



**MONONUCLEAR AND BINUCLEAR COPPER(II)
COMPLEXES OF BENZENE-1,2-DIOXYACETIC ACID
(bdoaH₂): X-RAY CRYSTAL STRUCTURES OF
[Cu(bdoa)(C₆H₅NH₂)₂]₂C₆H₅NH₂ AND [Cu₂(bdoa)(bipy)₄]
bdoa · 8.66H₂O (C₆H₅NH₂ = ANILINE, bipy = 2,2'-BIPYRIDINE)**

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Abstract—The copper(II) complex [Cu(bdoa)(H₂O)₂] (**1**; bdoaH₂ = benzene-1,2-dioxyacetic acid) reacts with aniline in an ethanol–water mixture to give [Cu(bdoa)(C₆H₅NH₂)₂]₂C₆H₅NH₂ (**2**). The X-ray crystal structure of **2** shows the asymmetric unit to contain two mononuclear [Cu(bdoa)(C₆H₅NH₂)₂] units and a solvate aniline molecule. Each copper(II) atom has essentially square planar coordination and is bonded to the nitrogen atoms of two *trans* aniline molecules and a single oxygen atom from each of the two carboxylate moieties of the bdoa²⁻ ligand. The ether oxygen atoms of the bdoa²⁻ bond only weakly to the metal, and one of the metals also interacts weakly with the solvate aniline. Compound **1** reacts with 2,2'-bipyridine (bipy) to form the binuclear copper(II) complex [Cu₂(bdoa)(bipy)₄]bdoa · 8.66H₂O (**3**). The X-ray crystal structure of **3** shows a discrete [Cu₂(bdoa)(bipy)₄]²⁺ dication, an uncomplexed bdoa²⁻ dianion and water molecules linked by O—H···O hydrogen bonding. The dication has two-fold crystallographic symmetry, and the coordination of the unique copper atom is N₄O₂ distorted octahedral. Only one of the carboxylate oxygens is strongly bonded and the other forms a weak interaction with the metal. Spectral, magnetic, conductivity, voltammetry and thermogravimetric data for the complexes are given.

The aryloxydicarboxylic acid benzene-1,2-dioxyacetic acid (bdoaH₂) is a multifunctional ligand in

that it has the potential to coordinate to metals in a number of different ways (Fig. 1). Recently,¹ we have shown that copper(II) acetate hydrate reacts with bdoaH₂ in water to produce the copper(II) complex [Cu(bdoa)(H₂O)₂] (**1**), and that **1** further

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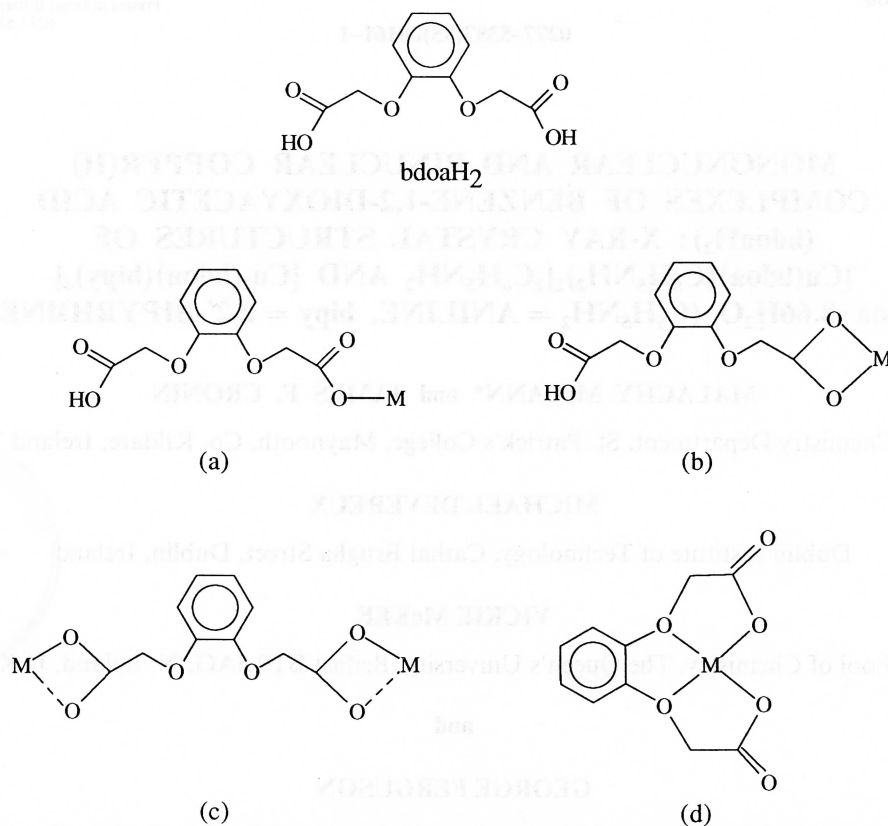


Fig. 1. Structure of bdoaH₂ and some of its possible coordination modes.

reacts with triphenylphosphine to give the crystallographically characterized tetrahedral copper(I) complex [Cu(bdoaH)(PPh₃)₃], in which the bdoaH⁻ ligand is coordinated to the metal by a single carboxylate oxygen atom [mode (a)]. Earlier studies² had revealed that **1** interacts with monodentate nitrogen-donor ligands to yield the copper(II) adducts [Cu(bdoa)(L)₂]·H₂O (L = pyridine or ammonia), and in the case of the bidentate chelating 1,10-phenanthroline (phen) ligand the binuclear copper(II) complex [Cu₂(bdoa)(phen)₄]bdoa·13H₂O formed. The X-ray crystal structure of the latter complex showed that the bdoa²⁻ ligand bridged the two metal centres, being coordinated to each copper atom by unsymmetrical chelating carboxylate groups [mode (c)].

As an extension of our studies into the coordination chemistry of bdoaH₂, we present here the synthesis, X-ray crystal structures and physical properties of new mononuclear and binuclear copper(II) complexes containing this versatile ligand.

