The Structure of 18-Molybdodisulphate(VI)(4−) Ion in $(NEt_4)_4S_2Mo_{18}O_{62}\cdot CH_3CN$†

Toshitaka Hori *
Department of Chemistry, College of Liberal Arts and Sciences, Kyoto University, Kyoto 606, Japan
Osamu Tamada
Institute of Earth Science, College of Liberal Arts and Sciences, Kyoto University, Kyoto 606, Japan
Sadayuki Himeno
Department of Chemistry, College of Liberal Arts, Kobe University, Kobe 657, Japan

The structure of $(NEt_4)_4S_2Mo_{18}O_{62}\cdot CH_3CN$ has been determined by the single-crystal *X*-ray method. The crystals are triclinic, space group $P\bar{1}$, with cell parameters a = 15.062(4), b = 23.296(4), c = 13.813(4) Å, and α = 97.66(4), β = 115.98(2), γ = 84.63(4)°, and Z = 2. The structure model was refined by full-matrix least squares to R' = 0.063 for 11 700 reflections with $F_o > 3\sigma(F)$. The existence of the $[S_2Mo_{18}O_{62}]^{4-}$ heteropolyanion in the crystals has been confirmed. It is composed of two SO_4 tetrahedra and eighteen MoO_6 octahedra linked to give the Dawson α-$[P_2W_{18}O_{62}]^{6-}$ structure. The anions are separated by NEt_4^+ cations and CH_3CN solvate molecules.

In parallel with extensive studies on heteropolymolybdate and/or-tungstate complexes which contain silicate, phosphate, germanate, or arsenate ion as the central tetrahedron, the occurrence of similar complexes containing sulphate ion, which would likely also to be a central tetrahedron, has long been sought by many investigators.[1]

With paramolybdate–SO_2 systems, Rosenheim[2] obtained pale yellow crystals having a composition of Mo/S^{IV} = 5/2. Later, Matsumoto *et al.*[3] substantiated, by an *X*-ray analysis, the molecular structure for the $[S_2Mo_5O_{21}]^{4-}$ heteropolyion where two $S^{IV}O_3$ trigonal pyramids were surrounded by five MoO_6 octahedra arranged in a zigzag ring. This fact may lead to a perspective for the occurrence of a family of molybdosulphates composed of the $S^{VI}O_4$tetrahedral ion as well as the $S^{IV}O_3$ pyramidal ion, from the analogy that the five-membered zigzag ring structure mentioned above has been established for both $[P_2Mo_5O_{23}]^{6-}$ and $[(HP)_2Mo_5O_{21}]^{4-}$ heteropolyions.[4,5] In these heteropolyions, P^VO_4 and $HP^{III}O_3$ tetrahedral ions similarly served as the respective central polyhedra, irrespective of the valence states of the P atoms, but reflecting the configurations of the O atoms around the P atoms.

More recent crystallographic studies[6] revealed the existence of $[SMo_3O_{13}]^{2-}$ and $[S_2V_2W_{16}O_{62}]^{6-}$ heteropolyions including $S^{VI}O_4$ tetrahedra.

Previously, we isolated[7] an orange-yellow material with the composition of Mo/S^{VI} = 9/1 from a Na_2MoO_4–H_2SO_4–CH_3CN system. It was crystallized into a form of $(NEt_4)_4S_2Mo_{18}O_{62}\cdot CH_3CN$. This can be reformulated as $[NEt_4]_4[(SO_4)_2(MoO_3)_{18}]\cdot CH_3CN$, therefore the anionic part of the salt is essentially the same as in $Na_6[(PO_4)_2(MoO_3)_{18}]\cdot 24H_2O$ obtained by Strandberg[8a] and $K_6[(PO_4)_2(WO_3)_{18}]\cdot 14H_2O$ by Dawson,[9] although the central PO_4 tetrahedra are replaced by SO_4 tetrahedra. In the present paper we report on the crystal structure of $(NEt_4)_4S_2Mo_{18}O_{62}\cdot CH_3CN$, which has revealed the existence of the $[(SO_4)_2(MoO_3)_{18}]^{4-}$ heteropolyion.

Experimental

Preparation of Single Crystals.—By treating the Na_2MoO_4–H_2SO_4–CH_3CN system as described previously[7] a yellow powder of $(NEt_4)_4S_2Mo_{18}O_{62}$ was prepared. Approximately 800 mg of the material were dissolved in neat CH_3CN (500 cm^3). The solution was, if necessary, filtered and allowed to stand in a chemical hood at ambient temperature. As the solvent evaporated spontaneously, the first crystals appeared after a few days. The orange transparent prisms were collected by filtration, followed by drying in the open air for a few hours [Found: C, 12.45; H, 2.30; Mo, 51.85; N, 2.15; S, 1.95. Calc. for $(NEt_4)_4S_2Mo_{18}O_{62}\cdot CH_3CN$: C, 12.20; H, 2.50; Mo, 51.65; N, 2.10; S, 1.90%].

Crystallography.—A transparent, prismatic crystal with approximate dimensions 0.80 × 0.30 × 0.14 mm elongated on c was mounted on a Rigaku-5UD four-circle diffractometer. The crystal was glued on a glass fibre parallel to the c axis. The intensity data showed no systematically absent reflections and the cell parameters indicated the triclinic system. The space group $P\bar{1}$ or $P1$ was, therefore, assigned to the crystal.

Corrections were made for Lorentz and polarization factors but not for absorption because of the rather small value of the linear absorption coefficient. The cell parameters were determined from 19 reflections in the range $42 < 2\theta < 49°$. The crystal data and experimental conditions are summarized in Table 1.

The collection of the data had to be accomplished within a few days after the preparation of the crystals because they had a tendency to decay due to the spontaneous release of CH_3CN even under ambient conditions. Owing to this the data were collected rather rapidly although a slightly poorer precision resulted.

Data processing. The Mo atoms were located from a Patterson synthesis on the assumption that the anion had the Dawson structure, and their positions were refined to R 0.287. The S, O, N, and C atoms were then located by synthesizing successively Fourier and Fourier difference maps. The Fourier syntheses were carried out by using the program FOURIER provided by Iitaka and Matsusaki.[10] No attempt to locate the H atoms was made.

The atomic scattering factors and dispersion corrections for neutral Mo, S, O, N, and C atoms were taken from ref. 11.

