Triguanidinium hexahydrogenhexamolybdocobaltate(III) tetrahydrate

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Crystals of the title compound, $(CH_6N_3)_3[H_6CoMo_6O_{24}]\cdot 4H_2O$, containing the well known B-type Anderson–Evans heteropolyoxometalate structure, were obtained by recrystallization of powder $(CH_6N_3)_3[H_6CoMo_6O_{24}]\cdot nH_2O$. The anion has a Co^{III} atom at an inversion center and has approximate $\bar{3}$ symmetry, with Co—O bond lengths in the range 1.905 (3)–1.918 (3) Å and Mo—O bond lengths in the ranges 1.704 (3)–1.722 (3) (Ot), 1.915 (3)–1.949 (3) (Ob), and 2.266 (3)–2.312 (3) Å (Oc), respectively.

Comment

We have recently reported the crystal structures of two guanidinium salts of polyoxometalates, *viz.* $(CH_6N_3)_8$-$[PtW_6O_{24}]$ (Lee, Jang *et al.*, 2003) and $(CH_6N_3)_8[SiPt_2$-$W_{10}O_{40}]\cdot 6H_2O$ (Lee, Joo *et al.*, 2003). The salts $(CH_6N_3)_4[GeMo_{12}O_{40}]$ (Strandberg & Hedman, 1982), $(CH_6N_3)_2[MoO_4]$ (Ozeki *et al.*, 1987), $(CH_6N_3)_4[Si$-$Mo_{12}O_{40}]\cdot H_2O$ (Ichida *et al.*, 1980), $(CH_6N_3)_4[As_2Mo_{18}O_{62}]\cdot$-$9H_2O$ (Ichida & Sasaki, 1983), and $(CH_6N_3)_6[V_{10}O_{28}]\cdot 6H_2O$ (Wang *et al.*, 1993) have been reported by others. Good crystals of guanidinium polyoxometalates can not always be obtained, but sometimes very stable single crystals are obtained by recrystallization. These salts were shown to be arresting crystal packing by hydrogen bonds and thermal behavior of crystalline water molecules were different from alkali metal salts.

