BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(1), 106—110 (1976) [Vol. 49, No. 1

The Crystal Structure of Ammonium Pentamolybdodisulfate(IV)(4-) Trihydrate $(NH_4)_4[S^{IV}{}_2Mo_5O_{21}]\cdot 3H_2O$

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(Received July 16, 1975)

The crystal of $(NH_4)_4S_2Mo_5O_{21}\cdot 3H_2O$ contains a discrete polyanion, $S_2Mo_5O_{21}{}^{4-}$, formed by reactions in an aqueous solution:

$$5Mo_7O_{24}{}^{6-} + 14SO_2 + 2H^+ \rightleftarrows 7S_2Mo_5O_{21}{}^{4-} + H_2O$$

or

$$5MoO_4{}^{2-} + 2SO_2 + 6H^+ \rightleftarrows S_2Mo_5O_{21}{}^{4-} + 3H_2O$$

It is orthorhombic, with the space group Pbcn and with $a=15.096(9)$, $b=13.375(8)$, $c=23.734(7)$ Å, $D_m=2.79$, and $D_x=2.79$ g cm^{-3} for $Z=8$. The crystal consists of $S_2Mo_5O_{21}{}^{4-}$ anions connected with each other by hydrogen bonds, with intervening water molecules and ammonium cations. In the polyanion, five MoO_6 octahedra are connected by edge sharing, and the two octahedra at the two ends are connected by corner sharing to complete the Mo_5O_{21} ring; the two SO_3 trigonal pyramids are attached to the ring from above and below the ring.

Three polymolybdosulfate(IV)(4—) ions, $S_2Mo_8O_{31}{}^{6-}$,1) $S_2Mo_5O_{21}{}^{4-}$,2) and $S_3Mo_{10}O_{40}{}^{8-}$,3) are found in the literature, but the existence of the last species was once regarded as doubtful.2) Our preparative work, together with powder X-ray diffraction and IR measurements, confirmed the first two polyanions as ammonium salts, $(NH_4)_6S_2Mo_8O_{31}\cdot 5H_2O$ and $(NH_4)_4S_2Mo_5O_{21}\cdot 3H_2O$.

Both samples were examined by means of the single crystal X-ray diffraction technique; the former was found only as twinned crystals. The present structure work deals with the structure of ammonium pentamolybdodisulfate(IV)(4—); the results show that the material is neither an inclusion nor a clathrate compound of SO_2 gas, but contains a discrete polyanion consisting of two SO_3 trigonal pyramids and five MoO_6 octahedra.

Experimental

Preparation. Crystals of $(NH_4)_4S_2Mo_5O_{21}\cdot 3H_2O$ were prepared according to the method described by Rosenheim:2) a 9 g portion of ammonium paramolybdate was dissolved in 30 ml of water, and SO_2 gas was dissolved in this solution; during this procedure the color of the solution gradually changed to yellow. After the solution had become saturated with SO_2, it was rapidly cooled in an ice–water bath; pale yellow needles of $(NH_4)_4S_2Mo_5O_{21}\cdot 3H_2O$ were thus obtained. If the solution was kept in a desiccator at room temperature, $(NH_4)_6S_2Mo_8O_{31}\cdot 5H_2O$ was crystallized. The results of the elemental analyses of $(NH_4)_4S_2Mo_5O_{21}\cdot 3H_2O$ were as follows: Found: Mo, 47.3; S, 6.4; N, 5.55; H, 1.91%. Calcd: Mo, 47.6; S, 6.4; N, 5.51; H, 2.18%.

The solid sample is stable in air and on X-ray irradiation at room temperature.

IR Measurement. The IR spectra were measured from 400 to 4000 cm^{-1} using Nujol mull and a KBr disk on a Hitachi EPI-G2 spectrometer.

