Crystal Structure of Sodium Tris(tetramethylammonium) Pentamolybdodisulfate(VI) Tetrahydrate, $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$ †

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The structure of $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$ has been determined by the single-crystal X-ray method: monoclinic, space group *P*2/*c*, $a = 29.25(2)$, $b = 12.85(1)$, $c = 18.24(1)$ Å, and $\beta = 123.89(2)°$ and $Z = 6$. The structure was refined by full-matrix least squares to $R' = 0.0678$ for 5532 reflections. The existence of the Strandberg-type heteropolyion $[S_2Mo_5O_{23}]^{4-}$ **1** in the crystals has been confirmed. The geometry of **1** was compared systematically with various analogues containing $S^{IV}O_3^{2-}$, PO_4^{3-}, $MePO_3^{2-}$ or $NH_3C_2H_4PO_3^{-}$ as the central polyhedron. The UV spectrum of the salts $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$ and $[NMe_4]_4S_2Mo_5O_{23}$ in neat MeCN, hence the kernel heteropolyion **1** showed absorption maxima at $\lambda = 213$ and 243 nm ($\varepsilon = 3.2 \times 10^4$ and 3.3×10^4 dm^3 mol^{-1} cm^{-1}). Spectroscopic measurements also indicate that **1** and $[Mo_6O_{19}]^{2-}$ form simultaneously in aqueous–MeCN media containing Mo^{VI} and H_2SO_4.

Previously, we reported that addition of certain organic solvents such as MeCN promoted the formation of a yellow $[S_2Mo_{18}O_{62}]^{4-}$ heteropolyion[1] from aqueous Mo^{VI}–H_2SO_4 solutions. An X-ray crystallographic study[2] showed that $[S_2Mo_{18}O_{62}]^{4-}$ has the same structure as that determined by Dawson[3] for $[P_2W_{18}O_{62}]^{6-}$ and that the sulfate ion in the former structure serves as the central tetrahedron in the same manner as the phosphate ion does in the latter. Therefore, we anticipated the existence of 12-molybdosulfate ions like $[SMo_{12}O_{40}]^{2-}$, which is structurally analogous to the well established Keggin-type[4] $[PMo_{12}O_{40}]^{3-}$.

Recently, we have isolated[5] a 12-molybdosulfate as $[NBu^n{}_4]_2SMo_{12}O_{40}$ from an aqueous–Me_2CO medium containing Mo^{VI}–V^{V}–H_2SO_4. Spectroscopic and electrochemical studies on the yellow salt strongly suggest the existence of $[SMo_{12}O_{40}]^{2-}$ with the Keggin-type structure.

In glacial acetic acid containing Mo^{VI}–H_2SO_4–$HClO_4$, Cartie[6] found two types of yellow molybdosulfate ion, which he isolated and characterized as $[NEt_4]_2SMo_{12}O_{40}$ and $[NEt_4]_3HS_2Mo_{18}O_{62}\cdot 3MeCO_2H$. These salts were assumed to contain, respectively, the Keggin and Dawson-type anions on the basis of their electrochemical properties, although the crystal structures have not yet been determined.

Similarly, EtOH aids the formation of yellow molybdosulfate ions although it is less effective than MeCN or Me_2CO. When EtOH is used the aqueous–EtOH medium containing the NMe_4^+ counter ion produces a colourless molybdosulfate ion[7] having the elemental composition ratio of Mo/S = 5:2.

On the basis of the results of the X-ray structure analysis on the salt, $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$, the presence in the salt of $[S_2Mo_5O_{23}]^{4-}$ **1** with the Strandberg-type structure[8] is herein reported. The geometric characteristics of **1** are compared with those of the isostructural ions $[S^{IV}{}_2Mo_5O_{21}]^{4-}$, $[P_2Mo_5O_{23}]^{6-}$, $[(MeP)_2Mo_5O_{21}]^{4-}$, and $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$. Ultraviolet spectroscopic evidence for the formation of **1** in an aqueous–MeCN medium is also discussed.

Experimental

Preparation of Materials.—Single crystals of $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$ were obtained according to a previously reported procedure[7] modified only in regard to temperature. A solution (80 cm^3) containing $Na_2MoO_4\cdot 2H_2O$ (4.8 g, 0.02 mol) and concentrated H_2SO_4 (5.6 cm^3, 0.1 mol) was mixed with EtOH (120 cm^3) and kept in the dark at *ca.* 25 °C for 15 min.‡ While stirring vigorously, the colourless solution was then treated with NMe_4Cl (2 g, 0.018 mol) and the resulting mixture was cooled to 15 °C for 15 min to initiate crystallization. Chilling overnight at 5 °C produced well shaped single crystals adequate for X-ray analysis. They were separated by filtration, washed with neat EtOH, and air-dried for several hours (Found: C, 11.70; H, 3.70; Mo, 39.05; N, 3.40; Na, 1.95; S, 5.05. Calc. for $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$: C, 11.70; H, 3.60; Mo, 39.00; N, 3.40; Na, 1.85; S, 5.20%).

In order to elucidate the UV spectroscopic characteristics of anion **1** in neat MeCN, the $[NMe_4]_4S_2Mo_5O_{23}$ salt was also prepared by the same procedure using Me_2CO in place of EtOH. A stirred solution (80 cm^3) containing $Na_2MoO_4\cdot 2H_2O$ (4.8 g) and concentrated H_2SO_4 (5.6 cm^3) was mixed with Me_2CO (120 cm^3). After the addition of NMe_4Cl (6 g, 0.055 mol), the colourless solution was kept at 5 °C for 3–4 h. The colourless and transparent crystals thus obtained were washed with EtOH. When exposed to air for 1 h, however, they became opaque and were converted into the anhydrous salt (Found: C, 15.65; H, 3.90; Mo, 39.20; N, 4.55; S, 5.20. Calc. for $[NMe_4]_4S_2Mo_5O_{23}$: C, 15.90; H, 4.00; Mo, 39.70; N, 4.65; S, 5.30%).

