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Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{Co}-\text{O}) = 0.003 \text{ \AA}$
H-atom completeness 0%
R factor = 0.031
wR factor = 0.082
Data-to-parameter ratio = 17.7

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

Tripotassium hexahydrogen hexamolybdocobaltate(III) heptahydrate, $\text{K}_3[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot 7\text{H}_2\text{O}$

The very stable title crystals, $\text{K}_3[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot 7\text{H}_2\text{O}$, that include the well known *B*-type Anderson–Evans heteropolyoxometalate, were obtained by recrystallization of powder $\text{K}_3[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot n\text{H}_2\text{O}$ at pH 3.5. The unit cell consists of two different crystallographically discrete $[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-}$ polyanions. The two anions have the Co atoms at inversion centers and have close to $\bar{3}m$ symmetry, with Co–O bond lengths in the range 1.898 (3)–1.912 (3) Å, Mo–O bond lengths in the ranges 1.700 (4)–1.726 (4), 1.895 (3)–1.960 (3) and 2.259 (3)–2.313 (3) Å.

Comment

Compounds having *B*-type Anderson–Evans structure heteropolyanions containing heteroatoms (Anderson, 1937; Tsigdinos, 1978) of a lower oxidation state, such as $[\text{H}_6\text{X}^n\text{Mo}_6\text{O}_{24}]^{(6-n)-}$ (X: Co^{2+} , Co^{3+} , Ni^{2+} , Fe^{3+}), do not usually form crystals suitable for structure determination. The reason for this is the weak bonding between the anions by six undissociated H atoms that are bound to O atoms in XO_6 . As a result, the crystals have a cleavage property like mica and form a plate-like powder. The typical *B*-type Anderson–Evans structure heteropolyanions containing Co^{3+} , such as (18-crown-6·K)₂·K $[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$ (Nagano *et al.*, 1990), $[\text{Ga}(\text{H}_2\text{O})_6]_3[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot 10\text{H}_2\text{O}$ (Panneerselvam *et al.*, 1996), $\text{Ba}_3[\text{H}_6\text{CoMo}_6\text{O}_{24}]_2 \cdot 20\text{H}_2\text{O}$ (Soriano-García *et al.*, 1996), $\text{Na}_3[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$ (Nolan *et al.*, 1998), and $\text{K}_3[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot \text{KNO}_3 \cdot 4\text{H}_2\text{O}$ (Lee & Joo, 2000), have bulky counter-cations or clusters of counter-cations with O atoms and double-salt formation acting as a separator between the anions in the crystal packing. The present crystals have two different crystallographically discrete $[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-}$ polyanions (Fig. 1), as found also in $\text{K}_3[\text{H}_6\text{AlMo}_6\text{O}_{24}] \cdot 7\text{H}_2\text{O}$ (Lee *et al.*, 1991). Two anions lie on inversion centers and are close to having $D_{3d}(\bar{3}m)$ symmetry. All atoms, except for the two central Co atoms, are located on general positions of the space group. The Co atoms lie on inversion centers at the center of the polyanions.

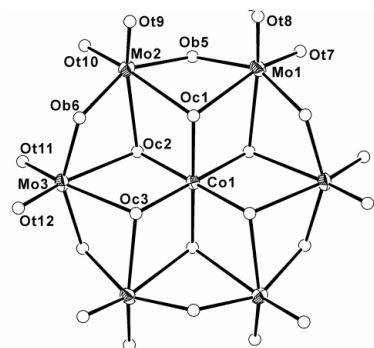
The labeling of the O atoms in the polyanion is the same as in the previous report (Lee & Joo, 2000). All average bond distances and angles show values similar to those found in $\text{Na}_3[\text{H}_6\text{CoMo}_6\text{O}_{24}] \cdot 8\text{H}_2\text{O}$. Detailed discussions related to the bond distances, angles and the position of six H atoms in the $[\text{H}_6\text{CoMo}_6\text{O}_{18}]^{3-}$ polyanion have been given by Nolan *et al.* (1998).

