Crystal and Molecular Structure and Properties of Ammonium Dimolybdate

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Crystals of ammonium dimolybdate are triclinic, space group $P\bar{1}$, $Z = 2$ with cell dimensions $a = 7.937(7)$, $b = 7.305(7)$, $c = 7.226(8)$ Å, $\alpha = 93.88(12)$, $\beta = 114.33(7)$, $\gamma = 82.58(13)°$. The structure was solved by Patterson and Fourier methods from diffractometer data and refined by least-squares techniques to R 0.066 for 988 reflections. The structure is isomorphous with that of potassium dimolybdate and different from that of sodium dimolybdate. It consists of infinite chains of edge-shared $[MoO_6]$ octahedra with adjacent pairs linked by $[MoO_4]$ tetrahedra. Ammonium ions occupy interchain positions. Its properties and spectra are compared with those of ammonium heptamolybdate. Dissolution of ammonium dimolybdate in water and its thermal decomposition are discussed.

AMMONIUM DIMOLYBDATE, $[NH_4]_2[Mo_2O_7]$, is used for the preparation of molybdenum-containing catalysts, molybdenum trioxide, and molybdenum metal. The only previous chemical and structural investigation is that of Ma,[1] who studied its thermal decomposition and reported its X-ray diffraction pattern. He gave no details of its preparation or source. It has been suggested [2] that the dimolybdates are mixtures of normal molybdates and heptamolybdates. We have determined the structure of ammonium dimolybdate by single-crystal X-ray analysis of crystals taken from a normal production batch (Climax Molybdenum, Rotterdam). We report also various properties of the compound.

EXPERIMENTAL

Preparation.—The compound crystallised from an ammoniacal molybdate solution at temperatures >75 °C (Found: H, 2.3; Mo, 56.5; N, 8.4%. Calc. for $H_8Mo_2N_2O_7$: H, 2.3; Mo, 56.5; N, 8.25%).

Physical Measurements.—I.r. spectra (KBr discs and Nujol mulls) were recorded on a Unicam SP 200 spectrophotomer. U.v. diffuse reflectance spectra were measured on a Unicam SP 700C spectrophotometer against magnesium oxide as standard. Thermogravimetric analyses were carried out with a Stanton thermobalance model TR 1.

Crystal Data.—$H_8Mo_2N_2O_7$, $M = 339.88$, Triclinic, $a = 7.937(7)$, $b = 7.305(7)$, $c = 7.226(8)$ Å, $\alpha = 93.88(12)$, $\beta = 114.33(7)$, $\gamma = 82.58(13)°$, $U = 379.3$ Å^3, $Z = 2$, $D_c = 2.97$, $D_m = 2.95(3)$, $F(000) = 464$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ (Mo-K_α) = 32.3 cm^{-1}. Spacegroup $P\bar{1}$, confirmed by the structure analysis.†

A crystal with dimension 0.4 × 0.3 × 0.4 mm was mounted with the b^* axis parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, a scintillation counter, and pulse-height discriminator. A molybdenum tube was used with a zirconium filter at the receiving slit. The stationary-crystal–stationary counter method was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were obtained for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of backgrounds as a function of 2θ. Several standard reflections were measured repeatedly during the course of the experiment, but no significant change in intensity was detected. 1375 independent reflections were measured with $2\theta < 50°$. No absorption or extinction corrections were applied. The standard deviation $\sigma(I)$ of a reflection was taken to be $[I + 2E + (0.03I)^2]^{\frac{1}{2}}$ where E is the estimated background of the reflection. 990 reflections having $I > 3\sigma(I)$ were considered observed and used in the subsequent refinement.

Structure Determination.—The positions of the two molybdenum atoms were determined from a Patterson function and Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least-squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of F_o and $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < 40$ and $\sqrt{w} = 40/F_o$ for $F_o > 40$. Calculations were made on an ATLAS computer at S.R.C. Chilton, Berkshire, with the programs described in ref. 4, and on an Elliott 4130 with the programs described in ref. 5. Atomic scattering factors for molybdenum, oxygen, and nitrogen were taken from ref. 6, together with corrections for the real and imaginary part of the anomalous dispersion for molybdenum. The anisotropic temperature factor is defined as $\exp -2\pi^2 \sum_i \sum_j h_i h_j b_i b_j U_{ij}$, $(i,j, = 1—3)$ where b_i is the i^{th} reciprocal cell dimension. The isotropic temperature factor is $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$. The molybdenum atoms were refined anisotropically and the light atoms isotropically to R 0.065. Anisotropic refinement on all atoms gave R 0.061. We did not think this to be a significant lowering of the R value considering the increased number of parameters and Table 1 therefore lists final atomic co-ordinates and thermal parameters from the mixed refinement. The zero reflections showed no large discrepancies. A difference Fourier showed no significant peaks; hydrogen atoms in the ammonium ion were not

