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Polyhedron 22 (2003) 2143–2153

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Malonate-based copper(II) coordination compounds: ferromagnetic coupling controlled by dicarboxylates

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Received 6 October 2002; accepted 23 December 2002

Abstract

Studies on structural and magnetic properties of polynuclear transition metal complexes, aimed at understanding the structural and chemical factors governing electronic exchange coupling mediated by multiatom bridging ligands, are of continuing interest to design new molecular materials exhibiting unusual magnetic, optical and electrical properties, bound to their molecular nature. Looking at potentially flexible bridging ligands, the malonate group seems a suitable candidate. The occurrence of two carboxylate groups in the 1,3 positions allows this ligand to adopt simultaneously chelating bidentate and different carboxylato bridging modes (*syn–syn*, *anti–anti* and *syn–anti* trough one or two carboxylate groups) In the course of our research we have structurally and magnetically characterized several carboxylato bridged copper(II) complexes. In the present study we start describing briefly the structure and the magnetic behaviour of the compounds, subsequently we analyze the magneto-structural correlations concluding that the parameter that governs, in first order, the magnetic interaction between metal centres is the relative position of the carboxylato bridge of the malonate respect to the copper(II) ions: equatorial–equatorial (strong interaction), equatorial–apical (weak interaction) and apical–apical (negligible interaction). Inside this division another parameters become important such as β (angle between copper(II) basal planes) in the equatorial–equatorial, or the distortion t in the equatorial–apical.

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Keywords: Copper(II) coordination compounds; Malonate ligands; Dicarboxylates; Ferromagnetism

1. Introduction

It has long been recognised that carboxylate bridges provide an efficient means for transmitting magnetic information in Cu(II) aggregates as demonstrated by the dinuclear copper acetate system [1–4]. Different coordination and bridging modes favour different forms of cooperative coupling [5–7]. As has been shown previously, a particularly attractive system for investigating how these bridging modes can be used to modulate the overall magnetic behaviour in coordination compounds involves Cu_4 unit into a cyclic structure [8–13]. In addition, the fact that the Cu(II) centres only carry one unpaired electron makes the interpretation of the magnetic behaviour simpler than in other cases where there are multiple unpaired electrons and several detailed studies of Cu_4 cyclic structures have been reported [14–16].

The malonate (dianion of the propanedioic acid, H_2mal) is a flexible and versatile ligand. The occurrence of two carboxylate groups in 1,3 positions allow this ligand to adopt simultaneously chelating bidentate and different carboxylato bridging modes (*syn–syn*, *syn–anti* and *anti–anti* through one or both carboxylate

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0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00203-1

groups) [17–30]. The ability of the carboxylato bridge to mediate significant ferro- or antiferromagnetic interactions [31–40] between the paramagnetic metal ions it bridges, enhances the interest in this ligand aiming at designing extended magnetic systems. In the context of our magneto-structural research with malonato-bridged homo- and heterometallic complexes [34–40], we have investigated the Cu(II) compounds.

The bisbidentate behaviour analogue to that exhibited by the oxalate is forbidden by steric reasons to malonate and this affects dramatically to the structure and properties of the malonato complexes. The malonate ligand occupies one or two coordination positions and neutralizes two positive charges of the metallic copper ion (Cu(II)), allowing the inclusion of other ligands in the coordination sphere of the metal. These complementary ligands can act as bridging or blocking ligands contributing to the interconnection or isolation of the spin carriers. Thus combining the malonate with other bridging and/or blocking ligands we have been able to prepare monomers, dimmers, trimers, tetramers, infinite chains, 2D and 3D arrays.

The magnetic coupling among the magnetic centres is given by the value of J (the intramolecular exchange interaction), being J negative or positive depending on the antiferro- or ferromagnetic character of the coupling, respectively. The magnitude of the interaction is governed by the overlap density, thus for the carboxylato bridge, it will be affected by the bridging modes that it can adopt.

In the course of our research we have structurally and magnetically characterized several carboxylato bridged copper(II) complexes, here we report the main aspects and conclusions of our magneto-structural research in copper(II) malonato complexes. We will start describing briefly the structure and the magnetic behaviour of the compounds, subsequently we will analyze the magneto-structural correlations.

2. Structure and magnetic properties

2.1. *Copper(II)-malonate*

2.1.1. *$[Cu(H_2O)_4][Cu(mal)_2(H_2O)_2]$ (**1**)*

The dinuclear complex **1** (Fig. 1) was firstly prepared by Chattopadhyay et al. [24]. The magnetic properties were studied by our group [40]. The neutral dinuclear entity consists of a diaquabis(malonato)–cuprate(II) anion and a tetraaquacopper(II) cation connected through a carboxylato group exhibiting the *anty–syn* bridging mode. The environment of the chelated copper(II) ion is octahedral, whereas the coordination of the other is square pyramidal.

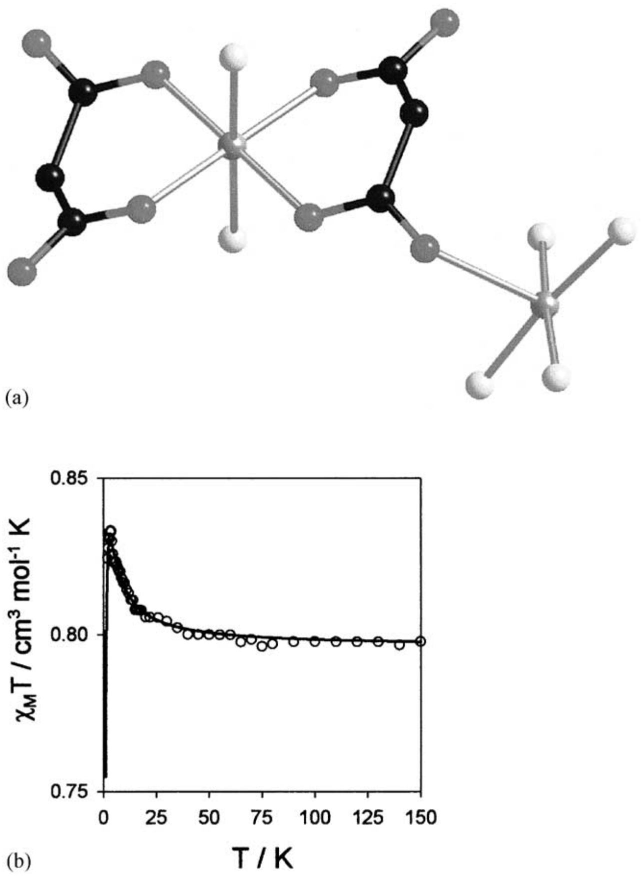


Fig. 1. (a) Perspective view of the dinuclear copper(II) units of compound $[Cu(H_2O)_4][Cu(mol)_2(H_2O)_2]$ (**1**) along with the copper(II) numbering scheme. (b) Thermal dependence of the $\chi_M T$ product for this compound.