Six non-acidic H atoms are also bound to the six central O_c atoms surrounding the Co^{III} atom. The packing diagram of the polyanion *A* is presented in Fig. 2 and shows the extensive hydrogen-bonding interactions by six non-acidic H atoms and water molecules. The polyanion *B* also shows the same

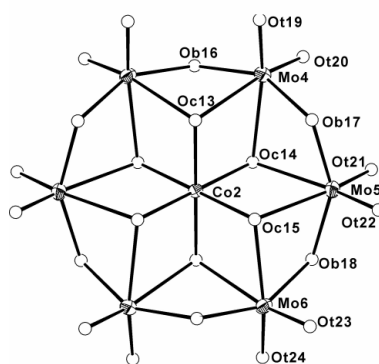
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Polyanion A



Polyanion B

Figure 1

Two discrete polyanion structures in $K_3[H_6CoMo_6O_{24}] \cdot 7H_2O$.

pattern. A list of all probable hydrogen-bond distances within 3.1 Å is given in Table 2. In particular, in all inter-anion links, such as $Oc1 \cdots Ot12$, $Oc2 \cdots Ot7$, $Oc13 \cdots Ot23$ and $Oc14 \cdots Ot22$, the hydrogen-bond distances are short.

There is no direct hydrogen-bond interaction between the polyanion A and polyanion B. The H atoms of Oc3 (anion A) and Oc15 (anion B) do not contribute to the inter-anion hydrogen bonding, but form strong hydrogen bonds with Ow1 and Ow5, respectively. Five water molecules form hydrogen bonds with Ob or Ot atoms in the anions. The hydrogen bonds between water molecules, such as $Ow2 \cdots Ow3$, $Ow3 \cdots Ow7$ and $Ow4 \cdots Ow6$, are also shown. K1 and K3 ions are coordinated by eight O atoms, such as $[K(Ot)_4(Ob)(Ow)_3]^+$, and the K2 ion is coordinated by nine O atoms, such as $[K(Ot)_4(Ob)(Ow)_4]^+$. The title crystals are stabilized by the formation of extensive hydrogen bonding and the effective packing of the bulky $[KO_{8-9}]^+$ clusters.

Experimental

The title compound was obtained by recrystallization of the powder $K_3[H_6CoMo_6O_{24}] \cdot nH_2O$ at pH 3.5. It was obtained by adding KCl to an $(NH_4)_3[H_6CoMo_6O_{24}]$ solution. $(NH_4)_3[H_6CoMo_6O_{24}] \cdot 7H_2O$ was obtained from the reaction of $(NH_4)_6[MoO_7O_{24}] \cdot 4H_2O$ with $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (Bauer & Drinkard, 1966) at pH 7.0.

Crystal data

$K_3[H_6CoMo_6O_{24}] \cdot 7H_2O$
 $M_r = 1268.03$
 Monoclinic, $P2_1/c$
 $a = 22.461$ (4) Å
 $b = 11.295$ (2) Å
 $c = 11.394$ (2) Å
 $\beta = 94.557$ (9)°
 $V = 2881.5$ (9) Å³
 $Z = 4$

$D_x = 2.923$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 30 reflections
 $\theta = 9.6$ – 10.4 °
 $\mu = 3.63$ mm⁻¹
 $T = 298$ (2) K
 Monoclinic, blue
 $0.25 \times 0.20 \times 0.20$ mm

Data collection

Stoe Stadi-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: numerical
 (*X-SHAPE*; Stoe & Cie, 1996)
 $T_{min} = 0.502$, $T_{max} = 0.669$
 6611 measured reflections
 6611 independent reflections
 5649 reflections with $I > 2\sigma(I)$

$\theta_{max} = 27.5$ °
 $h = -29 \rightarrow 29$
 $k = 0 \rightarrow 14$
 $l = 0 \rightarrow 14$
 3 standard reflections
 frequency: 60 min
 intensity decay: 3.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.082$
 $S = 1.11$
 6611 reflections
 374 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 11.8333P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.98$ e Å⁻³
 $\Delta\rho_{min} = -0.69$ e Å⁻³
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00144 (6)

Table 1

Selected bond lengths (Å).

