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Crystal structure of bis(tetra-*n*-butylammonium)dodecamolybdosulfate(VI)-(2−), $[NBu^n{}_4]_2[SMo_{12}O_{40}]$

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The structure of $[NBu^n{}_4]_2[SMo_{12}O_{40}]$ has been determined by the single-crystal X-ray method: cubic, space group *Fm*3*m*, $a = 18.824(1)$ Å and $Z = 4$. The structure model was refined by full-matrix least squares to $R = 0.0607$ and $R' = 0.0585$ for 320 independent reflections and 32 variables. The heteropolyion $[SMo_{12}O_{40}]^{2-}$ **1** contained in the crystals is a typical Keggin molecule with point symmetry $\bar{4}3m$ and located at sites of crystallographic *Fm*3*m* symmetry in two equally weighted orientations related by inversion at the S atom. The geometry is compared with those of the isomorphous Keggin molecules $[PMo_{12}O_{40}]^{3-}$ **2**, $[SiMo_{12}O_{40}]^{4-}$ **3** and $[GeMo_{12}O_{40}]^{4-}$ **4** as a function of the nature of the central heteroatom and in relation to the relative stability **1** ≪ **2** ≪ **3** < **4** in aqueous solution.

By previous, synthetic and X-ray crystallographic studies it was revealed that sulfate ions react with molybdate to produce the Dawson-type $[S_2Mo_{18}O_{62}]^{4-}$ and Strandberg-type $[S_2Mo_5O_{23}]^{4-}$ heteropolyions,[1] where the sulfate ions serve as the central tetrahedra in the same manner as phosphate ions do in the corresponding heteropolyions $[P_2Mo_{18}O_{62}]^{6-}$ and $[P_2Mo_5O_{23}]^{6-}$.[2,3] Unlike phosphate, however, the sulfate heteropolyions are favoured in aqueous solutions containing organic solvents such as MeCN, Me_2CO and EtOH. Although the effects due to the organic solvents are not fully understood yet, it is empirically expected that the Keggin-type $[SMo_{12}O_{40}]^{2-}$ **1** would also be derived from the reaction between sulfate and molybdate ions in the presence of certain organic solvents. In fact, Cartié[4] deduced the formation of **1** from a voltammetric measurement on the reaction products between sulfuric acid and sodium molybdate dissolved in glacial acetic acid dehydrated with anhydrous acetic acid. At the same time, he concluded that **1** would be a so-called Keggin-type heteropolyion, based both on the electrochemical characteristics and the IR spectrum observed for its tetraethylammonium salt. Being poorly soluble in various solvents, the tetraethylammonium salt has not yet been crystallized and hence the detailed, crystallographic nature of **1** is unknown apart from the fact that it is the first example of a dodecamolybdate complex including sulfate ion.

In parallel with this, a yellow salt of composition $[NBu^n{}_4]_2[SMo_{12}O_{40}]$ was isolated after treating sulfate ion with a mixture of molybdate and vanadates in aqueous Me_2CO solution.[5] It should be noted that, even in the presence of a fair amount of water, complex **1** can be formed with the aid of vanadate ion.[†] The tetrabutylammonium salt of **1** was readily soluble in neat Me_2CO and the solution gave well shaped crystals for X-ray structural analysis. Recently, Proust *et al.*[6] isolated the same salt from the reaction between $[NBu^n{}_4]_3[Mo_6O_{18}(NO)]$ and $(MeO)_2SO_2$ in an MeCN solution.

In the present paper we report the X-ray crystallographic analysis of $[NBu^n{}_4]_2[SMo_{12}O_{40}]$ and the detailed geometric characteristics of **1** having the so-called Keggin structure. The geometry is compared with a series of isomorphous Keggin molecules $[PMo_{12}O_{40}]^{3-}$ **2**,[7] $[SiMo_{12}O_{40}]^{4-}$ **3**[8] and $[GeMo_{12}O_{40}]^{4-}$ **4**[9] as a function of the natures of the central heteroions. The relative stability in the order **1** ≪ **2** ≪ **3** < **4** in aqueous solutions is related to the geometry of the individual heteropolyions.

