

The Structure of Tetraguanidinium α -Dodecamolybdosilicate Monohydrate, (CH₆N₃)₄[SiMo₁₂O₄₀].H₂O

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Abstract

Crystals of (CH₆N₃)₄[SiMo₁₂O₄₀].H₂O are triclinic, space group $P\bar{1}$, with $a = 13.372$ (3), $b = 21.016$ (5), $c = 12.083$ (2) Å, $\alpha = 120.60$ (2), $\beta = 123.46$ (1), $\gamma = 52.46$ (1)° and $Z = 2$. The structure was determined by the heavy-atom method and refined by the least-squares method to $R = 0.064$ for 11 608 independent reflexions collected by diffractometry. The heteropolyanion has a structure with point symmetry T (23), lower than the T_d ($\bar{4}3m$) of the ideal 'Keggin molecule', resulting from the dispositions of the Mo atoms. In accord with the decrease in symmetry of each MoO₆ octahedron, six different Mo—O distances are observed with the mean values: 1.69 (1), 1.84 (2), 1.86 (3), 1.98 (3), 2.00 (4) and 2.34 (1) Å. The bond orders are estimated to be approximately 2 (to the terminal O atom), 1, 1, $\frac{2}{3}$, $\frac{2}{3}$ (to the four bridging O atoms), and $\frac{1}{6}$ (to the interior O atom coordinated to the Si atom), respectively. No unusual interactions are found between the anion and its surroundings. The skeleton of the guanidinium ion takes D_{3h} ($\bar{6}m2$) symmetry, and the water molecule is non-structural and zeolitic.

Introduction

The heteropolyanions with the formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ ($X = B, Si, P, Ge, As$ and $M = Mo$ and W) are well known as 'Keggin structures'. Various chemical and physical properties have been investigated, especially for [SiMo₁₂O₄₀]⁴⁻ and [PMo₁₂O₄₀]³⁻ because of their importance in the analytical chemistry of Si and P (Strickland, 1952; Truesdale & Smith, 1975). The structures of [SiW₁₂O₄₀]⁴⁻, [PW₁₂O₄₀]³⁻ and [PMo₁₂O₄₀]³⁻ have been studied by X-ray diffractometry, because their crystals are more manageable than those of the others. As part of a series of investigations into structural differences caused by different elements at the common X site, the crystal structure of the title salt has been determined. The empirical equation of Schröder (1975) relating bond

distance and bond order was applied to interpret the results.

Experimental

From an aqueous solution of [SiMo₁₂O₄₀]⁴⁻ prepared according to *Inorganic Syntheses* (1939), the tetraguanidinium salt was precipitated by quantitative addition of guanidine hydrochloride. Yellow needles of the hexahydrate, described in *Gmelins Handbuch der Anorganischen Chemie* 53 (1974), were crystallized from the filtrate by standing for a day. Triclinic plates of the monohydrate were obtained by recrystallization of the precipitate obtained from water after a week. Of the two species, the latter was selected for the structure determination as it is more resistant to reduction and efflorescence than the former. The number of the water molecules was determined from a TGA–DSC diagram, which showed that the water molecules (0.9 weight%) were slowly lost from the crystal in the temperature range 353–403 K.

Preliminary cell dimensions and space group were determined from oscillation and Weissenberg photographs. The density of the crystals was measured by flotation in a mixture of diiodomethane and chloroform. A single crystal of dimensions 0.15 × 0.31 × 0.38 mm was used for the intensity measurement. The intensity data were collected on a Rigaku automated four-circle diffractometer using Mo $K\alpha$ radiation monochromated by a graphite plate, the θ – 2θ scan mode being employed. 12 815 independent reflections below $2\theta = 65^\circ$ with $|F| > 3\sigma(|F|)$ were regarded as observed and used for the structure determination and refinement.

The crystal data are: (CH₆N₃)₄[SiMo₁₂O₄₀].H₂O, $M_r = 2077.7$, triclinic, $a = 13.372$ (3), $b = 21.016$ (5), $c = 12.083$ (2) Å, $\alpha = 120.60$ (2), $\beta = 123.46$ (1), $\gamma = 52.46$ (1)°, $U = 2108$ Å³, $Z = 2$, $D_m = 3.18$, $D_x = 3.18$ Mg m⁻³, μ for Mo $K\alpha$ ($\lambda = 0.71069$ Å) = 3.41 mm⁻¹, space group $P\bar{1}$.