The magnetic behaviour is typical of a ferromagnetically copper(II) dimer (intradimer coupling constant of $J = +1.8$ cm^{-1}) with a weak intermolecular antiferromagnetic interaction.

2.1.2. *$\{[Cu(H_2O)_4]_2[Cu(mal)_2(H_2O)]\}[Cu(mal)_2(H_2O)_2]\{[Cu(H_2O)_4][Cu(mal)_2(H_2O)_2]\}$ (**2**)*

The compound **2** is built up by three units of different nuclearity [40]. A neutral entity, $[Cu(H_2O)_4][Cu(mal)_2(H_2O)]$ (the dinuclear complex explained previously), an anionic monomer $[Cu(mal)_2(H_2O)_2]$ and a cationic trinuclear unit $[Cu(H_2O)_4]_2[Cu(mal)_2(H_2O)_2]$ (Fig. 2). The mononuclear entity is formed by two malonate anions chelating one copper(II) ion. The di-, and trinuclear complexes are built up by joining one and two tetraaquacopper(II) cations to the mononuclear compound via *anti–syn* carboxylato bridging mode, respectively. The chelated copper(II) atom has an octahedral surrounding, and the adjacent Cu(II) have square-pyramidal environments.

The magnetic properties of this compound were explained on the basis of the sum of the magnetic susceptibility of the three units gives the total suscept-

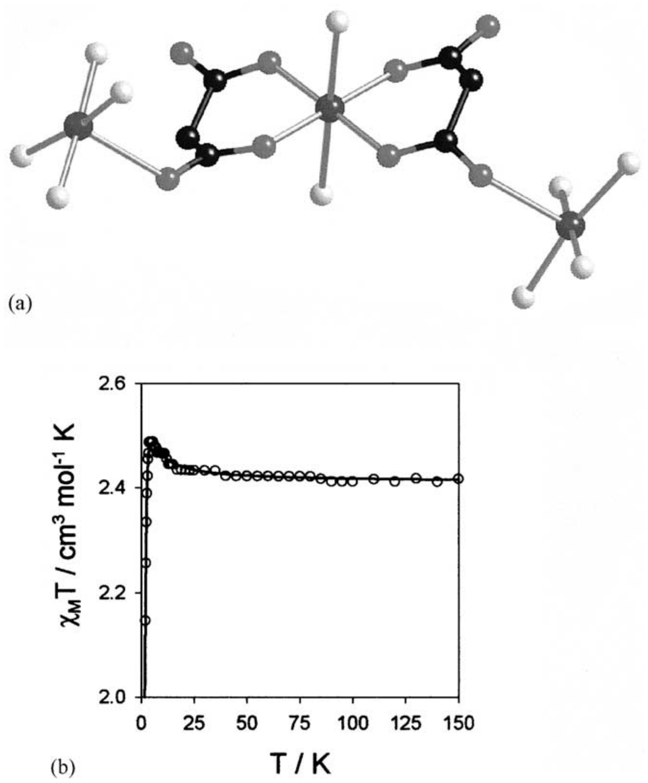
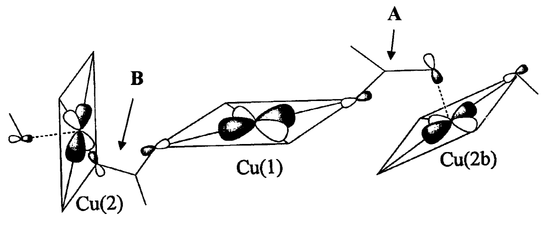


Fig. 2. (a) Perspective view of the trinuclear copper(II) units of compound $\{[Cu(H_2O)_4]_2[Cu(mal)_2(H_2O)]\}[Cu(mal)_2(H_2O)_2]\{[Cu(H_2O)_4][Cu(mal)_2(H_2O)_2]\}$ (**2**) (b) Thermal dependence of the $\chi_M T$ product for compound **2**.

ibility. The coupling constant of the trinuclear unit can therefore be found out and its value is $J = +1.2$ cm^{-1}.

2.1.3. $\{[Cu(H_2O)_3][Cu(mal)_2(H_2O)]\}_n$ (**3**)

The structure of **3** [40] (Fig. 3) consists of zigzag chains of copper(II) ions that exhibit a regular alternation of aquabis(malonate)copper(II) and triaquacopper(II) units, the former linked to the latter via two different OCO groups exhibiting the *anti*-*syn* bridging modes, one involves two equatorial oxygens of the Cu(II) ions (**B**) whereas the other involves an equatorial oxygen at one copper(II) and an apical oxygen at the other (**A**) (see Scheme 1). The two crystallographically independent copper(II) ions have distorted square pyramidal surroundings.



Scheme 1.

The magnetic behaviour of this compound reveals the occurrence of an overall ferromagnetic coupling. The model proposed to explain that magnetic properties is an alternating intrachain magnetic exchange model; with a Hamiltonian of the form:

$$\hat{H} = -J\sum_i[\hat{S}_{2i}\cdot\hat{S}_{2i-1} + \alpha\hat{S}_{2i}\cdot\hat{S}_{2i+1}]$$

where α is the alternation parameter (αJ equals to j).