Experimental

Preparation of materials

As reported previously, the salt $[NBu^n{}_4]_2[SMo_{12}O_{40}]$ was obtained by using $[NBu^n{}_4]Br$ as a precipitant from an aqueous Me_2CO solution consisting of Na_2MoO_4–NH_4VO_4–H_2SO_4, followed by successive washing with water, EtOH and MeCN.[5] The same salt is also obtainable according to Cartié's method[4] with a minor modification where the $LiClO_4$ was omitted and the precipitant $[NBu^n{}_4]Br$ was used in place of $[NEt_4][O_2CMe]$. One gram of the salt prepared by either method was dissolved in Me_2CO (100 cm^3) at ambient temperature and the solution concentrated by spontaneous evaporation in a chemical hood. After 3 d, when the solution volume had been reduced to approximately 60 cm^3, octahedral, lemon-yellow crystals appeared and grew to sizes of 0.2–0.5 mm in diameter until the mother-liquor started to change to orange-yellow.[‡] The crystals were collected by decantation and dried in the open air (Found: C, 16.80; H, 3.25; Mo, 49.80; N, 1.20; S, 1.35. Calc. for $[NBu^n{}_4]_2[SMo_{12}O_{40}]$: C, 16.65; H, 3.15; Mo, 49.90; N, 1.20; S, 1.40%). IR:[5] $\tilde{\nu}_{max}/cm^{-1}$ 1155vs, 982vs, 877s and 805vs.

Crystallography

A well shaped, octahedral crystal with approximate diameter 0.2 mm was glued to the end of a thin glass fibre and rotated along an axis perpendicular to one of the crystal faces. The rotating axis thus chosen was later found to be coincident with the [111] axis of the crystal.

Preliminary Weissenberg camera work showed cubic symmetry with systematic absences for $h + k, k + l, l + h = 2n + 1$, indicating possible space groups $F\bar{4}3m$, *F*432 and *Fm*3*m*; that initially assumed was $F\bar{4}3m$, (non-centrosymmetric) rather than *Fm*3*m* (centrosymmetric) based on the $\bar{4}$ point symmetry associated with the central SO_4 tetrahedra in the heteropolyions. As discussed later, however, *Fm*3*m* was finally

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[†] In the absence of vanadate the Dawson-type $[S_2Mo_{18}O_{62}]^{4-}$ ion forms predominantly; the essential role of the vanadate ion is not yet known.

[‡] On further concentration the crystals started to dissolve and the mother-liquor became orange-yellow. This is due to the conversion of complex **1** into the more stable Dawson-type $[S_2Mo_{18}O_{62}]^{4-}$ ion.

Table 1 Crystal data and the experimental parameters for $[NBu^n{}_4]_2[SMo_{12}O_{40}]$

Crystal size/mm	0.20 × 0.25 × 0.30
M	2308.26
Symmetry	Cubic
Space group	$Fm\bar{3}m$
a/Å	18.824(1)
U/Å^3	6670(1)
Z	4
D_m/g cm^{-3}	2.30
D_c/g cm^{-3}	2.30
$F(000)$	5752
μ(Mo-Kα)/cm^{-1}	22.43
Radiation (λ/Å)	Graphite-monochromated Mo-Kα (0.7107)
Scan technique	$2\theta-\omega$
Scan width, $\Delta\omega$/°	$(1.5 + 0.3\tan\theta)$
Scan speed/° min^{-1}	8
Scan range (2θ)/°	3–60
Collected reflections	15 914
Averaged reflections ($3 < 2\theta < 60°$) with $m3m$ symmetry	552
Reflections with $F_o > 3\sigma(F)$ ($3 < 2\theta < 50°$)	320
Final R'	0.0607
Final R	0.0585
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$