The refinement was carried in space group $P\bar{1}$ by using the RFINE4 program[12] with modifications by Horiuchi,[13] with reflections weighted by $1/\sigma^2(F)$, where $\sigma(F)$ was based on counting statistics.

The final fractional co-ordinates are listed in Table 2, inter-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

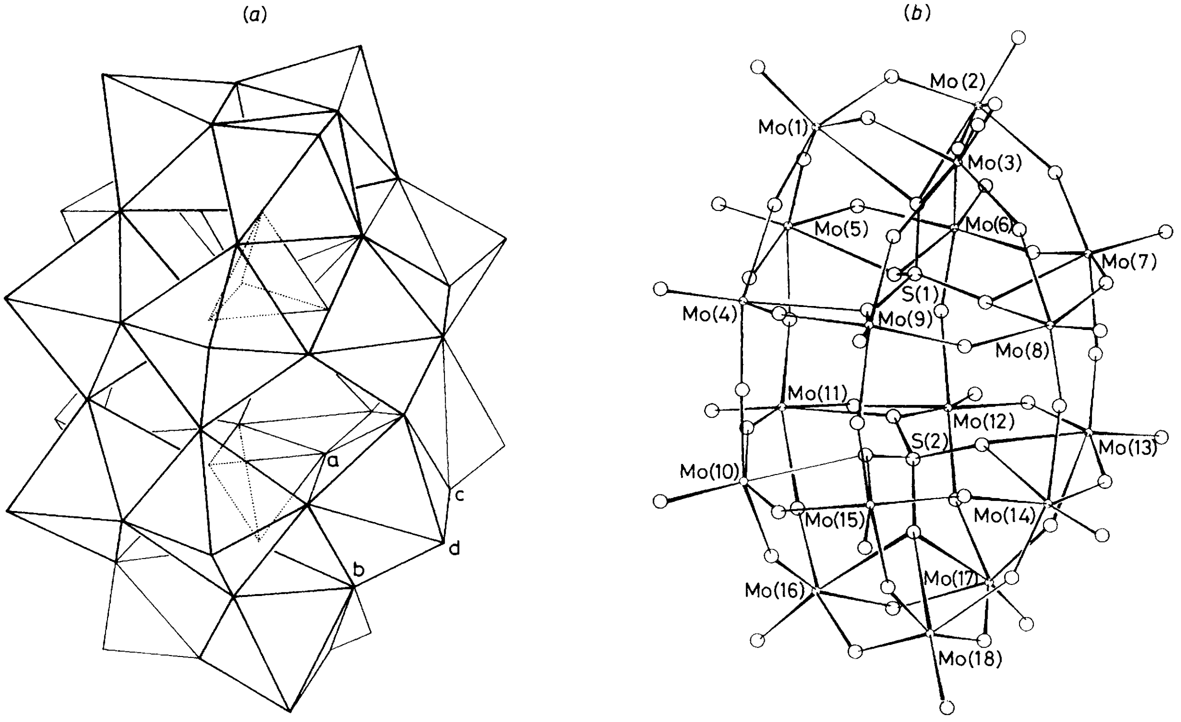

Figure 1. Polyhedral (*a*) and atom-and-bond representations (*b*) for the structure of $[S_2Mo_{18}O_{62}]^{4-}$, along with the numbering scheme for the Mo and S atoms and the designation for the O atoms in the polyhedra. The O atoms are designated by the numbers of the Mo atoms to which they are linked. The types of bonding of the O atoms are indicated by using lower case letters: O_a denotes oxygens which bridge the Mo atom and the central S atom; O_b and O_c, link MoO_6 octahedra by vertex and by edge, respectively, and O_d, are bonded to one Mo atom

Table 1. Crystal data and the experimental parameters for $(NEt_4)_4S_2Mo_{18}O_{62}\cdot CH_3CN$

Space group	$P\bar{1}(P1)$
a/Å	15.062(4)
b/Å	23.296(4)
c/Å	13.813(4)
α/°	97.66(4)
β/°	115.98(2)
γ/°	84.63(4)
U/Å^3	4 314(2)
M	3 345.1
Z	2
D_m/g cm^{-3}	2.56
D_c/g cm^{-3}	2.57
μ(Mo-K_α)/cm^{-1}	29.8
Radiation	Mo-K_α (graphite monochromated, λ = 0.7107 Å)
Scan technique	2θ—ω
Scan width/°	$\Delta\omega = (1.0 + 0.5 \tan \theta)$
Scan speed/° min^{-1}	10
Scan range (2θ)/°	2—50
Reflections collected	12 842
Reflections used [$F_o > 3\sigma(F)$]	11 700
R'	0.063
R	0.079
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting function	$w = 1/\sigma^2(F)$

atomic distances and bond angles, calculated by the program UMBADTEA,[14] in Tables 3 and 4, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

The crystals consist of $[S_2Mo_{18}O_{62}]^{4-}$ heteropolyanions, NEt_4^+ cations, and CH_3CN solvate molecules. The negative charge on the heteropolyion arises from the two SO_4^{2-} ions incorporated, and is neutralized by the four NEt_4^+ ions. The crystals become opaque and crumble as the CH_3CN molecules are lost.

Figure 1(*a*) illustrates the assemblage of eighteen MoO_6 octahedra and two SO_4 tetrahedra in the heteropolyion. The numbering scheme for the Mo and S atoms is given in Figure 1(*b*). It is evident from the Figures that the heteropolyion is isostructural with $[P_2Mo_{18}O_{62}]^{6-}$ and hence with $[P_2W_{18}O_{62}]^{6-}$. That is, the present heteropolyion is composed of two SMo_9O_{34} half units, each of which contains SO_4 as the central tetrahedron which is poly-co-ordinated by one triad and three pairs of edge-sharing MoO_6 octahedra. Since the latter pairs are linked further by sharing vertices, a hexagonal puckered ring is formed around the central tetrahedron. The mean plane for the ring and the displacements of the Mo atoms from the plane are given in the footnote on p. 1495. To complete the structure of the heteropolyion, the pairs of half-units are joined by sharing the six unshared oxygens, each exposed in the direction perpendicular to the puckered ring. According to Pope,[15] the heteropolyion should be referred to as the α isomer, since one of the half-units is eclipsed by the other.

