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Lee and Joo

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Tripotassium hexahydrogenhexamolybdocobaltate(III) potassium nitrate tetrahydrate, $K_3[H_6CoMo_6O_{24}] \cdot KNO_3 \cdot 4H_2O$

Uk Lee* and Hea Chung Joo

Department of Chemistry, Pukyong National University, 599-1 Daeyeon-dong Nam-ku, Pusan 608-737, Korea

Correspondence e-mail: uklee@mail.pknu.ac.kr

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The title double salt was obtained from the reaction of $Y(NO_3)_3$ and $K_6[H_4Co_2Mo_{10}O_{38}] \cdot 5H_2O$ at a pH of about 2.0. The $[H_6CoMo_6O_{24}]^{3-}$ anion is a typical B-type Anderson-structure heteropolyanion, and has an inversion center, with Co—O bond lengths in the range 1.907 (4)–1.919 (4) Å and Mo—O bond lengths in the ranges 1.709 (5)–1.721 (5), 1.902 (5)–1.951 (5) and 2.274 (4)–2.312 (4) Å.

Comment

Obtaining suitable crystals for the structure determination of some kinds of B-type Anderson-structure heteropolyanions, such as $[H_6X^{n+}Mo_6O_{24}]^{(6-n)-}$ ($X: Co^{2+}, Co^{3+}, Ni^{2+}, Fe^{3+}$) (Anderson, 1937), is difficult. The salts of these polyanions have a cleavage property like mica because of the repulsion of interanions by six undissociated H atoms bound to O atoms in XO_6 . The bulky counter-cation acts as a separator between the interanions in the crystal packing. Single crystals of some compounds, such as $(18\text{-crown-}6 \cdot K^+)_2K[H_6CoMo_6O_{24}] \cdot 12H_2O$ (Nagano *et al.*, 1990) and $[Ga(H_2O)_6]_3[H_6CoMo_6O_{24}] \cdot 10H_2O$ (Panneerselvam *et al.*, 1996), have been obtained. The role of potassium nitrate in the crystallization of these crystals is important.

The present polyanion is close to having $D_{3d}(\bar{3}m)$ symmetry. The definition of O atoms in the polyanion is the same as in the previous report (Panneerselvam *et al.*, 1996); O_n is a nitrate O atom. The Mo—O distances show a similar tendency to those found in $(18\text{-crown-}6 \cdot K^+)_2K[H_6CoMo_6O_{24}] \cdot 12H_2O$ (Nagano *et al.*, 1990), $Na_3[H_6CoMo_6O_{24}] \cdot 8H_2O$ (Nolan *et al.*, 1998) and $[Ga(H_2O)_6]_3[H_6CoMo_6O_{24}] \cdot 10H_2O$ (Panneerselvam *et al.*, 1996). KNO_3 not only contributes to the charge balance but also packs the cavity made by the polyanion with K^+ and O_w . The N and $ON17$ atoms are located on the twofold axis. Reasonable displacement parameters of $OW14$ and $OW15$ were obtained by reducing the occupancy to 0.5. The K1 and K2 ions are coordinated to O atoms as $[K1(O_i)_4-$

$(O_b)(O_w)(O_n)]^+$ and $[K2(O_i)_3(O_b)(O_w)(O_n)_3]^+$. The distances between K and O atoms are in the range 2.68–3.19 Å.

Experimental

The title compound was prepared by mixing hot aqueous solutions of $K_6[H_4Co_2Mo_{10}O_{38}] \cdot 5H_2O$ (0.5 mM per 20 ml) and $Y(NO_3)_3 \cdot 6H_2O$ (0.5 mM per 20 ml), adjusting the pH to about 2.0 with 3.0 M HNO_3 . The solution was concentrated to about 20 ml by heating it on a water bath. After a day, monoclinic pale-blue crystals and an unstable colorless by-product were obtained.

