



**SYNTHESIS, X-RAY CRYSTAL STRUCTURE AND
REACTIVITY OF THE POLYMERIC COPPER(II)
DICARBOXYLIC ACID COMPLEX $\{Cu_2(\eta^1\eta^1\mu_2-$
 $oda)_2(py)_4(H_2O)_2\}_n$ (odaH₂ = OCTANEDIOIC ACID,
py = PYRIDINE)**

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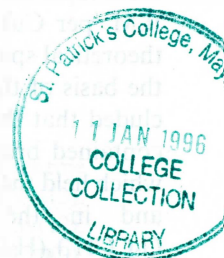
Abstract—An aqueous solution of the α,ω -dicarboxylic acid octanedioic acid (odaH₂) reacts with $[Cu_2(\mu-O_2CCH_3)_4(H_2O)_2]$ in the presence of an excess of pyridine (py) to give the crystalline copper(II) complex $\{Cu_2(\eta^1\eta^1\mu_2-oda)_2(py)_4(H_2O)_2\}_n$ (**1**). The structure of **1**, as determined by X-ray crystallography, consists of polymeric chains in which bridging oda^{2-} anions link two crystallographically identical copper atoms. The copper atoms are also ligated by two *transoidal* pyridine nitrogens and an oxygen atom from an apical water molecule, giving the metals an overall N₂O₃ square-pyramidal geometry. If the blue solid **1** is gently heated, or if it is left to stand in its mother liquor for prolonged periods, it loses one molecule of pyridine and half a molecule of water and the green complex $\{Cu(oda)(py)(H_2O)_{0.5}\}_n$ (**2**) is formed. Spectroscopic and magnetic data for both complexes are given, together with the electrochemical and thermogravimetric measurements for **1**.

Copper is an important trace element in almost all forms of life and it is the third most abundant element in the human body following iron and zinc.¹ Copper-containing metalloenzymes are now known to be involved in a variety of biological functions such as electron transfer, copper storage and many oxidase activities.² Anomalies in copper metabolism in humans, whether caused by a deficiency of, or an inability to absorb, the metal can lead to the development of Menke's disease.³⁻⁵ This dis-

order is characterized by severe neurologic, skeletal and developmental abnormalities.³ Near normal growth rates and the survival of animal models for this disease has been achieved by the administration of copper(II) salts in the presence of decanedioic acid $\{HO_2C(CH_2)_8CO_2H\}$.⁶ The nature of the copper complexes present in the system is not fully understood and, indeed, reports of copper complexes of this or similar long chained α,ω -dicarboxylic acid ligands are scarce.^{7,8}

Asai *et al.*⁷ have synthesized a range of polymeric copper(II) complexes of the formula $[Cu(O_2C)(CH_2)_nCO_2]$ ($n = 0-8$), and with the exception of

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the propanedioic acid complex all of these materials had effective magnetic moments in the range 1.20–1.45 B.M. per Cu. These values were similar to those reported⁹ for hydrated copper(II) acetate (1.4 B.M. per Cu) and considerably smaller than the theoretical spin-only value (1.73 B.M. per Cu). On the basis of the magnetic data these workers concluded that the polymeric complexes ($n = 0, 2-8$) contained bridging bidentate carboxylate ligands, which held the two metal centres in close proximity and in the same manner as in $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_4]$.^{10,11} The X-ray crystal structure of the copper(II) butanedioic acid complex $\{\text{Cu}_2(\mu\text{-O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)_2(\text{H}_2\text{O})_2\}_n$ showed it to consist of infinite chains of binuclear copper(II) units interconnected by the bridging bidentate dicarboxylate ligands.¹²

As part of our recent studies into the coordination chemistry of dicarboxylic acids,¹³⁻¹⁷ we have been examining the reactions of copper(II) salts with several relatively long-chained α,ω -dicarboxylic acids. $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ was found¹⁶ to react smoothly with $\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$ ($n = 5, 6$) to give polymeric copper(II) complexes similar to those described by Asai *et al.*⁷ These somewhat insoluble polymeric complexes then reacted with 1,10-phenanthroline (phen) to yield the highly soluble mononuclear species $[\text{Cu}(\eta^2\text{-O}_2\text{C}(\text{CH}_2)_n\text{CO}_2)(\text{phen})_2] \cdot x\text{H}_2\text{O}$ ($x = 8$). The X-ray crystal structures of the two complexes ($n = 5, x = 11.73$; $n = 6, x = 12$) show the copper centres ligated by the four nitrogen atoms of the two phenanthrolines and two oxygens from a single asymmetrically chelating carboxylate function of the dicarboxylate ligand, with the second carboxylate group of the diacid uncoordinated.¹⁶