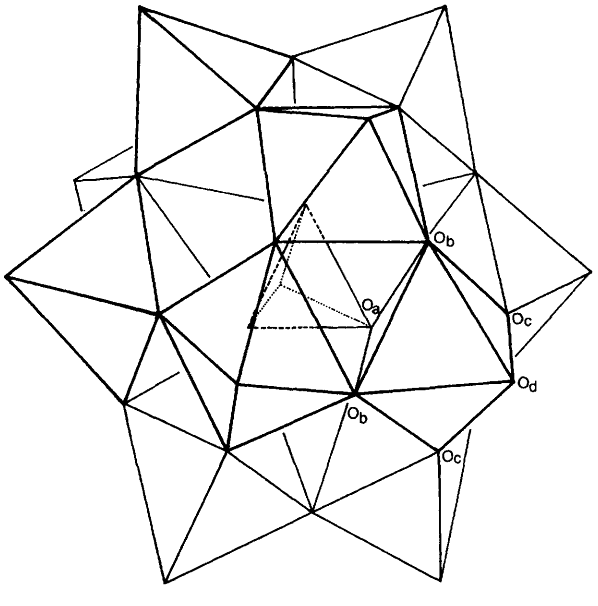

Fig. 1 Polyhedral representation of the structure of complex **1**, along with the designation of the O atoms where O_a denotes oxygens which bridge Mo (located at the centre of the MoO_6 octahedron) and the S atom (located at the centre of the SO_4 tetrahedron), O_b and O_c those linking MoO_6 octahedra by vertex and edge, respectively, and O_d those bonded to one Mo

Table 2 Interatomic distances (Å) and angles (°) for $[NBu^n{}_4]_2[SMo_{12}O_{40}]$

$Mo\cdots Mo^I$	3.581(1)	$S-O_a$	1.480(9)
$S\cdots Mo$	3.581(1)	N–C(1)	1.61(5)
$Mo-O_a$	2.52(1)	C(1)–C(2)^I	1.5(1)
$Mo-O_{b/c}{}^I$	1.891(8)	C(2)–C(3)^I	1.7(1)
$Mo-O_d$	1.649(1)	C(3)–C(4)^I	1.4(1)
$O_{b/c}{}^I-Mo-O_{b/c}{}^{II}$	86.9(5)	C(1)–N–C(1^{IV})	119.6(3)
$O_{b/c}{}^I-Mo-O_d$	103.6(4)	N–C(1)–C(2^I)	117(5)
$O_a-S-O_a{}^{III}$	109.5(8)	C(1)–C(2)–C(3^{II})	118(7)
O_a-Mo-O_d	160.2(1)	C(2)–C(3)–C(4^I)	118(6)

Symmetry codes: I z, x, y; II y, z, x; III $\bar{x}, \bar{y}, z$; IV $\frac{1}{2} - z, y, \frac{1}{2} - x$.

accepted. All the reflections were sharp and no super or diffuse reflections were observed in the oscillation and Weissenberg photographs. The intensity data were collected by using a Rigaku-AFC5S four-circle diffractometer. The crystal data and experimental parameters are summarized in Table 1.

Data processing. The Mo atoms were located by a Patterson map and the initial model refined to $R = 0.48$. The S, O and N atoms were then located by successive Fourier-difference maps. To locate the C atoms, Fourier maps were prepared for some planes perpendicular to the [111] axis, where each C appeared to be at three crystallographically equivalent positions with $\frac{1}{3}$ partial occupancy, as will be described later. No attempt to locate the H atoms was made. The total of 15 914 reflections measured at $2\theta < 60°$ were first converted into a set of 552 independent reflections by averaging the symmetrically identical reflections, and 320 reflections having $F_o > 3\sigma(F)$ were refined with unit weights using the program RADY.[10] The Fourier syntheses were carried out by using the program FRAXY.[11] Selected interatomic distances and angles, calculated by the program UMBADTEA,[12] are listed in Table 2.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/29.

