Reactions of *NNN'N'*-Tetra-alkylethylenediamines with Copper(II) Halides and the Crystal Structure of Bis(*NNN'N'*-tetraethylethylenediammonium) Hexa-μ-chloro-μ_4-oxo-tetra[chlorocuprate(II)]

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Controlled addition of *NNN'N'*-tetraethylethylenediamine (teed) or *NNN'N'*-tetramethylethylenediamine (tmed) to concentrated ethanolic solutions of copper(II) chloride produce a series of colour changes and allow isolation of the following compounds: (I) yellow $[\mathrm{teedH_2}^{2+}][\mathrm{CuCl_4}^{2-}]$, (II) garnet red $[\mathrm{teedH_2}^{2+}]_2[\mathrm{Cu_4OCl_{10}}^{4-}]$, (III) $\mathrm{CuCl_2(teed)}$, (IV) yellow $[\mathrm{tmedH_2}^{2+}][\mathrm{CuCl_4}^{2-}]$, (V) $\mathrm{CuCl_2(tmed)}$, and (VI) an ill-defined red product. With copper bromide solution and teed the products were (VII) dark purple $[\mathrm{teedH_2}^{2+}][\mathrm{CuBr_4}^{2-}]$, (VIII) pale violet $[\mathrm{teedH}^{+}][\mathrm{CuBr_3}^{-}]$, and (IX) $\mathrm{CuBr_2(teed)}$.

On heating the solids or ethanolic solutions of them, compounds (III) and (IX) gave the compounds (*NNN'*-triethylethylenediamine)$\mathrm{CuX_2}$ (X = Cl or Br), with evolution of acetaldehyde.

A three-dimensional crystal structure analysis on compound (II) has been carried out. Full-matrix least-squares refinement on 1478 diffractometer observations gave *R* 0·06. In a monoclinic unit cell having a = 14·46(2), b = 15·23(2), c = 17·59(2) Å, β = 104·55(3)°, and space group *C*2/*c*, *Z* = 4. The $[\mathrm{Cu_4OCl_{10}}^{4-}]$ ion is tetrahedral with two bridging chlorines and the oxygen atom lying on the crystallographic two-fold axis. The copper atoms have trigonal bipyramidal environments, surrounded by four chlorines and one oxygen at mean distances Cu–Cl(bridge) 2·40, Cu–Cl(terminal) 2·24, and Cu–O 1·92 Å. The quaternary nitrogen atoms are hydrogen-bonded to terminal chlorine atoms, N · · · Cl 3·14 and 3·17 Å.

The compounds *NNN'N'*-tetramethylethylenediamine (tmed) [1] and *NNN'N'*-tetraethylethylenediamine (teed), react with an equimolar amount of copper(II) chloride, chloride hydrate, or bromide in ethanol, to give $\mathrm{CuCl_2L}$ or $\mathrm{CuBr_2L}$. Attempts to add a second molecule of ligand failed; [2,3] this has been attributed to steric hindrance.[3] In a saturated aqueous solution of copper(II) chloride, addition of diamine leads to the precipitation of $\mathrm{Cu_2(OH)_3Cl}$.[4] The addition of a slight excess of fully substituted diamine to an aqueous, or alcoholic, solution of copper(II) salts with the less efficient co-ordinating anions, nitrate, perchlorate, or sulphate, yields the μ-hydroxy-bridged species $[\mathrm{LCu{\cdot}(OH)_2{\cdot}CuL}]\mathrm{X_2}$.[2,3]

We have observed that the controlled addition of tmed or teed to concentrated ethanolic solutions of copper(II) chloride provides a series of colour changes. The green solution is made progressively more yellow until a crystalline yellow solid (A) is precipitated. On addition of further ligand the colour darkens until a deep reddish-brown solution is obtained from which a viscous garnet liquid settles. This slowly crystallises to give a garnet solid (B), and the solution is dark green. Further addition of the ligand leads to the production of the 1 : 1 species. The reaction may be carried out as described, or stopped at any stage to isolate species. With copper(II) bromide where the colour changes are less explicit, two species have been isolated, dark purple lustrous flakes (C), and pale violet needles (D). Both have been shown to contain complex halogenocuprate ions.

