

Fig. 2. Vue en perspective du contenu de la maille.

dimères sont en coordinence cubique déformée, par rapport aux anions  $[\text{Ni}(\text{CN})_4]^{2-}$ , typique de la structure CsCl (Ouahab *et al.*, 1987). Les molécules de TMTTF présentent un recouvrement éclipsé (Fig. 2). Cette configuration maximise les interactions soufre-soufre (Lowe, 1980). Ainsi, les molécules ne sont pas planes et il en résulte des distances S...S intradimères de 3,327 (1) Å courtes par rapport à la séparation de van der Waals (3,70 Å).

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## The Structure of $\text{MoO}_2\text{DPO}_4 \cdot \text{D}_2\text{O}$ by Powder Neutron Diffraction

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**Abstract.**  $\text{MoO}_2\text{DPO}_4 \cdot \text{D}_2\text{O}$ ,  $M_r = 244.9$ , monoclinic,  $P2_1/m$ ,  $a = 6.7104$  (2),  $b = 6.3437$  (2),  $c = 6.9864$  (2) Å,  $\beta = 109.892$  (1)°,  $V = 279.7$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.90$  g cm<sup>-3</sup>,  $\lambda = 1.595$  Å,  $\mu = 0.010$  cm<sup>-1</sup>,  $T = 5$  K. The D-atom positions in  $\text{MoO}_2\text{DPO}_4 \cdot \text{D}_2\text{O}$  have been determined by powder neutron diffraction using the Rietveld profile refinement method. The structure of this material, formerly represented as  $\text{Mo}(\text{OH})_3\text{PO}_4$ , was found to consist of bent  $\text{MoO}_2$  groups coordinated by  $\text{D}_2\text{O}$  and linked into double chains by  $\text{PO}_3\text{OD}$  units. These double chains are held together by hydrogen bonds.

**Introduction.** A material of the composition  $2\text{MoO}_3 \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  was first reported by Schultz (1955). Kierkegaard (1958) subsequently studied the structure of this material by single-crystal X-ray diffraction and

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found it to consist of double chains of linked  $\text{MoO}_6$  octahedra and  $\text{PO}_4$  tetrahedra parallel to the crystal  $y$  axis. The refinement was unable to locate the H atoms and indeed considerable uncertainty remained in a number of the O-atom positions. Kierkegaard interpreted the results of this refinement as demonstrating the presence of  $\text{MoO}_3(\text{OH})_3$  octahedra, with a fairly regular octahedral coordination for molybdenum, linked by O– $\text{PO}_2$ –O units, and hence described the material as  $\text{Mo}(\text{OH})_3\text{PO}_4$ .

However, the infra-red spectrum of this material shows a very strong absorption at 1620 cm<sup>-1</sup> (Kierkegaard, 1962), indicative of water molecules in the structure. This prompted us to examine the structure of ' $\text{Mo}(\text{OH})_3\text{PO}_4$ ' by neutron diffraction in order to determine accurate oxygen positions and locate the H atoms.

**Experimental.** A sample of  $\text{MoO}_2\text{DPO}_4 \cdot \text{D}_2\text{O}$  was prepared following the method described by Kierkegaard (1958) but using fully deuterated materials.  $\text{MoO}_3$  was dissolved in  $\text{D}_3\text{PO}_4$  (85% w/v, >99% D, Aldrich) at 450 K. The cooled solution was diluted with  $\text{DNO}_3$  (50% w/v, >98.5% D, Koch-Light) and then refluxed. Approximately 5 g of a crystalline product was obtained on cooling to room temperature; this was filtered off in a glove box and washed with dried ether. Powder X-ray diffraction measurements using an INEL position-sensitive-detector-based system showed a single phase which could be indexed totally on the cell dimensions given by Kierkegaard.

Neutron diffraction measurements were carried out on the 5 g sample contained in a thin-walled vanadium can cooled to 5 K at atmospheric pressure. Data were collected on the high-resolution powder diffractometer D2B operating at a wavelength of 1.595 Å at the high-flux reactor of the Institut Laue-Langevin, Grenoble. The profile was obtained in  $2\theta$  steps of 0.025 between 0 and 160° over a period of 20 h. The data could be indexed completely, except for a few widely spaced peaks, using the lattice parameters obtained from the powder X-ray measurements in the space group  $P2_1/m$ . All the additional peaks were found to be the result of diffraction by the aluminium of the cryostat tail; these peaks were displaced slightly from the expected  $2\theta$  positions at low angles, owing to the off-centre nature of the diffraction. A version (Hewat, 1973) of the least-squares Rietveld (1969) profile refinement program running on the IBM 3090 at Southampton was used to fit the data. The profile points were weighted according to  $1/y_i$  where  $y_i$  was the number of counts at  $2\theta_i$  after correction for the background. The background was determined between peaks wherever possible at low angles and estimated at 5° intervals at higher  $2\theta$  values. Portions of the profile containing aluminium diffraction peaks were placed in excluded regions.

