

Crystal Structure and Magnetic Exchange Interaction in a Binuclear Copper(II) Schiff Base Complex with a Bridging *m*-Phenylenediamine Ligand

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Condensation of 2-hydroxy-3-methoxybenzaldehyde with *m*-phenylenediamine (1,3-diaminobenzene) (*m*-pda) gives the ligand [*N,N'*-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminobenzene] which reacts with cupric acetate to give the complex $[\text{Cu}_2(\text{L-}m\text{-pda})_2] \cdot 2\text{H}_2\text{O}$, [*L* = 2-hydroxy-3-methoxybenzaldehyde]. The molecular structure of the complex $[\text{Cu}_2(\text{L-}m\text{-pda})_2] \cdot 2\text{H}_2\text{O}$ has been determined by single-crystal X-ray analysis. $(\text{C}_{44}\text{H}_{40}\text{Cu}_2\text{N}_4\text{O}_8) \cdot 2\text{H}_2\text{O}$, triclinic, space group *P* $\bar{1}$. Two $[\text{Cu}(\text{L-}m\text{-pda})]$ fragments, related by an inversion center, are connected by *m*-phenylene groups to form a binuclear unit. The coordination geometry around each copper(II) can be described as a distorted tetrahedron formed by the N_2O_2 donor set of the Schiff base ligands. The intramolecular Cu...Cu separation is 7.401(6) Å. The magnetic susceptibility of the complex in the 5–301 K temperature range can be rationalized by the parameters $J = -0.4 \text{ cm}^{-1}$ and $g = 2.17$. This indicates a weak intramolecular antiferromagnetic interaction. Extended Hückel molecular orbital (EHMO) calculations have been performed in order to gain insight into the molecular orbitals that participate in the super-exchange pathway.

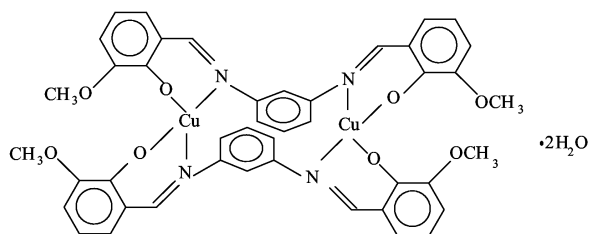
Key words: Dinuclear Copper(II) Complex, Antiferromagnetic Interactions, Super-Exchange Interactions, Schiff Base, Molecular Orbital Calculation

Introduction

Series of binuclear transition-metal complexes which display different physical properties have been investigated extensively in recent years. This is partly because of the use of such complexes to mimic aspects of bimetallic bio-sites in various proteins and enzymes [1, 2], and partly because of attempts to understand the structural and electronic factors that govern magnetic exchange phenomena [3–6]. The previous papers in this series have sought to establish various criteria for judging the viability of a particular single-atom or polyatomic bridging unit to support magnetic exchange interactions between two paramagnetic metal ions [7–9]. Many of the papers have been concerned with exchange interactions in binuclear copper(II) complexes and the results have indicated that the strength of the exchange interaction depends primarily upon the symmetry and energy of the copper(II)

ion ground state relative to the highest occupied molecular orbitals of the bridging moiety. The complexes exhibit ferromagnetic or antiferromagnetic character depending on their geometry.

Recently, we have studied the crystal structure and magnetic properties of μ -acetato-*N,N'*-bridged dicopper(II) complexes of 1,3-bis((5-bromo-2-hydroxybenzylidene)amino)-propan-2-ol, 1,3-bis((2-hydroxy-1-naphthylidene)amino)-propan-2-ol [7, 9] and μ -pyrazol-*N,N'*-bridged dicopper(II) complexes of 1,3-bis((3,5-dichlorosalicylidene)amino)-propan-2-ol, 1,3-bis((3,5-dibromosalicylidene)amino)-propan-2-ol [10] and 1,3-bis(2-hydroxy-3-methoxybenzylidene)propan-2-ol [11]. In this study, we present the synthesis, crystal structure and magnetic properties of a binuclear copper(II) complex, $[\text{Cu}_2(\text{L-}m\text{-pda})_2] \cdot 2\text{H}_2\text{O}$, [*L* = 2-hydroxy-3-methoxybenzaldehyde] of a Schiff base derived from *m*-phenylenediamine. We have measured the magnetic susceptibilities in the temperature



Scheme 1.

range 5–301 K to investigate the relationship between the magnetic properties and the molecular structure. We also performed EHMO calculations to determine the nature of the frontier orbitals and to clarify the influence of the bridging ligand *m*-phenylenediamine on the super-exchange interaction in the investigated complex.