Structure determination and refinement

The structure was solved by the heavy-atom method, the space group $P\bar{1}$ being assumed. Approximate positions of all the Mo atoms were deduced from three-dimensional Patterson maps. The other non-hydrogen atoms were located by successive Fourier syntheses and the block-diagonal least-squares method. All the H atoms were found from a difference Fourier synthesis. After inclusion of the H atoms with isotropic thermal parameters, further refinement was carried out. The final R and R_w values were 0.064 and 0.065, respectively, for 11 608 independent reflexions. The weighting scheme used was $w^{-1} = \sigma^2(F_o) + c|F_o|^2$,

where the value of c was 0.0004 estimated from fluctuations of the intensities of the standard reflexions. The atomic scattering factors for all atoms and corrections for anomalous scattering for the non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974). Table 1 lists the final positional parameters with their estimated standard deviations.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35097 (62 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$ for non-hydrogen atoms; $\times 10^3$ for H atoms) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Si	4268 (2)	2524 (1)	4829 (2)	OT(7)	6217 (6)	4609 (4)	8266 (6)
Mo(1)	1673 (1)	2542 (1)	4944 (1)	OT(8)	1038 (6)	5556 (4)	4539 (6)
Mo(2)	988 (1)	3016 (1)	2270 (1)	OT(9)	2501 (6)	4532 (4)	8851 (6)
Mo(3)	3068 (1)	1042 (1)	2546 (1)	OT(10)	5288 (5)	1589 (4)	8719 (5)
Mo(4)	5435 (1)	1141 (1)	2044 (1)	OT(11)	7444 (6)	-619 (3)	4665 (6)
Mo(5)	3580 (1)	3178 (1)	2200 (1)	OT(12)	9116 (5)	1726 (4)	8454 (6)
Mo(6)	6742 (1)	2465 (1)	4455 (1)	C(1)	610 (9)	5882 (6)	1655 (10)
Mo(7)	5266 (1)	4107 (1)	7146 (1)	C(2)	1633 (7)	1696 (5)	8008 (8)
Mo(8)	2085 (1)	4626 (1)	4928 (1)	C(3)	6782 (8)	3416 (5)	1593 (7)
Mo(9)	3113 (1)	4008 (1)	7580 (1)	C(4)	9165 (8)	1049 (6)	1492 (9)
Mo(10)	5173 (1)	1755 (1)	7410 (1)	N(1)	-437 (8)	6015 (7)	1778 (9)
Mo(11)	6573 (1)	425 (1)	4980 (1)	N(2)	511 (11)	5919 (8)	550 (11)
Mo(12)	7506 (1)	1906 (1)	7376 (1)	N(3)	1783 (9)	5695 (8)	2682 (12)
OI(1)	2971 (4)	2342 (3)	3955 (4)	N(4)	507 (7)	1831 (7)	6888 (8)
OI(2)	4810 (4)	2386 (3)	3755 (5)	N(5)	1732 (7)	1549 (7)	9017 (7)
