DOI: 10.1002/ejic.201100067

Synthesis, Crystal Structures and Magnetic Properties of a Phenoxo-Bridged Dinuclear Cu^{II} Complex and a Dicyanamide Bridged Novel Molecular Rectangle Based on It

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Keywords: Copper / Schiff bases / Magnetic properties

The phenoxo-bridged dinuclear Cu^{II} complex [$Cu_2L_2(NCNCN)_2$] (**1**) and the dicyanamide-bridged molecular rectangle [$Cu_4L_4\{\mu_{1,5}\text{-}(NCNCN)_2\}$]·$(ClO_4)_2(H_2O)_2$ (**2**) were synthesized using the tridentate reduced Schiff-base ligand HL {2-[(2-dimethylamino-ethylamino)methyl]phenol}. The complexes were characterized by X-ray structural analyses and variable-temperature magnetic susceptibility measurements. Complex **2** was formed through the joining of the phenoxo-bridged dinuclear Cu_2O_2 cores of **1** via the $\mu_{1,5}$-bridging mode of dicyanamide. The structural properties of the Cu_2O_2 cores in two complexes are significantly different. The geometry of the copper ions is distorted trigonal bipyramid in **1** but is nearly square-pyramidal in **2**. These differences have a marked effect on the magnetic properties of two compounds. Although both are antiferromagnetically coupled, the coupling constants (J = –185.2 and –500.9 cm^{-1} for **1** and **2**, respectively) differ considerably.

Introduction

The coordination-driven self-assembly of supramolecular entities of transition metals has received much attention during the past decades due to their potential for porosity and their consequent use in applications in various fields, including host-guest chemistry,[1] gas separation and storage,[2] ion recognition or ion exchange,[3] and optoelectronics or photovoltaics,[4] as well as catalysis.[5] The important aspects of this methodology are the rational design of structures of diverse shapes and sizes as well as functionalization by incorporating suitable functional groups.[6] By employment of a rational transition metal mediated approach, many finite and nanoscopic supramolecules have been prepared.[7]

Of the geometric shapes accessible through the directional bonding approach, tetranuclear squares have been the most broadly reported.[8] Other high-symmetry structures, such as triangles,[9] hexagons,[10] and dodecahedrons,[11] have also been recognized. As lower symmetry hosts can be expected to show enhanced guest selectivity, especially toward planar aromatic guests,[12] rectangles represent a crucial geometrical model in the development of this area. However, molecular rectangles have proven difficult to make because their formation generally requires the self-assembly of a metal precursor with two different types of ligands, which have tended to preferentially form separate discrete complexes.[13] Although, metallomacrocycles offer a half-way house in that they can provide rectangular shapes without the need for the combination of mixed ligands.[14] Most of the reported molecular rectangle-based coordination compounds have been prepared with the Ru, Rd, Ir, Pt and Pd metal ions and nitrogen donor symmetrical polypyridyl ligands have been used widely with these metal ions to prepare several 2D and 3D architectures.[15] However, synthesis of a molecular rectangular based on 1st transition metal ions are very rare.[15a]

The Schiff bases derived from the condensation of diamines and salicylaldehyde derivatives have been employed in the synthesis of many complexes with different transition metals,[16] among which the most frequent ones are the phenoxo-bridged copper(II).[17] In the field of molecular magnetism, phenoxo-bridged complexes are an important family of compounds. The magnetic properties of phenoxo-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 lengths, the Cu···Cu distances, Addison parameter and torsion angle are the parameters that have been postulated to influence the J values of the spin coupling.[17]

The pseudohalide ligand, dicyanamide, has been extensively used recently to generate a wide variety of polynu-

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clear compounds of different topologies and magnetic properties partly due to the discovery of long-range magnetic ordering in the M(dicyanamide)$_2$ compounds.[18] Over the past years or so, several new binding modes have been identified although the terminal and the $\mu_{1,5}$-mode seemingly appear on a more regular basis in the transition metal complexes. As in the $\mu_{1,5}$-bridging mode, the dicyanamide should act as a linear linker between two metal ions, it is of our interest to utilize it in the formation of molecular rectangle by joining phenoxo-bridged di-copper units and study in the changes of the magnetic coupling.