Dawson first proposed this structure for the $[P_2W_{18}O_{62}]^{6-}$ ion in relation to the Keggin structure which was known for $[PW_{12}O_{40}]^{3-}$ ion;[16] the former structure bears the PW_9O_{34} unit derived by removing the W_3O_{13} unit from the latter. In both types of structures, in fact, the PW_9O_{34} unit was retained with mostly the same dimensions. Such a structural relation was also found between $[P_2Mo_{18}O_{62}]^{6-}$ and $[PMo_{12}O_{40}]^{3-}$ ions[8] and between $[As_2W_{18}O_{62}]^{6-}$ and $[AsW_{12}O_{40}]^{3-}$.[17]

Table 2. Fractional atomic co-ordinates for $(NEt_4)_4S_2Mo_{18}O_{62}\cdot CH_3CN$

Atom	*x*	*y*	*z*
Mo(1)	0.852 7(1)	0.470 03(6)	0.279 3(1)
Mo(2)	0.946 7(1)	0.355 67(7)	0.164 4(1)
Mo(3)	0.053 6(1)	0.390 22(6)	0.440 2(1)
Mo(4)	0.691 1(1)	0.439 95(6)	0.410 8(1)
Mo(5)	0.616 4(1)	0.398 65(7)	0.119 6(1)
Mo(6)	0.713 3(1)	0.272 12(7)	0.035 7(1)
Mo(7)	0.945 3(1)	0.208 96(7)	0.236 1(1)
Mo(8)	0.015 4(1)	0.245 55(6)	0.509 8(1)
Mo(9)	0.907 8(1)	0.380 57(7)	0.593 9(1)
Mo(10)	0.524 1(1)	0.336 53(7)	0.438 0(1)
Mo(11)	0.443 4(1)	0.298 53(7)	0.144 4(1)
Mo(12)	0.540 5(1)	0.172 50(7)	0.060 8(1)
Mo(13)	0.772 8(1)	0.105 39(7)	0.253 1(1)
Mo(14)	0.842 3(1)	0.143 11(7)	0.526 2(1)
Mo(15)	0.740 9(1)	0.277 43(7)	0.622 0(1)
Mo(16)	0.395 7(1)	0.199 20(7)	0.309 8(1)
Mo(17)	0.528 8(1)	0.081 75(7)	0.255 4(2)
Mo(18)	0.594 0(1)	0.141 51(7)	0.518 1(1)
S(1)	0.816 5(3)	0.325 8(2)	0.315 5(3)
S(2)	0.640 8(3)	0.221 0(2)	0.340 9(4)
O_a(1,2,3)	0.885 1(7)	0.365 2(4)	0.309 5(8)
O_a(4,9)	0.793 1(8)	0.350 9(5)	0.405 1(9)
O_a(5,6)	0.730 4(7)	0.319 2(4)	0.216 1(8)
O_a(7,8)	0.871 1(8)	0.269 4(5)	0.344 8(9)
O_a(10,15)	0.655 9(7)	0.270 1(4)	0.423 3(8)
O_a(11,12)	0.592 3(7)	0.237 9(4)	0.229 0(8)
O_a(13,14)	0.735 9(8)	0.189 2(5)	0.364 2(9)
O_a(16,17,18)	0.574 3(8)	0.180 5(5)	0.354 3(9)
O_b(1,4)	0.787 8(8)	0.467 2(5)	0.360 8(9)
O_b(1,5)	0.729 6(8)	0.436 3(5)	0.162 8(9)
O_b(2,6)	0.829 9(7)	0.326 0(4)	0.080 8(9)
O_b(2,7)	0.984 1(8)	0.276 4(5)	0.216 2(9)
O_b(3,8)	0.061 6(8)	0.316 4(5)	0.473 2(9)
O_b(3,9)	0.979 9(8)	0.405 8(4)	0.535 5(9)
O_b(4,5)	0.622 9(8)	0.419 3(5)	0.261 6(9)
O_b(4,10)	0.621 4(8)	0.393 9(5)	0.443 0(9)
O_b(5,11)	0.520 6(8)	0.339 8(5)	0.114 2(9)
O_b(6,7)	0.819 3(8)	0.223 6(5)	0.123 5(9)
O_b(6,12)	0.617 7(8)	0.232 6(5)	0.035 9(9)
O_b(7,13)	0.869 0(8)	0.150 2(5)	0.264 5(9)
O_b(8,9)	0.963 9(8)	0.302 3(5)	0.579 3(9)
O_b(8,14)	0.939 3(8)	0.189 3(5)	0.505 3(9)
O_b(9,15)	0.807 6(8)	0.333 7(5)	0.610 2(9)
O_b(10,11)	0.480 7(8)	0.336 2(5)	0.282 2(9)
O_b(10,16)	0.457 4(8)	0.270 2(5)	0.410 9(9)
O_b(11,16)	0.393 4(8)	0.239 4(5)	0.204 9(9)
O_b(12,13)	0.670 4(8)	0.139 2(5)	0.136 3(9)
O_b(12,17)	0.500 0(8)	0.127 9(5)	0.131 4(9)
O_b(13,17)	0.654 0(8)	0.077 9(5)	0.269 4(9)
O_b (14,15)	0.823 5(8)	0.217 0(5)	0.600 7(9)
O_b(14,18)	0.276 5(8)	0.120 8(5)	0.515 6(9)
O_b(15,18)	0.647 4(8)	0.210 0(5)	0.585 5(9)
O_c(1,2)	0.904 9(9)	0.431 6(5)	0.176(1)
O_c(1,3)	0.976 3(8)	0.462 3(5)	0.380 5(9)
O_c(2,3)	0.058 3(8)	0.374 7(5)	0.308 0(9)
O_c(4,9)	0.803 1(7)	0.435 7(4)	0.547 9(8)
O_c(5,6)	0.631 6(8)	0.343 6(5)	0.010 9(9)
O_c(7,8)	0.029 8(8)	0.208 8(5)	0.382 2(9)
O_c(10,15)	0.616 6(8)	0.322 3(5)	0.574 3(9)
O_c(11,12)	0.441 2(8)	0.231 4(5)	0.039 7(9)
O_c(13,14)	0.839 3(8)	0.095 2(5)	0.406 2(9)
O_c(16, 17)	0.405 3(8)	0.125 4(5)	0.242 3(9)
O_c(16, 18)	0.465 6(8)	0.165 3(5)	0.454 0(9)
O_c(17, 18)	0.558 5(8)	0.077 3(5)	0.397 7(9)
O_d(1)	0.841 2(8)	0.539 0(5)	0.249 9(9)
O_d(2)	0.002 9(9)	0.355 6(5)	0.084(1)
O_d(3)	0.161 8(8)	0.414 6(5)	0.519 0(9)
O_d(4)	0.638 4(9)	0.503 8(5)	0.428(1)
O_d(5)	0.526 2(9)	0.441 3(5)	0.044(1)
O_d(6)	0.704 0(9)	0.252 8(5)	0.912(1)
O_d(7)	0.999 7(8)	0.160 6(5)	0.176(1)
O_d(8)	0.122 3(8)	0.229 0(5)	0.606 6(9)
O_d(9)	0.971 1(8)	0.401 5(5)	0.724 3(9)
O_d(10)	0.446 6(8)	0.384 6(5)	0.464 8(9)
O_d(11)	0.329 3(8)	0.326 5(5)	0.075(1)
O_d(12)	0.497 4(9)	0.138 9(5)	0.936(1)
O_d(13)	0.798 4(9)	0.043 3(5)	0.195(1)
O_d(14)	0.928 1(8)	0.109 8(5)	0.629 6(9)
O_d(15)	0.779 5(8)	0.280 8(5)	0.755(1)
O_d(16)	0.280 3(9)	0.204 9(5)	0.294(1)
O_d(17)	0.478 1(9)	0.019 4(5)	0.188(1)
O_d(18)	0.600 8(9)	0.107 4(5)	0.619(1)
N(1)	0.242(1)	0.489 0(6)	0.171(1)
C(11)	0.193(1)	0.455 3(9)	0.226(2)
C(12)	0.230(1)	0.391 8(9)	0.237(2)
C(13)	0.216(1)	0.459 8(8)	0.052(1)
C(14)	0.105(1)	0.458 3(9)	0.979(2)
C(15)	0.189(2)	0.550(1)	0.167(3)
C(16)	0.232(2)	0.590(1)	0.119(2)
C(17)	0.351(1)	0.487 5(8)	0.230(1)
C(18)	0.393(1)	0.514 8(8)	0.343(2)
N(2)	0.388(1)	0.322 7(7)	0.715(1)
C(21)	0.301(2)	0.294(1)	0.626(2)
C(22)	0.299(1)	0.287 3(9)	0.513(2)
C(23)	0.393(2)	0.318(1)	0.829(2)
C(24)	0.295(2)	0.348(1)	0.832(2)
C(25)	0.386(2)	0.384(1)	0.688(2)
C(26)	0.463(2)	0.420(1)	0.789(2)
C(27)	0.492(2)	0.294(1)	0.723(2)
C(28)	0.500(2)	0.230(1)	0.731(2)
N(3)	0.902(1)	0.818 2(8)	0.074(1)
C(31)	0.015(2)	0.821 8(9)	0.132(2)
C(32)	0.068(2)	0.796(1)	0.064(2)
C(33)	0.870(2)	0.755(1)	0.037(2)
C(34)	0.926(2)	0.714(1)	0.136(2)
C(35)	0.871(2)	0.842(1)	0.165(2)
C(36)	0.752(2)	0.844(1)	0.105(3)
C(37)	0.851(2)	0.848(1)	0.967(2)
C(38)	0.875(2)	0.912(1)	0.993(2)
N(4)	0.214(1)	0.058 1(7)	0.455(1)
C(41)	0.178(2)	0.026(1)	0.518(2)
C(42)	0.113(2)	0.062(1)	0.575(2)
C(43)	0.278(2)	0.106(1)	0.532(2)
C(44)	0.368(2)	0.086(1)	0.628(2)
C(45)	0.130(2)	0.080(1)	0.361(2)
C(46)	0.053(2)	0.036(1)	0.288(2)
C(47)	0.279(2)	0.012(1)	0.417(2)
C(48)	0.320(2)	0.038(1)	0.349(2)
N(5)	0.852(2)	0.065(1)	0.873(2)
C(51)	0.780(2)	0.079(1)	0.885(3)
C(52)	0.697(2)	0.093(1)	0.902(2)