OI(3)	3850 (4)	3474 (3)	5780 (4)	N(6)	2622 (8)	1774 (6)	8149 (7)
OI(4)	5456 (4)	1880 (3)	5795 (4)	N(7)	5676 (7)	3387 (6)	1215 (8)
OE(1)	415 (4)	3060 (3)	3528 (5)	N(8)	6894 (7)	3647 (5)	840 (7)
OE(2)	1373 (5)	1923 (3)	1513 (5)	N(9)	7824 (7)	3180 (5)	2712 (8)
OE(3)	2019 (5)	1470 (3)	3593 (5)	N(10)	8051 (8)	1046 (8)	1105 (8)
OE(4)	4285 (5)	2002 (4)	1141 (5)	N(11)	9349 (8)	1194 (8)	694 (10)
OE(5)	5272 (5)	3099 (4)	2984 (5)	N(12)	10084 (8)	935 (7)	2689 (9)
OE(6)	6827 (5)	1496 (4)	2961 (5)	OW	-549 (21)	159 (24)	3867 (42)
OE(7)	3729 (5)	4859 (3)	6258 (5)	H1(1)	-49 (11)	585 (8)	229 (12)
OE(8)	1915 (5)	4844 (3)	6543 (5)	H1(2)	-115 (10)	627 (7)	146 (10)
OE(9)	4454 (5)	4334 (3)	8341 (5)	H2(1)	37 (10)	607 (7)	-5 (11)
OE(10)	6075 (5)	655 (3)	6451 (5)	H2(2)	59 (10)	574 (7)	41 (10)
OE(11)	7923 (5)	719 (4)	6277 (5)	H3(1)	247 (10)	542 (7)	345 (11)
OE(12)	6971 (4)	1787 (3)	8344 (5)	H3(2)	196 (11)	583 (8)	275 (12)
OP(1)	1967 (5)	3467 (3)	6247 (5)	H4(1)	-18 (10)	241 (7)	679 (11)
OP(2)	2091 (5)	2999 (4)	1791 (5)	H4(2)	40 (11)	132 (8)	620 (12)
OP(3)	4674 (5)	582 (3)	3811 (5)	H5(1)	234 (11)	100 (8)	933 (12)
OP(4)	3960 (5)	1099 (3)	1786 (5)	H5(2)	126 (11)	199 (8)	954 (12)
OP(5)	2993 (5)	4075 (4)	3589 (5)	H6(1)	264 (11)	232 (7)	836 (11)
OP(6)	7591 (5)	1924 (4)	5766 (5)	H6(2)	333 (11)	131 (8)	797 (12)
OP(7)	5958 (5)	3483 (3)	5707 (5)	H7(1)	571 (10)	309 (7)	99 (11)
OP(8)	1161 (5)	4038 (3)	3763 (5)	H7(2)	484 (10)	364 (7)	114 (11)
OP(9)	4421 (5)	2979 (3)	7982 (5)	H8(1)	673 (9)	396 (6)	75 (9)
OP(10)	3467 (5)	1915 (3)	6203 (5)	H8(2)	718 (9)	351 (6)	45 (9)
OP(11)	6415 (5)	615 (3)	3534 (5)	H9(1)	859 (10)	287 (7)	308 (10)
OP(12)	6569 (5)	3032 (3)	7693 (5)	H9(2)	783 (10)	334 (6)	323 (10)
OT(1)	687 (5)	2554 (3)	5422 (5)	H10(1)	764 (10)	136 (7)	117 (10)
OT(2)	-557 (5)	3480 (4)	1178 (6)	H10(2)	772 (10)	73 (7)	80 (11)
OT(3)	2713 (6)	261 (4)	1374 (6)	H11(1)	968 (11)	98 (7)	42 (11)
OT(4)	6012 (6)	322 (4)	797 (5)	H11(2)	918 (10)	155 (7)	49 (11)
OT(5)	2824 (5)	3628 (4)	929 (6)	H12(1)	1037 (10)	116 (7)	323 (11)
OT(6)	7999 (5)	2546 (4)	4584 (5)	H12(2)	1061 (11)	60 (8)	299 (12)

Table 2. *Interatomic distances (Å) and bond angles (°) with estimated standard deviations in parentheses*