In this paper we report the syntheses, crystal structures, and magnetic properties of a phenoxo-bridged dinuclear Cu^{II} complex, $[Cu_2L_2(NCNCN)_2]$ (**1**) where HL is a reduced Schiff-base ligand, 2-[(2-dimethylamino-ethylamino)-methyl]phenol and a molecular rectangle, $[Cu_4L_4\{\mu_{1,5}\text{-}(NCNCN)_2\}]\cdot(ClO_4)_2(H_2O)_2$ (**2**) in which the dinuclear Cu_2O_2 cores of **1** are joined via the $\mu_{1,5}$-bridging mode of dicyanamide.

Results and Discussion

Synthesis of the Complexes

The condensation of *N*,*N*-dimethylethylenediamine in 1:1 molar ratio with salicylaldehyde afforded the Schiff base, 2-[(2-dimethylamino-ethylimino)methyl]phenol which on reduction with sodium borohydride readily produced the reduced Schiff base, HL (Scheme 1). HL on reaction with copper(II) perchlorate in presence of sodium dicyanamide in 1:1:1 and 2:2:1 molar ratios yielded compound **1** and **2**, respectively. Compound **2** was converted into **1** when a methanol solution of **2** was treated with an aqueous solution of sodium dicyanamide (1:2 molar ratio) and the resulting solution was evaporated slowly at room temperature.

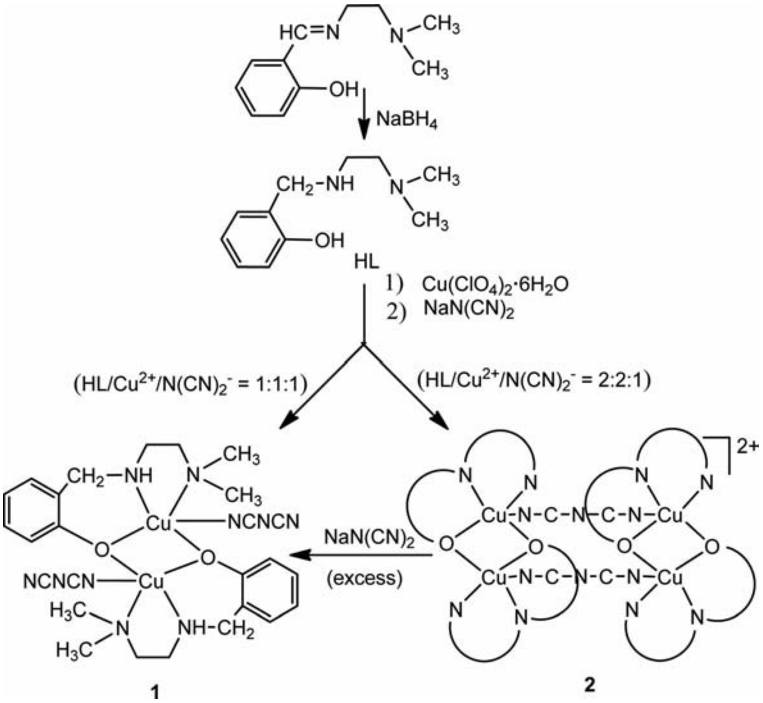
IR and Electronic Spectra

A moderately strong, sharp peak due to N–H stretching vibration at 3184, and 3238 cm^{-1} for complexes **1** and **2**, respectively, shows that the imine group of the Schiff base is reduced. The reduction of the imine group is also very clearly indicated by the absence of the strong band due to imine vibration which appears in the region 1620–1650 cm^{-1} for the complexes of the corresponding unreduced Schiff bases.[19] Both the complexes exhibit several ν_{C-N} bands[20] at 2286, 2223, 2167 cm^{-1} for **1** and 2293, 2221, 2161 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. The strong and single band at 1090 cm^{-1} for complex **2** indicates the presence of anionic perchlorate group.

The electronic spectra of these two compounds were recorded in acetonitrile solution. The electronic spectra show a single absorption band at 645 and 640 nm for compounds **1** and **2**, respectively. At higher energy region, the ligand to metal charge-transfer bands were located at 420 and 455 nm for compounds **1** and **2**, respectively.