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† This work was originally reported (A. W. Armour, Ph.D. Thesis, University of Reading, 1973) with different axes and atom numbering scheme. When we noticed the publication of the structure of potassium dimolybdate,[3] we changed the axes, $a^* \rightarrow a^* - c^*, b^* \rightarrow -b^*, c^* \rightarrow a^*$ to conform; likewise the atom numbering scheme. Cell dimensions for $K_2[Mo_2O_7]$ are 7.51, 7.24, 6.95 Å, 92, 112, 82.5°, $U = 347$ Å^3. R was 0.117 for 965 visually estimated reflections.

[1] E. Ma, *Bull. Chem. Soc. Japan*, 1964, **37**, 171, 648.

[2] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Interscience, London, 3rd edn., 1972, p. 951.

[3] S. A. Magarill and R. F. Klevtsova, *Sov. Phys. Cryst.*, 1972, **16**, 645.

[4] 'X-Ray '67' system of programmes, revised July 1970, J. C. Baldwin, R. V. Chostain, D. F. High, F. A. Kundell, and J. M. Stewart, University of Maryland Technical Report TR 67 58, 1967.

[5] Fourier programme, D. R. Russell; Local version of ORFLS, full-matrix least-squares programme, K. R. Busing, K. O. Martin, and H. A. Levy.

[6] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

discernible. In the final cycle of refinement no shift was $>0.001\sigma$. Molecular dimensions are given in Table 2.

TABLE 1

Final co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) for the atoms, with estimated standard deviations in parentheses

Atom	x	y	z	U
Mo(1)	0482(2)	3547(2)	1705(2)	*
Mo(2)	3005(2)	$-$0832(2)	2496(2)	*
N(1)	4435(20)	6170(21)	7768(23)	32(2)
N(2)	1553(20)	1587(20)	6963(22)	32(3)
O(1)	2560(16)	1545(16)	1652(17)	24(2)
O(2)	$-$0535(16)	2151(16)	2706(17)	29(3)
O(3)	1929(17)	4707(17)	3793(19)	33(3)
O(4)	4646(16)	$-$2143(16)	1783(17)	27(3)
O(5)	$-$0959(15)	1837(15)	$-$1213(16)	23(8)
O(6)	1413(15)	4652(15)	$-$0376(16)	23(2)
O(7)	3529(16)	$-$0933(16)	5040(18)	27(3)

* Anisotropic thermal parameters ($\times 10^4$) are:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo(1)	194(8)	168(8)	205(8)	128(5)	63(6)	106(6)
Mo(2)	166(7)	177(8)	203(8)	136(5)	67(6)	102(5)

TABLE 2

Bond lengths (Å) and angles (°) for ammonium dimolybdate. Bond lengths for potassium dimolybdate [3] are given in square brackets

(*a*) Distances

Mo(1)–O(1)	2.069(12) [2.17]
Mo(1)–O(2)	1.734(15) [1.76]
Mo(1)–O(3)	1.722(11) [1.75]
Mo(1)–O(5)	2.311(10) [2.27]
Mo(1)–O(6)	2.166(14) [2.17]
Mo(1)–O(6^{I})	1.840(10) [1.83]
Mo(2)–O(1)	1.822(12) [1.80]
Mo(2)–O(4)	1.744(12) [1.75]
Mo(2)–O(5^{II})	1.735(11) [1.77]
Mo(2)–O(7)	1.714(13) [1.78]
Mo(1) ··· Mo(1^{I})	3.146(2) [3.09]
Mo(1) ··· Mo(2)	3.496(2) [3.42]
Mo(1) ··· Mo(2^{II})	3.807(2) [3.78]