RESULTS AND DISCUSSION

[Cu(bdoa)(H₂O)₂] (**1**) reacts with an excess of aniline in an ethanol-water (10:1) mixture to give

the dark green copper(II) complex [Cu(bdoa)(C₆H₅NH₂)₂]₂C₆H₅NH₂ (**2**) in high yield. The X-ray crystal structure of **2** revealed that the asymmetric unit contains two mononuclear [Cu(bdoa)(C₆H₅NH₂)₂] complexes [designated Cu(1) and Cu(2)] and a solvate aniline molecule (Figs 1 and 2, Table 1). Each copper(II) atom has essentially square planar coordination and is bonded to the nitrogen atoms of two *trans* aniline molecules and a single oxygen atom from each of the two carboxylate moieties of the bdoa²⁻ ligand. The ether oxygen atoms of the bdoa²⁻ interact only weakly with the metal [mean Cu—O(ether) 2.48 Å] and Cu(2) also shows a weak interaction with the nitrogen atom of the solvate aniline [Fig. 2b, Cu(2)—N(70) 3.076(7) Å]. This quadridentate coordination mode of the bdoa²⁻ ligand in **2** is exactly that predicted by Suzuki *et al.*³ for the 1:1 complexes [M(bdoa)] which formed upon treating selected divalent alkaline earth and first-row transition metals with bdoaH₂.

The aromatic ring of one aniline ligand in each molecule of complex **2** sits above the phenyl ring of the bdoa²⁻ ligand and there is some suggestion of a π - π interaction. The second coordinated aniline is rotated almost 180° relative to the first and lies