Crystal Structures of the Complexes

Structure of $[Cu_2L_2(NCNCN)_2]$ (1). The structure of $[Cu_2L_2(NCNCN)_2]$ (**1**) is a centrosymmetric dimer, as



Scheme 1. Formation of the complexes.

shown in Figure 1 with each metal atom in a five-coordinate environment. Dimensions in the metal coordination sphere are given in Table 1.

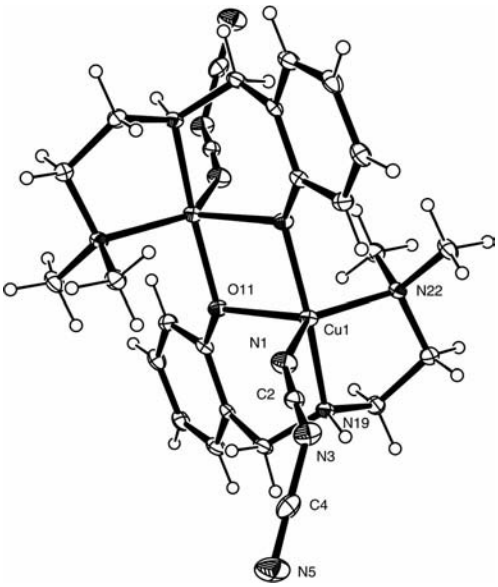


Figure 1. The crystal structure of **1** (ellipsoids at 30% probability).

Table 1. Bond lengths [Å] and angles [°] for complex **1**.

Cu(1)–O(11)^a	1.938(3)
Cu(1)–N(19)	1.971(3)
Cu(1)–N(1)	2.032(4)
Cu(1)–N(22)	2.082(3)
Cu(1)–O(11)	2.131(2)
O(11)^a –Cu(1)–N(19)	168.68(11)
O(11)^a–Cu(1)–N(1)	98.61(13)
N(19)–Cu(1)–N(1)	90.29(14)
O(11)^a–Cu(1)–N(22)	93.50(11)
N(19)–Cu(1)–N(22)	84.91(12)
N(1)–Cu(1)–N(22)	135.47(14)
O(11)^a–Cu(1)–O(11)	79.57(10)
N(19)–Cu(1)–O(11)	90.94(11)
N(1)–Cu(1)–O(11)	109.15(13)
N(22)–Cu(1)–O(11)	115.16(11)

Symmetry operation: a: 1 – x, 1 – y, 2 – z

The metal atom is bonded to the mononegative tridentate ligand, L via O(11) at 2.131(2), N(19) at 1.971(3) and N(22) at 2.082(3) Å, together with a bridging oxygen atom O(11)^a (a: 1 – x, 1 – y, 2 – z) from a second ligand at 1.938(3) Å and a terminal NCNCN ligand via N(1) at 2.032(4) Å. The two Cu atoms are separated by 3.129 Å and the Cu(1)–O(11)–Cu(1)^a angle is 100.43°. 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 –0.445(4), 0.501(3), –0.483(3), 0.428(2) Å, respectively. The deviation of Cu^{II} from the same plane is 0.2974(5) 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 an r.m.s. deviation of 0.0413(5) Å. The Addison parameter (τ) of the pentacoordinate Cu^{II} is 0.55 indicating also that the geometry is basically a distorted trigonal bipyramid with N(19) and O(11)^a occupying axial positions. 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(5)^c (c: 1 – x, 2 – y, 1 – z) with dimensions (Table 2) N···N 2.893(5) Å, H···N 2.07 Å and N–H···N 150° to result in a 1D supramolecular structure (Figure 2).

Table 2. Hydrogen bonding distances [Å] and angles [°] for the complexes **1** and **2**.

