The Crystal Structure of Copper(II) Tetraammine Nitrate*

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The room-temperature crystal structure of $Cu(NH_3)_4(NO_3)_2$ has been refined by the full-matrix least-squares method using three-dimensional Mo $K\alpha$ intensity data. The space group is probably *Pnnm* with lattice constants $a_o = 10.840$ (2), $b_o = 23.693$ (4) and $c_o = 6.902$ (2) Å with eight molecules in the cell. The two independent copper ions are each surrounded by four ammonia molecules (~ 2.0 Å) in a near square-planar arrangement and by two more distant O atoms at slightly unequal distances (~ 2.5 Å). The symmetry of the crystal at 77 K involves a simple shear of the room-temperature cell, becoming monoclinic $P2_1/n$ with $a = 23.6$ (1), $b = 10.75$ (5), $c = 6.77$ (3) Å, and $\beta = 94.3$ (1)°.

Introduction

Although $Cu(NH_3)_4(NO_3)_2$ exhibits magnetic properties attributable to a linear chain system (Rogers & Dempsey, 1967), no chemically bonded superexchange path similar to that found in various other Cu compounds (Lowndes, Finegold, Rogers & Morosin, 1969; Rogers, Finegold & Morosin, 1972) was suggested by our initial X-ray study (quoted by Rogers & Dempsey as private communication). In addition, that study suggested the structure was probably centrosymmetric rather than noncentrosymmetric as suggested by Karovicova & Madar (1960). This paper presents the recently refined crystal structure which it is hoped might stimulate other studies on the relationship between the crystal structure and magnetic properties.

Experimental data

Deep blue crystals of $Cu(NH_3)_4(NO_3)_2$ may be grown from an ammoniated aqueous solution of cupric nitrate by addition of alcohol with the rate of crystal growth being determined by the rate at which alcohol is added. Crystals were examined by X-ray photographic techniques to check the space group assignment [Karovicova & Madar (1960) preferred *Pnn*2 over *Pnnm*] as well as to ensure that a single crystal specimen rather than a twin was selected for our measurements. Thermal diffuse scattering along the c direction is evident in both precession and Weissenberg photographs; this scattering decreases with decreasing temperature. Careful examination of Laue as well as other photographs did not reveal evidence for the noncentrosymmetric space group; similarly, no evidence of piezoelectricity was observed. Upon cooling, the crystals transform to twinned specimens of monoclinic symmetry, $P2_1/n$ with 77 K lattice constants as given in the abstract. This reversible

transformation appears to involve a simple shear of the room temperature cell. The small, nearly insignificant changes in the intensities of *hkl* reflections (other than split spots in the photographs) suggest no large positional shifts of the cell contents.

Room temperature lattice constants given in the abstract were determined with Cu $K\alpha$ radiation (λ for $K\alpha_1 = 1.54050$ Å) by least-squares fit of 64 high 2θ values measured on *hk*0 and 0*kl* films taken with a 115 mm diameter Weissenberg camera with Straumanis film loading. Initially, Cu $K\alpha$ radiation was used to measure intensity data on which Friedel pairs could be compared. The number which deviated from the average values was insignificant, indicating the correct space group is probably the centric one, *Pnnm*. The data set on which this refinement is based consisted of θ–2θ scanned Mo $K\alpha$ intensities measured to $55°$ 2θ (on two quadrants) using a scintillation detector with pulse height discrimination. For the averages of 2205 unique intensities, 1642 were greater than 3σ where $\sigma = (N_{sc} + K^2 N_B)^{1/2}$ and N_{sc}, N_B, and K are the total scan count, background counts and the time ratio of the scan to background, respectively. Scattering factors were taken from Table 3.31A of *International Tables for X-ray Crystallography* (1962) and (for H) from Stewart, Davidson & Simpson (1965).

Initial Cu parameters for several models were determined from a Patterson Fourier synthesis and N and O coordinates introduced on the basis of subsequent difference syntheses. At each step, the model was subjected to least-squares refinement using isotropic thermal parameters. The function $\sum w(F_o - F_c)^2$ was minimized with $w = 1/\sigma^2$. For the model which was retained following such refinement, the difference synthesis showed peaks about the N (ammine) groups which were assigned as H positions and retained fixed in the subsequent least-squares refinement cycles using anisotropic thermal parameters. The final residual value, $R = \sum ||F_o| - |F_c||/\sum |F_o|$ was 0.065.