Experimental Section

Synthesis

2-Hydroxy-3-methoxy-benzaldehyde and 1,3-diaminobenzene were purchased from Aldrich. The yellow Schiff base ligand *N,N'*-bis(2-hydroxy-3-methoxy-benzylidene)-1,3-diaminobenzene was synthesized by reaction of these compounds in a 1:2 molar ratio at room temperature and obtained from the solution on cooling. For the preparation of the Cu(II) complex, the Schiff base ligand (1 mmol, 0.35 g) was dissolved in hot acetonitrile (50 ml) and a solution of Cu(CH₃COO)₂·H₂O (1 mmol, 0.20 g) in hot methanol (40 ml) was added. The resulting mixture was set aside for 3 d and the prismatic dark blue crystals which formed were filtered off and washed with cold ethanol (Scheme 1). C₄₄H₄₄N₄O₁₀Cu₂: calcd. C 55.75, H 4.68, N 5.91; found C 55.97, H 4.87, N 6.11.

X-ray structure determination

A crystal of dimensions 0.30 × 0.20 × 0.05 mm³ was mounted on an Enraf-Nonius CAD-4 diffractometer [12] (graphite monochromatized Mo-K_α radiation, λ = 0.71073 Å). Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections (2.32° ≤ θ ≤ 29.20°) carefully centred on the diffractometer. The standard reflections (103, 103̄, 222̄) were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. A total of 6257 reflections were recorded, with Miller indices *h*_{min} = −11, *h*_{max} = 4, *k*_{min} = −13, *k*_{max} = 13, *l*_{min} = −13, *l*_{max} = 13. The structure was solved by SHELXS-97 [13] and refined with SHELXL-97 [14]. The positions of the H atoms bonded to C atoms were calculated (C–H distance 0.96 Å), and refined using a riding model. H atom displacement parameters were re-

Table 1. Crystallographic data.

Sum formula	(C ₄₄ H ₄₀ Cu ₂ N ₄ O ₈)·2H ₂ O
<i>f</i> _w [g·mol ^{−1}]	947.94
Space group	<i>P</i> 1̄
<i>a</i> = 8.953(2) [Å]	α = 100.74(2) [°]
<i>b</i> = 11.264(1) [Å]	β = 105.23(10) [°]
<i>c</i> = 11.318(2) [Å]	γ = 103.47(3) [°]
Vol [Å ³]	1033(1)
<i>Z</i>	1
<i>D</i> _{calc} (g·cm ^{−3})	1.524
μ [cm ^{−1}]	1.039
<i>F</i> (000)	490
Index ranges	−11 ≤ <i>h</i> ≤ 4, −13 ≤ <i>k</i> ≤ 13, −13 ≤ <i>l</i> ≤ 13
Reflections collected	6257
Independent reflections	4038 [<i>R</i> (int) = 0.016]
Data / restraints / parameters	4038 / 0 / 313
Goodness-of-fit on <i>F</i> ²	0.972
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> = 0.0445, <i>wR</i> = 0.0769
Final <i>R</i> indices (all data)	<i>R</i> = 0.0617, <i>wR</i> = 0.1034
Largest diff. peak and hole [e·Å ^{−3}]	0.471 and −0.787