(I)
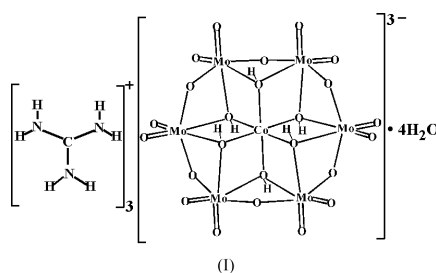
Several heteropolyoxometalates containing the $[H_6Co$-$Mo_6O_{24}]^{3-}$ polyanion, such as $(18$-crown-$6\cdot K^+)_2\cdot K[H_6$-$CoMo_6O_{24}]\cdot 12H_2O$ (Nagano *et al.*, 1990), $[Ga(H_2O)_6]_3[H_6Co$-$Mo_6O_{24}]\cdot 10H_2O$ (Panneerselvam *et al.*, 1996), $Na_3[H_6Co$-$Mo_6O_{24}]\cdot 8H_2O$ (Nolan *et al.*, 1998), $K_3[H_6CoMo_6O_{24}]\cdot$-$KNO_3\cdot 4H_2O$ (Lee & Joo, 2000), and $K_3[H_6CoMo_6O_{24}]\cdot 4H_2O$ (Lee *et al.*, 2001), have been reported. The $[H_6CoMo_6O_{24}]^{3-}$ anion is a typical B-type Anderson–Evans heteropolyanion structure (Anderson, 1937; Evans, 1948; Tsigdinos, 1978). Detailed discussions related to the position of six H atoms in the $[H_6CoMo_6O_{24}]^{3-}$ ion have been given by Nolan *et al.* (1998). Six non-acidic H atoms are bound to six central Oc atoms surrounding the Co^{III} atom. As expected, they were not
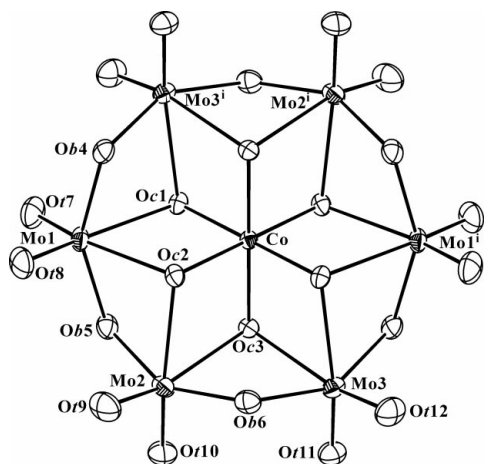
Figure 1
The anion structure in $(CH_6N_3)_3[H_6CoMo_6O_{24}]\cdot4H_2O$. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted. [Symmetry code: (i) $1 - x, -y, 1 - z$.]
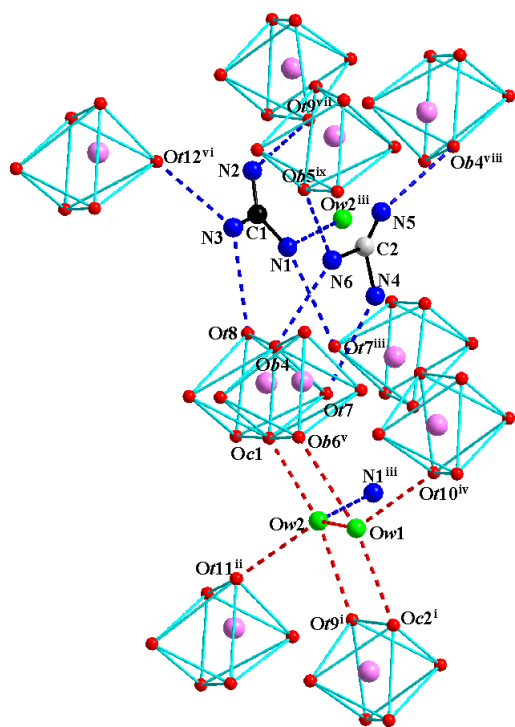

Figure 2
Formation of hydrogen bonds by guanidinium ions and water molecules. [Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, -y, 2 - z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $x - 1, y, -1 + z$; (v) $1 - x, -y, 1 - z$; (vi) $2 - x, -y, 1 - z$; (vii) $2 - x, 1 - y, 1 - z$; (viii) $1 - x, 1 - y, -z$; (ix) $x, y, z - 1$.]

substituted by guanidinium ion. The crystal structure of (I) is a good example of the packing and the hydrogen bonding found in the B-type Anderson–Evans heteropolyoxometalate structure and thermal behavior of water molecules. Here we report the crystal structure of (I), in which the replaceable cations were completely exchanged by guanidinium ions.

Fig. 1 shows the structure of the $[H_6CoMo_6O_{24}]^{3-}$ poly-anion. The labeling of the O atoms in the polyanion is the same as the labeling in the previous structure (Lee *et al.*, 2001).
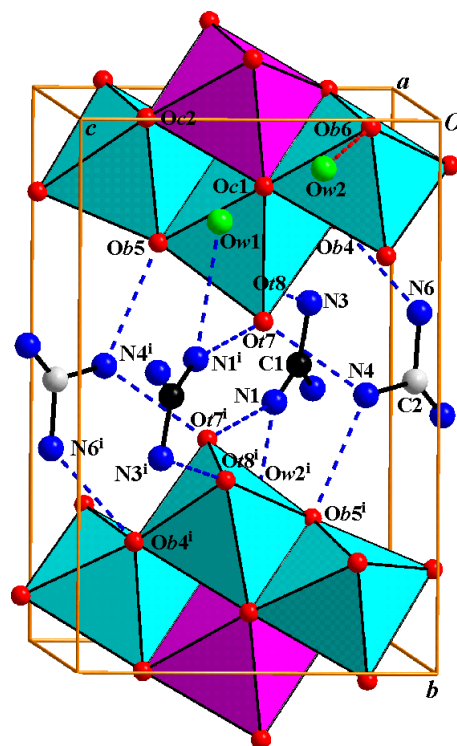

