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Crystal data for anhydrous lithium acetate.

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A crystallographic study has been made of anhydrous lithium acetate which is apparently the less common form of lithium acetate; most standard chemical works give data for the dihydrate only. The source of our material was a commercial compound sold as 'anhydrous lithium acetate'. This consisted of a fine hygroscopic powder with which was mixed a relatively few tiny colorless crystals. A chemical analysis of the crystals after they had been permitted to take on water from the atmosphere showed them to be the dihydrate. It was not possible to get a good chemical analysis of the original crystals, but their hygroscopic character suggested that they were either the anhydrous compound or a lower hydrate. They proved to have a lower density than the 1·30 g.cm.$^{-3}$ of the dihydrate (Amirthalingam & Padmanabhan, 1958), and by sifting the commercial powder and then floating the crystals in a liquid with a density lower than 1·30 g.cm.$^{-3}$, it was possible to obtain good crystals of the hygroscopic material. By heavy liquids the best specific gravity was determined to be 1·227 g.cm.$^{-3}$.

X-ray precession photographs using Cu radiation were taken of several of the crystals which were coated with a thin layer of transparent nail polish or of a plastic waterproof spray, Krylon, in order to protect them from moisture in the atmosphere. The crystals proved to be triclinic with:

$$a=9{\cdot}29,\ b=12{\cdot}13,\ c=6{\cdot}76\ \text{Å}\ .$$
$$\alpha=101^\circ\ 0',\ \beta=100^\circ\ 19',\ \gamma=105^\circ\ 5'.$$

The statistical tests of Howells, Phillips & Rogers (1950) showed the space group to be $P\overline{1}$. These cell dimensions yield, for an assumed composition of anhydrous lithium acetate and the measured specific gravity of 1·227 g.cm.$^{-3}$, 8·04 formula units in the unit cell. The density calculated for $Z=8$ is 1·221 g.cm.$^{-3}$, and this agreement between calculated and observed densities is our basis for concluding that the crystals are anhydrous lithium acetate and not some hydrate lower than the dihydrate. Powder data for this compound and for the dihydrate have been submitted for publication in the *A.S.T.M. Powder Data Card File*.

We attempted an analysis of the crystal structure by 2-dimensional Fourier methods, but we were unable to deduce a structure that would explain the observed intensities. Details of the investigation are to be found in Saunderson (1960). We plan no further work on this crystal.

One of us (C. S.) is grateful to Dr W. G. Schneider, Dr Maria Przybylska and Dr F. R. Ahmed of the National Research Council, Ottawa, for respectively suggesting the problem, guiding the work at some stages, and providing programs for the IBM 650. We also wish to thank Prof. C. B. Germain, Dr B. Noonan and Mr T. J. White of the University of Manitoba for computational assistance, and the National Research Council for financial support.

References

Amirthalingam, V. & Padmanabhan, V. M. (1958). *Acta Cryst.* **11**, 896.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

Saunderson, C. P. (1960). *An investigation of the crystal structure of anhydrous lithium acetate.* (Unpublished.) M.Sc. Thesis. University of Manitoba, Winnipeg.

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A note on the crystal structure of anhydrous copper sulphate.

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The crystal structure of $CuSO_4$, which crystallizes with the cell constants

$$a=8{\cdot}39,\ b=6{\cdot}69,\ c=4{\cdot}83\ \text{Å}$$

in the space group *Pnma* and $Z=4$, has been determined by Kokkoros & Rentzeperis (1958) by the method of trial and error. A $(2+2+2)$ coordination has been attributed to Cu in this structure, but copper has mostly been found to have four nearest coplanar neighbours, with two more at a rather greater distance, which complete a distorted octahedral coordination group (Wells, 1950; *cf.* also Gattow & Zemann, 1958). Recently Knox (1959) has reported a new kind of distortion for the octahedral copper(II) in K_2CuF_4, where Cu has been found to have a $(2+4)$ coordination with two nearest neighbours (Cu–F = 1·95 Å (2 ×)) and four at a slightly greater distance (Cu–F = 2·08 Å (4 ×)). Edwards & Peacock (1959) have also reported an identical coordination for Cu in $KCuF_3$ (Cu–F = 1·96 Å (2 ×) and 2·07 Å (4 ×)). Therefore it is of interest to investigate whether Cu has the usual $(4+2)$ coordination or the rarer type of $(2+4)$ coordination in $CuSO_4$. While there is no doubt that the structure determined by Kokkoros & Rentzeperis (K&R) is correct in principle it needs further refinement to establish the exact nature of the coordination polyhedron around copper.

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Table 1. *Final parameters*

4 Cu	(*a*)	0	0	0
4 S	(*c*)	0·185	0·250	0·445
4 O_I	(*c*)	0·141	0·250	0·755
4 O_{II}	(*c*)	0·375	0·250	0·439
8 O_{III}	(*d*)	0·129	0·069	0·307

Table 2. *Interatomic distances*

Coordination polyhedron around copper:

$\mathrm{Cu}-\mathrm{O}_{\mathrm{I}} = 2{\cdot}37$ Å (2 ×)
$\mathrm{Cu}-\mathrm{O}_{\mathrm{II}} = 2{\cdot}00$ (2 ×)
$\mathrm{Cu}-\mathrm{O}_{\mathrm{III}} = 1{\cdot}89$ (2 ×)

$\mathrm{O}_{\mathrm{II}}-\mathrm{O}_{\mathrm{III}} = 2{\cdot}72$

$\mathrm{O}_{\mathrm{II}}-\mathrm{O}'_{\mathrm{III}} = 2{\cdot}78$ Å
$\mathrm{O}_{\mathrm{I}}-\mathrm{O}_{\mathrm{II}} = 2{\cdot}68$
$\mathrm{O}_{\mathrm{I}}-\mathrm{O}_{\mathrm{III}} = 3{\cdot}13$
$\mathrm{O}_{\mathrm{I}}-\mathrm{O}'_{\mathrm{III}} = 2{\cdot}93$
$\mathrm{O}_{\mathrm{I}}-\mathrm{O}_{\mathrm{II}} = 3{\cdot}46$

