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The Crystal Structure of a Complex of Cupric Chloride and 1:2:4-Triazole

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The crystal structure of the 1:1 complex of cupric chloride and 1:2:4-triazole was determined in order to discover the nature of the bonding between the triazole molecules and the copper atoms. The unit-cell dimensions are:

$$a=6\cdot81,\ b=11\cdot39,\ c=7\cdot13\ \text{Å};\ \beta=96°\ 58'.$$

The space group is $I2/c$ and contains four units of $C_2N_3H_3.CuCl_2$. The copper atom has a distorted octahedral coordination group consisting of two N at 1·98 Å, two Cl at 2·34 Å, and two Cl at 2·77 Å. The structural unit is an infinite chain in which octahedral groups, joined by sharing edges, are also linked by triazole molecules.

Introduction

The 1:1 complex of cupric chloride and 1:2:4-triazole was first described by di Paolini & Goria (1932) who proposed a structure incompatible with modern ideas on the stereochemistry of divalent copper. Unit-cell dimensions were published by Sanero (1936). The present investigation was undertaken to determine the nature of the bonding between the triazole molecules and the copper atoms.

Experimental

The complex of cupric chloride and triazole, $C_2N_3H_3.CuCl_2$, was reported by Sanero (1936) to form pale-green transparent monoclinic prismatic crystals. The cell dimensions were given as

$$a=6\cdot92,\ b=11\cdot58,\ c=7\cdot24\ \text{Å};\ \beta=95°\ 41'.$$

A measured density of 2·362 g.cm.$^{-3}$ required four molecules of the complex in the unit cell.

The cell dimensions obtained in the present investigation, by measuring resolved $\alpha_1 : \alpha_2$ doublets on Weissenberg photographs, are

$$a=6\cdot81,\ b=11\cdot39,\ c=7\cdot13\ \text{Å},\ \text{with}\ \beta=96°\ 58'.$$

Systematic absences occur for reflexions with $h+k+l=2n+1$, and the only $h0l$ reflexions recorded are those with both h and l even, so that the space group is either Ic or $I2/c$.

The calculated density for four molecules of $C_2N_3H_3.CuCl_2$ is 2·462 g.cm.$^{-3}$; the density measured by flotation in a mixture of bromoform and acetone is 2·454 g.cm.$^{-3}$.

Zero-layer Weissenberg photographs about [b] and [c] were recorded, and layers 0 to 6 inclusive about [a]. The usual multiple-film and visual-estimation techniques were used to measure intensities, which were then corrected by Lorentz-polarization and rotation factors to obtain values for $F^2(hkl)$ and hence $|F(hkl)|$.

The values of $|F(hkl)|$ from the different layer-line photographs were brought to the same arbitrary scale by comparing common reflexions measured on layers about different axes.

About 610 reflexions are accessible with Cu $K\alpha$ radiation; some 55 reflexions with $h>6$ were not recorded. Of the 555 reflexions which could have been recorded on the photographs taken, 30 were too weak to measure. 10 very strong reflexions with low indices were omitted in the later stages of the least-squares refinement because of extinction, so that the final refinement is based on 515 measured hkl structure factors.

Structure determination

The systematic absences do not determine the space group uniquely, but the [a] and [b] Patterson projections indicate that the Cu and Cl atoms are in positions consistent with $I2/c$. If the Cu and Cl atoms are used to determine the phases the resulting structure will also have the symmetry of $I2/c$. If this is the true space group the triazole molecules must be in special positions, the most reasonable assumption being that they have two-fold symmetry and lie on diad axes.

If the true space group is Ic, one would expect this to become apparent firstly in attempting to refine the Cu and Cl coordinates, and secondly in the appearance of 'ghost' peaks for the atoms of the triazole molecule. Since no such difficulties appeared, and the vibration parameters are all uniform and quite small, the successful refinement confirms that the space group is $I2/c$.

Copper atoms lie at symmetry centres at $0, 0, 0$, $\frac{1}{2}, 0, 0$, $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, $0, \frac{1}{2}, \frac{1}{2}$; chlorine atoms lie in eight-fold general positions at x, y, z; $\frac{1}{2}+x, \bar{y}, z$; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}-x, y, \bar{z}$; and the positions $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$; etc. related by body-centering.

Peaks representing Cu–Cl vectors in the Patterson projections gave $x=0\cdot25$, $y=0\cdot072$, $z=0\cdot24$ as approximate Cl coordinates. The value of x was not necessarily exactly 0·25, since two peaks representing Cu–Cl vectors overlapped in the [c] Patterson projection. A portion of a three-dimensional Patterson section at $y=0{\cdot}072$ gave more accurate values of $x=0{\cdot}233$, $z=0{\cdot}240$ for Cl.