The analysis of data leads to $J = +3.0$ cm^{-1} for the **B** exchange pathway and $j = +1.9$ cm^{-1} for the **A**.

2.2. Copper(II)–malonate–ligand

Up to now we have seen that the copper(II) malonato complexes have revealed as magnetically interesting materials, so the use of appropriate ligands could enhance the dimensionality of these materials.

There are many copper(II) malonato complexes already prepared with different ligands, such us 1,10-phenantroline [41], 2-4,4′-diaminodiphenylmethane [42], diethylethylenediamine [43], methylethylenediamine [22], 1,3-diaminopropane [44], *N*1-isopropyl-2-methyl-propane-1,2-diamine [45], 1,3-diaminopropane [46], triphenylphosphino [47], tricyclohexyl-phosphinol [47], 4,4′-dimethyl-2,2′-bipyridine [48], 5,6-dimethyl-1,10-phenantroline [49], 2,2′-bipyridine [50,34], oxamide oxime [51], benzimidazole [25], 3,5-dimethyl-1H-pyrazole [52], imidazole [35], 2-methylimidazole [35], 4,4′-bipyridine [36] 2,4′-bipyridine [37], pyrazine [37], 2,2′-bipyrimidine [38].

But, most of these compounds are not magnetically characterized or they do not present interesting magnetic behaviours [38], or the malonato bridge does not play an important role in the magnetic exchange pathway [38]. Those compounds will not be analysed in this work.

Mainly the explanation of the magnetic properties of the malonato-bridged copper(II) complexes has been carried out by our group with just an exception [22].

2.2.1. $[Cu(Im)_2(mal)]_n$ (**4**) and $[Cu(2\text{-}MeIm)_2(mal)]_n$ (**5**) (Im = imidazole and MeIm = 2-methylimidazole)

The compounds **4** (Fig. 4) and **5** have a quite similar structure [35]. They consist of regular zig–zag chains that are linked through one malonate carboxylate group exhibiting the *anti*–*anti* conformation. Each copper(II) ion in **4** and **5** shows a distorted CuN_2O_3 square pyramidal geometry and each malonate group adopts simultaneously bidentate and monodentate coordination modes.

The shape of the magnetic χT versus T curves reveals the occurrence of significant ferromagnetic coupling between the copper(II) ions. The data were analyzed by means of Baker et al. [53] expression for a ferromag-

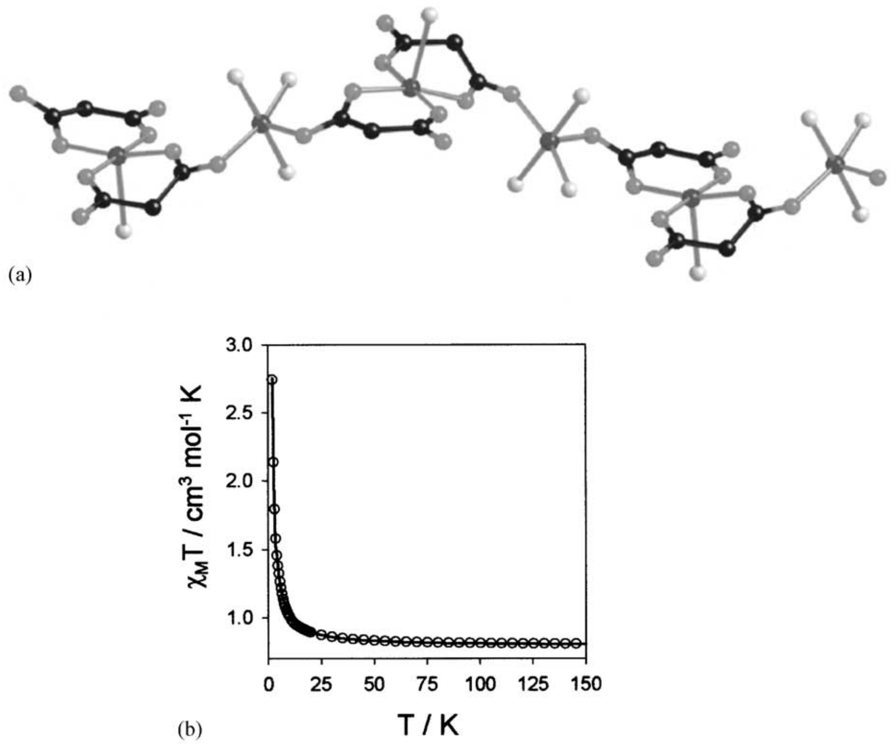


Fig. 3. (a) Perspective drawing of a fragment of the chain of compound $\{[Cu(H_2O)_3][Cu(mal)_2(H_2O)]\}_n$ (**3**). (b) Thermal dependence of the $\chi_M T$ product for compound **3**.

netic copper(II) uniform chain leading, to $J = +1.64$ cm^{-1} and $J = +0.39$ cm^{-1} for **4** and **5**, respectively.

2.2.2. *$\{[Cu(bpy)(H_2O)][Cu(bpy)(mal)(H_2O)]\}(ClO_4)_2$ (**6**) (bpy = 2,2′-bipyridine)*

There are three different malonato-bridged copper(II) complexes with 2,2′-bipyridine (Fig. 5), but only the two polymorphs of **6** have been magnetically characterized [34]. Although their structures and the spatial disposition are different, both can be considered as zig–zag chains with a very similar conformation. The chains exhibit a regular alternating of aqua(2,2-bipyridyl)(malonato)copper(II) and aqua(2,2′-bipyridyl)copper(II) units, the former being linked to the latter as a bis-monodentate ligand through two carboxylate–malonate oxygen atoms in a *cis* arrangement with the *anti–syn* coordination mode. The copper(II) ions present a distorted square pyramidal environment.