	D–H···A	D–H [Å]	A···H [Å]	D···A [Å]	∠ D–H–A [°]
1	N(19)–H(19)···N(5)^c	0.91	2.07	2.893(5)	150
2	N(19)–H(19)···N(5)^d	0.91	2.68	3.477(4)	147
	O(1)–H(1)···O(74)^e	0.87(4)	2.10(4)	2.932(5)	160(5)
	O(1)–H(2)···O(73)^f	0.84(4)	2.23(5)	2.972(5)	147(4)
	N(39)–H(39)···O(72)	0.91	2.14	3.005(3)	159

Symmetry operations: c: 1 – x, 2 – y, 1 – z; d: x, y – 1, z; e: 1 – x, 1 – y, 1 – z; f: x, y, 1 + z

Structure of [Cu$_4$L$_4${μ$_{1,5}$-(NCNCN)$_2$}]·(ClO$_4$)$_2$(H$_2$O)$_2$ (2): The structure of **2**, contains discrete tetranuclear cations, perchlorate anions and solvent water molecules. The cation is a centrosymmetric tetramer containing two independent copper atoms, both with square pyramidal geometries as shown in Figure 3. Dimensions in the metal coordination sphere are given in Table 3.

For both copper atoms, the equatorial plane consists of the three donor atoms of the ligand together with one bridging oxygen atom of a second ligand. The axial site is occupied by nitrogen of a bridging NCNCN ligand. Bond lengths in the metal coordination sphere are Cu(1)–O(11)

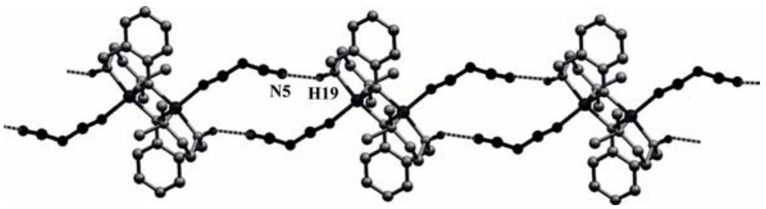


Figure 2. Hydrogen bonding polymeric structure of compound **1**; hydrogen atoms except H19 have been excluded for clarity.

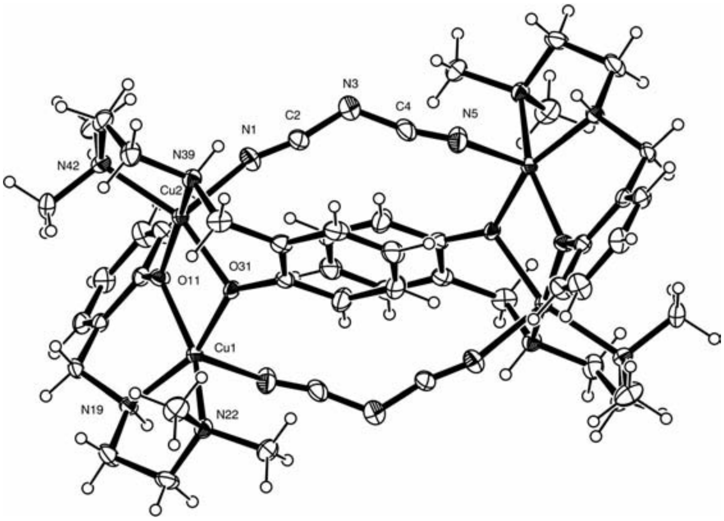


Figure 3. The crystal structure of **2** with ellipsoids at 30% probability.

Table 3. Bond lengths [Å] and angles [°] for complex **2**.

Cu(1)–N(5)^b	2.236(3)
Cu(1)–N(19)	2.014(2)
Cu(1)–N(22)	2.047(2)
Cu(1)–O(11)	1.966(2)
Cu(1)–O(31)	1.970(2)
Cu(2)–N(1)	2.165(2)
Cu(2)–N(39)	2.000(2)
Cu(2)–N(42)	2.055(2)
Cu(2)–O(11)	1.944(2)
Cu(2)–O(31)	1.986(2)
O(11)–Cu(1)–O(31)	76.77(8)
O(11)–Cu(1)–N(19)	91.01(8)
O(31)–Cu(1)–N(19)	158.89(9)
O(11)–Cu(1)–N(22)	157.19(9)
O(31)–Cu(1)–N(22)	98.18(9)
N(19)–Cu(1)–N(22)	86.40(9)
O(11)–Cu(1)–N(5)^b	102.39(10)
O(31)–Cu(1)–N(5)^b	107.05(9)
N(19)–Cu(1)–N(5)^b	92.25(11)
N(22)–Cu(1)–N(5)^b	100.35(10)
O(11)–Cu(2)–O(31)	76.89(8)
O(11)–Cu(2)–N(39)	159.89(9)
O(31)–Cu(2)–N(39)	91.18(9)
O(11)–Cu(2)–N(42)	98.27(9)
O(31)–Cu(2)–N(42)	156.22(9)
N(39)–Cu(2)–N(42)	86.09(9)
O(11)–Cu(2)–N(1)	103.27(9)
O(31)–Cu(2)–N(1)	100.28(10)
N(39)–Cu(2)–N(1)	94.69(9)
N(42)–Cu(2)–N(1)	103.48(11)