The data were also refined with the noncentrosymmetric *Pnn*2 space group. The R value of 0.051 was

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significantly smaller than that of the centric refinement based on the number of observed intensities and unknown parameters and yields an R index ratio suggesting that the structure might be noncentrosymmetric (Hamilton, 1965). Of the 25 'z' coordinates 6 differed by 3σ or more (with the maximum of 7σ) from the centric values and of the 36 zero-valued U_{13} and U_{23} parameters, only 4 differed by 3σ or more (maximum 5σ). However, it is believed that this result is an artifact of the large thermal motion of some of the O atoms since 4 of the 6 atoms with z coordinates significantly differing from zero have U_{33} values exceeding 0.10 Å^2. It is hence concluded on the basis of the various experimental methods explored that the structure is centric.

The positional and thermal parameters are given in Table 1 and the bond lengths and angles in Table 2.* Computations were performed with the X-RAY 72 System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Results

The crystal structure (Fig. 1) consists of two crystallographically independent $Cu(NH_3)_4(NO_3)_2$ units which differ in an interesting way. In each of these units, the copper ion is surrounded by four ammonia molecules at about 2.0 Å in a near square-planar arrangement and by two more distant O atoms (of the nitrate ion) at slightly unequal distances (near 2.5 Å). Such Cu–N distances are typical of reported values while the more

* A list of structure factors and parameters from the noncentric refinement has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31376 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

remote oxygen distances are certainly within the extreme values reported in Cu compounds (Morosin, 1969). However, the difference in the values of these more remote O atoms is unusual in that for Cu(1) it is 10 times the standard deviation while that for Cu(2) is almost 27 times the standard deviation. For both of these environments, the copper ion essentially lies on the least-squares plane of the N atoms (< 0.01 Å); this is consistent with the observation that a shorter remote

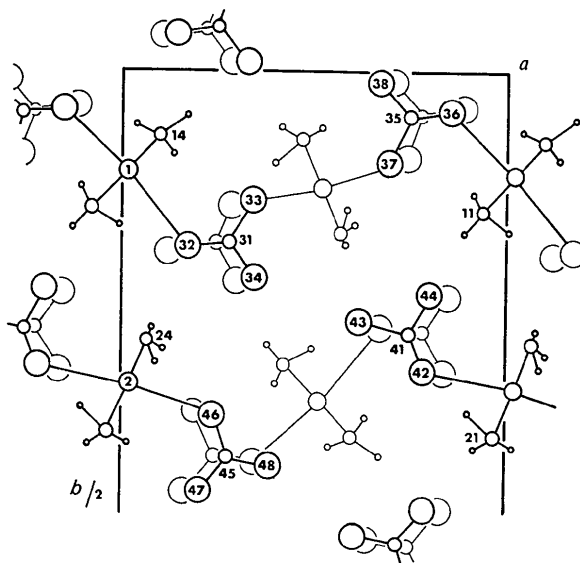Fig. 1. View along the c axis of $Cu(NH_3)_4(NO_3)_2$. Atoms in bold outline are situated about or on the mirror at $z=0$. The largest circles represent O atoms with subsequent smaller circles the Cu, N and H atoms, respectively. Note that, in projection, each nitrate ion is nearly in identical orientation with that above (and below) it.

Table 1. *Positional* ($\times 10^4$) *and thermal parameters for* $Cu(NH_3)_4(NO_3)_2$

