Crystal Structure of an Infinite Stair-type Chain Compound $[\{Cu_2(tc)_2(ClO_4)_2\}_n]$ (tc = thiochrome) †

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The infinite stair-type chain compound $[\{Cu_2(tc)_2(ClO_4)_2\}_n]$ (tc = thiochrome) crystallizes in the monoclinic space group $P2_1/c$ with $a = 9.50(1)$, $b = 22.79(1)$, $c = 7.889(6)$ Å, $\beta = 111.06(8)°$ and $Z = 2$ ($R = 0.068$, $R' = 0.070$). The dimeric units are mutually linked by the 2-hydroxyl group of the co-ordinated thiochrome, just like one step in a stairs. Each copper(I) atom in the unit has a three-co-ordinate T-shaped geometry with two nitrogen and one oxygen donor, providing a unique dimetal structure having a short Cu···Cu contact [2.476(3) Å]. Proton NMR spectra and cyclic voltammograms demonstrate that the species formed in solution is not polymeric but a low-molecular-weight dicopper complex, in which the 2-hydroxyethyl group is not co-ordinated. The cyclic voltammogram in the solid state gives a single quasi-reversible wave, indicating that the dicopper site undergoes redox reactions, whose stability is associated with the three-co-ordinate geometry and/or co-ordination of the alcohol group.

The great interest in low-dimensional metal-containing polymers stems from their potential to exhibit electrical, magnetic and optical properties usually displayed by metals,[1] from the unique and sometimes puzzling variation in their solid-state structures,[2,3] and also from the desire to control crystal packing in the solid state. Many metal-containing polymers[2,3] have been characterized by X-ray crystallography, but few of these have been obtained from rational and systematic syntheses. The rational synthesis of metal-containing polymers as well as the assembly of metal complexes has been one of the most difficult and challenging problems in solid-state co-ordination chemistry.

One of the most important aspects in the synthesis of metal-containing polymers is the design of a useful structural unit: polymers constructed from co-ordinatively unsaturated metal complex units are intriguing because various modes of polymerization can be expected owing to the various geometries of the metal. For instance, a square-planar metal complex can be stacked along the apical direction to give linear chain compounds.[1]

Copper(I) ion can readily provide lower co-ordination number complexes whose unsaturated structures range from linear to trigonal.[2,4] Among the copper(I)-containing polymers so far synthesised[2] there are few well characterized crystal structures where planar metal complex units are linked with each other in a horizontal direction. This is partly because planar dimetal complexes are rare. Recently, we have synthesised a planar dicopper(I) complex having a short metal–metal contact.[5] If by using this type of co-ordinatively unsaturated metal complex unit a polymer forms and simultaneously the crystal structure is well controlled it is a convenient and rational synthetic method in solid-state chemistry. As a first step, it is important to try linking this type of complex one-dimensionally along a metal–metal vector. This work, concerns the synthesis and characterization of this type of polymeric structure.

Experimental

All operations were carried out under an atmosphere of purified argon.

Materials.—All solvents used were dried and distilled under argon before use. The salt $[Cu(CH_3CN)_4]PF_6$ was prepared according to the literature,[6] $Cu(ClO_4)_2\cdot6H_2O$ and thiamine monohydrochloride were purchased from Wako. Thiochrome (tc) was prepared from thiamine monohydrochloride.[7] Its purity was checked by measuring the absorption band at 375 nm (log $\varepsilon = 4.2$).

Preparation of $[\{Cu_2(tc)_2(ClO_4)_2\}_n]$ **1**.—To a methanol solution (5 cm^3) of $Cu(ClO_4)_2\cdot6H_2O$ (4.63 mg, 2.5 mmol dm^{-3}) was added copper wire under an ethylene atmosphere, and the mixture was stirred for 0.5 h at 35 °C. After ethylene was replaced with argon and copper wire was removed, tc (2.18 mg, 1.67 mmol dm^{-3}) was added. The resultant yellow solution was layered with acetone, affording yellow brick-shaped crystals. A suitable crystal was used for X-ray diffraction data collection.

