Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Dipotassium heptahydrogenhexamolybdochromate(III) octahydrate, the first heptaprotonated Anderson-type polyoxometalate

Uk Lee

Department of Chemistry, Pukyong National University, 599-1 Daeyeon 3-dong Nam-ku, Pusan 608-737, Republic of Korea

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

Received 29 November 2006
Accepted 6 December 2006

The title compound, $K_2[H_7CrMo_6O_{24}]\cdot8H_2O$, contains an unexpectedly protonated polyanion, $[H_7CrMo_6O_{24}]^{2-}$ in the B series Anderson-type heteropolyoxomolybdate. It was obtained by recrystallizing $K_3[H_6CrMo_6O_{24}]\cdot nH_2O$ at pH 1.80. The asymmetric unit contains two crystallographically independent polyanions that have C_i ($\overline{1}$) symmetry. Six O atoms of the central CrO_6 octahedron and one atom of an edge-shared MoO_6 octahedron are protonated.

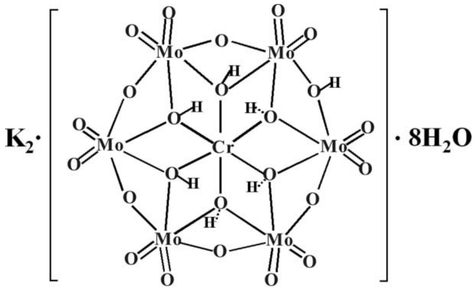
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(Cr–O) = 0.003 Å
H-atom completeness 83%
R factor = 0.029
wR factor = 0.073
Data-to-parameter ratio = 13.1

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

Comment

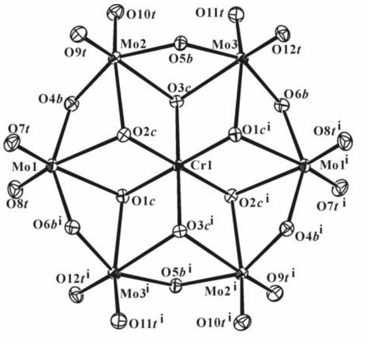
Since the first crystal structure report of $Na_3[Cr(OH)_6Mo_6O_{18}]\cdot8H_2O$ (Perloff, 1970), many crystal structures of B series Anderson-type (Anderson, 1937) heteropolyanions (Tsigdinos, 1978) consisting of a heteroatom X with a low oxidation state and a protonated polyanion with six H^+ of general formula $[X^{n+}(OH)_6Mo_6O_{18}]^{(6-n)-}$ [X: Co^{3+} (Nagano *et al.*, 1990; Nolan *et al.*, 1998; Lee *et al.*, 2001), Al^{3+} (Lee *et al.*, 1991), Rh^{3+} (Ozawa *et al.* 1991), Cu^{2+}(Ito *et al.*, 1989), Ni^{2+}(Lee *et al.*, 2004)] have been reported. Usually, these B series Anderson-type heteropolyanion species are isolated in a pH range of 3-4. The six H atoms attached to the O atoms of the central $[XO_6]$ octahedron are known to be non-acidic. For the past four decades, the existence of protonated species with more than seven H^+ has not been expected in the B series Anderson-type heteropolyoxomolybdate system.



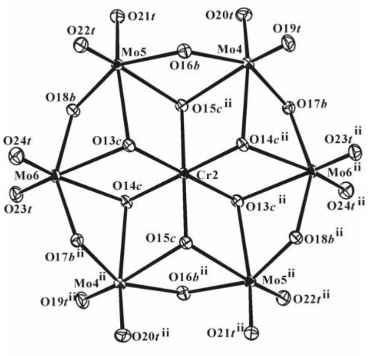
(I)

The title compound, dipotassium heptahydrogen hexamolybdochromate(III) octadecahydrate, $K_2[H_7CrMo_6O_{24}]\cdot8H_2O$, (I), has two crystallographically independent polyanions (Polyanion A and B; Fig. 1). All composite atoms, except for two central Cr atoms and two H atoms in the polyanion, are located in general positions, and the Cr atoms lie on inversion centres. The O atoms are labelled in the same way as previously by Lee *et al.* (2001), *viz*. O_c, O_b, O_t, and O_w.

The Mo3—O5$_b$, Mo4—O5$_b$, Mo4—O16$_b$ and Mo5—O16$_b$ bond distances are longer than the unprotonated Mo—O$_b$ bond distances and the bond angles at these O atoms are



Polyanion A



Polyanion B

Figure 1
Two discrete polyanion structures in (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms are not shown. [Symmetry codes: (i) $1 - x, -y, 2 - z$; (ii) $1 - x, 1 - y, 1 - z$.]