Thermal factors are of the form $\exp(-2\pi^2\sum\sum U_{ij}h_ih_ja_i^*a_j^*)$ in units 10^{-2} Å^2.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	138·8 (9)	1182·6 (4)	0	2·83 (7)	2·83 (7)	3·32 (8)	0·17 (3)	0	0
Cu(2)	157·4 (9)	3686·6 (4)	0	3·14 (7)	2·62 (7)	3·71 (8)	0·34 (3)	0	0
N(11)	−728 (4)	1623 (2)	2124 (7)	3·4 (2)	4·3 (2)	3·8 (2)	−0·3 (1)	0·8 (2)	0·2 (2)
N(14)	1001 (4)	750 (2)	2103 (8)	3·8 (2)	4·1 (2)	4·5 (2)	0·4 (1)	−0·6 (3)	0·6 (2)
N(21)	−385 (4)	4221 (1)	2115 (8)	3·9 (2)	3·6 (2)	6·1 (3)	0·4 (1)	−0·8 (2)	−1·2 (2)
N(24)	682 (4)	3148 (2)	2098 (8)	6·2 (3)	3·9 (2)	4·5 (2)	0·7 (2)	0·3 (2)	0·6 (2)
N(31)	2735 (5)	1984 (2)	0	3·6 (3)	3·6 (3)	3·4 (3)	−0·6 (2)	0	0
N(35)	7364 (6)	527 (2)	0	3·1 (3)	3·7 (3)	2·8 (3)	−1·0 (2)	0	0
N(41)	7327 (5)	3007 (2)	0	3·4 (2)	3·8 (3)	2·6 (3)	−0·3 (2)	0	0
N(45)	2729 (5)	4515 (2)	0	2·5 (3)	3·2 (2)	2·8 (3)	0·2 (2)	0	0
O(32)	1628 (5)	2027 (2)	0	3·1 (3)	3·9 (2)	9·5 (5)	−0·2 (2)	0	0
O(33)	3226 (6)	1495 (2)	0	5·2 (3)	6·3 (3)	8·2 (5)	3·0 (3)	0	0
O(34)	3439 (9)	2389 (3)	0	8·2 (7)	6·1 (4)	13·9 (8)	−3·4 (4)	0	0
O(36)	8496 (5)	432 (2)	0	2·8 (3)	3·9 (2)	9·1 (5)	−0·1 (2)	0	0
O(37)	6971 (5)	1016 (2)	0	4·7 (3)	3·5 (2)	6·9 (4)	1·3 (2)	0	0
O(38)	6653 (7)	137 (3)	0	5·5 (4)	7·3 (3)	13·5 (7)	−2·0 (4)	0	0
O(42)	7696 (6)	3497 (3)	0	6·9 (4)	5·5 (3)	9·3 (5)	−0·9 (3)	0	0
O(43)	6223 (6)	2914 (3)	0	4·2 (3)	9·2 (5)	7·6 (5)	−2·7 (4)	0	0
O(44)	8094 (9)	2621 (3)	0	9·6 (6)	7·5 (4)	13·1 (7)	5·7 (5)	0	0
O(46)	2385 (5)	4029 (2)	0	3·7 (3)	3·9 (2)	9·4 (5)	0·0 (2)	0	0
O(47)	1991 (6)	4883 (3)	0	4·9 (3)	4·7 (2)	12·8 (7)	1·7 (3)	0	0
O(48)	3878 (5)	4622 (3)	0	3·2 (3)	7·8 (4)	6·9 (4)	−2·7 (3)	0	0

Table 1 (cont.)

	x	y	z	U_{11}
H(11)	0	1800	2860	6·33
H(12)	−920	1400	2860	6·33
H(13)	−1110	1800	1430	6·33
H(14)	370	630	2860	6·33
H(15)	1300	1000	2620	6·33
H(16)	1700	490	1430	6·33
H(21)	370	4360	2860	6·33
H(22)	−680	3960	2860	6·33
H(23)	−810	4360	2140	6·33
H(24)	920	3450	2860	6·33
H(25)	780	3020	1430	6·33
H(26)	1040	3300	3810	6·33