To date no X-ray crystal structures of polymeric copper complexes of relatively long-chain α,ω -dicarboxylic acids have been reported in the literature. Herein we outline the synthesis, X-ray crystal structure, reactivity and physical properties of the polymeric copper(II) complex $\{\text{Cu}_2(\eta^1\eta^1\mu_2\text{-oda})_2(\text{py})_4(\text{H}_2\text{O})_2\}_n$ (**1**) [$\text{odaH}_2 = \text{octanedioic acid}$, $\text{HO}_2\text{C}(\text{CH}_2)_n\text{CO}_2\text{H}$, $\text{py} = \text{pyridine}$].

RESULTS AND DISCUSSION

Reaction of copper(II) acetate with an aqueous solution of odaH_2 (*ca* 1 : 2 mol ratio), followed by the addition of a large excess of pyridine (py), yields a deep blue solution from which blue crystals of the copper(II) complex $\{\text{Cu}_2(\eta^1\eta^1\mu_2\text{-oda})_2(\text{py})_4(\text{H}_2\text{O})_2\}_n$ (**1**) deposit on standing. The X-ray crystal structure of the complex is shown in Figs 1–3, and consists of linear polymeric chains in which brid-

ing oda^{2-} dianions link the metal centres. Each copper atom has N_2O_3 square-pyramidal coordination and is ligated by the nitrogen atoms of two *transoid* pyridines, an oxygen atom from an apical water molecule and a single carboxylate oxygen atom from each of the two *transoid* monodentate oda^{2-} ligands. In the coordination sphere of each metal the Cu—O(carboxylate) bond at 1.944(3) Å is shorter than the Cu—N bond at 2.030(3) Å, with the Cu—O(water) bond distance being the longest of all at 2.202(5) Å.

The IR spectrum of **1** contains distinctive $\nu_{\text{asym}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ bands at 1600 and 1395 cm^{-1} , respectively, giving a frequency difference (Δ) of 205 cm^{-1} , which reflects the monodentate nature of the carboxylate ligands.¹⁸ The magnetic moment of the complex (1.82 B.M. per Cu) is in the range expected for normal copper(II) complexes, i.e. those lacking Cu—Cu interactions.¹ In this lattice the Cu—Cu spacing is the length of the *b* axis (5.758 Å) and any interaction would be via the water bridge $\text{Cu—OH}_2 \cdots \text{Cu}$.

The polymeric dicarboxylate complex **1** is, as expected, insoluble in water and in common organic solvents. However, the complex is quite soluble in pyridine and in pyridine : water mixtures. Solutions of free odaH_2 and complex **1** in pyridine are essentially non-conducting ($\Lambda_{\text{M}} = 2.3$ and 2.5 $\text{S cm}^2 \text{mol}^{-1}$, respectively). In contrast, the free acid and complex **1** are both extensively ionically dissociated in a pyridine : water (1 : 1) mixture ($\Lambda_{\text{M}} = 189$ and 50 $\text{S cm}^2 \text{mol}^{-1}$, respectively).

Between the switching potentials of +50 and –2100 mV (*versus* Ag/AgCl), the cyclic voltammogram of a solution of free odaH_2 in pyridine (Fig. 4) showed a very large, irreversible reduction peak, A ($E_{\text{c}} = -1725$ mV), and two smaller irreversible oxidation peaks, B ($E_{\text{a}} = -800$ mV) and C ($E_{\text{a}} = -100$ mV). Peaks B and C are probably due to the oxidation of decomposition products arising from the irreversible reduction of the odaH_2 . In the potential range +1100 to –1200 mV the voltammogram of a pyridine solution of **1** (Fig. 5) contained two quasi-reversible $\text{Cu}^{2+}/\text{Cu}^+$ couples DE ($E_{\text{pa}} - E_{\text{pc}} = 330$ mV; $E_{1/2} = +307$ mV) and FG ($E_{\text{pa}} - E_{\text{pc}} = 220$ mV; $E_{1/2} = -237$ mV). Given that the metal centres in the solid polymer **1** are structurally identical, and also that conductivity measurements indicate that the complex does not ionically dissociate in pyridine, it is somewhat surprising that two distinct $\text{Cu}^{2+}/\text{Cu}^+$ couples are observed. Furthermore, as the difference in the $E_{1/2}$ potentials for the couples is quite large ($\Delta E_{1/2} = 544$ mV), this implies that the reduction of the first Cu^{2+} centre has a significant influence on the potential at which the second Cu^{2+} centre is reduced.

