Acta Cryst. (1960). **13**, 28

The Crystal Structure of the Cuprous Chloride Azomethane Complex

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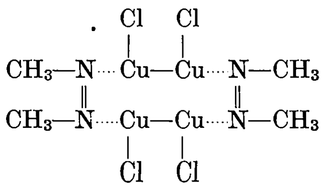
(*Received* 11 *May* 1959)

The structure of the cuprous chloride azomethane complex has been determined by an X-ray analysis in which the final parameters were evaluated from a least-squares treatment of the three-dimensional data. The crystal are triclinic, $a = 6{\cdot}87$, $b = 7{\cdot}03$, $c = 3{\cdot}82$ Å, $\alpha = 97^\circ\ 7'$, $\beta = 95^\circ\ 15'$, $\gamma = 111^\circ\ 45'$; space group $P\bar{1}$, with one formula unit ($Cu_2Cl_2 . C_2H_6N_2$) in the unit cell. The complex contains infinite copper–chlorine chains (Cu–Cl: 2·35 Å), running parallel to the c axis, which are joined in pairs by weaker copper–chlorine bonds (2·55 Å). The chains are further linked through *trans*-azomethane molecules by σ-type copper–nitrogen bonds (1·99 Å), which complete a distorted tetrahedral coordination around each copper atom.

Introduction

The red compound of composition CH_3NCuCl, formed by cuprous chloride and azomethane, was first prepared in crystalline form by Diels & Koll (1925) who drew attention to its similarity to the coloured intermediates observed during the course of the Sandmeyer reaction, and assigned to it the structure (I).



(I)

We have now determined its crystal structure. As suggested by Diels & Koll (1925), the azomethane molecules link pairs of copper atoms through Cu–N bonds. The cuprous chloride, however, exists not as discrete dimeric molecules but in the form of double-stranded infinite chains of alternating copper and chlorine atoms which bear a certain resemblance to the infinite three-dimensional network of cuprous chloride itself.

Crystal data

Cuprous chloride:
azomethane complex, $Cu_2Cl_2 . C_2H_6N_2$.
Triclinic, $a = 6{\cdot}867 \pm 0{\cdot}018$, $b = 7{\cdot}029 \pm 0{\cdot}018$, $c = 3{\cdot}821 \pm 0{\cdot}014$ Å; $\alpha = 97^\circ\ 7' \pm 3'$, $\beta = 95^\circ\ 15' \pm 6'$, $\gamma = 111'\ 45^\circ \pm 7'$.
Volume of unit cell $= 169 \pm 2$ Å^3.
Density (measured) $= 2{\cdot}48 \pm 0{\cdot}10$ g.cm.$^{-3}$.
Density (calculated) $= 2{\cdot}51 \pm 0{\cdot}03$ g.cm.$^{-3}$.
One formula unit per unit cell.
Systematic absences: None.
Space group: $P\bar{1}$ (assumed).
Absorption coefficient for Cu $K\alpha$ radiation $= 135{\cdot}5$ cm.$^{-1}$.

Experimental

The compound, prepared according to the method of Diels & Koll (1925), crystallized in the form of red laths which were mostly only a few microns thick and invariably slightly bent. The specimen on which most of the X-ray work was performed had a cross section of 0·08 mm. × 0·01 mm. normal to the needle axis. The cell constants were determined from precession and Weissenberg photographs calibrated against quartz ($a_0 = 4{\cdot}9126$ Å), aluminium ($a_0 = 4{\cdot}0489$ Å), and sodium chloride ($a_0 = 5{\cdot}6401$ Å); the density was measured by flotation in a mixture of chloroform and bromoform.

Because of the shape of the crystals, it was feasible to mount them only about the needle axis, c, for intensity measurements. Multiple film equi-inclination Weissenberg photographs were taken of the $hk0$, $hk1$ and $hk2$ layers. Integrated intensities of the $hk0$ reflexions with $\theta < 45^\circ$ were measured on the proportional-counter diffractometer developed in this laboratory by Arndt & Phillips (1957). Since the intensities obtained in this way are subject to the same Lorentz and polarization corrections as those on a zero-layer Weissenberg photograph, they were used to calibrate directly an $hk0$ film which was then used as a wedge in the visual estimation of the remaining reflexions by comparing spots of roughly the same size, shape, and intensity. In practice, this proved invaluable since the curvature of the crystal caused a wide variation in spot shape. Oscillation photographs were used to bring the relative intensities of reflexions in different layers to a common scale. For the final refinement, more accurate scaling was achieved by comparing the intensities of about 16 reflexions from each layer with those measured on the proportional-counter diffractometer. Lorentz and polarization corrections were applied to all intensities but no correc-

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tions were made for absorption. Copper $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å) was used throughout.

Structure analysis

The extreme shortness of the c axis enabled us to derive the structure from the Patterson projection $P(u, v)$ and from the generalized Patterson projections involving $hk1$ reflexions. For the projection $P(u, v)$, the observed values of $F^2(hk0)$ were converted to unitary structure factors and multiplied by

$$\exp\left(-2{\cdot}3\sin^2\theta\right).$$

The origin peak was removed. In the resulting function (Fig. 1) the four large peaks corresponding to Cu–Cu, Cu–Cl (twice) and Cl–Cl interactions are very prominent. The eight peaks corresponding to the interactions Cu–N, Cu–C, Cl–N, Cl–C (all twice) can also be recognised. Approximate x and y coordinates of all atoms (excluding hydrogen) were thus derived and subsequently refined by Fourier and difference-synthesis methods.