The magnetic properties of the two polymorphs are practically identical and the shape of the χT versus T curves is characteristic of the occurrence of weak ferro- and antiferromagnetic interactions in the high- and low-temperature ranges, respectively. Two failed attempts to explain these properties led us to the development of a new model, where two intrachain interactions are considered: one through the carboxylato in the *anti–syn* conformation (the ferromagnetic one) and another through the malonato skeleton in the *anti–anti* conformation (the antiferromagnetic one). According to the model, the copper(II) chain is made up by isosceles triangles sharing the two vertices of their base, the Hamiltonian describing this situation being:

$$\hat{H} = -\left[J_1 \sum_{i=1}^{n} \hat{S}_{2i} \cdot \hat{S}_{2i-1} + J_1 \sum_{i=1}^{n} \hat{S}_{2i} \cdot \hat{S}_{2i+1} + J_2 \sum_{i=1}^{n} \hat{S}_{2i-1} \cdot \hat{S}_{2i-1}\right]$$

There is no analytical expression to describe the magnetic behaviour of such a copper(II) chain, so we used a general numerical procedure [54] to obtain the values of the magnetic coupling constants. The results were $J_1 = +4.6$ cm^{-1} (for the *anti–syn* carboxylato bridge) and $J_2 = -4.2$ cm^{-1} (through malonato skeleton pathway).

2.2.3. *$[Cu_4(mal)_4(2,4'\text{-}bpy)_4(H_2O)_4]\cdot 8H_2O$ (7) (2,4′-bpy = 2,4′-bipyridine)*

The structure of complex **7** consists of small planar squares with copper(II) ions (Fig. 6) and malonato anions at each corner and side, respectively [37]. The 2,4′-bpy acts as a monodentate ligand being located in the same plane of the $[Cu_4(mal)_4]$ square. The only crystallographically independent copper(II) ion exhibits a slightly distorted square pyramidal surrounding. The carboxylato bridge in *anti–syn* conformation links the copper(II) ions.

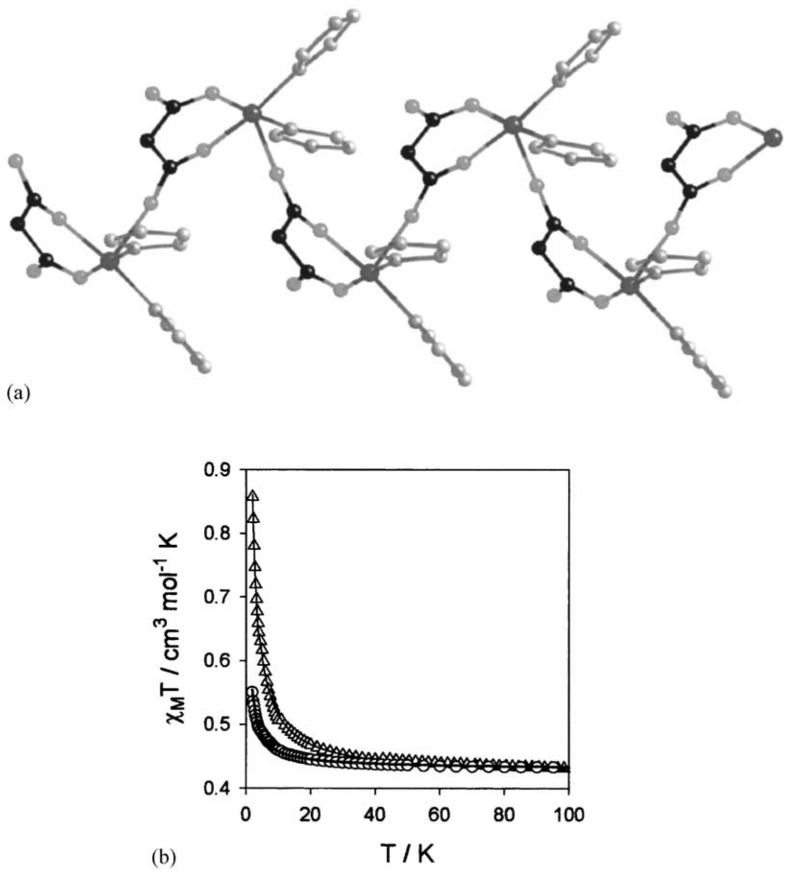


Fig. 4. (a) A view of the chain compound [Cu(Im)$_2$(mal)] (**4**) (b) Thermal dependence of the $\chi_M T$ product for compounds [Cu(Im)$_2$(mal)] (△) (**4**) and [Cu(MeIm)$_2$(mal)] (○) (**5**).

The compound behaves as a magnetically isolated square of four spin doublets interacting ferromagnetically. According to this, the Hamiltonian proposed is:

$$H = -J[S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4]$$

This fit through the expression led to $J = +12.3$ cm^{-1}.

2.2.4. [$Cu_2(mal)_2(H_2O)_2$(4,4′-bpy)] (*8*) (4,4′-bpy = 4,4′-bipyridine)

The compounds **8** [36] (Fig. 7) is made up by small planar squares as those of complex **7** linked through a bis-monodentate 4,4′-bipyridine ligand to form two-dimensional networks. Copper(II) surrounding and carboxylato bridging mode are also those of **7**.

The magnetic properties of compound **8** and **7** are quite similar, except for the antiferromagnetic behaviour coming from the decrease in the χT versus T curve at low-temperatures. The magnetic behaviour of **8** could be described as a quadratic layer of tetranuclear copper(II) units which are antiferromagnetically coupled through the bridging 4,4′-bpy. Since the value of the spin of the tetranuclear copper(II) unit is large enough as to be considered as a classic one ($S \geq 1.8$), the magnetic susceptibility data can be analyzed by means of the expression for a classic spin model derived by Curély [55]. This gives $J = +12.4$ cm^{-1} (for the carboxylate *anti–syn* bridge) and $j = -0.052$ cm^{-1} (through the 4,4′-bpy).

2.2.5. [$Cu_4(mal)_4(pyz)_2$]·$4H_2O$ (*9*) (pyz = pyrazine)

The crystal structure of **9** consists of a three-dimensional arrangement of copper(II) ions bridged by malonate and pyrazine ligands [37] (Fig. 8). The 3D arrangement is formed by layers linked via *anti–syn* carboxylate bridges. The layers are made up with small planar squares, similar to those of **7** and **8**, bound through a bis-monodentate pyrazine. Copper(II) surroundings are square pyramidal and the two different bridging modes present the *anti–syn* conformation.