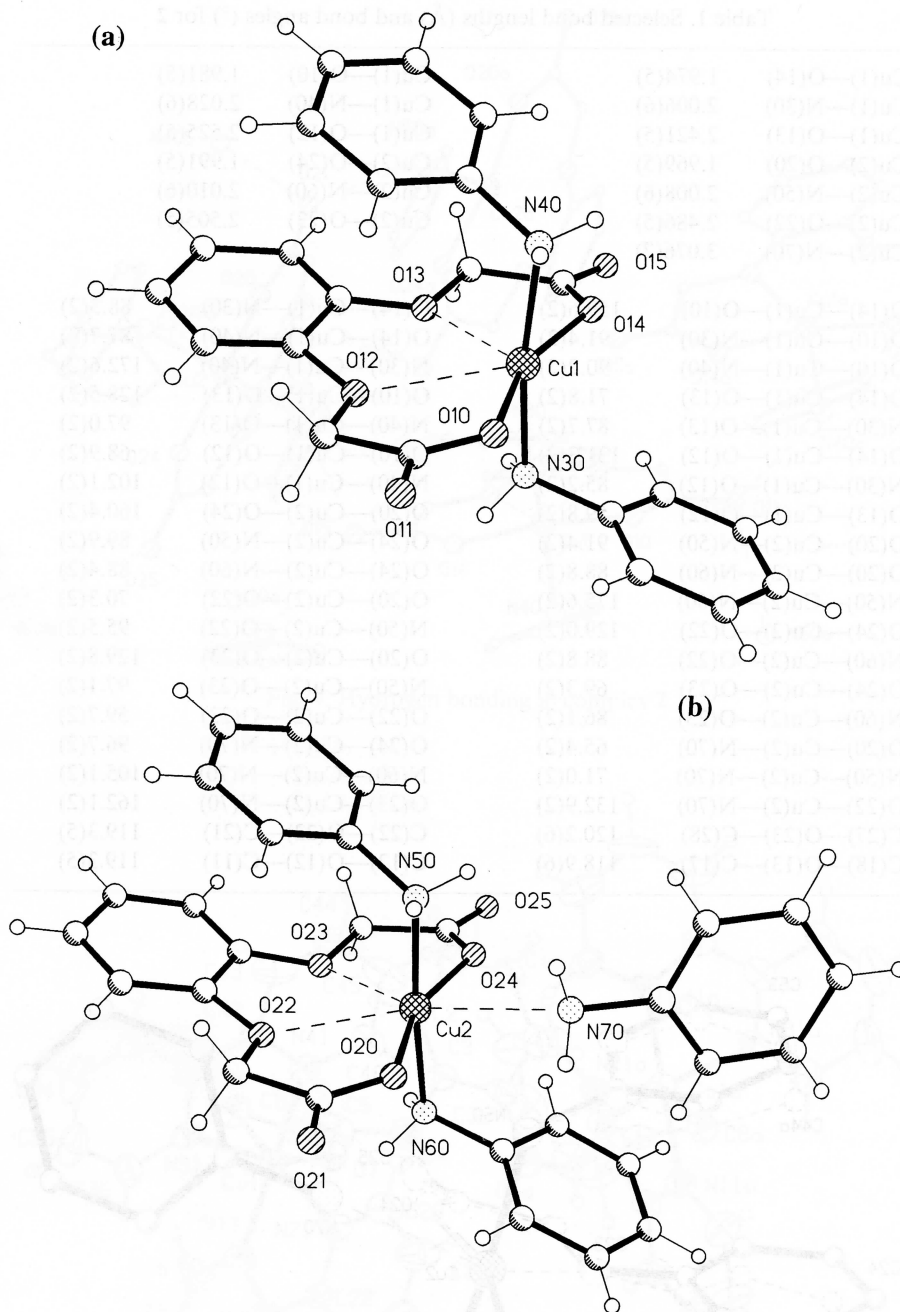


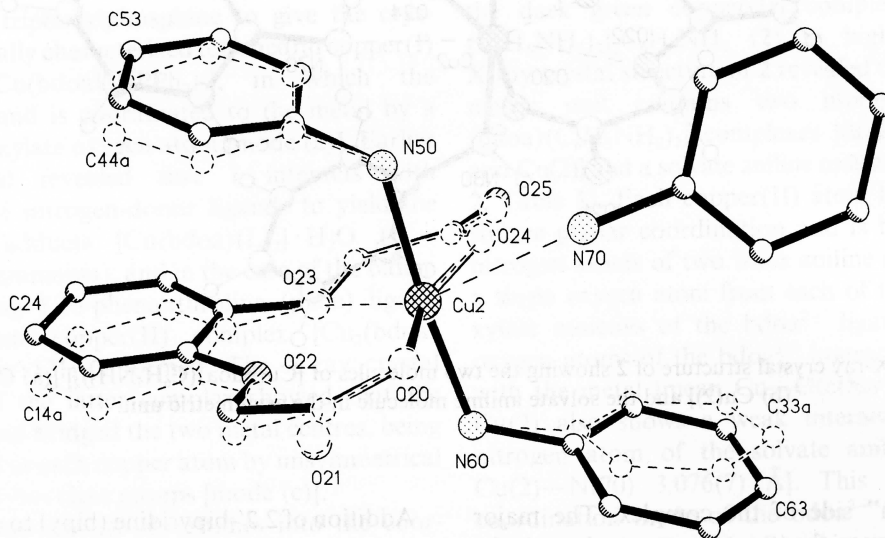
Fig. 2. X-ray crystal structure of **2** showing the two molecules of $[\text{Cu}(\text{bdoa})(\text{C}_6\text{H}_5\text{NH}_2)_2]$ [(a) Cu(1); (b) Cu(2)] and the solvate aniline molecule in the asymmetric unit.

on the "open" side of the complex. The major difference between the two copper complexes is the tilt of the aniline rings relative to the square plane about the metal, as illustrated in the superposition picture (Fig. 3). There is extensive hydrogen bonding throughout the structure of **2**, involving all of the "ketonic" oxygen atoms and aniline nitrogen atoms (Fig. 4). These hydrogen bonds link the structure into polymeric sheets lying in the xz plane but do not extend in the y direction.

Addition of 2,2'-bipyridine (bipy) to an ethanolic suspension of $[\text{Cu}(\text{bdoa})(\text{H}_2\text{O})_2]$ (**1**) (2 : 1 mol ratio) produces the blue-green crystalline complex $[\text{Cu}_2(\text{bdoa})(\text{bipy})_4]\text{bdoa} \cdot 8.66\text{H}_2\text{O}$ (**3**) in good yield. The X-ray crystal structure of the complex was determined, and due to the fact that the crystals lose some of their water molecules of crystallization very rapidly (with consequent decomposition), the X-ray measurements were carried out using a sealed capillary. Complex **3** comprises a discrete $[\text{Cu}_2$

Table 1. Selected bond lengths (Å) and bond angles (°) for **2**

Cu(1)—O(14)	1.974(5)	Cu(1)—O(10)	1.981(5)
Cu(1)—N(30)	2.006(6)	Cu(1)—N(40)	2.028(6)
Cu(1)—O(13)	2.421(5)	Cu(1)—O(12)	2.525(5)
Cu(2)—O(20)	1.969(5)	Cu(2)—O(24)	1.991(5)
Cu(2)—N(50)	2.008(6)	Cu(2)—N(60)	2.010(6)
Cu(2)—O(22)	2.486(5)	Cu(2)—O(23)	2.505(5)
Cu(2)—N(70)	3.076(7)		
O(14)—Cu(1)—O(10)	159.6(2)	O(14)—Cu(1)—N(30)	88.3(2)
O(10)—Cu(1)—N(30)	91.4(2)	O(14)—Cu(1)—N(40)	87.7(2)
O(10)—Cu(1)—N(40)	90.2(2)	N(30)—Cu(1)—N(40)	172.6(2)
O(14)—Cu(1)—O(13)	71.8(2)	O(10)—Cu(1)—O(13)	128.5(2)
N(30)—Cu(1)—O(13)	87.7(2)	N(40)—Cu(1)—O(13)	97.0(2)
O(14)—Cu(1)—O(12)	131.3(2)	O(10)—Cu(1)—O(12)	68.9(2)
N(30)—Cu(1)—O(12)	85.2(2)	N(40)—Cu(1)—O(12)	102.1(2)
O(13)—Cu(1)—O(12)	59.8(2)	O(20)—Cu(2)—O(24)	160.4(2)
O(20)—Cu(2)—N(50)	91.4(2)	O(24)—Cu(2)—N(50)	89.9(2)
O(20)—Cu(2)—N(60)	88.8(2)	O(24)—Cu(2)—N(60)	88.4(2)
N(50)—Cu(2)—N(60)	175.6(2)	O(20)—Cu(2)—O(22)	70.3(2)
O(24)—Cu(2)—O(22)	129.0(2)	N(50)—Cu(2)—O(22)	95.5(2)
N(60)—Cu(2)—O(22)	88.8(2)	O(20)—Cu(2)—O(23)	129.8(2)
O(24)—Cu(2)—O(23)	69.3(2)	N(50)—Cu(2)—O(23)	97.1(2)
N(60)—Cu(2)—O(23)	86.1(2)	O(22)—Cu(2)—O(23)	59.7(2)
O(20)—Cu(2)—N(70)	65.4(2)	O(24)—Cu(2)—N(70)	96.7(2)
N(50)—Cu(2)—N(70)	71.0(2)	N(60)—Cu(2)—N(70)	105.1(2)
O(22)—Cu(2)—N(70)	132.9(2)	O(23)—Cu(2)—N(70)	162.1(2)
C(27)—O(23)—C(28)	120.2(6)	C(22)—O(22)—C(21)	119.3(5)
C(18)—O(13)—C(17)	118.9(6)	C(12)—O(12)—C(11)	119.3(5)

Fig. 3. Superposition of the two molecules of complex **2**.