The geometrical structure factors for $I2/c$ are:

$$A(h\text{ even}) = +8\cos 2\pi(hx+lz)\cos 2\pi ky\,,$$
$$A(h\text{ odd}) = -8\sin 2\pi(hx+lz)\sin 2\pi ky\,.$$

Thus Cu at 0, 0, 0, etc., always makes a maximum positive contribution to structure factors with h even, and it may be assumed that large structure factors of this type are positive. Copper makes no contribution to structure factors with h odd, so that these signs must be deduced from the chlorine contributions. Since x and z for Cl are each about 0·25, the Cl contribution to structure factors with h odd is small unless l is even. Thus most of the structure factors with h even, and rather fewer than half of those with h odd, have their signs determined by Cu and Cl.

An [100] electron-density projection in which all the $F(0kl)$ were assumed to be positive indicated that the triazole molecules lay in the planes $z=0$, $z=\frac{1}{2}$, presumably on the diad axes at $\frac{1}{4}, y, 0$; etc. An [001] projection confirmed this since peaks with the same y-coordinates as in the [100] projection were observed in positions corresponding to two overlapping five-membered rings so that approximate values of x-coordinates for the light atoms could be measured.

With the aid of the light atom coordinates it was possible to derive the signs of most of the structure factors; refinement of the light atom and chlorine coordinates was continued by means of three-dimensional lines and sections and eventually by a three-dimensional least-squares method on the Dyestuffs Division 'Pegasus' computer.

The programmes for the least-squares refinement were written by D. W. J. Cruickshank of Leeds University and enabled anisotropic temperature factors to be refined for the copper and chlorine atoms, and individual isotropic temperature factors for the carbon and nitrogen atoms. The final agreement factor for $515F(hkl)$ was $R=10{\cdot}3\%$.

The atomic coordinates from the final cycle of refinement are given in Table 1. The estimated standard deviation for the coordinates of the Cl atom is 0·002 Å, and for the C and N atoms it is 0·01 Å.

Table 1. *Atomic coordinates*

Atom	x	y	z
Cu	0·000 Å	0·000 Å	0·000 Å
Cl	1·586	−0·824	1·710
N_1	1·012	1·706	0·029
C	0·666	2·951	0·047
N_2	1·702	3·746	0·000

The final values of the thermal vibration parameters are given in Table 2 and Table 3. In Table 2 the U_{ij} are the components (in Å²) of the mean square vibration-amplitude tensor referred to the reciprocal axes. In Table 3 the values of U are the mean square amplitudes (in Å²) of the isotropic vibration.

Table 3. *Isotropic thermal parameters* (*in* Å²)

Atom	N_1	C	N_2
U	0·0083	0·0141	0·0177

The value of $U=0{\cdot}0177$ Å² for N_2 corresponds to a value of $B=1{\cdot}4$ Å².

Description of the structure

Fig. 1 shows the unit cell of the structure projected down the c-axis. The smaller and larger solid black

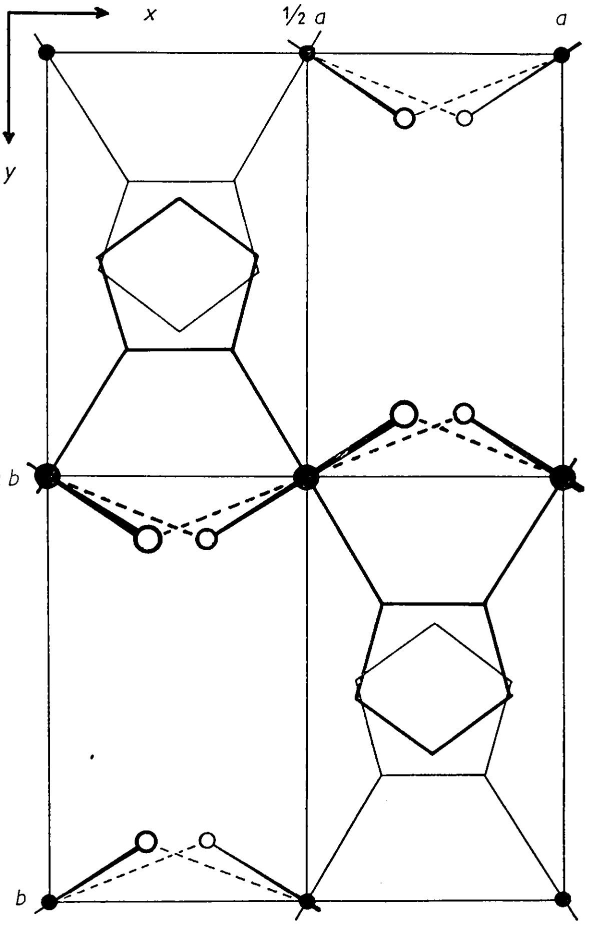

Fig. 1. Triazole–$CuCl_2$: c-axis projection; Cl atoms (open circles) displaced in [a]-direction to avoid overlapping.

