

First report of singly phenoxo-bridged copper(II) dimeric complexes: synthesis, crystal structure and low-temperature magnetic behaviour study†

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Three singly phenoxo-bridged dinuclear Cu(II) complexes [Cu₂(L)₂(SCN)(H₂O)](ClO₄) **1**, [Cu₂(L)₂(N₃)(H₂O)](ClO₄) **2**, [Cu₂(L)₂(NCO)(H₂O)](ClO₄) **3** (HL is the Schiff base ligand derived from O-vanillin and 2-aminomethyl ethylenediamine) have been synthesised and characterised by infrared, UV-Vis spectra, electrochemical study and single crystal X-ray diffraction study. In all the complexes (**1–3**), there are two geometrically different square pyramidal copper(II) centres, with N₃O₂ and N₂O₃ donor sets for the two Cu(II) centres. In the dimeric unit, the copper atoms are held together by only one distinct rare μ₂-phenolate oxygen of one Schiff base. The Cu–Cu distances are 3.291(2), 3.244(1) and 3.244(1) Å for complexes **1**, **2** and **3**, respectively, and the Cu–O–Cu angles are found to be 111.5(1), 109.3(2), 109.6(1)° for complexes **1**, **2** and **3**, respectively. Variable temperature magnetic susceptibility study on the complexes **1**, **2** and **3** indicate the presence of antiferromagnetic coupling between the Cu(II) centres with 2J values –109.8, –103.9 and –95.9 cm^{–1}, respectively.

Transition dinuclear metal complexes and ligands capable of yielding them have been attracting increasing interest in the field of synthetic and biological chemistry due to the key roles they play in many applications.^{1–10} In fact, dinuclear metal complexes have been used successfully for the recognition and assembly of external species of different natures, such as inorganic or organic substrates.^{1–4} Many metalloenzymes contain two divalent transition metal ions in close proximity and in most cases the two metal centres cooperate with each other¹¹ and they have contributed to a better knowledge of oxygen transport as well as of some industrial catalytic processes.^{12,13} The design of structural and functional model complexes of such dinuclear centres has been the subject of very extensive investigations.^{11,14,15}

In this context, recent emphasis has been placed on the detailed study of the properties of Cu(II) phenolate complexes because of their postulated involvement in a range of biological and catalytic processes. Thus, Cu(II) phenolate units have been proposed as intermediates in the catalytic cycles of metalloenzymes *e.g.* galactose oxidase, tyrosinase,^{16–19} in the biogenesis of novel metalloenzyme cofactors (*e.g.*, topaquinone in amine oxidases),^{20,21} and in synthetic catalysis such as alcohol oxidation^{22–25} and phenol polymerization.^{26–28} The distance between the two metal centres is crucial to allow the cooperation of both metal ions in the active (site) centre.²⁹

The known Cu(II)–phenolate complexes exhibit coordination numbers ranging from 4 to 6, as is typical for the

coordination chemistry of Cu(II). The phenolates in most of these compounds usually are incorporated as part of multidentate ligand systems^{26–28} and complexes with simple, exogenous phenolate ligands are less common.³⁰

Sanmartin *et al.* have reported the synthesis and crystal structure of one bischelical isocetes triangle core self-assembled by two μ-phenoxo bridges.³¹ Recently, the same group has communicated the trinuclear Cu(II) bischelate Cu₃(H₂L)(L)·2H₂O [H₄L = N,N'-bis(3-hydroxysalicylidene)-1,4-diaminobutane] complex.¹² Yang *et al.* have reported two compounds, [Cu₃(Sbal)₂(Phen)(H₂O)₂](ClO₄)₂·3H₂O and [Cu(H₂Sbal)₂(Phen)](ClO₄)₂, where two μ-phenoxo bridges are observed.³² Using an amino-phenolic ligand, Dapporto *et al.* have synthesised dinuclear zinc complexes assembling butanolate and azide anions, [Zn₂(HL)(CH₃CH₂CH₂CH₂O)](ClO₄)₂.¹ The authors also have done a CCDC search and shown that phenoxo bridging is generally always associated with some other kind of bridging featuring dinuclear metal complexes.^{1,33a} So, dinuclear singly phenoxo-bridged copper(II) complexes of Schiff base ligands are still very sparse in the literature.^{33b,34}

For the atoms which bridge between paramagnetic transition metal atoms, the magnetic interactions have been related to the magnitude of the bridging angle (φ) and other structural features. This has been especially studied for oxygen-bridged metal atoms such as Cu–O–Cu. Small φ angles near 96° should lead to strong ferromagnetic interactions, while larger values should make the interaction increasingly strongly antiferromagnetic.³⁵

In this paper, we describe the synthesis, characterisation and crystal structure and low temperature magnetic behaviour of three novel singly phenoxo-bridged dinuclear Cu(II) Schiff base

† Electronic supplementary information (ESI) available: structural data for compounds **1**, **3**, **2**. See <http://www.rsc.org/suppdata/nj/b3/b300217a/>

complexes. All the complexes show antiferromagnetic behaviour at low temperature.

Experimental

Materials and measurements

Reagent grade copper(II) perchlorate (Fluka), sodium thiocyanate, sodium azide, sodium cyanate (Aldrich), O-vanillin and 2-aminomethyl ethylenediamine (Fluka) were used as received. The solvents used were of reagent grade.

Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer as a KBr pellet and electronic spectra on a Perkin-Elmer Lambda-40 spectrophotometer using methanol as solvent. Elemental analyses were carried out on a Perkin-Elmer 2400-II instrument. Electrochemical studies were performed on a CH 600A cyclic voltammeter instrument using acetonitrile as solvent. EPR spectra were performed on a Bruker ER 420 model. Variable temperature magnetic susceptibilities were measured in the temperature range 5–300 K on a model CF-1 superconducting extracting sample magnetometer with powdered sample kept in a capsule for weighing. All data were corrected for diamagnetism of the ligands estimated from Pascal's constants.³⁶

Synthesis of the ligand and complexes

Synthesis of the Schiff base ligand. The Schiff base ligand $[(CH_3)_2NCH_2CH_2N=CHC_6H_3(OH)(OMe)]$ (LH) was obtained by refluxing a methanolic solution (25 ml) of O-vanillin (1 mmol) and 2-dimethylaminoethylamine (1 mmol) for 30 minutes. The resulting orange–yellow solution containing the ligand was used without further purification.

Caution! Perchlorate salts are potentially explosive and should be used in small quantity with much care.

Synthesis of the complexes

$[Cu_2(L)_2(SCN)(H_2O)](ClO_4)$ (1). To a methanolic solution of copper perchlorate (0.370 g, 1 mmol), methanolic solution of the Schiff base (1 mmol) was added. Then methanolic solution of sodium thiocyanate (0.081 g, 1 mmol) was added to the mixture with constant stirring. The resulting solution was stirred for 5 minutes at room temperature. After 3 days crystals suitable for X-ray diffraction were collected and the rest were filtered and air-dried.

Yield: 60%, Anal. calc. for $C_{25}H_{36}ClCu_2N_5O_9S$, C, 40.26; H, 4.83; N, 9.39; Cu, 17.05. Found: C, 40.31; H, 4.86; N, 9.36; Cu, 16.97%.

$[Cu_2(L)_2(N_3)(H_2O)](ClO_4)$ (2) and $[Cu_2(L)_2(NCO)(H_2O)](ClO_4)$ (3). The syntheses were carried out using the same procedure as in 1, by using sodium azide and sodium cyanate instead of sodium thiocyanate for 2 and 3 respectively. After 4 days single crystals suitable for X-ray diffraction were collected and the rest were filtered and air-dried.

Yield: 65%, Anal. calc. for $C_{24}H_{36}ClCu_2N_7O_9$, (2) C, 39.49; H, 4.94; N, 13.44; Cu, 17.43. Found: C, 39.67; H, 4.86; N, 13.66; Cu, 17.52%.

Yield: 70%, Anal. calc. for $C_{25}H_{36}ClCu_2N_5O_{10}$, (3) C, 41.14; H, 4.94; N, 9.60; Cu, 17.98. Found: C, 41.22; H, 4.86; N, 9.36; Cu, 17.86%.

X-Ray crystallography

The determination of the unit cell and the data collection for deep blue crystals of compounds 1, 2 and 3 were performed on a Siemens SMART CCD diffractometer and the data were collected using graphite-monochromatic $MoK\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K in the range of $1.25 < \theta < 23.0^\circ$ for 1, $1.98 < \theta < 25.10^\circ$ for 2, and $1.98 < \theta < 25.04^\circ$ for 3 respectively. The data sets were corrected by the SADABS program.^{37a} The structures of 1, 2 and 3 were solved by direct methods and refined by the full-matrix least-squares method with the SHELXTL-97^{37b} program package. The details of X-ray data collection and structure refinement of 1, 2 and 3 are given in Table 1.

CCDC reference numbers 214016, 214955, 214017 for 1, 2 and 3, respectively. See <http://www.rsc.org/suppdata/nj/b3/b300217a/> for crystallographic in .cif or other electronic format.

Results and discussion

Infrared spectra

The infrared spectra of all the three complexes 1, 2 and 3 are very much consistent with the structural data presented in this paper. The bands in the range 3524 and 1631 cm^{-1} for 1, 3547 and 1634 cm^{-1} for 2 and 3548 and 1635 cm^{-1} for 3 are attributable to O–H stretching and bending of water ligands or water of crystallisation. This also indicates the presence of

