

A new tetramolybdenumcobaltdiphosphonate, $\text{Na}_8[\text{CoMo}_4\text{O}_{12}\{\text{MeC}(\text{O})(\text{PO}_3)_2\}_2]\cdot 18\text{H}_2\text{O}$

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Key indicators

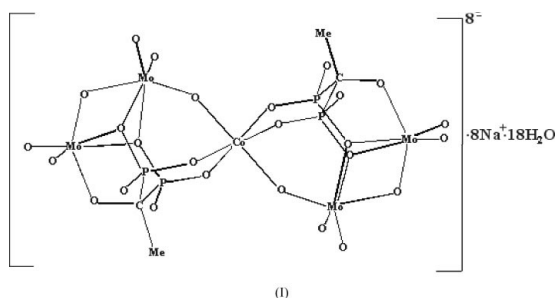
Single-crystal X-ray study
 T = 298 K
 Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
 H-atom completeness 15%
 R factor = 0.036
 wR factor = 0.069
 Data-to-parameter ratio = 15.0

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

A new tetramolybdate-diphosphate compound with the formula $\text{Na}_8[\text{CoMo}_4\text{O}_{12}\{\text{MeC}(\text{O})(\text{PO}_3)_2\}_2]\cdot 18\text{H}_2\text{O}$, octa-sodium(I) cobalt(II) tetramolybdenum(VI) bis(1-hydroxyethylidenediphosphate) octadecahydrate, has been synthesized under weakly acidic conditions (pH = 5.5–6.0). The $[\text{CoMo}_4\text{O}_{12}\{\text{MeC}(\text{O})(\text{PO}_3)_2\}_2]^{8-}$ anion comprises two $[\text{Mo}_2\text{O}_6\{\text{MeC}(\text{O})(\text{PO}_3)_2\}]^{5-}$ fragments linked by one six-coordinate Co^{II} atom. 1-Hydroxyethylidenediphosphate as a pentadentate ligand bonds to two pairs of face-sharing MoO_6 octahedra. The Co atom in the anion is situated on a centre of inversion.

Comment

In recent years, metal organophosphonate systems have received considerable attention because of their unusual structural chemistry and their applications as sorbents, catalysts and catalyst supports, and ion exchangers (Rodriguez, 1986; Rosenthal & Caruso, 1992; Burwell *et al.*, 1992; Cao & Mallouk, 1993). Furthermore, the organophosphonate group has also been shown to form molecular anion clusters with molybdenum (Kwak *et al.*, 1975; Stalick & Quicksall, 1976). In this kind of compound, it is normal to form Mo_5 (Yayasaki *et al.*, 1987; Finn & Zubieta, 2001), Mo_6 (Yayasaki *et al.*, 1987; Kortz & Pope, 1995; Cao *et al.*, 1993; Khan *et al.*, 1993), Mo_7 (Yayasaki *et al.*, 1987; Dumas *et al.*, 2002) polyoxomolybdates, the MoO_6 octahedra being linked by edge-sharing or angle-sharing.



The $\text{H}^+/\text{MoO}_4^{2-}/\text{hedp}$ ($\text{hedp} = 1\text{-hydroxyethylidenediphosphonate}$) acid system has been investigated previously (Tolkacheva *et al.*, 1992). The complexes are formed with $\text{Mo}:L$ ($L = \text{hedp}$) ratios of 1:2, 2:2, 2:1, 3:1 and 6:1, mainly depending on pH. A few transition metal–hedp complexes have been structurally characterized, including $M(\text{hedpH}_2)_2$ ($M = \text{Ni, Fe}$), $M_2(\text{hedpH}_2)_2$ ($M = \text{Cu, Fe}$) and $M_3(\text{hedpH}_2)_2$ ($M = \text{Cu}$) (Zheng *et al.*, 2002). A number of one-dimensional lanthanide–hedpH_n ($n = 1\text{--}3$; Nash *et al.*, 1998) compounds have also been structurally characterized. However, the transition metal/ $\text{MoO}_4^{2-}/\text{hedp}$ system has not been reported.

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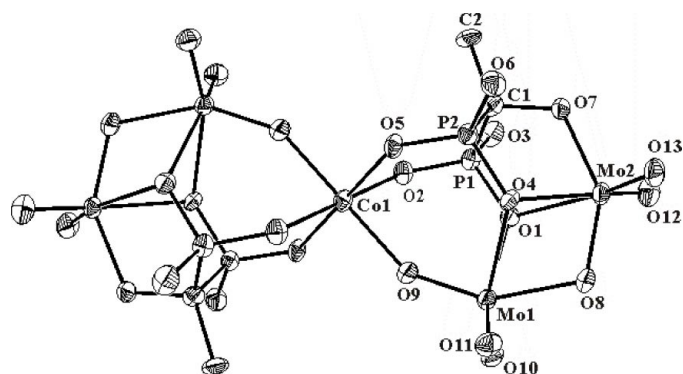


Figure 1
The anion of the title compound, with the atom-numbering scheme and 50%- probability displacement ellipsoids.