Co1—Oc1	1.899 (3)	Mo5—Oc15	2.309 (3)
Co1—Oc3	1.909 (3)	Mo5—Oc14	2.313 (3)
Co1—Oc2	1.912 (3)	Mo6—Ot24	1.707 (4)
Mo1—Ot8	1.706 (4)	Mo6—Ot23	1.713 (4)
Mo1—Ot7	1.715 (4)	Mo6—Ob16 ⁱⁱ	1.906 (3)
Mo1—Ob5	1.921 (3)	Mo6—Ob18	1.960 (3)
Mo1—Ob4	1.948 (3)	Mo6—Oc15	2.259 (3)
Mo1—Oc3 ⁱ	2.278 (3)	Mo6—Oc13 ⁱⁱⁱ	2.295 (3)
Mo1—Oc1	2.283 (3)	Oc1—Or12 ⁱⁱⁱ	2.720 (5)
Mo2—Or9	1.700 (4)	K1—Or22	3.151 (4)
Mo2—Or10	1.705 (4)	K1—Ow4	2.731 (5)
Mo2—Ob5	1.943 (3)	K1—Ow6 ^{iv}	2.775 (5)
Mo2—Ob6	1.956 (3)	K1—Ow2	2.834 (7)
Mo2—Oc2	2.294 (3)	K1—Or10	2.964 (4)
Mo2—Oc1	2.313 (3)	K1—Ob17	2.930 (4)
Mo3—Or11	1.710 (4)	K1—Or21 ^v	2.874 (4)
Mo3—Or12	1.715 (4)	K1—Or20 ^v	2.884 (4)
Mo3—Ob6	1.895 (3)	K2—Ob16 ^{vi}	2.705 (4)
Mo3—Ob4 ⁱ	1.948 (3)	K2—Ow6	2.739 (5)
Mo3—Oc3	2.273 (3)	K2—Or24 ^{vii}	2.739 (4)
Mo3—Oc2	2.286 (3)	K2—Ow7	2.966 (6)
Co2—Oc13	1.898 (3)	K2—Ow3	2.986 (7)
Co2—Oc15	1.908 (3)	K2—Ot20 ^{vi}	3.128 (4)
Co2—Oc14	1.910 (3)	K2—Or21 ^v	3.177 (4)
Mo4—Or20	1.707 (4)	K2—Or22 ^v	3.239 (4)
Mo4—Or19	1.713 (4)	K2—Ow5	3.293 (6)
Mo4—Ob17	1.930 (3)	K3—Ow3	2.639 (5)
Mo4—Ob16	1.947 (3)	K3—Ob6 ^{viii}	2.676 (4)
Mo4—Oc13	2.292 (3)	K3—Or8 ^{vi}	2.728 (4)
Mo4—Oc14	2.301 (3)	K3—Or11	2.832 (4)
Mo5—Or21	1.702 (4)	K3—Or12	3.165 (4)
Mo5—Or22	1.720 (4)	K3—Ow7	2.826 (5)
Mo5—Ob17	1.922 (3)	K3—Ow1	2.924 (4)
Mo5—Ob18	1.932 (3)	K3—Or9 ^{viii}	3.363 (5)

Symmetry codes: (i) $1 - x, -1 - y, 1 - z$; (ii) $-x, -1 - y, 1 - z$; (iii) $x, -\frac{3}{2} - y, \frac{1}{2} + z$; (iv) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (v) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (vi) $x, y, z - 1$; (vii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (viii) $x, -\frac{3}{2} - y, z - \frac{1}{2}$.