Symmetry operation: b: $-x, -y, 1 - z$

1.966(2), Cu(1)–N(19) 2.014(2) and Cu(1)–N(22) 2.047(2) Å to the tridentate ligand L with Cu(1)–O(31) 1.970(2) and Cu(1)–N(5)^b 2.236(3) Å to the bridging NCNCN ligand and Cu(2)–O(31) 1.986(2), Cu(2)–N(39) 2.000(2) and Cu(2)–N(42) 2.055(2) Å to the tridentate ligand L with Cu(2)–O(11) 1.944(2) and Cu(2)–N(1) 2.165(2) Å to the bridging NCNCN ligand. The four donor atoms in the equatorial plane show r.m.s. deviations of 0.031, 0.051 Å, respectively, with the copper atoms 0.365(1), 0.365(1) Å from the plane in the direction of the axial ligand. The overall geometry around copper(II) is nearly square pyramidal with Addison parameter τ = 0.03 and 0.06 for Cu(1) and Cu(2), respectively. In the compound the shortest Cu···Cu distances are 3.051 and 8.054 Å corresponding to the diphenoxo and dicyanamide bridges, respectively. The bridging Cu(1)–O(11)–Cu(2) and Cu(1)–O(31)–Cu(2) angles are 102.56 and 100.93°, respectively.

Thus by contrast with **1** in **2** the NCNCN ligand bridges two copper atoms. The perchlorates and water molecules are involved in intermolecular hydrogen bonding together with the two amine hydrogen atoms. N(19)–H(19) forms a weak hydrogen bond to N(5)^d (d: x, $y - 1$, z) with dimensions (Table 2) 3.477(4), 2.68 Å, 147° while N(39)–H(39)···O(72) is significantly stronger with dimensions, 3.005(3), 2.14 Å, 159°. In addition the water molecule forms hydrogen bonds to two oxygen atoms of the perchlorate, viz. O(1)–H(1)···O(74)^e (e: $1 - x$, $1 - y$, $1 - z$) and O(1)–H(2)···O(73)^f (f: x, y, $1 + z$) with dimensions 2.932(5), 2.10(4) Å, 160(5)° and 2.972(5), 2.23(5) Å, 147(4)°, respectively (Figure 4).

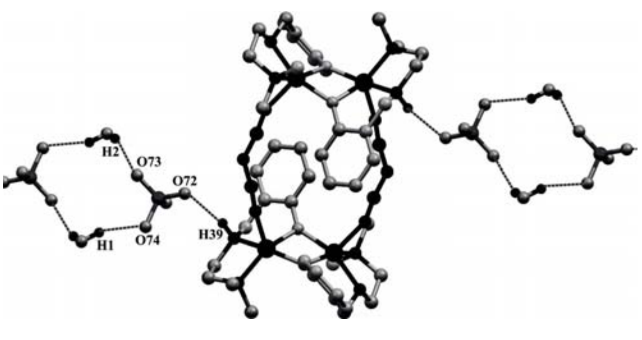


Figure 4. Hydrogen bonding polymeric structure of compound **2** (hydrogen atoms except H39 and those of water molecules omitted for clarity).

In both the structures the geometry of the NCNCN ligand is similar in spite of its different binding mode. Thus the Cu–N–C angles are 155.5(3)° in **1**, and 151.9(3), 138.0(3)° in **2** while the central C–N–C angles are 121.6(4)° in **1**, and 125.6(4)° in **2**.

