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## New Investigation of [(NH<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>](CuCl<sub>4</sub>)Cl at 20°C

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**Abstract.** Orthorhombic, *Pnma*;  $a = 7.1109$  (3),  $b = 23.6788$  (10),  $c = 7.3353$  (3) Å; C<sub>4</sub>H<sub>16</sub>N<sub>3</sub><sup>3+</sup>·CuCl<sub>4</sub><sup>2-</sup>·Cl<sup>-</sup>;  $Z = 4$ ;  $D_m = 1.85$  (2),  $D_x = 1.866$  (0) g cm<sup>-3</sup>;  $\mu(\text{Cu } K\alpha) = 122$  cm<sup>-1</sup>. The structure has been refined to  $R = 0.027$  for 1075 observed reflexions. All H atoms have been located, and a complex system of relatively strong N—H···Cl hydrogen bonds is described.

**Introduction.** The structure of diethylenetriammonium chlorocuprate(II) was determined originally by Ferguson & Zaslav (1971) (F&Z). It was refined to  $R = 0.10$  for 286 reflexions measured from precession photographs taken with Mo  $K\alpha$  radiation. No H atoms were located. In order to interpret the magnetic properties of this compound (Lossee & Hatfield, 1973; Larkworthy, 1974; Larkworthy & Yavari, 1976), a more accurate structure analysis was required. Crystals suitable for examination were obtained by addition of concentrated HCl to an aqueous solution of the compound until the first crystals were formed. Then, crystallization was allowed to take place by slow evaporation at room temperature, giving well formed, thin, yellow plates.

Cell dimensions were calculated by least-squares from the  $\theta$  values of the  $\alpha_1$  and  $\alpha_2$  peaks of 13 high-angle reflexions ( $\theta = 52$ – $67^\circ$ ) obtained at 20°C on a Siemens four-circle diffractometer (AED). The cell dimensions reported by F&Z at 20°C were  $a = 7.117$  (4),  $b = 23.78$  (1) and  $c = 7.342$  (4) Å, the value of  $b$  differing from that in the present investigation by more

than ten standard deviations. Diffractometer data provided 1204 intensities, of which 1075 were  $2.58\sigma$  above background (observational variances based on counting statistics) and classified as observed. Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å) and the five-value measurement method (Hoppe, 1965) with variable scan and scan speed to  $\theta = 70^\circ$  were used. A reference reflexion was measured periodically, and showed no significant change in intensity. The value of  $100\Sigma\sigma(F_o)/\Sigma(F_o)$  was 0.64% for the observed data.

Lorentz and polarization corrections were carried out. An analytical absorption correction gave maximum and minimum transmission factors for the correction of  $|F_o|$  of 0.629 (2,28,0) and 0.233 (200) respectively. Systematic absences,  $hk0$ ,  $h = 2n$ ;  $0kl$ ,  $k + l = 2n$ , indicated the space groups *Pnma* or *Pn2<sub>1</sub>a*; the former was chosen on the basis of an  $N(z)$  test (Howells, Phillips & Rogers, 1950), and confirmed by the structure analysis.

All non-hydrogen atoms were located by direct methods and refined by full-matrix least squares. The H atoms were located from a difference map and assigned isotropic temperature factors; their scattering factors were taken from Stewart, Davidson & Simpson (1965). The unrefined H parameters were considered the better estimates, since their inclusion in the least-squares calculations resulted in both chemically unreasonable N—H and C—H lengths (0.5–0.6 Å) and a rise in  $R$ . The anomalous scattering components given by Cromer & Liberman (1970) were included for Cu and Cl, as was an extinction parameter  $r^*$  (Larson, 1970). Both corrections resulted in improvements in the model.

The final refinement was carried out with the scattering factors for ionic Cu<sup>2+</sup> and Cl<sup>-</sup> (Cromer & Mann,

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1968): further significant improvements in the model suggested that they provided a better approximation than the neutral atomic species, in general agreement with Demuynck, Veillard & Wahlgren (1973) who gave formal charges on Cu and Cl in [CuCl<sub>4</sub>]<sup>2-</sup> of approximately +1.6 and -0.9 respectively. Attempts to correlate site occupancies with the charge distribution proved unsuccessful. A CNDO/2 calculation (Pople & Beveridge, 1970) for the cation in isolation gave charges of +0.08 on C(1), and C(2), -0.02 on N(2) and +0.02 on N(1). The majority of the total cationic charge resides on the H atoms which are bonded to N (see later).