Results and Discussion

Crystal structure of $[NBu^n{}_4]_2[SMo_{12}O_{40}]$

So-called Keggin molecules contain a tetrahedron-like SiO_4, GeO_4 and PO_4 at the centre. As illustrated in Fig. 1, the present molecule **1** contains an SO_4 tetrahedron at its centre and has $\bar{4}3m$ symmetry. Since the $[NBu^n{}_4]_2[SMo_{12}O_{40}]$ crystals have a face-centred cubic system, we started the structure determination by assuming the space group $F\bar{4}3m$ and by locating the Mo and O_d atoms at the (x, x, z) positions. This showed, however, that the z parameters for both atom types converged virtually to zero, *i.e.* $z = 0.000\,02$ and -0.011, respectively, suggesting strongly that the outer $Mo_{12}O_{36}$ moiety of **1** has $m3m$ point symmetry. In addition, the thermal parameters, B_{eq}, of the atoms in this moiety exhibited relatively large values (5–10 Å^2) in contrast to the S and O_a atoms in the central SO_4 (about 2 Å^2). There are two possible interpretations of these results.

One interpretation (an ordered model) is that complex **1** has point symmetry $\bar{4}3m$, but that the atoms in the $Mo_{12}O_{36}$ moiety deviate spatially to yield the large thermal parameters. The difficulty of this model, however, is that the Mo···Mo distances between neighbouring MoO_6 octahedra become uniform irrespective of the presence of their different types, *i.e.* sharing edges and vertices.

Evans and Pope[13] proposed another interpretation (a disordered model). According to them, a Keggin molecule of $\bar{4}$ symmetry has two different orientations in the crystals and one orientation is converted into the other by 90° rotation around the $\bar{4}$ axis. In the crystals these two orientations are present in equal proportion and show $4/m$ symmetry. For the crystals of $H_5[PV_2Mo_{10}O_{40}]$, $H_6[PV_3Mo_9O_{40}]$ and $[NBu_4]_3[PW_{12}O_{40}]$ (γ-type) which were originally described as containing Keggin-like molecules with approximate octahedral symmetry on crystallographic inversion centres, Evans and Pope[13] pointed out that the results were equally consistent with the presence of true Keggin molecules with approximately tetrahedral non-crystallographic symmetry in two equally weighted orientations differing by a 90° rotation about a local two-fold axis (or equivalently, by inversion at the central heteroatom). Weakley[14] reported the structure of $Ba_3[BCo(H_2O)W_{11}O_{39}]\cdot 26H_2O$ crystals, in which $[BCo(H_2O)W_{11}O_{39}]^{6-}$ with $\bar{4}$ point symmetry and itself derived through an inversion operation at the B atom occupied the $4/m$ site with equal weight.

Here, we adopted the disordered model, hence a space group of $Fm\bar{3}m$, and refined the model where the S atom is surrounded by eight O_a oxygens with partial occupancy of $\frac{1}{2}$ and the Mo, $O_{b/c}$, O_d atoms occupy the average positions of the two orientations of complex **1**. The anomalies of the thermal parameters (B_{eq} = 5.198, 6.80 and 10.12 Å^2 for Mo, $O_{b/c}$ and O_d atoms in the $Mo_{12}O_{36}$ moiety) and of the elongation in the z direction of the anisotropic thermal parameters [$U_{11} = U_{22}$ = 0.150, U_{33} = 0.17 for the O_d atom located at (x, x, 0)] are thus reasonably understood.

Fig. 2 illustrates the arrangements of the anion **1** and $[NBu^n{}_4]^+$ cations in the unit cell. The negative charge on **1** arising from the $SO_4{}^{2-}$ ion is neutralized by two $[NBu^n{}_4]^+$ ions. The ion $[SMo_{12}O_{40}]^{2-}$ **1** occupies the F centres of the cell and the $[NBu^n{}_4]^+$ enters into the cavities and is surrounded by four $[SMo_{12}O_{40}]^{2-}$ **1** ions. The centres of the cavities are at (0.25, 0.25, 0.25), (0.25, 0.25, 0.75), (0.25, 0.75, 0.25), (0.25, 0.75, 0.75), (0.75, 0.25, 0.25), (0.75, 0.25, 0.75), (0.75, 0.75, 0.25) and (0.75, 0.75, 0.75). In the unit cell, however, the larger cavity, centred at (0.5, 0.5, 0.5) and surrounded by six $[SMo_{12}O_{40}]^{2-}$ ions, is left unoccupied.