Table 2. *Anisotropic thermal parameters* (*in* Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu	0·0168	0·0093	0·0185	−0·0032	0·0070	−0·0013
Cl	0·0180	0·0106	0·0082	−0·0002	0·0099	−0·0030

circles represent Cu atoms at $z=0$, $z=\frac{1}{2}$, respectively, and the thinner and thicker pentagons represent triazole molecules lying very nearly in the planes $z=0$, $z=\frac{1}{2}$. The three kinds of open circles represent, in order of increasing size, Cl atoms near to $z = -\frac{1}{4}, +\frac{1}{4}, +\frac{3}{4}$ respectively; since $z=0{\cdot}240$ for Cl the medium circles near $y=\frac{1}{2}$ are at $z=0{\cdot}260$, and those near $y=0$, $y=1$ are at $z=0{\cdot}240$.

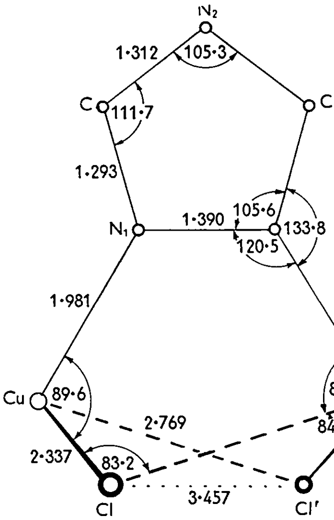

Fig. 2. Triazole–$CuCl_2$: bond-lengths (in Å) and bond-angles (in degrees).

Bond-lengths and bond-angles are shown in Fig. 2. The copper atoms, at centres of symmetry, have an octahedral coordination group consisting of two N atoms at 1·98 Å, two Cl atoms at 2·34 Å, and two Cl atoms at 2·77 Å.

The structural unit, shown diagrammatically in Fig. 3, is an infinite chain parallel to the *c*-axis, in which coordination octahedra are joined by sharing edges containing two Cl atoms. The octahedra are also linked along the chain through the vertices formed by the N atoms, since vertices of adjacent octahedra are occupied by adjacent N_1 atoms of one triazole molecule.

The direct link Cu–N–N–Cu distinguishes the chain of the triazole: $CuCl_2$ complex from otherwise similar chains found in such compounds as $CuCl_2.2H_2O$ (Harker, 1936), $CuCl_2(pyr)_2$ (Dunitz, 1957) etc.

As can be seen from Fig. 1, the triazole molecules of adjacent chains are parallel, with intermolecular contacts ranging from 3·53 Å ($N_1 \cdots N_2$) to 3·99 Å ($N_2 \cdots N_2$). Atom N_2 makes contacts of 3·33 Å with Cl atoms of two neighbouring chains and there are Cl ··· Cl contacts of 3·69 and 4·06 Å between Cl atoms of neighbouring chains in the *c*- and *b*-axis directions respectively.

The triazole molecules are symmetrical and lie on diad axes. They are planar to within 0·002 Å, but the plane of the molecule is twisted by $2\frac{1}{2}°$ about the diad axis out of the plane $z=0$. The simplest formulation of the triazole molecule consistent with the space group symmetry would have double bonds $N_1=C$ and $N_1'=C'$, but the lengths of $C–N_2$, $C'–N_2$, which are very little longer than $N_1–C$, indicate that these bonds also have considerable double-bond character.

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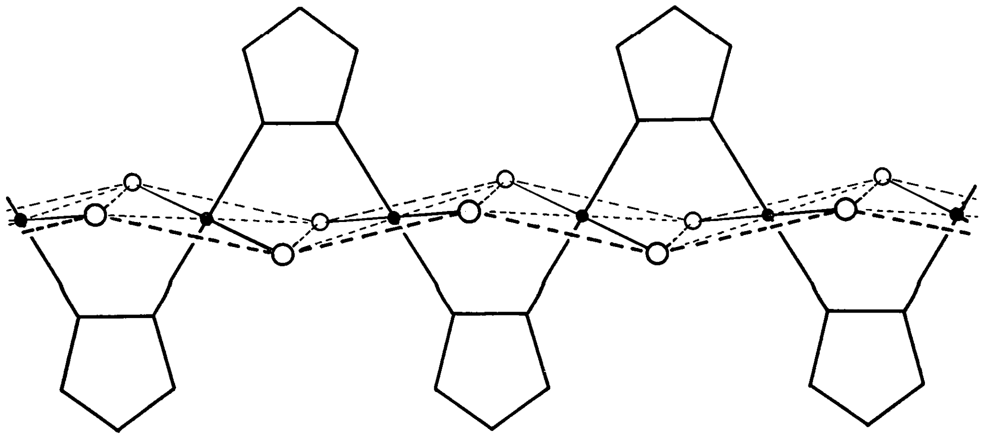

Fig. 3. Triazole–$CuCl_2$: structural unit.