(bdoa)(bipy)₄]²⁺ dication (Fig. 5, Table 2), an uncomplexed bdoa²⁻ dianion and water molecules linked by O—H···O hydrogen bonding. The dication has two-fold crystallographic symmetry with

the two-fold axis passing through the midpoints of the C(1)—C(1a) and C(3)—C(3a) bonds. The coordination of the unique copper atom is N₄O₂ distorted octahedral. Only one of the carboxylate

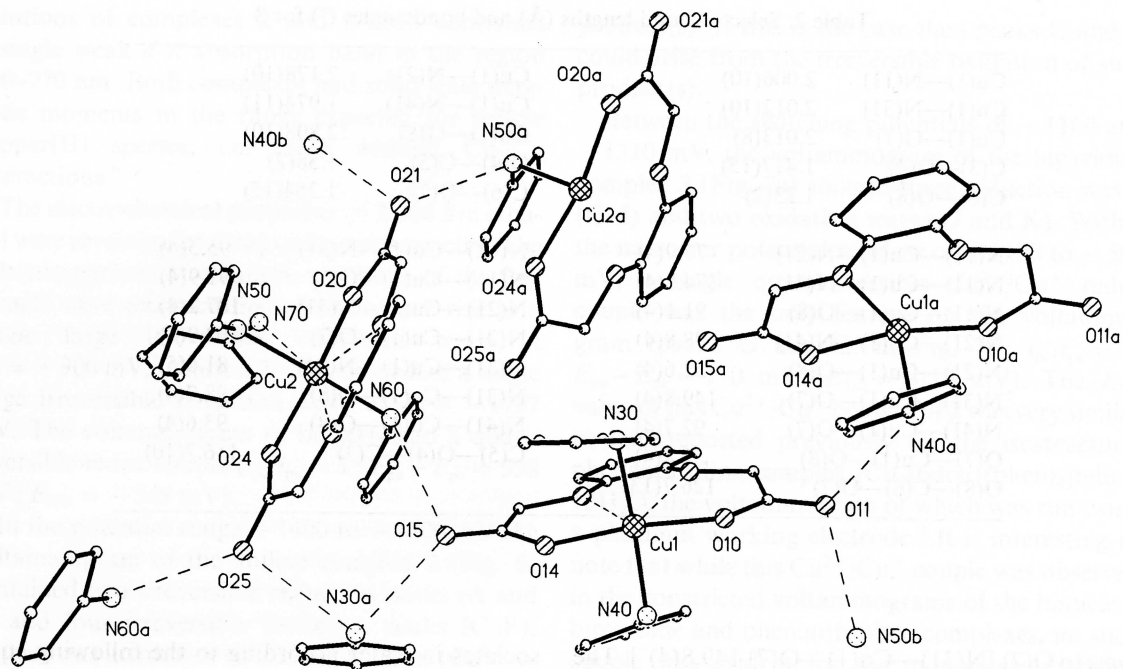


Fig. 4. Hydrogen bonding in complex 2.

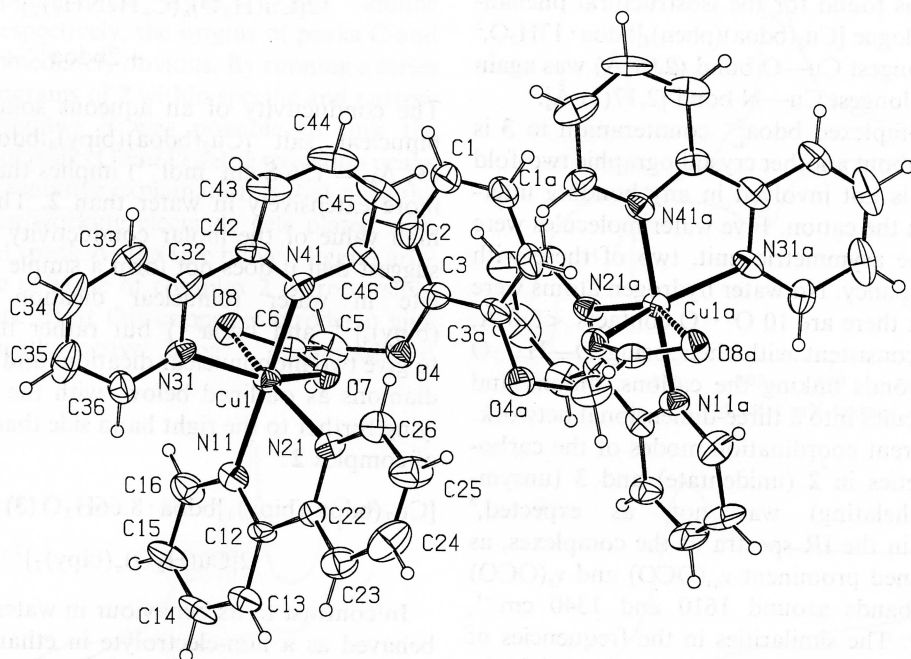


Fig. 5. Structure of the $[\text{Cu}_2(\text{bdoa})(\text{bipy})_4]^{2+}$ dication of **3** with the bdoa^{2-} counterion and water molecules omitted for clarity. Thermal ellipsoids are at the 30% probability level. The atoms whose labels terminate with an "a" are obtained from the coordinates of the asymmetric unit by the transformation $2-x, y, 1.5-z$.

oxygens is strongly bonded $[\text{Cu}(1)-\text{O}(7) 2.013(8) \text{ \AA}]$ and the other forms at best a weak interaction opposite nitrogen N(21) $[\text{Cu}(1)-\text{O}(8) 2.808(10) \text{ \AA}]$. Three of the four Cu—N bonds are similar in

length, namely $\text{Cu}(1)-\text{N}(11) 2.006(10)$, $\text{Cu}(1)-\text{N}(41) 1.974(11)$, $\text{Cu}(1)-\text{N}(31) 2.012(10) \text{ \AA}$; $\text{Cu}(1)-\text{N}(11)$ and $\text{Cu}(1)-\text{N}(41)$ are *trans* $[\text{N}(11)-\text{Cu}(1)-\text{N}(41) 174.8(4)^\circ]$ and N(31) is