Crystallography.—A prismatic crystal of $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$ with dimensions *ca.* 0.35 × 0.2 × 0.15 mm, elongated on the *a* axis and containing microscopically observable cracks in the (100) plane, was glued on a glass fibre with the direction parallel to the *b* axis and coincident with the rotation axis of the goniometer. Preliminary Weissenberg

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

‡ When exposed to daylight the solution produced a blue mixed-valence species of octadecamolybdodisulfate[7] which contaminated the desired crystals.

camera work showed monoclinic symmetry with systematic absences for $h0l$, $l = 2n + 1$ and presences for $0k0$, $k = 2n + 1$, indicating possible space groups $P2/c$, or Pc. All the reflections were sharp, and no super or diffuse reflections were observed in the *b*-axis oscillation and Weissenberg photographs. Using the same crystal, the complete intensity data were collected using a Rigaku-5UD four-circle diffractometer. The measurements were performed at a rather high rate of 6° min^{-1} because the crystal hydrate tends to dehydrate in open air.

Corrections were made for Lorentz and polarization factors. The Furnas correction for absorption was made around *b* axis according to North *et al.*[9] The cell parameters were determined from 20 reflections in the range $40 < 2\theta < 50°$. The crystal data and experimental conditions are summarized in Table 1.

Data processing. The space group was confirmed as $P2/c$ (centrosymmetric) based on the statistical probability of intensity distributions. According to Wilson,[10] the ratio $r = \langle|F|^2\rangle/\langle I\rangle$ may indicate the presence (=0.637) or absence (= 0.785) of a centre of symmetry. The r value calculated for the present crystal was 0.556. In addition, the zero-moment test reported by Howells *et al.*[11] was applied; the distributions calculated by using the RSWS-3 program[12] indicated the presence of a centre of symmetry.

Table 1 Crystal data and experimental parameters for $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$

M	1229.3
Crystal symmetry	Monoclinic
Space group	$P2/c$
a/Å	29.25(2)
b/Å	12.85(1)
c/Å	18.24(1)
β/°	123.89(2)
U/Å^3	5690(8)
Z	6
D_m/g cm^{-3}	2.15
D_c/g cm^{-3}	2.15
$F(000)$	3636
μ(Mo-Kα)/cm^{-1}	17.9
Radiation	Mo-Kα (graphite monochromated, $\lambda = 0.7107$ Å)
Scan technique	$2\theta-\omega$
Scan width/°	$\Delta\omega = (1.0 + 0.5 \tan\theta)$
Scan speed/° min^{-1}	6
Scan range (2θ)/°	0–50
Final R'	0.0678
Final R	0.0621
Function minimized	$\Sigma(|F_o| - |F_c|)^2$

The Mo atoms were located by a Patterson map, which was resolved manually assuming the approximately pentagonal Mo_5 groups confirmed by Strandberg[8] in a crystal of $Na_6P_2Mo_5O_{23}\cdot 13H_2O$. The initial model was thus refined to R 0.27. The S, Na, O, N and C atoms were then located by successive Fourier and Fourier difference maps. The Fourier syntheses were carried out by using the program FRAXY.[13] No attempt was made to locate H atoms. One of the eighteen independent C atoms, designated as C(185) in Table 2, was left unlocated. This was due to the low signal-to-noise ratio of the intensity data acquired rather rapidly to minimize the decay of the crystal by dehydration. Among 8752 reflections, 5532 with $F_o > 7$ and $F_o > 3\sigma(F)$ was refined, assigning unit weights for each reflection and in space group $P2/c$, using the program RADY.[14]

The final fractional coordinates are listed in Table 2, interatomic distances and bond angles calculated by the program RADY[14] in Tables 3 and 4, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

UV Spectroscopy.—The UV absorption spectra were measured with a Hitachi-3300 spectrophotometer using quartz cuvettes with light pathlengths of 10.0, 1.00, or 0.158 mm depending on sample absorbances. The MeCN solvent, purified by Dojin Kogyo, Kumamoto, Japan, was transparent at wavelengths $\lambda > 210$ nm.

Results and Discussion

Crystal Structure of $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$.—The crystal structure contains two heteropolyions, **1** and **1′**, which are essentially identical but independent crystallographically. The negative charges on each anion arise from SO_4^{2-} ions and are neutralized by NMe_4^+ and hydrated Na^+ ions.

Fig. 1(*a*) illustrates the assemblage of five MoO_6 octahedra and two SO_4^{2-} tetrahedra in **1**. The numbering scheme for the Mo and S atoms is given in Fig. 1(*b*). The designation for the O atoms is in accordance with that adopted by Strandberg[8] for $[P_2Mo_5O_{23}]^{6-}$. Anion **1** has a two-fold rotation axis passing through the Mo(3) and O(11a′) atoms. It is clear from Fig. 1 that **1**, hence **1′**, have the Strandberg-type structure.[8] Each anion has