Crystal Data. Preliminary photographs revealed that the crystal is orthorhombic, with the space group Pbcn. The unit-cell dimensions were refined with 12 θ values measured on a diffractometer with Mo$K\alpha$ radiation ($\lambda=0.7107$ Å). The crystal data are as follows:

$(NH_4)_4S_2Mo_5O_{21}\cdot 3H_2O$
F.W. = 1005.9
orthorhombic Pbcn
$a = 15.096(9)$ Å
$b = 13.375(8)$ Å
$c = 23.734(7)$ Å
$V = 4792.1$ Å^3
$D_m = 2.79$ g cm^{-3}
$D_x = 2.79$ g cm^{-3}
$Z = 8$
$\mu = 30.4$ cm^{-1} (for Mo$K\alpha$)

Data Collection. The intensity data were collected on a Rigaku four-circle automatic diffractometer with graphite-monochromated Mo$K\alpha$ radiation. The ω-2θ scan tachnique, with a scan rate of 2θ 2° min^{-1}, was employed. The scan range was determined for each reflection according to this formula: $\Delta\omega=1.4+0.6\tan\theta$, while the background was counted at each scan end for ten seconds. As a check on the crystal stability during the data collection, three standard reflections were monitored every 50 measurements, but no significant deterioration of the crystal was observed. After applying Lorentz and polarization corrections, 6698 $|F_o|$'s were obtained; of those, 3295 reflections with $|F_o|\geq 3\sigma(F)$ were used for further computation. The crystal used for the intensity measurement was pillar-shaped, approximately 0.3 mm long and 0.1 mm in diameter. No absorption correction was made because of the relatively low absorption coefficient.

Structure Determination

The structure was solved by the heavy atom method. Refinement with anisotropic temperature factors for the molybdenum in the anion and with isotropics for the sulfur and oxygen reduced R_1 to 0.112. This was followed by a difference Fourier synthesis, which revealed the positions of all the other non-hydrogen atoms. Eight peaks on the Fourier projection map were attributed to oxygen atoms of water and nitrogen atoms of ammonium cations.

In order to discern the nitrogen atoms in ammonium cations from the oxygens in water molecules, reference was made to the empirical effective radius for $NH_4{}^+$, which was determined from the $NH_4{}^+$-O distances in a number of ammonium salts.4) In crystals containing ammonium cations with high coordination numbers, such as 7, 8 or 9, as in the present crystal, the ammonium cations may be considered to be approximate spheres with an effective radius of 1.65 Å. Accordingly, interatomic distances shorter than 3.5 Å were assigned to nitrogen-oxygen contacts. The most probable assign-

