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Structurally diverse copper(II) herbicide complexes: mono- and bi-nuclear neutral or cationic complexes†

Catherine Dendrinou-Samara,[a] George Psomas,[a] Konstantinos Christophorou,[a] Vasilis Tangoulis,[b] Catherine P. Raptopoulou,[b] Aris Terzis[b] and Dimitris P. Kessissoglou *,[a]

[a] *Department of General and Inorganic Chemistry, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece*
[b] *NRCPS 'Demokritos', Institute of Materials Science, 15310 Aghia Paraskevi Attikis, Greece*

Copper complexes with the commercial auxin herbicides 2,3-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)propanoic acid and 2,2′-bipyridine (bipy) were prepared and characterized: $[Cu_2(Cl_2C_6H_3OCH_2CO_2)_4(MeOH)_2]$ **1**, $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}_2(bipy)(H_2O)]$ **2** and $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}(bipy)_2]Cl$ **3**. The available evidence supports a dimeric structure for complex **1** while the presence of bipy leads to monomeric forms. In dimethylformamide solution the binuclear complex is converted into a monomeric complex upon addition of a $> 1:2$ ratio of bipy. The ESR powder spectrum of compound **2** exhibits features characteristic of the presence of a $S = 1$ triplet state which may be assigned to a hydrogen-bond network. The crystal structures of the three complexes have been determined.

Many binuclear copper(II) carboxylate compounds have been isolated and their magnetostructural correlation studied.[1–3] In most cases the formula of the complexes is $Cu_2(O_2CR)_4L_2$ ($L = H_2O$, dmf = dimethylformamide, dmso = dimethyl sulfoxide, or py = pyridine). The isolation of mononuclear carboxylato-compounds has also confirmed the existence of uni- and bi-dentate co-ordination modes of the ligands.[4–7] The electrochemical behaviour of binuclear complexes as one means of determining reactivity differences between bi- and mono-nuclear complexes has also drawn great interest.[8–20] Phenoxyalkanoic acids interact with copper(II) ions to form complexes which have been shown to have diverse stereochemistries.[4,5,21–29]

We have initiated studies on the co-ordination chemistry of antiinflammatory carboxylate and hypoglycaemic sulfonylurea agents with Cu^{II} and d^{10} ions in an attempt to examine their mode of binding and possible synergetic effects.[30–34] In this paper we report the solid-state and solution behaviour of mono- and bi-nuclear copper(II) complexes with the commercial auxin herbicides 2,3-dichlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy)propanoic acid in the presence or not of bipy (2,2′-bipyridine), an antimicrobial agent, while the antimicrobial behaviour and possible structural relations are presented elsewhere.[35] We also report the molecular and the crystal structures of tetrakis(2,3-dichlorophenoxyacetato)bis(methanol)dicopper(II) **1**, aqua(2,2′-bipyridine)bis[2-(2,4-dichlorophenoxy)propanoato]copper(II) **2** and bis(2,2′-bipyridine)[2-(2,4-dichlorophenoxy)propanoato]copper(II) chloride **3**.

Results and Discussion

The synthesis of the binuclear complex **1** has been achieved *via* the reaction of $CuCl_2{\cdot}4H_2O$ with the sodium salt of the carboxylic acid. This involves deprotonation of the acid using NaOH or NaOMe as base [equations (1) and (2)]. The complex is a green crystalline solid soluble in dmf, dmso and py.

$$Cl_2C_6H_3OCH_2CO_2H + NaOMe \longrightarrow Cl_2C_6H_3OCH_2CO_2Na \quad (1)$$

Table 1 Selected bond distances (Å) and angles (°) of complex 1

Cu···Cu	2.637(1)	O(1)–C(1)	1.242(4)
Cu–O(1)	1.975(2)	O(2)–C(1)	1.259(3)
Cu–O(2′)	1.974(1)	O(4)–C(9)	1.246(4)
Cu–O(4)	1.977(2)	O(5)–C(9)	1.256(4)
Cu–O(5)	1.961(2)	O(7)–C(17)	1.420(5)
Cu–O(7)	2.101(2)		
O(1)–Cu–O(4)	92.0(1)	O(5)–Cu–O(7)	97.8(1)
O(1)–Cu–O(5)	88.2(1)	O(4)–Cu–O(2′)	88.7(1)
O(1)–Cu–O(7)	97.2(1)	O(2′)–Cu–O(5)	88.7(1)
O(4)–Cu–O(5)	168.2(1)	O(2′)–Cu–O(7)	94.8(1)
O(4)–Cu–O(7)	93.9(1)	O(1)–Cu–O(2′)	168.9(1)

$$4Cl_2C_6H_3OCH_2CO_2Na + 2CuCl_2 \longrightarrow [Cu_2(Cl_2C_6H_3OCH_2CO_2)_4(MeOH)_2] \quad (2)$$