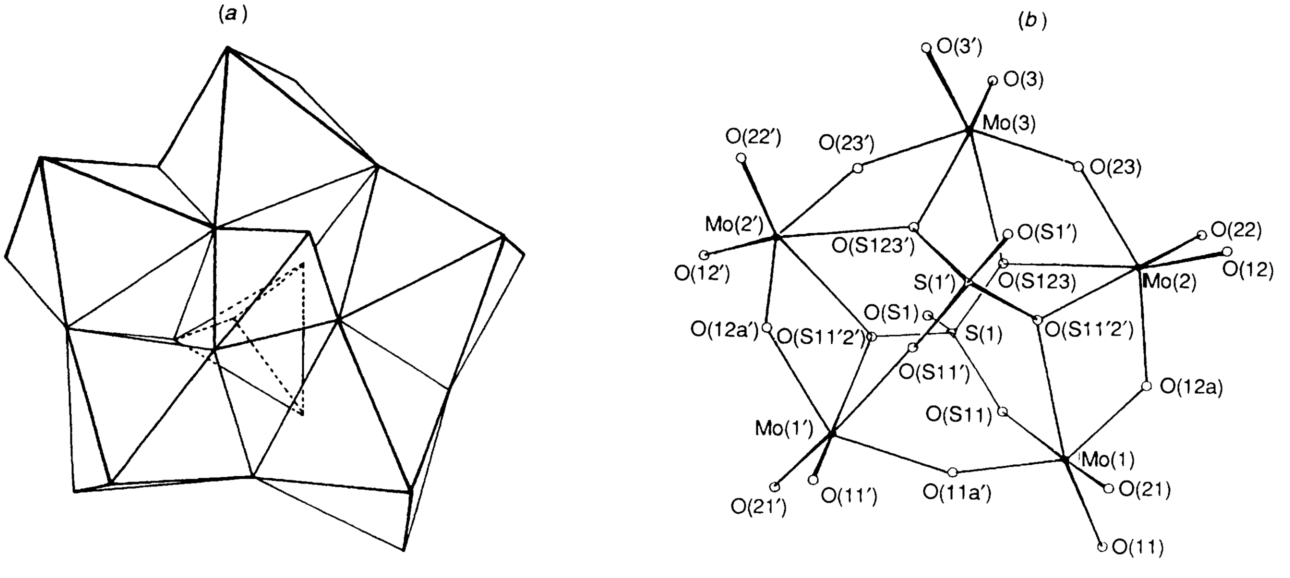

Fig. 1 Polyhedral (*a*) and atom-and-bond representation (*b*) for the structure of anion **1**, along with the numbering scheme for the Mo and S atoms in the polyhedra; O(S) denotes the SO_4 oxygen atoms

Table 2 Fractional atomic coordinates

Atom[a]	x	y	z	Atom[a]	x	y	z
Mo(1)	−0.031 17(6)	0.402 1(1)	0.130 4(1)	O(12a)	−0.047 7(5)	0.284 5(9)	0.056 1(8)
Mo(2)	−0.067 77(6)	0.146 6(1)	0.066 13(9)	O(23)	−0.064 9(4)	0.038 0(8)	0.142 0(7)
Mo(3)	0.000 00	−0.005 5(2)	0.250 00	O(48)	0.281 4(5)	0.439 0(9)	0.139 5(8)
Mo(4)	0.270 99(6)	0.338 2(1)	0.057 1(1)	O(45)	0.291 7(5)	0.200 9(9)	0.050 4(8)
Mo(5)	0.305 15(6)	0.086 6(1)	0.128 1(1)	O(56)	0.327 8(5)	0.040 4(9)	0.242 9(8)
Mo(6)	0.391 43(6)	0.088 5(1)	0.354 0(1)	O(67)	0.431 0(4)	0.209 3(9)	0.419 6(7)
Mo(7)	0.400 11(6)	0.334 7(1)	0.430 48(9)	O(78)	0.344 3(4)	0.436 9(8)	0.374 1(7)
Mo(8)	0.308 92(6)	0.486 8(1)	0.255 9(1)	Na(1)	0.189 2(3)	0.029 3(6)	0.279 6(5)
S(1)	0.069 3(2)	0.218 3(3)	0.252 5(3)	Na(2)	0.500 0	0.459 3(8)	0.250 0
S(2)	0.400 4(2)	0.300 6(3)	0.242 2(3)	O(W11)	0.224 5(6)	0.079(1)	0.705(1)
S(3)	0.268 8(2)	0.236 9(3)	0.245 6(3)	O(W21)	0.278 3(7)	0.005(1)	0.408(1)
O(S1)	0.121 7(5)	0.178(1)	0.279 6(8)	O(W31)	0.163 8(5)	0.045(1)	0.873 4(9)
O(S2)	0.458 1(5)	0.313(1)	0.281 4(8)	O(W41)	0.104 3(6)	−0.034(1)	0.164(1)
O(S3)	0.229 4(5)	0.166(1)	0.241 2(8)	O(W52)	0.473 6(6)	0.434(1)	0.829(1)
O(S11)	0.055 3(4)	0.312 6(9)	0.198 6(7)	O(W62)	0.414 2(9)	0.466(2)	0.639(1)
O(S11′2′)	0.067 9(5)	0.246 6(9)	0.331 1(7)	N(1)	0.251 9(7)	0.297(1)	0.503(1)
O(S123)	0.026 1(4)	0.137 7(8)	0.200 9(7)	N(2)	0.088 6(6)	0.242(1)	0.009(1)
O(S24)	0.367 4(4)	0.341 6(9)	0.151 5(7)	N(3)	0.405 2(6)	0.248(1)	−0.022(1)
O(S256)	0.385 5(4)	0.188 4(8)	0.239 1(7)	N(4)	0.136 6(6)	0.359(1)	0.737(1)
O(S278)	0.381 8(4)	0.359 7(8)	0.293 2(7)	N(5)	0.500 0	0.120(2)	0.750 0
O(S345)	0.273 4(4)	0.222 6(8)	0.167 9(7)	C(11)	0.305(1)	0.327(2)	0.578(2)
O(S367)	0.324 3(4)	0.217 3(8)	0.327 0(7)	C(21)	0.253(1)	0.325(3)	0.422(2)
O(S38)	0.254 3(4)	0.345 3(9)	0.246 1(7)	C(31)	0.206(1)	0.356(2)	0.496(2)
O(11)	−0.000 8(5)	0.485(1)	0.098 6(9)	C(41)	0.241(1)	0.183(3)	0.495(2)
O(21)	−0.094 2(5)	0.456(1)	0.084 0(9)	C(52)	0.118(1)	0.322(2)	0.080(2)
O(12)	−0.136 6(5)	0.148(1)	−0.010 7(8)	C(62)	0.128 4(8)	0.156(2)	0.028(1)
O(22)	−0.042 9(5)	0.079 3(9)	0.014 5(8)	C(72)	0.069(1)	0.287(2)	0.922(2)
O(3)	0.029 1(5)	−0.087(1)	0.213 6(8)	C(82)	0.042(1)	0.197(2)	0.012(2)
O(14)	0.281 8(5)	0.404(1)	0.987 3(8)	C(93)	0.426 7(9)	0.177(2)	0.058(2)
O(24)	0.201 8(5)	0.326(1)	0.997 2(9)	C(103)	0.433 4(9)	0.220(2)	0.933(1)
O(15)	0.242 8(5)	0.027(1)	0.068 6(9)	C(113)	0.344(1)	0.237(2)	0.912(2)
O(25)	0.345 8(5)	0.014(1)	0.108 8(8)	C(123)	0.418 8(9)	0.360(2)	0.009(2)
O(16)	0.378 6(5)	0.027(1)	0.423 4(8)	C(134)	0.156(1)	0.462(2)	0.782(2)
O(26)	0.443 4(5)	0.017(1)	0.363 1(8)	C(144)	0.186 2(9)	0.285(2)	0.783(2)
O(17)	0.457 4(5)	0.408(1)	0.483 0(8)	C(154)	0.116(1)	0.370(2)	0.641(2)
O(27)	0.391 2(5)	0.300(1)	0.512 1(9)	C(164)	0.091(1)	0.321(2)	0.745(2)
O(18)	0.256 9(5)	0.437(1)	0.741 8(9)	C(175)	0.462(2)	0.179(4)	0.758(3)
O(28)	0.355 8(5)	0.423(1)	0.768 3(8)	C(185)[b]			
O(11′)	0.000 0	0.434(1)	0.250 0				

