# Exchange Coupling in Dinuclear Copper(II) Complexes with Oxalato, Oxamidato and Oxamato Ligands

A. BENCINI, C. BENELLI, D. GATTESCHI, C. ZANCHINI
*I.S.S.E.C.C., C.N.R. and Department of Chemistry, University of Florence, Florence, Italy*
A. C. FABRETTI and G. C. FRANCHINI
*Institute of General Chemistry, University of Modena, Modena, Italy*

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*We have synthesized a series of dinuclear copper(II) complexes in which the metal ions are bridged by oxamidato, oxamato and oxalato ligands, with the purpose of studying the influence of the ligands on the extent of the antiferromagnetic coupling between the two metal ions. Magnetic susceptibility measurements between 77 and 300 K showed that the singlet–triplet splitting ranges from 330 cm$^{-1}$ to 550 cm$^{-1}$; J is found to increase in the order oxalato < oxamato < oxamidato.*

## Introduction

Exchange interaction propagated by multiatom bridges represents a challenge to chemists in order to design ligands which propagate the magnetic coupling between metal ions which are far apart [1–3]. In particular ligands which have a skeleton similar to that of the oxalate ion, Fig. 1, have been found to be extremely effective in transmitting exchange interactions between two copper atoms which are more than 500 pm apart [3–8]. In fact in a ditiooxamidato bridged complex the singlet–triplet splitting, J, has been found to be 594 cm$^{-1}$, with the two copper ions at 561 pm from each other [7]. An extended Hückel calculation showed that the reason for the strong coupling is the fact that the $x^2 - y^2$ metal orbitals and the last occupied in-plane MO's of the ligand are very close in energy, allowing a relatively strong covalency. Another factor favouring the coupling is the in-plane S–N overlap which contributes to the splitting of the MO's which are formed by the symmetric and antisymmetric contributions of the magnetic orbitals [7].

In order to collect more data on analogous series of complexes we have synthesized a series of copper(II) complexes with oxalato, oxamato and oxamidato bridges, and have studied the temperature dependence of the magnetic susceptibilities in order to learn how the magnetic coupling is affected by the nature of the donor atoms of the bridge ligand.

## Experimental

$[Cu_2(phen)_2oxam](NO_3)_2\cdot3H_2O$ and $[Cu_2(phen)_2oxamd](NO_3)_2\cdot1.5H_2O$ (oxam = oxamato; oxamd = oxamidato; phen = 1,10-phenanthroline) were synthesized by adding to a warm solution of 2 mmol of $Cu(NO_3)_2\cdot3H_2O$, 2 mmol of 1,10-phenanthroline and 1 mmol of the appropriate bridging ligand in 20 ml of water, a warm solution of 2 mmol of LiOH in 2 ml of water.

$[Cu_2(phen)_2oxal](NO_3)_2$ (oxal = oxalate) was prepared by adding to 15 ml of a water solution of 2 mmol of $Cu(NO_3)_2\cdot3H_2O$ and 2 mmol di 1,10-phenanthroline, 4 ml of a water solution of 1 mmol of $Na_2oxal$.

$[Cu_2(dpa)_2oxamd](NO_3)_2$ and $[Cu_2oxa](BPh_4)_2\cdot2CH_3COCH_3$ (dpa = 2,2′-dipyridyl-amine; bipy = 2,2′-bipyridyl; oxa = bis(6-ethyl-3,6-diazaoctyl)oxamidato(2$^-$)) were prepared as previously described [9, 10].

## Results and Discussion

Deprotonated oxamide (oxamd), oxamic acid (oxam), and oxalic acid (oxal) with 1,10-phenanthroline (phen) and copper(II) nitrate form complexes of the formula $[Cu_2L(phen)_2](NO_3)_2\cdot nH_2O$, which are assigned a structure analogous to that previously reported [11] for $[Cu_2(dpa)_2oxamd](NO_3)_2$ and $[Cu_2(bipy)_2oxamd](NO_3)_2\cdot3H_2O$, and which are shown schematically in Fig. 1 on the basis of the analytical and spectral data shown in Table I.

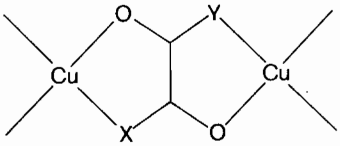

Fig. 1. Sketch of the oxalato-type bridge: X = Y = O oxalate, X = Y = NH oxamidato, X = NH; Y = O oxamato.

The infrared spectra show that the nitrato groups are ionic, and that the L ligands are in bridging positions, according to analogous reported data [9].