The experimental measurements of the magnetic properties reveal the coexistence of ferro- and antiferromagnetic interactions. According to the structure three different magnetic exchange pathways can be identified, two carboxylate *anti–syn* bridging modes: J_1 (the responsible of the small squares) and J_3 (the pathway that links the layers); and a pyrazine bridge J_2. However, there is no model to fit the magnetic properties of this three-dimensional compound with three magnetic exchange pathways, although the authors give a roughly evaluation of their magnitude.

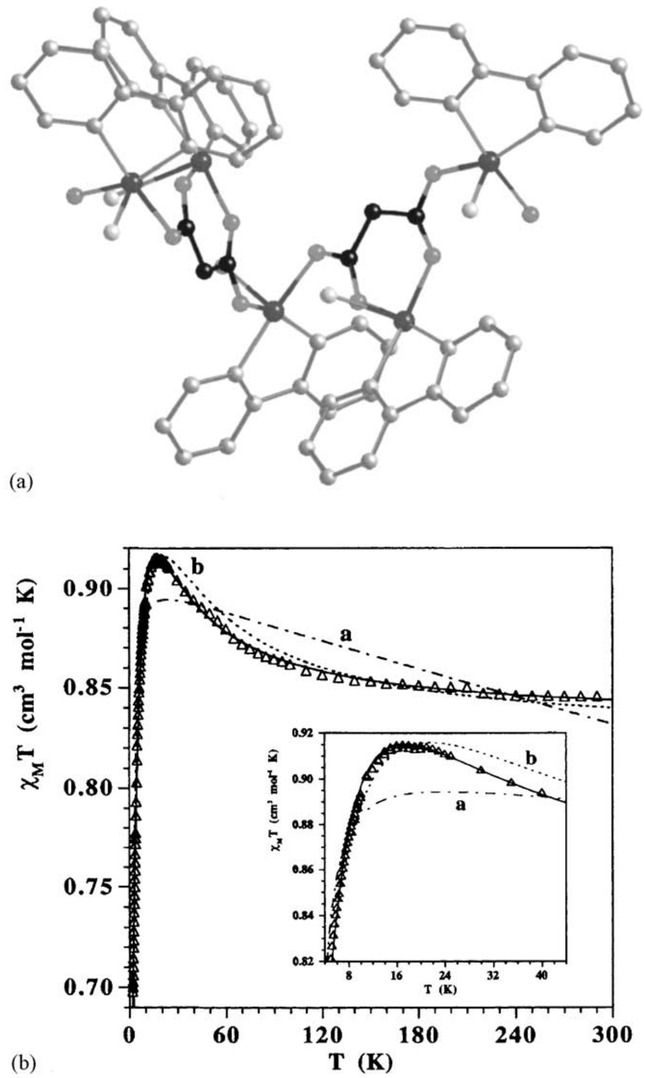


Fig. 5. (a) View of compound $\{[Cu(bpy)(H_2O)][Cu(bpy)(mal)(H_2O)]\}(ClO_4)_2$ (**6**). Hydrogen atoms and the perchlorate anions have been omitted for clarity. (b) Thermal dependence of the $\chi_M T$ product for compound **6**.

3. Magneto-structural correlations

The magnetic orbital at copper(II) atoms is defined by the short equatorial bonds, and it is of the $d_{x^2-y^2}$ type, with possibly some mixture of the d_{z^2} character in the axial position when the trigonal distortion defined by the τ factor [56] (τ ranges from 0, perfect square pyramid, to 1, perfect trigonal bipyramid) becomes important. Following the Kahn's orbital model [57], the magnetic coupling for a copper(II) dimer is decomposed in two terms, one antiferro- and the other ferromagnetic according to $J = J_{AF} + J_F$. The magnitude of the antiferromagnetic term is essentially governed by the square of the overlap integral between the two metal-centred magnetic orbitals, whereas that of the ferromagnetic one is very small.

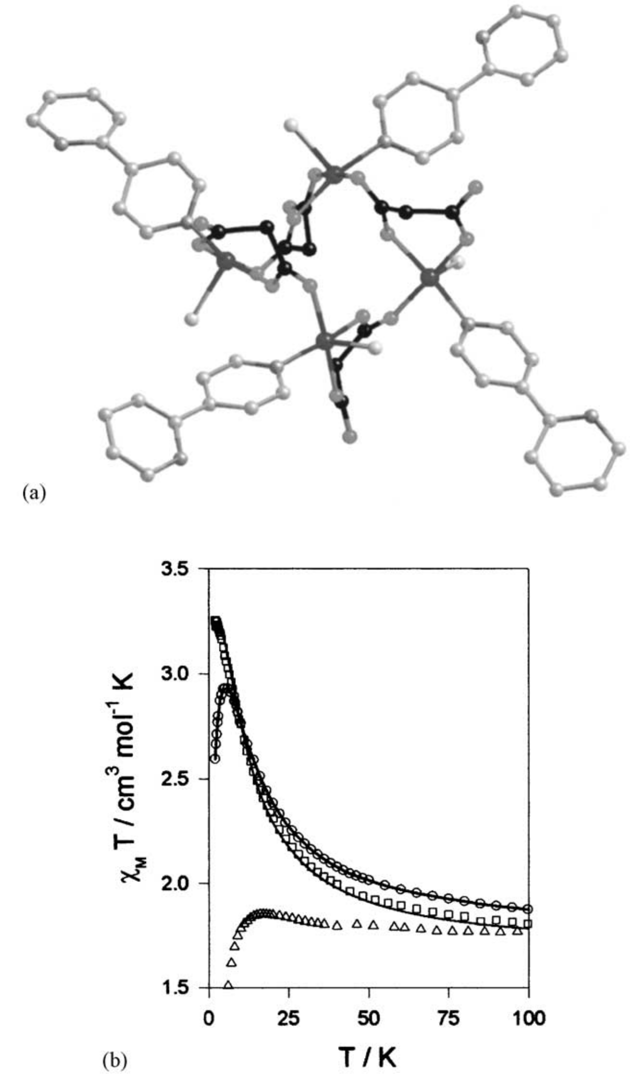


Fig. 6. (a) Perspective view of the tetramer unit of $[Cu_4(mal)_4(H_2O)_4(2,4'\text{-bpy})_4]\cdot 2H_2O$ (**7**). (b) Thermal dependence of the $\chi_M T$ product for compounds $[Cu_4(mal)_4(H_2O)_4(2,4'\text{-bpy})_4]\cdot 2H_2O$ (**7**) (□), $[Cu_4(mal)_4(H_2O)_4(4,4'\text{-bpy})_2]\cdot 2H_2O$ (**8**) (○) and $[Cu_4(mal)_4(pyz)_2]\cdot 4H_2O$ (**9**) (△)