TABLE 1

			Found				Calc.				*M*	
		Colour	C	H	N	Cu	C	H	N	Cu	Calc.	(*X*-Ray)
(I)	$[\mathrm{teedH_2}^{2+}][\mathrm{CuCl_4}^{2-}]$	Yellow	31·8	6·8	7·3	17·0	31·6	6·9	7·4	16·8	379·7	386
(II)	$[\mathrm{teedH_2}^{2+}]_2[\mathrm{Cu_4OCl_{10}}^{4-}]$	Garnet red	24·2	5·4	5·4	25·7	24·7	5·4	5·7	26·1	973·4	990
(III)	$\mathrm{CuCl_2(teed)}$	Marine blue	39·0	8·0	8·7	21·0	39·2	7·9	9·1	20·7		
(IV)	$[\mathrm{tmedH_2}^{2+}][\mathrm{CuCl_4}^{2-}]$	Yellow	21·9	5·6	8·7	19·5	22·2	5·6	8·7	19·6		
(V)	$\mathrm{CuCl_2(tmed)}$ [a]	Peacock blue	28·8	6·5	11·1	25·2	28·7	6·4	11·2	25·3		
			13·6	3·8	5·1		16·7	4·2	6·5	29·5	861·2 (if 4 Cu)	
(VI)	$\mathrm{CuCl_2(tmed)}$ ' cluster '	Garnet red	13·6	3·4	5·1	29·5						810
			13·8	4·0	5·4		13·4	3·2	5·2	35·5	536·6 (if 3 Cu)	
(VII)	$[\mathrm{teedH_2}^{2+}][\mathrm{CuBr_4}^{2-}]$	Dark purple	21·5	4·6	5·1	11·7	21·6	4·7	5·0	11·4		
(VIII)	$[\mathrm{teedH}^{+}][\mathrm{CuBr_3}^{-}]$	Pale violet	24·9	5·1	5·8	—	25·2	5·3	5·8	13·3	476·6	487
(IX)	$\mathrm{CuBr_2(teed)}$	Deep olive green–black	30·2	6·3	7·1	15·9	30·3	6·1	7·1	16·1		
(X)	$\mathrm{CuBr_2(treed)}$ [b]	Sage green	26·3	5·6	7·7	17·6	26·1	5·5	7·6	17·3		
(XI)	$\mathrm{CuBr_2(treed)}$ [b]	Emerald green	34·5	7·5	10·2	23·4	34·5	7·3	10·1	22·8		

[a] See ref. 1. [b] See ref. 29.

The thermal decomposition of $\mathrm{CuX_2(teed)}$ has been investigated and shown to produce acetaldehyde and *NNN'*-triethylethylenediamine copper(II) halide, $\mathrm{CuX_2(treed)}$.

In Table 1 the products are enumerated together with their colours, analyses, and where available, molecular weights by *X*-ray methods.

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[1] I. Bertini and F. Mani, *Inorg. Chem.*, 1967, **6**, 2032.

[2] P. Pfeiffer and H. Glaser, *J. Prakt. Chem.*, 1938, **151**, 134; W. Hatfield, T. S. Piper, and U. Klebunde, *Inorg. Chem.*, 1963, **2**, 629; D. W. Meek and S. A. Ehrhardt, *ibid.*, 1965, **4**, 584; J. L. Hall, L. K. Ross, and J. F. Gavlas, *Proc. West Va. Acad. Sci.*, 1967, **39**, 355.

[3] J. R. Wasson, T. P. Mitchell, and W. H. Bernard, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2865; T. P. Mitchell, W. H. Bernard, and J. W. Wasson, *Acta Cryst.*, 1970, *B*26, 2096.

[4] P. Tarte, *Spectrochim. Acta*, 1958, **13**, 107.

RESULTS AND DISCUSSION

Ligand Deficiency Reactions.—The first products isolated from the deficiency reactions, (A) and (C), were identified as the diammonium tetrahalogenocuprates. These are compounds (I), (IV), and (VII) of Table 1. For (I) *X*-ray methods established the formula weight and that no symmetry was required for $[teedH_2^{2+}][CuCl_4^{2-}]$; this was consistent with the reflectance spectra of all three compounds, *i.e.* there were no bands at *ca.* 10,000 cm^{-1} and so the geometry is probably distorted tetrahedral (D_{2d}) $[CuX_4^{2-}]$.[5,6]

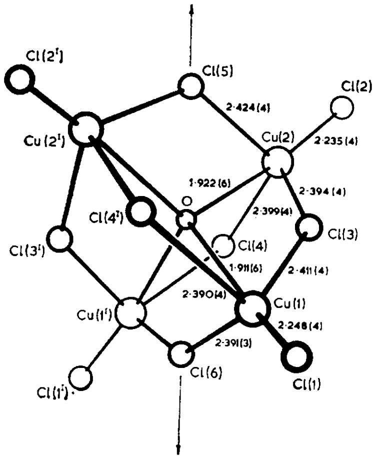

FIGURE 1 The anion $Cu_4OCl_{10}^{4-}$ in the garnet red compound (II) showing the designations of the atoms and bond lengths (Å) with their standard deviations in parentheses. Atoms Cl(5), O, and Cl(6) lie on a crystallographic two-fold axis, indicated by the arrows and this relates the other atoms in pairs, the Roman numeral superscript I indicates atoms at $-x, y, \frac{1}{2} - z$