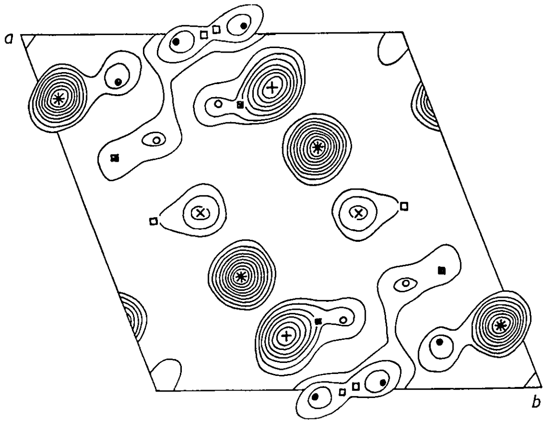


Fig. 1. Patterson projection P(u, v), contour intervals on arbitrary scale. The origin peak has been removed. The various interactions are shown as follows: Cu–Cu (+), Cl–Cl (×), Cu–Cl (✱), Cu–N (●), Cu–C (■), Cl–N (○), Cl–C (□).

To obtain the z coordinates, the generalised Patterson functions

$$
\begin{aligned}
{}_cP_1(u, v) &= \int_0^1 P(u, v, w)\,.\cos 2\pi w\,.\,dw \\
&= \frac{1}{A}\sum_{-h}^{+h}\sum_{-k}^{+k}|F(hk1)|^2\cos 2\pi(hu+kv) \\
{}_sP_1(u, v) &= \int_0^1 P(u, v, w)\,.\sin 2\pi w\,.\,dw \\
&= \frac{1}{A}\sum_{-h}^{+h}\sum_{-k}^{+k}|F(hk1)|^2\sin 2\pi(hu+kv)
\end{aligned}
$$

were computed with unmodified values of $F^2(hk1)$. Since the u and v coordinates of the vector peaks were known, the w coordinate of the peak at (u_1, v_1, w_1) could be found from the relation

$$w_1 = (1/2\pi)\tan^{-1}({}_sP_1(u_1, v_1)/{}_cP_1(u_1, v_1))\,.$$

The present case, with only eight atoms in the unit cell, is very favourable for resolution and indeed the w components of all but one of the twelve vectors appearing in $P(u, v)$ could be estimated directly from the maps (Fig. 2). From this information the z coordinates of all the atoms were derived.

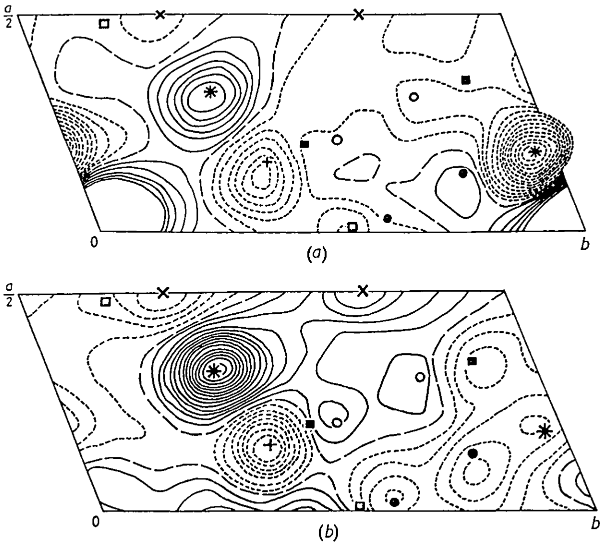


Fig. 2. Generalized Patterson projections (a) ${}_cP_1(u, v)$ and (b) ${}_sP_1(u, v)$. Contour intervals on arbitrary scale. Identification of interactions as in Fig. 1.

At this stage, the calculation of structure factors for a few general hkl planes indicated that the coordinates were sufficiently accurate to warrant proceeding directly to a three-dimensional refinement by the method of least squares. It was thought advisable, however, because of the wide variation in the quality of the intensity measurements derived from different sources, first to assign weights (indicated in Table 1) to the observed data in accordance with *a priori* estimates of their reliability. In assigning these

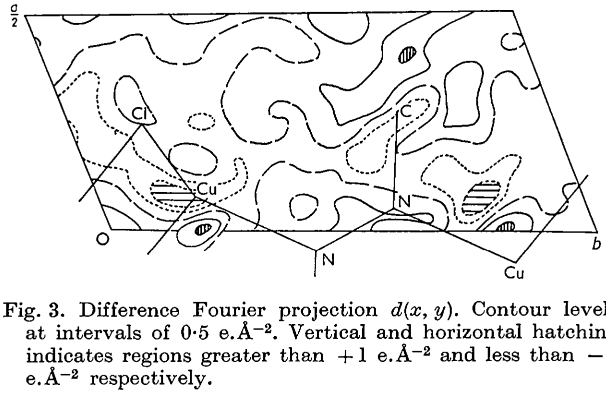


Fig. 3. Difference Fourier projection $d(x, y)$. Contour levels at intervals of 0·5 e.Å^{-2}. Vertical and horizontal hatching indicates regions greater than +1 e.Å^{-2} and less than −1 e.Å^{-2} respectively.