It is to be noted that in the dinuclear structure of **1** the two NCNCN groups are in opposite directions (*trans*) whereas in **2**, they orient themselves in the same direction (*cis*) to form the molecular rectangle.

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 K and 2–30 K, respectively. Plots of complexes **1** and **2** are shown in Figures 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 (0.66 $cm^3 mol^{-1} K$ for **1**, and 0.22 $cm^3 mol^{-1} K$ for **2**). When the samples are cooled, the $\chi_m T$ values decreased to zero at low temperatures. The shape of the curves indicates strong antiferromagnetic coupling in both cases.

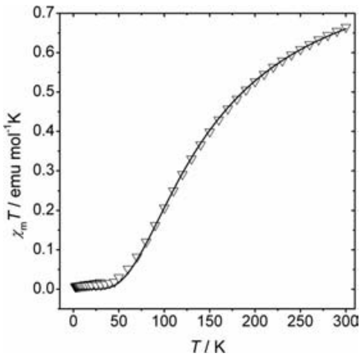


Figure 5. Plot of the $\chi_m T$ vs, T in the range 2–300 K for **1**.

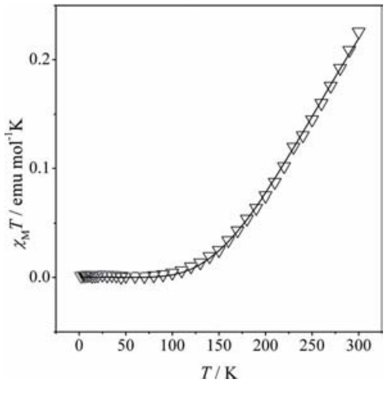


Figure 6. Plot of the $\chi_m T$ vs, T in the range 2–300 K for **2**.

Assuming the isotropic Hamiltonian $\boldsymbol{H} = -JS_1S_2$, the experimental data were fitted to the Bleaney–Bowers expression for an isotropically coupled pair of S = 1/2 ions, where the symbols have their usual meaning;[21] see Equation (1).

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

The best-fit parameters for reproducing satisfactorily the experimental data, as shown in Figures 5 and 6, are J = –185.2 cm^{-1} and g = 2.18 with $R = 7\times10^{-5}$ for **1**, J = –500.9 cm^{-1} and g = 2.10 with $R = 2\times10^{-5}$ for **2** [$R = \Sigma_i(\chi T_{icalc} - \chi T_{iexp})^2/\Sigma_i(\chi T_{iexp})^2$].

However, the structure of complex **2** comprises two dinuclear copper systems, in each of which the copper ions are bridged by a double μ-phenoxo and additional *double* μ-dicyanamide ligand bridge these dinuclear units giving the tetranuclear compound (see description of crystal structure). The dimer model reproduces very satisfactorily the magnetic behavior in the whole temperature range. This result is logical taking into account that the coupling though the dicyanamide-bridge is negligible compare to the high expected magnetic exchange through the double phenoxo-bridged, according to the structural parameters.

Magnetostructural Correlations

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

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

	1	2
J value [cm^{-1}]	–185.2	–500.9
τ (Addison parameter)	0.55	0.03 (Cu1)
		0.06 (Cu2)
Distances (Cu–O) [Å]	1.937	1.966
	2.131	1.944
		1.986
		1.970
Angles (Cu–O–Cu) [°]	100.43	102.56
		100.93
Torsion angle (Cu–O–Cu–O) [°]	0.0	12.94
		12.83