In this paper, we describe the synthesis and structure of $\text{Na}_8[\text{CoMo}_4\text{O}_{12}\{\text{MeC}(\text{O})(\text{PO}_3)_2\}_2]\cdot 18\text{H}_2\text{O}$.

Selected geometric parameters of the title compound are listed in Table 1. The anion $[\text{CoMo}_4\text{O}_{12}\{\text{MeC}(\text{O})(\text{PO}_3)_2\}_2]^{8-}$ and crystal packing of the compound are illustrated in Figs. 1 and 2. The tetramolybdocobalt diphosphonate polyanion, $[\text{CoMo}_4\text{O}_{12}\{\text{MeC}(\text{O})(\text{PO}_3)_2\}_2]^{8-}$, comprises a Co^{II} atom connecting two $[\text{Mo}_2\text{O}_6\{\text{MeC}(\text{O})(\text{PO}_3)_2\}]^{5-}$ fragments. Each of the fragments donates three oxo groups, two of them come from $\{\text{CPO}_3\}$ groups of the chelating hedp ligand and the third from the oxo group bridging to a molybdenum site. The anion is situated on a centre of inversion. Each of Mo^{6+} cation in the title compound has a distorted octahedral configuration with two apical $\text{Mo}\cdots\text{O}$ bonds of length 1.717 (4) and 1.731 (3) Å and four other $\text{Mo}\cdots\text{O}$ bonds with lengths ranging from 1.745 (3) to 2.419 (3) Å. Based on the valence-bond calculations, the bond values for the two molybdenum are 5.985 and 5.967, respectively, indicating that Mo atoms have oxidation state +6. Another structural feature in $[\text{CoMo}_4\text{O}_{12}\{\text{MeC}(\text{O})(\text{PO}_3)_2\}_2]^{8-}$ is the presence of a pair of face-sharing MoO_6 octahedra. Edge- and angle-sharing octahedra the normal connecting fashions in polyoxomolybdate anions, but face-sharing MoO_6 octahedra are rare. The two Mo atoms in the asymmetric unit of the title compound are non-bonded to each other, according to the average $\text{Mo}\cdots\text{Mo}$ distance of 3.24 (1) Å.

In contrast with the majority of diphosphonates, the short length of the $\text{MeC}(\text{O})$ - tether in hedp permits formation of stable six-membered rings with the metal ions. In Fig. 1, one can see that there are three types of six-membered rings in the anion, *viz.* $\text{Co}-\text{O}-\text{Mo}-\text{O}-\text{P}-\text{O}$, $\text{Co}-\text{O}-\text{P}-\text{C}-\text{P}-\text{O}$ and $\text{Mo}-\text{O}-\text{P}-\text{C}-\text{P}-\text{O}$.

Experimental

The title compound was synthesized by reacting Na_2MoO_4 , hedp and CoCl_2 in the ratio 12:1:1 at pH 5.5. The mixed solution was kept at 333 K for 2 h and was then filtrated. The clear filtrate was kept at room temperature. Within a few days, red block-shaped crystals formed in a very good yield. Elemental analysis results are in complete agreement with the structural composition of the title compound.

Crystal data

$\text{Na}_8[\text{CoMo}_4\text{O}_{12}\{\text{C}_2\text{H}_3\text{O}_7\text{P}_2\}_2]\cdot 18\text{H}_2\text{O}$
 $M_r = 1544.87$
 Monoclinic, $P2_1/n$
 $a = 9.660$ (3) Å
 $b = 22.381$ (8) Å
 $c = 10.441$ (4) Å
 $\beta = 99.049$ (5)°
 $V = 2229.3$ (14) Å³
 $Z = 2$

$D_x = 2.301$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2446 reflections
 $\theta = 2.3$ – 25.8 °
 $\mu = 1.80$ mm⁻¹
 $T = 298$ (2) K
 Block, red
 0.28 × 0.13 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\text{min}} = 0.632$, $T_{\text{max}} = 0.869$
 12 461 measured reflections

