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Synthesis, crystal structures and magnetic properties of two bis(μ-phenoxido)dicopper(II) complexes derived from reduced Schiff base ligands

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ABSTRACT

Two phenoxido bridged dinuclear Cu(II) complexes, $[Cu_2(L^1)_2(NCNCN)_2]$ (**1**) and $[Cu_2(L^2)_2(NCNCN)_2]\cdot 2H_2O$ (**2**) have been synthesized using the tridentate reduced Schiff-base ligands 2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol (HL^1) and 2-[1-(3-methylamino-propylamino)-ethyl]-phenol (HL^2), respectively. The complexes have been characterized by X-ray structural analyses and variable-temperature magnetic susceptibility measurements. Both the complexes present a diphenoxido bridging Cu_2O_2 core. The geometries around metal atoms are intermediate between trigonal bipyramid and square pyramid with the Addison parameters (τ) = 0.57 and 0.49 for **1** and **2,** respectively. Within the core the Cu–O–Cu angles are 99.15° and 103.51° and average Cu–O bond distances are 2.036 and 1.978 Å for compounds **1** and **2,** respectively. These differences have marked effect on the magnetic properties of two compounds. Although both are antiferromagnetically coupled, the coupling constants ($J = -184.3$ and $-478.4\ cm^{-1}$ for **1** and **2,** respectively) differ appreciably.

1. Introduction

Dinuclear copper(II) complexes with endogenous bridging phenoxido ligands are of ongoing interest due to their interesting magnetic properties [1,2]. These Cu(II) complexes also show remarkable non-magnetic properties, making them useful in metal extraction in hydrometallurgy [3], fluorescent sensors [4], heterogeneous catalysis [5], and show catechol oxidase activity [6]. The magnetic properties of bridged dinuclear copper(II) complexes have been extensively studied, most of them having a five-coordinate geometry around each copper ion [2,7]. Five-coordinate Cu(II) complexes are stereochemically flexible and they can be square pyramidal or trigonal bipyramidal, or almost anything in between. A considerable body of experimental evidence has been accumulated to elucidate the magnetostructural relationship. The magnetic properties of phenoxido-bridged complexes containing the Cu_2O_2 core depend on the structural properties of the core. Factors, such as the coordination geometry of the copper ions, the Cu–O–Cu angle, the Cu–O bond distances, the Cu···Cu distances, the out-of-plane shift of the phenyl group, Addison parameter (τ) and torsion angle are the parameters that have also been postulated to influence the J values of the spin coupling [2,7].

In this paper we report the syntheses, crystal structures, and magnetic properties of two phenoxido bridged dinuclear Cu(II) complexes, $[Cu_2(L^1)_2(NCNCN)_2]$ (**1**) and $[Cu_2(L^2)_2(NCNCN)_2]\cdot 2H_2O$ (**2**) obtained from the reduced Schiff base ligands 2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol (HL^1) and 2-[1-(3-methylamino-propylamino)-ethyl]-phenol (HL^2), respectively. The geometry around copper ion is intermediate between square pyramid and trigonal bipyramid for both the complexes. However, they show appreciable differences in bridging Cu–O distances and Cu–O–Cu angles. These differences are well reflected in their magnetic properties.

2. Experimental

The reagents and solvents used were of commercially available reagent quality.

2.1. Synthesis of the reduced Schiff base ligands (HL^1) 2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol and (HL^2) 2-[1-(3-methylamino-propylamino)-ethyl]-phenol

The Schiff base ligand was synthesized by refluxing a solution of 2-hydroxyacetophenone (0.60 mL, 5 mmol) and *N*,*N*-dimethylethylenediamine (0.54 mL, 5 mmol) in methanol (30 mL) for 1 h [8,9]. The solution was cooled to 0 °C and solid sodium borohydride (210 mg, 6 mmol) was added slowly to this methanolic solution with stirring. After completion of the addition, the resulting solution

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was acidified with concentrated HCl (5 mL) and then evaporated to dryness [10,11]. The reduced Schiff base ligand HL^1 was extracted from the solid mass with methanol and this methanol solution (ca. 20 mL) was used for preparation of the complexes. HL^2 was synthesized in the same way as HL^1 using *N*-methyl-1,3-propanediamine (0.52 mL, 5 mmol) instead of *N*,*N*-dimethylethylenediamine [12].

