Preparation and Crystal Structure of Bis-(2,2′-bipyridyl)copper(II) Bis-[dichlorocuprate(I)]

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The title compound has been prepared and its structure determined by *X*-ray diffraction. Crystals are triclinic, $a = 9{\cdot}40(2)$, $b = 10{\cdot}68(3)$, $c = 15{\cdot}34(4)$ Å, $\alpha = 122{\cdot}15°$, $\beta = 103{\cdot}67(13)°$, $\gamma = 105{\cdot}93(12)°$, $Z = 2$, space group $P\bar{1}$. The structure was determined from diffractometer data by Patterson and Fourier methods, and refined by full-matrix least-squares techniques to R 0·048 for 3184 observed reflections. The structure contains isolated linear $Cu^ICl_2^-$ ions, trigonal-bipyramidal $Cu^{II}(bipy)_2Cl$ groups, and infinite chains of alternating linear Cu^ICl_2 groups and Cu^ICl_4 double tetrahedra.

COMPOUNDS containing a metal in two valence states are of special interest because of the possibility of easy electron transfer between these states. Thus, a number of mixed copper(I)–copper(II) complex salts have been prepared and investigated,[1] *e.g.* salts with aminecopper(II) cations and halogenocopper(I) anions.[2] Baglio[3] *et al.* have solved the crystal structures of some of these salts, *e.g.* $[Cu(NH_3)_4][CuCl_2]_2,H_2O$, $[Cu(NH_3)_4][CuBr_2]_2$, and $[Cu(NH_3)_4][CuI_2]_2$. Meanwhile $Cu(en)_2(CuCl_2)_2{\cdot}CuCl$[4] and $Cu(phen)_2(CuCl_2)_2$ have been prepared and investigated. We now report the structure of $[Cu(bipy)_2][CuCl_2]_2$.

EXPERIMENTAL

Reagents.—Analytical reagent grade 2,2′-bipyridyl, copper chloride dihydrate, and potassium chloride were from Merck. Ethanol (95%) was distilled under oxygen-free nitrogen. Ether was purified by distillation and passed through a column containing neutral Al_2O_3 to remove peroxides and was stored over molecular sieve (4 Å). Water was boiled for ½ h, with passage of oxygen-free nitrogen, and then cooled and stored under nitrogen in a stoppered flask. Copper(I) chloride was prepared from $CuSO_4,5H_2O$, sodium chloride, and sulphur dioxide by the method of ref. 5. The white crystals were washed with ethanol and ether and dried at 10^{-3} Torr. When stored in a brown flask they showed no discolouration, even after 6 months, unlike commercial samples which could not therefore be used.

Synthesis.—All preparation was carried out under nitrogen. 2,2′-Bipyridyl (3·12 g, 0·02 mol), $CuCl_2,2H_2O$ (1·71 g, 0·01 mol), and KCl (3 g) were dissolved in a mixture (80 ml) of ethanol–water (3 : 5 v/v) containing 5 drops concentrated hydrochloric acid and stirred at 60 °C to give a dark green to blue solution. CuCl (1·9 g, 0·02 mol) and KCl (12 g) were then added to water (80 ml) acidified with 5 drops of concentrated hydrochloric acid, in an externally heated dropping funnel.

The clear, light yellow, solution obtained was heated to 60 °C and was added dropwise to the blue solution within 1 h. A black solid was precipitated, and after stirring at 60 °C for 3 h, was washed twice with ethanol–water (9 : 1), three times with ether, and finally dried at 10^{-3} Torr.

Crystals suitable for crystallographic investigation were obtained by lowering the reaction temperature to 40 °C and diluting the blue solution with ethanol (160 ml) and water (50 ml). Under these conditions only a few crystals appeared, together with green and yellow products which have not yet been examined. Crystals of $[Cu(bipy)_2][CuCl_2]_2$, [m.p. (decomp.) 190 ± 2 °C], were black, but dark green in transmitted light. They are stable in dry air (Found: Cu, 29·55; Cl, 22·35; N, 8·85. $C_{20}H_{16}Cl_4Cu_3N_4$ requires Cu, 29·55; Cl, 22·0; N, 8·7%) and have no piezoelectric properties.