Table 1 Crystallographic data for complexes 1, 2 and 3

Compound	1	2	3
Chemical formula	$C_{25}H_{36}ClCu_2N_5O_9S$	$C_{24}H_{36}ClCu_2N_7O_9$	$C_{25}H_{36}ClCu_2N_5O_{10}$
<i>M</i>	745.18	729.13	729.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$
<i>Z</i>	4	4	4
<i>a</i> /Å	16.605(1)	16.675(1)	16.738(1)
<i>b</i> /Å	13.775(1)	13.319(1)	13.286(1)
<i>c</i> /Å	13.789(1)	14.064(1)	14.082(1)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	102.184(1)	104.699(1)	104.88(1)
$\gamma/^\circ$	90	90	90
<i>T</i> /K	293(2)	293(2)	293(2)
<i>V</i> /Å ³	3082.8(1)	3021.2(1)	3026.5(2)
Total reflections collected	8518	9445	9793
No. of independent reflections	4281 [$R_{\text{int}} = 0.0807$]	5272 [$R_{\text{int}} = 0.0240$]	5279 [$R_{\text{int}} = 0.0210$]
Absorption coefficient μ/mm^{-1}	1.592	1.558	1.556
<i>F</i> (000)	1536	1504	1504
θ for data collection/ $^\circ$	1.25 to 23.00	1.98 to 25.10	1.98 to 25.04
<i>R</i> indices (all data)	$R1 = 0.1646$, $wR2 = 0.1410$,	$R1 = 0.0732$, $wR2 = 0.1369$	$R1 = 0.0664$, $wR2 = 0.1253$
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0821$, $wR2 = 0.1410$	$R1 = 0.0557$, $wR2 = 0.1224$	$R1 = 0.0513$, $wR2 = 0.1253$

hydrogen bonding in the complex.³² The complexes **1**, **2** and **3** show one strong band at 2078, 2068 and 2206 cm⁻¹, respectively, which indicate the presence of NCS, N₃ and NCO as terminal ligands. The bands at 2936, 2946 and 2937 cm⁻¹ are due to the imine stretching frequency for complexes **1**, **2**, **3** respectively. The phenolic C=O stretching is present at 1274 and 1286 cm⁻¹ for **1**, 1268 and 1288 cm⁻¹ for **2** and 1270 and 1289 cm⁻¹ for **3**.³² Bands in agreement with non-coordinated anions could also be observed for perchlorate compounds, 1172, 1161–1086, 969, 650, 455, 445 cm⁻¹.^{38,39} Ligand coordination to the copper centre is substantiated by two bands appearing at 465, 464, 465 (medium) and 355, 378, 369 (strong) cm⁻¹, for complexes **1**, **2** and **3**, attributable to $\nu(\text{Cu-N})$ and $\nu(\text{Cu-O})$, respectively.¹²

Electronic spectra

Although the electronic spectra of the copper complexes with multidentate Schiff base ligands are not in general good indicators of geometry,⁴⁰ they support the structural data.

The complexes display two strong absorption bands in the region 225, 276 nm for **1**, 236, 277 nm for **2** and 237, 279 nm for **3** respectively. These are clearly charge transfer in origin. The UV absorption bands observed at 378, 379 and 382 nm for complexes **1**, **2** and **3**, respectively, can be assigned to the charge transfer from the ligands to the Cu(II), transition. The band for an LMCT transition of the Cu–O–Cu skeleton is masked here by the other bands. As usual, all the spectra show very weak low-intensity absorption bands associated with d–d transitions at 640, 644 and 646 nm for complexes **1**, **2** and **3** respectively.^{1,11,30,32}

Electrochemical study

Electrochemical studies of the complexes were performed using acetonitrile as solvent and tetrabutylammonium perchlorate as supporting electrolyte at a scan rate of 50 mV sec⁻¹. Cyclic voltammetry on the complexes **1**, **2** and **3** show two reductive responses on the negative side of SCE (at -0.67, -1.24 V for complex **1**, -0.69, -1.27 V for complex **2** and -0.71, -1.30 V for complex **3**, respectively) both of which are irreversible in nature. The observed potential gaps (570, 580 and 590 mV for complex **1**, **2** and **3**, respectively) between the two reductions are considerably large and is believed to be due to the combined effect of the difference in coordination environment around the two copper centres and effective communication between them through the oxo-bridge. Two irreversible oxidation responses are also observed on the positive side of SCE and these are tentatively assigned to oxidation of the coordinated ligands.

Description of the crystal structures of the complexes **1**, **2** and **3**

The structures of **1**, **2** and **3** are identical, except for a slight difference in the bond parameters and the standard deviation, so we limit the description to structure **1**.

Crystal structure of complex **1**

The ORTEP representation of the binuclear unit for **1** is shown in Fig. 1 with important bond lengths and angles summarised in Table 2. The crystallographic cell diagram viewed down the *c*-axis is shown in Fig. 2. Complex **1** crystallises in a monoclinic system with space group *P*2(1)/*c*. There are two geometrically different square pyramidal copper(II) centres, with N₃O₂ donor set for Cu(1) and N₂O₃ donor set for Cu(2). In the dimeric unit, the copper atoms are held together by only one distinct rare μ_2 -phenolate oxygen of one Schiff base ligand. In the present case, the Cu1...Cu2 distance is 3.291(2) Å which is lower than similar complexes found in the literature.³⁴ For

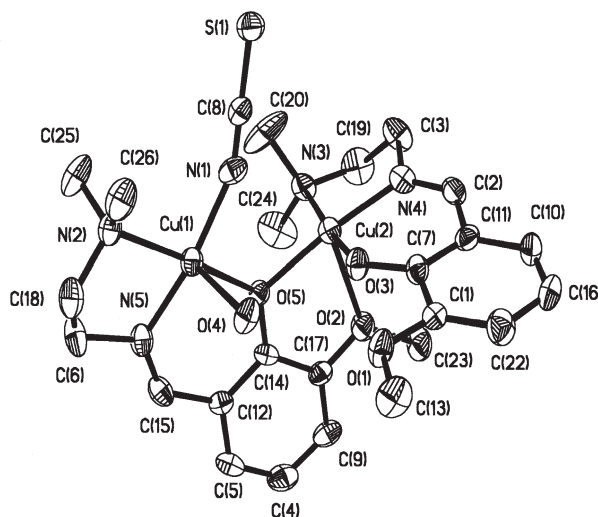


Fig. 1 ORTEP representations of the binuclear unit for **1** (30% probability ellipsoids, for clarity hydrogen atoms were omitted). (one ClO₄⁻ was omitted).