The synthesis of the mononuclear complexes has been achieved in two ways. (*i*) Template reaction of $CuCl_2{\cdot}4H_2O$, NaOH, bipy and 2-(2,4-dichlorophenoxy)propanoic acid results in the formation of the cationic complex **3**, equation (3).

$$Cl_2C_6H_3OCH(Me)CO_2H + NaOH + 2CuCl_2 + 2(bipy) \longrightarrow [Cu\{Cl_2C_6H_3OCH(Me)CO_2\}(bipy)_2]Cl \quad (3)$$

The compound is a 1:1 electrolyte in dmf or dmso solutions. (*ii*) Reaction of $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}_2(H_2O)_2]$ with bipy results in the formation of mononuclear neutral compound **2**, $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}_2(bipy)(H_2O)]$. This complex is blue crystalline solid, soluble in dmf and dmso and is not an electrolyte.

Structure of complex 1

The crystal structure of complex **1** is composed of centrosymmetric dimers. Four bidentate carboxylate anions form *syn-syn* bridges between isolated pairs of copper atoms separated by 2.637(1) Å. An ORTEP diagram of the complex appears in Fig. 1, and selected bond distances and angles are given in Table 1. The copper to carboxylate oxygen distances range from 1.961(2) to 1.977(2) Å. The metal atom is displaced 0.20 Å toward the MeOH ligand from the plane containing the

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† *Non-SI units employed:* $G = 10^{-4}$ T, $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

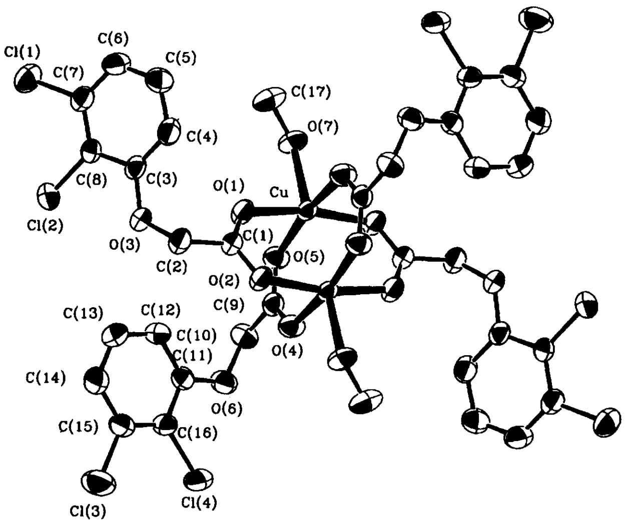


Fig. 1 An ORTEP[36] view of the structure of complex **1** showing the atom-labelling scheme

four co-ordinated carboxylate oxygen atoms. This structure is closely related to those of the carboxylate adducts $[Cu_2(O_2CR)_4L_2]$ (R = Me, $ClCH_2$, Et, 4-HOC_6H_4, H, FCH_2 or Ph; L = py, urea, dmso, quinoline or methylpyridine).[37–43]

The sum of all interatomic distances in the CuO_5 chromophore (half the Cu···Cu distance = 1.318 Å is included) is 11.306 Å, almost the same as the 11.34 Å average for a series of copper(II) binuclear carboxylate compounds.[2] The displacement of the copper atom from the basal plane (0.20 Å) is in the range 0.19–0.22 Å known for binuclear carboxylate complexes.[44] The eight oxygens of the four carboxylate groups create an oblique parallelepiped. The bridging path lengths of 6.44 and 6.45 Å are within the range observed for most other copper(II) carboxylate dimers.[44] The Cu···Cu distances (2.56–2.88 Å) of binuclear copper(II) carboxylates are the shortest among the oxo-bridged binuclear copper(II) compounds, 2.903–3.034 Å for dialkoxo-bridged, 3.244–3.529 Å for bis(heterocyclic *N*-oxide)-bridged and 2.98–3.383 Å for Schiff-base compounds.[44]

Structure of complex 2

In complex **2** the carboxylate group behaves as a unidentate ligand. An ORTEP diagram is given in Fig. 2, selected bond distances and angles in Table 2. In this complex the copper atom is five-co-ordinate and could be described as having a distorted square-pyramidal geometry. The changes in bond lengths described by the tetragonality[45] T^5 = 0.890 along with the trigonality index[46] [$\tau = (\varphi_1 - \varphi_2)/60$, where φ_1, φ_2 are the largest angles in the co-ordination sphere, τ = 0 for a perfect square pyramid, 1 for a perfect trigonal bipyramid] τ = (169.79 − 157.04)/60 = 0.2125 show the distortion away from the regular square-based pyramidal geometry.[47–51] Atoms N(1) and N(2) [2.013(2) and 2.044(2) Å] of the bipyridine molecule and the carboxylate oxygen atoms O(1) and O(4) [1.968(2) and 1.940(2) Å] occupy *cis* positions in the basal plane, while the water oxygen is 2.236(2) Å away. The unco-ordinated carboxylato-oxygen atoms O(2) and O(5) [Cu···O(2) 2.826, Cu···O(5) 3.365 Å] lie below and above the basal plane of the pyramid respectively (2.256 and 3.908). The ligand atoms which form this basal plane are not strictly coplanar. Atoms N(2) and O(4) are 0.155 and 0.133 Å below the plane and O(1) and N(1) are 0.122 and 0.157 Å above it, towards the apex. The Cu–O(w) distance [2.236(2) Å] is comparable with those observed for the methoxyacetato (2.24 Å)[7] or maleato (2.26 Å) analogues.[47]