X-*Ray Crystallographic Data.*—Crystals of cross-section 0·5 mm showing well developed faces were selected. The unit cell and space group were determined from oscillation, Weissenberg, and precession photographs, taken with filtered and crystal monochromatized Cu-K_α radiation.

Crystal Data.—$C_{20}H_{16}N_4Cl_4Cu_3$, $M = 644{\cdot}54$, Triclinic, (reduced cell) $a = 9{\cdot}40(2)$, $b = 10{\cdot}68(3)$, $c = 15{\cdot}34(4)$ Å, $\alpha = 122{\cdot}15(13)°$, $\beta = 103{\cdot}67(13)°$, $\gamma = 105{\cdot}93(12)°$, $U = 1107$ Å^3, $D_m = 2{\cdot}05$ g cm^{-3} (pycnometrically), $Z = 2$, $D_c = 1{\cdot}941$ g cm^{-3}, $F(000) = 572$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 34{\cdot}5$ cm^{-1}. Space group $P1$ (No. 1) or $P\bar{1}$ (No. 2), $P\bar{1}$ from structure analysis.

For intensity measurements a crystal was ground to an approximate sphere, diameter 0·5 mm. The intensities of all reflections with $2\theta < 52°$ were measured on a PDP8 computer-controlled Picker four-circle diffractometer by use of Mo-K_α graphite monochromatized radiation. A scintillation counter was used in conjunction with a pulse-height analyzer.

Intensities were corrected for Lorentz-polarization effects, and symmetry-related reflections were averaged. The standard deviation of the intensity, I, was calculated from $\sigma^2(I) = S + cB$ where S and B are the scan and background counts respectively, and c a scale factor which corrects for the difference in total scan time and total background time. Reflections with $I < 2{\cdot}5\ \sigma(I)$ were excluded from the computations. Reflections with computed $|F|$-values $<2{\cdot}1$ (close to the minimum observable) were also deleted. Of 8900 reflections measured, 3184 were used for the solution of the structure.

Structure Analysis.—The structure was determined by standard Patterson techniques in conjunction with successive series of electron density maps.

Refinement.—Constraints were introduced to decrease the number of variables. The two crystallographically independent bipyridyl molecules were constrained to be identical and each was constrained to have a two-fold symmetry axis. With isotropic thermal parameters R was 13% after three cycles. The function minimized was

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TABLE 1

Atomic co-ordinates, as fractions of the cell edges. Anisotropic thermal parameters, U_{ij} values,* are mean square amplitudes (Å^2), and isotropic thermal parameters † B/Å^2