The numbering scheme for the N and C atoms is given in Figure 3.

Based on these facts and the structure generalized as (P or As) (Mo or W)$_9$O$_{34}$, Baker and Figgis[18] explained comprehensively the wide occurrence of the 18- and 17-heteropolyions including their geometrical isomers.

As for the SiO_4 tetrahedron, however, the Keggin-type anion, *i.e.* [SiMo(or W)$_{12}$O$_{40}$]$^{4-}$, and its lacunary modifications such as $[SiW_9O_{34}]^{10-}$ ion[19] have been found to exist, but the Dawson-type anions are not yet known.

In contrast to this, the SO_4 tetrahedron was found to form the Dawson-type $[S_2V_2W_{16}O_{62}]^{6-}$ion [6b] along with a side product of the hexametalate $[VW_5O_{19}]^{3-}$. The present study has now revealed a second example of the Dawson-type ion based on the SO_4 tetrahedron. As reported before,[7] however, the ion is unstable in aqueous solutions and decomposes gradually to a mixture of isopolymolybdates. Because of the instability of Dawson-type heteropolymolybdate anions and the paucity of examples of heteropolyanions based on SO_4 tetrahedra, it has been assumed that the relatively small SO_4 group would be a less versatile constituent of heteropolyanions than SiO_4, AsO_4, or especially PO_4. The lower charge on SO_4^{2-} and consequently on the polyanion could also be a factor.