Mo(1)—Mo(2)	3.342 (1)	Mo(10)—Mo(11)	3.357 (1)	Mo(4)—Mo(11)	3.721 (1)	Si—Mo(4)	3.537 (2)
Mo(2)—Mo(3)	3.374 (1)	Mo(11)—Mo(12)	3.346 (1)	Mo(5)—Mo(8)	3.710 (1)	Si—Mo(5)	3.437 (2)
Mo(3)—Mo(1)	3.363 (1)	Mo(12)—Mo(10)	3.346 (1)	Mo(6)—Mo(7)	3.705 (1)	Si—Mo(6)	3.500 (2)
Mo(4)—Mo(5)	3.358 (1)	Mo(1)—Mo(9)	3.717 (1)	Mo(6)—Mo(12)	3.695 (1)	Si—Mo(7)	3.534 (2)
Mo(5)—Mo(6)	3.358 (1)	Mo(1)—Mo(10)	3.705 (1)	Mo(7)—Mo(12)	3.734 (1)	Si—Mo(8)	3.491 (2)
Mo(6)—Mo(4)	3.367 (1)	Mo(2)—Mo(5)	3.733 (1)	Mo(9)—Mo(10)	3.712 (1)	Si—Mo(9)	3.522 (2)
Mo(7)—Mo(8)	3.349 (1)	Mo(2)—Mo(8)	3.703 (1)	Si—Mo(1)	3.526 (2)	Si—Mo(10)	3.519 (2)
Mo(8)—Mo(9)	3.325 (1)	Mo(3)—Mo(4)	3.671 (1)	Si—Mo(2)	3.555 (2)	Si—Mo(11)	3.554 (2)
Mo(9)—Mo(7)	3.334 (1)	Mo(3)—Mo(1)	3.684 (1)	Si—Mo(3)	3.515 (2)	Si—Mo(12)	3.525 (2)
Mo(1)—OE(1)—Mo(2)	120.78 (4)	Mo(7)—OE(7)—Mo(8)	120.26 (5)	Mo(1)—OP(1)—Mo(9)	152.77 (4)	Mo(7)—OP(7)—Mo(6)	153.03 (4)
Mo(2)—OE(2)—Mo(3)	120.63 (5)	Mo(8)—OE(8)—Mo(9)	120.37 (4)	Mo(2)—OP(2)—Mo(5)	153.66 (4)	Mo(8)—OP(8)—Mo(3)	151.25 (4)
Mo(3)—OE(3)—Mo(1)	121.76 (4)	Mo(9)—OE(9)—Mo(7)	119.39 (4)	Mo(3)—OP(3)—Mo(11)	150.26 (4)	Mo(9)—OP(9)—Mo(10)	149.67 (4)
Mo(4)—OE(4)—Mo(5)	120.15 (4)	Mo(10)—OE(10)—Mo(11)	121.09 (4)	Mo(4)—OP(4)—Mo(2)	148.51 (4)	Mo(10)—OP(10)—Mo(1)	151.64 (4)
Mo(5)—OE(5)—Mo(6)	119.81 (5)	Mo(11)—OE(11)—Mo(12)	121.10 (4)	Mo(5)—OP(5)—Mo(8)	149.92 (4)	Mo(11)—OP(11)—Mo(4)	154.17 (4)
Mo(6)—OE(6)—Mo(4)	121.56 (4)	Mo(12)—OE(12)—Mo(10)	118.80 (4)	Mo(6)—OP(6)—Mo(12)	149.54 (4)	Mo(12)—OP(12)—Mo(7)	150.84 (4)