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu(1)	0·000000	0·000000	0·000000	0·058386	0·046969	0·060453	0·030705	0·036582	0·039368
Cu(2)	0·000000	0·000000	0·500000	0·034988	0·072079	0·066736	0·011051	0·056525	0·008680
Cu(3)	−0·009051	0·469216	0·226839	0·033246	0·035061	0·030737	0·021167	0·024494	0·021233
Cu(4)	0·342936	0·962359	0·488594	0·045134	0·053757	0·058684	0·263910	0·073566	0·027254
Cl(1)	0·079210	0·756144	0·316722	0·034091	0·027265	0·033965	0·014838	0·016935	0·016400
Cl(2)	0·245136	0·095560	0·625414	0·031871	0·039030	0·033843	0·180980	0·020986	0·015084
Cl(3)	0·491776	0·834399	0·519267	0·040483	0·041144	0·044198	0·024280	0·033550	0·025370
Cl(4)	0·246127	0·077285	0·025485	0·062739	0·065042	0·084605	0·038123	0·052131	0·050266
N(1)	0·064244	0·347888	0·282078	2·39					
C(11)	0·175226	0·292496	0·267563	3·20					
C(12)	0·197598	0·190873	0·292381	3·92	C(31)	0·290166	0·542035	0·190771	3·76
C(13)	0·092943	0·137402	0·329549	4·14	C(32)	0·372602	0·521822	0·126172	3·19
C(14)	−0·022757	0·191621	0·343999	3·65	C(33)	0·282135	0·416522	0·006430	3·36
C(15)	−0·033081	0·298138	0·321846	2·49	C(34)	0·110266	0·335650	−0·044015	2·84
H(11)	0·241756	0·318352	0·229617	6·21	C(35)	0·031177	0·357348	0·023814	2·05
H(12)	0·276243	0·137341	0·275518	7·97	H(31)	0·356915	0·608467	0·277921	2·74
H(13)	0·099729	0·052532	0·339924	5·50	H(32)	0·506193	0·578954	0·162620	7·93
H(14)	−0·084107	0·164325	0·373372	13·80	H(33)	0·346589	0·423583	−0·037300	10·00
N(2)	−0·149979	0·460197	0·304387	2·35	H(34)	0·051740	0·283867	−0·119916	4·95
C(21)	−0·246065	0·536944	0·321022	3·14	N(4)	−0·205105	0·310965	0·057680	2·41
C(22)	−0·344335	0·522772	0·372711	3·51	C(41)	−0·370263	0·239935	0·021419	3·15
C(23)	−0·347090	0·426283	0·405056	3·60	C(42)	−0·488333	0·135981	−0·094592	3·78
C(24)	−0·248427	0·347822	0·389385	3·25	C(43)	−0·434194	0·104148	−0·175901	3·16
C(25)	−0·148809	0·368384	0·337983	2·48	C(44)	−0·264117	0·176933	−0·139480	2·54
H(21)	−0·244478	0·609121	0·297305	8·85	C(45)	−0·152067	0·278011	−0·022194	2·25
H(22)	−0·434137	0·564685	0·375919	9·39	H(41)	−0·412177	0·270901	0·082264	5·38
H(23)	−0·420193	0·413297	0·441965	7·35	H(42)	−0·619749	0·083143	−0·123963	5·07
H(24)	−0·243525	0·291090	0·414269	5·65	H(43)	−0·521219	0·010885	−0·260899	4·17
N(3)	0·120661	0·457535	0·140231	2·40	H(44)	−0·229062	0·140565	−0·193136	3·16

* In the form $T = -2\pi^2(U_{11}h^2a^{*2} + \cdots\cdots + 2U_{12}hka^*b^* + \cdots)$. † In the form $B = 8\pi^2U^2$.

$\Sigma w(F_o - F_c)^2$ with unit weights. Refinement was continued with the constraints removed and with isotropic temperature factors for carbon and nitrogen, and anisotropic parameters for copper and chlorine. R was then <5%. Hydrogen atoms were introduced into the calculations by reinvoking the constraints, so that only four independent hydrogen atoms were introduced, C–H 1 Å being assumed. R was then 4·8%. In the final refinement, hydrogen positions and temperature factors were kept constant, but positional parameters for all other atoms were allowed to refine unconstrained. The final R was 4·8% (R' 5·3%). No allowance was made for the effects of absorption or extinction. A few least-squares refinements were also calculated allowing positional and thermal parameters to vary for the hydrogen atoms as well. No improvement in the R value was obtained. A final difference electron-density map was qualitatively featureless. Final atomic co-ordinates and thermal parameters are listed in Table 1. Observed and Calculated structure factors are listed in Supplementary Publication No. SUP 20913 (15 pp., 1 microfiche).* Figure 1 shows a drawing of the molecule and the atom numbering system used in the analysis.