In order to deduce the structural characteristics of $[S_2Mo_{18}$-

Table 3. Interatomic distances (Å)

Mo(1)···Mo(2)	3.429(3)	Mo(1)···Mo(3)	3.422(3)	Mo(1)···Mo(4)	3.775(3)
Mo(1)···Mo(5)	3.681(3)	Mo(2)···Mo(3)	3.435(3)	Mo(2)···Mo(6)	3.766(3)
Mo(2)···Mo(7)	3.687(3)	Mo(3)···Mo(8)	3.785(3)	Mo(3)···Mo(9)	3.700(3)
Mo(4)···Mo(5)	3.685(3)	Mo(4)···Mo(9)	3.438(2)	Mo(4)···Mo(10)	3.804(3)
Mo(5)···Mo(6)	3.454(3)	Mo(5)···Mo(11)	3.805(3)	Mo(6)···Mo(7)	3.699(3)
Mo(6)···Mo(12)	3.797(3)	Mo(7)···Mo(8)	3.456(3)	Mo(7)···Mo(13)	3.805(3)
Mo(8)···Mo(9)	3.687(3)	Mo(8)···Mo(14)	3.791(3)	Mo(9)···Mo(15)	3.804(3)
Mo(10)···Mo(11)	3.693(3)	Mo(10)···Mo(15)	3.441(2)	Mo(10)···Mo(16)	3.709(3)
Mo(11)···Mo(12)	3.444(3)	Mo(11)···Mo(16)	3.774(3)	Mo(12)···Mo(13)	3.700(3)
Mo(12)···Mo(17)	3.704(3)	Mo(13)···Mo(14)	3.455(3)	Mo(13)···Mo(17)	3.781(3)
Mo(14)···Mo(15)	3.693(3)	Mo(14)···Mo(18)	3.695(3)	Mo(15)···Mo(18)	3.782(3)
Mo(16)···Mo(17)	3.437(3)	Mo(16)···Mo(18)	3.429(3)	Mo(17)···Mo(18)	3.444(3)
Mo(1)···S(1)	3.586(5)	Mo(2)···S(1)	3.593(6)	Mo(3)···S(1)	3.591(5)
Mo(4)···S(1)	3.561(5)	Mo(5)···S(1)	3.522(4)	Mo(6)···S(1)	3.568(5)
Mo(7)···S(1)	3.529(3)	Mo(8)···S(1)	3.594(4)	Mo(9)···S(1)	3.563(5)
Mo(10)···S(2)	3.514(5)	Mo(11)···S(2)	3.564(4)	Mo(12)···S(2)	3.545(5)
Mo(13)···S(2)	3.595(5)	Mo(14)···S(2)	3.529(4)	Mo(15)···S(2)	3.599(5)
Mo(16)···S(2)	3.601(5)	Mo(17)···S(2)	3.608(5)	Mo(18)···S(2)	3.589(6)
S(1)–O_a(1,2,3)	1.47(1)	S(1)–O_a(4,9)	1.46(1)	S(1)–O_a(5,6)	1.418(9)
S(1)–O_a(7,8)	1.49(1)	S(2)–O_a(10,15)	1.46(1)	S(2)–O_a(11,12)	1.48(1)
S(2)–O_a(13,14)	1.47(1)	S(2)–O_a(16,17,18)	1.52(1)	S(1)···S(2)	3.918(7)
Mo(1)–O_a(1,2,3)	2.50(1)	Mo(2)–O_a(1,2,3)	2.53(1)	Mo(3)–O_a(1,2,3)	2.454(9)
Mo(4)–O_a(4,9)	2.48(1)	Mo(5)–O_a(5,6)	2.49(1)	Mo(6)–O_a(5,6)	2.50(1)
Mo(7)–O_a(7,8)	2.47(1)	Mo(8)–O_a(7,8)	2.448(9)	Mo(9)–O_a(4,9)	2.46(1)
Mo(10)–O_a(10,15)	2.46(1)	Mo(11)–O_a(11,12)	2.44(1)	Mo(12)–O_a(11,12)	2.45(1)
Mo(13)–O_a(13,14)	2.49(1)	Mo(14)–O_a(13,14)	2.43(1)	Mo(15)–O_a(10,15)	2.46(1)
Mo(16)–O_a(16,17,18)	2.49(1)	Mo(17)–O_a(16,17,18)	2.50(1)	Mo(18)–O_a(16,17,18)	2.44(1)
Mo(1)–O_b(1,4)	1.79(1)	Mo(1)–O_b(1,5)	1.992(9)	Mo(2)–O_b(2,6)	1.77(1)
Mo(2)–O_b(2,7)	2.01(1)	Mo(3)–O_b(3,8)	1.82(1)	Mo(3)–O_b(3,9)	2.04(1)
Mo(4)–O_b(1,4)	2.04(1)	Mo(4)–O_b(4,5)	1.87(1)	Mo(4)–O_b(4,10)	1.79(1)
Mo(5)–O_b(1,5)	1.81(1)	Mo(5)–O_b(4,5)	1.92(1)	Mo(5)–O_b(5,11)	2.05(1)
Mo(6)–O_b(2,6)	2.07(1)	Mo(6)–O_b(6,7)	1.90(1)	Mo(6)–O_b(6,12)	1.78(1)
Mo(7)–O_b(2,7)	1.82(1)	Mo(7)–O_b(6,7)	1.890(9)	Mo(7)–O_b(7,13)	2.04(1)
Mo(8)–O_b(3,8)	2.05(1)	Mo(8)–O_b(8,9)	1.84(1)	Mo(8)–O_b(8,14)	1.80(1)
Mo(9)–O_b(3,9)	1.79(1)	Mo(9)–O_b(8,9)	1.96(1)	Mo(9)–O_b(9,15)	2.05(1)
Mo(10)–O_b(4,10)	2.05(1)	Mo(10)–O_b(10,11)	1.96(1)	Mo(10)–O_b(10,16)	1.83(1)
Mo(11)–O_b(5,11)	1.79(1)	Mo(11)–O_b(10,11)	1.85(1)	Mo(11)–O_b(11,16)	2.05(1)
Mo(12)–O_b(6,12)	2.05(1)	Mo(12)–O_b(12,13)	1.91(1)	Mo(12)–O_b(12,17)	1.82(1)
Mo(13)–O_b(7,13)	1.80(1)	Mo(13)–O_b(12,13)	1.88(1)	Mo(13)–O_b(13,17)	2.07(1)
Mo(14)–O_b(8,14)	2.03(1)	Mo(14)–O_b(14,15)	1.95(1)	Mo(14)–O_b(14,18)	1.81(1)
Mo(15)–O_b(9,15)	1.79(1)	Mo(15)–O_b(14,15)	1.87(1)	Mo(15)–O_b(15,18)	2.07(1)
Mo(16)–O_b(10,16)	2.02(1)	Mo(16)–O_b(11,16)	1.81(1)	Mo(17)–O_b(12,17)	2.01(1)
Mo(17)–O_b(13,17)	1.80(1)	Mo(18)–O_b(14,18)	2.02(1)	Mo(18)–O_b(15,18)	1.80(1)
Mo(1)–O_c(1,2)	2.00(1)	Mo(1)–O_c(1,3)	1.782(9)	Mo(2)–O_c(1,2)	1.83(1)
Mo(2)–O_c(2,3)	1.986(9)	Mo(3)–O_c(1,3)	2.00(1)	Mo(3)–O_c(2,3)	1.84(1)
Mo(4)–O_c(4,9)	1.914(9)	Mo(5)–O_c(5,6)	1.92(1)	Mo(6)–O_c(5,6)	1.95(1)
Mo(7)–O_c(7,8)	1.86(1)	Mo(8)–O_c(7,8)	1.95(1)	Mo(9)–O_c(4,9)	1.87(1)
Mo(10)–O_c(10,15)	1.84(1)	Mo(11)–O_c(11,12)	1.98(1)	Mo(12)–O_c(11,12)	1.88(1)
Mo(13)–O_c(13,14)	1.94(1)	Mo(14)–O_c(13,14)	1.86(1)	Mo(15)–O_c(10,15)	1.94(1)
Mo(16)–O_c(16,17)	1.87(1)	Mo(16)–O_c(16,18)	2.03(1)	Mo(17)–O_c(16,17)	1.98(1)
Mo(17)–O_c(17,18)	1.83(1)	Mo(18)–O_c(16,18)	1.81(1)	Mo(18)–O_c(17,18)	2.00(1)
Mo(1)–O_d(1)	1.69(1)	Mo(2)–O_d(2)	1.67(2)	Mo(3)–O_d(3)	1.62(1)
Mo(4)–O_d(4)	1.66(1)	Mo(5)–O_d(5)	1.65(1)	Mo(6)–O_d(6)	1.65(1)
Mo(7)–O_d(7)	1.67(1)	Mo(8)–O_d(8)	1.63(1)	Mo(9)–O_d(9)	1.66(1)
Mo(10)–O_d(10)	1.67(1)	Mo(11)–O_d(11)	1.68(1)	Mo(12)–O_d(12)	1.66(1)
Mo(13)–O_d(13)	1.65(1)	Mo(14)–O_d(14)	1.67(1)	Mo(15)–O_d(15)	1.66(1)
Mo(16)–O_d(16)	1.65(1)	Mo(17)–O_d(17)	1.67(1)	Mo(18)–O_d(18)	1.66(2)
N(1)···C(12)	2.60(3)	N(1)···C(14)	2.60(2)	N(1)···C(16)	2.51(3)
N(1)···C(18)	2.51(2)	N(1)···O_c(1,2^{II})	4.85(2)	N(1)···O_d(2)	4.62(2)
N(1)···O_c(4,9^{I})	4.35(2)	N(1)···O_d(9^{I})	4.52(2)	N(1)···O_b(9,15^{I})	4.98(2)
N(1)···O_d(10)	4.71(2)	N(1)···O_b(10,11)	4.71(2)	N(1)···O_d(11)	4.13(2)
N(2)···C(22)	2.56(2)	N(2)···C(24)	2.54(4)	N(2)···C(26)	2.51(3)
N(2)···C(28)	2.59(3)	N(2)···O_d(3)	3.95(2)	N(2)···O_b(3,8)	4.58(2)
N(2)···O_d(4^{I})	4.64(2)	N(2)···O_d(5)	4.69(2)	N(2)···O_c(5,6)	4.13(2)