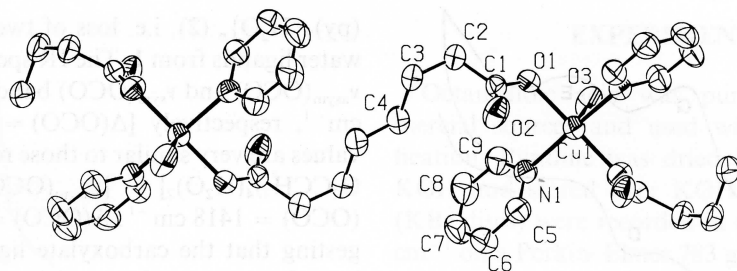


Fig. 1. X-ray crystal structure of $\{\text{Cu}_2(\eta^1\eta^1\mu_2\text{-oda})_2(\text{py})_4(\text{H}_2\text{O})_2\}_n$ (**1**), showing the numbering scheme and polymeric nature of the species. Selected bond distances (Å) and angles (°): Cu—O(1) 1.944(3), Cu—N 2.030(3), Cu—O(3) 2.202(5); O(1)—Cu—O(1*) 179.8(2), O(1*)—Cu—N(1) 91.39(12), O(1)—Cu—N(1) 88.62(12), O(1)—Cu—N(1*) 91.39(12), O(1*)—Cu—O(3) 89.90(9), N(1)—Cu—O(3) 95.22(10), N(1)—Cu—N(1*) 169.6(2) (*symmetry related).

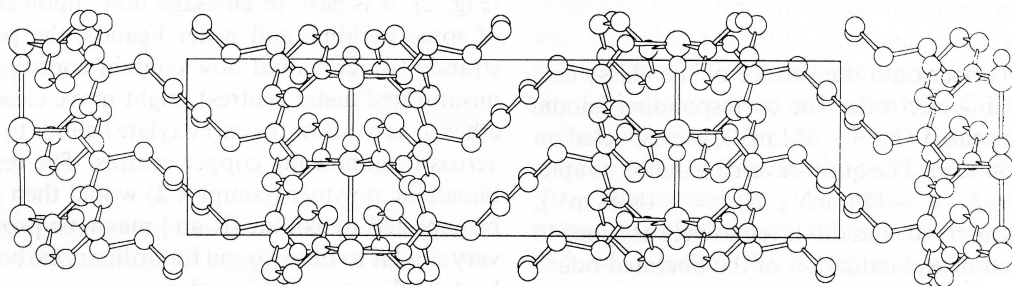


Fig. 2. View of **1** down the 001 direction, showing the stacking of the polymer chains. The Cu—OH₂ of one chain is directly above the Cu of an adjacent chain giving $\cdots\text{Cu—OH}_2\cdots\text{Cu—OH}_2\cdots\text{Cu—OH}_2\cdots$, etc.

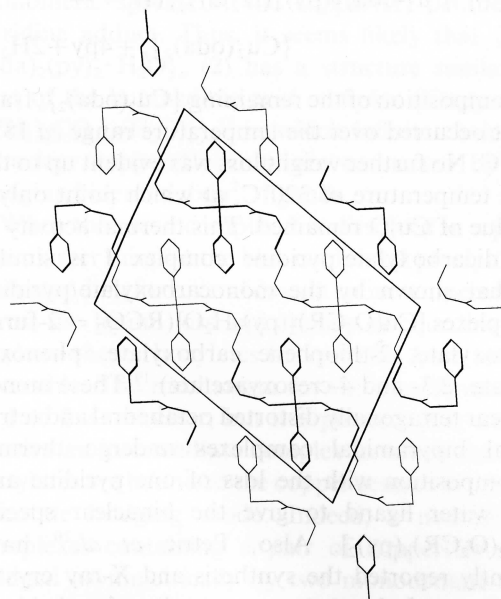


Fig. 3. View of **1** down the *b* axis showing the infinite polymer chains. The Cu—OH₂···Cu stacking is not visible in this orientation.