TABLE 1. FINAL POSITIONAL AND THERMAL PARAMETERS ($\times 10^4$) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	278(1)	1521(1)	1285(1)	11(1)	18(1)	6(0)	−1(1)	1(0)	0(0)
Mo(2)	1622(1)	538(1)	2270(1)	18(1)	24(1)	5(0)	0(1)	2(0)	3(0)
Mo(3)	3733(1)	1043(1)	1919(1)	13(1)	21(1)	6(0)	1(1)	−1(0)	0(0)
Mo(4)	3782(1)	2104(1)	612(1)	12(1)	15(1)	6(0)	−2(1)	2(0)	1(0)
Mo(5)	1715(1)	2040(1)	77(1)	14(1)	18(1)	5(0)	−1(1)	0(0)	2(0)
S(1)	2274(3)	37(3)	905(1)	15(1)	9(1)	5(0)	−1(1)	0(0)	−1(0)
S(2)	2203(3)	2828(3)	1526(2)	14(2)	10(2)	6(1)	0(2)	1(1)	−1(1)
O(1)	713(99)	1821(9)	558(5)	23(6)	12(7)	4(2)	2(5)	3(3)	−1(3)
O(2)	−326(8)	449(10)	1114(6)	9(5)	25(8)	10(3)	1(5)	−1(3)	−1(4)
O(3)	−517(9)	2400(11)	1357(7)	10(6)	26(8)	13(3)	0(5)	6(3)	0(4)
O(4)	586(8)	1306(10)	2030(6)	8(5)	27(8)	7(2)	6(5)	0(3)	−4(4)
O(5)	1219(9)	2879(10)	1497(6)	18(6)	15(6)	7(2)	6(6)	4(3)	2(4)
O(6)	1559(9)	480(10)	1318(5)	22(6)	18(7)	2(2)	−3(5)	0(3)	0(4)
O(7)	1744(12)	1008(15)	2935(6)	41(9)	67(13)	5(2)	2(10)	−3(4)	3(5)
O(8)	1139(11)	−619(12)	2380(8)	25(7)	34(9)	19(4)	−10(7)	2(5)	5(5)
O(9)	2807(10)	130(10)	2143(6)	26(7)	18(8)	7(2)	6(6)	2(3)	5(4)
O(10)	2421(9)	1945(10)	1913(6)	15(5)	14(7)	8(2)	4(5)	0(3)	2(4)
O(11)	4037(11)	1616(13)	2545(7)	35(9)	43(10)	11(3)	−6(8)	−5(4)	−3(5)
O(12)	4599(9)	225(10)	1809(7)	15(6)	26(9)	12(3)	6(6)	−2(3)	0(4)
O(13)	4046(9)	2098(10)	1397(6)	22(6)	13(7)	8(2)	−10(6)	−4(3)	1(4)
O(14)	3144(8)	608(10)	1028(5)	10(5)	19(7)	4(2)	3(5)	2(3)	2(3)
O(15)	4624(9)	1321(11)	375(6)	18(6)	23(8)	10(3)	−2(6)	3(3)	−2(4)
O(16)	4213(12)	3277(11)	462(8)	39(9)	14(8)	18(4)	−12(7)	2(5)	6(5)
O(17)	2986(9)	1947(9)	−26(6)	22(6)	13(7)	5(2)	0(5)	6(3)	3(4)
O(18)	2441(9)	2449(10)	925(6)	13(5)	8(6)	8(2)	7(5)	6(3)	3(4)
O(19)	1349(9)	1515(12)	−540(6)	20(6)	41(9)	5(2)	−3(7)	−3(3)	2(4)
O(20)	1612(11)	3284(11)	−58(7)	31(7)	20(8)	13(3)	−1(6)	−2(4)	14(4)
O(21)	1974(9)	401(10)	345(6)	24(6)	13(7)	6(2)	0(5)	−5(3)	−1(4)
N(1)	1970(19)	3388(19)	2974(11)	86(19)	48(16)	19(6)	−28(15)	14(8)	−12(8)
N(2)	241(12)	4202(13)	714(8)	19(8)	31(10)	9(3)	−5(7)	0(4)	0(5)
N(3)	4585(13)	3486(15)	3339(8)	37(10)	28(11)	13(4)	3(9)	0(5)	−3(6)
N(4)	2146(16)	830(20)	4190(10)	38(12)	78(19)	17(5)	−8(12)	−9(6)	3(9)
H_2O(1)	0(0)	0(0)	0(0)	30(10)	26(12)	11(4)	3(10)	0(6)	−2(7)
H_2O(2)	1638(12)	4225(13)	4037(8)	25(8)	48(12)	19(4)	3(8)	−1(5)	6(6)
H_2O(3)	0(0)	3367(22)	2500(0)	49(16)	59(20)	20(6)	0(0)	8(8)	0(0)
H_2O(4)	3755(14)	1571(16)	3711(8)	57(11)	61(13)	15(4)	−11(11)	9(6)	−4(6)

ment and the proposed model of the ammonium and water arrangement in the crystal are given in Table 1 and in Fig. 3.

After six cycles of refinement with anisotropic temperature factors, all the shifts in the parameters were less than their standard deviations and refinement was terminated. The final value of $R_1(=\sum[|F_o|-|F_c|]/\sum|F_o|)$ was 0.060, and that of $R_2(=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2})$ was 0.084.

In the block-diagonal least-squares refinement, the quantity minimized was $\sum w(|F_o|-k|F_c|)^2$; the weighting scheme adopted was $w=0.2$ for $|F_o|<75$ and $w=1.0$ for all the others.