Table 2 Selected bond distances (Å) and angles (°) of complex **2**

Cu–O(4)	1.940(2)	Cu–O(w)	2.236(2)
Cu–O(1)	1.968(2)	Cu···O(2)	2.826
Cu–N(2)	2.013(2)	Cu···O(5)	3.365
Cu–N(1)	2.044(2)		
O(4)–Cu–O(1)	96.81(9)	N(2)–Cu–N(1)	80.01(10)
O(4)–Cu–N(2)	169.79(9)	O(4)–Cu–O(w)	97.06(10)
O(1)–Cu–N(2)	90.88(9)	O(1)–Cu–O(w)	98.26(9)
O(4)–Cu–N(1)	90.37(9)	N(2)–Cu–O(w)	88.43(10)
O(1)–Cu–N(1)	157.04(9)	N(1)–Cu–O(w)	102.47(9)

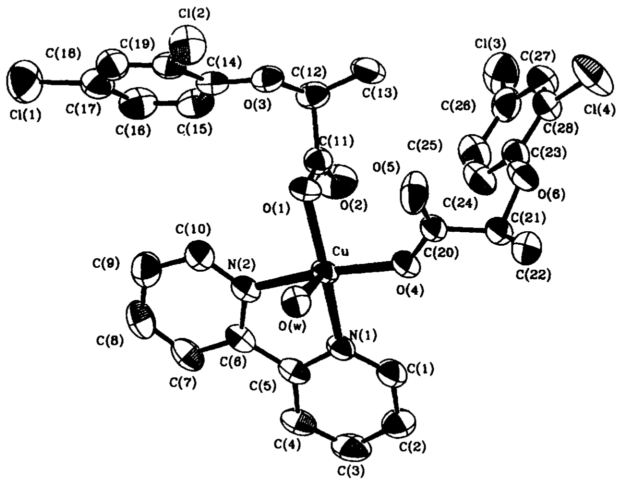
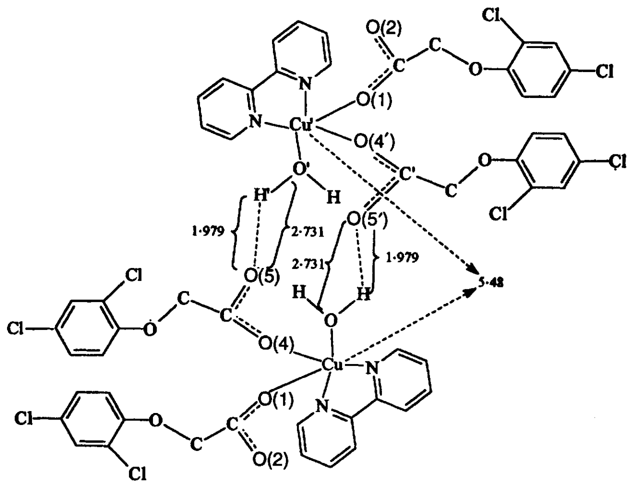


Fig. 2 An ORTEP view of the structure of complex **2** showing the atom-labelling scheme



Scheme 1

The O(5) of each molecule is hydrogen bonded to the water hydrogen of a neighbouring molecule at a distance H(w)···O(5′) of 1.979 Å, giving a dimeric arrangement with intradimer Cu···Cu separation of 5.48 Å, while the bridging path length [Cu–O–H···O(5′)–C′–O(4)′–Cu′] is 9.88 Å. The oxygen atom O(w) lies 2.731 Å away from O(5′) (Scheme 1). The copper atom is displaced 0.23 Å toward the water ligand. The *trans* N–Cu–O system of the basal plane gives angles of O(4)–Cu–N(2) 169.79(9) and O(1)–Cu–N(1) 157.04(9)°.

