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Structure of an Ammonium Molybdenyl Diphosphate: $(NH_4)_2MoO_2P_2O_7$

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Abstract. $(NH_4)_2MoO_2P_2O_7$, $M_r = 333{\cdot}925$, monoclinic, $C2/c$, $a = 13{\cdot}984\ (9)$, $b = 8{\cdot}297\ (6)$, $c = 15{\cdot}81\ (1)$ Å, $\beta = 99{\cdot}11\ (1)°$, $V = 1811\ (4)$ Å^3, $Z = 8$, $D_x = 2{\cdot}449$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}811$ mm^{-1}, $F(000) = 1296$, $T = 295$ K, final $R = 0{\cdot}021$ for 2728 independent observations. Isolated MoO_6 distorted octahedra share four of their oxygen atoms with three different P_2O_7 groups to build infinite ribbons spreading along the c axis. The two oxygen atoms of the molybdenyl group remain unshared. Along the c axis, large oblong channels delimited by the MoO_6–P_2O_7 ribbons are lined by the ammonium groups.

Introduction. Only some phosphates containing MoO_2 radicals have so far been characterized. The first structural studies, not very accurate, concerned the polyphosphate $MoO_2(PO_3)_2$ (Kierkegaard, 1962*a*) and the two monophosphates $NaMoO_2PO_4$ (Kierkegaard, 1962*b*) and $AgMoO_2PO_4$ (Kierkegaard & Holmin, 1965). Recently, a more accurate structural study of two compounds, $Ba(MoO_2)_2(PO_4)_2$ and $Pb(MoO_2)_2PO_4$, has been reported (Masse, Averbuch-Pouchot & Durif, 1985). In all these compounds the two oxygen atoms of the molybdenyl group correspond to short bonds with the molybdenum atoms and are not shared with the phosphorus atoms in the anionic network.

Experimental. Crystals of the title compound are obtained by a flux method. 2·5 g of MoO_3 is added to 10 g of $(NH_4)_2HPO_4$ in a graphite crucible. The two components are heated in air to 573 K. After two days, small colourless crystals appear in the flux. The flux is removed by hot water and crystals suitable for X-ray study are isolated. Density not measured. Monoclinic prism: 0·21 × 0·15 × 0·14 mm. Nonius CAD-4 diffractometer. Graphite monochromator. Systematic absences: hkl, $h+k = 2n$; $h0l$, $h = 2n$ and $l = 2n$. 22 reflexions ($10{\cdot}30 < \theta < 12{\cdot}85°$) for refining unit-cell dimensions. ω scan. 4248 reflexions measured ($3 < \theta < 30°$), $\pm hkl$, $h_{\max} = 22$, $k_{\max} = 13$, $l_{\max} = 25$. 3756 independent reflexions. Scan width: 1·20°, scan speed: 0·024 to 0·042° s^{-1}, background measuring time 14 to 25 s. Two orientation (02$\bar{9}$ and 0$\bar{2}\bar{9}$) and two intensity (044 and 0$\bar{4}$4) reference reflexions; no significant variations, Lorentz and polarization corrections, no absorption correction.

Table 1. *Final atomic coordinates and B_{eq} (B_{iso} for* H *atoms) for* $(NH_4)_2MoO_2P_2O_7$; *estimated standard deviations are given in parentheses*

$$B_{\text{eq}} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	B_{eq} or B_{iso} (Å^2)
Mo	0·38558 (1)	0·12662 (2)	0·36163 (1)	1·265 (2)
P(1)	0·37596 (4)	0·07256 (8)	0·15739 (3)	1·378 (8)
P(2)	0·04204 (4)	0·30821 (7)	0·42872 (3)	1·294 (8)
O(*E*11)	0·3834 (1)	0·0071 (2)	0·24955 (9)	1·69 (3)
O(*E*12)	0·2836 (1)	0·1586 (3)	0·1272 (1)	2·17 (3)
O(*E*13)	0·4649 (1)	0·1671 (2)	0·1453 (1)	1·64 (3)
O(*L*12)	0·1270 (1)	0·4135 (2)	0·3997 (1)	2·16 (3)
O(*E*21)	0·0498 (1)	0·4060 (2)	0·0837 (1)	1·67 (3)
O(*E*22)	0·4232 (1)	0·2277 (2)	0·47647 (9)	1·80 (3)
O(*E*23)	0·0355 (1)	0·1536 (2)	0·3802 (1)	2·42 (3)
O(1)	0·2785 (1)	0·0508 (3)	0·3806 (1)	2·29 (3)
O(2)	0·3524 (1)	0·3035 (2)	0·3127 (1)	2·21 (3)
N(1)	0·1385 (2)	0·1489 (3)	0·2318 (1)	2·52 (4)
N(2)	0·3559 (2)	0·4053 (3)	0·0209 (2)	2·57 (4)