[a] The O atoms in $[S_2Mo_5O_{23}]^{4-}$ polyhedra are designated by the numbers of the Mo atom(s) to which they are linked; the primed numbers indicate that the Mo atoms are those derived through the transformations of the coordinates as $\bar{x}$, y, $\frac{1}{2} - z$. For the water oxygens O(W) and tetramethylammonium carbons, designation is made by using the numbers of the Na and N atoms, to which the oxygens and the carbons are linked. The numbering scheme for the Na and N atoms is given in Fig. 3. [b] Unlocated (see text for details).

Table 3 Interatomic distances (Å)

Mo(1) ··· Mo(2)	3.449(3)	Mo(1) ··· Mo(1$^{\mathrm{I}}$)	3.673(3)	Mo(2) ··· Mo(3)	3.404(2)
Mo(4) ··· Mo(5)	3.419(3)	Mo(4) ··· Mo(8)	3.680(3)	Mo(5) ··· Mo(6)	3.428(3)
Mo(6) ··· Mo(7)	3.410(3)	Mo(7) ··· Mo(8)	3.407(2)	S(1) ··· Mo(1)	3.446(4)
S(1) ··· Mo(1$^{\mathrm{I}}$)	3.747(6)	S(1) ··· Mo(2)	3.644(4)	S(1) ··· Mo(2$^{\mathrm{I}}$)	3.458(6)
S(1) ··· Mo(3)	3.504(5)	S(2) ··· Mo(4)	3.422(4)	S(2) ··· Mo(5)	3.632(4)
S(2) ··· Mo(6)	3.501(5)	S(2) ··· Mo(7)	3.468(6)	S(2) ··· Mo(8)	3.702(6)
S(3) ··· Mo(4)	3.712(6)	S(3) ··· Mo(5)	3.464(6)	S(3) ··· Mo(6)	3.536(5)
S(3) ··· Mo(7)	3.641(4)	S(3) ··· Mo(8)	3.389(5)	S(1) ··· S(1$^{\mathrm{I}}$)	4.004(8)
S(2) ··· S(3)	3.971(8)	Mo(1)–O(S11)	2.40(1)	Mo(1$^{\mathrm{I}}$)–O(S11′2′)	2.55(1)
Mo(1)–O(11)	1.68(2)	Mo(1)–O(21)	1.69(1)	Mo(1)–O(11′)	1.882(4)
Mo(1)–O(12)	1.90(1)	S(1)–O(S1)	1.42(1)	S(1)–O(S11′2′)	1.50(2)
S(1)–O(S11)	1.47(1)	S(1)–O(S123)	1.49(1)	S(2)–O(S2)	1.43(1)
S(2)–O(S24)	1.47(1)	S(2)–O(S256)	1.50(1)	S(2)–O(S278)	1.52(2)
S(3)–O(S3)	1.43(2)	S(3)–O(S345)	1.51(2)	S(3)–O(S367)	1.489(9)
S(3)–O(S38)	1.46(1)	Na(1)–O(S1)	2.74(2)	Na(1)–O(S3)	2.43(2)
Na(2)–O(S2)	2.48(2)	Na(1)–O(W11$^{\mathrm{III}}$)	2.54(2)	Na(1)–O(W21)	2.36(2)
Na(1)–O(W31$^{\mathrm{III}}$)	2.41(2)	Na(1)–O(W41)	2.33(1)	Na(2)–O(W52$^{\mathrm{II}}$)	2.38(2)
Na(2)–O(W62$^{\mathrm{II}}$)	2.38(2)				