MoO₆ octahedra

	OT	OP ₁	OE ₁	OP ₂	OE ₂	OI
Mo(1)	OT(1)	OP(1)	OE(1)	OP(10)	OE(3)	OI(1)
	1.690 (7)	1.852 (7)	1.882 (7)	1.993 (7)	1.943 (7)	2.347 (6)
Mo(2)	OT(2)	OP(2)	OE(2)	OP(8)	OE(1)	OI(1)
	1.677 (8)	1.834 (7)	1.821 (7)	2.030 (7)	1.991 (7)	2.336 (6)
Mo(3)	OT(3)	OP(3)	OE(3)	OP(4)	OE(2)	OI(1)
	1.683 (8)	1.799 (7)	1.879 (7)	1.944 (7)	2.060 (7)	2.337 (6)
Mo(4)	OT(4)	OP(4)	OE(4)	OP(11)	OE(6)	OI(2)
	1.689 (8)	1.870 (7)	1.898 (7)	1.959 (7)	1.956 (8)	2.356 (7)
Mo(5)	OT(5)	OP(5)	OE(5)	OP(2)	OE(4)	OI(2)
	1.695 (9)	1.848 (7)	1.839 (8)	1.999 (7)	1.977 (7)	2.334 (7)
Mo(6)	OT(6)	OP(6)	OE(6)	OP(7)	OE(5)	OI(2)
	1.697 (8)	1.835 (8)	1.902 (8)	1.920 (7)	2.041 (8)	2.349 (7)
Mo(7)	OT(7)	OP(7)	OE(7)	OP(12)	OE(9)	OI(3)
	1.687 (8)	1.890 (7)	1.792 (7)	2.006 (7)	1.972 (7)	2.338 (6)
Mo(8)	OT(8)	OP(8)	OE(8)	OP(5)	OE(7)	OI(3)
	1.695 (8)	1.829 (7)	1.878 (7)	1.993 (7)	2.066 (7)	2.322 (6)
Mo(9)	OT(9)	OP(9)	OE(9)	OP(1)	OE(8)	OI(3)
	1.675 (8)	1.868 (7)	1.890 (7)	1.942 (7)	1.955 (7)	2.343 (6)
Mo(10)	OT(10)	OP(10)	OE(10)	OP(9)	OE(12)	OI(4)
	1.696 (8)	1.829 (7)	1.886 (7)	1.978 (7)	2.046 (7)	2.338 (6)
Mo(11)	OT(11)	OP(11)	OE(11)	OP(3)	OE(10)	OI(4)
	1.686 (8)	1.859 (7)	1.830 (8)	2.012 (7)	1.969 (7)	2.353 (6)
Mo(12)	OT(12)	OP(12)	OE(12)	OP(6)	OE(11)	OI(4)
	1.700 (9)	1.820 (7)	1.840 (7)	2.029 (8)	2.012 (8)	2.340 (6)

Mean angles in MoO₆ octahedra

OT—Mo—OP ₁	103.1 (11)
OT—Mo—OP ₂	99.7 (18)
OP ₁ —Mo—OE ₁	95.5 (23)
OP ₁ —Mo—OE ₂	157.9 (16)
OE ₁ —Mo—OE ₂	87.8 (24)

SiO₄ tetrahedron

Si	OI(1)	OI(2)	OI(3)	OI(4)
	1.627 (7)	1.641 (7)	1.622 (7)	1.632 (7)
OI(1)—Si—		108.9 (3)	110.3 (3)	109.1 (3)
OI(2)—Si—			109.0 (3)	109.7 (3)
OI(3)—Si—				109.8 (3)

Description and discussion of the structure

[SiMo₁₂O₄₀]⁴⁻ anion

Fig. 1 shows the structure of the [SiMo₁₂O₄₀]⁴⁻ anion. The interatomic distances and bond angles are given in Table 2. The molecule consists of an SiO₄ tetrahedron, of which the O atoms (OI) are shared with the surrounding twelve MoO₆ octahedra subdivided into four Mo₃O₁₃ units. Three MoO₆ octahedra in the

same unit are linked to one another by sharing edges (OE to OI), making one vertex (OI) common to them all. The four units join at the remaining two points (OP) and surround tetrahedrally the SiO₄ group. Polyhedral representations of the molecular structure are given in Fig. 2. The dispositions of the Si and O atoms approximately conform to point symmetry *T_d*. The mean value of 1.631 (7) Å for the Si—O distances agrees well not only with that of the [SiW₁₂O₄₀]⁴⁻ anion, 1.631 (11) Å, obtained by neutron diffraction

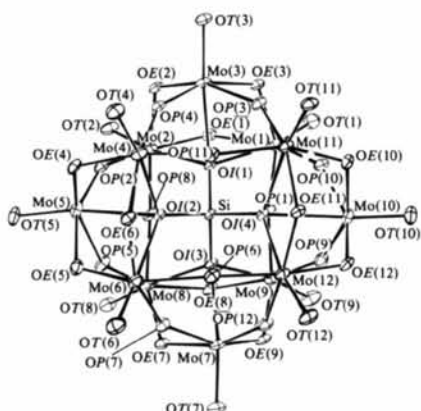


Fig. 1. The structure of the $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ anion with labelling of the atoms.