Table 2
 Hydrogen-bonding geometry (Å).

<i>D</i> ... <i>A</i>	<i>D</i> ... <i>A</i>
Oc1...Or12 ⁱ	2.720 (5)
Oc2...Or7 ⁱⁱ	2.676 (5)
Oc13...Or23 ⁱⁱⁱ	2.691 (5)
Oc14...Or22 ^{iv}	2.809 (5)
Ow1...Oc3 ^v	2.657 (5)
Ow1...Ob4 ^{vi}	2.781 (5)
Ow1...Ob4 ^{vii}	3.016 (5)
Ow2...Ow3	2.731 (8)
Ow2...Or19	2.811 (7)
Ow2...Or24 ⁱⁱⁱ	3.042 (8)
Ow3...Or24 ⁱⁱⁱ	3.002 (6)
Ow3...Or19 ^v	3.017 (7)
Ow3...Ow7	3.074 (8)
Ow4...Ob5 ⁱⁱ	2.744 (5)
Ow4...Or11	2.810 (5)
Ow4...Ow6	2.757 (6)
Ow5...Oc15 ^{viii}	2.636 (5)
Ow5...Ob18 ⁱⁱⁱ	2.779 (5)
Ow5...Ob18 ⁱⁱ	3.047 (5)
Ow6...Or20 ^{vi}	3.082 (6)
Ow6...Or8 ^{vi}	3.100 (6)
Ow7...Or9 ^{vi}	2.849 (7)

Symmetry codes: (i) $x, -\frac{3}{2}-y, \frac{1}{2}+z$; (ii) $x, -\frac{1}{2}-y, z-\frac{1}{2}$; (iii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (v) $x, -\frac{3}{2}-y, z-\frac{1}{2}$; (vi) $x, y, z-1$; (vii) $1-x, -1-y, 1-z$; (viii) $-x, -1-y, -z$.

The highest peak in the difference map is 0.86 Å from Oc14, and the largest hole is 0.92 Å from Ow5.

Data collection: *Stadi4* (Stoe & Cie, 1996); cell refinement: *Stadi4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997).

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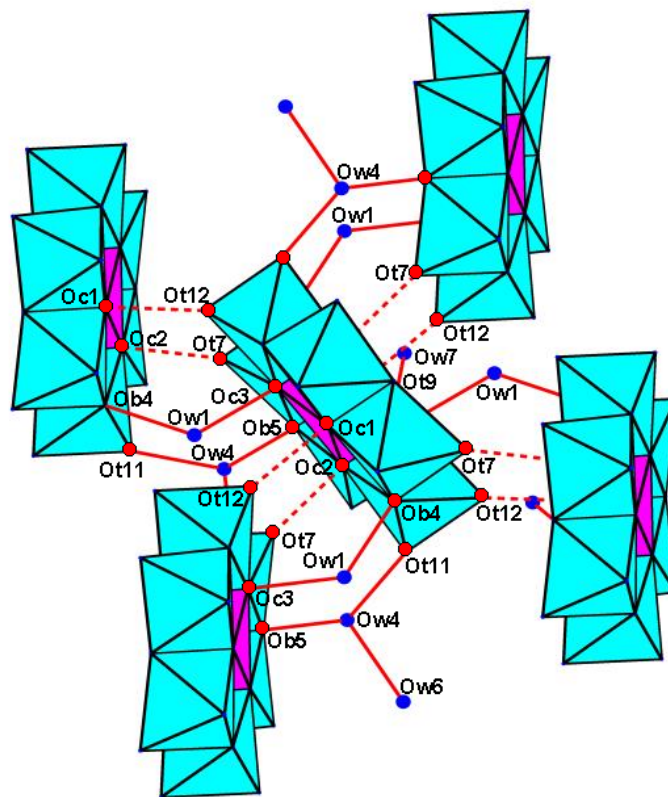


Figure 2
 The packing diagram of the polyanion *A* showing the hydrogen bonds.

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