*2.2. Synthesis of the complexes $[Cu_2(L^1)_2(NCNCN)_2]$ (**1**) and $[Cu_2(L^2)_2(NCNCN)_2]\cdot 2H_2O$ (**2**)*

An extracted methanol solution of HL^1 as prepared above was added to a solution of $CuCl_2\cdot 2H_2O$ (0.850 g, 5.00 mmol) in methanol (20 mL) and an aqueous solution (1 mL) of sodium dicyanamide (0.450 g, 5.00 mmol) was added to this mixture with stirring. The mixture was stirred for 1 h and filtered. The filtrate was kept undisturbed at room temperature. Green crystals of **1** suitable for X-ray diffraction were obtained on standing overnight in air. Complex **2** was synthesized as the same way of **1** by using HL^2 instead of HL^1. Green crystals of **2** suitable for X-ray diffraction were obtained after 1 day on slow evaporation of the solvent.

*2.2.1. Complex **1***

(Yield: 1.3140 g, 78%), *Anal.* Calc. for $C_{28}H_{38}Cu_2N_{10}O_2$: C, 49.91; H, 5.68; N, 20.79. Found: C, 49.85; H, 5.75; N, 20.75%. IR (KBr): ν(N–H), 3180 cm^{-1}, ν(C–N), 1594 cm^{-1}; λ_{max} (nm), [ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)] (methanol), 638 (358), 422 (1683).

*2.2.2. Complex **2***

(Yield: 1.330 g, 75%), *Anal.* Calc. for $C_{28}H_{42}Cu_2N_{10}O_4$: C, 47.38; H, 5.96; N, 19.73. Found: C, 47.31; H, 5.99; N, 19.66%. IR (KBr): ν(N–H), 3187 cm^{-1}, ν(C–N), 1592 cm^{-1}; λ_{max} (nm), [ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)] (methanol), 653 (391), 422 (2114).

2.3. Physical measurements

Elemental analyses (C, H and N) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr pellets (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanol (1200–350 nm) were recorded in a Hitachi U-3501 spectrophotometer. The magnetic measurements were carried out in the “Unitat de mesures magnètiques dels SCT (Universitat de Barcelona)” on polycrystalline samples (20 mg) with a Quantum Design SQUID MPMSXL magnetometer in an applied field of 10 000 and 500 G in the temperature ranges of 2–300 and 2–30 K, respectively. The diamagnetic corrections were evaluated from Pascal’s constants.

2.4. Crystal data collection and refinement

Crystal data for the two crystals are given in Table 1. 4309, 4723 data for **1** and **2**, respectively were collected with Mo Kα radiation at 150 K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD. Three hundred and twenty-one frames were measured with a counting time of 10 s. Data analyses were carried out with the CRYSALIS program [13]. The structures were solved using direct methods with the SHELXS-97 program [14]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The hydrogen atoms of the solvent water molecules in **2** were located in a difference Fourier maps and refined with distance constraints. Absorption corrections were carried out using the ABSPACK program [15]. The structures were refined on F^2 with SHELXS-97 [14] to R_1, 0.0386, 0.0549; wR_2, 0.0857, 0.1273, for 3201, 2072 reflections for **1**, **2**, respectively with $I > 2\sigma(1)$.

Table 1
Crystal data and structure refinement of complexes **1** and **2**.

	1	2
Formula	$C_{28}H_{38}Cu_2N_{10}O_2$	$C_{28}H_{42}Cu_2N_{10}O_4$
M	673.76	709.80
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	9.1566(4)	11.1055(10)
b (Å)	9.5443(4)	11.3769(9)
c (Å)	9.8732(4)	13.166(2)
α (°)	104.129(4)	90
β (°)	108.360(4)	102.410(16)
γ (°)	97.700(4)	90
V ($Å^3$)	773.03(6)	1624.6(3)
Z	1	2
D_{calc} ($g\ cm^{-3}$)	1.447	1.451
μ (mm^{-1})	1.419	1.358
F(000)	350	740
R_{int}	0.016	0.080
Total reflections	5465	10641
Unique reflections	4309	4723
$[I > 2\sigma(I)]$	3201	2072
R_1, wR_2	0.0386, 0.0857	0.0549, 0.1273
T (K)	150	150

3. Results and discussion

3.1. Synthesis of the complexes

The condensation of *N*,*N*-dimethylethylenediamine and *N*-methyl-1,3-propanediamine in 1:1 M ratio with 2-hydroxyacetophenone afforded the Schiff bases, 2-[1-(2-dimethylamino-ethylimino)-ethyl]-phenol and 2-[1-(3-methylamino-propylimino)-ethyl]-phenol, respectively which on reduction with sodium borohydride readily produced the reduced Schiff bases, HL^1 and HL^2 (Scheme 1). HL^1 and HL^2 on reaction with copper(II) chloride in presence of sodium dicyanamide in 1:1:1 M ratios yielded compound **1** and **2**, respectively (Scheme 1).