Table 2. Selected bond lengths (Å) and bond angles (°) for **3**

Cu(1)—N(11)	2.006(10)	Cu(1)—N(21)	2.178(10)
Cu(1)—N(31)	2.012(10)	Cu(1)—N(41)	1.974(11)
Cu(1)—O(7)	2.013(8)	Cu(1)—O(8)	2.808(10)
C(3)—O(4)	1.417(15)	O(4)—C(5)	1.38(2)
C(6)—O(8)	1.23(2)	C(6)—O(7)	1.254(15)
N(11)—Cu(1)—N(21)	77.9(4)	N(11)—Cu(1)—N(31)	95.5(4)
N(11)—Cu(1)—N(41)	174.8(4)	N(11)—Cu(1)—O(7)	91.9(4)
N(11)—Cu(1)—O(8)	91.1(4)	N(21)—Cu(1)—N(31)	107.2(4)
N(21)—Cu(1)—N(41)	98.8(4)	N(21)—Cu(1)—O(7)	102.9(4)
N(21)—Cu(1)—O(8)	152.6(4)	N(31)—Cu(1)—N(41)	81.6(5)
N(31)—Cu(1)—O(7)	149.8(4)	N(31)—Cu(1)—O(8)	98.7(4)
N(41)—Cu(1)—O(7)	92.7(4)	N(41)—Cu(1)—O(8)	93.6(4)
O(7)—Cu(1)—O(8)	51.8(4)	C(5)—O(4)—C(3)	116.7(10)
O(8)—C(6)—O(7)	126.7(13)		

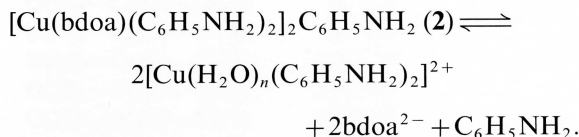
trans to O(7) [N(31)—Cu(1)—O(7) 149.8(4)°]. The Cu(1)—N(21) bond *trans* to the long (weak) Cu(1)—O(8) interaction is the longest at 2.178(10) Å, with N(21)—Cu(1)—O(8) 152.6(4)°. A similar situation was found for the isostructural phenanthroline analogue [Cu₂(bdoa)(phen)₄]bdoa · 13H₂O,² where the longest Cu—O bond (2.91 Å) was again *trans* to the longest Cu—N bond [2.17(1) Å].

The uncomplexed bdoa²⁻ counteranion in **3** is disordered about another crystallographic two-fold axis and it is not involved in any bonding interactions with the cation. Five water molecules were found in the asymmetric unit, two of these with partial occupancy. No water hydrogen atoms were located, but there are 10 O···O contacts <3.0 Å, which are consistent with their being O—H···O hydrogen bonds linking the cations, anions and water molecules into a three-dimensional network.

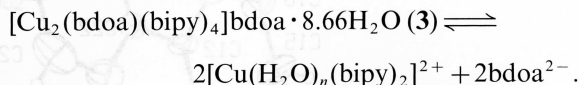
The different coordination modes of the carboxylate moieties in **2** (unidentate) and **3** (unsymmetrical chelating) was not, as expected,⁴ manifested in the IR spectra of the complexes, as each contained prominent $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ stretching bands around 1610 and 1340 cm⁻¹, respectively. The similarities in the frequencies of the OCO bands for the two complexes might be attributed to the fact that the chelating carboxylate groups in **3** are highly unsymmetrical (one short and one very long Cu—O bond) and that these carboxylates may indeed be viewed as being essentially pseudo-unidentate.

Whereas **2** was soluble in hot ethanol and hot water, complex **3** readily dissolved in these solvents at room temperature. The molar conductivity value for an aqueous solution of **2** ($\Lambda_{\text{M}} = 72 \text{ S cm}^2 \text{ mol}^{-1}$) suggests that the neutral complex partially dis-

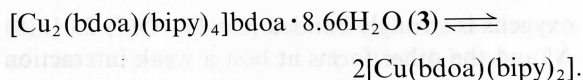
sociates in water according to the following equilibrium:



The conductivity of an aqueous solution of the binuclear salt [Cu₂(bdoa)(bipy)₄]bdoa · 8.66H₂O (**3**; $\Lambda_{\text{M}} = 156 \text{ S cm}^2 \text{ mol}^{-1}$) implies that it ionized more extensively in water than **2**. The relatively high value of the molar conductivity of **3** would suggest that it does not form a simple 1:1 electrolyte in water (binuclear dication [Cu₂(bdoa)(bipy)₄]²⁺ and bdoa²⁻) but rather it dissociates to give two mononuclear dications and two bdoa²⁻ dianions as outlined below, with the equilibrium lying further to the right hand side than in the case of complex **2**:



In contrast to its behaviour in water, complex **2** behaved as a non-electrolyte in ethanol. Surprisingly, the binuclear salt **3** also dissolved in ethanol to give a solution that was non-conducting. This suggests that **3** either forms the strongly associated ion pair⁵ ([Cu₂(bdoa)(bipy)₄]²⁺bdoa²⁻) in ethanol or that it dissociates to form non-ionized mononuclear products as shown below:



The electronic spectra of aqueous and ethanolic

solutions of complexes **2** and **3** each contained a single weak $d-d$ absorption band in the region 700–770 nm. Both complexes had solid state magnetic moments in the range expected for simple copper(II) species, i.e. those without Cu–Cu interactions.⁶

The electrochemical properties of **2** and **3** in ethanol were investigated using cyclic voltammetry. The voltammograms of ethanolic solutions of the free ligands were recorded first. Aniline gave rise to a single large irreversible oxidation wave at $E_a = +900$ mV,⁷ whilst 2,2'-bipyridine had a single large irreversible reduction wave at $E_c = -1797$ mV. The voltammogram of bdoaH₂ had a quasi-reversible redox couple ($i_{pc}/i_{pa} = 1$; $E_{pa} - E_{pc} = 338$ mV; $E_{1/2} = -548$ mV).