The atomic scattering factors used were taken from Ref. 5, while corrections of the effect of anomalous dispersion for molybdenum and sulfur were based on Ref. 6.

A difference Fourier synthesis was calculated with the reflections in the range of $0\leq\sin\theta\leq0.45$, but no definitive conclusion was drawn about the positions of hydrogens.

The final coordinates and temperature factors are listed in Table. 1. The observed and calculated structure factors are available at the office of this Bulletin as Document No. 7603.

The calculations were performed on a HITAC 8700/8800 computer at the Computer Centre of the University of Tokyo, using a local version of the UNICS programs.[7)]

Description and Discussion of the Structure

Molecular Structure. The $S_2Mo_5O_{21}^{4-}$ anion can be described as an assemblage of five distorted MoO_6 octahedra, which are joined through four sharings of edges and one corner sharing nearly on a plane to form a Mo_5O_{21} pentagon. The two SO_3 trigonal pyramids

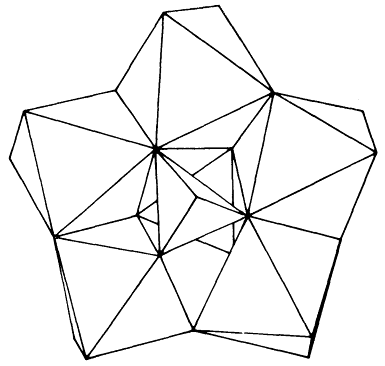

Fig. 1. The structure of $S_2Mo_5O_{21}^{4-}$ anion. Sulfur atoms occupy the apexes of the central trigonal pyramids. Five molybdenum atoms lie nearly on a plane to form a pentagon.

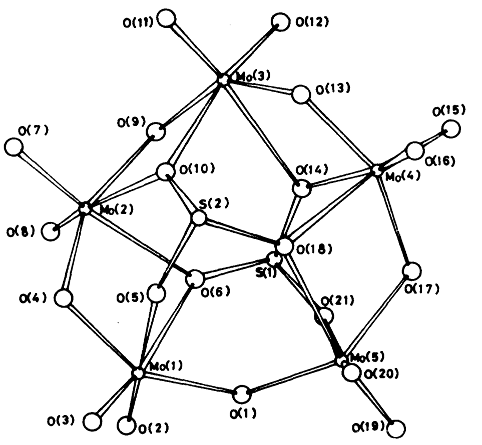

Fig. 2. The structure of $S_2Mo_5O_{21}^{4-}$ anion and its numbering scheme.

are situated so that the Mo_5O_{21} pentagon is capped on both sides by SO_3 pyramids through sharing the oxygens. Figures 1 and 2 show the structure of the anion and numbering scheme adopted for it. The five Mo atoms in the anion are almost co-planar. The equation of the plane through the molybdenum atoms obtained by the least-squares method is:

$$0.03055x - 0.92493y - 0.37892z + 2.82437 = 0.0$$

(x, y, and z are in Å unit)

while the deviations (Å) of each molybdenum from the plane are:

Mo(1) −0.2172, Mo(2) 0.1809, Mo(3) −0.0291
Mo(4) −0.1661, Mo(5) 0.2938

The vector from S(1) to S(2) is almost perpendicular to this plane; the angle between them is 89.25°. The anion has a pseudo twofold axis passing from Mo(3) to O(1).

The structure of the $S_2Mo_5O_{21}^{4-}$ anion is very similar to those of $P_2Mo_5O_{23}^{6-}$,[8] $HP_2Mo_5O_{23}^{5-}$,[9] and $H_2P_2Mo_5O_{23}^{4-}$ [10] (Fig. 3). However, the latter anions have hetero atom P's tetrahedrally coordinated by four oxygen atoms; that is, each phosphorus has one unshared atom, while the trigonal pyramidal SO_3 has no such terminal oxygen. The bond lengths and angles within the anion are listed in Tables 2 and 3. All the MoO_6 octahedra are disorted, and the Mo–O distances can be grouped into three groups, *i.e.*, Mo–O (unshared, terminal) 1.69—1.74 Å, Mo–O (shared between molybdenums) 1.89—1.95 Å, and Mo–O (shared between molybdenum and sulfur atom) 2.32—2.43 Å. These values are almost equal to the corresponding lengths in the $P_2Mo_5O_{23}^{6-}$ anions.[8–10]