The N atom of $[NBu^n{}_4]^+$ is located at special point on the [111] axis of the cell. The four zigzag chains of C_4H_9 groups extend outwards from the N atom, twisting around the [111] axis. The configuration of $[NBu^n{}_4]^+$ is illustrated in Fig. 3, where individual C atoms in each zigzag chain ocupy with $\frac{1}{3}$ weight the three equivalent positions related by 120° rotation around a [111] axis. Such a configuration is suggested from the Fourier maps synthesized for the planes perpendicular to the [111] axis, but the electron density due to the C atoms which is sketched in Fig. 4 is so diffuse that the accuracy in locating the C atoms is relatively low.

Geometrical characteristics of complex 1

In the Keggin molecule **1** consisting of one SO_4 tetrahedron and twelve MoO_6 octahedra there are twelve linkages between the central SO_4 and the neighbouring twelve MoO_6 and 24 linkages between the neighbouring MoO_6 octahedra; half of the latter are formed by sharing edges and the other half by sharing vertices.

As given in the first row of Table 3, the geometric characteristics of **1** are presented in terms of the Mo···S distance averaged over the twelve SO_4–MoO_6 linkages and the Mo···Mo distance averaged over the 24 MoO_6–MoO_6 linkages. These characteristics are compared with those of a series of isomorphous Keggin molecules, *viz.*, $H_3[PMo_{12}O_{40}]\cdot nH_2O$,[7] $[CH_6N_3]_4[SiMo_{12}O_{40}]\cdot H_2O$,[8a] $H_4[SiMo_{12}O_{40}]\cdot 13H_2O$[8b] and $Na_4[GeMo_{12}O_{40}]\cdot 8H_2O$.[9] By formulating the Keggin molecules as $[(X^{n+})Mo_{12}O_{40}]^{(8-n)-}$, the central heteroatom, X^{n+}, is replaced successively with S^{6+}, P^{5+}, Si^{4+} and Ge^{4+}, and their geometrical changes in terms of interatomic distances Mo··· X (denoted here as l_1), Mo··· Mo (l_2–l_4), X–O_a (l_5) and Mo–O_a (l_6) can be examined as a function of the nature of the X^{n+} atoms.

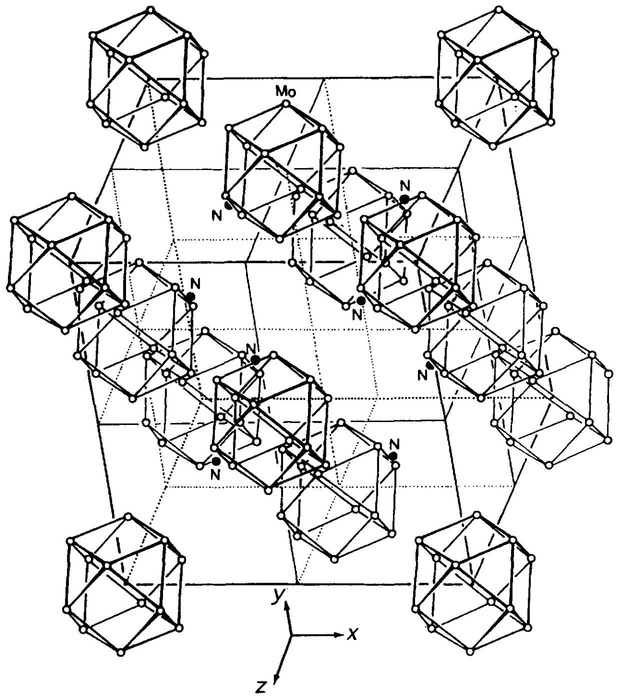

Fig. 2 The arrangement of $[SMo_{12}O_{40}]^{2-}$ and $[NBu^n{}_4]^+$ ions in the unit cell. For simplicity, the C atoms of the $[NBu^n{}_4]^+$ ions are omitted