In the potential range +1400 to -1700 mV the voltammogram of the aniline complex **2** (Fig. 6) contained two irreversible reduction peaks (A and B) and four irreversible oxidation peaks (C–F). Peak A was attributed to metal reduction ($\text{Cu}^{2+} \rightarrow \text{Cu}^0$) and B was due to reduction of the resulting lecomplexed bdoa²⁻ ligand (see later). Although peaks E and F were positively assigned to anodic metal stripping ($\text{Cu}^0 \rightarrow \text{Cu}^{2+}$) and aniline oxidation, respectively, the origins of peaks C and D are not immediately obvious. By running a series of voltammograms of **2** within specific and narrow potential windows it was possible to link the appearance of peaks C and D to the reduction peaks A and B. A tentative explanation is that once the glassy carbon working electrode gets plated with copper metal (peak A) the free bdoa²⁻ ligand arising from the collapse of complex **2** is irreversibly reduced (peak B) at this copper electrode to give electrochemically active bdoa²⁻ decomposition

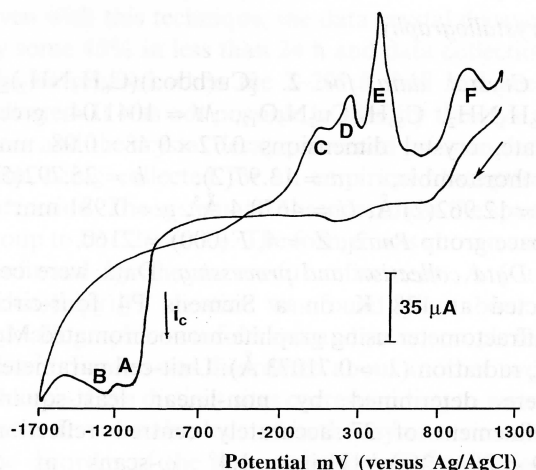


Fig. 6. Cyclic voltammogram of **2** in ethanol at a scan rate of 50 mV s^{-1} , and between the switching potentials of +1400 and -1700 mV. Potentials versus Ag/AgCl.

product(s). If this is the case then peaks C and D could arise from the irreversible oxidation of such product(s).

Between the switching potentials of +1100 and -1310 mV, the voltammogram of the bipyridine complex **3** (Fig. 7a) showed three reduction waves (G–I) and two oxidation waves (J and K). Within the narrower potential window of +1100 to -500 mV, a single quasi-reversible $\text{Cu}^{2+}/\text{Cu}^+$ redox couple was the only feature on the voltammogram (peaks G and G' in Fig. 7b: $i_{pc}/i_{pa} = 1$; $E_{pa} - E_{pc} = 170$ mV; $E_{1/2} = +12$ mV). The $E_{1/2}$ value of this $\text{Cu}^{2+}/\text{Cu}^+$ couple for **2** was very similar to that reported previously for the isostructural phenanthroline complex $[\text{Cu}_2(\text{bdoa})(\text{phen})_4]\text{bdoa} \cdot 13\text{H}_2\text{O}$, the voltammogram of which was run using a platinum working electrode.² It is interesting to note that while this $\text{Cu}^{2+}/\text{Cu}^+$ couple was observed in the constricted voltammograms of the binuclear bipyridine and phenanthroline complexes, no such couple was evident for the mononuclear aniline

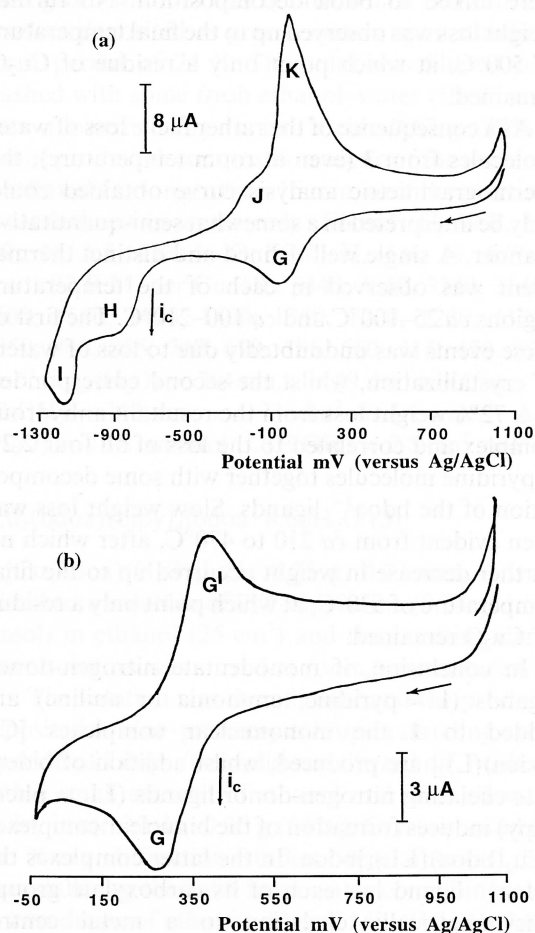


Fig. 7. Cyclic voltammograms of **3** in ethanol at a scan rate of 50 mV s^{-1} , and between the switching potentials of +1100 and -1310 mV (a) and +1100 and -500 mV (b). Potentials versus Ag/AgCl.

complex. The irreversible peaks H and I in the voltammogram of **3** (Fig. 7a) are attributed to plating of copper metal and reduction of decomplexed bdoa^{2-} , and these peaks appeared at similar potentials to the corresponding reduction peaks (A and B) in the voltammogram of **2**. Whilst the strong sharp peak K is due to copper stripping from the electrode surface, peak J is, again, cautiously ascribed to the irreversible oxidation of the organic by-product(s) arising from the reduction of the free bdoa^{2-} ligand. Given the fact that conductivity measurements for **2** and **3** in ethanol suggest that their structures in this solvent may not be too dissimilar ($[\text{Cu}(\text{bdoa})(\text{bipy})_2]$ and $[\text{Cu}(\text{bdoa})(\text{C}_6\text{H}_5\text{NH}_2)_2]$, respectively), then it is not surprising that the voltammograms of the two complexes share many common features.

A thermogravimetric study of **2** showed the loss of all five aniline ligands in a distinct single thermal event between *ca* 95 and 160°C. Two further stages in the weight loss (not perfectly resolved) occurred over the temperature range *ca* 160–320°C and these were linked to *bdoa* decomposition. No further weight loss was observed up to the final temperature of 500°C, at which point only a residue of Cu_2O remained.

As a consequence of the rather facile loss of water molecules from **3** (even at room temperature), the thermogravimetric analysis curve obtained could only be interpreted in a somewhat semi-quantitative manner. A single well-defined and distinct thermal event was observed in each of the temperature regions *ca* 25–100°C and *ca* 100–210°C. The first of these events was undoubtedly due to loss of waters of crystallization, whilst the second corresponded to a 72% weight loss from the resultant anhydrous complex and correlated to the loss of all four 2,2'-bipyridine molecules together with some decomposition of the bdoa^{2-} ligands. Slow weight loss was then evident from *ca* 210 to 470°C, after which no further decrease in weight occurred up to the final temperature of 530°C, at which point only a residue of Cu_2O remained.