Roman numeral superscripts denote transformations of the coordinates as follows: I $\bar{x}, y, \frac{1}{2} - z$; II $x, 1 - y, z - \frac{1}{2}$; III $x, \bar{y}, z - \frac{1}{2}$.

the distinguishable, pentagonal molybdate framework (called molybdenum ring, hereafter) made up of five MoO_6 octahedra, linked by sharing edges, except for one linkage between Mo(1) and Mo(1′) where the vertices are shared. A pair of SO_4^{2-} tetrahedra co-ordinate to the molybdenum ring from either side, three vertices of each SO_4^{2-} tetrahedron being shared with the ring and the last protruding outward from the ring plane.

The SO_4^{2-} tetrahedra in **1** and **1′** are slightly distorted, with the S–O distances varying in the range 1.42–1.51 Å and the O–S–O angles 107.0–112.5°.

The geometrical characteristics of both anions **1** and **1′** can be deduced by calculating the dimensions of the molybdenum rings and the orientation of the S–S vectors to the rings. According to ref. 15, the positions of the Mo atoms belonging to the respective molybdenum rings are approximated to planes. For **1**, plane (1) can be expressed as in equation (1) and for **1′**,

$$29.24X - 9.84Z + 2.46 = 0 \text{ with } S = 0.20 \qquad (1)$$

plane (2) can be expressed as in equation (2). Here, X, Y and Z

$$28.57X + 2.76Y - 10.12Z - 7.84 = 0 \text{ with } S = 0.19 \qquad (2)$$

are the fractional coordinates and S denotes the sum of the squares of the residuals. The displacements of the Mo atoms in **1** from plane (1) are shown in the first row of Table 5 and compared with those calculated for molybdenum rings in isostructural heteropolyions in various crystals including $[NH_4]_4S^{IV}{}_2Mo_5O_{21}\cdot 3H_2O$,[16] $Na_6P_2Mo_5O_{23}\cdot 13H_2O$,[8] $Na_4H_2P_2Mo_5O_{23}\cdot 10H_2O$,[17] $[NH_4]_5HP_2Mo_5O_{23}\cdot 3H_2O$,[18] $[NH_4]_4(MeP)_2Mo_5O_{21}\cdot 5H_2O$,[19] and $Na[NMe_4](NH_3C_2H_4P)_2Mo_5O_{21}\cdot 5H_2O$.[19] The displacements are smaller than 0.3 Å and occur in a direction coincident with the molybdenum planes. Table 5 also indicates that the paired heteroatoms in the heteropolyions are located approximately 2 Å from the respective planes, to which the S–S and P–P vectors are essentially perpendicular. In this respect, the molybdenum rings in the Strandberg-type heteropolyions closely resemble each other and no appreciable effect due to the nature of the central polyhedra can be observed.

By summing the interatomic distances between the Mo and S (or P) atoms in the molybdenum rings, the Strandberg-type heteropolyions can be envisaged as a pentagonal bipyramid, *viz.* a polyhedron having an external surface composed of ten triangular faces. The form for **1** is given in Fig. 2(*a*), where the edges of the bipyramid are represented by lower case letters. The lengths of the edges vary from 3.40 (*c* and *d*) to 3.75 Å (*j* and *k*), with an average value of 3.5 Å; the standard deviation of 0.1 Å indicates that the ten triangles are essentially equilateral. Polyhedral schemes can also be depicted for the other heteropolyions. In Fig. 2, **1** is compared with $[S^{IV}{}_2Mo_5O_{21}]^{4-}$ (*b*), $[P_2Mo_5O_{23}]^{6-}$ (*c*), $[(MeP)_2Mo_5O_{21}]^{4-}$ (*d*), or $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ (*e*), to illustrate the effects of replacement of the central polyhedron on the heteropolyion geometry.

First, it can be noted that edge *a* [in Fig. 2(*a*)] corresponding to the Mo–Mo distance between the two vertex-sharing MoO_6 octahedra is essentially unaffected by the replacement of SO_4^{2-} with any other polyhedron; the change is 0.026 Å or less [Fig. 2(*b*)–(*e*)]. Secondly, when the oxophosphorus ions are replaced by SO_4^{2-} ion as the central polyhedron, the distances between the respective pairs of the heteroatoms are elongated; the S–S distances are 0.18–0.25 Å longer than the corresponding P–P distances. Thirdly, as emphasized by the heavier lines in Fig. 2(*c*)–(*e*) the replacement of oxophosphorus ions by SO_4^{2-} also elongates edges *f*, *g*, *j*, *k*, *n* and *o* by 0.10–0.18 Å. In summary, exchanging the central polyhedra caused an appreciable deformation of the S(or P)–Mo–Mo triangle involving edge *a* in particular. The reason for this effect is not yet fully understood.

Fig. 3 shows the arrangement in the unit cell of anions **1** and **1′** with the counter ions of NMe_4^+ and hydrated Na^+. The molybdenum rings of the anions are not parallel to each other [see equations (1) and (2)] and, therefore, a zigzag chain having the sequence of ···-anion **1**–Na(1)–anion **1′**–Na(2)–anion **1′**–Na(1)··· is formed along the *a* axis. In the chain, a pair of oxygen atoms from SO_4^{2-} (designated S) extends toward each Na^+ ion with respective angles O(S1)–Na(1)–O(S3) 87.8 and O(S2)–Na(2)–O(S2^{I}) 81.4°. Each Na^+ ion is also associated with four water-oxygen atoms (W), providing a total of six oxygen atoms in the co-ordination sphere of each Na atom. These oxygen atoms form a rather distorted trigonal prism; for instance, Na(1) is faced by a pair of triangles formed by O(S1)–O(W31^{III})–O(W41) and O(S3)–O(W21)–O(W1^{III}). The oxygen atoms are arranged in a similar manner around atom Na(2).