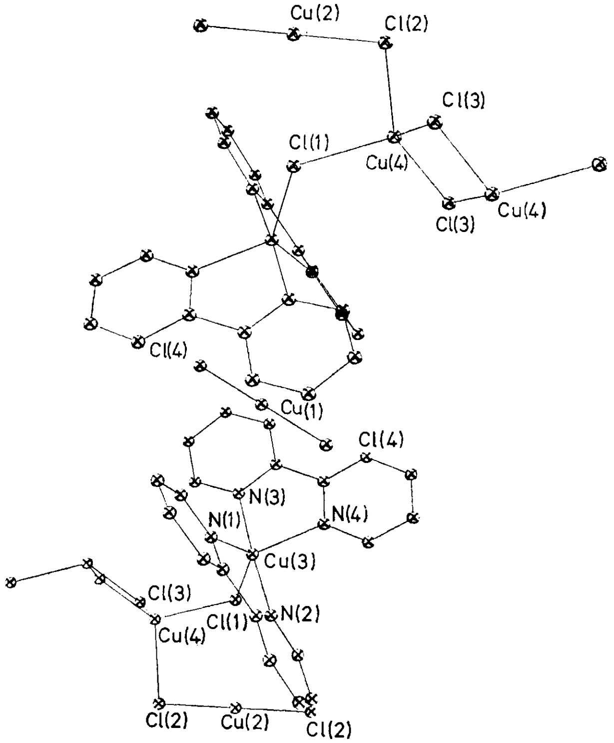

FIGURE 1 Diagram of the molecule showing the atom numbering system

Calculations.—The following computations were carried out on a Gier computer with programs: diffractometer output, M.S. Lehmahn; Wilson plot, intensity statistics, and structure factors, J. Danielsen; Patterson and Fourier syntheses, S. Lauesen. Other computations were carried out on a CDC 6400 as follows: constrained refinement, G. S. Pawley, modified by R. G. Hazell; unconstrained least squares, LINUS, Brookhaven National Laboratories; distances and angles, ORFFE, Brookhaven National Laboratory.

DISCUSSION

Description of Structure.—The structure contains isolated $Cu^{I}Cl_2^-$ ions, $Cu^{II}(bipy)_2Cl$ groups, and infinite chains built from Cu^{I} and Cl atoms. The chains contain sequences of arrangements of three copper and six

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

chlorine atoms. Edge-sharing double tetrahedra with chlorine atoms at the corners and copper atoms at the centres are linked together by copper atoms which, since they lie on crystallographic centres, must be co-linear with the chlorine atoms. The midpoint of the shared-edge of the double tetrahedron corresponds to a crystallographic centre of symmetry. The $Cu^{II}(bipy)_2$ groups are attached to the chains *via* chlorine atoms which are bound to the Cu^I atoms of the tetrahedra. All other chlorine atoms in the chain form bridges exclusively with Cu^I atoms. The arrangement of the chains is depicted in Figure 2.

isolated $CuCl_2^-$ ions link $[Cu(bipy)_2]^{2+}[CuCl_2]^-$ groups together by electrostatic forces.

The Cu(1)–Cl(4) distance in the isolated Cu^ICl_2 group is 2·091 Å. In the Cu^ICl_2 group which is embedded in the infinite chain, the Cu^I(2)–Cl(2) distance is 2·140 Å. Here the chlorine atom is bound also to a tetrahedrally co-ordinated Cu^I atom [Cu(4)] with a bond length of 2·393 Å. The other independent Cu–Cl distances of the tetrahedrally co-ordinated Cu^I atom are 2·339 Å to those [Cl(3)] connecting the two tetrahedra, and 2·384 Å to those [Cl(1)] which are also connected to the divalent copper atoms, Cu^{II}(3)–Cl(1) being 2·355 Å.