Table 1. *Observed and calculated structure factors*

The weight *w* was used in the expression $S=\Sigma w^2|\Delta F|^2$ for the quantity minimized by the least-squares analysis

k	*w*	F_o	F_c
0*k*0			
1α	30	19·0	+21·5
2α	22	39·0	−39·4
3α	22	39·2	−38·2
4α	30	13·5	−12·4
5α	30	17·3	+15·8
6	26	11·4	+9·4
7	6	<2	+1·8
8	19	1·6	−2·2
1*k*0			
−8	6	<2	−1·1
−7	2	<3	+0·2
−6α	30	3·7	+3·1
−5α	30	9·8	+9·4
−4α	30	21·3	−22·0
−3α	24	28·1	−27·6
−2α	28	23·9	+21·8
−1α	20	37·2	+39·7
0α	15	50·6	+54·8
1α	24	23·9	−24·8
2α	17	55·1	−59·0
3α	30	19·2	−19·8
4α	30	16·6	+15·3
5α	24	22·6	+22·0
6	25	3·4	+3·1
7	19	3·9	−3·7
2*k*0			
−8	19	5·8	−6·1
−7	2	<3	−1·0
−6α	30	4·0	+2·8
−5α	30	14·0	+13·9
−4α	30	7·1	−6·7
−3α	30	21·5	−22·5
−2α	30	21·0	+20·5
−1α	28	25·4	+21·2
0α	30	4·5	0·0
1α	22	35·3	−33·7
2α	30	20·2	−22·0
3α	30	12·0	+9·0
4α	30	19·2	+17·9
5	25	9·8	+11·0
6	19	6·0	+6·8
7	19	6·0	−6·8
3*k*0			
−8	25	8·3	−7·9
−7	25	7·2	−8·7
−6α	30	17·0	+15·3
−5α	30	11·9	+9·5
−4α	30	14·6	−13·7
−3α	26	30·6	−28·8
−2α	30	1·6	+0·5
−1α	30	15·1	+16·6
0α	30	14·2	+11·0
1α	30	15·6	−15·5
2α	30	2·8	−4·1
3α	30	12·2	+12·3
4	2	<3	+2·7
5	19	2·7	−1·6
6	19	4·8	−5·2
4*k*0			
−8	6	<2	−0·3
−7	25	14·9	+15·5
−6α	30	15·6	+14·2
−5α	30	8·3	−9·8
−4α	20	33·5	−32·8
−3α	30	20·5	−18·0
−2α	30	22·1	+22·2
−1α	30	22·9	+23·1
0α	30	15·6	+12·2
1α	30	10·1	−10·8
2α	30	12·9	−12·3
3	25	2·8	+3·2
4	19	2·8	−0·1
5	6	<2	−1·3
5*k*0			
−8	23	4·4	+5·5
−7	19	10·4	+9·8
−6	25	2·8	−2·8
−5α	30	18·2	−18·5
−4α	30	17·7	−20·8
−3α	30	3·9	+4·6
−2α	20	36·1	+37·2
−1α	30	15·3	+14·4
0α	30	10·8	−11·8
1α	30	15·3	−17·2
2	25	11·3	−9·2
3	19	4·0	+4·0
4	19	5·0	+4·9
6*k*0			
−8	19	1·6	+2·1
−7	19	3·4	+3·8
−6	19	7·1	−8·6
−5	25	10·7	−11·2
−4	25	2·8	+3·8
−3α	30	12·2	+13·0
−2α	30	16·6	+17·7
−1α	30	4·2	−3·3
0	25	18·1	−19·5
1	25	7·9	−9·0
2	19	4·0	+4·2
3	19	7·1	+7·9
7*k*0			
−7	19	1·9	+4·0
−6	2	<3	−1·1
−5	19	4·0	−5·4
−4	21	5·4	+5·6
−3	27	5·0	+6·5
−2	3	<3	−1·4
−1	19	7·5	−8·2
0	19	6·0	+6·2
1	19	2·8	+1·9
2	19	4·5	+6·3
8*k*0			
−6	6	<2	−0·3
−5	19	4·0	−5·4
−4	6	<2	−1·9
−3	6	<2	+2·3
−2	6	<2	+0·6
−1	6	<2	−2·5
0	19	2·9	+1·1
−8*k*1			
0	5	<2	−2·7
1	16	9·3	−11·6
2	16	4·4	−5·6
3	16	3·4	+5·6
4	18	8·4	+10·2
5	2	<3	+5·0
6	16	2·5	−2·6
−7*k*1			
−2	5	<2	+0·6
−1	2	<3	−1·9
0	18	4·8	−6·1
1	20	6·8	−7·7
2	3	<3	+2·0
3	22	13·0	+15·1
4	22	11·2	+12·2
5	20	6·6	−8·7
6	18	9·5	−11·1
7	16	2·5	−3·3
−6*k*1			
−3	2	<3	−2·2
−2	3	<3	+1·5
−1	2	<4	+1·5
0	2	<4	−4·6
1	3	<4	−0·2
2	22	8·3	+8·7
3	22	5·6	+6·1
4	2	<4	+3·2
5	22	12·5	−13·4
6	22	9·9	−11·7
7	16	4·8	+6·2
8	16	7·0	+6·6
−5*k*1			
−5	16	3·4	−5·1
−4	16	4·4	−6·2
−3	3	<3	+2·6
−2	22	9·4	+10·8
−1	22	11·2	+10·6
0	22	7·6	−9·9
1	22	14·1	−14·4
2	22	7·2	+8·9
3	22	4·4	+3·9
4	3	<3	−2·1
5	22	5·2	−4·7
6	3	<3	−3·3
7	16	8·0	+6·9
8	16	4·5	+4·3
−4*k*1			
−5	16	5·2	−7·3
−4	2	<3	+1·3
−3	16	19·5	+20·7
−2	22	12·7	+13·6
−1	22	6·0	−7·5
0	18	27·6	−26·8
1	18	27·6	−25·8
2	22	17·3	+20·2
3	18	26 2	+22·8
4	19	2·5	+0·9
5	16	7·7	−7·8
6	16	4·8	−3·4
7	16	3·9	+3·2
8	1	<4	−1·1
−3*k*1			
−6	16	3·4	−4·0
−5	3	<3	+1·4
−4	22	10·7	+9·9
−3	18	22·0	+23·8
−2	22	4·8	−3·4
−1	18	42·7	−44·2
0α	26	30·0	−29·6
1	22	9·7	+9·3
2	11	45·0	+46·7
3α	30	24·0	+23·4
4	19	12·8	−11·0
5	19	19·8	−21·3
6	16	6·4	−8·4
7	16	8·6	+7·8
−2*k*1			
−7	2	<3	−0·2
−6	2	<3	−2·2
−5	20	6·8	+6·3
−4	22	8·5	+7·4
−3	22	3·6	+5·6
−2	16	22·0	−20·3
−1α	20	42·7	−42·6
0α	30	2·0	+1·3
1α	20	49·6	+49·0
2α	20	49·6	+51·0
3	20	14·4	−15·0
4	13	33·8	−34·2
5	16	13·1	−13·6
6	16	3·4	+1·1
7	16	14·9	+13·6
−1*k*1			
−8	5	<2	+3·3
−7	3	<3	+0·4
−6	23	7·7	−8·1
−5	2	<4	−0·3
−4	22	6·8	+6·8
−3	22	3·8	+4·1
−2α	30	16·9	−17·1
−1	22	11·1	−12·6
0α	26	30·0	+30·7
1	22	22·6	+24·7
2α	30	13·7	+15·6
3	28	31·5	−32·3
4	28	31·5	−31·7
5	20	8·6	+8·7
6	18	14·4	+13·3
7	16	9·4	+8·0
0*k*1			
−8	3	<2	−0·2
−7	22	7·7	−7·4
−6	22	13·0	−12·4
−5	21	4·8	+5·4
−4	21	18·0	+20·0
−3α	30	21·5	+18·3
−2α	30	12·6	−17·4
−1	4	33·8	−31·8
0α	24	25·5	+23·9
1	7	<2	+3·0
2	22	6·0	−5·5
3α	30	12·2	−11·8
4	22	8·7	−8·9
5	20	12·6	+13·3
6	16	7·9	−8·1
7	1	<4	−1·1
1*k*1			
−8	16	6·7	−6·4
−7	18	10·1	−11·1
−6	18	3·9	−2·6
−5	18	26·2	+27·4
−4	18	24·6	+24·5