Table 3 (*continued*)

$N(2) \cdots O_d(6)$	4.60(2)	$N(2) \cdots O_b(6,12)$	4.87(2)	$N(2) \cdots O_d(8)$	4.37(2)
$N(2) \cdots O_d(10)$	4.37(2)	$N(2) \cdots O_c(10,15)$	4.64(2)	$N(2) \cdots O_b(10,16)$	4.75(2)
$N(3) \cdots C(32)$	2.56(3)	$N(3) \cdots C(34)$	2.62(4)	$N(3) \cdots C(36)$	2.49(4)
$N(3) \cdots C(38)$	2.52(4)	$N(3) \cdots O_d(2^{II})$	4.74(2)	$N(3) \cdots O_d(7^{IV})$	4.41(3)
$N(3) \cdots O_d(8^{I})$	4.86(3)	$N(3) \cdots O_d(11^{II})$	4.67(2)	$N(3) \cdots O_b(11,16^{II})$	4.60(2)
$N(3) \cdots O_d(14^{V})$	3.99(2)	$N(3) \cdots O_b(14,15^{V})$	4.70(2)	$N(3) \cdots O_d(15^{V})$	4.84(2)
$N(3) \cdots O_d(16^{II})$	4.57(2)	$N(4) \cdots C(42)$	2.69(4)	$N(4) \cdots C(44)$	2.55(3)
$N(4) \cdots C(46)$	2.55(3)	$N(4) \cdots C(48)$	2.56(4)	$N(4) \cdots O_d(7^{VI})$	4.59(2)
$N(4) \cdots O_c(7,8)$	4.21(2)	$N(4) \cdots O_d(8)$	4.63(2)	$N(4) \cdots O_c(13,17^{III})$	4.88(2)
$N(4) \cdots O_d(14^{III})$	4.41(2)	$N(4) \cdots O_b(14,18^{III})$	4.21(2)	$N(4) \cdots O_d(16)$	4.72(3)
$N(4) \cdots O_c(16,18)$	4.73(2)	$N(4) \cdots O_c(17,18^{III})$	4.40(2)	$N(4) \cdots O_d(18^{III})$	4.81(2)
$N(5)–C(51)$	1.17(5)	$N(5) \cdots C(52)$	2.54(5)	$N(5) \cdots O_d(6)$	4.79(3)
$N(5) \cdots O_b(6,7)$	4.85(3)	$N(5) \cdots O_d(7)$	4.20(3)	$N(5) \cdots O_d(13)$	4.95(4)
$N(5) \cdots O_d(14)$	4.28(4)	$N(5) \cdots O_b(14,18)$	4.77(3)	$N(5) \cdots O_d(18)$	4.02(3)

Roman numeral superscripts denote the transformations of the co-ordinates as follows: I $1 - x, 1 - y, 1 - z$; II $1 - x, 1 - y, \bar{z}$; III $1 - x, \bar{y}, 1 - z$; IV $2 - x, 1 - y, \bar{z}$; V $2 - x, 1 - y, 1 - z$; VI $x - 1, y, z$.