The final *R* was 0.027 ( $R = \Sigma|\Delta F|/\Sigma|F_o|$ ), the function minimized being  $\Sigma w(|F_o| - |F_c|)^2$  with  $w = 1/\{1 + [(|F_o| - 10)/28]^2\}$ ; a weighting analysis confirmed the suitability of this function.

**Discussion.** The results support the overall stereochemistry described by F&Z, with the diethylenetriammonium cation and the ionic Cl(3) lying on a crystallographic mirror plane and the CuCl<sub>4</sub> anion occupying a centrosymmetric site. The Cl(2) atoms form bridges between neighbouring CuCl<sub>4</sub> anions, the Cu and Cl(2) atoms forming approximately planar networks at  $b = 0$  and  $\frac{1}{2}$ ; the Cl(1) atoms extend above and

below these planes. The shortest Cu-Cu distance is 5.108 Å, and the -Cu-Cl(2)- sheets are separated by 11.8 Å in the *b* direction. Some of the packing features may be seen in Fig. 1.

The final positional parameters for the non-hydrogen atoms are given in Table 1:\* they exhibit many significant differences from those of F&Z, the greatest of them being over forty standard deviations for the *y* coordinate of Cl(2). The difference-map H atom coordinates and their assigned values of *U* are given in Table 2; the H atom peaks were strongly represented on the difference map.

Bond distances and angles (Table 3) are in fairly good agreement with the previous values but the Cu-Cl(1) distance [F&Z: 2.276 (9) Å], the Cu-Cl(2)···Cu bridging angle [F&Z: 166.5 (2)°] and the Cl(2)-Cu-Cl(1) angle [F&Z: 88.3 (1)°] are all significantly different.

An analysis of the N-H···Cl hydrogen bonds is presented in Table 4 together with the net charge on the

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32346 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

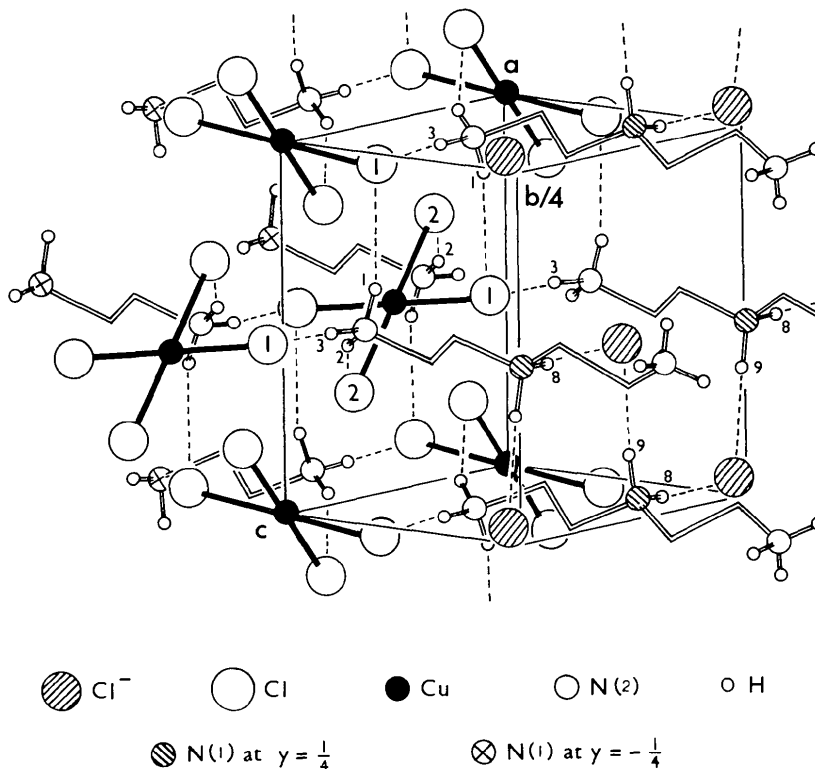


Fig. 1. Perspective drawing of a portion of the structure of [(NH<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>](CuCl<sub>4</sub>)Cl showing the hydrogen-bonding scheme: hydrogen bonds are denoted by dashed lines. All Cu atoms shown are in the plane at  $y = 0$ , and all Cl(3) atoms shown are in the *m* plane at  $y = \frac{1}{4}$ ; for clarity the CH<sub>2</sub> groups have been omitted.

H atoms obtained from a CNDO/2 calculation (Pople & Beveridge, 1970) for the cation in isolation; some details of the hydrogen bond scheme are shown in Fig. 1.