Physical Measurements.—Electronic absorption spectra were obtained with a Hitachi 260-10 spectrophotometer, infrared spectra as KBr disks with a JASCO 200S spectrometer. Proton and ^{13}C NMR spectra were obtained on a JEOL GSX 270 spectrometer operating in the Fourier-transform mode at 25 °C. Shifts at 23 °C are referenced against $SiMe_4$. For metal-free tc the observed ^1H NMR chemical shifts of H^4, H^8, C^9H_3, $C^{10}H_3$, H^{11} and H^{12} are δ 5.24, 8.01, 2.45, 2.22, 2.77 and 3.52 for $[^2H_4]$methanol solution, and 5.19, 8.02, 2.35, 2.21, 2.65 and 3.52 for $(CD_3)_2SO$ solution, respectively. The numbering of the protons corresponds to that of the carbons in Fig. 1(*a*). In the case of the copper(I) complex, the corresponding co-ordination shifts ($\delta_C = \delta_{complex} - \delta_{free\ ligand}$) are: 0.16, 0.41, 0.43, 0.11, 0.11 and 0.07 ppm for $[^2H_4]$methanol solution, 0.23, 0.32, 0.17, 0.06, 0.17 and 0.08 ppm for $(CD_3)_2SO$, respectively. The complex is sparingly soluble in methanol in contrast to the case of dimethyl sulphoxide.

Cyclic voltammograms were recorded with a Hokuto HA-104

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† thiochrome = 2-(2,7-Dimethyl-5*H*-pyrimido[4,5-*d*]thiazolo[3,2-*a*]-pyrimidin-8-yl)ethanol.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

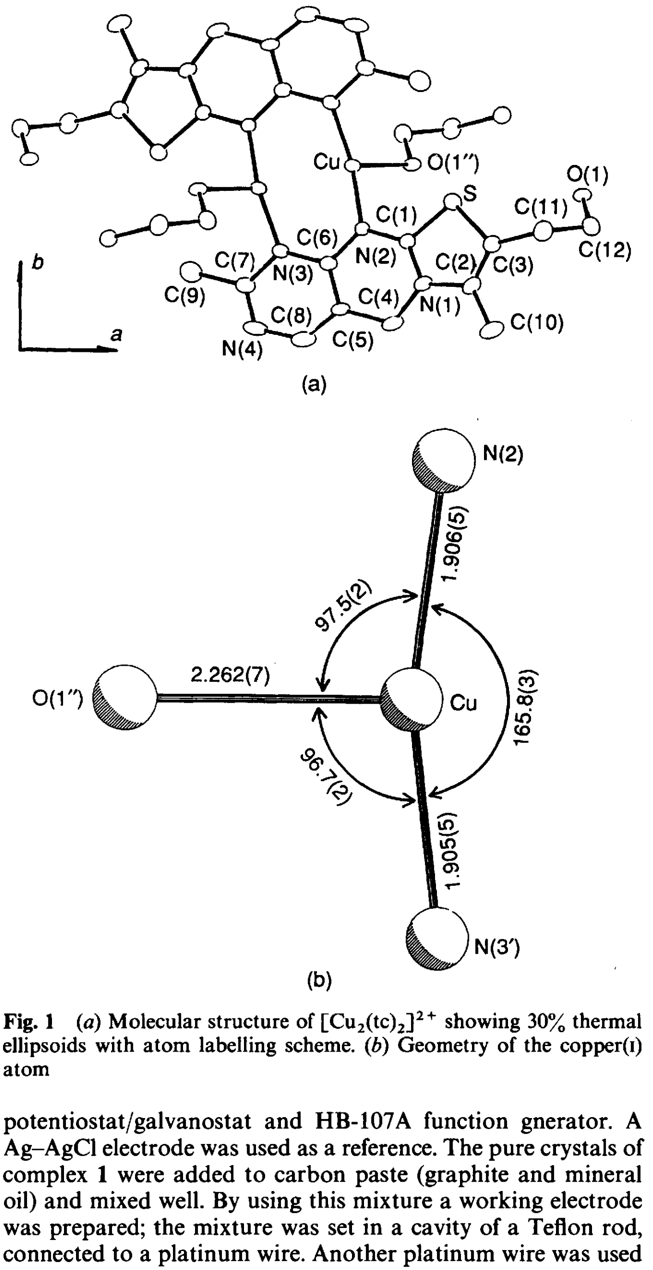

Fig. 1 (*a*) Molecular structure of [Cu$_2$(tc)$_2$]$^{2+}$ showing 30% thermal ellipsoids with atom labelling scheme. (*b*) Geometry of the copper(I) atom