Table 4. Bond angles(°)*

$O_a(1,2,3)–S(1)–O_a(4,9)$	106.7(7)	$O_a(1,2,3)–S(1)–O_a(5,6)$	111.0(7)
$O_a(1,2,3)–S(1)–O_a(7,8)$	107.6(7)	$O_a(4,9)–S(1)–O_a(7,8)$	107.9(7)
$O_a(1,2,3)–Mo(1)–O_b(1,4)$	81.3(5)	$O_a(1,2,3)–Mo(1)–O_b(1,5)$	79.2(4)
$O_a(1,2,3)–Mo(1)–O_c(1,2)$	72.5(5)	$O_a(1,2,3)–Mo(1)–O_c(1,3)$	72.7(4)
$O_a(1,2,3)–Mo(1)–O_d(1)$	171.9(6)	$O_a(5,6)–Mo(5)–O_b(1,5)$	83.7(4)
$O_a(5,6)–Mo(5)–O_b(4,5)$	80.1(4)	$O_a(5,6)–Mo(5)–O_b(5,11)$	77.4(4)
$O_a(5,6)–Mo(5)–O_c(5,6)$	73.3(4)	$O_a(5,6)–Mo(5)–O_d(5)$	169.2(5)
$N(5)–C(51)–C(52)$	177(4)		

* Values are selected for the $S(1)O_4$ tetrahedron, $Mo(1)O_6$ and $Mo(5)O_6$ octahedra, and the CH_3CN molecule.

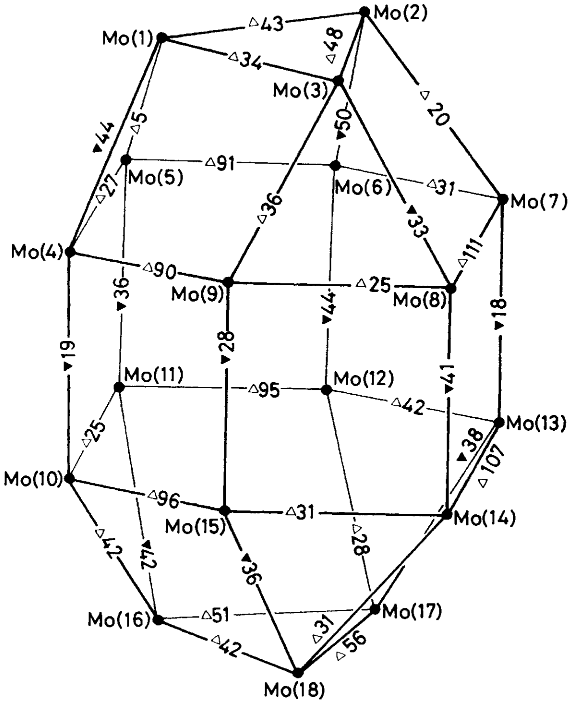

Figure 2. Comparison of dimensions of the molybdenum frameworks between the isostructural heteropolyions $[S_2Mo_{18}O_{62}]^{4-}$ (present study) and $[P_2Mo_{18}O_{62}]^{6-}$ (ref. 8*a*). From the Mo ··· Mo distance in the former ion the corresponding Mo ··· Mo distance in the latter ion is subtracted and the differences are indicated in terms of 10^{-3} Å. The positive and negative signs for the values are marked with △ and ▼, respectively

$O_{62}]^{4-}$, its dimensions can be compared with those of the stable isostructural $[P_2Mo_{18}O_{62}]^{6-}$ ion, regarding specifically the central tetrahedra, the molybdenum frameworks, and the MoO_6 octahedra. The SO_4 central tetrahedra in $[S_2Mo_{18}O_{62}]^{4-}$ have S–O distances of 1.42—1.52 Å and O–S–O angles of 106—111°, and are thus slightly distorted from a regular SO_4 tetrahedron having the S–O distance of 1.51 Å observed in H_2SO_4. The central tetrahedra are not only smaller than the regular $SO_4{}^{2-}$ ion but also smaller than PO_4 tetrahedra in $[P_2Mo_{18}O_{62}]^{6-}$ having P–O distances of 1.50—1.56 Å.[8a] Interestingly, even such smaller SO_4 tetrahedra are taken up into the 18 MoO_6 polyhedral frameworks in a similar manner to PO_4 tetrahedra.

In Figure 2 the dimensions of the molybdenum frameworks are compared for the two isostructural heteropolyions $[P_2Mo_{18}O_{62}]^{6-}$ and $[S_2Mo_{18}O_{62}]^{4-}$. First it can be pointed out that the Mo ··· Mo distances between the puckered rings in the latter ion are shorter by 0.018—0.044 Å than those in the former ion: in other words, the two SMo_9O_{34} half-units are closer upon complex formation. Correspondingly, the S ··· S distance of 3.92 Å in $[S_2Mo_{18}O_{62}]^{4-}$ (Table 3) is shorter by 0.23 Å than the P ··· P distance in $[P_2Mo_{18}O_{62}]^{6-}$.[8a] Undoubtedly, the contraction of these atomic distances originates from the smaller size of the SO_4 tetrahedra.*

In contrast, it can be seen in Figure 2 that the Mo ··· Mo distances within the compact triads and within the puckered rings of MoO_6 octahedra are lengthened and, simultaneously, the Mo ··· S distances in both the SMo_9O_{34} half-units are expanded. The increment in the Mo ··· S distances ranges from

