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Guanidinium Heptamolybdate Monohydrate

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Abstract. $[CH_6N_3]_6[Mo_7O_{24}].H_2O$, $C2/c$, $a = 11{\cdot}979\ (7)$, $b = 15{\cdot}955\ (15)$, $c = 19{\cdot}923\ (18)$ Å, $\beta = 92{\cdot}27\ (5)^\circ$, $V = 3805$ Å^3, $D_m = 2{\cdot}46$, $D_x = 2{\cdot}50$ Mg m^{-3}, $Z = 4$. Final $R = 0{\cdot}091$ for 1784 independent reflections. The $[Mo_7O_{24}]^{6-}$ isopolyanion, in which seven distorted MoO_6 octahedra share edges, is identical with the anion in the heptamolybdates of Na^+, K^+, and NH_4^+. The planar cations link the anions through an extensive network of hydrogen bonds.

Introduction. Sodium, potassium, ammonium and guanidinum paramolybdates, which crystallize from aqueous solutions acidified to H^+: $MoO_4^{2-} \simeq 1{\cdot}15$, were all at one time formulated $5M_2O.12MoO_3.nH_2O$ on the basis of chemical analysis (*Gmelins Handbuch der Anorganischen Chemie*, 1935). The first three were subsequently shown by single-crystal diffraction studies (the most recent have been by Sjöbom & Hedman, 1973; Evans, Gatehouse & Leverett, 1975) to contain the heptamolybdate anion $[Mo_7O_{24}]^{6-}$, whose existence in solution was also demonstrated by potentiometric and X-ray methods (Sasaki & Sillen, 1968; Johansson, Pettersson & Ingri, 1974). The possibility remained, however, that guanidinium paramolybdate contained a different anion, since (i) small errors in chemical analysis can radically alter the assigned formulae of isopolyanion salts, and (ii) instances of isomerism are known in the isopolymolybdate series, for instance α-$[Mo_8O_{26}]^{4-}$ (Fuchs & Hartl, 1976; Day, Fredrich, Klemperer & Shum, 1977), β-$[Mo_8O_{26}]^{4-}$ (Gatehouse, 1977) and $[Mo_4O_{13}^{2-}]_\infty$ (Gatehouse & Leverett, 1971).

Colourless elongated prisms, giving satisfactory analyses for $[CH_6N_3]_6[Mo_7O_{24}].H_2O$, were obtained on cooling a mixture of hot solutions of sodium heptamolybdate (approximately 0·3 *M* in Mo) and guanidinium chloride. Data were collected *via* equi-inclination multi-film Weissenberg photographs of the levels 0–10*kl* and *h*0–2*l* by use of Cu *Kα* radiation. Films were scanned by the SRC Microdensitometer Service, Daresbury Laboratory. Intensities were corrected for absorption ($\mu = 19{\cdot}6$ mm^{-1}). The Mo atoms were located in space group *Cc* by direct methods. All non-hydrogen atoms were located by difference syntheses alternating with cycles of least-squares refinement. It appears that the correct space group is $C2/c$, but that one of the four independent cations and the water molecule each have site-occupancy factors of 0·5 at general positions close to, and approximately related by, a centre of symmetry. Refinement in $C2/c$ terminated at $R = 0{\cdot}091$, $R_w = 0{\cdot}089$ [1784 independent reflections, 141 parameters, Mo anisotropic, O, C, and N isotropic, weighting factor $w = (1 + 0{\cdot}0133\ F^2)^{-1}$ in last cycle]. The *SHELX* 76 (Sheldrick, 1976) program was used in all calculations. Atomic

Table 1. *Atomic coordinates* (×10^4) *and isotropic thermal parameters* (×10^3)