potentiostat/galvanostat and HB-107A function gnerator. A Ag–AgCl electrode was used as a reference. The pure crystals of complex 1 were added to carbon paste (graphite and mineral oil) and mixed well. By using this mixture a working electrode was prepared; the mixture was set in a cavity of a Teflon rod, connected to a platinum wire. Another platinum wire was used as a counter electrode. By utilizing three-electrode systems and 0.1 mol dm^{-3} NaClO$_4$ aqueous solution, cyclic voltammograms were recorded, using a scan rate of 10 mV s^{-1} and scan range of −0.8 to 0.8 V. Ferrocene crystals in the paste were used as a standard.

Crystallography.—Crystal Data. C$_{12}$H$_{14}$ClCuN$_4$O$_5$S, monoclinic, space group $P2_1/c$, a = 9.50(1), b = 22.79(1), c = 7.889(6) Å, β = 111.06(8)°, U = 1595.9 Å^3, Z = 2, D_c = 1.770 g cm^{-3}, λ(Mo-Kα) = 0.710 73 Å, μ = 16.61 cm^{-1}, T = 25 °C.

X-Ray data collection. A single crystal (0.5 × 0.4 × 0.4 mm) of the compound was glued on top of a glass fibre and studied on a Rigaku 6B automatic diffractometer. Preliminary investigation revealed the crystal to be monoclinic. Unit-cell parameters were determined from a least-squares fit of 25 accurately centered reflections. Intensities were gathered in an ω–2θ scan mode. Lorentz, polarization and absorption corrections were applied. Of the 5306 unique reflections measured, 2529 with $F_o > 3\sigma(F_o)$ were used in the subsequent structure analysis. The Laue class and the axial dimensions were confirmed with oscillation photographs. From the systematic absences, the space group was uniquely determined to be $P2_1/c$.