Table 2. Atomic coordinates and equivalent isotropic displacement parameters.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	* <i>U</i> (eq)
Cu1	0.15254(8)	0.28253(6)	0.17413(6)	0.0338(2)
N1	−0.0032(5)	0.2450(3)	0.0043(3)	0.0314(10)
N2	0.2081(5)	0.4680(3)	0.2247(3)	0.0290(10)
O1	0.0487(4)	0.1326(3)	0.2091(3)	0.0408(9)
O2	0.3586(4)	0.2801(3)	0.2726(3)	0.0362(9)
O3	0.6179(4)	0.2238(3)	0.3674(3)	0.0506(11)
O4	−0.0590(4)	−0.0389(3)	0.3122(3)	0.0478(10)
O5	0.3069(5)	0.0637(4)	0.3776(5)	0.0608(14)
O6	0.5390(6)	0.1350(4)	0.6361(5)	0.0725(15)
C1	−0.1315(6)	0.1461(4)	−0.0429(5)	0.0321(13)
C2	−0.1824(6)	0.0518(4)	0.0194(5)	0.0310(13)
C3	−0.3299(7)	−0.0408(5)	−0.0445(5)	0.0420(15)
C4	−0.3922(7)	−0.1298(5)	0.0093(5)	0.0488(15)
C5	−0.3047(7)	−0.1296(4)	0.1311(5)	0.0449(15)
C6	−0.1575(6)	−0.0441(4)	0.1945(5)	0.0345(13)
C7	−0.0918(6)	0.0527(4)	0.1421(5)	0.0306(12)
C8	0.4862(6)	0.3755(4)	0.3303(4)	0.0299(12)
C9	0.6335(6)	0.3508(4)	0.3876(5)	0.0350(13)
C10	0.7713(6)	0.4455(5)	0.4542(5)	0.0370(13)
C11	0.7742(6)	0.5728(5)	0.4715(5)	0.0415(14)
C12	0.6378(7)	0.6004(5)	0.4173(5)	0.0364(14)
C13	0.4917(6)	0.5045(4)	0.3436(4)	0.0272(12)
C14	0.3521(6)	0.5418(5)	0.2934(4)	0.0312(13)
C15	0.0838(6)	0.5254(4)	0.1829(4)	0.0273(12)
C16	0.1113(6)	0.6235(4)	0.1245(4)	0.0285(12)
C17	0.0164(6)	0.3329(4)	−0.0704(4)	0.0297(12)
C18	0.1701(7)	0.3864(4)	−0.0748(5)	0.0349(13)
C19	0.1941(7)	0.4798(5)	−0.1382(5)	0.0365(14)
C20	−0.0678(7)	0.4752(4)	0.1906(4)	0.0333(13)
C21	−0.1149(7)	−0.1344(5)	0.3694(5)	0.0583(18)
C22	0.7560(7)	0.1864(5)	0.4175(6)	0.066(2)

$$*U(\text{eq}) = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j.$$

stricted to be 1.2 *U*_{eq} of the parent atom. The hydrogen atoms of the water molecule were located in the difference Fourier

maps calculated at the end of the refinement process as a small positive electron density and were not refined. The final positional parameters are presented in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 220656 [15].

Susceptibility measurements

Variable-temperature magnetic susceptibility measurements of a powdered sample were performed with a QUANTUM Design SQUID magnetometer in the temperature range 5–301 K. The applied field was about 2 T. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constant [16]. The effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$, where χ is the magnetic susceptibility per Cu(II) ion.

Molecular orbital calculations

Extended Hückel molecular orbital (EHMO) calculations have been performed in order to gain insight into the molecular orbitals that participate in the super-exchange pathway by using the Computer Aided Composition of Atomic Orbitals (CACAO) package programs [17]. The interatomic distances were taken from the X-ray results. Molecular orbital representations were plotted using the CACAO software [17].

Results and Discussion

X-ray crystal structure

A perspective drawing of the molecule is shown in Fig. 1 [18]. Selected bond lengths, angles and hydrogen-bonding interactions are summarized in Table 3. The molecule is a centrosymmetric dimer with the coordination centres bridged by two *m*-phenylene groups. The distance between the Cu1 and Cu1^a [symmetry transformation used to generate equivalent atoms: ^a($-x, -y + 1, -z$)] centres in the dimer is 7.401(6) Å. Also, the closest separation between Cu(II) ions belonging to neighbouring molecules in the unit cell is large (8.953(6) Å) and precludes significant intermolecular magnetic interactions. The coordination about each copper atom can be described as distorted tetrahedral since the angle between the two ligands is 51.5(1)°, and the dihedral angle between the corresponding [CuN₂O₂] coordination planes is 27.6(2)°. Each copper(II) ion is coordinated by two N_{imine} atoms and two O_{phenol} atoms. The atom with the greatest deviation from the [CuN₂O₂] coordination plane is the O1 atom at $-0.613(3)$ Å. The average Cu–O and Cu–N

Table 3. Selected bond lengths [Å] and angles [°] characterizing the inner coordination sphere of the copper(II) centre, and hydrogen – bonding interactions (see Fig. 1 for labelling scheme adopted).