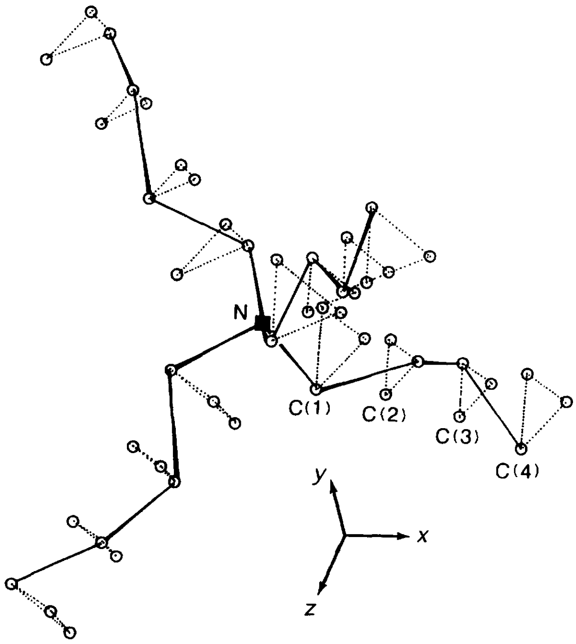

Fig. 3 The configuration of the $[NBu^n{}_4]^+$ ion, where the C_4H_9 groups extend outwards twisting around the [111] axis

First, when the oxidation state of X^{n+} decreases from +VI (for S) to +IV (for Si or Ge), l_1 decreases from a maximum of 3.581 Å (X = S^{6+}) to a minimum of 3.518 Å (X = Si^{4+}). In other words, the twelve Mo^{6+} atoms come closer to the central X^{n+} atom and the size of the $Mo_{12}O_{36}$ moiety of the Keggin

