Crystal Structure of a Linear Polymeric 1 :1 Adduct of Copper(I) Chloride and 2,3-Diazabicyclo[2,2,1]hept-2-ene

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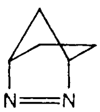
The crystal structure of the title compound has been determined by Patterson and Fourier methods from single-crystal photographic *X*-ray diffraction data, and refined by full-matrix least-squares methods to *R* 0·11 (401 reflections). Crystals are orthorhombic, space group $Pb2_1m$, a = 9·63(1), b = 10·64(1), c = 6·71(1) Å, Z = 4.

The structure comprises a linear chain of copper atoms alternately spaced at 3·32 and 3·39(1) Å, the copper atoms being spanned by ligand and chlorine bridges; the copper environment is basically a distorted tetrahedron: Cu–Cl 2·37 and 2·38(1), Cu–N 1·88 and 1·92(2) Å; N–Cu–N^{I} 128(1), Cl–Cu–Cl^{I}, 117(1), N–Cu–Cl, 100—106°.

ORGANIC ligand adducts of copper(I) halides often exist as polymers in which both halide and ligand function as bridging groups. In particular, the derivative of azomethane with copper chloride, $2CuCl,C_2H_6N_2$, exists as a two-dimensional infinite polymer with parallel [1] zig-zag ladders of alternately opposed Cu–Cl groups, which are crosslinked in the second dimension by azomethane molecules in the *trans*-configuration.[1] In 2,3-diazabicyclo[2,2,1]hept-2-ene (I) a similar C·N:N·C array is



(I)

found, differing in that the diaza-substituents are constrained to be *cis*. This molecule has been reported to yield an adduct $CuCl,C_5H_8N_2$, and we now report its structure determination.

The complex was prepared as red crystalline flakes as described in ref. 2; these were unsuitable for *X*-ray work and were recrystallized rapidly as compact prisms from hot acetonitrile.

EXPERIMENTAL

Photographic multiple-film equi-inclination Weissenberg data were collected on a single compact polyhedral crystal (approximated as a sphere 0·075 mm diameter for absorption correction purposes) about c and a for the layers $hk0$—3, 0—$4kl$; cell calibration was effected by the superposition of aluminium powder lines [$a(\mathrm{Al})_{298}$ = 4·0494 Å] on zero-layer photographs.

Crystal Data.—$C_5H_8ClCuN_2$, M = 230·6, Orthorhombic, a = 9·63(1), b = 10·64(1), c = 6·71(1) Å, U = 686 Å^3, D_m (flotation) = 1·88, Z = 4, D_c = 1·89 g cm^{-3}, $F(000)$ = 460. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 73·7 cm^{-1}. Space group $Pb2_1m$ (C_{2v}^2, No. 26) [non-standard setting of $Pmc2_1$: (x,y,z), $(x,y,\bar{z})$, $(x,\frac{1}{2}+y,\bar{z})$, $(\bar{x},\frac{1}{2}+y,z)$].

The data were estimated visually, corrected and processed, and the structure solved by Patterson and Fourier methods as previously described;[3] intensity statistics indicated the space group to be acentric and, of the two possibilities (Nos. 26 and 28), successful solution vindicated the choice of No. 26, the three-dimensional Patterson function being indicative of the ultimate special-position solution. The structure was refined by full-matrix least-squares, with all reflections allocated unit weights; the final R was 0·11, R' also 0·11 for the 401 observed reflections $\{R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}\}$. Anisotropic thermal parameters of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ were introduced for the copper and chlorine atoms. Final parameter shifts in the refinement were $<0{\cdot}005\sigma$; a final difference-Fourier map showed no significant features other than certain of the hydrogen atoms. Four reflections of low 2θ were deleted from the final data set owing to apparent extinction effects. Scattering factors for neutral atoms were taken from ref. 4, those for copper and chlorine being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[5] Results are shown in Tables 1—3, and a drawing of the molecule in the Figure.

TABLE 1

Atomic fractional positional ($\times 10^3$, for Cu $\times 10^4$) and thermal parameters with least-squares estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	U/Å^2
Cu	2210(4)	0	2528(9)	*
Cl(a)	373(1)	080(1)	500	*
Cl(b)	145(1)	142(1)	0	*
N(a)	063(2)	−036(2)	407(4)	5(5)
C(a1)	−090(3)	−039(2)	326(5)	16(7)
C(a2)	−151(4)	091(4)	384(6)	41(10)
C(a3)	−142(5)	−130(4)	500(—)	19(10)
N(b)	331(2)	−114(2)	096(4)	10(5)
C(b1)	439(3)	−203(3)	164(5)	17(7)
C(b2)	579(3)	−139(3)	119(5)	27(8)
C(b3)	440(4)	−306(3)	0	8(9)

* Anistropic thermal parameters ($\times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	16(2)	36(2)	12(2)	5(3)	8(3)	3(3)
Cl(a)	6(4)	24(5)	6(6)	−5(5)		
Cl(b)	12(5)	19(5)	10(6)	9(5)		

Computation was carried out on PDP 6 and CDC 6200 machines using programmes previously described, and those of the '*X*-Ray '72' system.[6] Structure factors are

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[1] I. D. Brown and J. D. Dunitz, *Acta Cryst.*, 1960, **13**, 28.