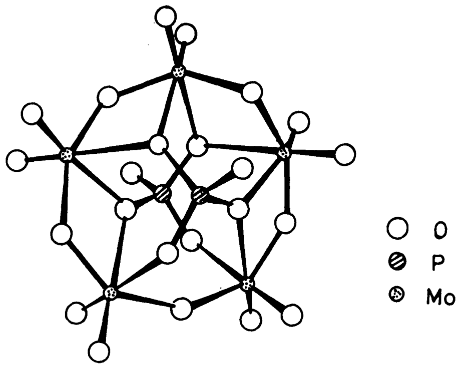

Fig. 3. The structure of $P_2Mo_5O_{23}^{6-}$anion.

Of the three S–O bondings of the SO_3 trigonal pyramid, two are relatively long; for example, the S(1)-O(6), S(1)-O(4) and S(2)-O(10), S(2)-O(18) distances are comparable to those in the SO_3^{2-} anions, while the other ones, S(1)-O(21) and S(2)-O(5), are as short as the S-O bonds in the SO_4^{2-} ions (1.47—1.49 Å).[11,12] These two types of bonds are different in their bonding schemes as well. O(6), O(14), O(10) and

TABLE 2. BOND DISTANCES (Å) WITHIN THE ANION WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Mo(1)···Mo(2)	3.364(2)	Mo(4)—O(13)	1.905(14)
Mo(2)···Mo(3)	3.361(2)	Mo(4)—O(14)	2.431(13)
Mo(3)···Mo(4)	3.413(2)	Mo(4)—O(15)	1.740(14)
Mo(4)···Mo(5)	3.368(2)	Mo(4)—O(16)	1.737(15)
Mo(5)···Mo(1)	3.662(2)	Mo(4)—O(17)	1.945(13)
		Mo(4)—O(18)	2.204(13)
Mo(1)—O(1)	1.890(13)		
Mo(1)—O(2)	1.748(14)	Mo(5)—O(17)	1.936(13)
Mo(1)—O(3)	1.688(14)	Mo(5)—O(18)	2.354(13)
Mo(1)—O(4)	1.851(13)	Mo(5)—O(19)	1.718(14)
Mo(1)—O(5)	2.359(13)	Mo(5)—O(20)	1.703(14)
Mo(1)—O(6)	2.384(13)	Mo(5)—O(21)	2.318(13)
		Mo(5)—O(1)	1.917(13)
Mo(2)—O(4)	1.957(13)		
Mo(2)—O(6)	2.264(12)	S(1)—O(6)	1.574(13)
Mo(2)—O(7)	1.708(16)	S(1)—O(14)	1.547(13)
Mo(2)—O(8)	1.713(17)	S(1)—O(21)	1.486(14)
Mo(2)—O(9)	1.894(15)		
Mo(2)—O(10)	2.391(13)	S(2)—O(5)	1.488(14)
		S(2)—O(10)	1.533(14)
Mo(3)—O(9)	1.931(14)	S(2)—O(18)	1.558(14)
Mo(3)—O(10)	2.318(13)		
Mo(3)—O(11)	1.733(17)		
Mo(3)—O(12)	1.725(14)		
Mo(3)—O(13)	1.937(14)		
Mo(3)—O(14)	2.367(12)		