Figure 3
The crystal packing of $(CH_6N_3)_3[H_6CoMo_6O_{24}]\cdot4H_2O$ in the unit cell shown as a polyhedral model. Violet and cyan octahedra are $[CoO_6]$ and $[MoO_6]$, respectively. Probable hydrogen bonds are shown as blue $(N\cdots O)$ and red $(O\cdots O)$ broken lines. [Symmetry code: (i) $1 - x, -y, 1 - z$.]

The distance ranges for $Co\cdots Mo$ and $Mo\cdots Mo$ are 3.2999 (9)–3.3319 (9) and 3.3081 (9)–3.328 (1) Å, respectively. The Co—O bond-length range is 1.905 (3)–1.918 (3) Å, and the three types of Mo—O bond-length ranges are 1.704 (3)–1.722 (3) (Ot), 1.915 (3)–1.949 (3) (Ob), and 2.266 (3)–2.312 (3) Å (Oc). The bond lengths and angles of (I) show a similar trend to values found in the literature, and the geometry of the guanidinium ions also agrees well with that in CH_6N_3Cl (Haas *et al.*, 1965) and $CH_6N_3(NO_3)$ (Katrusiak & Szafrański, 1994). There are one and a half crystallographically independent guanidinium $(CH_6N_3)^+$ ions in the asymmetric unit; cation is disordered over an inversion center.

Fig. 2 shows the hydrogen-bonding interaction of $(CH_6N_3)^+$ ions with O atoms of the anions and water molecules. The list of all probable hydrogen bonds with $N\cdots O$ and $O\cdots O$ distances less than 3.1 Å is given in Tables 1 and 2. An inter-anion hydrogen bond is formed by $Oc3$—H$\cdots Ot11$ [2.831 (4) Å]. All O atoms in the polyanion except $Oc3$ form strong N—H$\cdots$O and O—H$\cdots$O hydrogen bonds, with all N atoms of the guanidinium ions and all the water molecules. Each water molecule forms strong hydrogen bonds. As a result, the degradation temperature was very high (543 K) and those were decomposed with water molecules. All probable $N-O_{polyanion}$ hydrogen-bond distances fall into the range 2.78–3.10 Å, with N—H$\cdots$O angles varying between 119 and 177°. The crystal structure of (I) is stabilized by the formation of extensive N—H$\cdots$O and O—H$\cdots$O hydrogen-bond inter-

actions with the guanidinium ions and the water molecules of crystallization. Fig. 3 shows the unit-cell packing and probable hydrogen-bonding interactions in the crystal structure.

Experimental

A blue powder of (I) was obtained by adding a small excess stoichiometric amount of CH_6N_3Cl to a $K_3[H_6CoMo_6O_{24}]\cdot nH_2O$ solution (Lee *et al.*, 2001). Single crystals of (I) were obtained by recrystallizing the powdered crude sample from a boiling aqueous solution.

Crystal data

$(CH_6N_3)_3[H_6CoMo_6O_{24}]\cdot 4H_2O$	$Z = 1$
$M_r = 1276.95$	$D_x = 2.707$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.821 (1)$ Å	Cell parameters from 27
$b = 11.603 (3)$ Å	reflections
$c = 8.013 (1)$ Å	$\theta = 9.5–10.4°$
$\alpha = 93.93 (3)°$	$\mu = 2.96$ mm^{-1}
$\beta = 105.95 (1)°$	$T = 298 (2)$ K
$\gamma = 83.77 (1)°$	Polyhedron, blue
$V = 783.3 (2)$ Å^3	$0.38 \times 0.25 \times 0.19$ mm

Data collection

Stoe Stadi-4 diffractometer	$\theta_{max} = 27.5°$
$\omega/2\text{-}\theta$ scans	$h = -11 \rightarrow 11$
Absorption correction: numerical	$k = -15 \rightarrow 15$
(*X-SHAPE*; Stoe & Cie, 1996)	$l = 0 \rightarrow 10$
$T_{min} = 0.603$, $T_{max} = 0.678$	3 standard reflections
3588 measured reflections	frequency: 60 min
3588 independent reflections	intensity decay: 2.0%
3309 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0366P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$+ 2.8997P]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.15$	$(\Delta/\sigma)_{max} = 0.001$
3588 reflections	$\Delta\rho_{max} = 1.42$ e Å^{-3}
229 parameters	$\Delta\rho_{min} = -1.64$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å).