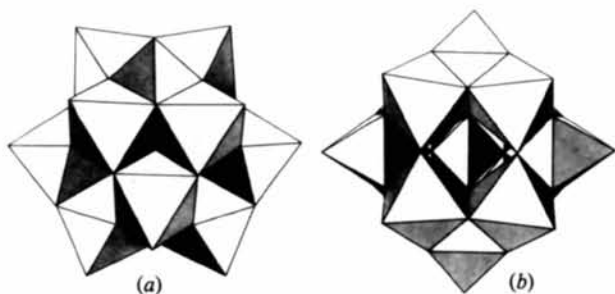


Fig. 2. Polyhedral representations of the anion projected along the (a) 3, and (b) 4 axes.

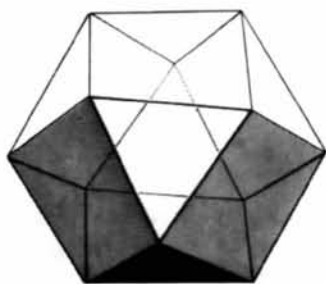


Fig. 3. Cubo-octahedron representation of the anion, showing molecular symmetry T .

(Smith, 1971), but also with those of orthosilicates, within the limits of error (Baur, 1978). However, the whole polyanion has a symmetry lower than the ideal Keggin molecule of point group T_d . There is a definite deviation of the Mo atoms from the corresponding mirror planes and 4 axes, as can be seen from the cubo-octahedron model in Fig. 3. A projection of the Mo_3O_{13} unit on a plane of the SiO_4 tetrahedron is given in Fig. 4. Three Mo atoms make an approximately equilateral triangle, rotated slightly around the three-fold axis. The lines joining each Mo atom to the center of the triangle are inclined at mean angle of 4.2° with

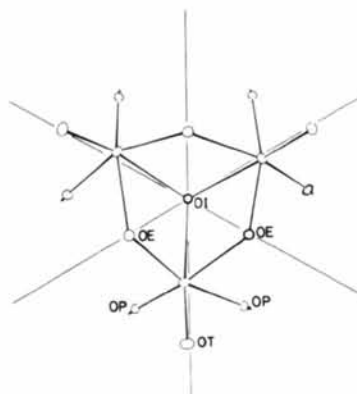
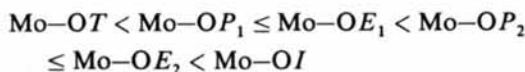


Fig. 4. An Mo_3O_{13} unit projected on a plane of the central tetrahedron, of which the three mirror planes are shown.

respect to the mirror planes of the SiO_4 tetrahedron. This means that the molecular symmetry of this anion is lowered from T_d ($4\bar{3}m$) to T (23), in a similar manner to $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]\cdot 13\text{--}14\text{H}_2\text{O}$ (d'Amour & Allmann, 1976). If a 12-heteromolybdate anion takes T_d symmetry, each Mo atom is required to be at the mid-point between two OP and two OE atoms, and the increasing order of the bond distances is always



whereas in the case of T symmetry, alternation between Mo--OP and Mo--OE is observed:



(the common subscripts for OP and OE indicate that they take the *cis* position with respect to each other). A bridging O atom (OP or OE) is bonded strongly to one Mo atom and weakly to the other.

To interpret the details of the polyanion structure of symmetry T , calculation of the bond orders for Mo--O have been performed, based on the empirical equation proposed by Schröder (1975):

$$d_{\text{Mo--O}} = 1.874 - 0.60_0 \log \text{BO}_{\text{Mo--O}},$$

where $d_{\text{Mo--O}}$ and $\text{BO}_{\text{Mo--O}}$ are the mean bond distance and bond order of Mo--O , respectively. The mean values of bond distances with corresponding bond orders and relevant bond angles are summarized in Table 3. They are also compared to those of $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]\cdot 13\text{--}14\text{H}_2\text{O}$ (d'Amour & Allmann, 1976) and $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]\cdot 29\text{--}30\text{H}_2\text{O}$ (Strandberg, 1975). As can be seen in Table 3, the Mo--OT bond can be regarded as a double bond in every case, while the Mo--OI bond (at the *trans* position to Mo--OT) is rather ionic. When the molecule takes symmetry T , both the Mo--OP (Si: 1.12 and 0.66, P: 1.1 and 0.7) and Mo--OE (Si: 1.05 and 0.62, P: 1.0 and 0.7) bonds have two different bond orders of approximately 1 and $\frac{2}{3}$ in each MoO_6 octahedron. However, average bond orders of Mo--OP (Si: 0.89, P: 0.9) and Mo--OE (Si:

Table 3. Comparison of bond distances (\AA), bond orders and bond angles ($^\circ$) in $[X^{n+}Mo_{12}O_{40}]^{(8-n)-}$ ions

Symmetry	$(CH_6N_3)_4[SiMo_{12}O_{40}] \cdot H_2O$		$H_3[PMo_{12}O_{40}] \cdot 13-14H_2O$		$H_3[PMo_{12}O_{40}] \cdot 29-30H_2O$	
	T		T		T_d	
Mo—OT	1.688 (7)	2.04	1.66	2.2	1.678	2.11
Mo—OP*	1.914	0.89	1.91	0.9	1.911	0.87
Mo—OP ₁	1.844 (24)	1.12	1.85	1.1		
Mo—OP ₂	1.984 (33)	0.66	1.96	0.7		
Mo—OE*	1.930	0.84	1.91	0.8	1.924	0.84
Mo—OE ₁	1.861 (34)	1.05	1.87	1.0		
Mo—OE ₂	1.999 (42)	0.62	1.97	0.7		
Mo—OI	2.341 (9)	0.17	2.43	0.1	2.435	0.11
Mo—O _{mean}	1.952	0.94	1.96	0.9 ₇	1.964	0.94
X—OI	1.631 (7)		1.54		1.542	
Mo—OP—Mo	151.3 (17)		152		151.3	
Mo—OE—Mo	120.5 (8)		125		126.0	

* Mean of following items when the molecular symmetry is T .

0.84, P: 0.8) agree well with those in the case of T_d symmetry (0.87 and 0.84). In every case, the average bond order around the bridging O atom is less than 1.0. The O—Mo—O chains composing the present anion and other polymolybdate frameworks are not rigid, and the transformation of a symmetric bridging oxygen into an asymmetric one can be caused easily by packing effects in the crystals. The asymmetric *trans* $[-O^{2/3}Mo^{\perp}O-]_n$ chains are also found in $Na_3[PMo_9O_{31}(H_2O)_3] \cdot 12-13H_2O$ (Strandberg, 1974; Hedmann, 1978) and $Na_3[PMo_9O_{31}(H_2O)_3] \cdot nH_2O$ (d'Amour, 1976). As has been mentioned, this oxygen bridge seems to be symmetric in all W analogues (d'Amour, 1976; d'Amour & Allmann, 1976). Apart from the asymmetry, all parameters of the $[SiMo_{12}O_{40}]^{4-}$ anion are quite similar to those of the $[SiW_{12}O_{40}]^{4-}$ anion, including the $M-M$ and $Si-M$ distances.

The influences of the different hetero atoms X in polymolybdates are reflected most obviously in the bond distances $X-OI$ and $Mo-OI$ and the bond angle $Mo-OE-Mo$. The $X-OI$ bonds are shorter than the sums of the covalent radii of the X and O atoms. The differences in the $Mo-OI$ (bond orders to Si: 0.17, P: 0.12) lengths and $Mo-OE-Mo$ angles are certainly caused by the $X-OI$ distances and the formal oxidation numbers of the hetero atoms.

Guanidinium ions and water molecule

A projection of the crystal structure along c^* is shown in Fig. 5. There are four crystallographically independent guanidinium $CH_6N_3^+$ ions and one water molecule in the asymmetric unit. The mean values of the C—N distances, 1.32 (2) \AA , and N—C—N angles, 120.0 (8) $^\circ$, in each cation agree with those in CH_6ClN_3 , 1.323 (6) \AA and 119.9 (6) $^\circ$ (Haas, Harris & Mills, 1965). The skeleton, comprising three equivalent C—N bonds which are shorter than single bonds, has D_{3h} symmetry. However, the coordinates of the H