	x	*y*	*z*	*U* (Å^2)
Mo(1)	5000	4549 (1)	2500	0·0232 (11)*
Mo(2)	2956 (1)	4230 (1)	3626 (1)	0·0306 (8)*
Mo(3)	5212 (1)	3157 (1)	3805 (1)	0·0273 (8)*
Mo(4)	7229 (1)	3212 (1)	2758 (1)	0·0259 (8)*
O(1)	4165 (11)	5216 (9)	2948 (8)	32 (3)
O(2)	6021 (10)	4168 (9)	3179 (7)	27 (3)
O(3)	4049 (9)	3532 (8)	3018 (7)	22 (2)
O(4)	2184 (13)	3508 (12)	4028 (9)	44 (4)
O(5)	2425 (13)	5194 (11)	3881 (9)	43 (4)
O(6)	4317 (11)	4134 (10)	4151 (8)	33 (3)
O(7)	6241 (13)	3317 (11)	4433 (9)	41 (4)
O(8)	4438 (13)	2331 (12)	4086 (9)	41 (4)
O(9)	6043 (11)	2564 (9)	3170 (8)	29 (3)
O(10)	2197 (11)	4182 (9)	2753 (8)	31 (3)
O(11)	7829 (12)	2412 (11)	2329 (8)	39 (4)
O(12)	8131 (12)	3404 (10)	3435 (8)	36 (3)
N(1)	1247 (15)	381 (14)	4479 (11)	41 (4)
N(2)	2391 (17)	591 (15)	3573 (12)	49 (5)
N(3)	2523 (17)	1466 (15)	4513 (12)	48 (5)
N(4)	−1214 (17)	1682 (15)	4124 (12)	49 (5)
N(5)	108 (17)	1894 (15)	3352 (12)	47 (5)
N(6)	189 (15)	2622 (13)	4339 (11)	39 (4)
N(7)	5939 (16)	915 (15)	2682 (11)	48 (5)
N(8)	5000	−282 (23)	2500	54 (8)
N(9)†	1593 (37)	4150 (34)	184 (25)	44 (10)
N(10)†	279 (38)	4983 (36)	−372 (28)	60 (12)
N(11)†	74 (38)	4587 (38)	751 (28)	61 (12)
C(1)	2065 (18)	801 (15)	4201 (12)	39 (5)
C(2)	−303 (16)	2063 (13)	3912 (12)	32 (4)
C(3)	5000	511 (20)	2500	34 (6)
C(4)†	668 (31)	4625 (27)	192 (22)	30 (8)
Aq†	−1534 (39)	6162 (39)	−58 (28)	68 (14)

* Equivalent isotropic thermal parameters defined by $U_{\rm eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

† Site-occupancy factor 0·5.

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Table 2. *Bond lengths* (Å) *in the* $[Mo_7O_{24}]^{6-}$ *anion*

	$CH_6N_3^+$ salt[a]		NH_4^+ salt[b]	Na^+ salt[c]
Point symmetry	2[d]	*mm*[e]	*mm*[e]	*mm*[e]
Mo(1)–O(1)	1·732 (14)	1·73	1·74	1·76
Mo(2)–O(4)	1·698 (17)	1·70	1·72	1·72
Mo(2)–O(5)	1·747 (18)	1·75	1·75	1·72
Mo(3)–O(7)	1·740 (17)	1·73	1·72	1·74
Mo(4)–O(12)	1·722 (17)			
Mo(3)–O(8)	1·718 (17)	1·71	1·73	1·70
Mo(4)–O(11)	1·710 (16)			
Mo(1)–O(2)	1·888 (15)	1·89	1·90	1·89
Mo(2)–O(6)	1·909 (15)	1·92	1·92	1·92
Mo(2)–O(10)	1·932 (16)			
Mo(3)–O(6)	2·028 (15)	2·01	1·97	1·98
Mo(4)–O(10^{i})	1·990 (17)			
Mo(3)–O(9)	1·894 (13)	1·93	1·92	1·92
Mo(4)–O(9)	1·963 (13)			
Mo(1)–O(3)	2·256 (13)	2·26	2·25	2·26
Mo(2)–O(1)	2·561 (14)	2·56	2·53	2·56
Mo(2)–O(3)	2·133 (12)	2·13	2·16	2·16
Mo(3)–O(2)	2·279 (13)	2·28	2·29	2·29
Mo(4)–O(2)	2·284 (13)			
Mo(3)–O(3)	2·140 (13)	2·17	2·18	2·16
Mo(4)–O(3^{i})	2·193 (17)			

(*a*) This work. (*b*) Evans, Gatehouse & Leverett (1975). (*c*) Sjöbom & Hedman (1973). (*d*) Actual point symmetry. (*e*) Ideal point symmetry, bond lengths averaged.

Table 3. *Other interatomic distances* (Å) *and angles* (°)