3.2. IR and electronic spectra

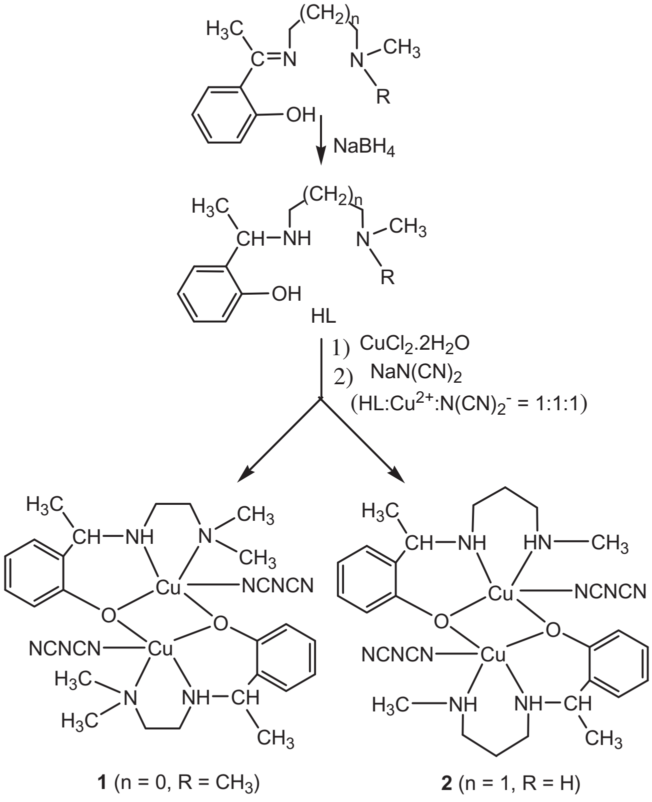
A moderately strong, sharp peak due to N–H stretching vibration at 3180, and 3187 cm^{-1} for complexes **1** and **2**, respectively shows that the imine group of the Schiff base is reduced. Both the complexes exhibit several $\nu_{C\equiv N}$ bands at 2275, 2227, 2163 cm^{-1} for **1** and 2268, 2220, 2153 cm^{-1} for **2** which are attributed to $\nu_{sym} + \nu_{asym}$ (CN), ν_{asym} (CN) and ν_{sym} (CN) modes of the bridging dicyanamide ligand, respectively [16,17].

The electronic spectra of these two compounds were recorded in methanol solution. The electronic spectra show a single absorption band at 638 and 653 nm for compounds **1** and **2**, respectively. At higher energy region, the ligand to metal charge transfer bands were located at 422 nm for the compounds.

*3.3. Description of structures of complexes **1** and **2***

The structure of $[Cu_2(L^1)_2(NCNCN)_2]$ (**1**) is a centrosymmetric dimer as shown in Fig. 1 with each metal atom in a five-coordinate environment. Dimensions in the metal coordination sphere are given in Table 2.

The metal atom is bonded to the tridentate ligand L^1 via O(11) at 2.128(2), N(19) at 1.986(2) and N(22) at 2.072(2) Å, together with a bridging oxygen atom $O(11)^a$, (a = 1 − *x*, 1 − *y*, 1 − *z*) from a second ligand at 1.945(2) Å and a terminal NCNCN ligand via



Scheme 1. Formation of the complexes.

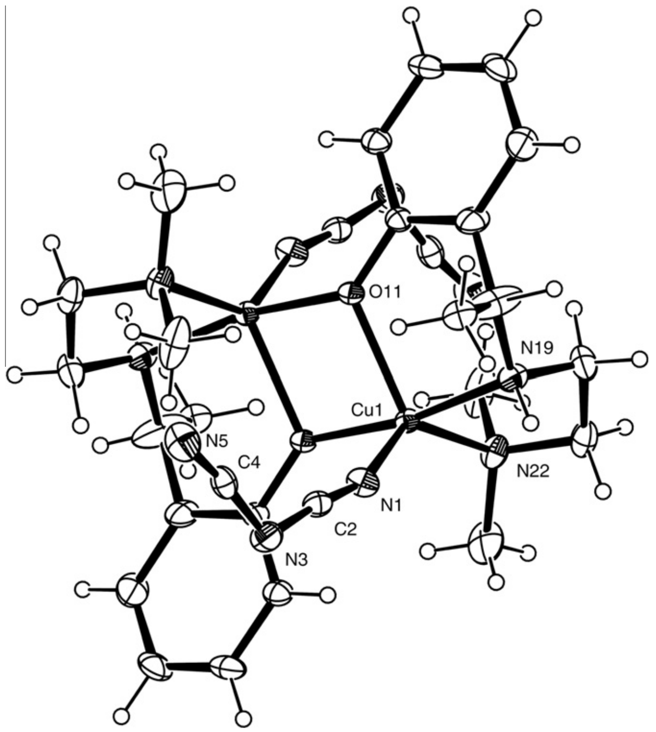


Fig. 1. The structure of **1** with ellipsoids at 30% probability.