Crystal structure solved by Patterson function and successive difference-Fourier syntheses; anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms. Unit weights, final $R = 0{\cdot}021$ ($wR = 0{\cdot}024$) for 2728 reflexions [$I > 3\sigma(I)$]. Extinction coefficient refined: $8{\cdot}72 \times 10^{-7}$ (Stout & Jensen, 1968). $S = 0{\cdot}912$. Max. $\Delta/\sigma = 0{\cdot}13$ [B_{iso} of H(24)]. Max. peak height in final difference Fourier synthesis: 0·252 e Å^{-3}. Final R value: 0·032 for the complete set of independent reflexions (3756 observations). H atoms located by difference Fourier map and refined isotropically. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1977) *SDP* employed for all calculations. Computer used: MicroVAXII.

Discussion. Table 1 reports the final atomic coordinates and bond angles of the atomic arrangement.* Fig.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51236 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1 represents the projection of the structure of $(NH_4)_2MoO_2P_2O_7$ along the *b* axis and shows clearly the ribbons of MoO_6 octahedra linked to P_2O_7 groups running along the *c* axis.

Each MoO_6 octahedron has four of its oxygen atoms shared with four PO_4 tetrahedra belonging to only three different P_2O_7 groups; two oxygen atoms O(1) and O(2) of the molybdenyl group are not linked to phosphorus atoms. The MoO(1) and MoO(2) distances are significantly shorter (Mo—O = 1·692 Å) than the others (Mo—O = 2·079 Å).

Each P_2O_7 group is linked to three MoO_6 octahedra. The interatomic distances and bond angles of this group are similar to those encountered in other known diphosphates. The mean P—O distance is here 1·532 Å against 1·543 Å for the P—O general mean of a great number of diphosphates already studied.

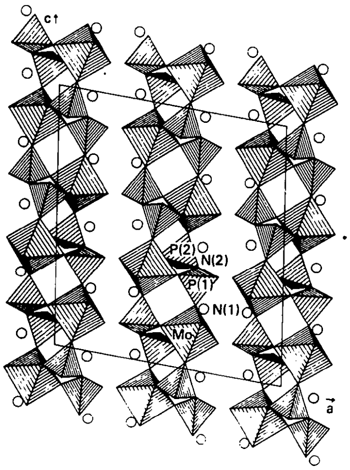

Fig. 1. Projection along the *b* axis of the atomic arrangement of $(NH_4)_2MoO_2P_2O_7$.

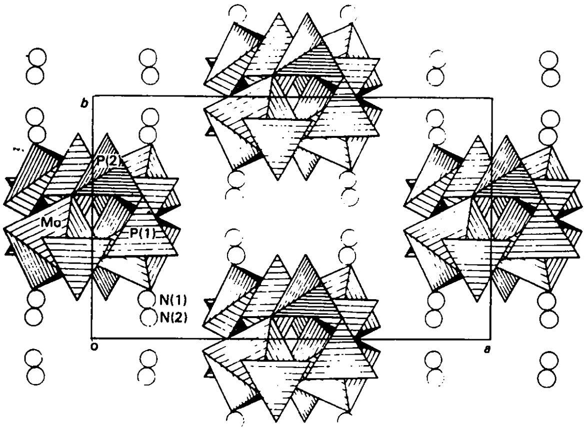

Fig. 2. Projection along the *c* axis of the atomic arrangement of $(NH_4)_2MoO_2P_2O_7$.