(*b*) Angles

O(1)–Mo(1)–O(2)	95.9(6)	O(5)–Mo(1)–O(6^{I})	83.3(4)
O(1)–Mo(1)–O(3)	94.7(5)	O(6)–Mo(1)–O(6^{I})	76.8(5)
O(1)–Mo(1)–O(5)	75.8(4)	O(1)–Mo(2)–O(4)	112.2(6)
O(1)–Mo(1)–O(6)	76.9(5)	O(1)–Mo(2)–O(5^{II})	107.1(5)
O(1)–Mo(1)–O(6^{I})	149.1(5)	O(1)–Mo(2)–O(7)	111.5(6)
O(2)–Mo(1)–O(3)	103.9(6)	O(4)–Mo(2)–O(5^{II})	105.1(6)
O(2)–Mo(1)–O(5)	82.7(5)	O(4)–Mo(2)–O(7)	113.2(5)
O(2)–Mo(1)–O(6)	161.0(5)	O(5^{II})–Mo(2)–O(7)	107.1(6)
O(2)–Mo(1)–O(6^{I})	103.8(5)		
O(3)–Mo(1)–O(5)	169.1(6)	Mo(1)–O(1)–Mo(2)	127.8(8)
O(3)–Mo(1)–O(6)	94.3(6)	Mo(1)–O(5)–Mo(2^{II})	139.9(7)
O(3)–Mo(1)–O(6^{I})	103.1(6)	Mo(1)–O(6)–Mo(1^{I})	103.2(6)
O(5)–Mo(1)–O(6)	78.5(4)		

Roman numeral superscripts are defined in footnote to Table 3.

Observed and calculated structure factors are listed in Supplementary Publication No SUP 21275 (4 pp., 1 microfiche).*

DISCUSSION

The structure of ammonium dimolybdate consists of discrete $[NH_4]^+$ and infinite chains of $[Mo_2O_7]^{2-}$ ions, the chains comprising pairs of edge-shared distorted $[MoO_6]$ octahedra, and having adjacent pairs linked by distorted $[MoO_4]$ tetrahedra (Figure 1).† The chain comprises equal numbers of $[MoO_4]$ and $[MoO_6]$ units. In each tetrahedron and octahedron there are two terminal oxides. Each of the remaining oxides bridges two molybdenum atoms. The structure is thus equivalent to that found for potassium dimolybdate [3] and different from that of sodium dimolybdate which consists of an infinite chain of corner shared octahedra bridged by shared $[MoO_4]$ tetrahedra.[7] It can be concluded that the type of dimolybdate structure depends on the size of the cation [8] and that the dimolybdate chains of $Na_2[Mo_2O_7]$ are unstable in the presence of cations larger than sodium.

The dimensions of the anion in the present structure are compared to those of potassium dimolybdate in Table 2. There are a few significant differences in bond length (maximum variation 0.10 Å) but the agreement is quite good.‡ Mo–O bond lengths follow the expected pattern.[9] The shortest bonds are to terminal oxides (1.714—1.744 Å), there being no significant difference between such bonds in the octahedron or tetrahedron. Bonds are lengthened by bridging and also by the *trans*-effect of terminal oxides. Mo(2)–O(5^{II}) is the same length as a terminal bond presumably because the Mo(1)–O(5) bond of 2.311(10) Å is so long. The Mo–O bonds between the edge-shared $[MoO_6]$ octahedra are alternatively long and short [2.166(14), 1.840(10) Å]. The ring Mo(1), O(6), Mo(1^{I}), O(6^{I}) is perforce planar.

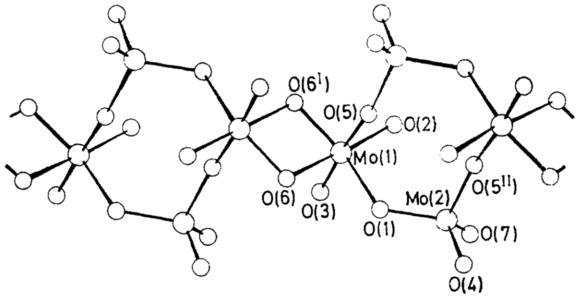

FIGURE 1 The $[Mo_2O_7]^{2-}$ anion together with atomic numbering scheme

The octahedron is considerably distorted owing to the steric requirements for the bridging and the variations in

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10pp. are supplied as full size copies).