double phenoxo-bridging, the Cu–Cu distances are in the range 2.901–3.345 Å.⁴¹ The Cu1–O5–Cu2 angle is 111.5(1)° taking Cu(1)–O(5) and Cu(2)–O(5) distances 1.996(6) and 1.985(6) Å respectively. This Cu–O–Cu angle value is very small compared to similar complexes³⁴ but larger than double phenoxo-bridged complexes where the values generally lie between 95.7–107.5°.^{41–44} The Cu–O distances are also comparable to the similar complexes.⁴¹

In our case, the two Schiff base molecules behave in a different way. One of the Schiff bases acts as a tetradentate one while the other acts in a tridentate fashion with a non-bonded (–OMe) group. One perchlorate is also present in the lattice which is not shown in Fig. 1.

The geometry of the Cu(1) centre is best described as a distorted (4 + 1) (NNNO + O) square-based pyramid. The four atoms constituting the basal plane are the phenolic oxygen (O5) atom, two nitrogen (N2 and N5) atoms of one Schiff base and the N(1) atom of the monodentate thiocyanate ligand. The axial site is occupied by the O(4) atom of the coordinated water molecule. The Cu(1) atom lies not in the basal plane but slightly out of it at a distance of 0.1496 Å. In the basal plane, the average bond distances (Å) are Cu(1)–N(1) = 1.952(10), Cu(1)–N(2) = 2.077(8), Cu(1)–N(5) = 1.933(9), Cu(1)–O(5) = 1.996(6). The axial distance is Cu(1)–O(4) = 2.260(6) Å, which is slightly longer than the basal bond lengths. The bond lengths are slightly higher than double phenoxo-bridged complexes.^{41,43,44} The deviation from the

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

Cu(1)–N(5)	1.933(9)	Cu(2)–O(3)	1.936(6)
Cu(1)–N(1)	1.952(10)	Cu(2)–N(4)	1.937(9)
Cu(1)–O(5)	1.996(6)	Cu(2)–O(5)	1.985(6)
Cu(1)–N(2)	2.077(8)	Cu(2)–N(3)	2.070(8)
Cu(1)–O(4)	2.260(6)	Cu(2)–O(2)	2.334(7)
		Cu(1)–Cu(2)	3.291(2)
N(5)–Cu(1)–N(1)	167.0(4)	O(3)–Cu(2)–N(4)	91.3(3)
N(5)–Cu(1)–O(5)	91.1(3)	O(3)–Cu(2)–O(5)	90.6(3)
N(1)–Cu(1)–O(5)	89.9(3)	N(4)–Cu(2)–O(5)	172.1(3)
N(5)–Cu(1)–N(2)	84.9(4)	O(3)–Cu(2)–N(3)	172.8(3)
N(1)–Cu(1)–N(2)	93.1(4)	N(4)–Cu(2)–N(3)	84.9(3)
O(5)–Cu(1)–N(2)	174.2(3)	O(5)–Cu(2)–N(3)	94.0(3)
N(5)–Cu(1)–O(4)	98.1(3)	O(3)–Cu(2)–O(2)	91.5(3)
N(1)–Cu(1)–O(4)	94.9(3)	N(4)–Cu(2)–O(2)	96.7(3)
O(5)–Cu(1)–O(4)	86.6(2)	O(5)–Cu(2)–O(2)	75.6(3)
N(2)–Cu(1)–O(4)	98.0(3)	N(3)–Cu(2)–O(2)	95.0(3)
Cu(2)–O(5)–Cu(1)	111.5(3)		

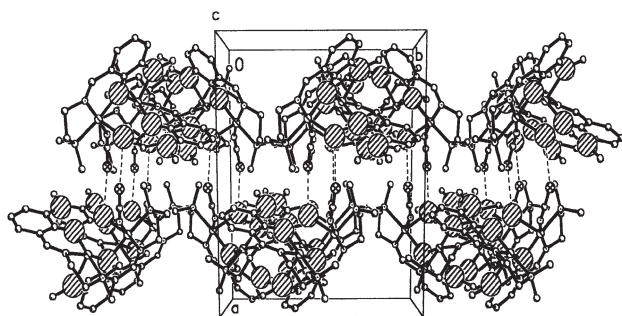


Fig. 2 Cell diagram of **1** viewed down the *c*-axis.

square pyramidal geometry is also indicated by the bond angles involving the atoms in the *cis* positions which vary from 84.9(4)–93.1(4)° as well as the angles involving the *trans* positions that vary to a large extent from 167.0(4)–174.2(3)°. All the angles are more or less comparable to those compounds in the literature.^{28,31,32,34,41–46}