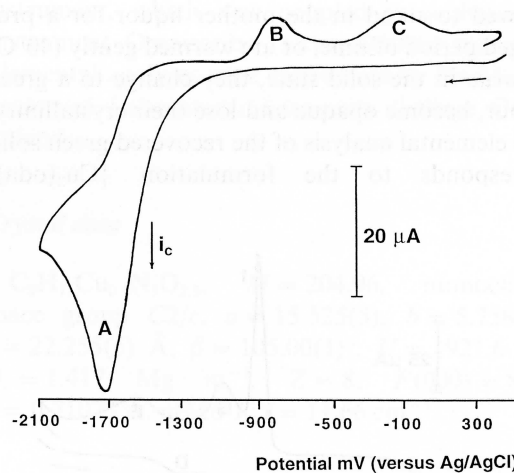


Fig. 4. Cyclic voltammogram of free odaH₂. Switching potentials were +500 and -2100 mV; and scan rate = 20 mV s⁻¹.

When the cathodic switching potential in the voltammogram of **1** is extended from +1100 to -2100 mV an irreversible reduction peak, H ($E_c = -1736$ mV), is observed (Fig. 6) due to the plating of

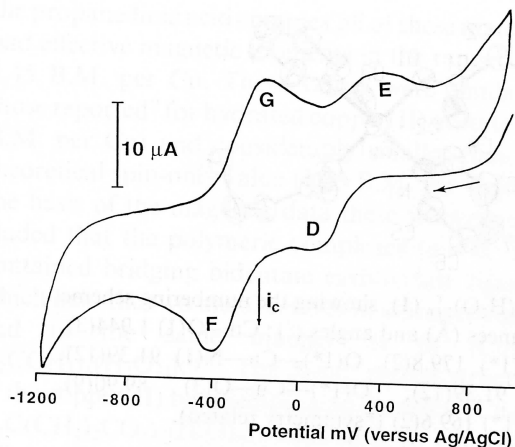


Fig. 5. Cyclic voltammogram of **1**. Switching potentials were +1100 and -1200 mV, and scan rate = 50 mV s⁻¹.

metallic copper onto the surface of the glassy carbon working electrode. The corresponding anodic stripping peak, I ($E_a = -361$ mV), was detected on the reverse scan. The quasi-reversible redox couple, JK ($E_{Pa} - E_{Pc} = -184$ mV; $E_{1/2} = -1868$ mV), was also observed, and this is tentatively assigned to the reduction and oxidation of the liberated oda^{2-} ligand. It should be noted that the electrochemical behaviour of the oda^{2-} ion at the copper coated working electrode is quite different to that of $odaH_2$ at a glassy carbon electrode.

The blue crystals of **1** are relatively air-stable at room temperature. However, if they are either allowed to stand in the mother liquor for a prolonged period of time, or are warmed gently (40°C) *in vacuo* in the solid state, they change to a green colour, become opaque and lose their crystallinity. The elemental analysis of the recovered green solid corresponds to the formulation $\{Cu_2(oda)_2$

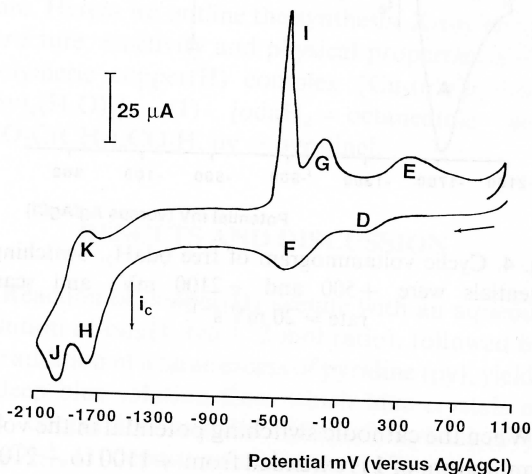
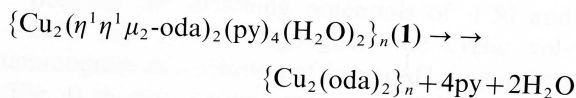


Fig. 6. Cyclic voltammogram of **1**. Switching potentials were +1100 and -2100 mV, and scan rate = 50 mV s⁻¹.