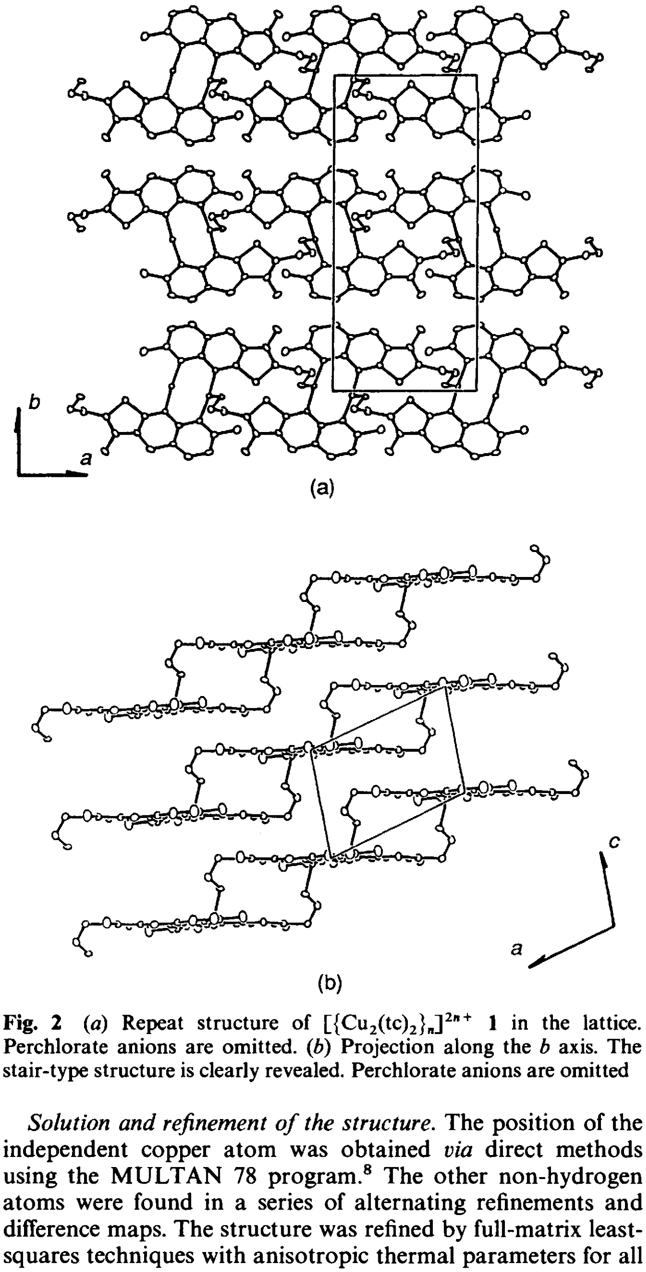

Fig. 2 (*a*) Repeat structure of [{Cu$_2$(tc)$_2$}$_n$]$^{2n+}$ **1** in the lattice. Perchlorate anions are omitted. (*b*) Projection along the *b* axis. The stair-type structure is clearly revealed. Perchlorate anions are omitted

Solution and refinement of the structure. The position of the independent copper atom was obtained *via* direct methods using the MULTAN 78 program.[8] The other non-hydrogen atoms were found in a series of alternating refinements and difference maps. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. All atoms of a perchlorate anion (A) were found. Towards the end of the development of the structure, four substantial difference peaks were observed around the chlorine atom of the perchlorate anion. These sites were modelled as oxygen atoms and the site occupancies were set as 70 and 30% for models A and B. The two ClO$_4^-$ are related by a rotation (*ca.* 63°) around the Cl atom. All hydrogen atoms of the thiochrome were placed in calculated positions and their parameters refined with fixed isotropic thermal parameters. Finally two cycles of refinement led to convergence at $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.0680$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.0697$, with $w^{-1} = [\sigma^2(F_o) + 0.015F_o^2]$.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Structure of [{Cu$_2$(tc)$_2$(ClO$_4$)$_2$}$_n$].—ORTEP diagrams of complex 1 are shown in Figs. 1 and 2. Fractional coordinates and selected bond distances and angles are presented in Tables 1 and 2, respectively.

The structure comprises an infinite array of [Cu$_2$(tc)$_2$]$^{2+}$

Table 1 Atomic positional parameters for [{$Cu_2(tc)_2(ClO_4)_2$}$_n$]

Atom	x	y	z
Cu	0.132 37(8)	0.484 63(3)	0.034 2(1)
Cl	0.763 3(2)	0.365 52(9)	0.359 5(3)
S	0.463 8(2)	0.528 51(8)	0.266 2(3)
N(1)	0.380 0(6)	0.633 9(2)	0.227 5(7)
N(2)	0.180 4(5)	0.564 5(2)	0.101 6(7)
N(3)	−0.067 0(6)	0.594 9(2)	−0.015 7(7)
N(4)	−0.134 3(8)	0.695 2(3)	−0.033(1)
O(1)	0.782 1(6)	0.517 9(2)	0.198 8(7)
C(1)	0.325 1(7)	0.580 1(3)	0.187 1(8)
C(2)	0.536 4(8)	0.635 5(3)	0.325(1)
C(3)	0.597 5(8)	0.582 0(3)	0.360(1)
C(4)	0.284 1(9)	0.686 0(3)	0.167(1)
C(5)	0.123 0(7)	0.668 5(3)	0.086 8(9)
C(6)	0.079 2(7)	0.610 0(3)	0.055 6(8)
C(7)	−0.169 8(8)	0.639 5(3)	−0.059(1)
C(8)	0.013(1)	0.708 8(4)	0.039(1)
C(9)	−0.0333 3(8)	0.623 5(3)	−0.135(1)
C(10)	0.609(1)	0.693 2(4)	0.383(1)
C(11)	0.759 9(8)	0.564 1(4)	0.464(1)
C(12)	0.850 1(8)	0.556 9(4)	0.346(1)
O(2A)	0.913 9(8)	0.355 4(4)	0.375(1)
O(3A)	0.689(1)	0.322 9(4)	0.417(1)
O(4A)	0.684(1)	0.388 7(8)	0.186(1)
O(5A)	0.763(1)	0.414 0(5)	0.464(2)
O(2B)	0.862(3)	0.343(1)	0.527(3)
O(3B)	0.853(4)	0.392(2)	0.282(4)
O(4B)	0.682(2)	0.326 6(9)	0.236(3)
O(5B)	0.679(2)	0.413 8(9)	0.390(4)