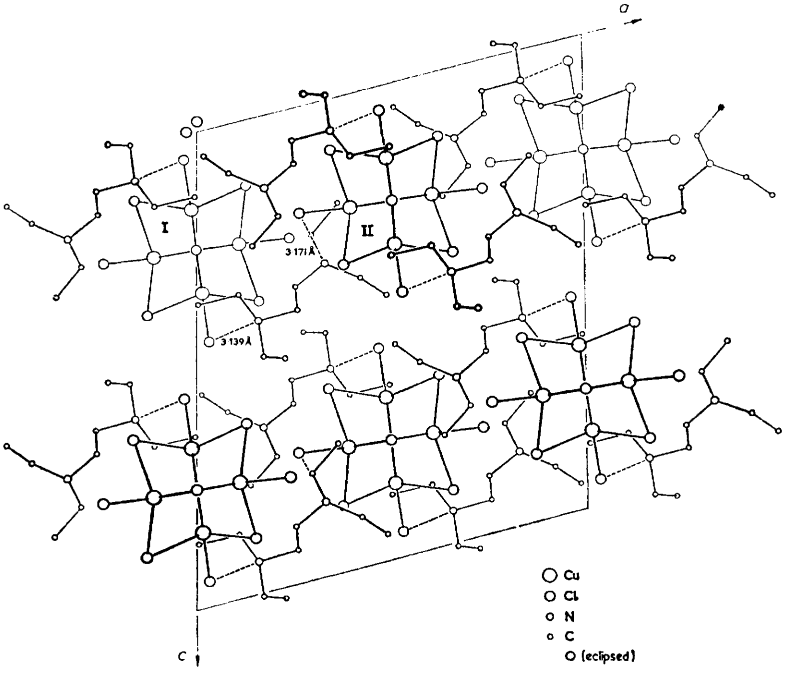

FIGURE 3 The structure of $[teedH_2^{2+}]_2[Cu_4OCl_{10}^{4-}]$ projected down the *b* axis. Broken lines indicate one set of N–H · · · Cl hydrogen bonds. The Roman numeral II indicates atoms at $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

The garnet-red products, (B), were not analogous for the two bases. With teed and copper(II) chloride a well-defined crystalline solid, (II), was obtained. It has been identified unequivocally by crystal structure analysis as $[teedH_2^{2+}]_2[Cu_4OCl_{10}^{4-}]$ with the anion, shown in Figure 1, similar to that of the tetramethylammonium salt.[7] The cation is shown in Figure 2 and the packing of the ions in Figure 3. There are four formula units in the monoclinic unit cell, space group *C2/c*, so no symmetry is required for the cation but the anion is on a crystallographic two-fold axis. The cation (Figure 2) has a *trans*-conformation about the central carbon–carbon bond. Most of the bond lengths are within the normal range;[8] the apparently very short

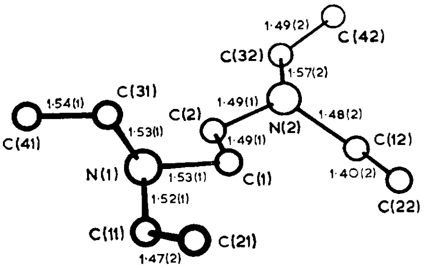

FIGURE 2 The cation $Et_2NH{\cdot}[CH_2]_2{\cdot}NHEt_2^{2+}$ showing the designations of the atoms and the bond lengths

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[5] R. D. Willett, O. Liles, and C. Michelson, *Inorg. Chem.*, 1967, **6**, 1885.

[6] J. C. Barnes, *J. Inorg. Nuclear Chem.*, 1969, **31**, 95.

[7] J. A. Bertrand and J. A. Kelley, *Inorg. Chem.*, 1969, **8**, 1982.

[8] *Chem. Soc. Special Publ.*, No. 18, 1965.

C(12)–C(22) bond is between two atoms with large vibration parameters and may be a consequence of libration. Each nitrogen atom has three carbon atoms pyramidally arranged, as indicated by the bond angles in Table 2. N(1) makes a contact of 3·139(9) Å with Cl(1) in a position completing a tetrahedron and implying the existence of N–H · · · Cl hydrogen bonding. Similarly N(2) appears to be hydrogen-bonded to Cl(2^{II}) at 3·171(11) Å. These interactions in the *ab* plane presumably reinforce the main electrostatic bonding in the crystal. The copper atoms are in a trigonal bipyramidal environment with the unshared Cu–Cl bond lengths, 2·242(4) Å, significantly shorter than the shared ones, 2·409(4) Å, confirming the results of ref. 7. The Cu–O bonds, 1·917(6) Å, gave a broad adsorption band at 548 cm^{-1} in the i.r. spectrum.