$(py)_2 \cdot H_2O\}_n$ (**2**), i.e. loss of two pyridine and one water ligands from **1**. The IR spectrum of **2** exhibits $\nu_{asym}(OCO)$ and $\nu_{sym}(OCO)$ bands at 1600 and 1430 cm^{-1} , respectively [$\Delta(OCO) = 170$ cm^{-1}]. These values are very similar to those reported for $[Cu_2(\mu-O_2CCH_3)_4(H_2O)_2]$ [$\nu_{asym}(OCO) = 1603$; $\nu_{sym}(OCO) = 1418$ cm^{-1} ; $\Delta(OCO) = 185$ cm^{-1}],¹¹ suggesting that the carboxylate ligands in **2** are also bound to the metal centres in a bridging bidentate mode. Further support for such a binuclear structure stems from the observed room temperature magnetic moment of **2** (1.34 B.M. per Cu), which indicates that there is strong antiferromagnetic coupling between adjacent metal centres.^{1,18} Considering the close interchain proximity of the copper centres (5.758 Å) in the solid state structure of **1** (Fig. 2), it is easy to envisage how, upon the loss of some pyridine and water ligands, the polymer strands (which would now contain coordinatively unsaturated metal centres) might move closer together so as to allow the carboxylate ligands to bridge across neighbouring copper centres. The resulting bimetallic polymer (complex **2**) would then indeed be expected to exhibit IR and magnetic properties very similar to those found for ordinary carboxylate bridged dicopper(II) complexes.

A thermogravimetric study of $\{Cu_2(\eta^1\eta^1\mu_2-oda)_2(py)_4(H_2O)_2\}_n$ (**1**) (Fig. 7) shows that over the temperature range *ca* 54–146°C there are two thermal events (not perfectly resolved) corresponding in total to the loss of the four pyridine and two water ligands.



Decomposition of the remaining $\{Cu_2(oda)_2\}_n$ fragment occurred over the temperature range *ca* 185–246°C. No further weight loss was evident up to the final temperature of 320°C, at which point only a residue of Cu_2O remained. This thermal activity of the dicarboxylate/pyridine complex **1** is similar to that shown by the monocarboxylate/pyridine complexes $[Cu(O_2CR)_2(py)_2H_2O](RCO_2 = 2\text{-furan carboxylate, 2-thiophene carboxylate, phenoxyacetate, 2,3- and 4-cresoxyacetate})$.¹⁹ These mononuclear tetragonally distorted octahedral and tetragonal bipyramidal complexes undergo thermal decomposition with the loss of one pyridine and one water ligand to give the binuclear species $[Cu_2(O_2CR)_4(py)_2]$. Also, Petric *et al.*²⁰ have recently reported the synthesis and X-ray crystal structure of the green, tetracarboxylate-bridged dicopper(II) complex $[Cu_2(\mu-O_2C(CH_2)_6CH_3)_4(py)_2]$ containing the relatively long-chained monocarboxylic acid octanoic acid. It was reported that