Table 2 Selected bond distances (Å) and angles (°) for [{$Cu_2(tc)_2(ClO_4)_2$}$_n$]*

Cu–N(2)	1.906(5)	Cu′–N(3)	1.905(5)
Cu–O(1″)	2.262(7)	S–C(1)	1.709(6)
N(1)–C(2)	1.407(8)	C(6)–N(2)	1.371(8)
C(6)–N(3)	1.342(8)	N(3)–C(7)	1.364(9)
C(12)–O(1)	1.419(9)	Cu ··· Cu′	2.476(3)
N(2) ··· N(3)	2.302(7)		
N(2)–Cu–N(3′)	165.8(3)	N(2)–Cu–O(1″)	97.5(2)
N(3′)–Cu–O(1″)	96.7(2)	C(1)–N(2)–C(6)	115.3(5)
C(6)–N(3)–C(7)	117.1(6)	N(2)–C(6)–N(3)	116.1(5)
C(1)–N(2)–Cu	119.5(4)	C(7)–N(3)–Cu′	120.3(5)
N(2)–Cu–Cu′	85.0(2)	N(3)–Cu′–Cu	88.6(2)

* Single and double primes denote atoms translated by a centre of symmetry and the other centre of symmetry, respectively.

units linked by the 2-hydroxyethyl group of the co-ordinated tc. The [$Cu(tc)_2$]$^{2+}$ unit is centrosymmetric and the midpoint of the Cu–Cu′ vector occupies a crystallographic centre of inversion. The Cu–Cu′ vector and the two tc ligands without the respective hydroxyethyl groups define a plane, the average mean deviation from planarity being 0.2 Å. The two copper atoms deviate by 0.17 Å above and below the plane, respectively, due to the binding to the hydroxy oxygen atom. The planar moiety of complex **1** is very similar to [$Cu_2(napy)_2$]$^{2+}$ (napy = 1,8-naphthyridine),[5] which has a nearly perfect planar structure.

Although there is little difference in bond distances and angles between these two complexes, there is a great difference in the co-ordination number: the copper(I) geometry in the [$Cu_2(tc)_2$]$^{2+}$ unit is a T-shape [Fig. 1(*a*)] with a N_2O donor set, in [$Cu_2(napy)_2$]$^{2+}$ the copper(I) is two-co-ordinate. The N(2)–Cu–N(3′) angle [165.8(3)°] is relatively small for a T-shape copper(I) complex, being comparable with those of [$Cu_2L(pyz)$] (167.6°)[9] and [CuL']BF_4 (169.1°) {L = the condensation product of 2-hydroxy-5-methylisophthalaldehyde and 2(2′-aminoethyl)pyridine, pyz = pyrazine, L^1 = bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ether}.[10] The terminal Cu–N(2) and Cu–N(3′) bond distances [1.906(5) and 1.905(5) Å] are shorter than those found in tetrahedral copper(I) complexes, while the bridge Cu–O(1″) [2.262(7) Å] is longer than that of a terminal Cu–O bond. This aspect is characteristic of T-shaped copper(I) complexes in contrast to Y-shaped ones.[11]

There are two interesting features of this structure. First, the co-ordination of the oxygen atom linking the [$Cu_2(tc)_2$]$^{2+}$ units apparently does not influence the Cu ··· Cu′ contact distance [2.476(3) Å], which is shorter than that in [$Cu(napy)_2$][ClO_4]$_2$ (2.506 Å).[5] Comparison of the bond distances and angles of these two complexes reveals no significant differences except for the spatial distance between N(2) and N(3): co-ordinated tc gives 2.302(7) Å, while napy gives 2.343(8) Å. This is associated with the shorter contact.