According to literature data the exchange coupling in dinuclear complexes with Cu_2O_2 core depends on several factors. Magnetostructural correlations in dinuclear copper(II) complexes bridged equatorially by pairs of hydroxide[22] or alkoxide[23,24] groups show that the major factor controlling spin coupling between the S = 1/2 metal centers is the Cu–O(R)–Cu angle. Hatfield and Hodgson found a linear correlation between the experimentally exchange coupling constant and the Cu–O–Cu bond angle.[22] In general the larger Cu–O–Cu angle, favors large AF J values. Thompson et al. found strong differences in μ-hydroxo, μ-alkoxo and μ-phenoxo.[25] It is apparent that the slopes (of J vs. Cu–O–Cu angle) of the hydroxide and alkoxide cases are comparable, but absolute values of $-J$ are larger for the alkoxide. In general, all the alkoxo and phenoxo-bridged complexes show stronger antiferromagnetic coupling than the hydroxo-bridged ones (from a theoretical or experimental point of view).[26] The slope for the phenoxide system is smaller and absolute values of $-J$ are inherently larger.[25]

The main conclusion for phenoxo systems is that strong antiferromagnetic exchange will dominate in these complexes.[25] However, recently three ferromagnetic bis-phenoxo-bridged copper(II) complexes have been reported and theoretically studied.[17b,27]

Another important structural factor in pentacoordinate Cu^{II} complexes is the Addison parameter (τ).[28] The increasing of τ diminishes the antiferromagnetic coupling.[29] Finally, the torsion of the Cu_2O_2 dihedral angle is important: when this torsion angle is not zero the ferromagnetic term increases.[30]

Complexes **1** and **2**, have different structural parameters (see Table 4). This feature explains their different J values (–185.2 and –500.9 $cm^3 mol^{-1}$ for **1** and **2**, respectively). The parameter τ for **2** is very low, 0.03 (average), whereas is intermediate, 0.55, for **1**, indicating that for **2** the magnetic orbital is almost exclusively $d_{x^2-y^2}$, perfectly directed to the Cu–O–Cu bonds, whereas for complex **1** the magnetic orbital is a mixture (almost 50%) of $d_{x^2-y^2}$ and d_{z^2}, being this mixture not so well directed to the Cu–O–Cu bonds. The AF character is, thus, enhanced for **2**. Furthermore, the high value of the Cu–O–Cu angle of 101.74° (average) for **2** and 100.43° for **1** also favours the more AF character of **2** (see above). The torsion angle, which is equal to 0° for complex **1** and 12.88° (average) for complex **2**, does not change this tendency.

Conclusions

The tridentate reduced Schiff-base ligand HL {2-[(2-dimethylamino-ethylamino)methyl]phenol} with Cu^{II} and dicyanamide anions afforded a phenoxo-bridged dinuclear Cu^{II} complex and a novel molecular rectangle which is formed through the joining of the phenoxo-bridged dinuclear Cu_2O_2 cores of **1** via the $\mu_{1,5}$-bridging mode of dicyanamide. The formation of this dicyanamide-bridged molecular rectangle is unprecedented. Although a $\mu_{1,5}$-dicyanamide-bridged tetranuclear Cu^{II} complex is reported[31] but in that compound the axial-equatorially bridged dicyanamide is severely bent and the tetranuclear structure is far from a rectangular shape. In compound **2** the dicyanamide acts as a linear linker through coordination to the axial positions of Cu^{II} and to facilitate such coordination the geometry around Cu^{II} in the Cu_2O_2 core changes significantly from distorted trigonal bipyramid in **1** to nearly square pyramid in **2**. The structural changes of the Cu_2O_2 core have pronounced effect on the magnetic coupling that can be explained by the well-established magneto-structural correlations of such compounds considering the bridging angles, Cu–O distances and Addison parameters. Thus we have shown here that dicyanamide can acts as a linear linker to produce molecular rectangle having Cu_2O_2 core and structures of the two compounds show that although the tridentate ligand is identical in both, the geometry around Cu^{II} is adjusted as per requirement of the molecular structure.

Experimental Section

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

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 acetonitrile (1200–350 nm) were recorded with 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 10000 and 500 G in the temperature ranges of 2–300 and 2–30 K, respectively. The diamagnetic corrections were evaluated from Pascal's constants.

Synthesis of the Reduced Schiff-Base Ligand (HL) 2-[(2-Dimethylamino-ethylamino)methyl]phenol: The Schiff-base ligand was synthesized by refluxing a solution of salicylaldehyde (0.52 mL, 5 mmol) and *N,N*-dimethylethylenediamine (0.54 mL, 5 mmol) in methanol (30 mL) for one hour.[32] 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 was acidified with concentrated aqueous HCl (5 mL) and then evaporated to dryness.[32,33] The reduced Schiff-base ligand HL was extracted from the solid mass with methanol and this methanol solution (ca. 20 mL) was used for preparation of complexes.