TABLE 2

(*a*) Bond angles (°) in the [$Cu_4OCl_{10}{}^{4-}$] cluster

Cl(1)–Cu(1)–Cl(3)	95·0(1)	Cl(2)–Cu(2)–Cl(5)	96·8(2)
Cl(1)–Cu(1)–Cl(6)	94·7(1)	Cl(2)–Cu(2)–Cl(3)	94·4(1)
Cl(1)–Cu(1)–Cl(4)	97·7(1)	Cl(2)–Cu(2)–Cl(4)	94·5(1)
Cl(1)–Cu(1)–O	177·0(2)	Cl(2)–Cu(2)–O	178·5(3)
Cl(3)–Cu(1)–Cl(6)	123·2(1)	Cl(3)–Cu(2)–Cl(5)	114·2(1)
Cl(3)–Cu(1)–Cl(4^{I})	112·3(1)	Cl(3)–Cu(2)–Cl(4)	127·5(1)
Cl(6)–Cu(1)–Cl(4^{I})	121·4(1)	Cl(5)–Cu(2)–Cl(4)	115·9(1)
Cl(3)–Cu(1)–O	84·9(2)	Cl(3)–Cu(2)–O	85·1(1)
Cl(6)–Cu(1)–O	82·8(3)	Cl(5)–Cu(2)–O	84·7(3)
Cl(4^{I})–Cu(1)–O	85·1(2)	Cl(4)–Cu(2)–O	84·7(1)
Cu(1)–O–Cu(2^{I})	108·9(4)	Cu(2)–O–Cu(1)	108·8(1)
Cu(1)–Cl(3)–Cu(2)	80·9(2)	Cu(2)–Cl(4)–Cu(1^{I})	81·2(2)
Cu(1)–Cl(6)–Cu(1^{I})	82·8(1)	Cu(2)–Cl(5)–Cu(2^{I})	80·9(3)

(*b*) Bond angles (°) in the cation

N(1)–C(1)–C(2)	107·7(9)	N(2)–C(2)–C(1)	114·7(10)
C(11)–N(1)–C(31)	110·7(9)	C(12)–N(2)–C(32)	114·5(13)
C(1)–N(1)–C(11)	109·9(8)	C(2)–N(2)–C(12)	114·3(11)
C(1)–N(1)–C(31)	111·8(9)	C(2)–N(2)–C(32)	106·5(10)
N(1)–C(11)–C(21)	116·2(10)	N(2)–C(12)–C(22)	120·1(16)
N(1)–C(31)–C(41)	112·7(10)	N(2)–C(32)–C(42)	112·8(12)

Angles involved in N–H · · · Cl hydrogen bonding

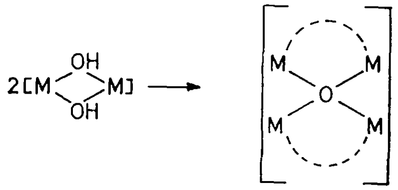
C(1)–N(1) · · · Cl(1)	111·7(6)	C(2)–N(2) · · · Cl(2^{II})	88·5(7)
C(11)–N(1) · · · Cl(1)	103·7(6)	C(12)–N(2) · · · Cl(2^{II})	135·5(10)
C(31)–N(1) · · · Cl(1)	108·7(6)	C(32)–N(2) · · · Cl(2^{II})	92·2(7)

Reflectance spectra determined in the range 10,000—20,300 cm^{-1} showed one absorption for the cluster compound. This band, attributed to *d–d* transitions, is broad and the maximum is at 11,200 cm^{-1}, as in $Cu_4OCl_6(Ph_3PO)_4$.[9] It is at lower energy than that in Cu_4OCl_6(2-methylpyridine)$_4$ (13,600 cm^{-1}),[10] as might be expected for comparison of nitrogen-bonded with oxygen- or chlorine-bonded ligands. A broad band, with an indistinct shoulder *ca.* 19,300 cm^{-1} occurs in the u.v. region and is likely to be due to charge-transfer transition.

For the other base, tmed, the compound (B) was ill-defined, the *X*-ray and analytical data being in conflict [see (VI) of Table 1]. It consistently gave C, H, and N analyses compatible with the formulation [Cu_3Cl_6(OH)][tmedH] but an *X*-ray molecular weight of 810. It might be analogous with [Cu_3L_3(OH)][SO_4], prepared by the reaction of pyridine-2-aldoxime, (L), and copper(II) sulphate,[11] and shown by *X*-ray crystal structure analysis [12] to contain 16·3 molecules of water. Our *X*-ray molecular weight would require 15 molecules of water, or 6 molecules of ethanol of crystallisation to agree with the formulation derived from C, H, N analyses from powdered samples. The i.r. spectrum showed the broad Cu–O band at 550 cm^{-1}, together with bands at 3460 and 3540 cm^{-1}. Evaporation of the green solution above the crystals gave a pale green powder with i.r. spectrum as described for $Cu_2(OH)_3Cl$.[4]

The nature of the species identified suggests that they are the products of a controlled hydrolysis of the copper(II) halide.