Crystal data

$K_3[H_6CoMo_6O_{24}] \cdot KNO_3 \cdot 4H_2O$
 $M_r = 1315.09$
 Monoclinic, $C2/c$
 $a = 24.191$ (3) Å
 $b = 10.9675$ (16) Å
 $c = 11.6115$ (15) Å
 $\beta = 106.644$ (9)°
 $V = 2951.6$ (7) Å³
 $Z = 4$

$D_x = 2.959$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 26 reflections
 $\theta = 9.6$ – 10.5 °
 $\mu = 3.692$ mm⁻¹
 $T = 298$ (2) K
 Monoclinic, pale blue
 $0.20 \times 0.15 \times 0.07$ mm

Data collection

Stoe Stadi-4 diffractometer
 ω - 2θ scans
 Absorption correction: numerical (Stoe & Cie, 1996)
 $T_{min} = 0.463$, $T_{max} = 0.650$
 3148 measured reflections
 3148 independent reflections
 2574 reflections with $I > 2\sigma(I)$

$\theta_{max} = 27.45$ °
 $h = -31 \rightarrow 30$
 $k = 0 \rightarrow 14$
 $l = 0 \rightarrow 15$
 3 standard reflections
 frequency: 60 min
 intensity decay: 2.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.119$
 $S = 1.087$
 3148 reflections
 206 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0530P)^2 + 53.7384P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 1.88$ e Å⁻³
 $\Delta\rho_{min} = -1.60$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co—OC1	1.907 (4)	Mo3—OB4	1.929 (5)
Co—OC3	1.910 (4)	Mo3—OB6	1.947 (4)
Co—OC2	1.919 (4)	Mo3—OC3 ⁱ	2.290 (4)
Co—Mo1	3.3091 (7)	Mo3—OC1	2.312 (4)
Co—Mo2	3.3106 (7)	K1—OW14	2.627 (16)
Co—Mo3	3.3123 (7)	K1—OB6 ⁱⁱ	2.690 (5)
Mo1—OT7	1.715 (5)	K1—OT10 ⁱⁱⁱ	2.760 (6)
Mo1—OT8	1.721 (5)	K1—ON16 ^{iv}	2.786 (8)
Mo1—OB4	1.921 (5)	K1—OT7	2.915 (6)
Mo1—OB5	1.951 (5)	K1—OW14 ^v	3.100 (19)
Mo1—OC2	2.274 (4)	K1—OT12 ⁱⁱ	3.197 (6)
Mo1—OC1	2.293 (4)	K1—OT8	3.205 (6)
Mo1—Mo3	3.2994 (9)	K1—OW13 ^{vi}	3.207 (8)
Mo1—Mo2	3.3282 (9)	K2—OW15	2.645 (18)
Mo2—OT10	1.712 (5)	K2—OT7 ⁱⁱ	2.781 (6)
Mo2—OT9	1.718 (5)	K2—OB4	2.819 (5)
Mo2—OB6 ⁱ	1.902 (5)	K2—OM16	2.826 (7)
Mo2—OB5	1.947 (5)	K2—ON16 ^{iv}	2.859 (10)
Mo2—OC2	2.274 (4)	K2—OM17 ^{iv}	2.888 (2)
Mo2—OC3	2.298 (4)	K2—OT12 ^v	2.996 (6)
Mo2—Mo3 ⁱ	3.3045 (9)	K2—OT12 ⁱⁱ	3.075 (7)
Mo3—OT11	1.709 (5)	N—ON17	1.239 (15)
Mo3—OT12	1.719 (5)	N—ON16 ^{vii}	1.232 (9)

Mo1—Co—Mo2	60.368 (16)	Co—Mo1—Mo2	59.839 (15)
Mo1—Co—Mo3	59.775 (15)	ON16 ^{vi} —N—ON16	122.1 (13)
Mo2—Co—Mo3	120.140 (15)	ON16 ^{vii} —N—ON17	119.0 (7)
Mo3—Mo1—Mo2	120.00 (2)	ON16—N—ON17	119.0 (7)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $x, -y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$; (iv) $1 - x, -y, 2 - z$; (v) $1 - x, y, \frac{3}{2} - z$; (vi) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (vii) $1 - x, y, \frac{5}{2} - z$.

The rather low completeness of 93.05% for $\theta_{\max} = 27.45^\circ$ is due to the omission of the off-center reflections. The highest peaks in the difference map are 1.29 Å from OW15 and 0.91 Å from K2, and the largest hole is 0.79 Å from K2. H atoms were not included in the structure model.

Data collection: *STADIA* (Stoe & Cie, 1996); cell refinement: *STADIA*; 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).

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