Similarly, the geometry around Cu(2) can also be described as a distorted (4 + 1) (NNOO + O) square-based pyramid. The four atoms constituting the basal plane are the phenolic oxygen [O(5)] atom, two nitrogens [N(3) and N(4)] of another Schiff base and the O(3) atom of the second phenolate oxygen atom which does not take part in bridging but remains bonded with Cu(2) only. Here the axial site is occupied by the O(2) atom of the coordinated methoxy (–OMe group) of the first Schiff base. As usual, here the Cu(2) atom also lies 0.0157 Å out of the mean basal plane. In the basal plane, the average bond distances (Å) are, Cu(2)–N(3) = 2.070(8), Cu(2)–N(4) = 1.937(9), Cu(2)–O(3) = 1.936(6), Cu(2)–O(5) = 1.985(6). The axial distance is Cu(2)–O(4) = 2.260(6) Å, which is slightly longer than the basal bond lengths. The bond lengths are slightly higher than double phenoxo-bridged complexes.^{41,43,44} The deviation from the square pyramidal geometry is also indicated by the bond angles involving the atoms in the *cis* positions which vary from 84.9(3)–94.0(3)° as well as the angles involving the *trans* positions that vary from 172.1(3)–178.8(3)°. All the angles are more or less comparable to those compounds in the literature.^{28,31,32,34,41–46}

Compounds **2** and **3** are iso-structural to that of the above-described compound **1**, except they contain the N₃[–] and OCN[–] anion in **2** and **3**, respectively, instead of the SCN[–] anion in **1**. The bond lengths and angles in the counterpart are also comparable. The symmetry expanded structures and the coordination environments around Cu^{II} atoms in **2** and **3** are shown in Fig. 3 and 4 respectively. Selected bond lengths and angles for

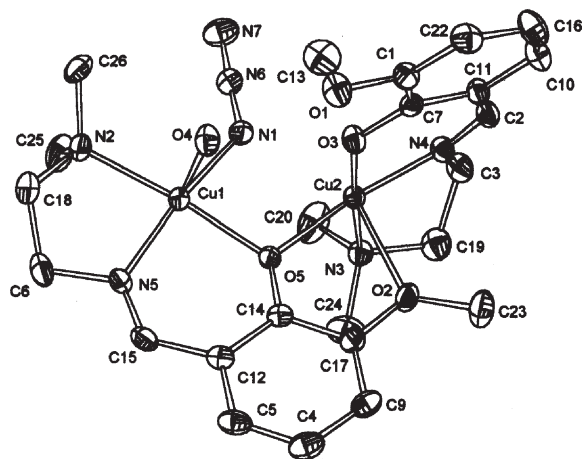


Fig. 3 ORTEP representations of the binuclear unit for **2** (30% probability ellipsoids, for clarity hydrogen atoms were omitted). (one ClO₄[–] was omitted).

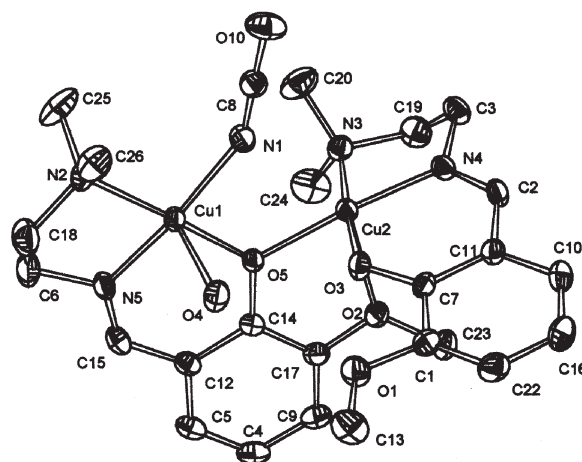


Fig. 4 ORTEP representations of the binuclear unit for **3** (30% probability ellipsoids, for clarity hydrogen atoms were omitted). (one ClO₄[–] was omitted).

compounds **2** and **3** are given in Tables 3 and 4, respectively. A comparison of the coordination environments for Cu(1) and Cu(2) in **1**, **2** and **3** is summarised in Table 5.

Magnetic properties and EPR spectral studies

Magnetic measurements were carried out on polycrystalline powder samples ranging from 5.0 to 300 K at 10 KG applied field. Compounds **1**, **2** and **3** show an almost identical behavior with very slight differences. In Fig. 5 we represent only the magnetic behavior of **1** in the forms of $\chi_M T$ vs. *T* and χ_M vs. *T* plots. Fig. 6 and Fig. 7 represent the magnetic behavior of **2** and **3**, respectively, in the forms of $\chi_M T$ vs. *T* and χ_M vs. *T* plots.