The unit cell contains two such zigzag chains which are identical and mutually interchangeable through the *c*-glide symmetry operation. The NMe_4^+ ions link these chains.

Viewing the whole cell in Fig. 3 along the *c*-axis, it appears that two rather diffusive layers are formed. One contains the Mo and S atoms and the other interstitial layer contains the NMe_4^+ and Na^+ ions. The microscopically observable cracks in the crystals seem to be generally parallel to these layers.

Table 4 Bond angles (°)*

O(11′)–Mo(1)–O(11)	104.7(6)	O(11′)–Mo(1)–O(21)	100.4(6)
O(11′)–Mo(1)–O(S11)	79.3(4)	O(11′)–Mo(1)–O(12)	139.9(6)
O(S1)–S(1)–O(S11)	112.5(9)	O(S1)–S(1)–O(S11′2′)	110.7(7)
O(S1)–S(1)–O(S123)	109.5(7)	O(S11)–S(1)–O(S11′2′)	107.0(8)
O(S1)–Na(1)–O(S3)	87.8(5)	O(W11^{III})–Na(1)–O(S3)	80.3(7)
O(W21)–Na(1)–O(S3)	86.3(7)	O(W31^{III})–Na(1)–O(S3)	151.4(7)
O(W41)–Na(1)–O(S3)	115.6(8)		

* Values are selected for $Mo(1)O_6$ and $S(1)O_4$ polyhedra and the Na(1) co-ordination sphere. Roman numeral superscripts as in Table 3.

Table 5 The configuration of the Mo and S (or P) atoms and the orientation of the S–S (or P–P) vectors to the molybdenum rings in various Strandberg-type heteropolyions

Heteropolyion	Distance [a] from the respective ring plane/Å							Angle [b]/°
	Mo(1)	Mo(2)	Mo(3)	Mo(2′)	Mo(1′)	S(1)	S(1′)	
1 in $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$ (present study)	0.264 △	0.172 ▼	0.000	0.172 △	0.264 ▼	2.001 △	2.001 ▼	89.44
$[S^{IV}{}_2Mo_5O_{21}]^{4-}$ in $[NH_4]_4S_2Mo_5O_{21}\cdot 3H_2O$	[Mo(5)]	[Mo(4)]	[Mo(3)]	[Mo(2)]	[Mo(1)]	[S(1)]	[S(2)]	
(ref. 16)	0.255 △	0.164 ▼	0.006 ▼	0.175 △	0.260 ▼	2.044 △	1.971 ▼	89.25
$[P_2Mo_5O_{23}]^{6-}$ in $Na_6P_2Mo_5O_{23}\cdot 13H_2O$	[Mo(3′)]	[Mo(2′)]	[Mo(1)]	[Mo(2)]	[Mo(3)]	[P′]	[P]	
(ref. 8)	0.227 △	0.150 ▼	0.000	0.150 △	0.227 ▼	1.911 △	1.911 ▼	88.24
$[(MeP)_2Mo_5O_{21}]^{4-}$ in $[NH_4]_4(MeP)_2Mo_5O_{21}\cdot 5H_2O$	[Mo(2)]	[Mo(3)]	[Mo(4)]	[Mo(5)]	[Mo(1)]	[P(1)]	[P(2)]	
(ref. 19)	0.225 △	0.134 ▼	0.024 ▼	0.173 △	0.240 ▼	1.879 △	1.897 ▼	90.0
$[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ in	[Mo(2)]	[Mo(3)]	[Mo(4)]	[Mo(5)]	[Mo(1)]	[P(1)]	[P(2)]	
$Na[NMe_4](NH_3C_2H_4P)_2Mo_5O_{21}\cdot 5H_2O$ (ref. 19)	0.192 △	0.121 ▼	0.010 ▼	0.148 △	0.198 ▼	1.845 △	1.907 ▼	88.23

[a] The marks of △ and ▼ indicate that the Mo, S and P atoms are located on opposite sides of the molybdenum ring plane. The atoms in square brackets are as in Fig. 2. [b] Values are for the angles between the S–S (or P–P) vector and the molybdenum ring plane in the respective heteropolyion.