[2] O. Diels, J. H. Blom, and W. Knoll, *Annalen*, 1925, **442**, 242.

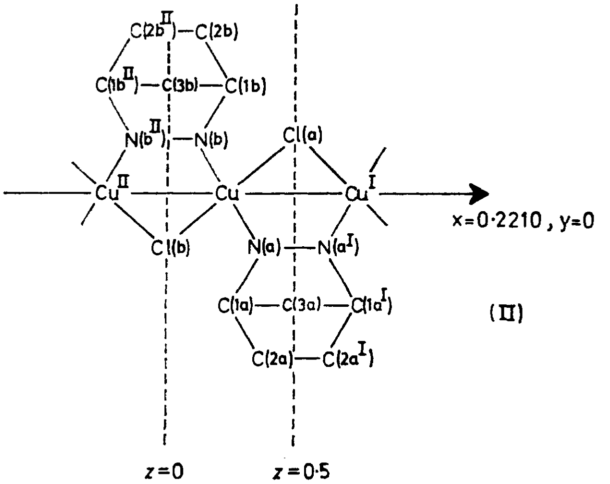
[3] See *e.g.*, P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 2239.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[6] *X*-Ray System of programs, version of June 1972, Technical Report TR 192 of the Computer Science Centre, University of Maryland, U.S.A.

listed in Supplementary Publication No. SUP 21033 (5 pp., 1 microfiche).* Atomic numbering is shown in (II).



(II)

DISCUSSION

The derivative is an infinite one-dimensional polymer, with the chain of copper atoms running parallel to *c* and segmented at the copper atoms; the halves of each segment are related by *ab* mirror planes midway between the copper atoms. Within each segment, the copper atoms are bridged by a chlorine atom, located on the mirror plane, and a ligand, bisected by it. The ligand double-bond and the chlorine are approximately opposed, the nitrogen atoms lying 0·43 Å out of the Cu–Cl–Cu$^{\mathrm{I}}$ planes. Thus only half of each Cu ··· Cu segment is crystallographically independent; however, alternate segments are non-equivalent. Slight but significant differences are found in the Cu ··· Cu$^{\mathrm{I}}$ distances of each segment type [3·32(1) and 3·39(1) Å]; the Cu–Cl–Cu$^{\mathrm{I}}$ angles vary correspondingly [88·8(4) and 90·7(4)°]. The approximate Cu_2N_2Cl planes within each segment lie approximately in the *ac* and *bc* planes, the angle between the alternate CuClCu$^{\mathrm{I}}$ planes being 85·5°.

TABLE 2

Molecular geometry

(*a*) Distances (Å)

Cu–N(a)	1·88(2)	C(a1)–C(a2)	1·55(5)
Cu–N(b)	1·92(2)	C(a1)–C(a3)	1·60(4)
Cu–Cl(a)	2·37(1)	C(a2)–C(a2$^{\mathrm{I}}$)	1·55(6)
Cu–Cl(b)	2·38(1)	N(b)–N(b$^{\mathrm{II}}$)	1·29(4)
Cu–Cu$^{\mathrm{I}}$	3·32(1)	N(b)–C(b1)	1·48(4)
Cu–Cu$^{\mathrm{II}}$	3·39(1)	C(b1)–C(b2)	1·54(4)
N(a)–N(a$^{\mathrm{I}}$)	1·25(3)	C(b1)–C(b3)	1·55(4)
N(a)–C(a1)	1·57(4)	C(b2)–C(b2$^{\mathrm{II}}$)	1·59(5)

(*b*) Angles (°)