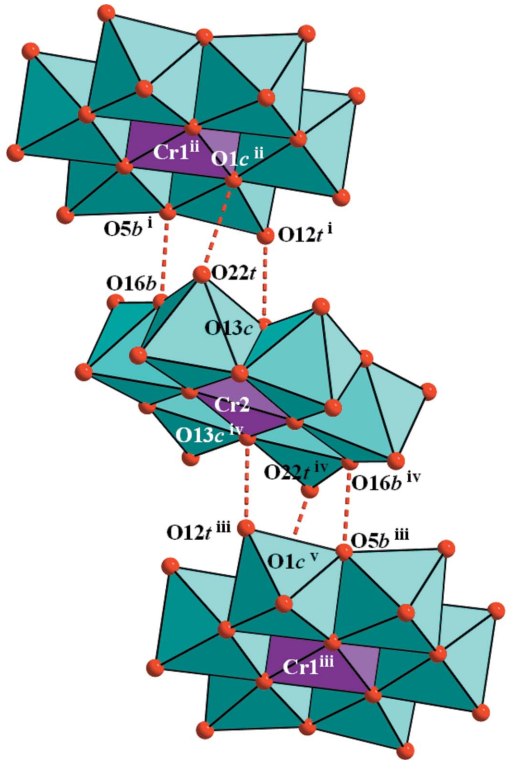


Figure 2
Polyhedral view of the heteropolyanions in (I) with O···O contacts of the inter-polyanion hydrogen bonds shown as dashed lines. [Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x, y, z - 1$; (iii) $x, 1 + y, z$; (iv) $1 - x, 1 - y, 1 - z$; (v) $1 - x, 1 - y, 2 - z$.]

smaller than at the unprotonated O atoms (Table 1). Polyanions *A* and *B* are connected by strong hydrogen bonds. K^+ ions are coordinated by eight O atoms, *viz*. $[K1(O_t)_4(O_w)_4]^+$ and $[K2(O_t)_4(O_b)(O_w)_3]^+$ in the distance range 2.724 (3)–3.081 (3)Å.

Experimental

The title compound was obtained by recrystallization from an aqueous solution of $K_3[H_6CoMo_6O_{24}]\cdot n H_2O$ (Lee *et al.*, 2001) at pH 1.80.

Crystal data

$K_2[H_7CrMo_6O_{24}]\cdot 8H_2O$
$M_r = 1241.02$
Triclinic, $P\overline{1}$
$a = 10.4733$ (6) Å
$b = 10.8698$ (6) Å
$c = 12.6540$ (7) Å
$\alpha = 99.309$ (1)°
$\beta = 94.465$ (1)°
$\gamma = 99.256$ (1)°

$V = 1395.08$ (14) Å^3
$Z = 2$
$D_x = 2.954$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 3.40$ mm^{-1}
$T = 173$ (2) K
Block, purple
0.32 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
$T_{\min} = 0.380$, $T_{\max} = 0.512$

10855 measured reflections
5360 independent reflections
5200 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 26.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.074$
$S = 1.19$
5360 reflections
408 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 4.6144P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.85$ e Å^{-3}
$\Delta\rho_{\min} = -0.85$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0065 (2)

Table 1
Selected geometric parameters (Å, °).

Cr1—O1*C*	1.969 (3)	Mo3—O3*C*	2.236 (3)
Cr1—O2*C*	1.976 (3)	Mo3—O5*B*	2.000 (3)
Cr1—O3*C*	1.975 (3)	Mo3—O6*B*	1.882 (3)
Cr2—O13*C*	1.974 (3)	Mo4—O16*B*	1.993 (3)
Cr2—O14*C*	1.980 (3)	Mo4—O17*B*	1.921 (3)
Cr2—O15*C*	1.978 (3)	Mo4—O14*C*$^{\rm ii}$	2.309 (3)
Mo1—O1*C*	2.305 (3)	Mo4—O15*C*$^{\rm ii}$	2.275 (3)
Mo1—O2*C*	2.324 (3)	Mo5—O13*C*	2.306 (3)
Mo1—O4*B*	1.943 (3)	Mo5—O15*C*$^{\rm ii}$	2.272 (3)
Mo1—O6*B*$^{\rm i}$	1.965 (3)	Mo5—O16*B*	2.000 (3)
Mo2—O2*C*	2.295 (3)	Mo5—O18*B*	1.900 (3)
Mo2—O3*C*	2.283 (3)	Mo6—O13*C*	2.310 (3)
Mo2—O4*B*	1.915 (3)	Mo6—O14*C*	2.302 (3)
Mo2—O5*B*	1.986 (3)	Mo6—O17*B*$^{\rm ii}$	1.917 (3)
Mo3—O1*C*$^{\rm i}$	2.324 (3)	Mo6—O18*B*	1.965 (3)
Mo1—O1*C*—Mo3$^{\rm i}$	91.44 (11)	Mo5—O13*C*—Mo6	92.44 (10)
Mo2—O2*C*—Mo1	92.13 (11)	Mo6—O14*C*—Mo4$^{\rm ii}$	91.62 (10)
Mo3—O3*C*—Mo2	97.78 (11)	Mo5$^{\rm ii}$—O15*C*—Mo4$^{\rm ii}$	97.58 (11)
Mo2—O4*B*—Mo1	119.10 (15)	Mo4—O16*B*—Mo5	117.88 (14)
Mo2—O5*B*—Mo3	117.37 (14)	Mo6$^{\rm ii}$—O17*B*—Mo4	118.96 (14)
Mo3—O6*B*—Mo1$^{\rm i}$	118.93 (14)	Mo5—O18*B*—Mo6	119.15 (14)