The results in Table 4 represent N...H and N...Cl distances for which the N...Cl contact is equal to or less than the sum of the corresponding van der Waals radii. They may be divided into three classes: strong bonds, of their type, for which H...Cl  $\lesssim$  2.5 Å and the average N—H—Cl = 165°, and which include the ionic Cl(3) species; bonds of lower strength, for

Table 1. Atomic coordinates, with e.s.d.'s in parentheses

	x	y	z
Cu	0	0	0
Cl(1)	0.01964 (9)	0.09562 (2)	0.04211 (8)
Cl(2)	0.23623 (7)	-0.01297 (2)	0.20638 (8)
Cl(3)	0.04914 (13)	$-\frac{1}{4}$	0.03825 (13)
N(1)	0.4832 (4)	$-\frac{1}{4}$	0.0435 (4)
N(2)	0.5176 (3)	-0.0930 (1)	-0.0219 (3)
C(1)	0.5544 (4)	-0.1969 (1)	-0.0406 (4)
C(2)	0.4615 (4)	-0.1481 (1)	0.0562 (4)

Table 2. Hydrogen positional coordinates and assigned thermal parameters ( $\times 10^2$ )

$$T = \exp[-8\pi^2 U^2 (\sin^2 \theta) / \lambda^2].$$

	x	y	z	U(Å <sup>2</sup> )
H(1)	0.480	-0.097	-0.120	4.70
H(2)	0.465	-0.063	0.025	4.70
H(3)	0.650	-0.087	-0.030	4.70
H(4)	0.490	-0.150	0.155	5.11
H(5)	0.335	-0.148	0.055	5.11
H(6)	0.525	-0.195	-0.155	4.68
H(7)	0.685	-0.195	-0.025	4.68
H(8)	0.370	$-\frac{1}{4}$	0.030	3.78
H(9)	0.510	$-\frac{1}{4}$	0.165	3.78

Table 3. Bond distances (Å) and bond angles (°) with e.s.d.'s in parentheses

Symmetry code: (i)  $\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$ ; (ii)  $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$ ;  
(iii)  $x, -\frac{1}{2} - y, z$ .

Cu—Cl(1)	2.3106 (6)	N(1)—C(1)	1.490 (3)
Cu—Cl(2)	2.2821 (6)	C(1)—C(2)	1.508 (4)
Cu—Cl(2')	2.8725 (6)	C(2)—N(2)	1.478 (3)
N(1)—H(8)	0.81	N(2)—H(3)	0.96
N(1)—H(9)	0.91	C(2)—H(4)	0.75
N(2)—H(1)	0.77	C(2)—H(5)	0.90
N(2)—H(2)	0.87	C(1)—H(6)	0.87
		C(1)—H(7)	0.94
Cl(1)—Cu—Cl(2)	90.00 (2)	C(1)—N(1)—C(1 <sup>iii</sup> )	115.3 (2)
Cl(2)—Cu—Cl(2')	89.87 (2)	N(1)—C(1)—C(2)	107.7 (2)
Cu—Cl(2)—Cu <sup>ii</sup>	164.50 (2)	C(1)—C(2)—N(2)	112.0 (2)

Table 4. N—H...Cl geometry, for N...Cl < 3.4 Å

Symmetry code (continued): (iv)  $\frac{1}{2} + x, y, \frac{1}{2} - z$ ; (v)  $1 - x, \bar{y}, \bar{z}$ ;  
(vi)  $\frac{1}{2} + x, y, \frac{1}{2} - z$ .

	H...Cl*	N—H*	$\hat{H}^*$	N...Cl	Net charge on H
N(1)—H(9)—Cl(3 <sup>iv</sup> )	2.19	0.91	175	3.104 (3)	0.23
N(1)—H(8)—Cl(3)	2.28	0.81	172	3.087 (3)	0.21
N(2)—H(3)—Cl(1)	2.36	0.96	165	3.295 (2)	0.27
N(2)—H(2)—Cl(2')	2.42	0.87	155	3.225 (2)	0.26
N(2)—H(1)—Cl(1 <sup>vi</sup> )	2.48	0.77	159	3.210 (2)	0.24†
N(2)—H(3)—Cl(2)	2.81	0.96	116	3.346 (2)	
N(2)—H(2)—Cl(2)	3.00	0.87	108	3.372 (2)	
N(2)—H(3)—Cl(2')	3.01	0.96	104	3.372 (2)	
N(2)—H(2)—Cl(2)	3.27	0.87	88	3.346 (2)	
N(2)—H(1)—Cl(2)	3.35	0.77	83	3.346 (2)	
N(2)—H(3)—Cl(1 <sup>vi</sup> )	3.37	0.96	72	3.210 (2)	
N(2)—H(1)—Cl(2')	3.56	0.77	59	3.225 (2)	
N(2)—H(1)—Cl(1)	3.60	0.77	60	3.295 (2)	
N(2)—H(2)—Cl(1 <sup>vi</sup> )	3.63	0.87	55	3.210 (2)	
N(2)—H(2)—Cl(1)	3.78	0.87	46	3.295 (2)	
N(2)—H(3)—Cl(2')	3.84	0.96	45	3.225 (2)	
N(2)—H(1)—Cl(2')	4.06	0.77	25	3.372 (2)	

\* E.s.d. approximately 0.02 Å and 1°.