The overlap is minimized when the orthogonality of the magnetic orbitals occurs. This orthogonality could be accidental or strict [57]. The latter involves the transformation of the orbitals in different irreducible representations of the symmetry group adapted to the system (i.e. different magnetic orbitals, such as $d_{x^2-y^2}$ versus d_{xy}, which is usually found in heterometallic complexes). However the accidental deals with the spatial orthogonality of the same magnetic orbitals (see Scheme 2).

The magneto-structural correlations of carboxylate-bridged systems have been studied previously, but in the case of dicarboxylates with a mean interest in oxalate bridged complexes [60]. Then the features achieved in these works have been extrapolated to the rest of dicarboxylates with three, four or more carbon atoms.

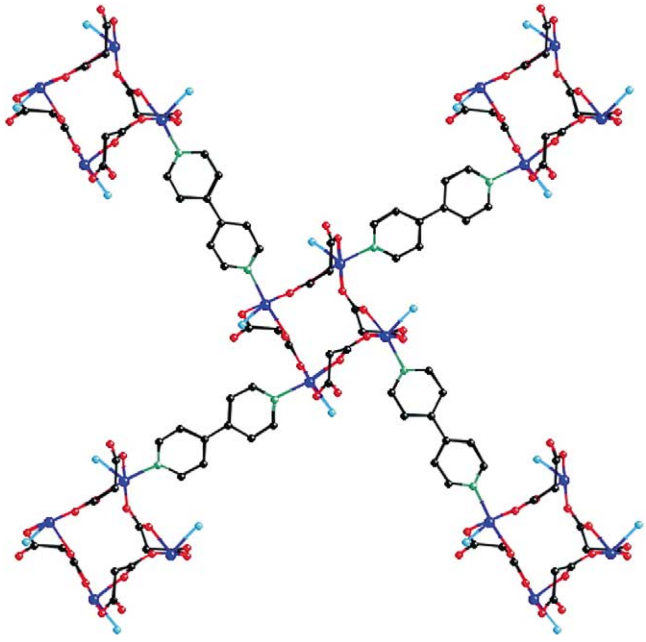


Fig. 7. View of the two-dimensional compound in $[Cu_4(mal)_4(H_2O)_4(4,4'\text{-}bpy)_2]\cdot 2H_2O$ (**8**)

We are going to analyze first our compounds in the light of these assumptions, and then we will introduce other parameters (see Table 1) that cannot be ignored to explain properly the magnetic properties of the compounds.

3.1. On the basis of carboxylate-bridging mode

Carboxylate bridge is a versatile anion that can assume many types of bridging conformations, the most important being *anti–anti*, *anti–syn* and *syn–syn* (Scheme 3). It is assumed that copper(II) complexes with *anti–syn* conformation exhibit very weak magnetic exchange interactions, whereas *syn–syn* and *anti–anti* conformations mediate large and weak to medium antiferromagnetic interactions, respectively [58,59].

According to this, compounds **4** and **5** should exhibit an antiferromagnetic behaviour, but they do not. At the same time, the remaining compounds bridged by a carboxylato in the *anti–syn* conformation should show weak interaction whatever the nature, ranging J from $+3$ to -45 cm^{-1} [61,62]. But, complexes **6**, **7** and **8** have a magnetic exchange as large as $J \approx +12.5$ cm^{-1}. These wrong conclusions are due to an oversimplification of the system produced by the extrapolation of the results from the oxalate complexes.

3.2. On the basis of the relative position of the bridge respect to the copper(II) environment

Attending to the relative positions of the oxygens of the OCO bridge, there are three relative orientations of

Table 1
List of parameters of the compounds

Compound	α_1 (°)	α_2 (°)	Bridge conformation	d_1 (Å)	d_2 (Å)	β (°) [a]	Position of the oxygen bridge atom in copper(II) environment	τ (Cu1) [b]	τ (Cu2) [b]	J (cm^{-1})
1	126.0	120.5	*anti–syn*	1.952	2.383	49.3	equatorial–apical	octahedral	0.05	+1.8
2	126.5	124.8	*anti–syn*	1.941	2.381	56.5	equatorial–apical	octahedral	0.12	+1.2
3A	124.5	116.9	*anti–syn*	1.931	2.185	85.9	equatorial–apical	0.24	0.28	+1.9
3B	124.5	118.4	*anti–syn*	1.945	1.990	85.9	equatorial–equatorial	0.24	0.28	+3.0
4	125.7	226.9	*anti–anti*	1.962	2.394	55.4	equatorial–apical	0.02	0.02	+1.6
5	123.8	228.1	*anti–anti*	1.961	2.270	82.7	equatorial–apical	0.18	0.18	+0.4
6	128.5	127.6	*anti–syn*	1.918	1.978	≈ 80.5	equatorial–equatorial	0.05	0.28	+4.6
7	120.9	111.0	*anti–syn*	1.963	1.986	70.5	equatorial–equatorial	0.15	0.15	+12.3
8	121.3	109.9	*anti–syn*	1.984	1.957	72.6	equatorial–equatorial	0.14	0.14	+12.4

The parameters are defined in Scheme 4.

[a] Angle subtended by the basal planes of the copper(II) ions linked by the carboxylate bridge.