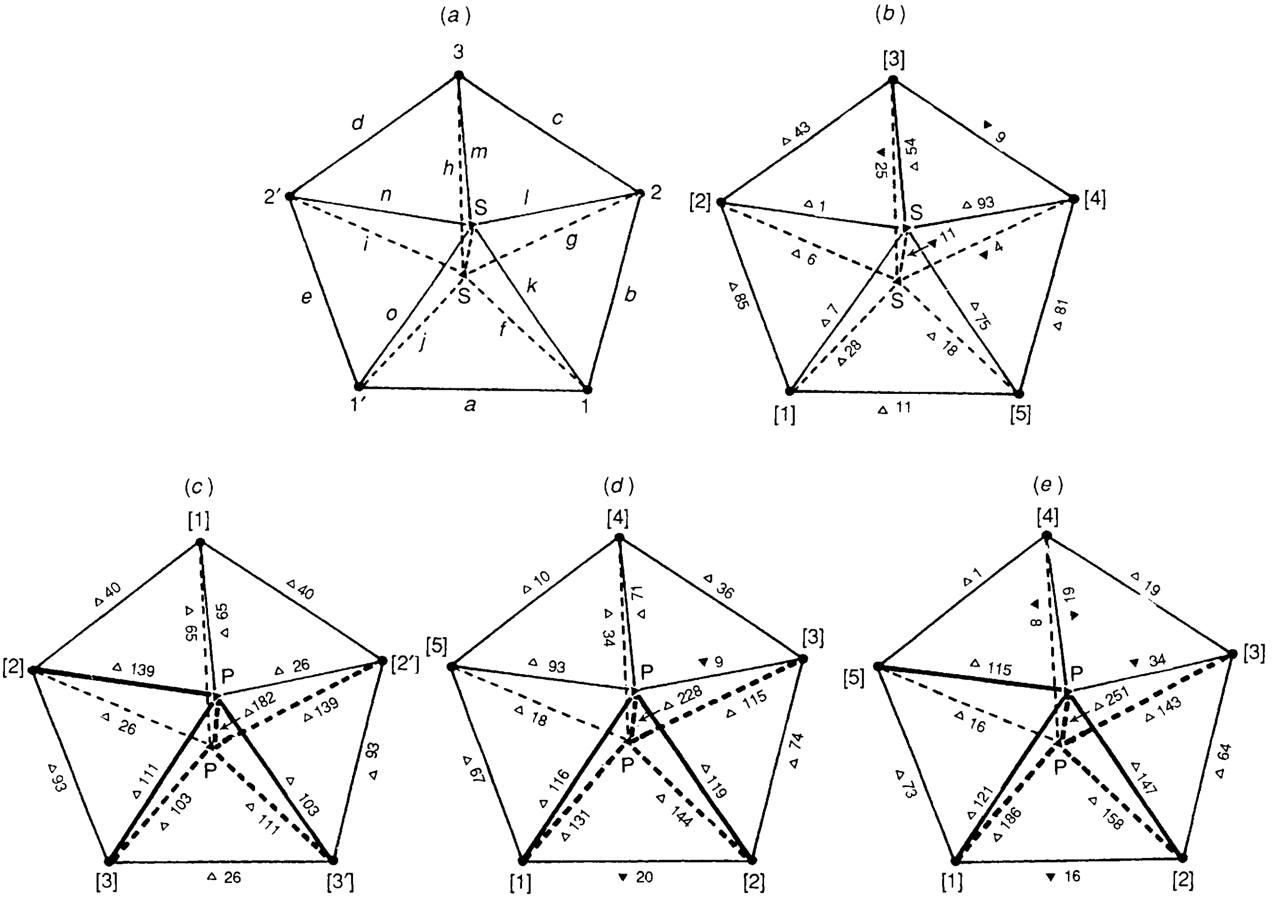

Fig. 2 Geometric comparisons of the molybdenum rings in various Strandberg-type heteropolyions; **1** is envisioned as (*a*). From the Mo–Mo, Mo–S and S–S distances in **1**, the corresponding Mo–Mo, Mo–S (or Mo–P) and S–S (or P–P) distances in $[S^{IV}{}_2Mo_5O_{21}]^{4-}$ (*b*), $[P_2Mo_5O_{23}]^{6-}$ (*c*), $[(MeP)_2Mo_5O_{21}]^{4-}$ (*d*) and $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ (*e*) are subtracted, and the differences indicated in terms of 10^{-3} Å. The positive and negative signs for the values are indicated by △ and ▼, respectively. The heavier lines indicate differences in distances which are larger than 100 × 10^{-3} Å. The atom numbers in square brackets for Mo and S (or P) are those used originally by the investigators of the respective heteropolyions and only rotated so as to parallel the numbering scheme adopted herein