TABLE 3. BOND ANGLES (°) WITHIN THE ANION WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Mo(1)···Mo(2)···Mo(3)	108.67(6)	O(11)—Mo(3)—O(12)	102.15(74)
Mo(2)···Mo(3)···Mo(4)	109.25(6)	O(11)—Mo(3)—O(13)	99.30(71)
Mo(3)···Mo(4)···Mo(5)	108.19(6)	O(12)—Mo(3)—O(13)	100.41(62)
Mo(4)···Mo(5)···Mo(1)	104.95(6)	O(12)—Mo(3)—O(14)	89.54(55)
Mo(5)···Mo(1)···Mo(2)	105.16(6)	O(13)—Mo(3)—O(14)	72.49(50)
		O(13)—Mo(4)—O(14)	71.47(51)
O(2)—Mo(1)—O(3)	103.00(65)	O(13)—Mo(4)—O(18)	82.19(54)
O(2)—Mo(1)—O(6)	87.16(55)	O(13)—Mo(4)—O(16)	97.23(66)
O(2)—Mo(1)—O(4)	103.01(60)	O(13)—Mo(4)—O(15)	99.25(62)
O(2)—Mo(1)—O(1)	98.23(60)	O(14)—Mo(4)—O(18)	70.86(46)
O(3)—Mo(1)—O(4)	100.98(62)	O(14)—Mo(4)—O(17)	89.04(49)
O(3)—Mo(1)—O(5)	82.49(57)	O(14)—Mo(4)—O(15)	85.69(55)
O(3)—Mo(1)—O(1)	101.02(61)	O(18)—Mo(4)—O(17)	73.58(51)
O(4)—Mo(1)—O(5)	76.41(52)	O(18)—Mo(4)—O(16)	102.92(62)
O(4)—Mo(1)—O(6)	70.98(52)	O(17)—Mo(4)—O(16)	99.73(64)
O(5)—Mo(1)—O(6)	87.45(46)	O(17)—Mo(4)—O(15)	97.74(60)
O(5)—Mo(1)—O(1)	79.78(51)	O(16)—Mo(4)—O(15)	101.80(69)
O(6)—Mo(1)—O(1)	82.66(51)	O(17)—Mo(5)—O(21)	78.89(50)
O(4)—Mo(2)—O(10)	83.40(49)	O(18)—Mo(5)—O(17)	70.30(50)
O(4)—Mo(2)—O(6)	72.11(48)	O(18)—Mo(5)—O(21)	84.68(46)
O(8)—Mo(2)—O(7)	103.64(76)	O(18)—Mo(5)—O(1)	83.91(51)
O(8)—Mo(2)—O(9)	99.44(70)	O(19)—Mo(5)—O(17)	100.63(60)
O(8)—Mo(2)—O(4)	100.25(67)	O(19)—Mo(5)—O(21)	84.28(56)
O(8)—Mo(2)—O(6)	95.87(62)	O(19)—Mo(5)—O(1)	101.01(61)
O(7)—Mo(2)—O(9)	98.74(68)	O(20)—Mo(5)—O(19)	102.09(66)
O(7)—Mo(2)—O(4)	99.31(65)	O(20)—Mo(5)—O(18)	88.70(58)
O(7)—Mo(2)—O(10)	89.03(61)	O(20)—Mo(5)—O(17)	97.43(61)
O(9)—Mo(2)—O(10)	72.20(54)	O(20)—Mo(5)—O(1)	100.97(63)
O(9)—Mo(2)—O(6)	82.56(53)	O(21)—Mo(5)—O(1)	79.90(52)
O(10)—Mo(2)—O(6)	72.18(43)		
O(9)—Mo(3)—O(10)	73.35(53)	O(6)—S(1)—O(14)	106.10(70)
O(9)—Mo(3)—O(12)	100.80(63)	O(6)—S(1)—O(21)	103.05(74)
O(9)—Mo(3)—O(14)	79.51(51)	O(14)—S(1)—O(21)	105.43(73)
O(10)—Mo(3)—O(13)	79.93(52)	O(5)—S(2)—O(10)	106.13(76)
O(10)—Mo(3)—O(14)	78.56(44)	O(5)—S(2)—O(18)	101.68(76)
O(11)—Mo(3)—O(9)	103.66(72)	O(10)—S(2)—O(18)	104.41(73)
O(11)—Mo(3)—O(10)	90.11(66)		