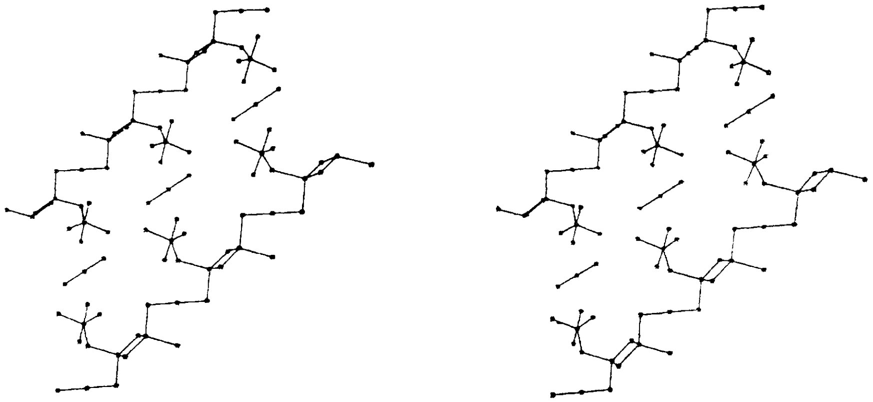

FIGURE 2 Projection of selected parts of the structure showing the arrangement of the infinite $CuCl_2^-$ chains and their connection to the $Cu(bipy)_2^{2+}$ groups. Isolated $CuCl_2^-$ ions are seen to be embedded between the chains. Carbon and hydrogen atoms are omitted

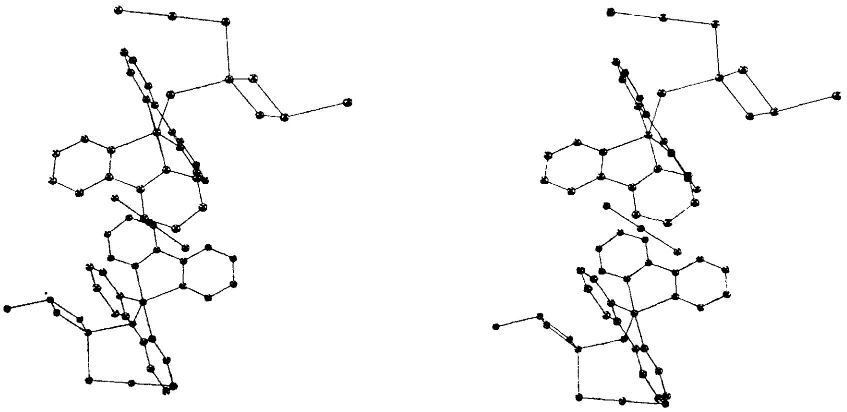

FIGURE 3 Projection of the content of a unit cell. Hydrogen atoms have been omitted

Isolated $CuCl_2^-$ ions with copper at a centre of symmetry are caged in by two $Cu(bipy)_2Cl$ groups which are related *via* the centre of symmetry. The chlorine atoms of the $CuCl_2^-$ group are in van der Waals contact with hydrogen and carbon atoms of the bipyridyl groups and are screened from contact with the infinite copper–chlorine chains. Figure 3 shows the contents of a unit cell. The packing appears to be governed by the following principles: the infinite copper–chlorine chains may be represented by stoicheiometry and charge as $(CuCl_2^-)_\infty$ units; $Cu(bipy)_2^{2+}$ ions are attached to the chains *via* chlorine ions, one Cu^{2+} group per $CuCl_2^-$ unit; and

The four nitrogen atoms of the two bipyridyl groups and the chlorine atom occupy the apices of a trigonal bipyramid with the Cu^{II} atom at the centre. The four Cu^{II}–N distances fall into two sets. The *trans*-distances are 1·99 Å. The Cu^{II}–Cl vector is coplanar with two Cu^{II}–N vectors of mean length 2·075 Å. Each bipyridyl group has one short and one long N–Cu bond. The difference between the two sets of Cu^{II}–N distances is 18σ as estimated by the least-squares computations and is probably therefore of physical significance. Bond distances are given in Table 2. In the two bipyridyl groups, the mean C–N distance is 1·345(8) Å, and mean

C–C distance 1·378 Å. Each pyridine ring is planar, but the two pyridine rings in a bipyridyl molecule are mutually twisted by 6°.

Among other mixed-valence copper(I)–copper(II) compounds for which structure determinations have been carried out[6] is tri-μ-thiocyanato-triamminecopper(I) copper(II). Mixed-valence compounds are, in general, strongly coloured and the present compound is no exception, although the interaction between the copper atoms in different valence states must be small because of the fairly large copper(II)–copper(I) separations (4·06 and 4·36 Å).