$[Cu_2L_2(NCNCN)_2]$ (1): An extracted methanol solution of HL as prepared above was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1.850 g, 5 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 after 2 d on slow evaporation of the solvent.

Complex 1: Yield 1.275 g (79%). $C_{26}H_{34}Cu_2N_{10}O_2$ (645.71): calcd. C 48.36, H 5.31, N 21.69; found C 48.31, H 5.37, N 21.62. IR (KBr): $\tilde{\nu}$ = 3184 (N–H), 1594 cm^{-1} [ν(C–N)]. UV (acetonitrile): λ_{max} (ε_{max}) = 645 (300), 420 nm (1970).

$[Cu_4L_4\{\mu_{1,5}\text{-}(NCNCN)_2\}]\cdot(ClO_4)_2(H_2O)_2$ (2): Another extracted methanol solution of HL (20 mL) prepared using the same quantity of reactants as stated above, was added to a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1.850 g, 5 mmol) in methanol (20 mL) and an aqueous solution (0.5 mL) of sodium dicyanamide (0.225 g, 2.5 mmol) was added to this mixture with stirring. The mixture was stirred for 2 h and filtered. The filtrate was kept undisturbed at room temperature. Brown crystals of **2** suitable for X-ray diffraction were obtained after 3 d on slow evaporation of the solvent.

Complex 2: Yield 1.290 g (74%). $C_{48}H_{72}Cl_2Cu_4N_{14}O_{14}$ (1394.27): calcd. C 41.35, H 5.21, N 14.06; found C 41.28, H 5.28, N 14.01. IR (KBr): $\tilde{\nu}$ = 3238 (N–H), [ν(C–N)], 1597 cm^{-1}. UV (acetonitrile): λ_{max} (ε_{max}) = 640 (823), 455 nm (3858).

Crystal Data Collection and Refinement: Crystal data for the two crystals are given in Table 5. 3971, 8382 data for **1**, and **2**, respectively were collected with Mo-K_α radiation at 150 K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned in a distance of 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analyses were carried out with the CrysAlis[34] program. The structures were solved by direct methods with the Shelxs97[35] program. 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.[36] The structures were refined on F^2 with Shelxl97[35] to R_1 = 0.0565, 0.0462, wR_2 = 0.1217, 0.1058 for 2242, 4759 reflections for **1**, **2**, respectively, with $I > 2\sigma(I)$.

Table 5. Crystal data and structure refinement of complexes **1** and **2**.

	1	**2**
Formula	$C_{26}H_{34}Cu_2N_{10}O_2$	$C_{48}H_{72}Cl_2Cu_4N_{14}O_{14}$
M	645.72	1394.26
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	8.1856(11)	10.8446(5)
b [Å]	8.8309(10)	10.9487(5)
c [Å]	10.3860(14)	12.6664(6)
α [°]	79.795(10)	92.702(4)
β [°]	73.285(12)	92.016(4)
γ [°]	84.600(10)	90.656(4)
V [Å^3]	706.93(16)	1501.08(12)
Z	1	1
D_c [g cm^{-3}]	1.517	1.542
μ [mm^{-1}]	1.548	1.559
$F(000)$	334	720
R(int)	0.048	0.031
Total reflections	5048	10622
Unique reflections	3971	8382
$I > 2\sigma(I)$	2242	4759
R_1, wR_2	0.0565, 0.1217	0.0462, 0.1048
Temperature [K]	150	150

CCDC-801230 (for **1**), -801231 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Government of India, Council of Scientific and Industrial Research (CSIR) for a Senior Research Fellowship to A. B., Sanction No. 09/028 (0717)/2008-EMR-I. We also thank the British Engineering and Physical Sciences Research Council (EPSRC) and the University of Reading for funds for the X-Calibur system and the Spanish Government (grant CTQ2009-07264) for financial support.

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Received: January 20, 2011