Table 1 (*cont.*)

k	*w*	F_o	F_c
−3	22	5·8	−6·1
−2α	20	36·6	−37·6
−1	10	53·6	−50·4
0α	24	26·2	+25·4
1	18	28·8	+30·6
2α	30	3·4	+1·4
3	22	5·1	−6·3
4	22	5·1	−4·0
5	1	< 6	+4·1
6	1	< 5	−1·0
7	3	< 3	−2·0
2*k*1			
−8	15	7·9	−6·4
−7	3	< 3	−1·5
−6	12	8·4	+9·3
−5	18	27·3	+29·6
−4	22	6·9	+4·1
−3	16	46·3	−46·4
−2	6	40·6	−37·3
−1α	30	4·5	−1·9
0α	20	48·0	+46·8
1α	30	31·1	+31·5
2	22	5·5	−7·1
3	22	17·4	−18·0
4	22	8·5	−9·7
5	1	< 5	+4·0
6	2	< 4	+1·1
3*k*1			
−8	16	2·6	−3·5
−7	16	5·6	+5·0
−6	16	8·5	+8·5
−5	16	8·5	+8·3
−4	16	13·4	−13·1
−3α	26	33·8	−38·0
−2	22	5·2	−5·9
−1	10	37·1	+33·9
0	10	39·0	+40·3
1	1	< 5	−2·6
2	16	22·4	−24·3
3α	30	14·9	−13·5
4	2	< 3	−1·8
5	16	8·5	+8·9
6	2	< 3	+4·3
4*k*1			
−8	16	5·6	−5·4
−7	2	< 3	+0·5
−6	22	4·8	+4·9
−5	22	2·9	+1·0
−4	22	10·6	−10·1
−3	23	11·4	−10·8
−2	19	15·9	+12·7
−1	17	20·7	+18·8
0	16	9·0	+9·2
1	16	16·2	−16·7
2	16	16·2	−19·5
3	1	< 5	+2·7
4	16	8·2	+7·9
5	1	< 3	+5·7
5*k*1			
−8	16	7·7	−6·7
−7	3	< 3	+0·7
−6	22	8·8	+8·7
−5	22	8·9	+7·2
−4	22	4·9	−5·5
−3	22	9·5	−9·3
−2	23	8·0	+7·2