4434 independent reflections
 2784 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.058$
 $\theta_{\text{max}} = 26.4$ °
 $h = -12 \rightarrow 11$
 $k = -27 \rightarrow 12$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.069$
 $S = 0.85$
 4434 reflections
 295 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0182P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.005$
 $\Delta\rho_{\text{max}} = 0.61$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.67$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Mo1—O11	1.729 (3)	Co1—O5	2.064 (3)
Mo1—O10	1.730 (3)	Co1—O5 ⁱ	2.064 (3)
Mo1—O9	1.746 (4)	Co1—O2	2.160 (3)
Mo1—O8	2.068 (3)	Co1—O2 ⁱ	2.160 (3)
Mo1—O4	2.339 (3)	P1—O3	1.515 (4)
Mo1—O1	2.418 (3)	P1—O2	1.516 (4)
Mo2—O12	1.717 (4)	P1—O1	1.568 (4)
Mo2—O13	1.719 (4)	P1—C1	1.824 (5)
Mo2—O8	1.841 (3)	P2—O5	1.507 (3)
Mo2—O7	1.984 (3)	P2—O6	1.512 (4)
Mo2—O4	2.335 (3)	P2—O4	1.562 (3)
Mo2—O1	2.345 (3)	P2—C1	1.830 (5)
Co1—O9	2.038 (3)	O7—C1	1.446 (6)
Co1—O9 ⁱ	2.038 (3)		
O11—Mo1—O10	105.17 (16)	O12—Mo2—O1	94.95 (15)
O11—Mo1—O9	103.01 (17)	O13—Mo2—O1	160.21 (14)
O10—Mo1—O9	103.78 (17)	O8—Mo2—O1	73.65 (13)
O11—Mo1—O8	96.33 (15)	O7—Mo2—O1	77.55 (13)
O10—Mo1—O8	92.92 (15)	O4—Mo2—O1	70.27 (11)
O9—Mo1—O8	149.92 (14)	O9—Co1—O9 ⁱ	180.0 (2)
O11—Mo1—O4	90.49 (14)	O9—Co1—O5	88.69 (13)
O10—Mo1—O4	158.27 (14)	O9 ⁱ —Co1—O5	91.31 (13)
O9—Mo1—O4	86.80 (13)	O9—Co1—O5 ⁱ	91.31 (13)
O8—Mo1—O4	70.05 (12)	O9 ⁱ —Co1—O5 ⁱ	88.69 (13)
O11—Mo1—O1	157.41 (14)	O5—Co1—O5 ⁱ	180.0 (2)
O10—Mo1—O1	92.64 (14)	O9—Co1—O2	84.68 (13)
O9—Mo1—O1	85.68 (14)	O9 ⁱ —Co1—O2	95.32 (13)
O8—Mo1—O1	68.49 (12)	O5—Co1—O2	92.80 (12)
O4—Mo1—O1	68.96 (11)	O5 ⁱ —Co1—O2	87.20 (12)
O12—Mo2—O13	104.74 (18)	O9—Co1—O2 ⁱ	95.32 (13)
O12—Mo2—O8	103.33 (16)	O9 ⁱ —Co1—O2 ⁱ	84.68 (13)
O13—Mo2—O8	103.17 (16)	O5—Co1—O2 ⁱ	87.20 (12)
O12—Mo2—O7	97.90 (16)	O5 ⁱ —Co1—O2 ⁱ	92.80 (12)
O13—Mo2—O7	97.40 (15)	O2—Co1—O2 ⁱ	180.0 (2)
O8—Mo2—O7	145.36 (14)	P1—O1—Mo2	112.84 (17)
O12—Mo2—O4	165.20 (15)	P1—O1—Mo1	127.57 (18)
O13—Mo2—O4	90.01 (15)	Mo2—O1—Mo1	85.74 (11)
O8—Mo2—O4	73.83 (13)	P1—O2—Co1	127.0 (2)
O7—Mo2—O4	78.65 (12)		

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

The H atoms on C atoms were treated as riding, with C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$ of the parent atom. The positions of the water H atoms could not be located.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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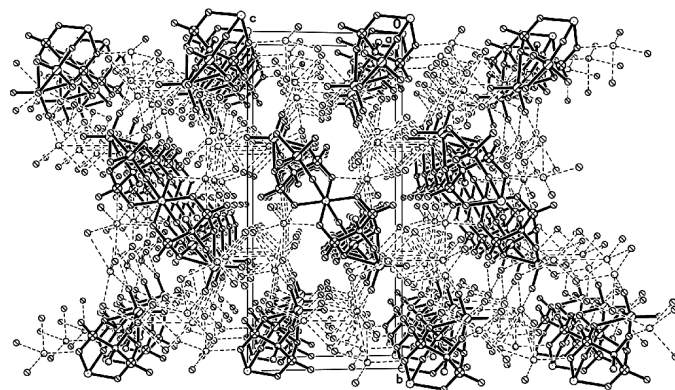


Figure 2
Packing diagram of the title compound, viewed down the *a* axis.