Table 2
Bond distances (Å) and angles (°) for complexes **1** and **2**.

	1 (*n* = 2)	**2** (*n* = 3)
Cu(1)–O(11)[a]	1.945(2)	2.005(2)
Cu(1)–N(19)	1.986(2)	2.031(3)
Cu(1)–N(1)	2.048(2)	2.246(4)
Cu(1)–N(2n)	2.072(2)	2.007(3)
Cu(1)–O(11)	2.128(2)	1.952(2)
O(11)[a]–Cu(1)–N(19)	169.48(7)	145.47(12)
O(11)[a]–Cu(1)–N(1)	96.39(7)	100.99(11)
N(19)–Cu(1)–N(1)	91.11(8)	111.01(13)
O(11)[a]–Cu(1)–N(2n)	94.61(7)	99.88(11)
N(19)–Cu(1)–N(2n)	85.14(8)	93.66(13)
N(1)–Cu(1)–N(2n)	135.31(8)	88.65(13)
O(11)[a]–Cu(1)–O(11)	80.85(6)	76.49(10)
N(19)–Cu(1)–O(11)	90.17(7)	91.31(11)
N(1)–Cu(1)–O(11)	104.29(7)	88.57(12)
N(2n)–Cu(1)–O(11)	120.20(7)	174.92(12)

Symmetry operation: a = (1 − *x*, 1 − *y*, 1 − *z*) in **1** and a = (−*x*, 2 − *y*, −*z*) in **2**.

N(1) at 2.048(2) Å. The two Cu atoms are separated by 3.103 Å and the Cu(1)–O(11)–Cu(1)[a] angle is 99.15(6)°. If the geometry around Cu(II) is considered as square pyramidal, the deviations of the coordinating atoms N(1), N(19), N(22), O(11)[a] from the least-square mean plane through them are −0.4504(19), 0.4980(19), −0.4845(19), 0.4369(15) Å, respectively. The deviation of Cu(II) from the same plane is 0.3023(3) Å in the direction of chelating oxygen atom O(11) which may be considered as axially coordinated. However, the geometry around Cu(II) can be described better as trigonal bipyramid with O(11), N(1), and N(22) make up the equatorial plane which together with Cu(II) provide a r.m.s. deviation of 0.0388(3) Å. The Addison parameter (τ) of the penta-coordinated Cu(II) is 0.57 indicating that the geometry is a distorted trigonal bipyramid with N(19) and O(11)[a] occupying axial positions with the trans N(19)–Cu–O(11)[a] angle of 169.48(7)°. The trigonal bipyramidal geometry also explain the apparently anomalous shorter Cu–O(11)[a] bond length in this compound, as for the d^9 system the axial bonds are longer in square pyramidal or octahedral geometry but are shorter in trigonal bipyramidal arrangement. While there is no short contact between N(5) and metal atoms, N(5) does act as acceptor to form an intermolecular hydrogen bond. Thus the proton on N(19) forms a hydrogen bond to N(3)[b] (b = −*x*, 1 − *y*, 1 − *z*) with dimensions (Table 3) N···N 3.086(3) Å, H···N 2.18 Å and N–H···N 171° to result in a zig-zag 1-D supramolecular structure (Fig. 2).

The structure of $[Cu_2(L^2)_2(NCNCN)_2]\cdot 2H_2O$ (**2**) contains a centrosymmetric binuclear dimer with solvent water molecules shown in Fig. 3.