Bond lengths			
Cu1–O1	1.893(3)	C1–N1	1.306(6)
Cu1–O2	1.898(4)	C14–N2	1.300(6)
Cu1–N1	1.958(4)	C7–O1	1.298(5)
Cu1–N2	1.964(4)	C8–O2	1.288(5)
Angles			
O1–Cu1–O2	91.2(1)	O1–Cu1–N1	94.5(2)
O2–Cu1–N2	93.8(2)	N1–Cu1–N2	100.4(2)
O1–Cu1–N2	143.8(2)	N1–Cu1–O2	146.9(2)
Hydrogen bonds ^a			
D	A	H	D···A [Å]
O5	O4	H5a	2.37(1)
O5	O3	H5b	2.42(1)
O5	O1	H5b	2.77(1)
O5	O2	H5b	2.19(1)
O5	O1	H5a	2.44(1)
O6	O3	H6b	2.99(1)
O6	O5	H6b	1.89(1)
O6	O5	H6a	2.12(1)
			D–H···A [°]
			160.8(1)
			133.2(1)
			95.7(1)
			156.6(1)
			129.8(1)
			113.3(1)
			173.3(1)
			161.9(1)

^a (A = acceptor, D = donor atom).

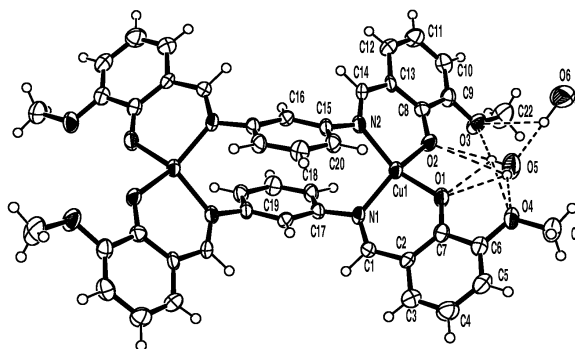


Fig. 1. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms are presented as spheres of arbitrary radii. Hydrogen bonding interactions are represented by broken lines.

distances are 1.896(4) and 1.961(4) Å, respectively. The N1–Cu1–N2 and O1–Cu1–O2 angles are 100.4(2) and 91.2(1)°, respectively. Those distances and angles are in the range of those of conventional Schiff base copper(II) complexes of similar coordination [18–21].

The bridging phenylene rings form dihedral angles of 45.5(3) and 61.4(2)° with the two chelate rings to which they are attached and are mutually parallel, the interplanar separation being 3.433 Å. This distance is larger than the corresponding value of 3.05 Å for a similar copper(II) complex [20], but smaller than 3.717 Å observed for a similar cobalt(II) complex [22].

There are two non-coordinating water molecules in the crystal structure, which are linked *via* six hydrogen bonds between the O5 and O6 atoms of the water molecules and the O atoms of the ligand, O5–H_a···O4 [2.37(1)], O5–H_b···O3 [2.42(1)], O5–H_b···O1 [2.77(1)], O5–H_b···O2 [2.19(1)], O5–H_a···O1 [2.44(1)], O6–H_b···O3 [2.99(1)], O6–H_b···O5 [1.89(1)], and O6–H_a···O5 [2.12(1) Å] (Table 3).

Magnetic properties

Magnetic susceptibility measurements for a powdered sample were carried out by the SQUID based magnetometer in the temperature range 5–301 K. The magnetic susceptibilities are shown as a function of temperature in Fig. 2, and the magnetic moments are shown as a function of temperature in Fig. 3. The magnetic susceptibility data were fitted by using the Curie-Weiss law, $\chi = C/(T + \theta)$ leading to $C = \frac{N\mu_B^2}{3k} = 0.125$ and a Curie-Weiss constant $\theta = -0.4$ K. In addition, the data were fitted using the Bleaney-Bowers equation [23]

$$\chi = \frac{N_L g^2 \mu_B^2}{3kT} \left[1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} + N_a \quad (1)$$

and the isotropic (Heisenberg) exchange Hamiltonian $H = -2JS_1 \cdot S_2$, where $-2J$ corresponds to the energy separation between spin-singlet and -triplet states, for two interacting $S = 1/2$ centres. N_a is the temperature-independent paramagnetism and its value is $6 \cdot 10^{-5}$ cm³/mol for each copper atom. Least squares fitting of the data leads to $J = -0.4$ cm⁻¹, $g = 2.17$. Magnetic moments were obtained from the relation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$. The magnetic moment at 301 K is about 2.75 B.M., and 2.56 B.M. at 5 K.