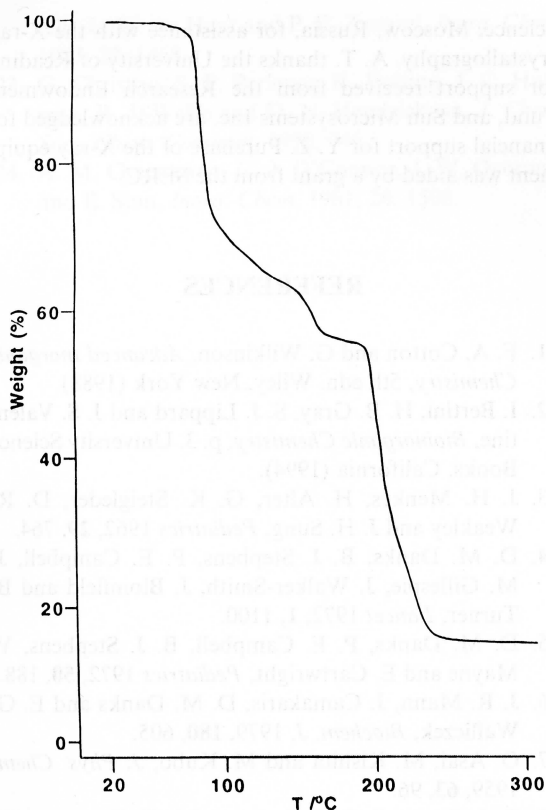


Fig. 7. Thermogravimetric analysis curve for **1**. Heating rate = $10^\circ\text{C min}^{-1}$.

EXPERIMENTAL

Octanedioic acid was purchased from commercial sources and used without further purification. Pyridine was dried by distillation from KOH and stored over KOH pellets. IR spectra (KBr discs) were recorded in the region $4000\text{--}200\text{ cm}^{-1}$ on a Perkin-Elmer 783 grating spectrometer, and electronic spectra of pyridine and water/pyridine (1:1) solutions of complex **1** were obtained using a Milton Roy Spectronic 3000 array. Solid-state, room-temperature magnetic susceptibility measurements were made on a Johnson-Mathey magnetic susceptibility balance, and conductivity measurements (25°C and 1.0 mM concentration) were obtained using an AGB model 10 conductivity meter. The cyclic voltammogram of **1** was recorded (*ca* 20°C and under N_2) using an EG&G Model 264A polarographic analyser, and the data was analysed using the EG&G Condecon software package. A glassy carbon disc and a platinum wire were used as the working and counter electrodes, respectively. Potentials are quoted with respect to a silver/silver chloride reference electrode (3.5 M aqueous KCl), against which the ferrocene/ferrocenium(1+) couple had $E_{1/2} = +593\text{ mV}$. Tetrabutylammonium perchlorate (0.1 M) in pyridine was used as the supporting electrolyte/solvent system and the sample concentration was 4.0 mM . Thermogravimetric analyses (in air) were performed on a Stanton Redcroft TG 750/770 instrument, which was coupled to a Houston Instrument Omniscrite (series D5000) recorder. Elemental analyses were carried out by the Micro-analytical Laboratory, University College Cork, Ireland.

Crystal data

$\text{C}_9\text{H}_{11}\text{Cu}_{0.5}\text{N}_1\text{O}_{2.5}$, $M = 204.96$, monoclinic, space group $C2/c$, $a = 15.525(5)$, $b = 5.758(3)$, $c = 22.255(5)\text{ \AA}$, $\beta = 105.00(1)^\circ$, $U = 1921.6\text{ \AA}^3$, $D_c = 1.417\text{ Mg m}^{-3}$, $Z = 8$, $F(000) = 852$, $\lambda = 0.71073\text{ \AA}$, $\mu(\text{Mo-K}\alpha) = 11.66\text{ cm}^{-1}$.

Data collection and processing

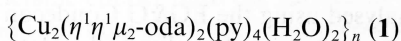
A dark blue crystal of approximate size $0.1 \times 0.3 \times 0.3\text{ mm}$ was mounted on a Mar Research image plate scanner, and graphite monochromated Mo- K_α radiation was used to measure 95.2° frames with an exposure time of 120 s per frame. Data were processed using the XDS package to give 9392 reflections, of which 1454 were unique [$R(\text{int}) = 4.61$].

during the work up of this complex blue crystals initially formed, and these were presumed to be a monomeric species of the copper(II) octanoate/pyridine adduct. Thus, it seems likely that $\{\text{Cu}_2(\text{oda})_2(\text{py})_2 \cdot \text{H}_2\text{O}\}_n$ (**2**) has a structure similar to that of the butanedioic acid complex $\{\text{Cu}_2(\mu\text{-O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)_2(\text{H}_2\text{O})_2\}_n$ ¹² in which infinite chains of binuclear copper(II) units are connected by the bridging bidentate bda^{2-} ligands.