The metal coordination spheres show the same bonding pattern as **1**, but the geometry is very different as indicated by the bond angles compared in Table 2. The metal atom is bonded to the tridentate ligand L^2 which has one extra methylene group compared to L^1, via O(11) at 1.952(2), N(19) at 2.031(3) and N(23) at 2.007(3) Å, together with a bridging oxygen atom O(11)[a] (a = −*x*, 2 − *y*, −*z*) from a second ligand at 2.005(2) Å and a terminal NCNCN ligand via N(1) at 2.246(4) Å. The two Cu atoms are separated by 3.108 Å and the Cu(1)–O(11)–Cu(1)[a] angle is 103.52(11)°. If the geometry around Cu(II) is considered as square pyramidal, the deviations of the coordinating atoms O(11), N(19), N(23), O(11)[a] from the least-square mean plane through them are 0.336(2), −0.276(3), 0.253(3), −0.313(2) Å, respectively. The deviation of Cu(II) from the same plane is 0.2547(5) Å in the direction of N(1) of NCNCN ligand which may be considered as axially coordinated. However, the geometry around Cu(II) can be described better as trigonal bipyramid with N(1), N(19), and O(11)[a] make up the equatorial plane which together with Cu(II) provide a r.m.s. deviation of 0.1305(5) Å. The Addison parameter (τ) of the penta-coordinated Cu(II) is 0.49 indicating that the geometry is a distorted trigonal bipyramid with O(11) and N(23) occupying axial positions. As in **1**, there is no short contact between N(5)

Table 3
Hydrogen bonding distances (Å) and angles (°) for the complexes **1** and **2**.

Complex	D–H···A	D–H (Å)	A···H (Å)	D···A (Å)	∠D–H–A (°)
1	N(19)–H(19)···N(3)[b]	0.91	2.18	3.086(3)	171
2	N(23)–H(23)···N(5)[c]	0.91	2.26	3.159(6)	168
	O(1)–H(1)···N(3)[a]	0.87	2.13	2.992(6)	172
	O(1)–H(2)···N(5)[c]	0.92	1.90	2.757(6)	156
	N(19)–H(19)···O(1)	0.91	2.08	2.938(5)	158

Symmetry operation:

[a] (−*x*, 2 − *y*, −*z*).

[b] (−*x*, 1 − *y*, 1 − *z*).

[c] (*x* − 1/2, 5/2 − *y*, *z* + 1/2).

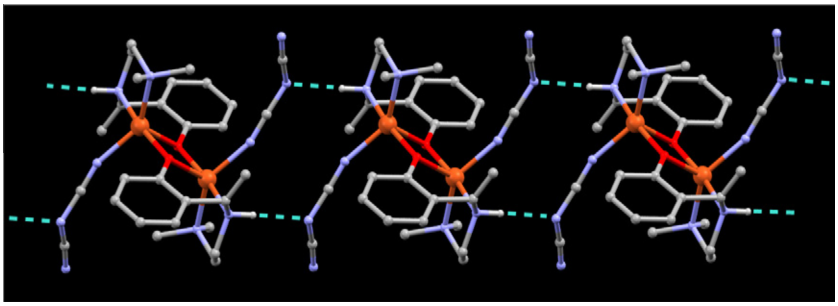


Fig. 2. Hydrogen bonding polymeric structure of compound **1**; hydrogen atoms except H19 have been excluded for clarity.

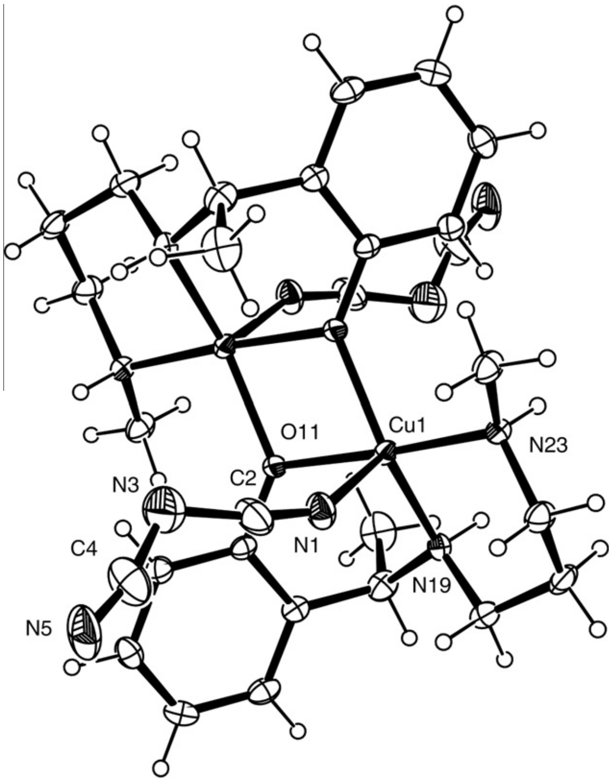


Fig. 3. The structure of **2** with ellipsoids at 30% probability.