TABLE 4. INTERMOLECULAR CONTACT DISTANCES LESS THAN 3.1 Å WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

N(1)···H_2O(2)	2.804(33)	H_2O(1)···O(1)			2.975(13)
N(1)···H_2O(3^{i})	3.013(32)	H_2O(1)···O(16^{viii})			2.818(16)
N(1)···H_2O(9^{ii})	3.081(30)	H_2O(2)···N(1)			2.804(33)
N(2)···H_2O(5)	2.961(23)	H_2O(2)···O(17^{iv})			2.778(23)
N(2)···H_2O(3)	3.074(24)	H_2O(2)···N(2^{i})			2.897(25)
N(2)···H_2O(20)	3.025(25)	H_2O(2)···N(4^{ii})			2.849(32)
N(2)···H_2O(2^{i})	2.897(25)	H_2O(3)···O(5)			3.078(15)
N(2)···H_2O(12^{ii})	2.948(24)	H_2O(3)···O(12^{ii})			3.036(29)
N(2)···H_2O(15^{ii})	2.959(23)	H_2O(4)···O(11)			2.803(26)
N(2)···H_2O(15^{iii})	2.837(24)	H_2O(4)···N(3)			2.986(30)
N(3)···H_2O(19^{iv})	3.011(25)	H_2O(4)···N(4)			2.858(33)
N(3)···H_2O(2^{v})	2.935(25)	H_2O(4)···O(20^{iv})			2.979(27)
N(3)···H_2HO(8^{ii})	2.791(27)	i	−x	y,	0.5−z
N(3)···H_2O(13^{vi})	2.848(25)	ii	0.5−x,	0.5+y,	z
N(3)···H_2H_2O(4)	2.986(30)	iii	−0.5+x,	0.5−y,	−z
N(4)···H_2O(7)	3.051(29)	iv	0.5−x,	0.5−y,	0.5+z
N(4)···H_2O(20^{iv})	2.849(30)	v	0.5+x,	0.5+y,	0.5−z
N(4)···H_2O(2^{i})	2.885(28)	vi	1.0−x,	y,	0.5−z
N(4)···H_2O(2^{viii})	2.840(32)	vii	x,	−y,	0.5+z
N(4)···H_2O(4)	2.858(33)	viii	0.5−x,	−0.5+y,	z
H_2O(1)···O(2)	2.757(14)	xi	−x,	−y,	−z