The expression  $M = \sum_i w_i [y_i(\text{obs}) - cy_i(\text{calc})]^2$  was minimized, where  $w_i$  is the weighting function and  $c$  the scale factor. Scattering lengths were taken as Mo 6.95, O 5.807, D 6.67 and P 5.13 fm. Initial refinements were based on the structure determined by Kierkegaard with no deuterium position included, varying the profile parameters, scale factor, half-width parameters, cell constants and zero point. This yielded  $R_{wp} \equiv 100 \{ \sum_i w_i [ |y_i(\text{obs}) - cy_i(\text{calc})| ]^2 / \sum_i w_i y_i(\text{obs})^2 \}^{1/2}$  in excess of 30%. Refinement of the Mo, P and O positional parameters reduced  $R_{wp}$  to around 25%. At this stage a Fourier difference map was derived using the calculated and observed intensities. A D-atom position was located in proximity to O3, which is bound to P, with two further possible sites approximately 1 Å distant from O6, which is bound to Mo. D atoms were introduced into the refinement on these sites in the  $y = 0.25$  plane. Subsequent refinement resulted in a

Table 1. Fractional atomic coordinates and  $B_{eq}$  values with e.s.d.'s in parentheses

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Mo	0.27699 (43)	0.25000	0.17815 (53)	1.70 (13)
P	0.66761 (46)	0.25000	0.66692 (48)	0.97 (14)
O1	0.67911 (39)	0.43443 (34)	0.81103 (29)	1.14 (10)
O2	0.46572 (44)	0.25000	0.48227 (41)	2.65 (17)
O3	0.84126 (55)	0.25000	0.56977 (53)	0.80 (13)
O4	0.20143 (48)	0.25000	0.91289 (41)	1.25 (14)
O5	0.60644 (56)	0.25000	0.15486 (87)	2.15 (18)
O6	0.04725 (54)	0.25000	0.22267 (46)	2.25 (17)
D1	0.98517 (48)	0.25000	0.68544 (40)	2.15 (17)
D2	0.73357 (58)	0.25000	0.28638 (59)	2.82 (17)
D3	0.65392 (71)	0.25000	0.03969 (67)	4.85 (23)

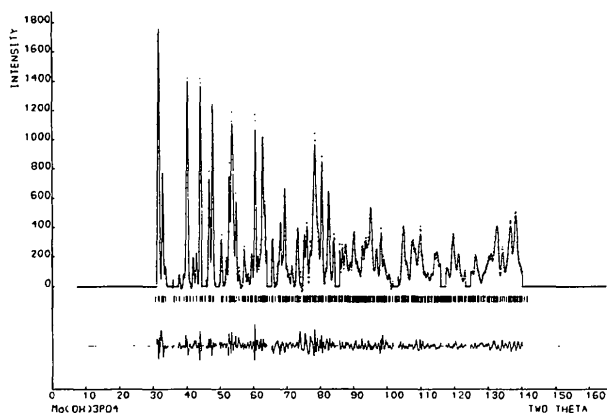


Fig. 1. Observed (points), calculated (upper continuous line) and difference (lower continuous line) profiles for  $\text{MoO}_2\text{DPO}_4 \cdot \text{D}_2\text{O}$ . Ticks mark the position of each reflection in the profile.

reduction of  $R_{wp}$  to 12% and produced chemically reasonable D-atom positions. Finally anisotropic temperature factors were introduced and refined yielding a final  $R_{wp}$  of 9.2% and  $R_N \equiv 100 \{ \sum_i w_i [ |I_i(\text{obs}) - cI_i(\text{calc})| ]^2 / \sum_i w_i I_i(\text{obs})^2 \}^{1/2} = 4.4\%$ . The final atomic positions are given in Table 1 together with their e.s.d.'s; parameter shifts in the last cycle of refinement were  $< 0.05\sigma$ .\* Fig. 1 shows the final fit to the profile. Attempts to refine the structure in the lower-symmetry space group  $P2_1$  which allows the atoms to move out of the  $y = 0.25$  plane produced no significant (Hamilton, 1965) improvement.