† H atoms below this line repeat by symmetry.

which 2.5  $\lesssim$  H...Cl  $\lesssim$  3.5 Å and the average N—H—Cl = 95°; the other interactions listed, for which H...Cl > 3.5 Å, cannot, on account of their unreasonable geometry, be considered to be significant. It is interesting that, apart from the bridging Cl(2), each Cl is involved in two strong hydrogen bonds. It seems probable that the bridging interaction itself precludes the formation of a second significant bond to Cl(2).

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## 9-Methylrubro fusarin: 5,6-Dihydroxy-8-methoxy-2,9-dimethyl-4*H*-naphtho[2,3-*b*]pyran-4-one

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**Abstract.** C<sub>16</sub>O<sub>5</sub>H<sub>14</sub>, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 10.910 (5), *b* = 8.245 (5), *c* = 14.459 (8) Å, β = 99.24 (3)°, *Z* = 4, *U* = 1284 Å<sup>3</sup>, *D<sub>x</sub>* = 1.48 g cm<sup>-3</sup>. The structure was determined by direct methods and refined to an *R* of 0.065 for 834 unique diffractometer data. The ring system is essentially planar and there are no intermolecular hydrogen bonds.

**Introduction.** Structural studies by spectroscopic means on this natural product were not conclusive (Keogh & de Gil, 1977). The present crystallographic study was undertaken to provide information on the structure of the molecule.

A crystal 0.25 × 0.25 × 0.30 mm was mounted along *a* on a Norelco Pailred diffractometer and 2299 intensities were collected with Mo *K*α radiation (graphite monochromator). Averaging equivalent reflexions after application of *Lp* corrections gave 834 unique data with *I* > 3σ(*I*). No absorption corrections were applied. The structure was solved by direct methods, all the data being used in the calculation of the overall scale and temperature factors by Wilson's method, the *F*'s normalized in parity groups and the geometry of the molecule taken into account. The phase solution with the highest 'combined figure of merit' obtained from the application of *MULTAN* to 200 reflexions with *E* > 1.69 gave an *E* map from which the positions of all the ring atoms were obtained. The terminal atoms were found by successive Fourier syntheses. The structure was refined by full-matrix least squares with isotropic temperature factors for all the atoms in the rings (anisotropic for the terminal atoms). All the H atoms were inserted in geometrically cal-

culated positions, except those of the two hydroxyl groups which were in the positions located from a difference map. Unit weights were used throughout the refinement which finally converged to an *R* of 0.065.

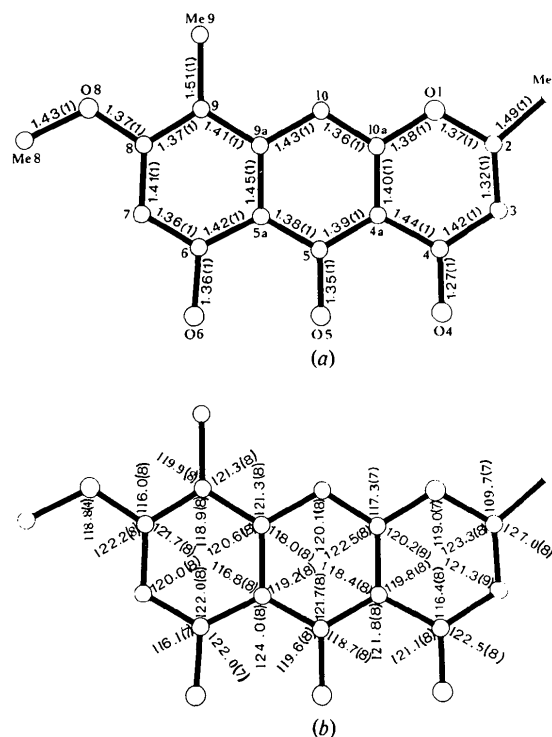


Fig. 1. (a) Bond lengths (Å) and (b) bond angles (°) for 9-methylrubro fusarin.