Symmetry codes: (i) $-x + 1, -y, -z + 2$; (ii) $-x + 1, -y + 1, -z + 1$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*C*—H1···O22$_{t}^{\mathrm{iii}}$	0.73 (5)	2.10 (5)	2.796 (4)	160 (5)
O5*B*—H5···O16*B*$^{\mathrm{iv}}$	0.71 (8)	1.79 (8)	2.475 (4)	163 (13)
O13*C*—H13···O12$_{t}^{\mathrm{iv}}$	0.98	1.81	2.733 (4)	155
O16*B*—H16···O5*B*$^{\mathrm{iv}}$	0.83 (8)	1.65 (8)	2.475 (4)	175 (11)
O25$_{w}$—H25*B*···O21$_{t}$	0.97	2.22	2.844 (4)	121
O25$_{w}$—H25*A*···O20$_{t}$	0.97	1.86	2.828 (4)	172
O26$_{w}$—H26*A*···O4*B*$^{\mathrm{i}}$	0.97	2.07	2.755 (4)	127
O27$_{w}$—H27*B*···O32$_{w}$	0.75 (6)	2.10 (6)	2.842 (6)	174 (7)
O28$_{w}$—H28*B*···O31$_{w}^{\mathrm{v}}$	0.96	1.83	2.719 (5)	153
O28$_{w}$—H28*A*···O12$_{t}^{\mathrm{vi}}$	0.96	1.95	2.789 (4)	144
O29$_{w}$—H29*A*···O11$_{t}^{\mathrm{i}}$	0.96	2.19	2.957 (5)	136
O29$_{w}$—H29*B*···O29$_{w}^{\mathrm{vii}}$	0.96	2.50	2.968 (8)	110
O29$_{w}$—H29*B*···O10$_{t}^{\mathrm{i}}$	0.96	2.01	2.928 (5)	160
O30$_{w}$—H30*B*···O32*w*	0.96	2.51	2.953 (6)	108
O30$_{w}$—H30*B*···O7$_{t}$	0.96	2.57	3.069 (6)	113

Symmetry codes: (i) $-x+1, -y, -z+2$; (iii) $x, y, z+1$; (iv) $-x+1, -y, -z+1$; (v) $-x+1, -y+1, -z+2$; (vi) $x, y+1, z$; (vii) $-x+2, -y+1, -z+2$.

H atoms were located in difference Fourier maps, but only H1, H5, H16 and H27*B* were refined isotropically. Other H atoms were placed in calculated positions and included in the refinement of the riding-motion approximation, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{O})$. The site occupancy of H5 and H16 is 0.5 because they are mutally disordered. The H atoms of O31$_{w}$ and O32$_{w}$ could not be located in an electron density map and were excluded from the refinement.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

References

Anderson, J. S. (1937). *Nature (London)*, **140**, 850.

Brandenburg, K. (1998). *DIAMOND*. Version 2.1. Crystal Impact GbR, Bonn, Germany.

Bruker (1997). *SMART* and *SAINT*. Versions 5.0. Bruker AXS Inc., Madison, Wisconsin, USA.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Ito, F., Ozeki, T., Ichida, H., Miyamae, I. & Sasaki, Y. (1989). *Acta Cryst.* C**45**, 946-947.

Lee, H. Y., Park, K. M. & Lee, U. (1991). *Acta Cryst.* C**47**, 1959–1961.

Lee, U. & Joo, H. Y. (2004). *Acta Cryst.* E**60**, i33–i36.

Lee, U., Joo, H. Y., Kwon, J. S. & Cho, M. A. (2001). *Acta Cryst.* E**57**, i112–i114.

Nagano, O., Lee, U., Ichida, H. & Sasaki, Y. (1990). *Bull. Korean Chem. Soc.* **11**, 15–19.

Nolan, A. L., Allen, C. C., Burns, R. C., Craig, D. C. & Lawrance, G. A. (1998). *Aust. J. Chem.* **51**, 825–834.

Ozawa, Y., Hayashi, Y. & Isobe, K. (1991). *Acta Cryst.* C**47**, 637–638.

Perloff, A. (1970). *Inorg. Chem.* **9**, 2228–2239.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (1999). *SADABS*. University of Göttingen, Germany.

Tsigdinos, G. A. (1978). *Top. Curr. Chem.* **76**, 36–40.