Secondly, the co-ordinated oxygen is not anionic (O^-) but neutral OH. There are many instances of Cu^{II}–(OH)R bonds, where the bond distance ranges from 2.375 to 1.991 Å.[12] On the other hand, a direct Cu^{I}–(OH)R bond is quite uncommon except for a weak contact such as a solvating alcohol (Cu^{I} ··· O 2.6 Å).[13] Thus, no comparison of this distance, 2.262(7) Å, can be made but this is rare and clear evidence of a Cu^{I}–(OH)R bond.

As shown in Figs. 1 and 2 the dinuclear copper units are linked by alcohol oxygen atoms from neighbouring dinuclear units on both sides, giving an infinite chain structure along the *a* axis. The mode of polymerization is stair-type, quite a novel structure there being only few stair-like chain structures in copper(I) compounds.[14,15] Each planar dimer moiety of complex **1** comprises one step. The distance between neighbouring two steps in a chain is 4.5 Å. The nearest-neighbour chain is related by a *c*-axis translation. Hence, there are no interactions among the chains. This is due to the presence of perchlorate anions between them. The closest O(ClO_4) ··· Cu distance is 4.07 Å, indicative of no anion co-ordination. Consequently, the structure is best described as infinite polycation chains with anion columns along these chains.

Preparation and Characterization of [{$Cu(tc)$}$_2$][ClO_4]$_2$.—Complex **1** crystallizes from acetone–methanol solution. The solution species was examined by ^1H NMR spectroscopy. Dissolution of **1** in methanol, acetone and dimethyl sulphoxide gave essentially similar NMR spectra, revealing a single species. The observed chemical shifts and co-ordination shifts ($\delta_c = \delta_{complex} - \delta_{free\ ligand}$) are listed in the Experimental section. Inspection of the δ_c indicates co-ordination of N(2) and N(3) because of the large δ_c values of the ring protons (H^4 and H^8) and the neighbouring methyl group (C^9H_3) in contrast with those of $C^{10}H_3$ and the hydroxyethyl protons. A decrease in δ_c from H^{11} to H^{12} clearly indicates no co-ordination of the hydroxy oxygen to the copper(I) atom, in contrast to the solid state. The cyclic voltammogram of the methanol solution gives two quasi-reversible waves [$E_{\frac{1}{2}}$ = 0.46 (ΔE_p = 0.07) and 0.50 V (ΔE_p = 0.16 V) *vs.* Ag–AgCl). On the basis of NMR results, the two waves arise from stepwise redox reactions of the two copper sites in a dicopper complex. Consequently, the solution species is [$Cu_2(tc)_2$]$^{2+}$, where the two copper atoms are bridged by two *trans* tc ligands through their nitrogen atoms. Thus dissolution breaks the Cu–O bond in **1**.

Electrochemical Properties of Complex **1**.—From the result in solution, it is impossible to obtain cyclic voltammograms of [{$Cu_2(tc)_2(ClO_4)_2$}$_n$] in solution. The cyclic voltammogram of a carbon paste containing crystalline **1** was measured as mentioned in the Experimental section. Before this experiment, the same technique was applied to ferrocene, chosen as a

