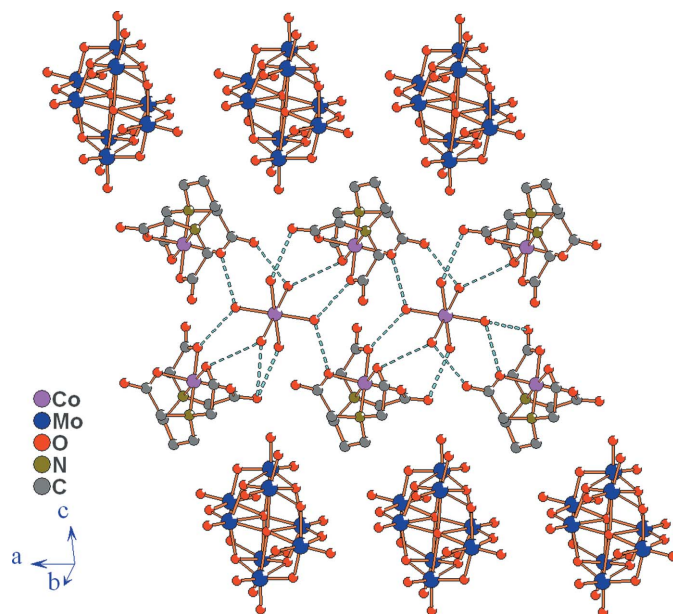


Figure 2

A view of the one-dimensional chain structure of hydrogen bonds (dashed lines) connecting $\text{Co}(\text{dpta})^-$ and $[\text{Co}(\text{H}_2\text{O})]^{2+}$ units surrounded by octamolybdate anions.

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O}23-\text{H}2 \cdots \text{O}10^i$	0.85	2.34	2.921 (5)	126
$\text{O}23-\text{H}3 \cdots \text{O}4$	0.85	2.36	3.131 (5)	151
$\text{O}23-\text{H}1 \cdots \text{O}12^j$	0.85	2.47	2.947 (4)	116
$\text{O}23-\text{H}2 \cdots \text{O}4^i$	0.85	2.29	2.994 (5)	141
$\text{O}24-\text{H}4 \cdots \text{O}21^{ii}$	0.89	1.92	2.814 (5)	173
$\text{O}24-\text{H}6 \cdots \text{O}22^{iii}$	0.92	1.91	2.826 (5)	175
$\text{O}24-\text{H}5 \cdots \text{O}7^i$	0.91	2.18	2.897 (5)	135
$\text{O}25-\text{H}7 \cdots \text{O}19^{iv}$	0.84	2.46	3.298 (6)	170
$\text{O}25-\text{H}8 \cdots \text{O}21$	0.84	2.09	2.836 (6)	147
$\text{O}26-\text{H}9 \cdots \text{O}25$	0.85	2.48	2.851 (8)	107
$\text{O}27-\text{H}12 \cdots \text{O}18$	0.87	2.14	2.960 (5)	158
$\text{O}27-\text{H}12 \cdots \text{O}16$	0.87	2.49	3.208 (5)	140
$\text{O}27-\text{H}11 \cdots \text{O}26$	0.85	1.86	2.702 (5)	177
$\text{O}28-\text{H}14 \cdots \text{O}19^{iii}$	0.89	1.96	2.848 (5)	173
$\text{O}28-\text{H}13 \cdots \text{O}15$	0.85	2.14	2.950 (5)	160

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O29–H16 \cdots O14 ⁱⁱ	0.83	1.95	2.776 (4)	178
O29–H15 \cdots O17 ⁱⁱⁱ	0.90	1.85	2.739 (4)	172
O30–H18 \cdots O26 ⁱ	0.85	2.36	2.904 (6)	122
O30–H17 \cdots O5 ⁱⁱ	0.86	2.06	2.907 (5)	170

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x, -y + 1, -z$.

Methylene H atoms were placed at calculated positions ($C-H = 0.97 \text{ \AA}$) and were allowed to ride on the carrier C atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All the other H atoms were located in a difference Fourier map and refined in their as-found positions ($O-H = 0.83\text{--}0.92 \text{ \AA}$) with a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Notably, this compound clearly must contain four additional protons for charge neutrality. The octamolybdate ion is too weak a base to bind extra protons and the four terminal O atoms of $\text{Co}(\text{dpta})_4$ form bonds to C of 1.52 valence units, which means that they are not likely to be hydrogen-bond donors. Similarly it is difficult for an H_3O^+ group to coordinate to Co^{II} . This leaves the free water molecules providing the only sites for the extra protons. The H_3O^+ ions are not easy to identify, probably because the structure contains only weak acceptors. However there are many $H \cdots O$ distances in the range 2.0–3.0 \AA , which suggests that the effective charge of the H_3O^+ ions is spread over many very weak $H \cdots O$ interactions. Under these conditions it becomes difficult to identify the hydronium groups from their chemistry alone and one must rely on the electron density, which

may also not give a clear answer in the presence of Mo and Co. In view of such considerations, the most suitable O23 and O24 atoms are assigned to be hydronium O atoms and six H atoms were located in the difference Fourier map and attached to atoms O23 and O24.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Bergerhoff *et al.*, 1996); software used to prepare material for publication: *SHELXTL*.

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