Structure of complex 3

In complex **3** the carboxylate group behaves as a unidentate ligand. An ORTEP diagram appears in Fig. 3, selected bond distances and angles in Table 3. In this complex the copper atom is five-co-ordinate and could be described as having a

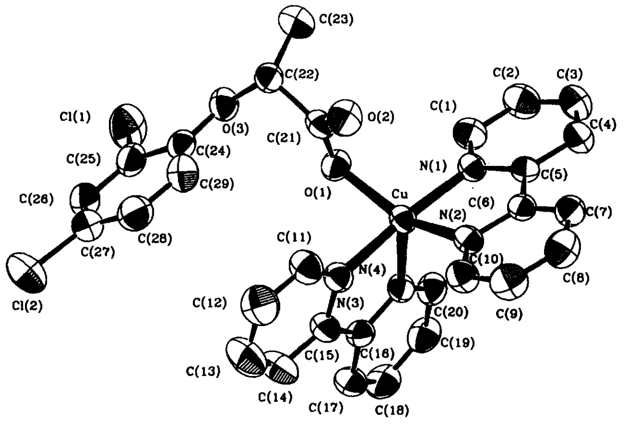


Fig. 3 An ORTEP view of the structure of complex **3** showing the atom-labelling scheme

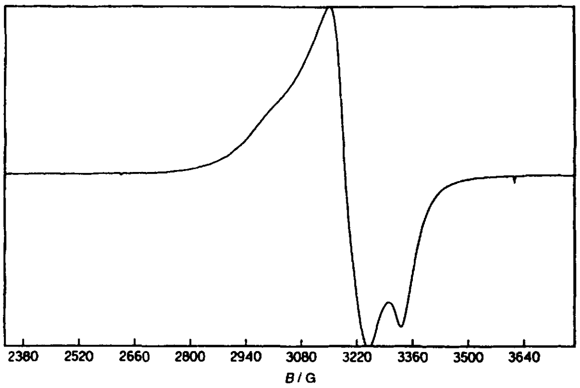


Fig. 4 The X-band powder ESR spectrum of complex **3** at 4 K

Table 3 Selected bond distances (Å) and angles (°) of complex **3**

Cu–N(4)	2.161(3)	Cu–N(1)	1.983(3)
Cu–O(1)	2.000(3)	Cu–N(3)	1.996(3)
Cu–N(2)	2.033(3)	Cu···O(2)	2.766
N(4)–Cu–O(1)	96.4(1)	N(3)–Cu–N(1)	175.2(1)
N(4)–Cu–N(3)	78.9(1)	N(4)–Cu–N(1)	98.8(1)
O(1)–Cu–N(3)	89.9(1)	O(1)–Cu–N(1)	94.6(1)
N(2)–Cu–N(1)	80.7(1)	N(2)–Cu–N(3)	96.1(1)
O(1)–Cu–N(2)	152.2(1)	N(2)–Cu–N(4)	111.4(1)

highly distorted square-pyramidal geometry with $\tau = (175.2-152.2)/60 = 0.3833$ and $T = 0.926$. Atoms N(1) and N(2) [1.983(3) and 2.033(3) Å] of one bipyridine molecule, N(3) [1.996(3) Å] of the second bipy and the carboxylate oxygen atom O(1) [2.000(3) Å] occupy the four positions in the basal plane, while N(4) of bipy is 2.161(3) Å away on the apex. A similar arrangement of two bipy molecules has been observed in a series of $[Cu(bipy)_2X]^+$ complexes.[48–51] The unco-ordinated carboxylato-oxygen atom O(2) [Cu···O(2) 2.766 Å] lies below the basal plane of the pyramid (2.317 Å). The *trans* atom system of the basal plane gives angles of O(1)–Cu–N(2) 152.2(1) and N(1)–Cu–N(3) 175.2(1)°. This cationic unit $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}(bipy)_2]^+$ is neutralized by a chloride ion 5.50 Å away from the metal atom.

Powder ESR spectra (4 K)

The polycrystalline ESR spectrum of complex **3** is rhombic,[49,50] $g_1 = 2.017$, $g_2 = 2.103$ and $g_3 = 2.243$ (Fig. 4) with R [$(g_2 - g_1)/(g_3 - g_2)$ where $g_3 > g_2 > g_1$] 0.642. The lowest g value only slightly above 2.00 is consistent with an approximate d_{z^2} ground state for the CuN_4O chromophore, but with such clearly rhombic, rather than axial, g factors this cannot be equated with a trigonal-bipyramidal stereochemistry as it involves a clear distortion towards square pyramidal with τ and R values 0.38 and 0.64 respectively.

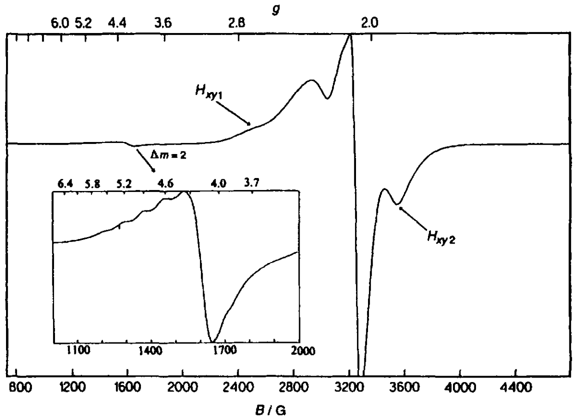


Fig. 5 The X-band powder ESR spectrum of complex **2** at 4 K. Inset: enlargement of the ESR signal at 1600 G