The hydrolysis of copper(II) has been shown to produce polymeric species.[13] The formation of [$Cu_3(OH)_4{}^{2+}$], [$Cu_2(OH)_2{}^{2+}$], and a series of [$Cu_n(OH)_{2n-2}{}^{2+}$] ($n \geqslant 4$), complexes have been suggested [13,14] on the basis of the 'core plus links' hypothesis.[15] The reaction of tmed with copper(II) in aqueous solution proceeds *via* ligated hydroxo-species such as [Cu(OH)(tmed)(H_2O)$^+$] and [{Cu(OH)(tmed)}$_2{}^{2+}$].[16,17] It is therefore probable that the cluster complexes are formed by aggregation and condensation (dehydroxylation) processes (1). The hydrolysis products include protons and halide ions, facilitating protonation of the diamine and formation of polyhalogenocuprates respectively.



(1)

Copper(II) bromide reacts with bromide ion in non-aqueous solution to give [$CuBr_4{}^{2-}$] and [$CuBr_3$(solvent)$_2{}^-$].[18] The latter species may be present in the solutions from which we obtained the second product of the deficiency reaction of teed with copper(II) bromide, the pale violet needles, (D). This was characterised as compound (VIII) by chemical analysis and preliminary *X*-ray investigation, which showed that it must be monomeric [teedH$^+$][$CuBr_3{}^-$] and not contain the dimeric anion [$Cu_2Br_6{}^{2-}$] postulated for $KCuBr_3$.[19] There is an ambiguity in the space group; in one case the monomeric units need no symmetry but in the other the [$CuBr_3{}^-$] entity must be planar with a two-fold axis of symmetry.

The existence of [CuX_3L^-] has also been proposed [20]

[9] J. A. Bertrand, *Inorg. Chem.*, 1967, **6**, 495.

[10] N. S. Gill and M. Sterns, *Inorg. Chem.*, 1970, **9**, 1619.

[11] R. Beckett, R. Colton, B. F. Hoskins, R. L. Martin, and D. G. Vince, *Austral. J. Chem.*, 1969, **22**, 2527.

[12] R. Beckett and B. F. Hoskins, *J.C.S. Dalton*, 1972, 291.

[13] D. D. Perrin, *J. Chem. Soc.*, 1960, 3189.

[14] H. Otaki, *Inorg. Chem.*, 1968, **7**, 1205.

[15] L. G. Sillen, *Acta Chem. Scand.*, 1954, **8**, 299.

[16] R. L. Gustafson and A. E. Martell, *J. Amer. Chem. Soc.*, 1959, **81**, 525.

[17] E. Arenare, P. Paoletti, A. Dei, and A. Vaccia, *J.C.S. Dalton*, 1972, 736.

[18] J. C. Barnes and D. N. Hume, *Inorg. Chem.*, 1963, **2**, 444.

[19] R. D. Willett, C. Dwiggins, jun., R. F. Kruh, and R. E. Rundle, *J. Chem. Phys.*, 1963, **38**, 2429.

[20] C. Furlani and G. Morpugo, *Theor. Chim. Acta*, 1963, **1**, 102.

as a possible species in the decomposition of $[CuX_4^{2-}]$ in the absence of an excess of halide ions in solution. The change of colour, from light yellow to deep brown, for $[CuCl_4^{2-}]$ in solution is attributed to solvolysis;[20] we have observed that unless solvent is rapidly removed from the yellow complexes then there is an increase in the intensity of a brown colouration and the solid material becomes viscous. The yellow complex will slowly yield the garnet red complex if set aside in ethanolic solution in air.

The preparation of KBr discs of (A) caused a colour change from yellow to red, and in the i.r. spectrum of $tmedH_2^{2+}$ salt a doublet appeared at 510, 533 cm^{-1} and water bands at 3500 and 1605 cm^{-1} which were absent in the yellow salt. This suggests a hydrolytic reaction, although bromide interaction[21] cannot be totally excluded.

Polynuclear copper–oxygen clusters involving tetrahedral oxygen have been prepared from a wide range of reagents[7,9,10,22-24] and fall into two classes. $[Cu_4OCl_6$-(2-methylpyridine)$_4]$ has been shown to come from water in the reaction system;[10] $[Cu_4OX_6$(pyridine)$_4]$ has been prepared from the reaction of copper(II) halide with the aromatic base in the presence of sodium hydroxide or water.[22,23] $[Me_4N]_4[Cu_4OCl_{10}]$ was prepared by the heating under reflux of $CuCl_2$,CuO and $[Me_4N]Cl$ in methanol, and so approximates to the reaction of basic copper(II) chloride with the ammonium salt.[7,25] It has been found that the use of non-stoicheiometric reagents in this reaction was necessary to prevent the precipitation of a green-yellow impurity, believed to be $[Me_4N]_2$-$[CuCl_4]$.[25] These preparations, we believe, support the view that similar cluster complexes should be expected in reactions of copper with conditions suitable for a controlled base hydrolysis. The mode of preparation of (II) also lends credance to the proposition[10] that the complex of formula Cu_4OBr_6(pyridine)$_4$ prepared from the reaction of pyridine and excess of $CuBr_2$ in 95% ethanol is of the cluster type.[26]