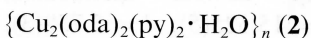
When the green complex **2** is dissolved in a pyridine:water mixture the blue complex **1** precipitates after standing for several days at room temperature. Thus, the ligand loss and change of coordination mode of the carboxylates for complex **1** are totally reversible. The mechanism for the transformation of **1** to **2** is not clear, but it is possible that it may involve an intermediate complex in which the carboxylates are bound to the copper centres in a monodentate bridging mode. Indeed, a number of complexes containing a pair of copper(II) ions bridged asymmetrically by two monodentate carboxylates have been reported²¹⁻²⁶ and Lippard and coworkers²⁷ have recently described this movement from monodentate bridging carboxylate to other binding modes as the "carboxylate shift".

Structure analysis and refinement

The structure was solved by the direct method of SHELX86 and refined using SHELXL (courtesy of Professor G. M. Sheldrick, University of Göttingen), by full-matrix least-squares of 119 variables to a final R value of 0.0484 for reflections with $|F_o| > 4\sigma(F)$. All atoms were revealed by difference Fourier maps. Non-hydrogen atoms were refined anisotropically, and the thermal parameters of hydrogen atoms were fixed at a value of 1.2 of that of the adjacent non-hydrogen atom. The final difference Fourier map had a largest peak at $0.487 \text{ e } \text{Å}^{-3}$. The water hydrogen has not been included as it was not satisfactorily located in the final difference map, although there were several small peaks in the vicinity of O3. It is presumed disordered.



$[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ (0.5 g, 1.25 mmol) and octanedioic acid (0.5 g, 2.87 mmol) were refluxed together in water (100 cm^3) for 1 h. The condenser was removed periodically to allow liberated acetic acid to escape. To the refluxing suspension was added pyridine (10 cm^3 , 0.124 mol) and the resulting dark blue solution was refluxed for a further 2 h. The solution was filtered whilst hot and upon standing for *ca* 72 h blue crystals of **1** deposited. The crystals were filtered off, washed with ice-cold water and then air-dried. Yield 0.44 g (43%). Found: C, 52.1; H, 5.9; N, 6.8. Calc: C, 52.5; H, 5.9; N, 6.8%; $\mu = 1.82 \text{ B.M. per Cu}$; IR: 3650–2800, 2940, 2850, 1600, 1490, 1460, 1400, 1310, 1280, 1220, 1150, 1140, 1070, 1045, 1015, 880, 860, 760, 735, 695, 640, 440, 310, 270 cm^{-1} . UV-vis (py:H₂O, 1:1): $\lambda = 632 \text{ nm}$, $\epsilon = 104 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, (py): $\lambda_{d-d} = 657 \text{ nm}$, $\epsilon = 104 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.



Blue crystals of complex **1** were warmed to *ca* 40°C *in vacuo* for 6 h. The crystals turned green and became opaque (lost their crystallinity) to give **2** in quantitative yield. Alternatively, **2** can also be prepared by allowing **1** to stand in its mother liquor for a prolonged period of time. Found: C, 49.3; H, 5.6; N, 4.2. Calc: C, 48.2; H, 5.6; N, 4.3% $\mu = 1.34 \text{ B.M. per Cu}$; IR: 2920, 2840, 1600, 1425, 1315, 1280, 1220, 1135, 1070, 1055, 870, 825, 760, 740, 690, 645, 425, $365, 280 \text{ cm}^{-1}$. UV-vis (py:H₂O, 1:1): $\lambda_{d-d} = 631 \text{ nm}$, $\epsilon = 86 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