The X-band ESR spectrum of a polycrystalline sample of complex **2** indicates the presence of magnetic exchange (Fig. 5). Using the approach employed by Wasserman *et al.*[52] for the spectra of randomly oriented organic triplets, we assign the pair of bands at 2500 and 3580 G as the $\Delta m = 1$ transitions H_{xy1} and H_{xy2}. Setting $E = 0$ and using the equations (4)–(7) we

$$H_{xy1}^2 = \left(\frac{g_e}{g_\perp}\right)^2 H_0(H_0 - D) \tag{4}$$

$$H_{xy2}^2 = \left(\frac{g_e}{g_\perp}\right)^2 H_0(H_0 - D) \tag{5}$$

$$H_{z1} = (g_e/g_z)|H_0 - D| \tag{6}$$

$$H_{z2} = (g_e/g_z)(H_0 + D) \tag{7}$$

obtain $g_\perp = 2.196$ and the zero-field splitting parameter $D = 0.108\ cm^{-1}$. Assignment of the absorption centred at 1600 G to the $\Delta m = 1$ transition H_{z1} seems unlikely because this would require an abnormally high value of $g_\parallel = 2.79$. Moreover, we were unable to detect the corresponding high-field line H_{z2}. The band at lowest field may be assigned to the $\Delta m = 2$ transition between the $|-1>$ and $|+1>$ levels. Such 'half-field' transitions have been observed recently in a series of double 1,2,4-triazole-N^1,N^2-bridged binuclear copper(II) compounds,[53,54] while similar copper nuclear hyperfine splitting on the 'half-field' band has been observed in binuclear copper(II) complexes[55] diluted in $[Zn(pyo)_2(ONO_2)_2]$ (pyo = pyridine *N*-oxide) diamagnetic host. The commonly used formula (8),

$$D = 3g^2\beta^2/2r^3 \tag{8}$$

where β' is the Bohr magneton, which correlates the D splitting with the distance r between two unpaired electrons is not appropriate for distances greater than 5 Å. For such distances better results are obtained using the formula[44] (9) which

$$\text{r.i.} = \frac{A}{r^6}\left(\frac{9.1}{\nu}\right)^2 \tag{9}$$

correlates the relative intensity (r.i.) of the half-field transition, intensity of $\Delta M_s = 2$/total intensity of $\Delta M_s = 1$, with the distance r, where ν is the spectrometer operating frequency, in our case 9.4331 GHz, and $A = 21 \pm 2$. By using the ratio of the intensities for two portions of the spectrum some correction factors, which are required for accurate intensity determination,

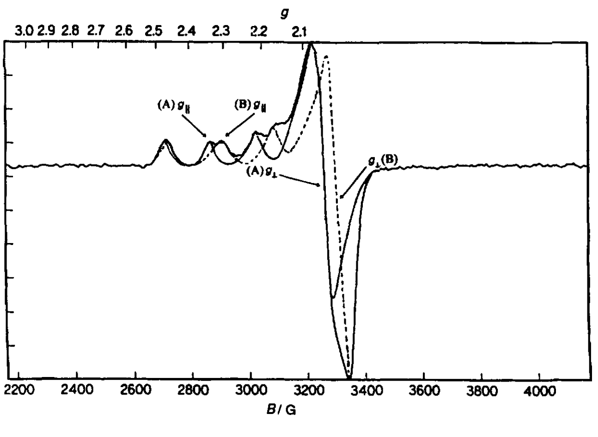


Fig. 6 The X-band powder ESR spectrum of complex **2** as a dmf glass at 4 K. (A) Elongated-octahedral environment, (B) distorted-octahedral environment

are eliminated. In the present spectrum the relative intensity is 0.7×10^{-4} and the calculated Cu · · · Cu separation, r, is 5.5 Å, in excellent agreement with the crystallographic data (5.48 Å). The isotropic signal with $g_\parallel = 2.302$ and $g_\perp = 2.072$ may be assigned to a mononuclear species with $S = \frac{1}{2}$. The observation of a triplet state due to the presence of a hydrogen-bond network is unique.

Glass ESR spectra (4 K)

Rapidly frozen samples of complex **2** exhibit spectra like the one shown in Fig. 6. The glass spectra obtained are axial without any feature suggesting a dimeric form. This is further support for the conclusion that the features characteristic for the presence of a dimeric form in the powder ESR spectrum come from the hydrogen-bond network. They can be described by the spin Hamiltonian (10). The numerical value of $G = (g_\parallel - 2)/(g_\perp - 2)$, for $A = 5.62$ and $B = 5.92$, indicates that exchange-coupling effects invalidate the use of the observed g values to propose a square-pyramidal or octahedral environment in solution.[48–51,56,57] However the presence of clear axial signals consistent with a $d_{x^2-y^2}$ ground state, in contrast to the powder spectra which suggest an approximate d_{z^2} ground state, supports a rearrangement of the copper environment to octahedral. The most interesting features of these spectra (Fig. 6) is that the ESR signal consists of two features corresponding to two types of complex. One feature (A) is consistent with an elongated-octahedral environment with basal bipy molecules, $g_\parallel = 2.281$, $g_\perp = 2.050$ and $A_\parallel = 156$ G (145.4×10^{-4} cm^{-1}), while the values $g_\parallel = 2.237$, $g_\perp = 2.040$ and $A_\parallel = 184$ G (171.6×10^{-4} cm^{-1}) suggest a distorted-octahedral structure (B)[48–51] with smaller T^6. The ESR spectrum of complex **3** in frozen solution is a typical axial spectrum with $g_\parallel = 2.252$, $g_\perp = 2.042$ and $A_\parallel = 165$ G (153.8×10^{-4} cm^{-1}).