Table 2. Bond lengths and angles

Cu(1)–N(11)	2·029 (4) Å	N(11)–Cu(1)–N(14)	87·4 (2)°
Cu(1)–N(14)	2·008 (5)	N(11)–Cu(1)–N(11′)	92·5 (2)
Cu(1)–O(32)	2·571 (5)	N(14)–Cu(1)–N(14′)	92·6 (2)
Cu(1)–O(36)	2·517 (5)	N(11)–Cu(1)–O(32)	83·8 (1)
		N(11)–Cu(1)–O(36)	92·0 (1)
		N(14)–Cu(1)–O(32)	96·0 (1)
		N(14)–Cu(1)–O(36)	88·2 (1)
		O(32)–Cu(1)–O(36)	173·9 (2)
Cu(2)–N(21)	2·020 (5)	N(21)–Cu(2)–N(24)	87·7 (2)
Cu(2)–N(24)	2·012 (5)	N(21)–Cu(2)–N(21′)	92·6 (2)
Cu(2)–O(46)	2·547 (5)	N(24)–Cu(2)–N(24′)	92·1 (2)
Cu(2)–O(42)	2·706 (7)	N(21)–Cu(2)–O(46)	94·4 (2)
		N(24)–Cu(2)–O(46)	86·2 (2)
		N(21)–Cu(2)–O(42)	79·5 (2)
		N(24)–Cu(2)–O(42)	100·0 (2)
		O(42)–Cu(2)–O(46)	171·0 (2)
N(31)–O(32)	1·204 (8)	O(32)–N(31)–O(33)	119·5 (6)
N(31)–O(33)	1·275 (8)	O(32)–N(31)–O(34)	123·6 (6)
N(31)–O(34)	1·227 (9)	O(33)–N(31)–O(34)	116·9 (7)
N(35)–O(36)	1·248 (8)	O(36)–N(35)–O(37)	120·6 (6)
N(35)–O(37)	1·234 (7)	O(36)–N(35)–O(38)	119·4 (6)
N(35)–O(38)	1·203 (9)	O(37)–N(35)–O(38)	120·0 (7)
N(41)–O(42)	1·228 (8)	O(42)–N(41)–O(43)	119·4 (6)
N(41)–O(43)	1·216 (9)	O(42)–N(41)–O(44)	118·7 (7)
N(41)–O(44)	1·235 (9)	O(43)–N(41)–O(44)	122·0 (7)
N(45)–O(46)	1·211 (7)	O(46)–N(45)–O(47)	119·5 (6)
N(45)–O(47)	1·184 (9)	O(46)–N(45)–O(48)	119·5 (6)
N(45)–O(48)	1·271 (8)	O(47)–N(45)–O(48)	121·0 (6)

O distance (< 2·45 Å) is necessary before an interaction sufficient to displace the copper ion from the nitrogen plane is found (Morosin & Howatson, 1970). The other interesting feature of the crystal packing consists of the nearly identical orientation of the nitrate ion with respect to that either above or below it. Later it is speculated that this may have an influence on the one-dimensional nature of the magnetic properties.

The N–O distances in the nitrate ions differ over the range 1·184 to 1·275 Å. Such large variations are not unusual, though, in general, trends in the N–O distance can be correlated to various aspects of the bonding network of the crystal structure, such as metal–oxygen or hydrogen bonding interactions (Morosin, 1970). In fact, distances over 1·3 Å have been reported when the O is bonded to the metal ion and the generally smaller values found in this compound suggests the Cu–O interactions are weak. The N–O distances involving O atoms not bonded to the copper ions appear to fall above the linear relationship

for N–O distance vs. O–H···O distance examined previously (Morosin, 1970); however, it is possible that in this compound there may be a weak interaction between the stacked, nearly identically oriented nitrate ions.

Employing the unrefined H positions and examining distances as well as angles, a reasonable choice for the hydrogen bonding network may be made. In Table 3, the choices for N(11) and N(14) are clear cut while those for N(21) and N(24) appear to involve bifurcated bonds [O(37a) and O(38a) for H(21); O(47d) and O(38e) for H(23); and O(37a) and possibly O(46) for H(24)].

The thermal parameters of the O atoms deviate significantly from isotropic values and the large values are consistent with the temperature-dependent diffuse scattering observed on the photographs. Of the O atoms bonded to the copper ion, O(42) involves the longest Cu–O separation and has the largest values for parameters in the ab plane.

Table 3. Probable hydrogen bonds

N(11)–O(43a)	3·101 (6) Å	N(14)–O(48a)	3·174 (6) Å
N(11)–O(46a)	3·241 (7)	N(14)–O(42a)	3·249 (7)
N(11)–O(44b)	3·063 (8)	N(14)–O(36c)	3·202 (6)
N(21)–O(37a)	3·287 (7)	N(24)–O(46)	3·139 (7)
N(21)–O(38a)	3·341 (8)	N(24)–O(32)	3·195 (6)
N(21)–O(33a)	3·018 (7)	N(24)–O(37a)	3·145 (6)
N(21)–O(47d)	3·110 (7)	N(24)–O(43a)	3·270 (7)
N(21)–O(38e)	3·251 (8)		

$$
\begin{array}{llll}
a & -\tfrac{1}{2}+x, & \tfrac{1}{2}-y, & \tfrac{1}{2}-z \\
b & -1+x, & y, & z \\
c & 1-x, & -y, & -z \\
d & -x, & 1-y, & -z \\
e & \tfrac{1}{2}-x, & \tfrac{1}{2}+y, & \tfrac{1}{2}+z
\end{array}
$$