At 300 K, the $\chi_M T$ values per dimer are 0.6733, 0.7063 and 0.7032 emu K mol^{–1} for complexes **1**, **2** and **3**, respectively; these values are smaller than that expected for two uncoupled *S* = 1/2 spins (0.75 emu K mol^{–1}). $\chi_M T$ decreases rapidly with decreasing temperature to reach a plateau at ca. 20 K giving values of 0.0161, 0.0133 and 0.0208 emu K mol^{–1} for **1**, **2** and **3** respectively, which indicate the existence of antiferromagnetic coupling. The plateau observed at low temperature may be due to the non coupled Cu(II) ions in the polycrystalline powder sample. The magnetic susceptibility data were quantitatively analysed by simply treating as an interacting dimer (eqn. (1)).

$$\chi_M = (1 - \rho)(2Ng^2\mu_B^2/kT)[3 + \exp(-2J/KT)]^{-1} + \rho Ng^2\mu_B^2/2kT \quad (1)$$

Table 3 Selected bond lengths and angles for complex **2**

Cu(1)–N(5)	1.944(4)	Cu(1)–Cu(2)	3.244(1)
Cu(1)–N(1)	1.971(4)	Cu(2)–O(3)	1.941(3)
Cu(1)–O(5)	1.975(3)	Cu(2)–N(4)	1.946(4)
Cu(1)–N(2)	2.064(4)	Cu(2)–O(5)	2.003(3)
Cu(1)–O(4)	2.318(4)	Cu(2)–N(3)	2.090(4)
		Cu(2)–O(2)	2.370(4)
N(5)–Cu(1)–N(1)	167.88(19)	O(3)–Cu(2)–N(4)	91.81(16)
N(5)–Cu(1)–O(5)	90.67(16)	O(3)–Cu(2)–O(5)	89.44(14)
N(1)–Cu(1)–O(5)	84.58(16)	N(4)–Cu(2)–O(5)	173.09(16)
N(5)–Cu(1)–N(2)	85.32(19)	O(3)–Cu(2)–N(3)	176.10(16)
N(1)–Cu(1)–N(2)	98.77(19)	N(4)–Cu(2)–N(3)	84.31(18)
O(5)–Cu(1)–N(2)	175.01(16)	O(5)–Cu(2)–N(3)	94.45(16)
N(5)–Cu(1)–O(4)	97.49(17)	O(3)–Cu(2)–O(2)	87.83(15)
N(1)–Cu(1)–O(4)	93.38(17)	N(4)–Cu(2)–O(2)	99.05(16)
O(5)–Cu(1)–O(4)	86.81(14)	O(5)–Cu(2)–O(2)	74.21(13)
N(2)–Cu(1)–O(4)	96.65(16)	N(3)–Cu(2)–O(2)	93.12(16)

Table 4 Selected bond lengths and angles for complex **3**

Cu(1)–N(5)	1.936(4)	Cu(1)–Cu(2)	3.244(1)
Cu(1)–N(1)	1.959(4)	Cu(2)–N(4)	1.934(4)
Cu(1)–O(5)	1.982(3)	Cu(2)–O(3)	1.944(3)
Cu(1)–N(2)	2.082(4)	Cu(2)–O(5)	1.989(3)
Cu(1)–O(4)	2.324(3)	Cu(2)–N(3)	2.085(4)
		Cu(2)–O(2)	2.367(3)
N(5)–Cu(1)–N(1)	168.62(18)	N(4)–Cu(2)–O(3)	91.91(15)
N(5)–Cu(1)–O(5)	90.65(15)	N(4)–Cu(2)–O(5)	173.64(14)
N(1)–Cu(1)–O(5)	88.16(15)	O(3)–Cu(2)–O(5)	89.25(13)
N(5)–Cu(1)–N(2)	84.68(17)	N(4)–Cu(2)–N(3)	84.14(16)
N(1)–Cu(1)–N(2)	95.82(17)	O(3)–Cu(2)–N(3)	175.86(15)
O(5)–Cu(1)–N(2)	174.42(14)	O(5)–Cu(2)–N(3)	94.81(14)
N(5)–Cu(1)–O(4)	96.94(16)	N(4)–Cu(2)–O(2)	99.15(14)
N(1)–Cu(1)–O(4)	94.31(16)	O(3)–Cu(2)–O(2)	88.31(14)
O(5)–Cu(1)–O(4)	87.25(13)	O(5)–Cu(2)–O(2)	74.63(12)
N(2)–Cu(1)–O(4)	96.33(15)	N(3)–Cu(2)–O(2)	93.52(15)

where we take into account a proportion of a monomeric impurity ρ , for which the susceptibility is assumed to follow the Curie law $\chi = (N\mu_B^2 g^2 / kT)$. The parameters N , μ_B and k in eqn. (1) have their usual meanings, $2J = \text{singlet-triplet splitting}$. Least-square fitting of all experimental data leads to the following parameters: $g = 2.05$, $2J = -109.8 \text{ cm}^{-1}$ and $\rho = 0.019$ for complex **1**, $g = 2.08$, $2J = -103.9 \text{ cm}^{-1}$ and $\rho = 0.015$ for complex **2** and $g = 2.06$, $2J = -95.9 \text{ cm}^{-1}$ and $\rho = 0.022$ for complex **3** with the agreement factor $R = \sum[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calcd}}]^2 / \sum[(\chi_M)_{\text{obs}}^2]$ inferior in all the cases to $R = 1.2 \times 10^{-6}$.