k	*w*	F_o	F_c
−1	1	< 6	+2·6
0	1	< 6	−4·0
1	1	< 6	−5·3
2	1	< 5	−3·1
3	22	6·7	+6·5
4	2	< 3	+4·9
6*k*1			
−8	16	3·4	−2·2
−7	16	8·3	+8·7
−6	18	10·2	+9·9
−5	2	< 4	+0·9
−4	20	9·1	−9·8
−3	19	14·5	−13·8
−2	1	< 6	+3·2
−1	16	5·5	+7·4
0	1	< 5	+0·8
1	1	< 5	+0·7
2	1	< 4	+0·6
3	2	< 3	+0·9
7*k*1			
−7	16	7·4	+9·3
−6	2	< 4	+3·1
−5	21	8·9	−10·5
−4	22	9·5	−10·1
−3	20	5·7	−2·7
−2	20	8·6	+8·4
−1	20	9·5	+9·5
0	2	< 4	+1·0
1	3	< 3	−3·8
8*k*1			
−6	2	< 3	−2·4
−5	16	6·7	−8·7
−4	16	4·4	−2·6
−3	16	5·2	+6·9
−2	16	7·3	+8·3
−1	2	< 3	+1·0
−8*k*2			
1	5	< 2	+0·9
2	2	< 3	+2·0
3	2	< 3	−0·7
4	2	< 3	−0·1
5	5	< 2	+1·5
−7*k*2			
−2	5	< 2	−2·4
−1	15	6·4	+7·0
0	15	9·6	+11·2
1	2	< 3	−0·6
2	15	9·5	−10·1
3	15	6·1	−5·6
4	2	< 3	+2·8
5	2	< 3	+0·8
6	2	< 3	+2·2
−6*k*2			
−3	5	< 2	−0·6
−2	15	7·0	+8·7
−1	15	11·3	+12·8
0	2	< 3	+1·7
1	15	13·7	−14·0
2	15	18·0	−17·3
3	1	< 5	−3·9
4	15	15·0	+18·3
5	15	8·4	+8·5

k	*w*	F_o	F_c
6	2	< 3	−4·1
7	5	< 2	−1·4
−5*k*2			
−4	5	< 2	+0·8
−3	15	5·9	+4·6
−2	15	7·5	+9·7
−1	20	6·5	+6·8
0	20	16·5	−16·1
1	16	27·6	−25·1
2	3	< 3	+1·2
3	20	15·1	+14·5
4	20	19·6	+20·6
5	1	< 5	+4·3
6	15	15·0	−14·9
7	15	7·2	−7·0
−4*k*2			
−5	5	< 2	+0·7
−4	2	< 3	−2·0
−3	15	3·7	+2·8
−2	2	< 3	+0·8
−1	3	< 3	−1·5
0	20	11·7	−11·4
1	20	18·0	−16·5
2	20	18·5	+19·0
3	17	23·4	+23·6
4	20	5·7	+2·7
5	15	13·2	−12·8
6	15	15·7	−14·0
7	2	< 3	−0·4
−3*k*2			
−6	15	3·1	+2·3
−5	15	4·2	−4·9
−4	15	12·7	−12·4
−3	3	< 3	+3·3
−2	20	9·3	+10·2
−1	3	< 3	+1·7
0	3	< 3	−1·6
1	20	10·8	−8·8
2	20	10·9	+10·3
3α	30	10·3	+10·1
4	20	7·2	−6·4
5	15	14·7	−13·2
6	2	< 3	−4·6
7	15	8·8	+9·6
−2*k*2			
−7	15	2·5	+2·2
−6	18	7·2	−6·9
−5	20	11·3	−11·4
−4	22	9·8	−8·7
−3	22	17·8	+18·8
−2α	18	29·7	+29·3
−1	20	2·3	−2·8
0	16	23·4	−22·6
1α	30	21·1	−18·8
2	20	7·8	+9·0
3	20	9·8	+6·7
4	1	< 5	−0·1
5	1	< 5	−0·6
6	1	< 5	−2·5
7	15	6·0	+6·1
−1*k*2			
−7	5	< 2	−2·5
−6	20	12·7	−12·6
−5	20	7·0	−5·5

k	*w*	F_o	F_c
−4	20	12·8	+13·2
−3	18	29·4	+31·4
−2α	30	16·2	+13·8
−1	15	32·5	−32·6
0	13	39·6	−39·7
1	20	11·3	−12·8
2α	24	30·6	+32·6
3	20	18·3	+19·6
4	20	6·0	−4·3
5	1	< 5	−2·5
6	15	6·0	−5·7
7	2	< 3	0·0
0*k*2			
−8	5	< 2	−0·7
−7	3	< 3	−2·1
−6	20	6·0	−6·4
−5	20	5·9	+5·4
−4	20	16·2	+19·6
−3	20	16·8	+18·2
−2α	30	19·5	−20·0
−1	5	45·1	−50·7
0	20	10·9	−8·4
1	12	22·1	+21·7
2	14	29·7	+36·0
3α	30	10·1	+11·1
4	20	19·8	−19·9
5	15	10·8	−10·5
6	2	< 3	−1·9
1*k*2			
−8	5	< 2	+1·8
−7	3	< 3	+0·1
−6	20	4·2	−4·1
−5	20	6·5	+5·2
−4	20	5·6	+7·3
−3	20	3·1	−0·5
−2α	30	17·9	−18·3
−1	12	28·0	−28·7
0α	24	23·0	+21·2
1	14	30·1	+32·8
2α	30	8·3	+8·8
3	18	11·7	−12·0
4	15	17·5	−19·3
5	1	< 5	−2·9
6	15	5·4	+5·2
2*k*2			
−8	15	2·7	+2·3
−7	15	3·0	−4·0
−6	18	11·3	−11·4
−5	20	5·6	+2·6
−4	20	9·5	+10·0
−3	20	3·3	+0·1
−2	5	< 2	−2·9
−1α	30	8·7	−8·7
0α	30	13·2	+12·1
1α	30	11·7	+12·1
2	20	9·6	−7·3
3	20	12·7	−12·9
4	2	< 3	−5·5
5	15	7·0	+7·4
3*k*2			
−8	15	4·4	−4·4
−7	20	8·7	−9·0
−6	20	8·6	−8·5
−5	20	9·9	+11·4
−4	14	20·1	+21·5
−3	3	< 3	+0·5