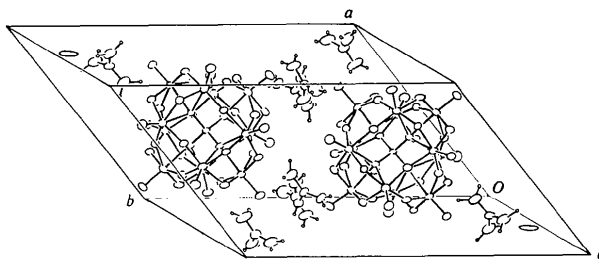


Fig. 5. The crystal structure projected along the c^* axis.

atoms are not accurate, and they lie out of the molecular plane. The IR spectrum (ν_{N-H} 3300 ~ 3500 cm^{-1} , $\nu_{C=N}$ 1660 cm^{-1}) of the compound agrees with that of $CH_6ClN_3O_4$ (Bonner & Jordan, 1975). None of the H atoms was found to be in the direction of any O atom.

The water molecule is zeolitic and has no interactions within a 3.2 \AA radius, except with the other water molecule in the unit cell. The two water molecules are paired at distances of 2.7 \AA and aligned approximately parallel to the c axis.

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The programs in the local version of *UNICS* (Sakurai, 1967), and *ORTEP* (Johnson, 1965) were used. All calculations were carried out on the HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo.

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A Neutron Diffraction Study of the Effect of Deuteration in Bis(3-amino-3-methyl-2-butanone oximato)nickel(II) Chloride Monohydrate

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Abstract

$[\text{Ni}(\text{C}_5\text{H}_9\text{D}_2\text{N}_2\text{O})_2\text{D}]^+\text{Cl}^-\cdot\text{D}_2\text{O}$, $\text{C}_{10}\text{H}_{18}\text{D}_5\text{N}_4\text{NiO}_2^+\text{Cl}^-\cdot\text{D}_2\text{O}$, monoclinic, $P2_1$, $a = 11.033$ (4), $b = 12.940$ (5), $c = 5.862$ (2) Å, $\beta = 101.97$ (1)°, $Z = 2$, $\rho_{\text{obs}} = 1.42$ (1), $\rho_{\text{calc}} = 1.424$ (2) Mg m^{-3} . The structure was solved directly from neutron data. The effects of deuteration on the short hydrogen bond [$\text{O}\cdots\text{O} = 2.439$ (8) Å] are examined by comparison with the corresponding normal hydrogen compound which crystallizes in $P2_1/c$. The bond is much more asymmetric with $\text{O}-\text{D} = 1.058$ (9) and $\text{D}\cdots\text{O} = 1.391$ (10) Å compared to $\text{O}-\text{H} = 1.187$ (5) and $\text{H}\cdots\text{O} = 1.242$ (5) Å. All water and amine deuterons are involved in hydrogen bonds with the chloride ion, the water molecule, or one of the oxime O atoms. The $\text{Ni}-\text{N}(\text{oxime})$ [1.860 (9) Å] and $\text{Ni}-\text{N}(\text{amine})$ [1.896 (1) Å] distances are slightly shorter than those in the normal hydrogen form. Distances within the ligand are equivalent within experimental error to those in the normal hydrogen form.

Introduction

The effect of deuteration on short symmetry-free hydrogen bonds has not been extensively studied, and the effect of deuteration is expected to yield significant information concerning the nature of the potential well describing the hydrogen position in various types of hydrogen bonds (e.g. Singh & Wood, 1969). An especially notable study of a short symmetry-free hydrogen bond has been carried out by Takusagawa & Koetzle (1979) on quinolinic acid at four temperatures. In that study the deuterium atom was found to shift slightly closer (~ 0.02 Å) to one O atom at all temperatures, and no significant change in the $\text{O}\cdots\text{O}$ distance was observed on deuteration at any of the temperatures from 35 K to 298 K. Similar effects were observed at room temperature for imidazolium hydrogen maleate (Hussain, Schlemper & Fair, 1980).

Bis(3-amino-3-methyl-2-butanone oximato)nickel(II) chloride monohydrate $\{[\text{Ni}(\text{ao})_2-\text{H}]^+\text{Cl}^-\cdot\text{H}_2\text{O}\}$ has a symmetry-free $\text{O}\cdots\text{O}$ hydrogen bond [2.420 (3) Å]