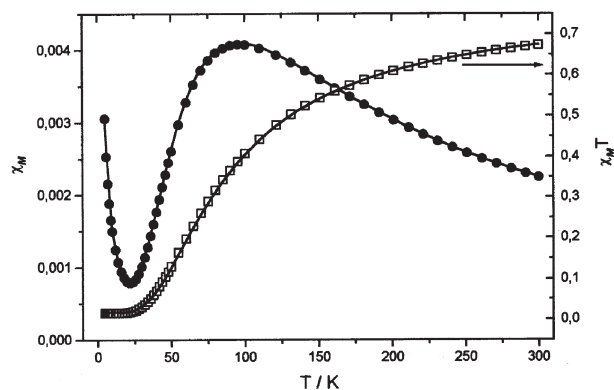
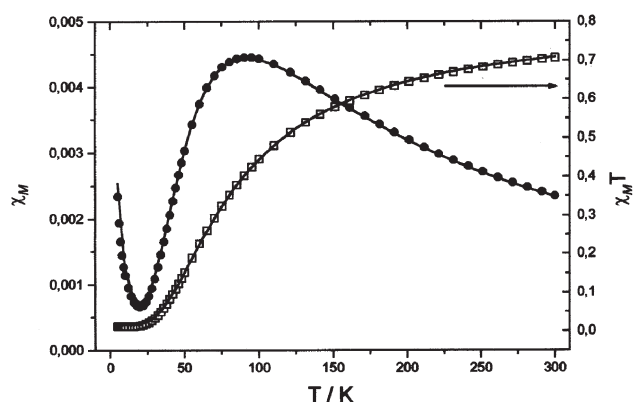
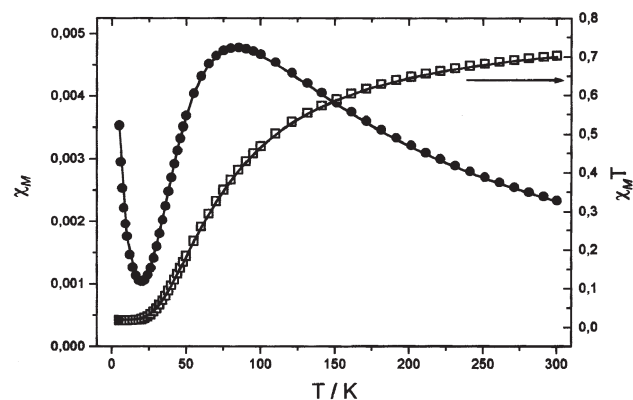
The EPR spectra of the three binuclear Cu(II) complexes registered are exactly the same, because they have almost identical coordination polyhedra. The polycrystalline EPR spectrum at room temperature gives a broad signal for the three complexes with $g = 2.098$ and $\Delta H = 516.67 \text{ G}$ for **1**, $g = 2.1232$ and $\Delta H = 360 \text{ G}$ for **2** and $g = 2.0909$ and $\Delta H = 475 \text{ G}$ for **3** respectively. These values are slightly high compared to those found above.

Magneto-structural correlation

Dinuclear copper(II) complexes in which the metals are bridged by only a *single* hydroxo, alkoxo or phenoxo-oxygen group are relatively rare,^{34,42,45–50} and a none straightforward correlation between structure and magnetism has been developed. However, similar compounds with *double* (OR) groups have been extensively studied. It is well known that the magnetic behavior of divalent copper complexes bridged equatorially by a pair of hydroxide,^{51–54} alkoxide,^{55,56} or phenoxide^{41,43,44,57–64} oxygen atoms is highly dependent on the Cu–O–Cu bridge angle. Also it can be influenced but in smaller measure by the Cu–O(bridge) distance, the Cu...Cu separation, the geometry around the copper(II) center, and the geometry around the bridging oxygen atom. As in all the cases,

Table 5 The comparison of the coordination environments for Cu(1) and Cu(2) in **1**, **2** and **3** respectively

1	2	3			
Cu(1)–N(5)	1.933(9)	Cu(1)–N(5)	1.944(4)	Cu(1)–N(5)	1.936(4)
Cu(1)–N(1)	1.952(10)	Cu(1)–N(1)	1.971(4)	Cu(1)–N(1)	1.959(4)
Cu(1)–O(5)	1.996(6)	Cu(1)–O(5)	1.975(3)	Cu(1)–O(5)	1.982(3)
Cu(1)–N(2)	2.077(8)	Cu(1)–N(2)	2.064(4)	Cu(1)–N(2)	2.082(4)
Cu(1)–O(4)	2.260(6)	Cu(1)–O(4)	2.318(4)	Cu(1)–O(4)	2.324(3)
Cu(1)–Cu(2)	3.290(2)	Cu(1)–Cu(2)	3.244(1)	Cu(1)–Cu(2)	3.244(1)
Cu(2)–O(3)	1.936(6)	Cu(2)–O(3)	1.941(3)	Cu(2)–N(4)	1.934(4)
Cu(2)–N(4)	1.937(9)	Cu(2)–N(4)	1.946(4)	Cu(2)–O(3)	1.944(3)
Cu(2)–O(5)	1.985(6)	Cu(2)–O(5)	2.003(3)	Cu(2)–O(5)	1.989(3)
Cu(2)–N(3)	2.070(8)	Cu(2)–N(3)	2.090(4)	Cu(2)–N(3)	2.085(4)
Cu(2)–O(2)	2.334(7)	Cu(2)–O(2)	2.370(4)	Cu(2)–O(2)	2.367(3)