N(a)–Cu–N(b)	128·3(9)	C(a1)–C(a3)–C(a1$^{\mathrm{I}}$)	94(3)
N(a)–Cu–Cl(a)	100·8(8)	C(a3)–C(a1)–C(a2)	104(3)
N(a)–Cu–Cl(b)	105·9(7)	C(a1)–C(a2)–C(a2$^{\mathrm{I}}$)	105(3)
N(b)–Cu–Cl(a)	105·5(8)	Cu–N(b)–N(b$^{\mathrm{II}}$)	123(2)
N(b)–Cu–Cl(b)	100·3(8)	Cu–N(b)–C(b1)	128(2)
Cl(a)–Cu–Cl(b)	117·3(4)	N(b$^{\mathrm{II}}$)–N(b)–C(b1)	108(2)
Cu–N(a)–N(a$^{\mathrm{I}}$)	123(2)	N(b)–C(b1)–C(b2)	105(2)
Cu–N(a)–C(a1)	125(2)	N(b)–C(b1)–C(b3)	104(2)
N(a$^{\mathrm{I}}$)–N(a)–C(a1)	110(2)	C(b1)–C(b3)–C(b1$^{\mathrm{II}}$)	91(2)
N(a)–C(a1)–C(a2)	104(2)	C(b3)–C(b1)–C(b2)	99(3)
N(a)–C(a1)–C(a3)	93(2)	C(b1)–C(b2)–C(b2$^{\mathrm{II}}$)	102(2)

Roman numeral superscripts denote the following transformations relative to *x*, *y*, *z*:

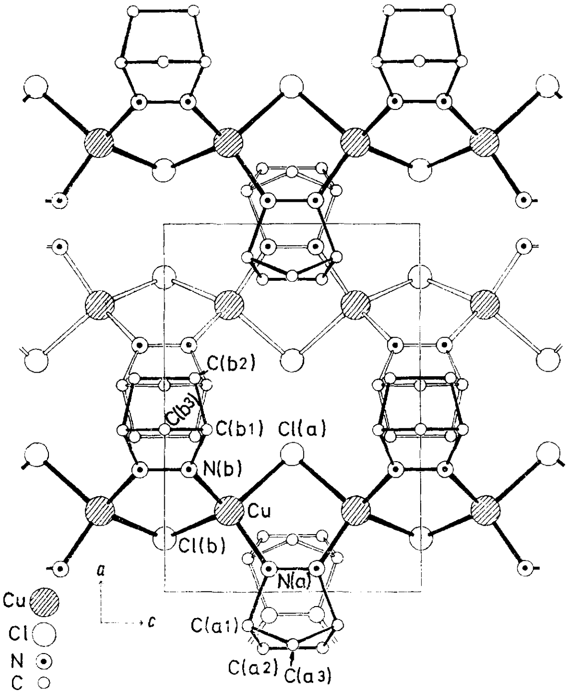
I $x, y, 1 - z$ II $x, y, \bar{z}$

TABLE 3

Equations of best least-squares planes in the form $pX + qY + rZ = s$, with deviations (Å) of relevant atoms in square brackets. The orthogonal (Å) frame (X,Y,Z) is defined by the transformation: $X = ax$, $Y = by$, $Z = cz$

	p	*q*	*r*	*s*
Plane (i): Cu, Cl(a)Cu$^{\mathrm{I}}$	−0·5035	0·8640	0·0000	−1·0714
[Cl(b) 1·67, N(a) 0·43, C(a1) 1·15, C(a2) 2·64, C(a3) 0·56, C(b1) −2·93, C(b2) −3·02, C(b3) −3·88]				
Plane (ii): Cu, Cl(b), Cu$^{\mathrm{II}}$	0·9006	0·4346	0·0000	1·9166
[Cl(a) 1·69, N(a) −1·54, C(a1) −2·88, C(a2) −2·81, C(a3) −3·75, N(b) 0·43, C(b1) 0·95, C(b2) 2·46, C(b3) 0·49]				

Angle between planes (i) and (ii): 85·5°



The unit cell contents, projected down *b*, showing atomic numbering. Atoms denoted by I and II in Table 2 are generated by the mirror planes at *c* = 0·5 and 0 respectively

The co-ordination of the copper atom is a highly distorted tetrahedron, the co-ordination positions being occupied by two crystallographically distinct chlorine

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).

atoms and two crystallographically distinct nitrogen atoms (Table 2). Bridging Cu–Cl distances in adduct derivatives of CuCl vary widely depending on ligand type and numbers and the nature of the bridging; the values [2·37(1) and 2·38(1) Å] in the present structure are not unusual.[7] Within the ligands the –N=N– distances [1·25(3) and 1·29(3) Å] are not significantly different from that in the azomethane complex [1·26(3) Å] and the remainder of the geometry is typical of the strained polycyclic system. The copper–nitrogen distances [1·88(2) and 1·92(2) Å] are significantly shorter than in the azomethane derivative [1·99(2) Å]; this, together with the small Cu–Cl–Cu^{I} angles suggests enhanced copper–nitrogen bond-order in the present complex, although the reason for this is not clear.

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[7] See *e.g.*, V. G. Albano, P. L. Bellon, G. Ciani, and M. Manassero, *J.C.S. Dalton*, 1972, **171**, ref. 23.