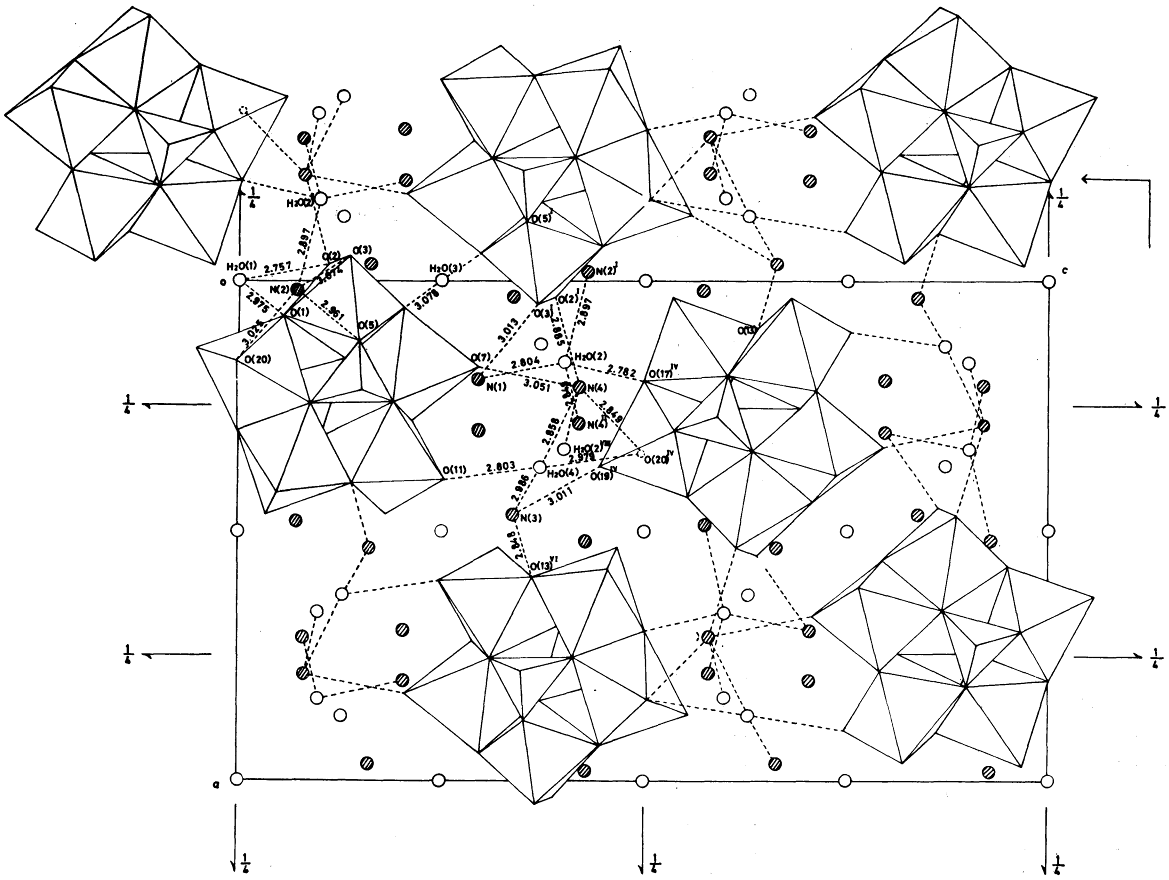

Fig. 4. The crystal structure of $(NH_4)_4S_2Mo_5O_{21}\cdot 3H_2O$. Open circles represent oxygen atoms in the water molecules and shaded circles nitrogen atoms. Only seven anions which lie in the range $y=0.0$—0.5 are depicted for easy viewing.

O(18), all of which make long S–O bonds, are all shared by two Mo atoms, whereas O(21) and O(5) are each bonded to only one Mo atom and make shorter bonds with the sulfur atom. This relation between the S–O lengths and the bonding schemes of the SO_3^{2-} ions corresponds to the general tendency of the elongating effect of a metal atom attached to the oxygen in SO_3^{2-}.[12] The IR spectra of the sample compound show a strong band at *ca.* 1020 cm^{-1} which is assigned to the S–O stretching of the short S–O bonding according to the relationship between the S–O lengths and the stretching frequencies.[11] It does not seem that either of the two lone pairs of S atoms coordinates to any particular atom. The crystal is held by hydrogen bondings between the anions, the cations, and the water of crystallization. Probable hydrogen bondings and van der Waals contacts less than 3.1 Å are given in Fig. 4 and Table 4.

References

1) A. Rosenheim, *Z. Anorg. Chem.* **7**, 177 (1894).
2) A. Rosenheim, *ibid.*, **15**, 183 (1897).
3) E. Péchard, *Ann. Chim. Phys.*, [6], **30**, 401 (1893).
4) A. A. Khan and W. H. Baur, *Acta Crystallogr.*, **B28**, 683 (1972).
5) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1962) Vol. III.
6) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
7) "The Universal Crystallographic Computation Program System," Crystallographic Society of Japan (1967).
8) R. Strandberg, *Acta Chem. Scand.*, **27**, 1004 (1973).
9) J. Fischer, L. Ricard, and P. Toledano, *J. Chem. Soc., Dalton Trans.*, **1974**, 941.
10) B. Hedman, *Acta Chem. Scand.*, **27**, 3335 (1973).
11) B. Nyberg and R. Larsson, *ibid.*, **27**, 63 (1973).
12) P. Kierkegaard, L. O. Larsson, and B. Nyberg, *ibid.*, **26**, 218 (1973).