Thermal Decomposition.—Samples of $CuCl_2$(tmed) and $CuCl_2$(teed) were dried at 90° before analysis. No change was observed for the former complex but a tarry residue remained for $CuCl_2$(teed). Ethanol extraction of this residue gave a bright green solid having an $\rangle$N–H stretching frequency in the i.r. and identical with an authentic sample of $CuCl_2$(treed). A similar reaction was observed for $CuBr_2$(teed).

Attempts to recrystallise both $CuCl_2$(teed) and $CuBr_2$(teed) from ethanol followed a similar pattern. In both cases the treed adduct was recovered whereas for the tmed analogues the CuX_2(tmed) species remained. The conversion occurred readily in hot ethanol or slowly in cold ethanol (*ca.* 1 week, depending upon concentration).

$CuCl_2$(teed) was prepared in an ice-bath, but if the solution was allowed to warm too much, black specks were observed in the product. If the compound was prepared in hot ethanol the dark green solution paled and often heating for 10—20 min gave a dark red solution. On cooling a green colour returned and crystals of $CuCl_2$(treed) were obtained, together with a tarry residue.

Gas chromatographic analysis of the vapours above $CuCl_2$(teed) heated to 90° for 10 min were collected in a liquid oxygen trap and showed a compound whose mass spectrum indicated molecular weight 44. The spectrum was identical with that of an authentic sample of acetaldehyde. A major late-running peak was identified as teed. In the absence of air only a very small peak was observed for acetaldehyde, although teed was still a major peak. It is suggested that the oxidative production of acetaldehyde is catalysed by the $CuCl_2$.

The reaction is similar to that of $CuCl_2$ and triethylamine,[27] in which an oxidative deprotonation of NEt_3 is postulated. If this reaction is carried out in ethanol a red solution * is observed on heating on a steam-bath.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Diffuse reflectance spectra were measured using a Unicam SP 500 spectrophotometer. Microanalyses were carried out by the University College London Microanalytical Laboratory, and mass spectrometry by the A.R.C. Mass Spectrometry Service, Food Research Institute.

The compounds were prepared by adding ligand dropwise to ethanolic solutions of the copper(II) halide in air and isolation of products was as described in the text. The 1 : 1 complexes were prepared by the methods of refs. 1 and 29.

Preliminary *X*-ray investigations were made with Cu-K_α radiation for oscillation and Weissenberg photographs. For compound (II) final unit-cell dimensions were obtained[30] from 15 accurately centred reflections on a Picker automatic four-circle diffractometer.

Crystal Data.—*Compound* (I), *yellow. NNN'N'*-Tetra-

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* The dissolution of copper in carbon tetrachloride–n-butylamine solutions saturated with oxygen at a total pressure of 1 atmosphere has as its rate-determining step the formation of CuCl on the metal surface. Immediately after adding the amine to the solution the copper surface is coated with a dark red layer; this persists until all amine is used.[28]

[21] W. H. Watson, *Inorg. Chem.*, 1969, **8**, 1879.

[22] B. T. Kilbourn and J. D. Dunitz, *Inorg. Chim. Acta*, 1967, **1**, 209.

[23] H. Bock, H. T. Dieck, H. Pyttlik, and M. Schneller, *Z. anorg. Chem.*, 1968, **357**, 54.

[24] J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 1970, **4**, 526.

[25] J. A. Barnes, G. W. Inman, and W. E. Hatfield, *Inorg. Chem.*, 1971, **10**, 1725.

[26] C. F. Harris and E. Sinn, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 125.

[27] J. F. Weiss, G. Tollin, and J. T. Yoke, *Inorg. Chem.*, 1964, **3**, 1344.

[28] E. W. Jones, W. J. Lautenberger, P. A. Willermet, and J. G. Miller, *J. Amer. Chem. Soc.*, 1970, **92**, 2946.

[29] F. Hein and W. Rittersdorf, *Z. anorg. Chem.*, 1961, **308**, 133.

[30] *X*-RAY ARC, IBM 1130 Program System for Crystallography, compiled by B. L. Vickery, D. Bright, and P. R. Mallinson; including least-squares program BLOK by B. L. Vickery, Fourier program FODAP by A. Zalkin and D. Bright, Picker setting program PICK 3 by W. C. Hamilton and D. Bright, data reduction program PRED by B. L. Vickery and P. R. Mallinson, mean planes program MPLN (NRC 22) by M. E. Pippy and R. F. Ahmed, intermolecular contacts program BANGL by D. Bright.

ethylethylenediammonium tetrachlorocuprate, $C_{10}H_{26}Cl_4CuN_2$, $M = 379{\cdot}5$, Monoclinic, $a = 8{\cdot}92$, $b = 10{\cdot}52$, $c = 19{\cdot}80$ Å, $\beta = 108°$, $U = 1764$ Å^3, D_m (flotation) $= 1{\cdot}45$, $Z = 4$, $D_c = 1{\cdot}43$. Space group $P2_1/c$. No molecular symmetry required.