**Discussion.** A diagram of the structure is shown in Fig. 2. Table 2 contains bond angles and distances of interest. The  $y = 0.25$  plane contains all of the atoms except O1 which links together layers of this type related by the twofold axis. Some of the O-atom

\* Lists of anisotropic thermal parameters and measured and calculated intensities at each profile point have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51016 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

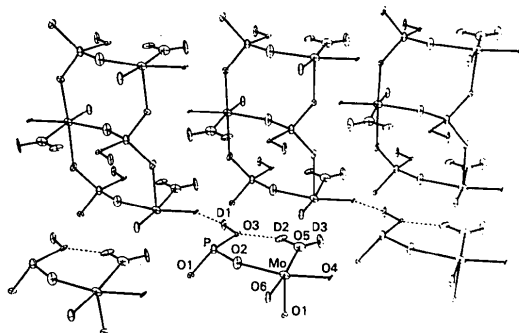


Fig. 2. Portion of the structure MoO<sub>2</sub>DPO<sub>4</sub>·D<sub>2</sub>O viewed obliquely to the  $y=0.25$  plane. The hydrogen bonds are represented by broken lines.

Table 2. Bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Mo—O1	2.021 (4)	P—O1	1.528 (3)
Mo—O2	2.071 (4)	P—O2	1.520 (4)
Mo—O4	1.747 (3)	P—O3	1.535 (4)
Mo—O5	2.271 (6)	O3—D1	1.027 (4)
Mo—O6	1.673 (3)	O5—D2	1.019 (6)
D1—O4	1.750 (4)	O5—D3	0.961 (6)
D2—O3	1.862 (4)	D2—D3	1.621 (4)
O4—Mo—O6	104.1 (9)	D2—O5—D3	109.9 (9)
O6—Mo—O2	95.2	P—O3—D1	107.7
O4—Mo—O5	82.1	O3—D1—O4	169.1
O2—Mo—O5	78.6	O5—D2—O3	149.5
O1—Mo—O2	86.1	O1—P—O2	112.9
O1—Mo—O4	91.5	O1—P—O3	114.6
O1—Mo—O5	82.5	O2—P—O3	102.5
O1—Mo—O6	97.2		

positions determined were significantly displaced from those obtained by Kierkegaard. The Mo environment consists of two short bonds to O4 and O6 typical of a bent molybdenyl group, three normal Mo—O bonds linking to phosphate groups and a more weakly bound D<sub>2</sub>O molecule with an Mo—O distance of 2.27 Å. The phosphate group is protonated as is found in other transition-metal phosphates, for example Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. The P—O—H group hydrogen bonds reasonably strongly to O4, which is the sole interaction between the double chains.

The water-molecule geometry is typical for this species in hydrated inorganic compounds; it is held in the  $y=0.25$  plane by a weak hydrogen bond between D2 and O3. The presence of this structural feature fits with the strong absorption at 1620 cm<sup>-1</sup> in the IR spectrum which is due to the H<sub>2</sub>O symmetric bend.

The coordination geometry of Mo is similar to that observed in molecular Mo[(CH<sub>3</sub>)<sub>2</sub>NCHO]<sub>2</sub>O<sub>2</sub>Cl<sub>2</sub> (Flo-

rian & Corey, 1968) where a bent MoO<sub>2</sub> group coordinated to oxygen and chlorine in an approximately octahedral environment. In MoO<sub>2</sub>DPO<sub>4</sub>·D<sub>2</sub>O, however, the phosphate groups link the molybdenyl moieties into infinite chains.

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## Redetermination of the Structure of Gd<sub>2</sub>CuO<sub>4</sub>: A Site Population Analysis

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**Abstract.** In view of recent interest in compounds of the type Ln<sub>2</sub>CuO<sub>4</sub> (where Ln = lanthanide), a single-crystal X-ray study has been performed for the redetermination of the structure of Gd<sub>2</sub>CuO<sub>4</sub> including a site population analysis.  $M_r = 442.04$ , tetragonal, *I4/mmm*,

$a = 3.892$  (1),  $c = 11.878$  (3) Å,  $V = 179.91$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 8.15$  g cm<sup>-3</sup>, Mo  $K\alpha_1$ ,  $\lambda = 0.70926$  Å,  $\mu = 423.5$  cm<sup>-1</sup>,  $F(000) = 378$ ,  $T = 295$  K,  $R = 2.8\%$ , 102 unique reflections used for refinement. The structure consists of a two-dimensional edge-linked square-planar network of [CuO<sub>2</sub>]<sup>2-</sup> groups which are linked by planes of Gd, O and Gd atoms. The oxygen coordination environment around the Gd<sup>3+</sup> cations is cubic. The

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