† *Note added at proof*: Since this paper was submitted, an independent determination of the structure of $[NH_4]_2[Mo_2O_7]$ has been publshed (I. Knöpnadel, H. Hartl, W.-D. Hunnius, and J. Fuchs, *Angew. Chem.*, 1974, **86**, 894). The results are in agreement with those reported here.

‡ $[NH_4]^+{}_6[Mo_7O_{24}]^{6-}$ and $K^+{}_6[Mo_7O_{24}]^{6-}$ ions are also isomorphous but there are quite marked differences (*sic*) between dimensions in the two structure (E. Shimao, *Bull. Chem. Soc. Japan*, 1967, **40**, 1609; B. M. Gatehouse and P. Leverett, *Chem. Comm.*, 1968, 901).

[7] M. Seleborg, *Acta Chem. Scand.*, 1967, **21**, 499.

[8] B. M. Gatehouse and P. Leverett, *J. Chem. Soc.* (*A*), 1971, 2107.

[9] P. C. H. Mitchell, *Quart. Rev.*, 1966, **20**, 103.

Mo–O bond lengths; as usual, angles subtended by pairs of terminal bonds are the largest. The $[Mo_2O_7]^{2-}$ polyhedra form a continuous chain along the *b* axis. The two independent ammonium ions occupy positions between these chains. The closest N ··· O contacts are listed in Table 3; N(1) has seven such contacts of 2.81—3.07 Å, the next closest being at 3.48 Å. N(2) also has seven close contacts of 2.86—3.15 Å with the next closest at 3.46 Å. These values are longer than the minimum K ··· O distances (2.6 Å) in $K_2[Mo_2O_7]$ suggesting that the ammonium ion is the larger of the two cations. Also this is in accordance with ammonium molybdate having the larger unit-cell volume by *ca.* 9%. These values for N ··· O contacts found in the present compound are usually considered to be hydrogen-bond distances.[10] There are only a few short O ··· O interanion contacts though the smallest (2.87 Å) is remarkably short (see Table 3). A packing diagram down *b** is given in ref. 3.

TABLE 3

Intermolecular contacts (Å), standard deviations are ⩽0.02 Å

(*a*) N ··· O contacts <3.80 Å

$N(1) \cdots O(3)$	2.96	$N(2) \cdots O(2)$	2.86
$N(1) \cdots O(7^{III})$	2.81	$N(2) \cdots O(3)$	3.46
$N(1) \cdots O(4^{IV})$	3.02	$N(2) \cdots O(7)$	2.91
$N(1) \cdots O(6^{V})$	3.51	$N(2) \cdots O(1^{V})$	3.15
$N(1) \cdots O(1^{VII})$	2.96	$N(2) \cdots O(5^{V})$	2.79
$N(1) \cdots O(3^{VII})$	3.48	$N(2) \cdots O(6^{V})$	2.87
$N(1) \cdots O(6^{VII})$	3.05	$N(2) \cdots O(4^{VIII})$	2.85
$N(1) \cdots O(4^{VIII})$	2.94	$N(2) \cdots O(3^{IX})$	3.51
$N(1) \cdots O(2^{IX})$	3.07	$N(2) \cdots O(2^{X})$	3.00
		$N(2) \cdots O(7^{X})$	3.78

(*b*) Others <3.80 Å, excluding O ··· O contacts in the same polymeric anion

$N(1) \cdots N(1^{VI})$	3.48	$O(4) \cdots O(7^{VIII})$	3.13
$N(2) \cdots N(2^{X})$	3.78	$O(7) \cdots O(7^{VIII})$	2.87
$O(7) \cdots O(1^{VIII})$	3.04	$O(3) \cdots O(2^{IX})$	3.71
$O(4) \cdots O(3^{VIII})$	3.67	$O(2) \cdots O(7^{X})$	3.61

Roman numeral superscripts represent the following equivalent positions relative to the reference set at *x,y,z:*

I	$-x, 1-y, -z$	VI	$1-x, 1-y, 2-z$
II	$-x, -y, -z$	VII	$1-x, 1-y, 1-z$
III	$x, 1+y, z$	VIII	$1-x, -y, 1-z$
IV	$x, 1+y, 1+z$	IX	$-x, 1-y, 1-z$
V	$x, y, 1+z$	X	$-x, -y, 1-z$