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REFERENCES

1. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn. Wiley, New York (1988).
2. I. Bertini, H. B. Gray, S. J. Lippard and J. S. Valentine, *Bioinorganic Chemistry*, p. 3. University Science Books, California (1994).
3. J. H. Menkes, H. Alter, G. K. Steigleder, D. R. Weakley and J. H. Sung, *Pediatrics* 1962, **29**, 764.
4. D. M. Danks, B. J. Stephens, P. E. Campbell, J. M. Gillespie, J. Walker-Smith, J. Blomfield and B. Turner, *Lancet* 1972, **1**, 1100.
5. D. M. Danks, P. E. Campbell, B. J. Stephens, V. Mayne and E. Cartwright, *Pediatrics* 1972, **50**, 188.
6. J. R. Mann, J. Camakaris, D. M. Danks and E. G. Walliczek, *Biochem. J.* 1979, **180**, 605.
7. O. Asai, M. Kishita and M. Kubo, *J. Phys. Chem.* 1959, **63**, 96.
8. E. J. Baran, S. B. Etcheverry, M. H. Torre and E. Kremer, *Polyhedron* 1994, **13**, 1859.
9. B. C. Guha, *Proc. R. Soc. (London)* 1951, **A206**, 353; B. N. Figgis and R. L. Martin, *J. Chem. Soc.* 1956, 3837.
10. J. N. van Niekerk and F. R. L. Schoening, *Nature* 1953, **171**, 36.
11. J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.* 1953, **6**, 227.
12. B. H. O Connor and E. N. Maslen, *Acta Cryst.* 1966, **20**, 824.
13. M. McCann, M. Devereux, C. Cardin and M. Convery, *Polyhedron* 1994, **13**, 221.
14. M. Devereux, M. McCann, J. F. Cronin, C. Cardin, M. Convery and V. Quillet, *Polyhedron* 1994, **13**, 2359.
15. M. T. Casey, M. McCann, M. Devereux, M. Curran, C. Cardin, M. Convery, V. Quillet and C. Harding, *J. Chem. Soc., Chem. Commun.* 1994, 2643.
16. M. McCann, J. F. Cronin, M. Devereux and G. Ferguson, *Polyhedron* 1995, **14**, 2379.
17. M. Devereux, M. Curran, M. McCann, M. T. Casey and V. McKee, *Polyhedron* 1995, **14**, 2247.
18. R. C. Mehrotra and R. Bohra, *Metal Carboxylates*. Academic Press, New York (1983) and refs therein.
19. A. Valent, J. Sokolík, V. Seressová and J. Krätzmár-Šmogrovič, *Thermal Anal., Proc. Int. Conf. 4th* (1974) (Edited by I. Buzas), Vol. 1, p. 885. London, U.K. (1975).
20. M. Petrič, I. Leban and P. Šegedin, *Polyhedron* 1993, **12**, 1973.
21. J. N. Brown and L. M. Trefonas, *Inorg. Chem.* 1973, **12**, 1730.
22. B. Chiari, W. E. Hatfield, O. Piovesana, T. Taran-

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iversity of Reading
earch Endowment
e acknowledged for
of the X-ray equip-
SERC.

Advanced Inorganic
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ard and J. S. Valen-
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. Steigleder, D. R.
ics 1962, **29**, 764.
P. E. Campbell, J.
J. Blomfield and B.

B. J. Stephens, V.
etrics 1972, **50**, 188.
M. Danks and E. G.
, 605.
bo, *J. Phys. Chem.*

M. H. Torre and E.
359.
(on) 1951, **A206**, 353;
J. Chem. Soc. 1956,

Schoening, *Nature*

L. Schoening, *Acta*

, *Acta Cryst.* 1966,

Cardin and M. Con-

. Cronin, C. Cardin,
polyhedron 1994, **13**,

Devereux, M. Curran,
illet and C. Harding,
1994, 2643.

I. Devereux and G.
2379.

McCann, M. T. Casey
5, **14**, 2247.

Metal Carboxylates.
83) and refs therein.
ová and J. Krátsmár-
Proc. Int. Conf. 4th
ol. 1, p. 885. London,

Cardin, *Polyhedron* 1993,

as, *Inorg. Chem.* 1973,

Piovesana, T. Taran-

telli, L. W. ter Haar and P. F. Zanazzi, *Inorg. Chem.* 1983, **22**, 1468.

23. G. Christou, S. P. Perlepes, K. Foltg, J. C. Huffman, R. J. Webb and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.* 1990, 746.

24. A. M. Greenaway, C. J. O'Connor, J. W. Overman and E. Sinn, *Inorg. Chem.* 1981, **20**, 1508.

25. B. Chiari, J. H. Helms, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem.* 1986, **25**, 870.

26. B. Chiari, J. H. Helms, O. Piovesana, T. Tarantelli and P. F. Zanazzi, *Inorg. Chem.* 1986, **25**, 2408.

27. R. L. Rardin, W. B. Tolman and S. J. Lippard, *New J. Chem.* 1991, **15**, 417.