Mo1—Mo2	3.328 (1)	Mo3—Ot12	1.704 (3)
Mo2—Mo3	3.317 (1)	Mo3—Ot11	1.722 (3)
Mo1—Mo3^i	3.3081 (9)	Mo3—Ob4^i	1.920 (3)
Co—Mo1	3.2999 (9)	Mo3—Ob6	1.938 (3)
Co—Mo2	3.3191 (9)	Mo3—Oc1^i	2.307 (3)
Co—Mo3	3.3319 (9)	Mo3—Oc3	2.308 (3)
Co—Oc1	1.905 (3)	Oc3—Ot11^{ii}	2.831 (4)
Co—Oc2	1.909 (3)	C1—N2	1.295 (7)
Co—Oc3	1.918 (3)	C1—N3	1.323 (7)
Mo1—Ot7	1.711 (3)	C1—N1	1.331 (7)
Mo1—Ot8	1.712 (3)	C2—N5	1.08 (1)
Mo1—Ob5	1.921 (3)	C2—N6	1.427 (8)
Mo1—Ob4	1.934 (3)	C2—N4	1.473 (9)
Mo1—Oc1	2.266 (3)	Ow1—Oc2^{iii}	2.814 (5)
Mo1—Oc2	2.312 (3)	Ow1—Ot10^{iv}	2.765 (5)
Mo2—Ot10	1.706 (3)	Ow1—Ob6^i	2.956 (5)
Mo2—Ot9	1.707 (3)	Ow1—Ow2	2.843 (6)
Mo2—Ob6	1.915 (3)	Ow2—Oc1	2.638 (4)
Mo2—Ob5	1.949 (3)	Ow2—Ot9^{iii}	2.837 (5)
Mo2—Oc2	2.302 (3)	Ow2—Ot11^{ii}	2.937 (5)
Mo2—Oc3	2.308 (3)	Ow2—N1^v	2.930 (7)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$b\cdots$Ot7^i	0.86	2.46	3.044 (6)	126
N2—H2$b\cdots$Ot9^{iii}	0.86	2.26	3.094 (7)	164
N3—H3$a\cdots$Ot12^{iii}	0.86	2.02	2.855 (6)	163
N3—H3$b\cdots$Ot8	0.86	2.10	2.900 (6)	155
N4—H4$a\cdots$Ob5^i	0.86	1.96	2.78 (1)	159
N4—H4$b\cdots$Ot7	0.86	2.17	2.96 (1)	152
N5—H5$b\cdots$Ob4^{iv}	0.86	2.34	2.95 (1)	128
N6—H6$a\cdots$Ob5^v	0.86	1.94	2.803 (9)	177
N6—H6$b\cdots$Ob4	0.86	2.04	2.852 (9)	158
N6—H6$a\cdots$Ot10^v	0.86	2.54	2.941 (9)	110

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

The guanidiniun ion that is disordered over an inversion center was fixed at $(\frac{1}{2}, \frac{1}{2}, 0)$ and refined with geometrical restraints. All H atoms were placed in calculated positions, with N—H distances of 0.86 Å and H—N—H angles of 120°. They were included in the refinement in the riding-motion approximation, with $U_{iso} = 1.2U_{eq}(N)$. The highest peak in the difference map is 0.43 Å from N5, and the largest hole is 0.42 Å from N5.

Data collection: *Stadi*4 (Stoe & Cie, 1996); cell refinement: *Stadi*4; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

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