**Fig. 5** The $\chi_M T$ vs. T and χ_M vs. T plots for complex **1**.**Fig. 6** The $\chi_M T$ vs. T and χ_M vs. T plots for complex **2**.**Fig. 7** The $\chi_M T$ vs. T and χ_M vs. T plots for complex **3**.

the magnetostructural correlations in bis(μ -phenoxide)-bridged macrocyclic dinuclear copper(II) complexes have been studied,⁴⁴ and a linear relationship between the exchange integral ($2J$) and the phenoxide bridging angle (θ) was observed; $2J = -31.95\theta + 2462$. If this relationship holds for complexes **1**, **2** and **3** ($\theta = 111.5(1)$, $109.3(2)$ and $109.6(1)^\circ$, respectively), a $2J$ value of *ca.* -1200 cm^{-1} is anticipated. The relatively weak antiferromagnetic interaction ($2J = -109.8$, -103.9 and -95.9 cm^{-1} for **1**, **2** and **3**, respectively) found experimentally appeared to be less than the prospective one using the previous relationship.

The relatively small magnitudes of the exchange coupling constants found can be understood in terms of the geometrical distortions, which affect the copper coordination spheres, the geometries of the bridges, and the planarity on the bridge core. In **1**, **2** and **3**, the coordination geometry around each

Table 6 Main molecular parameters which affect antiferromagnetic coupling

Compound	$\alpha(\text{Cu}_1\text{--OCu}_2)/^\circ$	$\tau_{\text{Cu}1}/\tau_{\text{Cu}2}/^\circ$	$\delta(^{\circ})^a$	$\lambda(^{\circ})^b$	$2J/\text{cm}^{-1}$	Ref.
$[\text{Cu}_2\text{L}(\text{N}_3)_2.5](\text{ClO}_4)_{0.5}(\text{H}_2\text{O})^c$	134.5(4)	distorted (sp)	—	83.6(4)	−280	6
	132.3(5)	distorted (sp)	—	71.4(4)		
Complex 1	111.5(1)	0.12/0.01	18.2	81.2(3)	−109.8	This work
Complex 2	109.3(2)	0.10/0.05	17.1	81.6(2)	−103.9	This work
Complex 3	109.6(1)	0.10/0.04	16.5	81.8(2)	−95.9	This work

LH = 2,6-bis((N-methylpiperazino)methyl)-4-chlorophenol.^a Out-of-plane shift angle: dihedral angle formed between the (μ -phenoxide) and Cu1–Cu2–O5 planes. ^b Dihedral angle between two adjacent basal planes. ^c This compound contains two different dinuclear molecules in the asymmetric unit.

copper ion is slightly distorted square pyramidal (*cf.* structure description). The $d_{x^2-y^2}$ magnetic orbitals (containing the unpaired electron) point toward the bridging phenoxide oxygen atoms. This situation is favourable to strong antiferromagnetic interactions. On the other hand, it is interesting to note that the dihedral angle (λ) between the adjacent basal planes such as N1–N2–N5–O5 and N3–N4–O3–O5 is large in **1**, **2** and **3**; equal to 81.2(3), 81.6(2) and 81.8(2)°, respectively. This situation without a doubt reduces dramatically the overlap between magnetic orbitals. However there is sufficient overlap of each $\text{Cu}(d_{x^2-y^2})$ orbital with the phenoxide oxygen p orbital to generate negative J values of intermediate magnitude, *i.e.* −109.8, −103.9 and −95.9 cm^{-1} . Undoubtedly, the J value would have been more negative if the basal planes had been coplanar.^{65,66} Another significant feature observed in **1**, **2** and **3**, which can reduce any antiferromagnetic term, is associated with the dihedral angle (δ) between the plane formed by Cu1–Cu2–O5 and the O5–C14–C17–C12 plane, which is 18.2(2), 17.1(3), and 16.5(2)° for **1**, **2** and **3** respectively. Since these values are $>0^\circ$, they must increase the ferromagnetic contribution, which effectively reduces the antiferromagnetic contribution as previously reported.^{67,68} In Table 6, we have gathered some structural parameters of the complexes **1**, **2**, **3** and a similar complex reported in the literature.³⁴ The most important difference is observed in the angle α (Cu1–O–Cu2); this is *ca.* 110° in **1**, **2** and **3**, while in $[\text{Cu}_2\text{L}(\text{N}_3)_2.5](\text{ClO}_4)_{0.5}(\text{H}_2\text{O})$ it is *ca.* 134 and 132°. A smaller value of α would cause a diminution of the antiferromagnetic coupling. The experimental $2J$ values are consistent with this observation. Obviously, more examples are aimed at relating magnetic properties and structural features for this type of bridging.

Conclusion

Here we present the synthesis, electrochemical study, crystal structure and low-temperature magnetic study of three dimeric singly phenoxo-bridged copper(II) complexes. From the foregoing discussion it is found that the phenoxo group of one Schiff base coordinates to two copper(II) centres. All the complexes show moderate antiferromagnetic behaviour at low temperature and magnetic interaction is dependent on the phenoxo bridge between the copper(II) centres. Thiocyanate, azide or cyanate act as terminal ligands.

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