[b] Distortion of the copper(II) environment (see text).

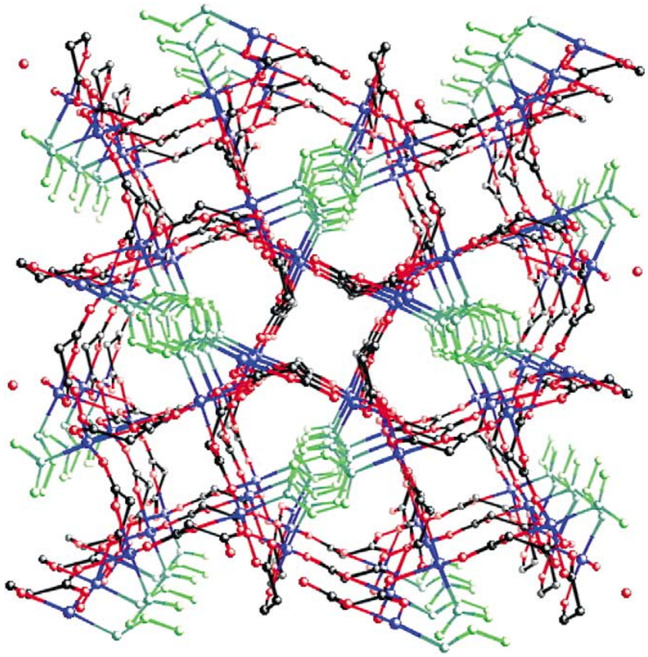


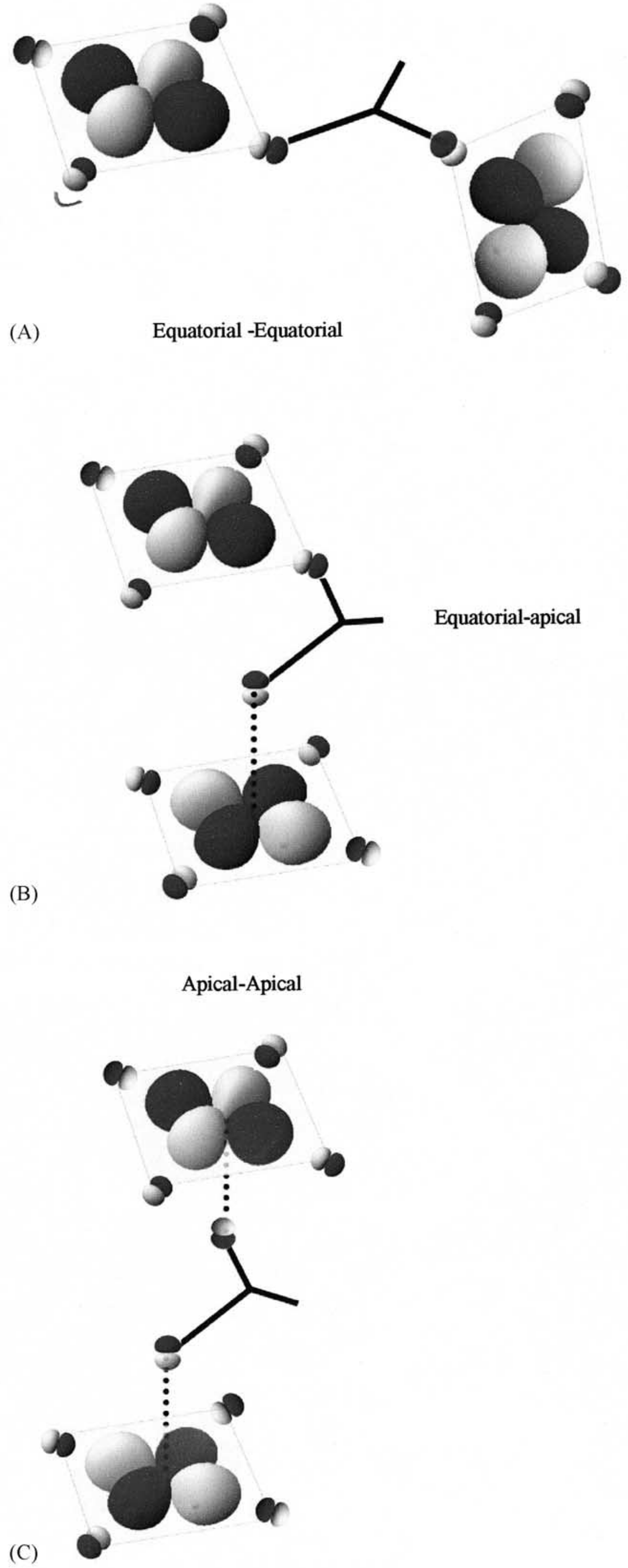
Fig. 8. A view of the 3D structure in compound $[Cu_4(mal)_4(pyz)_2]\cdot 4H_2O$ (**9**) where the square grids layers are stacked along the *c* axis showing the π–π overlap between pairs of pyrazine molecules.

the bridge respect to copper(II) ions involved in the Cu–O–C–O–Cu exchange pathway: equatorial–equatorial (most common in the case of oxalates), equatorial–apical and apical–apical (Scheme 2).

