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A ferrimagnetic cyclic tetranuclear copper(II) complex: *cyclo*-[tetrakis(μ-η³-hydroxyethanoato-1κ*O*:2κ²*O*′,*O*″)tetrakis-(1,10-phenanthroline)tetracopper] tetranitrate dihydrate. Structural and magnetic properties†

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Received 2nd July 2001, Accepted 11th March 2002
First published as an Advance Article on the web 26th April 2002

The crystal structure and magnetic analysis of a cyclic tetranuclear copper(II) complex with formula $[Cu_4(phen)_4(glyOH)_4](NO_3)_4\cdot 2H_2O$, where phen = 1,10-phenanthroline and glyOH = glycolate are described. Copper atoms are connected through bridging carboxylate groups from chelated glycolate units, forming a butterfly-type framework. Magnetic measurements as a function of temperature (2–300 K) and at 10, 100 and 1000 G were performed. The behaviour of the $\chi T-T$ curves is characteristic of ferrimagnetic-type coupling. Several theoretical magnetic models were tested to study the experimental data. A tetranuclear model of $S = 1/2$ coupled spins in a C_{2v} symmetry, is the one that better describes the magnetic response of the solid product over the whole range of experimental conditions explored. This model allows us to suggest the existence of a very weak antiferromagnetic coupling for two different pairs of Cu(II) centers, and a weak ferromagnetic coupling between those pairs. Besides this, negligible magnetic coupling at the mean field level is proposed. It is important to point out that although the system is homonuclear, with coordination spheres which are chemically equivalent for all the metallic centers, and which shows (at room temperature) equivalent internuclear distances between first neighbouring copper atoms, different types of intramolecular magnetic coupling are inferred. To our knowledge, the complex here studied appears to be the first case of a cyclic tetranuclear Cu(II) system showing global ferrimagnetic coupling.

Introduction

Copper ternary complexes of the type [Cu(N–N)(O–O)], where (N–N) is 2,2′-bipyiridine or 1,10-phenanthroline, have been widely studied in solution due to their enhanced thermodynamic stability, attributed to the π-acceptor character of the N–N ligand. Sigel[1,2] has explained this based on the hard–soft acid–base (HSAB) principle, assuming $Cu(N–N)_{(aq)}{}^{2+}$ is a harder acid than $Cu_{(aq)}{}^{2+}$. This makes the former preferred over the latter by hard bases such as oxygen donors. This effect has also been observed in the solid state through far-IR studies.[3] Also, a recent DFT study has shown that while global hardness calculated for $Cu(N–N)_{(aq)}{}^{2+}$ is not larger than that for $Cu_{(aq)}{}^{2+}$, local hardness on the copper atom is indeed larger when 1,10-phenanthroline is bound to it.[4]

Equilibrium[1,5] and structural[6] studies on complexes of this type have included different O–O ligands, such as acetylacetonate, salicylaldehydate, oxalate, malonate, *etc.* In order to broaden the range of this type of complexes, we are now interested in introducing α-hydroxy acids as the O–O donor ligands. While X-ray diffraction structure determination of related complexes such as aqua(glycolato)(5,6-dimethyl-1,10-phenanthroline)copper(II) nitrate and aqua(lactato)(1,10-phenanthroline)copper(II) nitrate show they are monomeric[7] (the same as all the other known ternary copper complexes with phenanthrolines and O–O donors), the compound described here possesses a rather unusual structure, forming a highly symmetrical cyclic tetranuclear cationic complex, *cyclo*-[tetrakis(μ-η³-hydroxyethanoato-1κ*O*:2κ²*O*′,*O*″)tetrakis(1,10-phenanthroline)tetracopper] tetranitrate dihydrate.

A large number of carboxylate-bridged polynuclear copper complexes have been described in the literature,[8a] although up until now only one cyclic tetranuclear copper species with carboxylate bridges has been reported.[8b] Since magnetic coupling is commonly exhibited by polynuclear carboxylate-bridged complexes, a temperature and magnetic field dependent study of the magnetic susceptibility was performed on the title complex, with very interesting results, that show unusual global ferrimagnetic coupling for a cyclic homonuclear Cu(II) system.