The magnetic properties of $Cu(NH_3)_4(NO_3)_2$ are those consistent with a linear chain system (Rogers & Dempsey, 1967); however, no clear chemically linked superexchange path or chain is found in the structure. One notes, however, that the nitrate ion involves resonant structures for which the π orbital might overlap sufficiently in the similarly oriented stacked arrangement and possibly provide a weak interaction along the c direction. Such interactions are believed responsible for the one-dimensional metallic properties of some TCNQ salts (Garito & Heeger, 1974). If then the Cu(2)–O(42) distance is sufficiently longer than the remaining Cu–O distances to make this interaction ineffective as an exchange path, one would have such a one-dimensional ribbon. It is noted that such an arrangement for magnetic structure would involve two different magnetic sites which should be observable in a typical resonance experiment.

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Polytypic Structures of n-C₂₈H₅₈ (Octacosane) and n-C₃₆H₇₄ (Hexatriacontane)

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Octacosane ($C_{28}H_{58}$) and hexatriacontane ($C_{36}H_{74}$) obtained by crystallization at room temperature from light petroleum solutions are polytypic modifications of the monoclinic structures. Their structure is a stacking of alternate monoclinic layers, related one to the other by a twofold axis perpendicular to the (001) plane. Space group *Pbca*, $Z = 4$. Cell parameters $a = 7.42$, $b = 5.59$, $c = 66.50$ or 84.50 Å for $C_{28}H_{58}$ and $C_{36}H_{74}$ respectively. The paraffinic chains are regular with C–C and C–H mean distances of 1.526 and 1.00 Å. The mean C–C–C angle is 113.9°. Thermal motion is anisotropic, weak in the direction of the chain. Lateral contacts between chains are the same in this structure as in the monoclinic structure.

Introduction

In a previous growth kinetics study of n-$C_{36}H_{74}$ crystallizing from light petroleum solutions (Simon, Grassi & Boistelle, 1974) we had to identify the crystalline phase by X-ray diffraction, since two polymorphic modifications are known. With identical morphologies (rhombic platelets), the polymorphs differ only in the orientation of the paraffinic chains: in the monoclinic phase the chains are inclined relative to the (001) plane (Shearer & Vand, 1956), whereas in the orthorhombic phase they are perpendicular to this plane (Teare, 1959). The crystals obtained belonged to neither phase, but to a new orthorhombic phase, space group *Pbca* with $a = 7.42$, $b = 5.59$, $c = 84.5$ Å, $Z = 4$. By comparison of these parameters with those of the monoclinic phase, we made the hypothesis that the new phase was a polytypic modification. But, due to the low thicknesses of the crystals, it was not possible to support this hypothesis by a structure determination. The same abnormal orthorhombic phase was later obtained with n-$C_{28}H_{58}$ in another growth kinetics study (Doussoulin, 1975; Boistelle & Doussoulin, 1976). Owing to the better quality of the crystals and to their greater thickness, it was then possible to perform a structure determination. The present study is a first contribution to the problem of polytypism in n-paraffins.

Experimental data

According to the crystallization conditions (temperature, nature of the solvent, purity of the products) a given paraffin crystallizes in different polymorphic structures (Holder & Winckler, 1965; Smith, 1953). For this reason we describe exactly the experimental conditions.

Light petroleum, frequently used as a solvent for paraffins, is a comparatively complex mixture. The commercially available product (Prolabo), has a mean molar mass of 78.5 g, and contains essentially pentane, 2-methylpentane, cyclopentane, and 3-methylpentane in the proportions of 39.4, 27.4, 12.2, 8.1 moles per 100 moles of solvent. As for the paraffins, their purity is better than 95% (Fluka), the 'impurities' probably being paraffins with slightly different numbers of carbon atoms in the chain.

Morphology

Octacosane and hexatriacontane crystals, obtained at 20°C by slow evaporation or slow cooling of the solution, are (001) rhombic platelets with [110] edges, the acute angle of the lozenge being about 72°. Observation of the (001) surfaces by electron microscopy with the platinum–carbon replica technique is comparatively easy only for $C_{36}H_{74}$, owing to its higher