and metal atoms, but it acts as acceptor to two intermolecular hydrogen bonds, one involving an amino hydrogen and the second the solvent water molecule O(1). Dimensions for N(23)–H(23)···N(5)^{c} (c = *x* − 1/2, 5/2 − *y*, *z* + 1/2) are 3.159(6) Å, 2.26 Å, 168° and for O(1)–H(2)···N(5)^{c} (c = *x* − 1/2, 5/2 − *y*, *z* + 1/2) are 2.758(6), 1.90 Å, 156°. There are two additional hydrogen bonds, first from N(19)–H(19) to the water molecule O(1) with dimensions 2.938(6), 2.08 Å, 158° and second from O(1)–H(1) to the central nitrogen N(3)^{a} (a = −*x*, 2 − *y*, −*z*) of the NCNCN ligand with dimensions 2.992(6), 2.13 Å, 172°. These hydrogen-bonding interactions lead to the formation of a 2D network (Fig. 4).

3.4. Magnetic properties

Temperature-dependence molar susceptibility measurements of powdered samples **1** and **2** were carried out in an applied field of 10000 and 500 G in the temperature range of 2–300 and 2–30 K, respectively. Plots of complexes **1** and **2** are shown in Figs. 5 and 6, respectively, in both cases $\chi_m T$ being the magnetic susceptibility per Cu_2 unit. At room temperature the $\chi_m T$ values are far from 0.75 cm^3 mol^{-1} K ($g = 2.00$) for a non-interacting Cu_2 unit (0.60 cm^3 mol^{-1} K for **1**, and 0.31 cm^3 mol^{-1} K for **2**). When the samples are cooled, the $\chi_m T$ values decreases to zero at low temperatures. The shape of the curves indicates strong antiferromagnetic coupling in both cases.

Assuming the isotropic Hamiltonian $H = -JS_1S_2$, the experimental data were fitted to the Bleaney–Bowers expression for an isotropically coupled pair of $S = 1/2$ ions (Eq. (1)) [18], where the symbols have their usual meaning.

$$\chi_m = \frac{Ng^2\mu_B^2}{kT}\,\frac{2\exp(J/kT)}{1+3\exp(J/kT)} \qquad (1)$$

The best-fit parameters for reproducing satisfactorily the experimental data, as shown in Figs. 5 and 6, are $J = -184.3$ cm^{-1} and $g = 2.07$ with $R = 5 \times 10^{-5}$ for **1**, $J = -478.4$ cm^{-1} and $g = 2.22$ with $R = 3 \times 10^{-5}$ for **2**, $R = \Sigma_i(\chi T_{icalc} - \chi T_{iexp})^2/\Sigma_i(\chi T_{iexp})^2$.

3.4.1. Magneto-structural correlations

In Table 4 we have indicated the main structural parameters of complexes **1** and **2** that can influence the corresponding *J* values.

According to literature data the exchange coupling in dinuclear complexes with Cu_2O_2 core depends on several factors: the Cu–O(R)–Cu angle, the Cu–O distance and geometrical distortions.

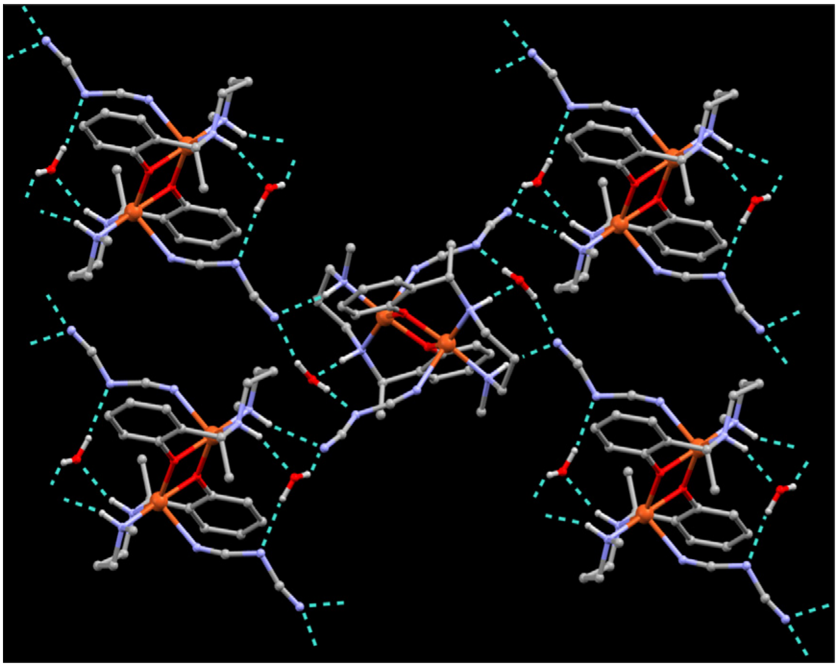


Fig. 4. Hydrogen bonding polymeric structure of compound **2**; hydrogen atoms except H19, H23, and those of water molecules omitted for clarity.