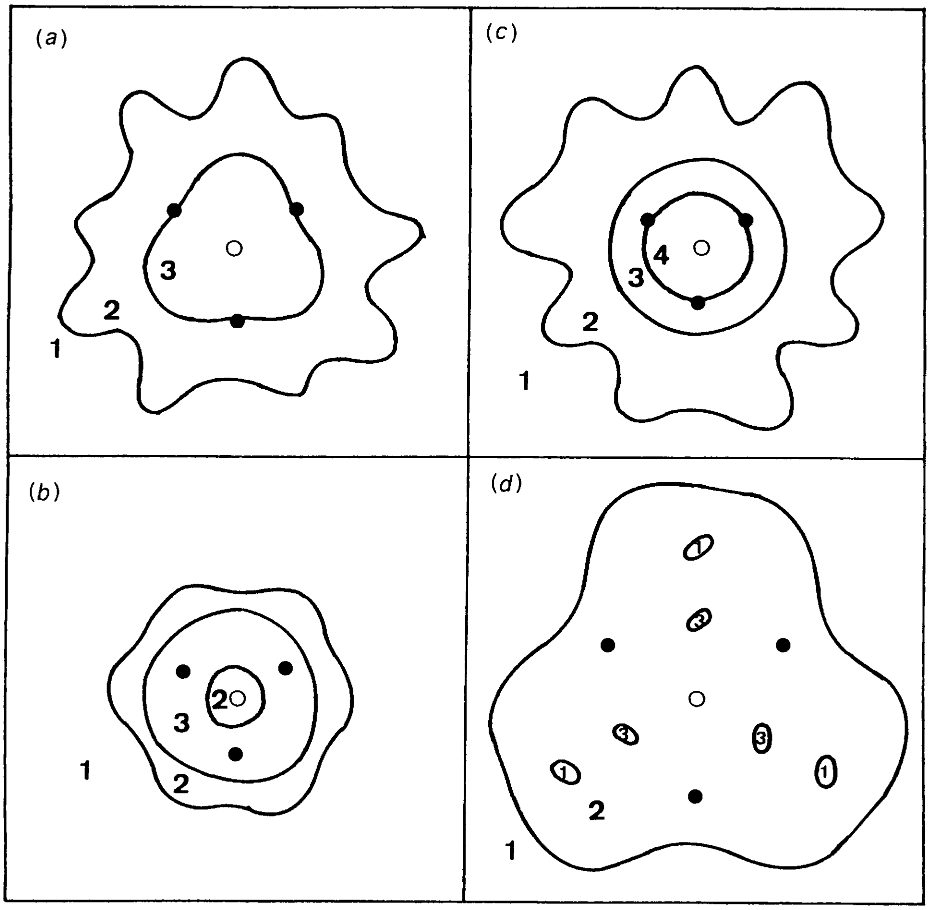

Fig. 4 Fourier maps synthesized for planes perpendicular to the [111] axis. Contour lines of electron density arising from atoms C(1)–C(4) are sketched in terms of e Å^{-3}, in (*a*)–(*d*). The open and closed circles indicate the positions of the [111] axis and the centres of the atoms, respectively

Table 3 Geometric characteristics of Keggin molecules $[(X^{n+})Mo_{12}O_{40}]^{(8-n)-}$

Heteroatom	Average interatomic distance (minimum, maximum)/Å						
(X^{n+})	Mo ··· X(l_1)	Mo ··· Mo(l_2)[a]	Mo ··· Mo(l_3)[a]	Mo ··· Mo(l_4)[b]	X–O$_a$(l_5)	Ref.	
S^{6+}	3.581	—	—	3.581	1.480	2.52	This work
P^{5+}	3.564 (3.562, 3.565)	3.420 (3.418, 3.421)	3.705 (3.702, 3.706)	3.563	1.542	2.435 (2.433, 2.436)	7
Si^{4+}	3.518 (3.437, 3.555)	3.352 (3.325, 3.374)	3.708 (3.671, 3.734)	3.530	1.631 (1.622, 1.641)	2.341 (2.322, 2.356)	8(*a*)
Ge^{4+}	3.528 (3.507, 3.561)	3.347 (3.317, 3.381)	3.736 (3.677, 3.779)	3.541	1.731 (1.724, 1.742)	2.289 (2.257, 2.316)	9

[a] Averages of the twelve Mo ··· Mo distances between neighbouring MoO$_6$ octahedra which are, respectively, linked by O$_b$ and O$_c$ atoms as in Fig. 1.
[b] Average of the total 24 Mo ··· Mo distances between neighbouring MoO$_6$ octahedra.

molecules is decreased. At the same time, the Mo ··· Mo distances l_2 and l_3 are decreased, the former more than the latter. The changes are simply related to the decrease in the electrostatic repulsion between the Mo^{6+} and the central X^{n+} atoms.

The stability of these Keggin molecules is also known in the solution states. In aqueous solution, for instance, the formation and the dissociation of $[SiMo_{12}O_{40}]^{4-}$ **3** were investigated by Strickland,[15] who observed that dissociation in aqueous solutions became first noticeable when the ion was dissolved at concentrations lower than 5 × 10^{-5} mol dm^{-3} and that even it had been degraded entirely to a mixture of molybdate and silicate by the addition of 24 equivalents of alkali the greater part of the ion could be reformed by adding 24 equivalents of hydrochloric acid. This means that this ion has such stability so as to be formed almost quantitatively from a molybdate concentration as low as 6 × 10^{-4} mol dm^{-3}. As for $[GeMo_{12}O_{40}]^{4-}$ **4**, Jakubiec and Boltz reported[16] that it could be formed quantitatively from 3.68 × 10^{-5} mol dm^{-3} molybdate. In this sense, the relative stability is **3** < **4** since the latter forms from a lower concentration of molybdate.