Sulphate tetrahedron:

$\mathrm{S}-\mathrm{O}_{\mathrm{I}} = 1{\cdot}54$ Å
$\mathrm{S}-\mathrm{O}_{\mathrm{II}} = 1{\cdot}59$
$\mathrm{S}-\mathrm{O}_{\mathrm{III}} = 1{\cdot}46$ (2 ×)

$\mathrm{O}_{\mathrm{I}}-\mathrm{O}_{\mathrm{III}} = 2{\cdot}48$ (2 ×)
$\mathrm{O}_{\mathrm{I}}-\mathrm{O}_{\mathrm{II}} = 2{\cdot}49$
$\mathrm{O}_{\mathrm{II}}-\mathrm{O}_{\mathrm{III}} = 2{\cdot}48$ (2 ×)
$\mathrm{O}_{\mathrm{III}}-\mathrm{O}_{\mathrm{III}} = 2{\cdot}42$

Primes denote equivalent atoms.

The structure was refined by Fourier and difference syntheses using the intensity data published by K&R. Structure factors were calculated using the atomic scattering curves for Cu^+ and O from the work of Berghuis *et al.* (1955) and for S from the work of Viervoll & Øgrim (1949). The curves were modified for O^- and S^{+2}. The final parameters obtained are given in Table 1. Table 2 gives the interatomic distances. The values of the reliability index *R*, obtained for the zones [010] and [001] are $0{\cdot}14_3$ and $0{\cdot}16_5$ respectively, as against $0{\cdot}19_3$ and $0{\cdot}19_6$ obtained by the previous workers. Further refinement of the structure was not possible with the present intensity data. The probable error in the location of the atoms is estimated to be 0·03–0·05 Å.

From the interatomic distances given in Table 2 it is seen that $\mathrm{Cu}-\mathrm{O}_{\mathrm{II}}$ distance has decreased from 2·15 Å (K&R) to 2·00 Å; the $\mathrm{Cu}-\mathrm{O}_{\mathrm{III}}$ and $\mathrm{Cu}-\mathrm{O}_{\mathrm{I}}$ distances have increased from 1·87 and 2·36 Å (K&R) to 1·89 and 2·37 Å. These changes in the interatomic distances indicate with great probability that Cu has neither the (2 + 2 + 2) coordination as given by the previous authors, nor the new type of (2 + 4) coordination, but the usual (4 + 2) coordination, although the Cu–O distances in the square planar coordination are not observed to be exactly equal.

I am greatly indebted to Prof. J. Zemann for suggesting the problem and guiding, to Dr W. H. Baur for many helpful discussions and to the Free and Hanseatic City of Hamburg for awarding a scholarship.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A.L. (1955). *Acta Cryst.* **8**, 478.
Edwards, A. J. & Peacock, R. D. (1959). *J. Chem. Soc.* 4126.
Gattow, G. & Zemann, J. (1958). *Acta Cryst.* **11**, 866.
Knox, K. (1959). *J. Chem. Phys.* **30**, 991.
Kokkoros, P. A. & Rentzeperis, P. J. (1958). *Acta Cryst.* **11**, 361.
Viervoll, H. & Øgrim, O. (1949). *Acta Cryst.* **2**, 277.
Wells, A. F. (1950). *Structural Inorganic Chemistry*, 2nd ed., p. 618 ff. Oxford: University Press.

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On the unit cell of Mallinckrodt's UO_3.

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The X-ray powder diffraction pattern of Mallinckrodt's UO_3 has recently been interpreted (Connolly, 1959) in terms of a monoclinic unit cell. Connolly drew attention to a number of remarkable split lines and ascribed these to pseudorhombic symmetry. However, this interpretation is weakened by an overwhelming number of multiple indexings. The total number of triplets listed is about $\frac{1}{4}$ of the number of available triplets, but this figure drops to 10% if the number of observed lines is put instead. Moreover, the first 'split line', consisting of the strong 4th and 5th line, is not even remotely accounted for by the indices stated, for which wrong calculated values are given. Only (300) with $\sin^2\theta = 0{\cdot}0314$ is acceptable here, so that one strong line remains unexplained.

A new interpretation for the same data is proposed now, based upon the quadratic form

$$10^4 \sin^2\theta = q = 124{\cdot}75(h^2 + k^2) + 2{\cdot}5hk + 14{\cdot}95l^2,$$

with $h + k + l$ even. It accounts for 44 lines, which is 36% of the number of available triplets. Six lines must be ascribed to impurities. They occur at the higher angles and their intensity is from '*w*' to '*vvw*' except for $q = 1896$ and 2109. These two figure as 'medium' in Connolly's list, but they are not mentioned at all in earlier otherwise similar data (Dawson *et al.*, 1956).

Positive features of the present interpretation are:

(*a*) The split lines stand out unambiguously as hkl, $h\bar{k}l$ doublets caused by pseudosymmetry.
(*b*) The number of molecules in the body-centered unit cell

$$a = b = 6{\cdot}90,\quad c = 19{\cdot}92\ \text{Å},\quad \alpha = \beta = 90,\quad \gamma = 90{\cdot}57^\circ,$$

corresponding to the above quadratic form, is $Z = 15$ according to the density used by Connolly, and $Z = 16{\cdot}7$ if the UO_3 volume is taken to be equal to its value in α-UO_3. Both figures suggest $Z = 16$. The lattice is actually face-centered orthorhombic