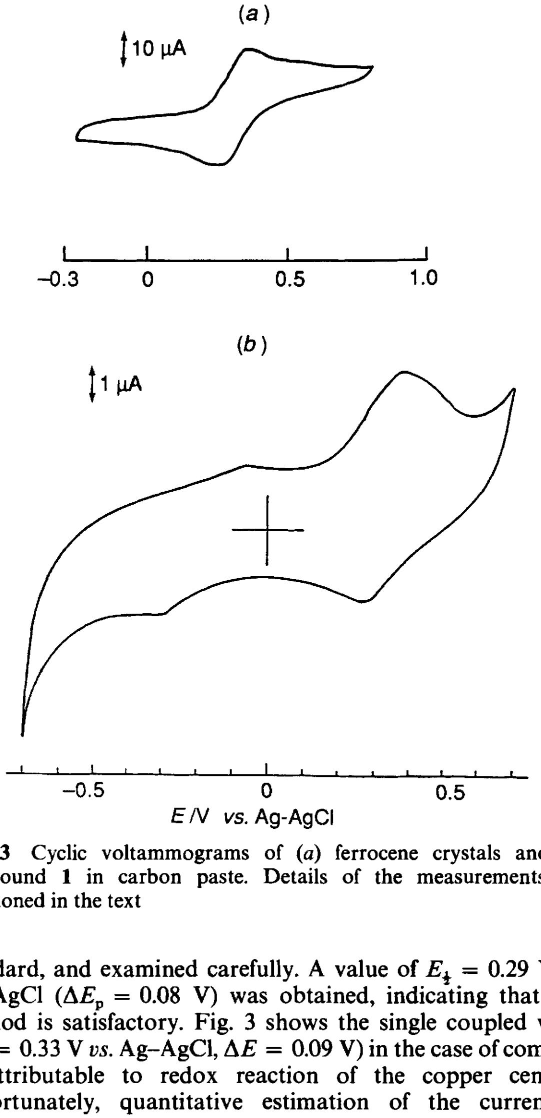

Fig. 3 Cyclic voltammograms of (*a*) ferrocene crystals and (*b*) compound **1** in carbon paste. Details of the measurements are mentioned in the text

standard, and examined carefully. A value of $E_{\frac{1}{2}} = 0.29$ V *vs.* Ag–AgCl ($\Delta E_p = 0.08$ V) was obtained, indicating that this method is satisfactory. Fig. 3 shows the single coupled wave ($E_{\frac{1}{2}} = 0.33$ V *vs.* Ag–AgCl, $\Delta E = 0.09$ V) in the case of complex **1**, attributable to redox reaction of the copper centre.* Unfortunately, quantitative estimation of the current is impossible because the concentration of the compound on the surface of the electrode, and hence the stoichiometry of electron transfer involved, is not known. This couple might correspond to the reactions $Cu^ICu^I \rightleftharpoons Cu^{II}Cu^I$ or $Cu^ICu^I \rightleftharpoons Cu^{II}Cu^{II}$. The good reversibility is attributable to the three-co-ordinate geometry, which both copper-(I) and -(II) favour. Otherwise, the role of the dissociable alcoholic proton of the third ligand is not negligible, probably existing as OH for Cu^I but O^- for Cu^{II}.

Conclusion

By using planar dicopper(I) complex units an infinite-chain polymer has been synthesised. This implies that a planar fused ligand having a substituent with a bridging ability such as tc is quite useful for rational synthesis of organometallic polymers. The compound obtained here is a rare polymer of a dicopper unit with short metal–metal contacts. It undergoes reversible redox reaction at the copper even in the solid state, attributable to the specific structure, such as three-co-ordination and/or co-ordination of the alcoholic OH group to the copper atom.

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References

1 J. S. Miller, *Extended Linear Chain Compounds*, Plenum, New York, 1981–1983, vols. 1–3.
2 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, New York, vols. 3–5, pp. 533–774.
3 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 1984.
4 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley-Interscience, New York, 1988.
5 M. Munakata, M. Maekawa, S. Kitagawa, M. Adachi and H. Masuda, *Inorg. Chim. Acta*, 1990, **167**, 181.
6 D. F. Shriver, *Inorganic Syntheses*, Wiley-Interscience, New York, 1979, vol. 19, p. 90.
7 G. E. Risinger and P. N. Parker, *Experientia*, 1965, **21**, 305.
8 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq and M. M. Woolfson, MULTAN 78. A System of Computer Programs for Automatic Solution of Crystal Structure from X-Ray Diffraction Data, Universities of York and Louvain, 1978.
9 R. G. Gagne, R. P. Kreh and J. A. Dodge, *J. Am. Chem. Soc.*, 1979, **101**, 6917.
10 T. N. Sorrell and M. R. Malachowski, *Inorg. Chem.*, 1983, **22**, 1883.
11 M. Munakata, M. Maekawa, S. Kitagawa, S. Matsuyama and H. Masuda, *Inorg. Chem.*, 1989, **28**, 4300.
12 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
13 M. G. B. Drew, P. C. Yates, J. Trocha-Grimshaw, K. P. McKillop and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1985, 262.
14 J. A. Campbell, C. L. Raston and A. H. White, *Aust. J. Chem.*, 1977, **30**, 1937.
15 P. C. Healy, C. Pakawatchai, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1905.

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* Both pure carbon paste and carbon paste containing only the ligand, tc, gave no waves in this region.