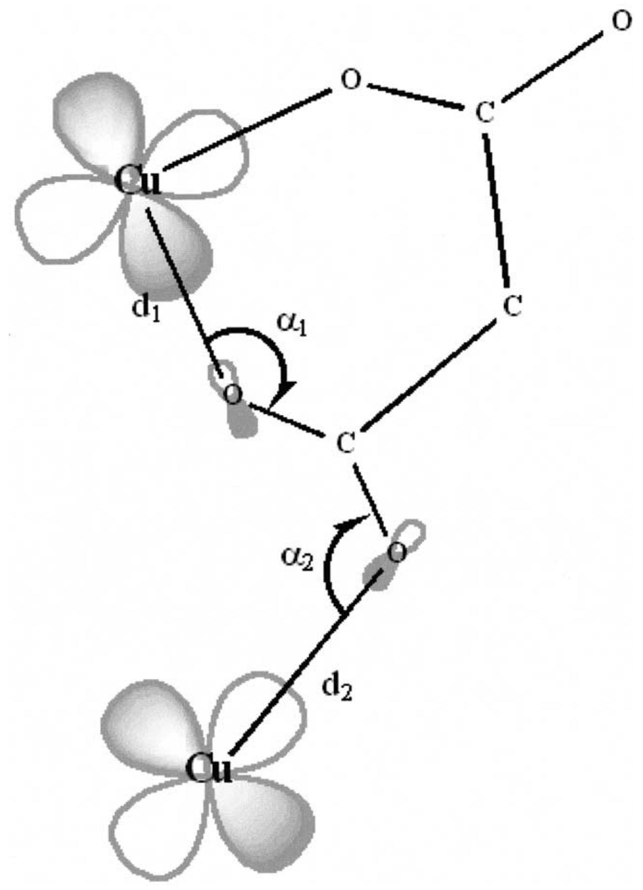
In **6**, **7**, **8** and **3B** the Cu–O–C–O–Cu involves two equatorial oxygen atoms contributing to the largest *J*, because the singly occupied orbitals interact directly through the bridge. At the same time *β* (angle subtended by the basal planes of the interacting copper(II) ions) ranges from 70 to 86° making the orbitals to minimize their overlap in such an extent that the ferromagnetic contribution becomes predominant.

The other complexes **1**, **2**, **4**, **5**, and the bridge **3A** involve equatorial–apical pathway. As far as we know this linkage will always give a weak ferromagnetic interaction if the copper(II) environments are not highly distorted. In the light of structural features, it is evident that the $d_{x^2-y^2}$ copper(II) orbitals are mismatched for interaction to take place between them through the carboxylate group, since the exchange pathway involves an equatorial position on one copper (x^2-y^2 direction) and an axial position on the other copper atom (z^2 direction). Deviations from the idealized symmetry might allow some mixture with the d_{z^2} orbital, but in any case the overlap would be weak. This would lead to a negligible antiferromagnetic contribution so that the ferromagnetic one becomes predominant.

The apical–apical pathway does not connect the magnetic orbitals of the copper(II) ions, then we expect the interaction to be negligible; although the apical–



Scheme 2.



Scheme 4.

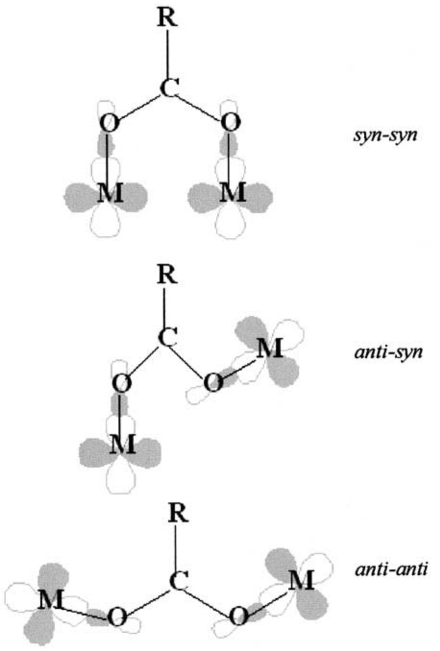
apical pathway has not been yet encountered in our compounds.

3.3. On the basis of other structural parameters

The structural parameters β, and τ can govern the nature and the magnitude of the interaction.

We can see this focusing on compounds **4** and **5**, in which both exhibit the *anti–anti* and apical–equatorial conformation, leading to a ferromagnetic coupling; but **4** shows a greater J value than **5**. From Table 1, the distortion parameter (τ) is 0.02 and 0.18 for **4** and **5**, respectively. This leads to a major z^2 character in compound **5**, and hence a larger overlap and a greater value of the antiferromagnetic contribution. A major distortion could cause this term to be greater than the ferromagnetic one, leading to an overall antiferromagnetic interaction, although the magnitude of the interaction is remained weak.

In compounds with equatorial–equatorial linkages the most important structural parameter is β. If β approximates to 90° the magnitude of the interaction decreases and the ferromagnetic term becomes predominant. But when β deviates from that angle, the antiferromagnetic term grows and can be greater than the ferromagnetic one, the coupling becoming stronger.



Scheme 3.

Other structural parameters could slightly tune the magnitude of the interaction, such as α_2. Thus a trend in this angle could be stated: decreasing α_2, (an increase of the *anti–syn* character) a greater value of the ferromagnetic coupling is encountered, as is observed in **3B**, **6**, **7** and **8** (equatorial–equatorial) and in **1**, **2** and **3A** (equatorial–axial).

However, as can be seen in Table 1, many parameters can be simultaneously responsible of the magnitude of the magnetic interaction.

4. Conclusion

The malonate is a very versatile ligand, allowing the out-of-plane conformation of the *anti–syn* and *anti–anti* modes. Hence, the magneto-structural assumptions applied to the oxalate bridge cannot be longer extended to more flexible ligands such as malonate, due to the oversimplification it implies.

We can conclude that the parameter that governs, in first order, the magnetic interaction between metal centres is the relative position of the carboxylato bridge of the malonate respect to the copper(II) ions: equatorial–equatorial (strong interaction), equatorial–apical (weak interaction) and apical–apical (negligible interaction). Inside this division another parameters become important such as β (angle between copper(II) basal planes) in the equatorial–equatorial, or the distortion in τ the equatorial–apical.

The synthesis and characterization of compounds of this family, and the wideness of this study to other flexible dicarboxylic ligands will allow these remarks to be definitely settled.

Acknowledgements

The financial support provided by the Gobierno Autónomo de Canarias (Project PI2000/135) and the Spanish Dirección General de Investigación (Ministerio de Ciencia y Tecnología), through project BQU2001-3794, are gratefully acknowledged. J.P. also thanks Ministerio de Educación y Cultura for the predoctoral fellowship AP2001-3322 and F.S.D. thanks the Consejería de Educación, Cultura y Deportes (Gobierno Autónomo de Canarias) for a project-fellowship (PI2000/135).

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