Compound (II), *garnet red*. *Bis*(*NNN'N'*-tetraethylethylenediammonium) hexa-μ-chloro-μ_4-oxo-tetra[chlorocuprate-(II)], $C_{20}H_{52}Cl_{10}Cu_4N_4O$, $M = 973{\cdot}4$, Monoclinic, $a = 14{\cdot}46(2)$, $b = 15{\cdot}23(2)$, $c = 17{\cdot}59(2)$ Å, $\beta = 104{\cdot}55(3)°$, $U = 2895{\cdot}4$ Å^3, D_m (flotation) $= 2{\cdot}19$, $Z = 4$, $D_c = 2{\cdot}23$, $F(000) = 1968$. Space group $C2/c$ determined by structure analysis. Mo-K_α (Zr-filtered) radiation, $\lambda(K_{\alpha 1}) = 0{\cdot}70930$, $\lambda(K_{\alpha 2}) = 0{\cdot}71359$ Å (1 Å $= 10^{-10}$ m); μ(Mo-K_α) $= 19{\cdot}5$ cm^{-1}, no absorption correction applied.

Compound (VIII), *pale violet needles*. (2-Diethylaminoethyl)diethylammonium tribromocuprate(II), $C_{10}H_{25}Br_3CuN_2$, $M = 476{\cdot}6$, Monoclinic, $a = 12{\cdot}65$, $b = 10{\cdot}32$, $c = 14{\cdot}00$ Å, $\beta = 109°$, $U = 1730$ Å^3, D_m (flotation) $= 1{\cdot}87$, $Z = 4$, $D_c = 1{\cdot}83$. Space group Cc or $C2/c$ from systematic absences: hkl with $h + k$ odd and $h0l$ with l odd. No symmetry required in Cc and a centre or a two-fold axis for each ion in $C2/c$.

Crystal Structure Determination.—For intensity measurements on compound (II) the crystal was set in a random orientation with respect to the goniometer axes to minimise the risk of double reflection. Observations were made on the hkl and $\bar{h}kl$ reflections with a scintillation counter through a pulse-height discriminator. The θ—2θ scan mode was used at 1° min^{-1} from 0·5 below the $K_{\alpha 1}$ peak to 0·5° above the $K_{\alpha 2}$ peak. Background counts of 25 s were taken at either end of the scan. Three reference reflections (008, $\bar{4}42$, and 620) were measured every 50 and used to put all observations on the same scale. The observations were processed [30] to give a set of intensities for which I, the net intensity was $> 3\sigma(I)$ where $\sigma^2(I) = [c + 0{\cdot}25(t_c/t_b)^2(B_1 + B_2)]$ where c is the total integrated count obtained in time t_c and B_1 and B_2 are background counts each obtained in time t_b. Lorentz and polarisation factors were applied and square roots taken to give 1478 values of $|F_o|$ from 2965 original intensity measurements.

TABLE 3(a)

Fractional atomic co-ordinates (× 10⁴) with standard deviations in parentheses unless the parameter was not refined

	x/a	y/b	z/c
Cu(1)	130(1)	2402(0)	3420(1)
Cu(2)	1116(1)	970(1)	2628(1)
Cl(1)	327(2)	3283(2)	4474(2)
Cl(2)	2436(2)	157(2)	2775(2)
Cl(3)	1585(2)	1586(2)	3921(2)
Cl(4)	1250(2)	1630(2)	1422(2)
Cl(5)	0	−241(3)	2500
Cl(6)	0	3580(3)	2500
O	0	1697(6)	2500
N(1)	1609(6)	4916(6)	4357(5)
N(2)	3311(7)	3634(7)	3455(6)
C(1)	2606(8)	4641(8)	4293(7)
C(2)	2499(9)	3823(9)	3815(8)
C(11)	1683(9)	5401(10)	5127(6)
C(21)	2224(11)	6232(10)	5229(9)
C(31)	1094(9)	5480(7)	3659(7)
C(41)	47(8)	5672(9)	3661(7)
C(12)	4225(13)	3428(13)	4031(12)
C(22)	4780(14)	4105(13)	4453(11)
C(32)	2952(11)	2902(9)	2820(10)
C(42)	3615(11)	2758(11)	2305(9)
H(11)	3033	4555	4793
H(21)	2883	5090	4024
H(12)	2414	3337	4158
H(22)	1888	3855	3419
H1(11)	1966	4988	5572
H2(11)	1026	5482	5199
H1(31)	1118	5166	3173
H2(31)	1439	6015	3650
H1(12)	4083	2905	4351
H2(12)	4609	3063	3698
H1(32)	2906	2339	3104
H2(32)	2307	3012	2525