Extended Hückel molecular orbital calculations (EHMO)

We have carried out EHMO calculations in order to gain insight into the MO's that participate in the super-exchange pathway. An energy difference of 0.140 eV is obtained between the HOMO and the LUMO (Fig. 4). The LUMO is a symmetrical orbital combination, whereas the HOMO is an asymmetrical combination. As can be observed, the Cu metal centres use $d_{x^2-y^2}$ type orbitals for a π interaction with p_N orbitals of the *m*-phenylenediamine bridging fragment.

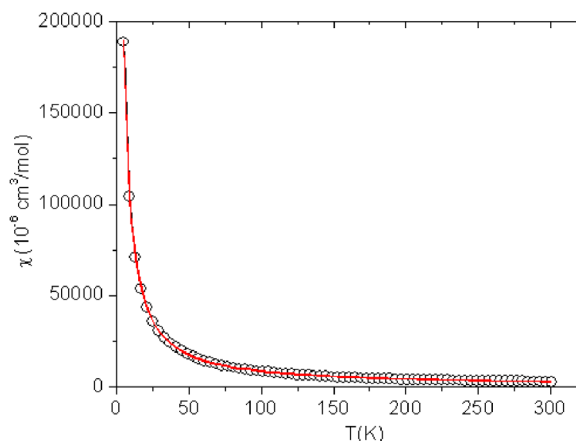


Fig. 2. Molar susceptibility per copper(II) vs. temperature curve.

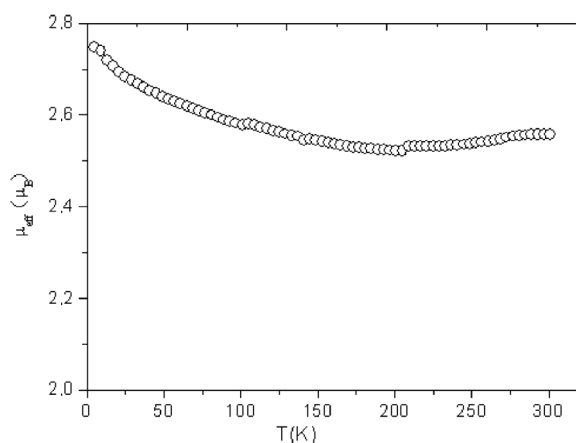


Fig. 3. Magnetic moment per copper(II) vs. temperature curve.

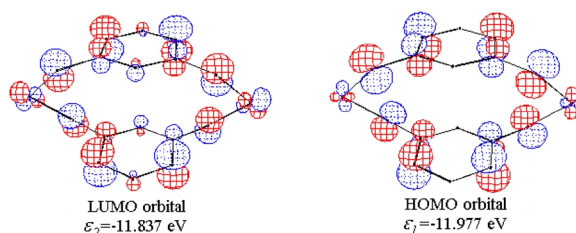


Fig. 4. Drawing of HOMO and LUMO frontier orbitals (for orbitals contributing more than 1%).

A qualitative relationship

A qualitative relationship between the magnitude of ground-state magnetic exchange interaction and separation between the two one-electron reduction waves can be set out for binuclear copper(II) complexes. A

molecular orbital approach can be used to assess the antiferromagnetic contribution to a magnetic exchange interaction. In a dinuclear copper(II) species, each copper(II) ion has one unpaired electron in an essentially *d*-type orbital and, to first order, the antiferromagnetic interaction reflects the level of interaction of the two unpaired-electron orbitals. The interaction between the two copper(II) *d* orbitals is effected by an interaction with the appropriate molecular orbitals of the bridging group. If the two copper(II) ion coordination geometries in a binuclear complex are square planar, then two molecular orbitals, ϕ_1 and ϕ_2 , will form as linear combinations of the two $d_{x^2-y^2}$ orbitals.

$$\phi_1 \approx d_{x^2-y^2}^a + d_{x^2-y^2}^b$$

$$\phi_2 \approx d_{x^2-y^2}^a - d_{x^2-y^2}^b$$

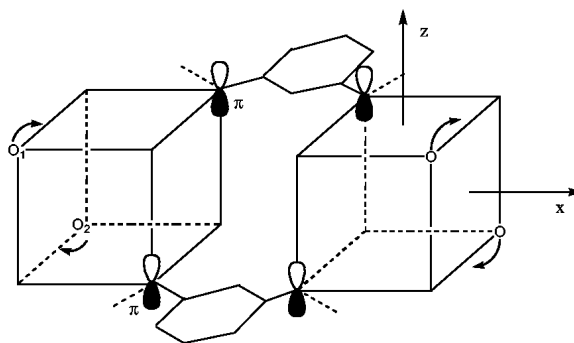
According to Hoffman and co-workers [24,25] in dinuclear complexes strong antiferromagnetism is observed if the energy separation of the symmetric and antisymmetric combination of the two molecular orbitals is large, irrespective of the fact which combination is lower in energy. The coupling constant is expressed as

