symmetry, since sulphate tetrahedra in the same mirror plane are now related only by the translation $a/2+c/2$. The structure adjusts itself, accordingly, to the new degree of freedom by a slight departure of the lattice from orthogonality.

Up till now, the anhydrous sulphates of divalent magnesium, manganese, iron and nickel are only known to occur in the A form, those of copper and zinc only in the B form. Polymorphism has been reported only for anhydrous cobalt sulphate, but it is difficult to see why the divalent cobalt atom should be egregious in this respect. Further work may well reveal that the other anhydrous sulphates in this series exhibit the same or at least similar kinds of polymorphism.

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The Structure of Ammonium Copper Sulphate $(NH_4)_2Cu(SO_4)_2 . 6H_2O$

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The structure of ammonium copper sulphate is shown to be very similiar to that of the nickel and magnesium ammonium sulphates except for the tetragonal distortion of the water molecule octahedra surrounding the copper ions. The orientation of the octahedron is in good agreement with paramagnetic resonance measurements and a reason for the poorer stability of the copper salt is suggested.

Introduction

Ammonium copper sulphate, a member of the isomorphous series known as Tutton salts, has a structure of particular interest because of the tetragonal distortion of the crystal field on the copper ion as revealed by paramagnetic resonance studies (Bleaney, Penrose & Plumpton, 1949). The structures of the corresponding nickel and magnesium salts of the series have already been described (Grimes, Kay & Webb, 1963; Margulis & Templeton, 1962), and as the procedure adopted to determine the structure of the copper salt was essentially the same as that used for the nickel salt, only the final results and conclusions are presented here.

Table 1. *Atomic coordinates and their standard deviations for ammonium copper sulphate*

	x/a	$\sigma x/a$	y/b	$\sigma y/b$	z/c	$\sigma z/c$
Ni	0	—	0	—	0	–
S	0·0878	±0·0013	0·6394	±0·00095	0·252	±0·0019
NH_4	0·1296	±0·0037	0·3498	±0·0028	0·3550	±0·006
O(1)	0·0857	±0·0037	0·7276	±0·0025	0·4030	±0·006
O(2)	0·1133	±0·0036	0·6753	±0·0026	0·0364	±0·007
O(3)	0·2217	±0·0037	0·5707	±0·0027	0·3687	±0·007
O(4)	−0·0520	±0·0036	0·5735	±0·0026	0·2135	±0·007
H_2O(1)	−0·1678	±0·0036	0·1070	±0·0025	0·0281	±0·007
H_2O(2)	0·1691	±0·0036	0·1189	±0·0026	0·1697	±0·007
H_2O(3)	0·0017	±0·0038	−0·0633	±0·0023	0·2987	±0·007

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Crystal data

Crystals of ammonium copper sulphate are monoclinic with space group $P2_1/a$. There are two molecules in the unit cell which has the dimensions $a = 9{\cdot}208 \pm 0{\cdot}002$, $b = 12{\cdot}349 \pm 0{\cdot}002$, $c = 6{\cdot}293 \pm 0{\cdot}002$ Å assuming Tutton's (1916) value for $\beta = 106°9'$. These lattice parameters give a calculated density of 1·919 $g.cm^{-3}$, which is 0·3% smaller than Tutton's measured value of 1·925 $g.cm^{-3}$. Bhowink (1961) obtained values of 9·27, 12·50, 6·33 Å and 106°5′ for a, b, c, and β respectively and these give a calculated density which is 2·7% smaller than Tutton's value.

The structure was determined from electron-density maps of the (100), (010) and (001) projections and from least-squares adjustment of the atomic positions using 300 reflexions. The final R index was 0·11. The atomic coordinates with their standard deviations are given in Table 1 and Tables 2 and 3 give some interatomic separations for comparison with the corresponding nickel and magnesium salts. Fig. 1 shows the projection of the structure onto (001).