$$H = g_\parallel \mu_B S_z H_z + g_\perp \mu_B (S_x h_x + S_y H_y) + A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y) \quad (10)$$

Magnetic measurements

Complexes **2** and **3**, with a d^9 configuration of the central atom, are considered to have magnetic moments close to the spin-only value, 1.73 μ_B, at room temperature. The observed value for **3**, 1.70 μ_B is consistent with a monomeric form[58,59] while that of **2**, 1.53 μ_B, indicates a magnetic exchange in accordance with the ESR data. The binuclear copper(II) compound shows subnormal magnetic moments at room temperature, 1.39 μ_B, due to copper–copper magnetic exchange consistent with those reported previously.[58]

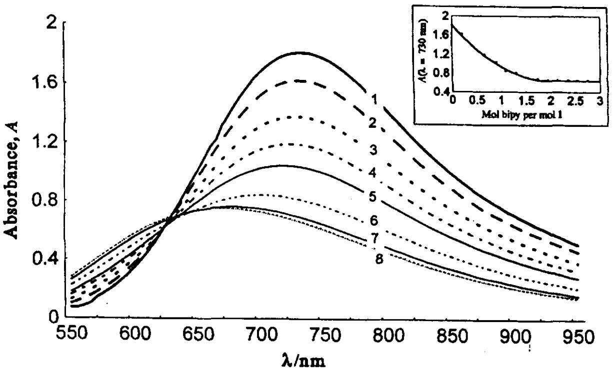


Fig. 7 The UV/VIS spectra of the titration of complex **1** with bipy. Curves: (1) 0.35 mmol of bipy added to an initial (70 cm^3) volume of **1** (5×10^{-3} mol dm^{-3}) in dmf; (2) 0.070 mmol of bipy; (3) 0.14 mmol of bipy; (4) 0.21 mmol of bipy; (5) 0.35 mmol of bipy; (6) 0.455 mmol of bipy; (7) 0.595 mmol of bipy; (8) 0.700 mmol of bipy. Inset: UV/VIS titration curve at 730 nm

Electronic absorption spectra

The electronic spectra of all the complexes prepared have been recorded by solution techniques using dmf as solvent and as Nujol mulls. In dmf solution **1** exhibits a broad absorption, band I, at 730 nm, a shoulder, band II, at 335 nm and a strong band, III, at 288 nm. The absorption coefficients are given in Table 4. The spectrum is also very similar to that recorded as a Nujol mull.

Dimeric copper(II) carboxylate complexes have been shown to exhibit an extra band (compared to the mononuclear complexes) at about 330 nm both in solution and in the crystalline phase. It is suggested[60] that band I could be assigned to a $d_{xz,yz} \longrightarrow d_{x^2-y^2}$ transition, II to a $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition[60] or to a transition to a doubly excited state,[61] of the type $(d_{z^2} \longrightarrow d_{x^2-y^2})^2$, without ruling out a charge-transfer assignment.[62] Band III has been assigned to a carboxylate-to-copper(II) charge-transfer transition since no significant solvent effect on this band was observed.[63] The neutral monomeric complex **2** exhibits a broad absorption band at 662 nm and a strong band at 302 nm, indicating that in dmf the complex retains the monomeric form. The ionic complex **3** exhibits an additional broad band at 914 nm as is expected for a *cis* distorted-octahedral complex of the type [Cu(bipy)$_2$L]Cl (L = ONO$^-$ or CO$_2$$^-$). When bipy is titrated into a solution of [Cu$_2$(Cl$_2$C$_6$H$_3$OCH$_2$CO$_2$)$_4$(MeOH)$_2$] in dmf the spectra shown in Fig. 7 are obtained. The isosbestic point at 640 nm demonstrates that this complex and [Cu(Cl$_2$C$_6$H$_3$OCH$_2$CO$_2$)$_2$(bipy)(H$_2$O)] are the only copper-containing species in solution.

Experimental

Materials

The chemicals for the synthesis of the compounds were used without further purification. Acetonitrile was distilled from calcium hydride and MeOH from magnesium and were stored over 3 Å molecular sieves. Diethyl ether (anhydrous grade) and absolute ethanol were used without further purification. The carboxylic acids, bipy, and CuCl$_2$·2H$_2$O were obtained from Aldrich Co. All chemicals and solvents were reagent grade.