Mo(1)···Mo(2)	3·424 (2)	Mo(2)···Mo(4^{i})	3·201 (2)
Mo(1)···Mo(3)	3·421 (2)	Mo(3)···Mo(4)	3·256 (2)
Mo(1)···Mo(4)	3·440 (2)	Mo(3)···Mo(4^{i})	4·187 (3)
Mo(2)···Mo(3)	3·207 (2)		
O(1)–Mo(1)–O(1^{i})	104·1 (1·0)	O(6)–Mo(3)–O(9)	155·5 (6)
O(4)–Mo(2)–O(5)	104·5 (8)	O(9)–Mo(4)–O(10^{i})	153·4 (7)
O(7)–Mo(3)–O(8)	104·7 (9)	O(3)–Mo(1)–O(3^{i})	88·0 (6)
O(11)–Mo(4)–O(12)	105·1 (7)	O(1)–Mo(2)–O(3)	69·4 (5)
O(2)–Mo(1)–O(2^{i})	142·4 (7)	O(2)–Mo(3)–O(3)	71·3 (5)
O(6)–Mo(2)–O(10)	148·4 (6)	O(2)–Mo(4)–O(3^{i})	70·7 (6)
C(1)–N(1)	1·33 (3)	C(3)–N(7)	1·33 (3)
C(1)–N(2)	1·37 (3)	C(3)–N(8)	1·27 (5)
C(1)–N(3)	1·34 (3)	C(4)–N(9)	1·34 (7)
C(2)–N(4)	1·33 (3)	C(4)–N(10)	1·33 (7)
C(2)–N(5)	1·27 (3)	C(4)–N(11)	1·35 (6)
C(2)–N(6)	1·35 (3)		
O(6)···N(1^{ii})	3·10 (5)	O(9)···N(7)	2·81 (4)
O(6)···N(1^{iii})	2·94 (4)	O(5)···N(7^{v})	3·14 (5)
O(2)···N(2^{ii})	2·89 (4)	O(10)···N(8^{iv})	2·79 (4)
O(8)···N(3)	2·84 (4)	O(5)···N(9^{vi})	3·01 (5)
O(4)···N(3^{iii})	2·91 (4)	O(7)···N(9^{i})	2·99 (5)
O(5)···N(4^{ii})	2·91 (4)	O(5)···N(10^{vii})	3·03 (5)
O(7)···N(4^{iii})	2·88 (4)	Aq···N(10)	2·96 (6)
O(11)···N(5^{iv})	2·98 (4)	O(5)···N(11^{iv})	3·26 (5)
O(1)···N(5^{ii})	3·00 (4)	O(12)···N(11^{iv})	3·25 (5)
O(4)···N(6)	2·87 (4)	O(5)···Aq^{iv}	3·04 (4)
O(8)···N(6^{iii})	3·15 (5)	O(7)···Aq^{viii}	2·93 (4)

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

coordinates are listed in Table 1, and derived dimensions in Tables 2 and 3.*

Discussion. The heptamolybdate anion is indeed present in guanidinium paramolybdate (Fig. 1). Here it has crystallographic point symmetry 2, but as in the Na^+, K^+ and NH_4^+ salts it approximates to point symmetry *mm*. The dimensions (Tables 2 and 3) are similar to those found by Sjöbom & Hedman (1973) and Evans, Gatehouse & Leverett (1975). The seven MoO_6 octahedra form a compact group by edge sharing. These octahedra are highly distorted; each Mo atom is displaced from the octahedron centre towards the periphery of the anion. Thus, the bonds around each Mo (Fig. 1 and Table 2) fall into three groups: (i) a short *cis* pair (Mo–O 1·70–1·75 Å, O–Mo–O 104·1–105·1°), terminal except for Mo(1) which shares all attached O atoms; (ii) a pair of medium length (1·89–2·03 Å), 142–153° apart and each *cis* to both short bonds; and (iii) a long pair (2·13–2·56 Å), each *trans* to a short bond. Consequently, the anion may be described in the following alternative way. A boat-like Mo_6O_{18} ring is formed from six tetrahedra sharing corners. Each of these Mo atoms forms an additional long bond to an O atom of a seventh tetrahedron [Mo(1)] above the centre of the boat. Two extra O atoms [O(3), O(3^{i})], each forming four long bonds, complete the sixfold coordination of the Mo atoms.

There are six cations per anion, so the latter is unprotonated. The lengths of the shorter N···O contacts (Table 3) and their directions close to the cation planes indicate an extensive network of hydrogen bonds linking the cations and anions in three dimensions. The only N atoms not involved are N(2), and possibly also N(11) which makes only weak contacts with anion O atoms. The half molecule of

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35762 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

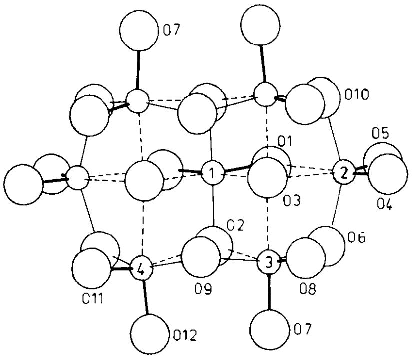

Fig. 1. The $[Mo_7O_{24}]^{6-}$ anion. Heavy, light and dashed lines indicate short, medium and long bonds (see *Discussion*).

water is weakly bonded to N(10) of the half-cation across a centre of symmetry, and to two anion O atoms.

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