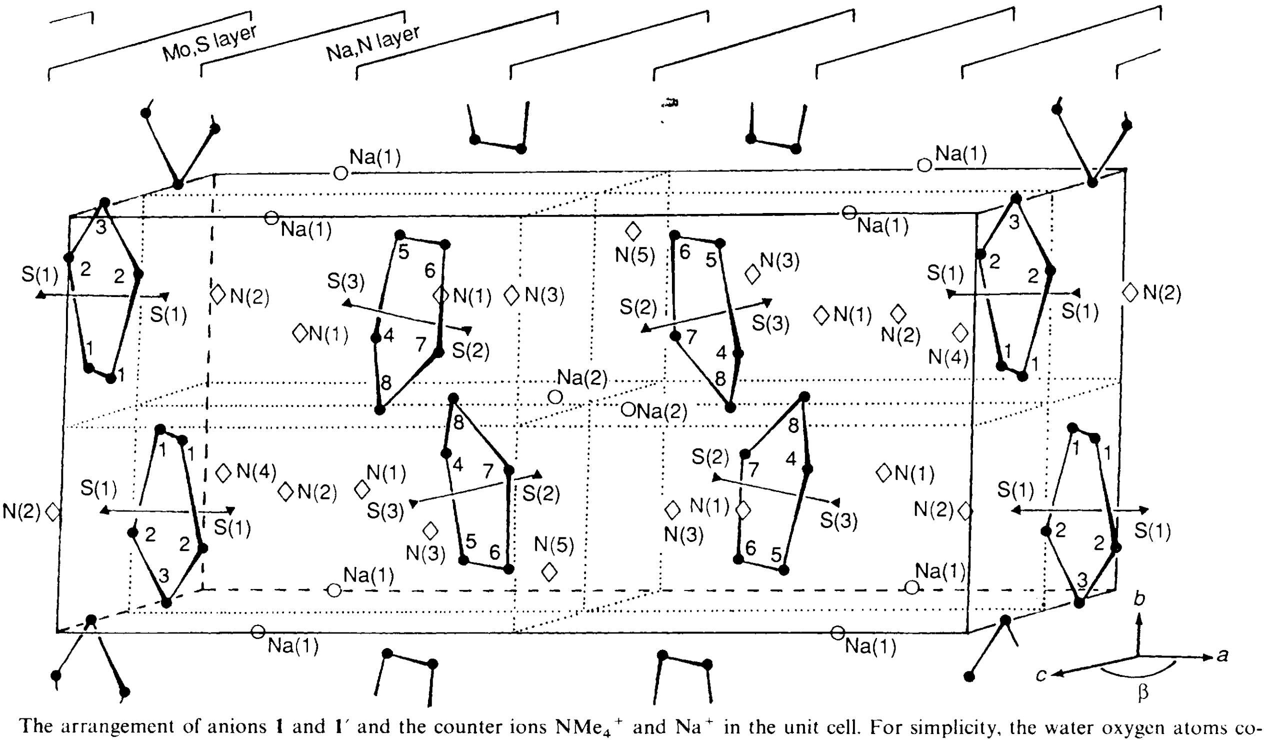

Fig. 3 The arrangement of anions **1** and **1′** and the counter ions NMe_4^+ and Na^+ in the unit cell. For simplicity, the water oxygen atoms co-ordinating to the Na^+ ions and the C atoms of the NMe_4^+ ions are omitted. The layer structure running parallel to the (100) plane is indicated at the top of the Figure

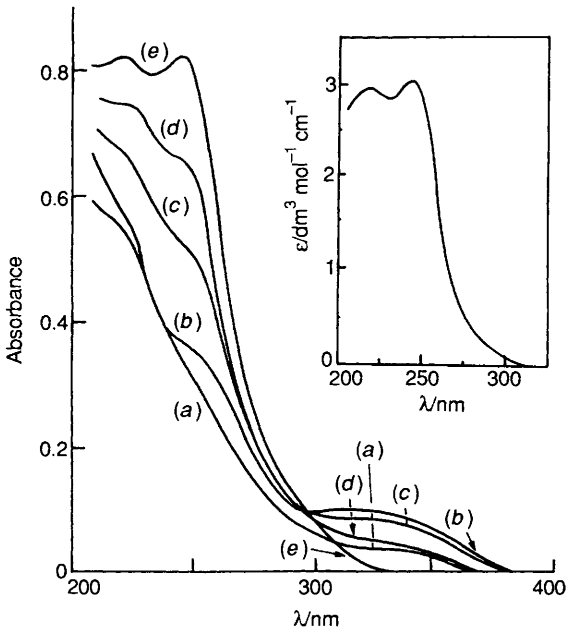

Fig. 4 Spectral representation of the reversible equilibrium between **1** and $[Mo_6O_{19}]^{2-}$ ions as a function of H_2SO_4 concentration in solutions composed of 60% (v/v) MeCN and 10 mmol dm^{-3} Mo^{VI}: $[H_2SO_4]$ 8 (*a*), 15 (*b*), 30 (*c*), 50 (*d*) and 125 mmol dm^{-3} (*e*). The spectral measurements were made by using a cuvette with a light pathlength of 0.154 mm and at 25 °C. Inset: UV absorption spectrum of $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$ and $[NMe_4]_4S_2Mo_5O_{23}$ dissolved in neat MeCN

Formation of Anion **1** *in Aqueous*-MeCN *Media*.—The UV spectra of the synthesized salts $Na[NMe_4]_3S_2Mo_5O_{23}\cdot 4H_2O$ and $[NMe_4]_4S_2Mo_5O_{23}$ in neat MeCN were measured. Both salts are soluble up to *ca*. 3.5 × 10^{-4} mol dm^{-3} in MeCN, and the spectra of these solutions conformed to Beer's law. The inset in Fig. 4 illustrates the spectroscopic characteristics of the salts, hence those of the kernel anion **1** in MeCN solutions; the absorption maxima appear at $\lambda = 213$ and 243 nm with respective molar absorption coefficients $\varepsilon = 3.2 \times 10^4$ and 3.3×10^4 dm^3 mol^{-1} cm^{-1}.

The UV spectroscopic measurements were also made for a series of solutions containing 60% (v/v) MeCN, 10 mmol dm^{-3} Mo^{VI}, and varying concentrations of H_2SO_4, the spectra being superimposed in Fig. 4. At low H_2SO_4 concentrations, the solutions are colourless [curve (*a*)]. At about 15 mmol dm^{-3} H_2SO_4 the solutions became pale yellow and show three absorption maxima at $\lambda = 222$, 257 and 325 nm [curve (*b*)], which are attributed to the formation of $[Mo_6O_{19}]^{2-}$ ion.[20] At higher H_2SO_4 concentrations the solutions become colourless again and the absorption maxima shift to $\lambda = 213$ and 243 nm [curves (*c*)–(*e*)], showing an isosbestic point at around $\lambda = 295$ nm. Curve (*e*) is the fully developed UV spectrum in 125 mmol dm^{-3} H_2SO_4 and virtually identical to the spectrum of **1** (inset in Fig. 4). A reversible equilibrium between **1** (colourless) and $[Mo_6O_{19}]^{2-}$ (yellow) in aqueous MeCN solutions can thus spectroscopically be revealed.

Acknowledgements

We are grateful to Dr. S. Sasaki of the Japanese National Laboratory of High Energy Physics for preparing and revising the computer programs used and to Dr. K. Tomita for his support and use of the X-ray facilities at Kyoto University. Support (Grant No. 0130004) from the Japanese Ministry of Education, Sciences and Culture is also gratefully acknowledged.

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Received 21*st May* 1991; *Paper* 1/02386A