Table 1 (*cont.*)

k	w	F_o	F_c	k	w	F_o	F_c	k	w	F_o	F_c	k	w	F_o	F_c
−2	20	11·3	−12·2	−4	20	13·5	+11·9	−5	20	9·5	+9·2	−4	22	6·4	−6·7
−1	22	14·4	−12·2	−3	20	14·0	−13·6	−4	20	6·0	−6·0	−3	20	8·7	−9·0
0	3	< 3	+2·6	−2	18	22·3	−21·3	−3	20	17·2	−19·7	−2	20	6·9	+5·6
1	3	< 3	+3·6	−1	20	11·3	−9·1	−2	20	7·4	−7·7	−1	20	10·3	+11·5
2	3	< 3	−1·6	0	20	10·8	+11·9	−1	20	5·9	+7·0	0	20	2·8	+4·1
3	3	< 3	0·0	1	20	10·2	+10·7	0	20	13·4	+14·8	1	15	2·3	−3·1
4	7	< 2	+0·2	2	3	< 3	+0·6	1	20	7·5	+7·3				
5	5	< 2	+4·4	3	7	< 2	+0·4	2	20	5·1	−6·1	7k2			
				4	5	< 2	−2·6	3	5	< 2	−5·0	−6	5	< 2	+1·6
4k2												−5	5	< 2	−0·5
−8	15	7·7	−8·2	5k2				6k2				−4	5	< 2	−0·1
−7	20	6·0	−5·3	−8	15	4·2	−4·2	−7	5	< 2	+1·9	−3	5	< 2	−0·5
−6	20	6·0	+5·7	−7	7	< 2	+1·5	−6	20	2·8	+3·1	−2	15	2·8	+3·4
−5	20	17·0	+17·6	−6	20	9·3	+9·7	−5	3	< 3	−4·7	−1	15	2·2	+3·2

The intensities of reflections labelled α were measured on the proportional-counter diffractometer

Table 2. *Positional parameters from the final least-squares analysis*

Origin at centre of symmetry

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Copper	0·0737	0·1932	−0·1655	0·003 Å	0·003 Å	0·004 Å
Chlorine	0·2486	0·1462	0·3604	0·005	0·005	0·005
Nitrogen	−0·0477	0·4030	−0·0201	0·016	0·013	0·016
Carbon	−0·2665	0·3207	0·0494	0·019	0·020	0·024

Table 3. *Anisotropic temperature-factor parameters*

	B_{hh}	B_{kk}	B_{ll}	B_{hk}	B_{kl}	B_{lh}
Copper	0·0419	0·0442	0·1062	0·0433	0·0187	0·0298
Chlorine	0·0337	0·0395	0·0699	0·0272	0·0070	0·0232
Nitrogen	0·0463	0·0290	0·0707	0·0331	−0·0119	0·0285
Carbon	0·0286	0·0432	0·1322	0·0395	−0·0211	0·0605
Isotropic $B = 4·04$ Å^2	0·0364	0·0350	0·1030	0·0278	0·0202	0·0178

The temperature factor is expressed in the form:

$$2^{-(B_{hh}h^2+B_{kk}k^2+B_{ll}l^2+B_{hk}hk+B_{kl}kl+B_{lh}lh)}\,.$$

weights, we were guided by the following considerations:—intensities which were measured on the proportional-counter diffractometer or which had been subject to several independent measurements were regarded as especially reliable. On the other hand, low weight was given to reflexions of poor shape, whether due to the curvature of the crystal, to the separation of the α_1 and α_2 components at high values of sin θ, or to the distortions that occur on upperlevel Weissenberg photographs. A reduction in weight was also made for strong reflexions for which extinction effects might be appreciable. In the final refinement, the unobserved reflexions were treated as having an F value of $F_{\text{min.}}/\sqrt{3}$ with weight inversely proportional to $F^2_{\text{min.}}$.

Three rounds of least-squares analysis were made on the computer DEUCE at the National Physical Laboratory. The computer programme, which was devised by Dr J. S. Rollett (unpublished work) refines both positional and anisotropic temperature-factor parameters for all the atoms simultaneously, taking account, for each atom, of the cross terms between its x, y and z parameters as well as those between its temperature-factor components. The final values of the parameters, given in Tables 2 and 3, were used to calculate a set of structure factors, which is given, together with the observed set, in Table 1. The calculated structure factors are based on the atomic scattering factors of Berghuis *et al.* (1955). The hydrogen atoms of the methyl group were not included, although there are faint indications of them in the final difference synthesis $d(x, y)$ (Fig. 3) based on these structure factors.