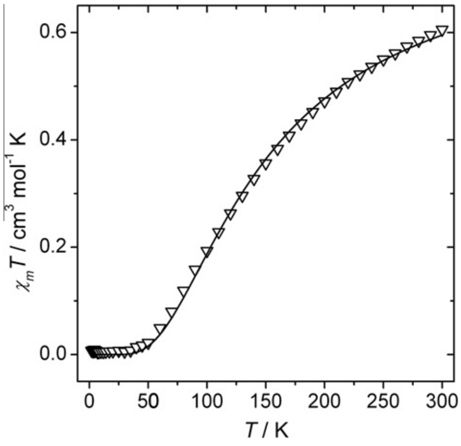


Fig. 5. Plot of the $\chi_m T$ vs. T in the range 2–300 K for **1**.

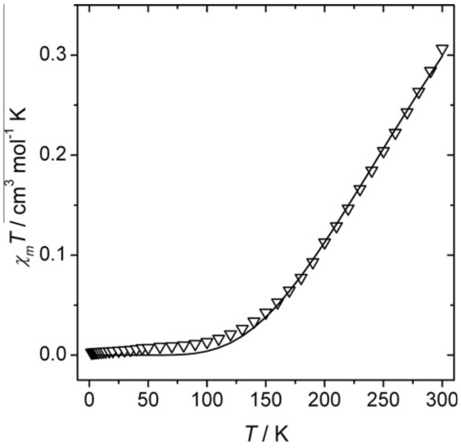


Fig. 6. Plot of the $\chi_m T$ vs. T in the range 2–300 K for **2**.

Table 4
Selected structural parameters for complexes **1** and **2** related to their magnetic data.

	Complex **1**	Complex **2**
J value (cm^{-1})	−184.3	−478.4
τ (Addison parameter)	0.57	0.49
Distances (Cu–O) (Å)	1.945	1.951
	2.128	2.005
Angles (Cu–O–Cu) (°)	99.15	103.51

Indeed, magnetostructural correlations in dinuclear copper(II) complexes bridged equatorially by pairs of hydroxido [19,20], alkoxido [21,22] and phenoxido [23] groups show that the most important factor is the Cu–O(R)–Cu angle, having a quasi-linear correlation between the experimentally exchange coupling constant and the Cu–O(R)–Cu bond angle. In general the larger Cu–O(R)–Cu angle favors large AF J values. There are, on the other hand, strong differences in μ-hydroxido, μ-alkoxido and μ-phenoxido: from theoretical or experimental point of view all the alkoxido and phenoxido-bridged complexes show stronger antiferromagnetic coupling than the hydroxido-bridged ones [23,24]. However, several compounds have been found to deviate from this linear relationship. The reasons that have been given for these deviations are mainly the geometrical distortions [7], such as the variations in Cu–O bond distances and/or the distortion of the square pyramidal geometry towards trigonal bipyramid. A survey of the magnetic and structural properties of the dinuclear phenoxido-bridged Cu(II) complexes reveal that when the Cu–O bond distance is less than 1.98 Å strong antiferromagnetic coupling is observed and the strength of the coupling is linearly dependent on the Cu–O bond lengths.

In our present work, complex **2** shows strong antiferromagnetic coupling with $J = -478.4$ cm^{-1}. Considering both the high Cu–O–Cu angle (103.51°) and the short average Cu–O bond distance (1.978 Å), such strong antiferromagnetic coupling is not surprising. On the contrary, the coupling in **1** is much less ($J = -184.3$ cm^{-1}) and it can be well correlated with its smaller Cu–O–Cu angle (99.15°) and longer average Cu–O distance (2.036 Å). Finally, in penta-coordinated Cu(II) complexes the Addison parameter (τ) is also important in determining the magnitude of coupling [25]: increasing of τ diminishes the antiferromagnetic coupling [26]. The slightly higher τ value (0.57) of **1** compare to **2** (0.49) may also contribute in diminishing the magnitude of coupling.