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* The two puckered rings belonging to $[S_2Mo_{18}O_{62}]^{4-}$ ion are approximated to the respective planes according to ref. 20; for the Mo(*n*) atoms with $n = 4$—9, plane I can be expressed as $11.68X + 16.19Y - 6.55Z - 12.69 = 0$ with $S = 0.21$ and for the Mo(*n*) atoms with $n =$ 10—15 plane II can be expressed as $11.67X + 16.22Y - 6.55Z - 8.89 = 0$ width $S = 0.20$. Here, *X*, *Y*, and *Z* are the fractional co-ordinates and *S* denotes the sum of the squares of the residuals. The planes are thus mostly parallel to each other and the distance between them is approximately 3.8 Å. The deviations (Å) of the Mo atoms from the respective planes are: plane I, Mo(4) −0.18, Mo(5) 0.18, Mo(6) −0.19, Mo(7) 0.19, Mo(8) −0.19, and Mo(9) 0.19; plane II, Mo(10) −0.18, Mo(11), 0.18, Mo(12) −0.18, Mo(13) 0.18, Mo(14) −0.18, and Mo(15) 0.18. Similarly puckered rings were observed for the $[P_2Mo_{18}O_{62}]^{6-}$ ion. The present $[S_2Mo_{18}O_{62}]^{4-}$ clearly resembles $[P_2Mo_{18}O_{62}]^{6-}$ and differs from $[P_2W_{18}O_{62}]^{6-}$ (refs. 8*a* and 9, respectively). Pope[15a] discussed the chirality of $[P_2Mo_{18}O_{62}]^{6-}$, and Garvey and Pope[21] measured an induced optical activity due to a Pfeiffer effect in the presence of brucine (2,3-dimethoxystrychnidin-10-one). Such induced optical activity was not observed for the present ion, its optical nature therefore being ambiguous.

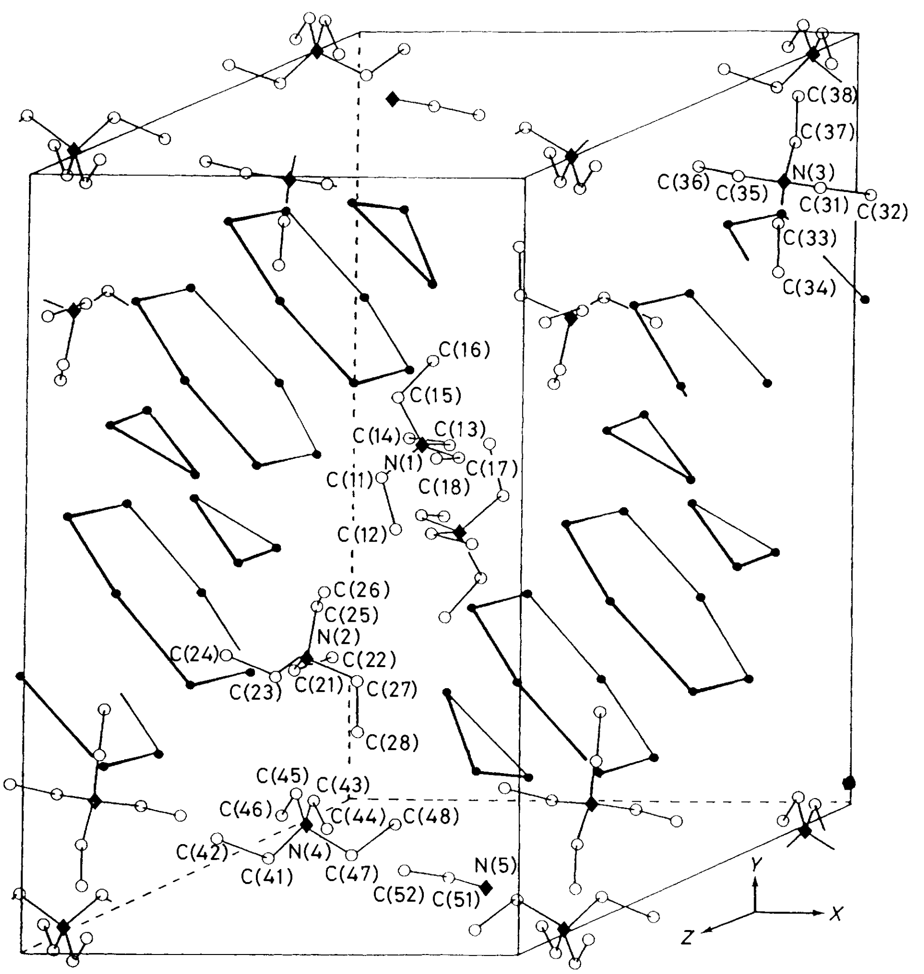

Figure 3. Numbering scheme for the N and C atoms and the location of the NEt_4^+ ions and the CH_3CN molecules in the unit cell. For simplicity, only the molybdenum frameworks are indicated with solid circles and the S and O atoms are omitted

a minimum of 0.055 Å [Mo(5) ··· S(1)] to a maximum of 0.104 Å [Mo(15)–S(2)]. Such expansions of the Mo ··· S distances may effectively moderate the coulombic repulsion which is intensified between Mo^{6+} and S^{6+}rather than between Mo^{6+} and P^{5+}.

As can be seen from the Mo–O distances (Table 3) and the O–Mo–O angles (Table 4), the MoO_6 octahedra are all distorted. The distances varing from 1.62 to 2.35 Å can be grouped into three categories: short 1.62—1.69 Å for Mo–O_d, intermediate 1.77—2.07 Å for Mo–O_b and Mo–O_c, and long 2.43—2.53 Å for Mo–O_a. Of these, the first two are well in accord with the values observed for the corresponding bonds in $[P_2Mo_{18}O_{62}]^{6-}$, but the last is 0.04—0.18 Å longer than the corresponding Mo–O_a distances in $[P_2Mo_{18}O_{62}]^{6-}$. The elongation of the Mo–O_a bonds allows the relatively small SO_4 tetrahedra to be incorporated into the Mo framework.

Figure 3 shows the location of NEt_4^+ ions and CH_3CN molecules in the crystals, along with the numbering scheme for the N and C atoms. In the crystals the cations are found in cavities made of the O atoms (mainly O_d atoms) donated from the heteropolyions. The radius of the cavities is approximately 4.6 ± 0.3 Å obtained by averaging the atomic distances between the N atom in NEt_4^+ and its neighbouring O atoms.

The CH_3CN molecule has a quite regular shape compared to that observed in other organic crystals.[22] The molecule with an approximate length of 2.54 Å [C(52) ··· N(5) in Table 3] is located in a cavity surrounded by seven O atoms such as $O_d(6)$, $O_b(6,7)$, $O_d(7)$, $O_d(13)$, $O_d(14)$, $O_b(14,18)$, and $O_d(18)$ of the heteropolyion. As mentioned above, when the CH_3CN molecule is lost the crystals decay to a yellow powder. However, the powdered salt reverts to the crystals in CH_3CN solution, indicating that the conformation of the heteropolyion is retained entirely in both powdered and crystal forms.

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