The electronic spectra, given in Table I, are characterized by one broad band in the visible region, with the maximum of absorption shifting to higher frequencies in the order oxal < oxam < oxamd, in agreement with previous observations [9]. A comparison of the absorption spectra of the three oxamidato complexes shows that the maximum is at 17,400, 14,700 and 17,800 $cm^{-1}$ for $[Cu_2(phen)_2oxamd](NO_3)_2 \cdot 1.5H_2O$, $[Cu_2(dpa)_2oxamd](NO_3)_2$ and $[Cu_2oxa](BPh_4)_2 \cdot 2CH_3COCH_3$ respectively. The crystal structure of $[Cu_2(dpa)_2oxamd](NO_3)_2$ showed that the copper(II) ions are five coordinated [11], with a monodentate nitrato group in the axial position of a square pyramid while for compound $[Cu_2oxa](BPh_4)_2 \cdot 2CH_3COCH_3$ the crystal structure showed an essentially square planar geometry [10]. Therefore it seems reasonable to ascribe the lower frequency of the maximum of the (dpa) complex to the five coordination [12] and assign square planar geometry to $[Cu_2(phen)_2oxamd](NO_3)_2 \cdot 1.5H_2O$ on the basis of the similarity of its electronic spectra to those of $[Cu_2oxa](BPh_4)_2 \cdot 2CH_3COCH_3$. By extension also $[Cu_2(phen)_2oxam](NO_3)_2 \cdot 3H_2O$ and $[Cu_2(phen)_2oxal](NO_3)_2$ are assigned a similar structure, although the possibility of weak axial interactions cannot be completely ruled out [13].

The room temperature magnetic moments are all below the value expected for single copper(II) ions, showing the existence of a substantial antiferromagnetic coupling. The EPR spectra are in general not different from those expected for mononuclear copper complexes, as was previously observed [10]. The spectra of $[Cu_2(phen)_2oxamd](NO_3)_2 \cdot 1.5H_2O$ however do show some evidence of triplet character, as shown in Fig. 2. The low field feature shows a hyperfine splitting into seven components, as expected for two equivalent copper(II) ions [14], and also a fine splitting of 50–55 G. On decreasing the temperature the spectra disappear, in accord with a strong antiferromagnetic coupling. The relevant EPR parameters are given in Table I. Although all these complexes do show large antiferromagnetic coupling in the ground state, the interactions in the excited states (*i.e.* interactions between the $x^2 - y^2$ orbital of one and xz, yz, $z^2$, or xy orbitals in the other ion) are weak, thus leaving only dipolar contributions to the zero-field splitting tensor [10]. Since the metal–metal distance is larger than 500 pm, the expected contribution to D is of the order of 125 G, so that the fine structure can be hidden in most cases due to the large linewidth.

The magnetic susceptibility of all the complexes decreases with temperature in the range 77–300 K but no maximum is achieved (Fig. 3). The experimental points were fit to the Bleaney–Bowers relation

TABLE I. Analytical, Spectral and Magnetic Data.

| | | Analytical data | | | Infrared spectra[c] | | | Electronic[a] spectra | Magnetic susceptibility[d] | | EPR data[b] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | $\nu$(NH) | $\nu_{as}$(CO) | $\nu_{sym}$(CO) | $10^3$ $cm^{-1}$ | J, $cm^{-1}$ | g | $g_\parallel$ | $g_\perp$ | D(G) |
| $[Cu_2(phen)_2oxal](NO_3)_2$ | Calc. | 44.6 | 2.3 | 12.0 | | 1642 | 1355,1320 | 14.8 | 330(20) | 2.10 | 2.26 | 2.08 | |
| | Found | 44.3 | 2.3 | 11.8 | | | | | | | | | |
| $[Cu_2(phen)_2oxam](NO_3)_2 \cdot 3H_2O$ | Calc. | 41.5 | 3.1 | 13.0 | 3200 | 1636,1608 | 1340 | 16.0 26.3sh | 400(30) | 2.10 | 2.25 | 2.07 | 52 |
| | Found | 41.4 | 2.9 | 13.0 | | | | | | | | | |
| $[Cu_2(phen)_2oxamd](NO_3)_2 \cdot 1.5H_2O$ | Calc. | 43.1 | 2.9 | 15.5 | 3230 | 1628,1608 | 1340 | 17.4 | 510(35) | 2.10 | 2.22 | 2.06 | |
| | Found | 43.0 | 2.9 | 15.5 | | | | | | | | | |
| $[Cu_2(dpa)_2oxamd](NO_3)_2$ | Calc. | 38.9 | 3.0 | 20.6 | 3320,3262,3202 | 1650,1625,1610 | 1348 | 14.7 27.1 | 480(35) | 2.11 | 2.25 | 2.08 | |
| | Found | 38.8 | 3.0 | 20.4 | | | | | | | | | |
| $[Cu_2oxa](BPh_4)_2 \cdot 2CH_3COCH_3$ | Calc. | 69.0 | 7.2 | 6.7 | 3212 | 1666 | 1310 | 17.8 27.4 | 550(40) | 2.10 | 2.26 | 2.05 | |
| | Found | 69.0 | 7.3 | 6.9 | | | | | | | | | |

[a] Spectra of the solids. [b] Polycrystalline powder EPR spectra. [c] Nujol; $\nu$(NH) is N–H stretch, $\nu_{as}$(CO) is CO antisymmetric stretch and $\nu_{sym}$(CO) is the CO symmetric stretch. [d] Estimated error in parenthesis.