Similarly, it is known[17] that $[PMo_{12}O_{40}]^{3-}$ **2** forms partially from a molybdate concentration of 6 × 10^{-4} mol dm^{-3} and requires for its full formation the presence of either 0.01 mol dm^{-3} molybdate[18] or certain water-miscible organic solvents along with 10^{-4} mol dm^{-3} molybdate.[19] The ion $[SMo_{12}O_{40}]^{2-}$ is less stable compared with **2** because it shows little sign of formation in aqueous solutions even in the presence of 0.05 mol dm^{-3} molybdate and first emerges in the presence of both 0.05 mol dm^{-3} molybdate and more than 50% organic solvents such as MeCN and Me$_2$CO. In summary, the relative stability of the series of Keggin molecules is **1** ≪ **2** ≪ **3** < **4** in aqueous solutions.

The stability seems to depend more on the arrangement of the anionic O^{2-} atoms rather than that of the cationic Mo^{6+} and X^{n+} atoms. From Table 3, we can compare the X–O_a distance, l_5, which represents the size of the central tetrahedron in the Keggin molecules. When $X = S^{6+}$ l_5 is the shortest at 1.48 Å. To co-ordinate such a small SO_4 tetrahedron the Mo–O_a bonds (l_6) stretch to 2.52 Å. This seems to be the main reason for the poor stability of **1** among the series of Keggin molecules. The unusually long distance of l_6 is, however, gradually shortened when larger tetrahedra such as PO_4, SiO_4, GeO_4 are introduced in place of SO_4. Of ions **1**–**4** the last is the most stable and is not hydrolysed even in aqueous solutions at pH 2–4.

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References

1 T. Hori, S. Himeno and O. Tamada, *J. Chem. Soc., Dalton Trans.*, 1989, 1491; 1992, 275.
2 R. Strandberg, *Acta Chem. Scand., Ser. A*, 1975, **29**, 350.
3 R. Strandberg, *Acta Chem. Scand.*, 1973, **27**, 1004; J. Fischer, L. Ricard and P. Toledano, *J. Chem. Soc., Dalton Trans.*, 1974, 941.
4 B. Cartié, *J. Chem. Res.*, 1988, (*S*) 289; (*M*) 2262.
5 S. Himeno, K. Miyashita, A. Saito and T. Hori, *Chem. Lett.*, 1990, 799.
6 A. Proust, R. Thouvenot, F. Robert and P. Gouzerh, *Inorg. Chem.*, 1993, **32**, 5299.
7 R. Strandberg, *Acta Chem. Scand., Ser. A*, 1975, **29**, 359.
8 (*a*) H. Ichida, A. Kobayashi and Y. Sasaki, *Acta Crystallogr., Sect. B*, 1980, **36**, 1382; (*b*) M. Feist, V. N. Molchanov, L. P. Kazanskii, E. A. Torchenkova and V. I. Spitsyn, *Zh. Neorg. Khim.*, 1980, **25**, 741 (*Russ. J. Inorg. Chem.*, 1980, **25**, 401).
9 R. Strandberg, *Acta Crystallogr., Sect. B*, 1977, **33**, 3090.
10 S. Sasaki, KEK Internal Report, National Laboratory of High Energy Physics, Tsukuba, 1987, vol. 3.
11 S. Sasaki, personal communication.
12 L. W. Finger, Program for computing bond angles and distances and thermal ellipsoids with error analysis, University of Minnesota, 1968.
13 H. T. Evans, jun., and M. T. Pope, *Inorg. Chem.*, 1984, **23**, 501.
14 T. J. R. Weakley, *Acta Crystallogr., Sect. C*, 1984, **40**, 16.
15 J. D. H. Strickland, *J. Am. Chem. Soc.*, 1952, **74**, 862, 868.
16 R. Jakubiec and D. F. Boltz, *Anal. Chem.*, 1969, **41**, 78.
17 T. Fujinaga, M. Koyama and T. Hori, *Talanta*, 1971, **18**, 960.
18 A. Halász and E. Pungor, *Talanta*, 1971, **18**, 557.
19 T. Hori and T. Fujinaga, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1380.

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