4. Conclusions

The tridentate reduced Schiff-base ligands 2-[1-(2-dimethylamino-ethylamino)-ethyl]-phenol (HL^1) and 2-[1-(3-methylamino-propylamino)-ethyl]-phenol (HL^2) with Cu(II) and dicyanamide anions have afforded two related phenoxido bridged dinuclear Cu(II) complexes. The relatively high Addison parameter (τ) of both complexes indicates that the environment around the copper ions is an intermediate between the trigonal bipyramid and a square based pyramid. The τ values of majority of the reported literature structures of Cu_2O_2 type complexes show that the copper environment exhibits a square pyramidal geometry with slight distortion towards trigonal bipyramidal geometry. The high τ value is rarer and is adopted from complexes containing bulky and rigid ligands such as diketones, bipyridines or ligands containing imine functional groups. The present study shows that Cu(II) complexes with larger τ can be obtained with the help of more flexible reduced Schiff base ligand as is reflected from our present work. The antiferromagnetic coupling in one of the complexes (**2**) is rather strong in spite of the high τ value. This apparent anomaly can be explained considering the relatively wide bridging Cu–O–Cu angle and short Cu–O bond distances.

Acknowledgments

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Appendix A. Supplementary material

CCDC 798704 and 798705 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.026.

References

[1] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.
[2] D. Venegas-Yazigi, D. Aravena, E. Spodine, E. Ruiz, S. Alvarez, Coord. Chem. Rev. 254 (2010) 2086 (and references therein).
[3] R.J. Gordon, J. Campbell, D.K. Henderson, D.C.R. Henry, R.M. Swart, P.A. Tasker, F.J. White, J.L. Wood, L.J. Yellowlees, Chem. Commun. (2008) 4801.
[4] S. Khatua, S.H. Choi, J. Lee, J.O. Huh, Y. Do, D.G. Churchill, Inorg. Chem. 48 (2009) 1799.
[5] M. Mijanuddin, A.D. Jana, M.G.B. Drew, C.S. Hong, B. Chattopadhyay, M. Mukherjee, M. Nandi, A. Bhaumik, M. Helliwell, G. Mostafa, M. Ali, Polyhedron 28 (2009) 665.
[6] K.S. Banu, T. Chattopadhyay, A. Banerjee, S. Bhattacharya, E. Suresh, M. Nethaji, E. Zangrando, D. Das, Inorg. Chem. 47 (2008) 7083.
[7] M. Stylianou, C. Drouza, Z. Viskadourakis, J. Giapintzakis, A.D. Keramidas, Dalton Trans. (2008) 6188.
[8] S. Naiya, C. Biswas, M.G.B. Drew, C.J. Gómez-García, J.M. Clemente-Juan, A. Ghosh, Inorg. Chem. 49 (2010) 6616.
[9] C. Biswas, M.G.B. Drew, S. Asthana, C. Desplanches, A. Ghosh, J. Mol. Struct. 965 (2010) 39.
[10] A. Biswas, M.G.B. Drew, C.J. Gómez-García, A. Ghosh, Inorg. Chem. 49 (2010) 8155.
[11] A. Biswas, M.G.B. Drew, A. Ghosh, Polyhedron 29 (2010) 1029.
[12] S. Naiya, M.G.B. Drew, C. Estarellas, A. Frontera, A. Ghosh, Inorg. Chim. Acta 363 (2010) 3904.
[13] CRYSALIS, Oxford Diffraction Ltd., Abingdon, UK, 2006.
[14] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.
[15] ABSPACK Program for Absorption Corrections, Oxford Diffraction, Abingdon, UK, 2007.
[16] S. Banerjee, S. Sen, S. Basak, S. Mitra, D.L. Hughes, C. Desplanches, Inorg. Chim. Acta 361 (2008) 2707.
[17] G.A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chem. Commun. 9 (2006) 441.
[18] B. Bleaney, K.D. Bowers, Proc. R. Soc. London, Ser. A 214 (1952) 451.
[19] V.H. Crawford, H.W. Richardson, J.R. Wason, D.J. Hodgson, W.E. Hatfield, Inorg. Chem. 15 (1976) 2107.
[20] D.J. Hodgson, Prog. Inorg. Chem. 19 (1975) 173.
[21] L. Merz, W. Haase, J. Chem. Soc., Dalton Trans. (1980) 875.
[22] M. Handa, N. Koga, S. Kida, Bull. Chem. Soc. Jpn. 61 (1988) 3853.
[23] L.K. Thompson, S.K. Mandal, S.S. Tandon, J.N. Bridson, M.K. Park, Inorg. Chem. 35 (1996) 3117.
[24] H. Astheimer, W. Haase, J. Chem. Phys. 85 (1986) 1427.
[25] A.W. Addison, T.N. Rao, J. Reedjik, J. van Rijn, C.G. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[26] A. Rodríguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, Inorg. Chem. 41 (2002) 3769.