Table 2. *Bond lengths and angles in ammonium copper sulphate*

Cu-H_2O(1) = 2·06 ± 0·03 Å
Cu-H_2O(2) = 2·19 ± 0·04
Cu-H_2O(3) = 2·04 ± 0·03

H_2O(1)-H_2O(2) = 3·03 ± 0·05 Å
H_2O(1)-H_2O(3) = 3·05 ± 0·04
H_2O(2)-H_2O(3) = 2·98 ± 0·05

H_2O(1)-Cu-H_2O(2) = 90° 10′ ± 30′
H_2O(1)-Cu-H_2O(3) = 91° 30′ ± 20′
H_2O(2)-Cu-H_2O(3) = 89° 50′ ± 40′

O(1)-S-O(2) = 110° 20′ ± 1°
O(1)-S-O(3) = 107° 30′
O(1)-S-O(4) = 109° 40′
O(2)-S-O(3) = 107°
O(2)-S-O(4) = 109°
O(3)-S-O(4) = 108° 10′

O(1)-O(2) = 2·48 ± 0·12 Å
O(1)-O(3) = 2·36
O(1)-O(4) = 2·42
O(2)-O(3) = 2·42
O(2)-O(4) = 2·48
O(3)-O(4) = 2·43

S-O(1) = 1·44 ± 0·06 Å
S-O(2) = 1·52
S-O(3) = 1·50
S-O(4) = 1·49

Table 3. *Hydrogen bond distances and angles in ammonium copper sulphate*

O(2)-H_2O(1)-O(4) 108° 40′	H_2O(1)-O(2) 2·75 Å	H_2O(1)-O(4) 2·54 Å
O(2)-H_2O(2)-O(3) 121°	H_2O(2)-O(2) 2·69 Å	H_2O(2)-O(3) 2·85 Å
O(1)-H_2O(3)-O(3) 98° 20′	H_2O(3)-O(1) 2·73 Å	H_2O(3)-O(3) 2·74 Å

Discussion of the structure

To the authors' knowledge this is the first structure analysis of a salt in which the copper ion is surrounded by six water molecules, and the main difference between its structure and those of nickel and magnesium ammonium sulphates is in the bond lengths of the octahedra of water molecules around the bivalent cation, these lengths being different in the three salts. The orientation of the octahedron is very nearly the same in all three cases, but in the copper salt the water molecules form a tetragonally elongated octahedron with the Cu-H_2O(2) separation greater than the Cu-H_2O(1) and Cu-H_2O(3) separations. These are equal to within the experimental accuracy, and thus four water molecules are situated at the corners of a square, at a distance of 2·05 Å from the copper ion. The other two water molecules lie on a perpendicular through the centre of the square and at a distance of 2·19 Å from the copper ion. This may be compared with their positions in the nickel and magnesium salts where the water molecules form a nearly regular octahedron around the bivalent ions with a nickel to water separation of 2·04 Å and a magnesium to water separation of 2·07 Å.

The tetragonal distortion of the octahedron is due to the Jahn–Teller effect, and is always found in octahedrally coordinated copper salts but is usually more pronounced than in this salt. For example, in $CuSO_4 . 5H_2O$ (Bacon & Curry, 1962), the average copper to oxygen separation in the plane of the squares is 1·97 Å and perpendicular to the square is 2·41 Å. This is not directly comparable with the results for copper ammonium sulphate since in copper sulphate the atoms perpendicular to the plane of the square are sulphate oxygen atoms.

The water molecule positions in the copper salt are sufficiently different from those in the nickel and magnesium salts to lead to a possible difference in the hydrogen bonding. Thus the hydrogen bond distances of 2·69 and 2·54 ± 0·05 Å in the copper salt are smaller than the corresponding distances in the nickel and magnesium salts which are 2·81 and 2·62 ± 0·04 Å and 2·844 and 2·722 ± 0·006 Å respecti-