Physical measurements

Infrared spectra (400–4000 cm^{-1}) were recorded on a Perkin-Elmer FT-IR 1650 spectrometer with samples prepared as KBr pellets, UV/VIS spectra on a Shimadzu-160A dual-beam spectrophotometer and ESR spectra on a Bruker ESR 300 spectrometer equipped with a Varian variable-temperature controller (diphenylpicrylhydrazyl was used as an external

Table 4 Electronic spectra and spin-Hamiltonian parameters of the copper(II) complexes in dmf solution

Complex	UV/VIS, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	$g_{\parallel}$	$g_{\perp}$	$10^4 \times A_{\parallel}$/cm^{-1}	G
1	730 (160)	—	—	—	—
	335 (sh) (503)				
	288 (2073)				
2	662 (80)	2.281(A)	2.050(A)	145.4(A)	5.62
	302 (2500)	2.237(B)	2.040(B)	171.6(B)	5.92
3	914 (35)	2.252	2.042	153.8	5.95
	704 (80)				
	320 (2040)				

Table 5 Crystallographic data for complexes 1–3

	1	2	3
Formula	$C_{36}H_{36}Cl_8O_{16}Cu_2$	$C_{28}H_{24}Cl_4CuN_2O_7$	$C_{31}H_{37}Cl_3CuN_4O_8$
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Crystal system	Triclinic	Triclinic	Triclinic
M	1135.39	705.83	763.54
a/Å	9.4831(8)	11.469(6)	12.803(2)
b/Å	9.6204(9)	14.095(8)	15.012(3)
c/Å	13.385(1)	10.887(6)	10.734(2)
α/°	86.966(3)	89.28(2)	109.464(7)
β/°	110.670(3)	62.05(1)	107.750(6)
γ/°	91.838(3)	76.37(2)	96.155(7)
U/Å^3	1140.80	1501(2)	1801.7
Z	1	2	2
D_m/g cm^{-3}	1.64	1.55	1.38
D_c/g cm^{-3}	1.653	1.562	1.407
μ/cm^{-1}	14.70	11.32	8.80
Weighting scheme	Unit weights[a]	$a = 0.0216, b = 1.1524$[b]	$a = 0.1093, b = 0.4787$[b]
R or $R1$	0.0320[c]	0.0365[d]	0.0542[d]
R' or $wR2$	0.0345	0.0908	0.1513

[a] $w = 1/[\sigma^2(F_o) + F_c^2]$. [b] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. [c] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [d] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|)$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

standard). Room-temperature magnetic measurements were carried out by Faraday's method using mercury tetrathiocyanatocobaltate(II) as a calibrant. The C, H and N elemental analysis were performed on a Perkin-Elmer 240B elemental analyser; Cu was determined by atomic absorption spectroscopy on a Perkin-Elmer 1100B spectrophotometer. Electric conductance measurements were carried out with a WTW model LF 530 conductivity outfit and a type C cell, which had a cell constant of 0.996. This represents a mean value calibrated at 25 °C with potassium chloride. All temperatures were controlled with an accuracy of ± 0.1 °C using a Haake thermoelectric circulating system.

The sodium salts of the carboxylic acids were prepared by the reaction of the acid with NaOH or NaOMe in methanol. The white solids were recrystallized from methanol and dried in the air.

Syntheses

Tetrakis(2,3-dichlorophenoxyacetato)bis(methanol)dicopper(II) 1. 2,3-Dichlorophenoxyacetic acid (2.21 g, 10 mmol) in MeOH (50 cm^3) was dissolved and NaOMe (0.54 g, 10 mmol) was added. After 30 min of stirring $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol) in MeOH (25 cm^3) was added dropwise. The reaction mixture was stirred at room temperature for 1 h and left for slow evaporation. Green *crystals* of $[Cu_2(Cl_2C_6H_3OCH_2CO_2)_4(MeOH)_2]\cdot 2MeOH$ **1** suitable for X-ray crystallography were deposited in a few days. Yield 70% (Found: C, 37.6; H, 3.40; Cu, 10.7. $C_{36}H_{36}Cl_8Cu_2O_{16}$ requires C, 38.05; H, 3.15; Cu, 11.2). $\tilde{\nu}_{max}$/cm^{-1}(KBr pellet): $\nu_{asym}(CO_2)$ 1620vs, $\nu_{sym}(CO_2)$ 1425vs.