Accuracy

The reliability factor ($R = \Sigma|\Delta F|/\Sigma|F_o|$) for the 521 reflexions on the $hk0$, $hk1$ and $hk2$ layers is 0·109. For the 91 reflexions measured on the proportional-counter diffractometer $R = 0·068$. The standard deviations of the positional parameters, calculated by the standard method from the final least-squares analysis, are given in Table 2. Interatomic distances and angles are given in Table 4 together with their standard deviations. These are probably somewhat underestimated since no account has been taken of the uncertainties in the lattice parameters which are of the order of 0·5%. For the sake of completeness, the

Table 4. *Interatomic distances and angles*

Unprimed atoms are those at the positions in Table 2. Primed atoms are related to these by inversion through the origin. Other atoms are indicated by the appropriate vector translation from these positions

(*a*) Interatomic distances

Cu–Cl	$2{\cdot}368 \pm 0{\cdot}006$ Å
Cu–Cl($00\bar{1}$)	$2{\cdot}319 \pm 0{\cdot}006$
Cu–Cl′	$2{\cdot}547 \pm 0{\cdot}006$
Cu–N	$1{\cdot}993 \pm 0{\cdot}016$
N–N′(010)	$1{\cdot}257 \pm 0{\cdot}030$
N–C	$1{\cdot}459 \pm 0{\cdot}026$
Cl–C(100)	$3{\cdot}473 \pm 0{\cdot}022$
Cl–C(101)	$3{\cdot}754 \pm 0{\cdot}022$
Cu–Cu(001)	3·821
Cu–Cu′	$3{\cdot}008 \pm 0{\cdot}006$
Cu–Cu′($00\bar{1}$)	$3{\cdot}271 \pm 0{\cdot}006$
Cl–Cl(001)	3·821
Cl–Cl′	$3{\cdot}891 \pm 0{\cdot}010$
Cl–Cl′(001)	$3{\cdot}609 \pm 0{\cdot}010$

(*b*) Bond angles

Cl–Cu–Cl($00\bar{1}$)	109° 14′ ± 13′
Cl′–Cu–Cl($00\bar{1}$)	95° 39′ ± 12′
Cl′–Cu–Cl	104° 37′ ± 12′
N–Cu–Cl($00\bar{1}$)	132° 7′ ± 28′
N–Cu–Cl	107° 3′ ± 28′
N–Cu–Cl′	104° 2′ ± 28′
Cu–Cl–Cu(001)	109° 14′ ± 13′
Cu′–Cl–Cu(001)	84° 21′ ± 11′
Cu′–Cl–Cu	75° 23′ ± 10′
Cu–N–N′(010)	125° 56′ ± 1° 14′
Cu–N–C	116° 4′ ± 1° 13′
N′(010)–N–C	118° 0′ ± 1° 33′

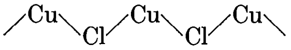
The standard deviations shown above do not include the uncertainties in the measurement of the cell constants which are of the order of 0·5%.

anisotropic temperature factors are listed in Table 3. These we believe, are influenced by various systematic errors in our observations, particularly by the effects of absorption, by incorrect scaling of the different layers, and by the omission of reflections with $l \geq 3$. We should, therefore, not place much reliance upon the numerical values and regard them simply as additional parameters introduced into the least-squares analysis in order to reduce the sum of the residuals.

Discussion

The two components, cuprous chloride and azomethane, can be recognised in the crystalline complex as distinct entities which interact with each other only through the close contacts between each copper atom and a nitrogen atom in the nearest azomethane molecule. Thus it is reasonable to consider the complex as a molecular compound and to discuss, first, the structural features of the two components separately.

The cuprous chloride occurs in the complex in the form of infinite chains



$$\diagup \mathrm{Cu} \diagdown_{\mathrm{Cl}} \diagup \mathrm{Cu} \diagdown_{\mathrm{Cl}} \diagup \mathrm{Cu} \diagdown$$

running parallel to the *c* axis. Within each chain, the two Cu–Cl distances are 2·32 Å and 2·37 Å and the angles at both copper and chlorine are tetrahedral. These chains, then, are just the same as those which would be obtained by isolating individual chains, running parallel to a face diagonal, from the cubic sphalerite-like structure of crystalline cuprous chloride itself, as shown in Fig. 4(*a*). The Cu–Cl distance in cuprous chloride is 2·35 Å, the same (within experimental error) as in the infinite CuCl chains in this complex.

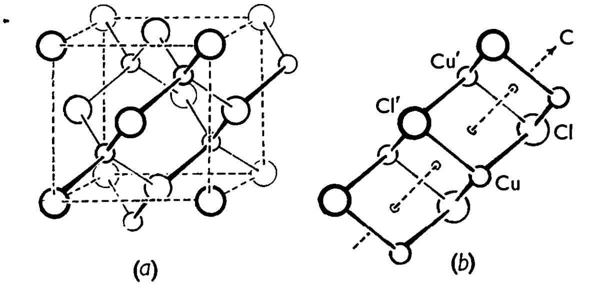


Fig. 4. Arrangement of adjacent Cu–Cl chains in (*a*) cubic CuCl structure and (*b*) CuCl azomethane complex.

The individual chains are connected in pairs, copper atoms of one chains being in register with the chlorine atoms of the other, to form the double stranded arrangement shown in Fig. 4(*b*). The inter-chain Cu–Cl distances are 2·55 Å, appreciably longer than those in the chains, and the additional angles formed at both types of atom deviate markedly from tetrahedral. Such a deviation is in fact required by the inversion points which relate the atoms of one chain to those of its neighbour. For since the four atoms Cu, Cu′, Cl, Cl′ in Fig. 4(*b*) must form a parallelogram, one of the angles Cl′–Cu–Cl or Cu–Cl′–Cu′, must be $\leq \pi/2$. The relationship between the two individual chains in the double strand is thus quite different from that which exists between a pair of parallel chains in cuprous chloride.