In conclusion, if monodentate nitrogen-donor ligands (L = pyridine, ammonia or aniline) are added to **1** the mononuclear complexes $[\text{Cu}(\text{bdoa})(\text{L})_2]$ are produced, whilst addition of bidentate chelating nitrogen-donor ligands (LL = phen, bipy) induces formation of the binuclear complexes $[\text{Cu}_2(\text{bdoa})(\text{LL})_4]\text{bdoa}$. In the latter complexes the bdoa^{2-} ligand has each of its carboxylate groups unsymmetrically chelating to a metal centre, whereas in the mononuclear complexes the two ethereal oxygens together with one oxygen atom from each of the two carboxylate moieties of the bdoa^{2-} bond to the metal.

EXPERIMENTAL

$[\text{Cu}(\text{bdoa})(\text{H}_2\text{O})_2]$ (**1**) was prepared as described previously,² and benzene-1,2-dioxyacetic acid (bdoaH_2) was purchased from Lancaster and used without further purification. For conductivity and voltammetry measurements the ethanol used was distilled from the magnesium ethoxide Grignard reagent. IR spectra (KBr discs) were recorded in the region 4000–200 cm^{-1} on a Perkin–Elmer 783 grating spectrometer, and solution electronic spectra were obtained using a Milton Roy Spectronic 3000 Array. Conductivity readings (10^{-3} M solutions; 25°C) were taken with an AGB model 10 conductivity meter. Solid-state room temperature magnetic susceptibilities were made on a Johnson–Matthey magnetic susceptibility balance. Cyclic voltammograms were recorded (*ca* 20°C under nitrogen) using an EG&G model 264A polarographic analyser and the data 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. Tetra-*n*-butylammonium perchlorate/ethanol (0.1 M) was used as the supporting electrolyte/solvent system, and sample concentration was 4.0 mM. Potentials were recorded with respect to a silver–silver chloride reference electrode (3.5 M KCl), against which the ferrocene/ferrocenium(1+) couple had $E_{1/2} = +509$ mV. Thermogravimetric analyses were performed under N_2 on a Stanton Redcroft TG 750/770 instrument which was coupled to a Houston Instrument Omniscrite (series D5000) recorder. Heating rate was 5°C min^{-1} . Elemental analyses were carried out by the Microanalytical Laboratory, University College Cork, Ireland.

Crystallography

Crystal data for 2. $[\text{Cu}(\text{bdoa})(\text{C}_6\text{H}_5\text{NH}_2)_2]$ ₂ $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_{50}\text{H}_{51}\text{Cu}_2\text{N}_5\text{O}_{12}$, $M = 1041.04$, green plate, crystal dimensions $0.72 \times 0.48 \times 0.08$ mm, orthorhombic, $a = 13.97(2)$, $b = 25.792(5)$, $c = 12.962(2)$ Å, $U = 4670.4$ Å³, $\mu = 0.981$ mm⁻¹, space group $Pna2_1$, $Z = 4$, $F(000) = 2160$.

Data collection and processing. Data were collected at 128 K on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were determined by non-linear least-squares refinement of 37 accurately centred reflections ($9 < 2\theta < 26^\circ$). Using 1.4° ω -scans at 5° min^{-1} , 3358 reflections were collected in the range $4 < 2\theta < 50^\circ$; 2905 unique reflections ($R_{\text{int}} = 0.024$) were used in the refinement. Crystal

EXPERIMENTAL

as prepared as described from benzene-1,2-dioxyacetic acid from Lancaster and used as received. For conductivity and viscosity the ethanol used was anhydrous. The ethoxide Grignard reagent was prepared from sodium ethoxide Grignard reagent (discs) were recorded in a Perkin-Elmer 783 spectrophotometer. Electronic spectroscopy was done on a Milton Roy Spectronic 2000. Conductivity readings (10^{-3} M solution) were done with an AGB model 10 conductivity cell at room temperature. Titrations were made on a Johnson-Matthey titration balance. Cyclic voltammetry was recorded (*ca* 20°C) under nitrogen on a model 264A polarograph. The data were analysed using the software package. A glassy carbon electrode was used as the reference electrode, respectively. The electrolyte was perchlorate/ethanol (0.1 M) and the supporting electrolyte/solvent concentration was 4.0 mM. The scan rate with respect to a silver-silver chloride electrode (3.5 M KCl), was 100 mV/s. Thermogravimetric analysis was done under N_2 on a Stanton Instruments instrument which was calibrated with a standard instrument Omniscrite 100. The heating rate was 5°C/min. The experiment was carried out by the University College

stability was monitored by recording three check reflections every 97 reflections and no significant variation was observed. The data were corrected for Lorentz and polarization effects and a semi-empirical laminar absorption correction was applied ($T_{\max} = 0.959$, $T_{\min} = 0.710$).

Structure solution and refinement. The structure was solved by direct methods,⁸ which revealed most of the structure, and the remaining non-hydrogen atoms were located from difference Fourier maps. Hydrogen atoms were inserted at calculated positions with isotropic temperature factors 1.2 times the equivalent isotropic U of their carrier atoms. The non-hydrogen atoms were refined with anisotropic atomic displacement parameters, except for C(10) and C(30), for which anisotropic refinement led to "non-positive definite" ellipsoids. All the data were used for refinement on F^2 , which converged with $R_w = 0.0833$, GOF = 1.065 and the conventional $R = 0.0355$ [$I > 2\sigma(I)$] for 607 parameters. The final difference map showed no residual electron density greater than ± 0.4 e \AA^{-3} . All programmes used in the structure refinement are contained in the SHELXL-93 package.⁹

Crystal data for 3. $[\text{Cu}_2(\text{bdoa})(\text{bipy})_4]\text{bdoa} \cdot 8.66\text{H}_2\text{O}$, $\text{C}_{60}\text{H}_{65.32}\text{Cu}_2\text{N}_8\text{O}_{20.66}$, $M = 1356.2$, blue-green block, crystal dimensions $0.37 \times 0.30 \times 0.21$ mm, monoclinic, $a = 16.932(2)$, $b = 24.427(2)$, $c = 16.440(2)$ \AA , $\alpha = \gamma = 90^\circ$, $\beta = 101.883(11)^\circ$, $U = 6654.1(13)$ \AA^3 , $\mu = 0.716$ mm^{-1} , space group $C2/c$, $Z = 4$, $F(000) = 2818$.