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* $(NH_4)_2MoO_2P_2O_7$; *estimated standard deviations are given in parentheses*

MoO_6 octahedron

Mo	O(*E*11)	O(*E*13)	O(*E*21)	O(*E*22)	O(1)	O(2)
O(*E*11)	2·026 (2)	2·813 (2)	2·783 (2)	3·987 (2)	2·745 (2)	2·714 (3)
O(*E*13)	84·93 (6)	2·138 (2)	2·722 (2)	2·714 (2)	3·800 (2)	2·778 (3)
O(*E*21)	83·26 (6)	78·60 (6)	2·160 (2)	2·879 (3)	2·665 (2)	3·837 (3)
O(*E*22)	165·37 (7)	82·04 (7)	87·65 (7)	1·994 (2)	2·752 (2)	2·696 (2)
O(1)	94·68 (8)	165·13 (8)	86·59 (8)	96·21 (8)	1·694 (8)	2·640 (3)
O(2)	93·39 (8)	92·31 (8)	170·54 (8)	93·75 (8)	102·54 (9)	1·690 (2)

Mo—P(1)	3·2416 (5)	Mo—P(2)	3·4866 (6)
Mo—P(1)	3·4247 (6)	Mo—P(2)	3·3528 (5)

P_2O_7 group

P(1)	O(*E*11)	O(*E*12)	O(*E*13)	O(*L*12)
O(*E*11)	1·543 (2)	2·532 (2)	2·524 (2)	2·466 (2)
O(*E*12)	113·4 (1)	1·486 (2)	2·506 (2)	2·459 (3)
O(*E*13)	111·68 (9)	113·6 (1)	1·507 (2)	2·508 (2)
O(*L*12)	103·6 (1)	105·8 (1)	107·9 (1)	1·595 (2)

P(2)	O(*E*21)	O(*E*22)	O(*E*23)	O(*L*12)
O(*E*21)	1·505 (2)	2·508 (2)	2·520 (3)	2·528 (2)
O(*E*22)	111·4 (1)	1·530 (2)	2·455 (2)	2·477 (2)
O(*E*23)	114·6 (1)	108·7 (1)	1·491 (2)	2·501 (3)
O(*L*12)	109·0 (1)	104·6 (1)	108·0 (1)	1·599 (2)

P(1)—P(2)	2·9107 (8)	P(1)—O(*L*12)—P(2)	131·3 (1)

NO_n coordination polyhedra

N(1)—O(*E*11)	3·007 (3)	N(2)—O(*E*12)	2·928 (3)
N(1)—O(*E*12)	2·814 (3)	N(2)—O(*E*12)	2·850 (3)
N(1)—O(*E*23)	2·940 (3)	N(2)—O(*E*13)	3·025 (3)
N(1)—O(*E*23)	2·774 (3)	N(2)—O(*E*23)	2·871 (3)
N(1)—O(1)	2·927 (3)	N(2)—O(1)	2·888 (3)
N(1)—O(2)	2·958 (3)		

	N—H	H···O	N—O	N—H···O
N(1)—H(11)···O(*E*23)	0·80 (3)	2·01 (3)	2·774 (3)	161 (4)
N(1)—H(12)···O(*E*12)	0·85 (5)	1·97 (5)	2·814 (3)	170 (4)
N(1)—H(13)···O(*E*11)	0·86 (5)	2·18 (5)	3·007 (3)	161 (4)
N(1)—H(14)···O(1)	0·69 (5)	2·49 (5)	2·927 (3)	123 (5)
N(2)—H(21)···O(*E*23)	0·89 (6)	2·05 (6)	2·871 (3)	152 (5)
N(2)—H(22)···O(*E*13)	0·98 (6)	2·53 (6)	3·025 (3)	111 (4)
O(*E*21)		2·56 (6)	3·441 (3)	149 (4)
O(*E*22)		2·53 (6)	3·418 (3)	150 (4)
N(2)—H(23)···O(*E*12)	0·75 (4)	2·16 (4)	2·850 (3)	152 (5)
N(2)—H(24)···O(*E*12)	0·81 (6)	2·21 (6)	2·928 (3)	149 (6)

The ammonium ions are lining the channels (Fig. 2) delimited by the anionic ribbons. In a range of 3 Å, N(1) is surrounded by six oxygen atoms while N(2) has only five oxygen neighbours. The complete hydrogen-bonding scheme is given in Table 2. By means of these bonds, the NH_4 ions ensure the three-dimensional cohesion of the atomic arrangement.

The situation of the H(22) hydrogen atom inside the hydrogen-bond network is not clear. The shortest N(2)—O distance [N(2)—O(*E*13) = 3·025 Å] which seems to be the most appropriate for the H bridge has a corresponding N—H···O angle of 111° which is difficult to accept. The two other N—O distances: N(2)—O(*E*21) and N(2)—O(*E*22) (3·441 and 3·418 Å) in spite of being much longer seem the most appropriate giving respective N—H···O angles of 149 and 150°, thus building a bifurcated bridge. It should be noticed that the isotypic potassium compound exists.