TABLE 2

Bond lengths (Å) with estimated standard deviations, in parentheses

N(1)–C(11)	1·341(9)	H(31)–C(31)	1·017
C(11)–C(12)	1·377(11)	H(32)–C(32)	1·071
C(12)–C(13)	1·387(12)	H(33)–C(33)	1·022
C(13)–C(14)	1·374(11)	H(34)–C(34)	0·990
C(14)–C(15)	1·370(10)	N(4)–C(41)	1·339(9)
C(15)–N(1)	1·354(8)	C(41)–C(42)	1·386(10)
H(11)–C(11)	1·027	C(42)–C(43)	1·369(11)
H(12)–C(12)	1·051	C(43)–C(44)	1·381(10)
H(13)–C(13)	1·016	C(44)–C(45)	1·388(9)
H(14)–C(14)	0·890	C(45)–N(4)	1·342(8)
N(2)–C(21)	1·359(9)	C(45)–N(4)	1·342(8)
C(21)–C(22)	1·380(10)	C(45)–C(35)	1·474(8)
C(22)–C(23)	1·358(11)	H(41)–C(41)	1·026
C(23)–C(24)	1·392(11)	H(42)–C(42)	1·064
C(24)–C(25)	1·403(10)	H(43)–C(43)	1·014
C(25)–N(2)	1·330(8)	H(44)–C(44)	0·892
C(25)–C(15)	1·478(9)	Cu(1)–Cl(4)	2·091(2)
H(21)–C(21)	1·011	Cu(2)–Cl(2)	2·140(2)
H(22)–C(22)	1·058	Cu(3)–N(1)	2·063(5)
H(23)–C(23)	1·014	Cu(3)–N(2)	1·995(5)
H(24)–C(24)	0·877	Cu(3)–N(3)	1·986(5)
N(3)–C(31)	1·356(8)	Cu(3)–N(4)	2·086(5)
C(31)–C(32)	1·363(10)	Cu(3)–Cl(1)	2·355(2)
C(32)–C(33)	1·379(10)	Cu(4)–Cl(1)	2·384(2)
C(33)–C(34)	1·374(10)	Cu(4)–Cl(2)	2·393(2)
C(34)–C(35)	1·376(9)	Cu(4)–Cl(3)	2·339(2)
C(35)–N(3)	1·343(8)		

The divalent copper is five-co-ordinate, a co-ordination number now well established for it.[6]

In most simple copper(I) compounds, copper is tetrahedrally connected to other atoms in the solid state. Copper(I) chloride has the wurtzite structure[8] with Cu–Cl 2·34 Å. In the gaseous phase it is trimeric forming a ring-shaped molecule[9] with Cu–Cl 2·16 Å. Numerous crystallographic investigations confirm, however, the general impression that tetrahedral co-ordination around copper is the preferred arrangement in copper(I) compounds. On the other hand, evidence from solution chemistry points towards a characteristic co-ordination number of two,[10] although there is evidence for a maximum co-ordination number of four. Isolated $CuCl_2^-$ groups have been reported recently[11] in diethyl-[2-(diphenylphosphine oxide)ethyl]ammonium dichlorocuprate(I). A Cu–Cl bond length of 2·09 Å was reported which is in complete agreement with the value found in this investigation and for chloro[dodeca(dimethylamino)-cyclohexaphosphazene-*NNNN*]copper(II) dichlorocuprate(I), $[\{N_6P_6(NMe_2)_{12}\}Cu^{II}Cl][Cu^{I}Cl_2]$.[12] In this last-named compound, which also contains copper in two valence states, the copper(II) atom is bonded to four nitrogen atoms of the phosphazene ring and to one chlorine atom in a distorted square-pyramidal arrangement with the chlorine atom occupying the apical position.

The most unusual structural feature of the present compound is the alternating co-ordination numbers two and four in the copper(I) chlorine chain. We do not know of other examples of this kind of diversity in the stereochemistry of copper(I) compounds

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[3/865 *Received, 25th April,* 1973]

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