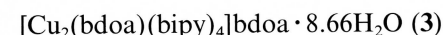
Data collection and processing. Data were collected at 294 K on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71067$ \AA). The crystals lost water rapidly on standing in air, and for the data collection a small block was cut from a larger crystal and sealed in a capillary with some mother liquor. Even with this technique, the data crystal decayed by some 45% in less than 24 h and data collection was terminated when the $2-20^\circ$ θ shell had been collected. It was not possible to identify the crystal faces and the crystal decay prevented ψ -scan data from being collected for an empirical absorption correction. The systematic absences allow the space group to be $C2/c$ or Cc . The former was chosen and confirmed by the successful refinement. A $[\text{Cu}_2(\text{bdoa})(\text{bipy})_4]^{2+}$ dication was found lying about a crystallographic two-fold axis and an uncomplexed bdoa^{2-} dianion was disordered about another two-fold axis. Five distinct sites corresponding to water molecules were also located in the asymmetric unit. The disorder of the uncomplexed bdoa^{2-} dianion was allowed for in the SHELXL-93⁹ refinement by appropriate constraints. Attempts at refining the structure in the Cc space group (which would

require no symmetry for the cation or disorder for the anion) led to nonsensical thermal parameters and was abandoned. Occupancy parameters for all five water oxygens were refined initially, but only two of them had values significantly less than unity. Analysis of the structure with PLATON¹⁰ reveals that there are eight (symmetry related) voids, each of volume 29 \AA^3 in the unit cell, and this loose packing is undoubtedly the reason for the rapid decay of the crystals of the complex when exposed to air.

Structure solution and refinement. The structure was solved by the Patterson heavy atom method. All the data were used for refinement on F^2 with $R1$, R_w and GOF = 0.096, 0.270 and 1.14, respectively. The density range in the final difference map was -0.400 to 0.915 e \AA^{-3} .



$[\text{Cu}(\text{bdoa})(\text{H}_2\text{O})_2]$ (**1**; 0.5 g, 1.54 mmol) and aniline (1.5 cm^3) were refluxed together in an ethanol-water (10:1) mixture (55 cm^3) for 15 min. The dark green solution was filtered whilst hot and the product deposited as green crystals upon standing for a period of 24 h. The solid was filtered off, washed with some fresh ethanol-water (10:1) and then allowed to dry in air. Yield: 0.62 g (77%). Note: product decomposition occurs if the reaction is refluxed for longer than 15 min, or if the reaction is carried out in water only. Found: C, 57.7; H, 4.9; N, 6.5. Calcd: C, 57.7; H, 4.9; N, 6.7%. $\mu = 1.82$ B.M. per Cu. IR: 3440, 3350, 3240, 3140, 1600, 1500, 1410, 1400, 1340, 1260, 1220, 1125, 1050, 940, 825, 740, 690, 585, 550, 515, 420, 320 cm^{-1} . $\lambda_{\text{d-d}}(\text{H}_2\text{O}) = 764$ nm, $\epsilon = 49$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, (EtOH) = 743 nm, $\epsilon = 71$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$. $\Lambda_{\text{M}}(\text{H}_2\text{O}) = 72$ $\text{S cm}^2 \text{mol}^{-1}$, (EtOH) = 2 $\text{S cm}^2 \text{mol}^{-1}$.



$[\text{Cu}(\text{bdoa})(\text{H}_2\text{O})_2]$ (**1**; 0.25 g, 0.77 mmol) was added to a solution of 2,2'-bipyridine (0.24 g, 1.54 mmol) in ethanol (25 cm^3) and the resulting dark green solution was stirred at room temperature for 6 h. The solution was then filtered and the product deposited as blue-green crystals upon standing over a period of 7 days. The solid was filtered off, washed with a small amount of ethanol and then allowed to dry in air. Yield: 0.35 g (64%). Crystals suitable for X-ray diffraction studies were obtained by recrystallizing the solid from water containing one to two drops of ethanol. Found: C, 49.6; H, 3.8; N, 7.8. Calcd: C, 53.1; H, 4.9; N, 8.3%. It should be noted that discrepancies between found and calculated analytical figures for **3** are probably attributable to the fact that the complex tended to lose

$[\text{Cu}(\text{bdoa})(\text{C}_6\text{H}_5\text{NH}_2)_2]_2$
 $M = 1041.04$, green
 0.48×0.08 mm,
 $b = 25.792(5)$,
 $\mu = 0.981$ mm^{-1} ,
 $D_x = 2160$.

Data were collected on a Siemens P4 four-circle diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation. The cell parameters were refined by least-squares on all observed reflections. The data were scanned at 5° and collected in the ω scan. The reflections were indexed and refined. Crystal

water molecules of crystallization fairly rapidly upon standing in the laboratory atmosphere. $\mu = 1.79$ B.M. per Cu. IR: 3680–2700, 1610, 1495, 1465, 1435, 1410, 1325, 1245, 1210, 1120, 1035, 1020, 1005, 895, 815, 765, 725, 680, 650, 625, 415, 285 cm^{-1} . $\lambda_{d-d}(\text{H}_2\text{O}) = 733\text{ nm}$, $\epsilon = 183\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$, $(\text{EtOH}) = 700\text{ nm}$, $\epsilon = 164\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$. $\Lambda_{\text{M}}(\text{H}_2\text{O}) = 156\text{ S cm}^2\text{ mol}^{-1}$, $(\text{EtOH}) = 2\text{ S cm}^2\text{ mol}^{-1}$.

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