Results and discussion

Crystallography

A summary of crystallographic data is presented in Table 1, and selected geometric parameters in Table 2. The asymmetric unit for the title compound contains one Cu(II) ion, one *o*-phenanthroline ligand, one glycolate ligand, one nitrate ion and 0.5 water molecule, with all atoms in general positions. The cationic moiety, $[Cu(o\text{-}phen)(glyOH)]^+$ lies close to the $\bar{4}$ crystallographic axis of the $P\bar{4}2_1c$ space group, yielding a cyclic tetramer $[Cu_4(o\text{-}phen)_4(glyOH)_4]^{4+}$, depicted in Fig. 1, in which the copper atoms are bridged by carboxylates in a *syn*,*anti* fashion. Each Cu(II) ion is then crystallographically equivalent

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† Electronic supplementary information (ESI) available: the crystal packing in $[Cu_4(o\text{-}phen)_4(glyOH)_4]^{4+}$. See http://www.rsc.org/suppdata/dt/b1/b105735a/

DOI: 10.1039/b105735a

Table 1 Summary of crystallographic data

Empirical formula	$C_{56}H_{48}Cu_4N_{12}O_{26}$
Formula weight	1558.22
Crystal system	Tetragonal
Space group	$P\bar{4}2_1c$
a/Å	20.995(2)
c/Å	7.2370(10)
Volume/Å^3	3190.0(6)
Z, ρ_{calc}/g cm^{-3}	2, 1.623
μ/mm^{-1}	1.409
2θ Range/°	4.00–50.0
Reflections collected	4051
Independent reflections[a]	1956 ($R_{int} = 0.0325$)
Final R indices [$I > 2\sigma(I)$][a]	$R_1 = 0.0401$, $wR_2 = 0.1095$
Final R indices (all data)[a]	$R_1 = 0.0506$, $wR_2 = 0.1159$
Goodness-of-fit, S[a]	1.060

[a] $R_{int} = \Sigma|F_o^2 - \langle F_o^2\rangle|/\Sigma F_o^2$; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F^2_o)^2]^{1/2}$; $S = [\Sigma w(F_o^2 - F_c^2)^2/m - n]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for $[Cu_4(o\text{-phen})_4(glyOH)_4](NO_3)_4{\cdot}2H_2O$ with s.u. in parenthesis[a]

Cul–019#1	1.965(4)	Cul–O15	1.966(4)
Cul–N1	1.994(4)	Cul–N12	2.021(5)
Cul–O18	2.343(4)	O15–C16	1.255(6)
C16–O19	1.271(7)	C16–C17	1.500(8)
C17–O18	1.430(7)	O19–Cul#2	1.965(4)
O19#1–Cul–N1	93.3(18)	O19#1–Cul–O15	90.9(17)
O19#1–Cul–N1	93.3(18)	O15–Cul–N1	174.3(19)
O19#1–Cul–N12	162.2(18)	O15–Cul–N12	94.9(18)
N1–Cul–N12	82.0(18)	O19#1–Cul–O18	106.2(15)
O15–Cul–O18	76.6(15)	N1–Cul–O18	98.6(17)
N12–Cul–O18	91.5(17)		
C16–O15–Cul	120.6(4)	O15–CI6–O19	122.1(5)
O15–C16–C17	121.9(5)	O19–C16–C17	116.0(5)
O18–C17–C16	110.9(5)	C17–O18–Cul	107.5(3)
C16–O19–Cul#2	123.9(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-y + 1, x + 1, -z + 2$. #2: $y - 1, -x + 1, -z + 2$.