TABLE 3(b)

Vibration parameters (Å ×10³)*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	39(1)	35(1)	30(1)	−1(1)	5(1)	−6(1)
Cu(2)	31(1)	39(1)	32(1)	7(1)	2(1)	−1(1)
Cl(1)	56(2)	43(2)	36(2)	−6(2)	16(2)	−7(2)
Cl(2)	38(2)	64(2)	41(2)	22(2)	1(2)	−4(2)
Cl(3)	42(2)	45(2)	30(2)	11(2)	−2(1)	−2(2)
Cl(4)	43(2)	58(2)	40(2)	17(2)	16(2)	9(2)
Cl(5)	44(3)	31(3)	115(5)	0	13(3)	0
Cl(6)	68(4)	31(3)	30(3)	0	−5(2)	0
O	29(6)	35(6)	23(6)	0	0(5)	0
N(1)	35(6)	44(6)	26(5)	−2(5)	0(5)	−2(5)
N(2)	46(7)	58(8)	52(7)	5(6)	18(6)	2(6)
C(1)	22(7)	62(9)	55(9)	−6(7)	3(6)	2(8)
C(2)	44(9)	66(9)	63(10)	−11(8)	19(7)	−23(9)
C(11)	64(10)	111(13)	18(7)	5(10)	10(7)	−8(8)
C(21)	104(13)	66(10)	70(11)	−42(10)	18(9)	−40(9)
C(31)	70(10)	36(8)	42(8)	−6(7)	5(7)	0(7)
C(41)	33(8)	72(10)	56(9)	25(7)	4(7)	7(8)
C(12)	100(17)	168(22)	141(20)	96(15)	47(14)	113(16)
C(22)	111(17)	156(20)	93(15)	−38(15)	−43(12)	−22(14)
C(32)	94(14)	39(9)	117(15)	−14(9)	14(11)	−13(10)
C(42)	83(12)	98(13)	87(13)	−1(11)	50(10)	−23(11)
H(11)	51					
H(21)	51					
H(12)	51					
H(22)	51					
H1(11)	51					
H2(11)	51					
H1(31)	51					
H2(31)	51					
H1(12)	51					
H2(12)	51					
H1(32)	51					
H2(32)	51					

* In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

For the hydrogen atoms a constant value of U_{iso} was assumed.

Systematic absences of reflections hkl with $h + k$ odd, $h0l$ with l odd, and $0k0$ with k odd correspond to two space groups Cc and $C2/c$.

A Patterson synthesis was computed [30] and showed the copper atoms related by the two-fold axis, establishing the space group as $C2/c$. Successive Fourier and difference-Fourier syntheses gave the positions of all the atoms other than hydrogen. Refinement was carried out by use of full-matrix least-squares with isotropic thermal parameters for all atoms. A difference-Fourier synthesis suggested the use of anisotropic thermal parameters for copper and chlorine and possibly also the cation group. Refinement by block-diagonal least-squares allowing for anisotropic vibrations of all atoms and anomalous dispersion of copper reduced R to 0·069. Hydrogen atoms were included in calculated positions [30] assuming C–H 0·95 Å and in order to complete tetrahedral arrangements about C(11), C(31), C(12), C(32), C(1), and C(2). They were assigned isotropic vibration parameters and their parameters were not refined. The function refined by least-squares was $R' = \Sigma w(|F_o| - |F_c|)^2$ where the weighting function w was adjusted to give constant values of R' in ranges of $\sin\theta/\lambda$ and of $|F_o|$. The final scheme was $w = 1/\sigma^2_{\text{counting}}\ (4{\cdot}15-0{\cdot}134F_o + 0{\cdot}00296F_o^2)$. Refinement converged at R 0·063, R' 0·089 and the most significant shift was 0·36 of the corresponding estimated standard deviation. To obtain more realistic standard deviations a final cycle of full-matrix refinement was carried out [31] and the corresponding bond lengths and angles with their standard deviations were calculated [31] and are given in Figures 1 and 2 and Table 2.

Final observed and calculated structure factors were obtained from the parameters in Table 3 with scattering factors for copper corrected for anomalous dispersion,[32] carbon, nitrogen, oxygen, and chlorine from ref. 33, and hydrogen from ref. 34. They are listed in Supplementary Publication No. SUP 20497 (12 pp., 1 microfiche).*

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[31] IBM 360 and CDC 6600, full-matrix least-squares program NUCLS by R. J. Doedens and J. A. Ibers; interatomic distances and errors ORFFE by W. R. Busing, K. O. Martin, and H. A. Levy.

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

[33] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, pp. 202—206.

[34] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.