Ammonium dimolybdate is the first example of a dimolybdate which crystallises with a chain structure from an aqueous solution. Usually such polymolybdates contain discrete polyanions, *e.g.* $[Mo_7O_{24}]^{2-}$ and $[Mo_8O_{26}]^{4-}$, and are hydrated, whereas polymolybdates crystallised from melts, *e.g.* $Na_2[Mo_2O_7]$ from $Na_2[MoO_4]$ and MoO_3, have infinite-chain structures.[8] Formation of the ammonium dimolybdate chain depends on crystallisation from a hot solution and the presence of ammonium ions. Solid ammonium dimolybdate is in equilibrium with the saturated solution only at >50 °C. At <50 °C ammonium heptamolybdate is the only stable solid in equilibrium with saturated solutions for a wide range of ammonia concentrations.[11] We have observed that, qualitatively, the rate of dissolution of ammonium dimolybdate in water is less than that of ammonium heptamolybdate. According to its u.v. spectrum the solution at 20 °C contains only heptamolybdate ions. So for ammonium di-, but not ammonium hepta-, molybdate, dissolution involves breakage of Mo–O bonds and is slow.

Physical Properties.—I.r. spectrum. The i.r. spectra of ammonium di- and hepta-molybdates, and of sodium molybdate in the Mo–O stretching region (700—1000 cm^{-1}), are shown in Figure 2. Although their structures are different, that of the heptamolybdate consisting of linked $[MoO_6]$ octahedra only, their i.r. spectra are similar. Predictions of polymolybdate structures on the basis of i.r. spectra are likely to be unreliable [12] however, and it was because of this and of differences in *X*-ray powder patterns that we determined the structure of the dimolybdate by *X*-ray diffraction. The $[MoO_4]$ tetrahedra of ammonium dimolybdate are not discrete anions, as in *e.g.* sodium and calcium molybdates, and so the i.r. spectrum of ammonium dimolybdate does not show the strong band in the 800 cm^{-1} region, typical of ionic molybdates (see Figure 2).

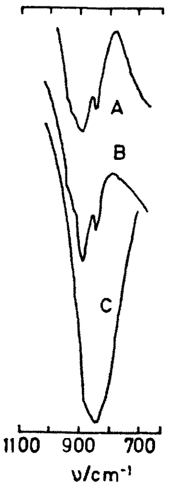

FIGURE 2 I.r. spectra of (A) ammonium heptamolybdate, (B) ammonium dimolybdate, (C) sodium molybdate

U.v. spectra. The reflectance spectra of the di- and hepta-molybdates were similar (peaks at *ca.* 37 000 and 32 000 cm^{-1}) as expected for systems containing $[MoO_6]$ octahedra.[13]

Thermal decomposition. In agreement with earlier work we found by thermogravimetric analysis that the thermal decomposition of ammonium dimolybdate proceeded as in reaction (1). Formation of molybdenum

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[10] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

[11] W. F. Barry and C. J. Hallada, 'Phase Diagram of the Ammonium Polymolybdates,' Report L 297 2, Climax Molybdenum, New York, 1968.

[12] K. B. Andras, H. Sandor, and H. Erzsebet, *Magyar Kem. Folyoirat*, 1971, **77**, 418.

[13] J. H. Ashley and P. C. H. Mitchell, *J. Chem. Soc. (A)*, 1968, 2822; 1969, 2730.

trioxide involves the building up of structures based on

$$[NH_4]_2[Mo_2O_7] \xrightarrow{260\ ^\circ C} [NH_4]_2[Mo_3O_{10}] \xrightarrow{300\ ^\circ C} [NH_4][Mo_8O_{26}] \xrightarrow{420\ ^\circ C} MoO_3 \quad (1)$$

edge-shared $[MoO_6]$ octahedra (MoO_3 and the octamolybdate) through an intermediate structure based on edge-shared $[MoO_6]$ octahedra and $[MoO_5]$ square pyramids (the trimolybdate).[14] Formation of the trimolybdate is in agreement with the known stability of the structure in the presence of large cations (K^+, Rb^+, Cs^+, and now NH_4^+).[8]

We thank Climax Molybdenum Co. Ltd. for financial support (to A. A. and P. C. H. M.).

[4/2245 *Received*, 31*st October*, 1974]

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[14] M. Seleborg, *Acta Chem. Scand.*, 1966, **20**, 2195; B. M. Gatehouse and P. Leverett, *J. Chem. Soc.* (*A*), 1968, 1398.