Aqua(2,2′-bipyridine)bis[2-(2,4-dichlorophenoxy)propanoato]copper(II) 2. 2-(2,4-Dichlorophenoxy)propanoic acid (2.35 g, 10 mmol) was dissolved in MeOH (50 cm^3) and NaOMe (0.54 g, 10 mmol) added. After 30 min of stirring $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol) in MeOH (25 cm^3) was added dropwise. The reaction mixture was stirred for 1 h and reduced in volume under vacuum. Microcrystalline $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}_2(H_2O)_2]$ was deposited and filtered off. Yield 70%. This complex (3 mmol) was dissolved in MeCN (50 cm^3) and bipy (0.47 g, 3 mmol) in MeCN (25 cm^3) was added. The mixture was stirred for 1 h and left for slow evaporation. Blue *crystals* of $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}_2(bipy)(H_2O)]$ **2** suitable for X-ray analysis were deposited in 1 week. Yield 60% (Found: C, 46.9; H, 3.60; Cu, 9.60; N, 4.25. $C_{28}H_{24}Cl_4CuN_2O_7$ requires C, 47.6; H, 3.40; Cu, 9.00; N, 4.00%). $\tilde{\nu}_{max}$/cm^{-1} (KBr pellet): $\nu_{asym}(CO_2)$ 1638vs; ν(C=N) 1477vs, 1446vs; $\nu_{sym}(CO_2)$ 1388vs.

Bis(2,2′-bipyridine)[2-(2,4-dichlorophenoxy)propanoato]copper(II) chloride 3. 2-(2,4-Dichlorophenoxy)propanoic acid (2.35 g, 10 mmol) was dissolved in MeOH (50 cm^3) and NaOMe (0.54 g, 10 mmol) added. After 30 min of stirring $CuCl_2 \cdot 2H_2O$ (0.85 g, 5 mmol) and bipy (1.56 g, 10 mmol) in MeOH (25 cm^3) were added dropwise. The reaction mixture was refluxed for 1 h. The blue solution was reduced in volume and left for slow evaporation. Blue *crystals* of $[Cu\{Cl_2C_6H_3OCH(Me)CO_2\}(bipy)_2]Cl \cdot 3H_2O \cdot 2MeOH$ **3** suitable for X-ray analysis were deposited in a few days. Yield 60% (Found: C, 48.1; H, 5.20; Cu, 7.95; N, 7.05. $C_{31}H_{37}Cl_3CuN_4O_8$ requires C, 48.7; H, 4.85; Cu, 8.30; N, 7.35%). $\tilde{\nu}_{max}$/cm^{-1} (KBr pellet): $\nu_{asym}(CO_2)$ 1590vs; ν(C=N) 1477vs, 1444vs; $\nu_{sym}(CO_2)$ 1404vs.

Crystallography

A green prismatic crystal with approximate dimensions $0.12 \times 0.22 \times 0.50$ mm for complex **1** and blue ($0.10 \times 0.40 \times 0.50$ mm) for **2** were mounted in air and a pale blue prismatic crystal ($0.15 \times 0.23 \times 0.50$ mm) for **3** was mounted in capillary. Diffraction measurements were made at 298 K on a Crystal Logic dual-goniometer diffractometer using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å) for 2 and on a P2_1 Nicolet diffractometer upgraded by Crystal Logic using Zr-filtered Mo-Kα radiation for **1** and **3**. Crystal data and data-collection parameters are in Table 5. Unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11° < 2\theta < 23°$. Intensity data were recorded using θ–2θ scans to $2\theta_{max} = 50°$ with scan speed $1.8° \min^{-1}$ for **1**, $2.8° \min^{-1}$ for **2** and $1.5° \min^{-1}$ for **3** and scan range $2.5 + \alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 showed $< 3.0\%$ intensity fluctuation and no decay. Lorentz-polarization and ψ-scan absorption corrections were applied using Crystal Logic software. Scattering factors were taken from ref. 64.

Symmetry-equivalent data for complex **1** were averaged with $R_{int} = 0.0193$ to give 3956 independent reflections from a total 4210 collected, for **2** with $R_{int} = 0.0118$ (5278 independent, a total 5569) and for **3** with $R_{int} = 0.0202$ (5994 independent, total 6249). The structures were solved by direct methods using the programs SHELXS 86.[65] Complexes **2** and **3** were refined by full-matrix least-squares techniques on F^2 with SHELXL 93[66] using 5278 and 5982 reflections and refining 475 and 481 parameters respectively, while **1** was refined by full-matrix least-squares techniques on F with SHELX 76[67] using reflections ~ 3421 with $F_o > 6\sigma(F_o)$, and refining 336, 475 and 481 parameters. All hydrogen atoms were located from difference maps and their positions refined isotropically. All non-hydrogen atoms were refined anisotropically. For **1** the final values for R, R' and goodness of fit, for all data, are 0.0407, 0.0430, 0.94 respectively. The maximum and minimum residual peaks in the final difference map were 0.989 and -0.548 e Å^{-3}. The largest shift/e.s.d. in the final cycle was 0.035. For **2** the final values were 0.0443, 0.0988 and 1.079 for $R1$, $wR2$ and goodness of fit, the maximum and minimum residual peaks were 0.700 and -0.375 e Å^{-3} and the largest shift/e.s.d. was 0.012. For **3** the corresponding values for $R1$, $wR2$ and goodness of fit, for all data, were 0.0769, 0.1818, 1.148, the maximum and minimum residual peaks were 0.618 and -0.538 e Å^{-3} and the largest shift/e.s.d. was 0.029.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/177.

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