$$2J = 2K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)^2}{J_{aa} - J_{ab}} \quad (2)$$

where, K_{ab} , J_{aa} and J_{ab} are the exchange integral and one-centre and two-centre Coulomb repulsion integrals, respectively, and ε_1 and ε_2 are the energies of the two orbitals ϕ_1 (HOMO) and ϕ_2 (LUMO), respectively. The value of K_{ab} is always positive, so the first term in (2) contributes to the ferromagnetic interaction, while the second term, which is always positive, contributes to the antiferromagnetic interaction. From the above expression (2) for the exchange parameter, it is seen that the binuclear complex with the greater antiferromagnetic interaction has the larger $(\varepsilon_1 - \varepsilon_2)$ energy difference. Very recently, we have studied the crystal structures and magnetic properties of $(\mu\text{-hydroxo})(\mu\text{-acetato})$ and $(\mu\text{-hydroxo})(\mu\text{-pyrazolato})$ bridged dicopper(II) complexes [9–11]. For these binuclear copper complexes the $(\varepsilon_1 - \varepsilon_2)$ energy differences were found to be 0.605, 0.645 [9] 0.648 [11] and 1.11 eV [10].

Conclusion

In general, several structural features of binuclear copper(II) complexes are thought to regulate the



Scheme 2.

strength of exchange coupling interactions: (i) the dihedral angle between the two coordination planes, (ii) planarity of the bonds around the bridging atom, and (iii) the bridging atom(s) and bridging angles [26,27]. But, the variation of the strength of the super-exchange interaction cannot be explained completely by the structural features of binuclear copper(II) complexes. A different approach must be discussed to clarify the origin of the super-exchange mechanism of this system.

In the light of the value of the exchange constant J , two points deserve to be discussed: (i) the exchange pathway between the two paramagnetic copper(II) ions and (ii) the variation of the antiferromagnetic coupling of the copper(II) ions. Dealing with the first point, studies of magnetic exchange between paramagnetic metal ions exhibiting a tetrahedral environment are very scarce [28,29]. Tetrahedral Cu(II) complexes present magnetic orbitals of t_2 symmetry and, as such, the π interaction with ligands can be very important. In addition, it has been suggested that the magnetic interaction through extended bridging ligands having a π -conjugated system is mediated *via* the delocalized π framework [29–31]. In fact, the EHMO calculations [17] on the *m*-phenylenediamine bridging fragment show that the HOMOs are of π symmetry. Scheme 2 can be used to describe the magnetic interaction therein. One can see that the overlap between the $3d_{xy}$ orbital of the metal ion and the p orbital of the bridging ligand is greater than that involving $3d_{xz}$ and $3d_{yz}$, whereas the overlap with the phenolato-oxygen orbitals (p_x , p_y and p_z) is identical for the three $3d$ orbitals. In this respect, the trend of the orbital energy will be $\varepsilon_{dxy} > \varepsilon_{dxz} \approx \varepsilon_{dyz}$ and due to the larger overlap between the d_{xy} orbital and those of the bridging ligand this $3d_{xy}$ orbital will be mainly responsi-

ble for the magnetic interaction [32, 33]. In the investigated copper(II) complex, a distortion of the tetrahedron occurs, consisting of a shift of the phenolato oxygen atoms in such a way that they are occupying the middle point of the edge of a cube as shown in Scheme 2. Such a distortion in the copper(II) family causes a larger interaction between the d_{xz} orbital and those of the phenolato oxygen atoms, and raise the energy of this orbital placing it above d_{xy} . However, this distortion does not modify significantly the overlap between the d_{xz} orbital and those of the bridging ligand. So, the electronic configuration for the copper(II)

complex exhibiting the above-mentioned distortion is $(d_{z^2})^2(d_{x^2-y^2})^2(d_{yz})^2(d_{xy})^2(d_{xz})^1$.

On the second key point, the dependence of the J parameter on the metal ion for a given ligand is explained by a qualitative relationship. Our results strongly suggest that the antiferromagnetic interaction in the dinuclear compound must be mediated by the delocalized π framework of the *m*-phenylenediamine fragment.

Acknowledgement

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