The azomethane molecules are strictly coplanar and must occur in the *trans*-configuration by virtue of the inversion points which occur at the centre of each N = N bond. The planar *trans*-structure has previously been reported from an electron-diffraction study of isolated azomethane molecules (Boersch, 1935) in the vapour phase. For the N = N distance we obtain $1{\cdot}26 \pm 0{\cdot}03$ Å which may be compared with previously observed distances of $1{\cdot}25 \pm 0{\cdot}04$ Å in difluorodiazine, F_2N_2 (Bauer, 1947), $1{\cdot}24 \pm 0{\cdot}05$ Å in gaseous azomethane (Boersch, 1935), 1·23 Å in both *cis*- and *trans*-azobenzene (Hampson & Robertson, 1941; de Lange, Robertson & Woodward, 1939) and $1{\cdot}26 \pm 0{\cdot}03$ Å in azo-*bis*-N-chloroformamidine (Bryden, 1958). The N–C distance is $1{\cdot}46 \pm 0{\cdot}03$ Å compared with the distances $1{\cdot}47 \pm 0{\cdot}06$ Å in gaseous azomethane and $1{\cdot}47 \pm 0{\cdot}02$ Å in methyl azide (Pauling & Brockway, 1937). The N = N − C angle is 118 ± 2°. These results indicate that no gross changes in the dimensions of the azomethane molecule occur on molecular compound formation, but they are not sufficiently accurate to reveal any small distortions which might take place.

Formally, azomethane could complex with Cu^+ either through its empty, antibonding π^*-orbitals (electron transfer from Cu^+ to $-N=N-$) or through its unshared pair (electron transfer from N to Cu^+). Both types of bonding are known to occur in cuprous compounds with other unsaturated ligands. Thus, complexes of cuprous chloride with 2-butyne and with 1:6-heptadiyne are of the π-type (Carter & Hughes, 1957), while σ-bonding occurs in potassium cuprocyanide, $KCu(CN)_2$, (Cromer, 1957) where each copper atom is σ-bonded to two carbon atoms and one nitrogen atom of three different cyanide anions.

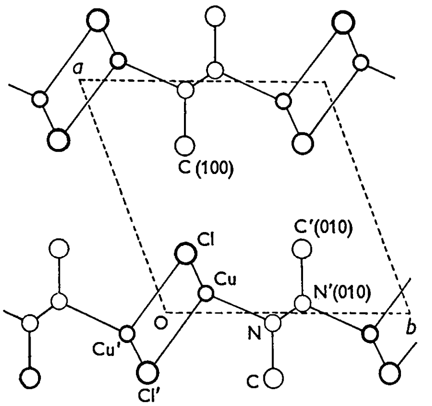


Fig. 5. View of the structure in projection down *c* axis.

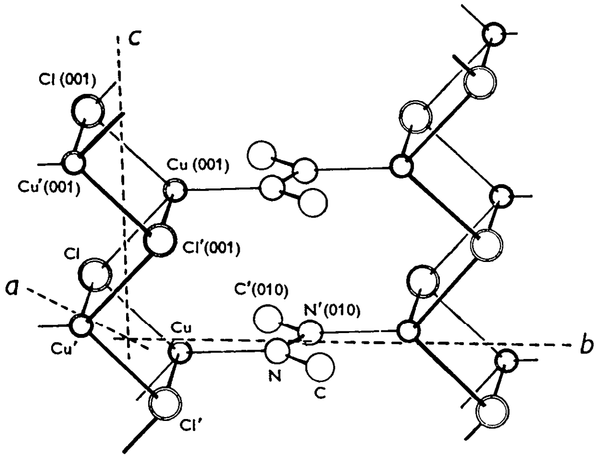


Fig. 6. View of the structure showing azomethane molecules linking CuCl chains. Labelling of the atoms corresponds, as does that in Fig. 5, to the labelling used in Table 4.

The only bonding contact between the azomethane and cuprous–chloride components in the present structure (see Figs. 5 and 6) occurs in the N–Cu distance of 1·99 ± 0·02 Å, somewhat shorter than the N–Cu distance of 2·05 ± 0·02 Å in potassium cuprocyanide (Cromer, 1957) or the sum of the standard tetrahedral covalent radii, 0·70 Å for N and 1·35 Å for Cu (Pauling, 1940). The bonded copper atom is coplanar with the azomethane molecule (the methyl group is 0·02 Å from the plane of the copper and nitrogen atoms). Moreover, the three angles N–N–Cu, Cu–N–C and C–N–N are all close to 120°. We can therefore assume that the unshared pair of electrons on each nitrogen atom interacts specifically with a cuprous ion forming a dative σ-bond which provides the principal cohesive force between the components. Each copper atom thus has four neighbours, three chlorine atoms and a nitrogen atom, in a distorted tetrahedral arrangement. Each chlorine atom is in Van der Waals contact with two methyl groups belonging to different azomethane molecules and thus achieves a 5-fold coordination (three copper atoms at 2·32, 2·37 and 2·55 Å and two methyl groups at 3·47 and 3·75 Å).

We have to acknowledge our thanks to Dr R. Lister and to Miss D. Meuche for preparing the complex. One of us (I.D.B.) is also indebted to the Department of Scientific and Industrial Research (D.S.I.R.) for a maintenance grant, and to the Managers of the Royal Institution for the facilities to carry out this research.

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