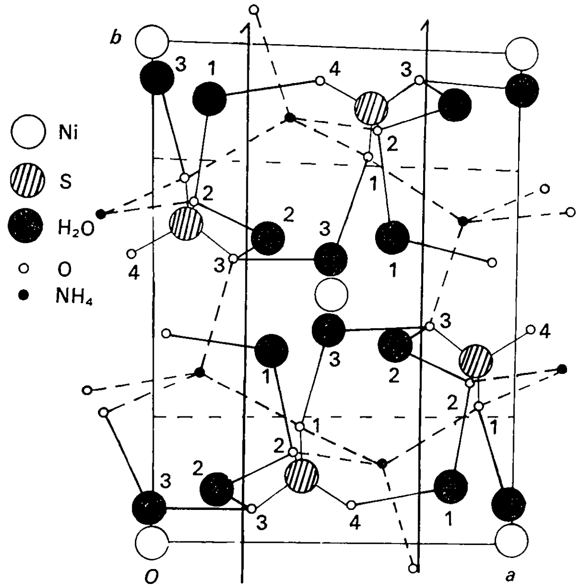

Fig. 1. Projection of structure on (001) (hydrogen bonds shown).

vely. Thus the copper salt appears to be rather tightly packed into the structure and the $H_2O(1)-O(4)$ bond length (2·54 Å) is exceptionally short. It is so short, that not only is it unlikely that a hydrogen bond will form but there is probably some repulsion between the two atoms. The authors suggest that this tighter packing and resultant strain is one of the reasons for the much poorer stability of the copper salt than that of the nickel salt to dehydration (Caven & Ferguson, 1922) even though the heats of hydration of the hexahydrated copper and nickel ions are practically identical (Griffith & Orgel, 1957). The close approach of $H_2O(1)$ and O(4) does not, in this case, lead to extra stability since it is imposed by the packing of sulphate group tetrahedra and $Cu(H_2O)_6$ octahedra and is not due to attractive forces between $H_2O(1)$ and O(4). Half of the hydrogen bonds lie across the $\bar{2}01$ plane and the average separation of the closest atoms across this plane in the copper salt is significantly smaller than in the nickel and magnesium salts (2·66 in comparison with 2·74 and 2·78 Å respectively). This may explain the poorer cleavage of the copper salt on this plane.

The bonding of the ammonium group to the sulphate oxygen atoms is very similar to that in the nickel and magnesium salts, so the cleavage parallel to (010) in the three salts is explained (Grimes, Kay & Webb 1963).

Paramagnetic resonance measurements on copper ammonium sulphate are given by Bleaney, Penrose & Plumpton (1949). They found that the angle between the projection of the tetragonal axis of the complex onto the *ac* plane and the *c* axis was 77°. The angle which the tetragonal axis makes with the *ac* plane was not measured at room temperature, but at 90 °K it was found to be 40° and in other copper Tutton salts at room temperature it was found to be approximately 40°. When these angles are calculated using the position of $H_2O(2)$, and assuming that the tetragonal axis of the complex passes through the oxygen atom of this water molecule, they are found to be $68° \pm 6°$ and $42° \pm 2°$ respectively. As with the nickel salt, the true symmetry of the copper complex must be less than orthorhombic owing to the non-symmetrical arrangement of the hydrogen atoms of the water molecules around the copper ion. However the orientation of the approximately tetragonally distorted octahedron confirms the paramagnetic resonance measurements.

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The Crystal Structure of the Centrosymmetric Photodimer of Cyclopentenone*

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The crystal structure of the centrosymmetric photodimer of cyclopentenone, $C_{10}H_{12}O_2$, has been determined from the three-dimensional X-ray diffraction data. The crystals are monoclinic, space group $P2_1/n$, with two molecules in the unit cell with dimensions

$$a=6{\cdot}78,\ b=7{\cdot}23,\ c=8{\cdot}67\ \text{Å};\ \beta=98{\cdot}9°.$$

The carbon–carbon bond lengths in the cyclobutane ring are 1·54 and 1·59 Å.

Introduction

Many α,β-ethylenic carbonyl compounds dimerize in the presence of ultraviolet radiation to yield derivatives of cyclobutane (Yates & Jorgenson, 1963). These dimers have been investigated by a variety of physical and chemical techniques, but no crystal structure has been reported. Eaton (1962) found that cyclopentenone yields two dimers, $C_{10}H_{12}O_2$, upon ultraviolet irradiation, and assigned them structures (I) and (II) primarily on the basis of chemical evidence. The present paper describes the crystal structure determination of

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