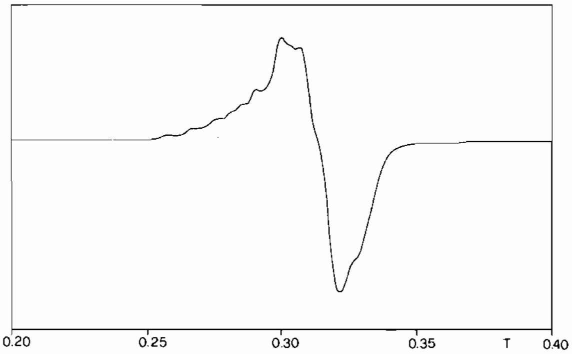

Fig. 2. Polycrystalline powder EPR spectra of $[Cu_2(phen)_2$-$oxamd](NO_3)_2 \cdot 1.5H_2O$ at liquid nitrogen temperature.

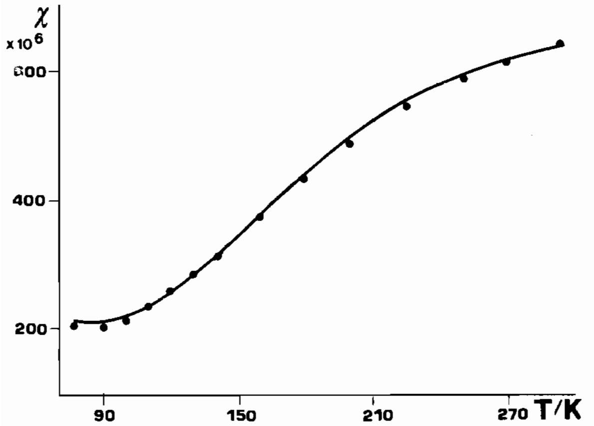

Fig. 3. Corrected molar magnetic susceptibility *vs.* temperature for $[Cu_2(phen)_2oxam](NO_3)_2 \cdot 3H_2O$.

[15] through a least squares procedure. The spin hamiltonian was in the form $H = J\ S_1 \cdot S_2$. In general it was found that the fit was rather insensitive to the g values, and also in some cases the quality of the fit was not excellent. It must be considered that the diamagnetic correction [16] is of the same order of the observed uncorrected molar susceptibility, and in some cases even larger, thus giving a large uncertainty on the corrected values.

Another source of error may come from the presence of paramagnetic impurities (monomeric species?) which are responsible for the fact that the compounds stay paramagnetic down to low temperatures. Therefore the estimated J values are reliable within 5–10%. The calculated g and J values are given in Table I. It is apparent that the antiferromagnetic coupling increases dramatically in the order oxal < oxam < oxamd, as was previously suggested on the basis of room temperature magnetic susceptibility data alone [9]. The increase of the J value in the series of phen complexes is to be compared to the increase in the frequency of the maximum in the electric absorption spectra. Since the structures remain presumably constant in the series, as discussed above, the increase in the absorption frequency is indicative of an increase in the in-plane ligand field on passing from oxal to oxam and oxamd, and this in turn determines a stronger antiferromagnetic coupling, as was shown in an angular overlap treatment of the magnetic coupling in dinuclear copper(II) complexes [17].

Comparing the J value of $[Cu_2(phen)_2oxal]$-$(NO_3)_2$ with those reported for complexes in which the oxalato ligand is bridging two copper ions in such a way that the oxygen atoms are pointing towards the lobes of the two magnetic orbitals, we find that the present value, 330 $cm^{-1}$, is intermediate between $J = 272\ cm^{-1}$ reported for $CuC_2O_4 \cdot 1/3H_2O$ [18, 19] and $J = 385\ cm^{-1}$ reported for $[tmen(H_2O)Cu(C_2O_4)$-$Cu(H_2O)tmen](ClO_4)_2 \cdot 1.25H_2O$ [3] (tmen = 1,1,4,-4-tetramethylethylenediamine). It can be assumed that structural variations in the series may determine the variations in the J values, but lack of X-ray data prevents us from discussing this point further.

The J values which we have determined for the oxamidato bridged complexes also show some variability, the largest value, $J = 550\ cm^{-1}$, being obtained for the chelating ligand oxa. It is worth noting that this J value falls very close to the maximum value thus far observed for this kind of complexes, $J = 594\ cm^{-1}$ [19].

Comparing $[Cu_2oxa](BPh_4)_2 \cdot 2CH_3COCH_3$ with $[Cu_2(dpa)_2oxamd](NO_3)_2$ for both of which the crystal structures are available [10, 11], we see that the large J value observed for the former could be due to the shorter Cu–O and Cu–N bond distances observed in that case and also to the fact that the coordination around copper is more regularly planar. In fact $[Cu_2(dpa)_2oxamd](NO_3)_2$ is square pyramidal with the copper atom 22 pm displaced towards the axial ligand, determining a mismatch of the lobes of the magnetic orbitals and the ligand orbitals, thus decreasing the antiferromagnetic coupling.

## Acknowledgement

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