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Le Phosphite Acide de Lanthane Monohydraté

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Abstract. $La(HPO_3H)_3.H_2O$, $M_r = 399{\cdot}81$, triclinic, $P\bar{1}$, $a = 8{\cdot}054\ (2)$, $b = 9{\cdot}672\ (3)$, $c = 7{\cdot}224\ (2)$ Å, $V = 458{\cdot}15$ Å^3, $\alpha = 111{\cdot}35\ (2)$, $\beta = 75{\cdot}77\ (2)$, $\gamma = 118{\cdot}66\ (2)°$, $Z = 2$, $D_m = 2{\cdot}88\ (1)$, $D_x = 2{\cdot}906$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 7{\cdot}14$ mm^{-1}, $F(000) = 380$, $T = 293$ K, $R = 0{\cdot}038$ for 868 independent reflexions. The structure consists of three phosphite anions connected by a strong hydrogen bond. The La^{3+} cation is coordinated by seven O atoms of phosphite anions and one O atom of the water molecule.

Introduction. Une précédente étude nous a permis de mettre en évidence l'existence de plusieurs types de sels acides ou neutres d'éléments de terres rares. Ces composés sont différents de par leur degré d'hydratation ou le nombre d'atomes d'hydrogène acide (Larbot, Battou, Durand & Cot, 1982). Les phases déjà isolées sont du type: $MH(PO_3H)_2.1{\cdot}5H_2O$ avec $M =$ La ou Ce; $La(HPO_33H)_3.H_2O$, $Ce_2(PO_3H)_3.4H_2O$ ou $MH(PO_3H)_2.2H_2O$ avec $M =$ La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb ou Lu. L'étude structurale de $NdH(PO_3H)_2.2H_2O$ montre la présence de groupements $H_2P_2O_6^{2-}$ obtenus par la mise en jeu d'une liaison hydrogène entre deux anions PO_3H^{2-} (Loukili, Durand, Rafiq & Cot, 1988).

La structure cristalline de $La(HPO_3H)_3.H_2O$ est un nouvel exemple d'arrangement dans cette famille de sels acides de terres rares.

Partie expérimentale. Les cristaux en fines aiguilles se forment par évaporation lente d'une solution obtenue par dissolution de l'oxyde La_2O_3 dans l'acide phosphoreux H_2PO_3H. En respectant la stoechiométrie, la phase que l'on obtient, de structure triclinique, correspond à la formule $La(HPO_3H)_3.H_2O$. Paramètres de maille déterminés par enregistrement en chambre de Weissenberg (symétrie triclinique $P\bar{1}$) affinés par la méthode des moindres carrés à partir du spectre de poudre, densité mesurée par pycnométrie dans le benzène à 293 K, axe d'allongement *c*, dimensions du cristal 0,2 × 0,015 × 0,015 mm, diffractomètre Enraf–Nonius CAD-4, mesures d'intensité effectuées au minimum d'absorption (mode aiguille) avec balayage ω–θ, $\theta < 30°$, largeur de balayage 1,20°; trois réflexions contrôle mesurées toutes les heures, pas de variation d'intensité supérieure à 0,3%; 3130 réflexions mesurées, 868 réflexions indépendantes conservées avec $\sigma(I)/I < 0{,}3$; corrections de Lorentz et de polarisation mais pas d'absorption; structure résolue par la méthode de Patterson tridimensionnelle; affinement des paramètres atomiques (sauf pour les atomes d'hydrogène) par la méthode des moindres carrés basée sur *F*; facteurs de diffusion atomique de Doyle & Turner (1968) et de Stewart, Davidson & Simpson (1965) pour les atomes d'hydrogène de PO_3H positionnés par synthèse différence de Fourier, mais non affinés; autres atomes d'hydrogène non observés; cycles finals d'affinement anisotrope pour tous les atomes sauf ceux d'hydrogène; pas de pondération, résidu final de la synthèse de Fourier = 1,36 e Å^{-3}; *R* final 0,038; calculateur utilisé IBM 3081.

Discussion. Le Tableau 1 rassemble les valeurs des paramètres atomiques de position en fin d'affinement.* La Fig. 1 représente la projection de la structure sur le plan *yOz*. Cette structure peut être décrite à partir de trois tétraèdres HPO_3H^- centrés en P(1), P(2) et P(3).

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* Les listes des facteurs de structure et des paramètres thermiques anisotropes ont été déposés au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 51223: 7 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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