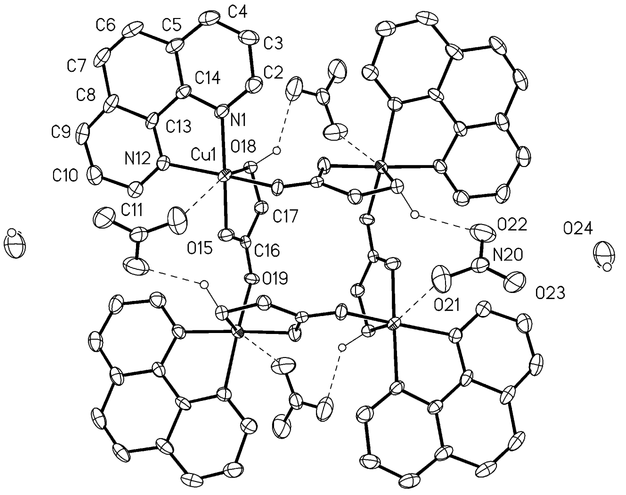

Fig. 1 Cyclic tetrameric unit of $[Cu_4(o\text{-phen})_4(glyOH)_4](NO_3)_4$.

within the tetramer. It is important to mention that attempts to lower the local symmetry by refining the structure in sub-space groups of $P\bar{4}2_1c$ were unsuccessful.

Each Cu atom is bound to the bidentate *o*-phen ligand (NI, N12) and the glycolate fragment through the hydroxyl function (O18) and two O atoms of the carboxylic function (O15 and O19); one of these, O19, arises from the glycolate ligand of a neighbouring Cu atom. In this way, the metal ion displays an almost square pyramidal coordination geometry, remarkably similar to the many known monomeric complexes of the type $[Cu(o\text{-phen})(O–O)]NO_3$.[6] The base of the pyramid is formed by N1, N12, O15 and O19′ (the prime denotes symmetry code $-y + 1, x + 1, -z + 2$), with bond lengths in the expected short range 1.965(4)–2.021(5) Å. The Cu atom is displaced by 0.11 Å out of the mean plane formed by N1, N12, O15 and O19′. Each neighbouring pair of these planes makes an angle of 44.5° with each other. The apical position is occupied by the hydroxyl function, with a Cu1–O18 distance of 2.343(4) Å. Approximately *trans* to O18 appears an O atom of the nitrate ion. However, the separation from the metal center cannot be considered as a bond distance, Cu1–O21 = 2.778(7) Å. Due to its bridging character, the carboxylic group of the glycolate ligand presents a delocalized π system rather than a formal double bond: C16–O15 and C16–O19 distances are similar, 1.255(6) and 1.271(7) Å, respectively.

The four Cu(II) ions in the tetramer do not lie in the same plane, but form a butterfly-type system (Fig. 2), with two Cu atoms above the mean plane formed by the four atoms (displacement of 0.65 Å) while the other two are below this plane (displacement of −0.65 Å). The shortest metal–metal contact is 5.0157(10) Å for first neighbour Cu atoms (*e.g.*, Cu1 and Cu1A) in the cycle, while two opposite Cu atoms (*e.g.*, Cu1 and Cu1C) are separated by 6.8502(13) Å. No short intermolecular contacts are observed in the lattice, the cations being well separated.

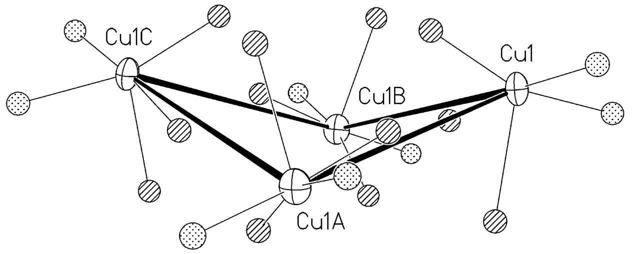

Fig. 2 Butterfly-type system in $[Cu_4(o\text{-phen})_4(glyOH)_4]^{4+}$.

The crystal packing (see ESI †) is stabilized by the stacking of the *o*-phen π systems of equivalent tetramers along the short *c* axis of the tetragonal cell: the shortest separation between the centroids of the aromatic rings in the cell is 3.63 Å, close to the distance between the planes in graphite,[9] 3.35 Å. A number of weak hydrogen bonds which implicate O21, O22 (nitrate ion) and O15 (carboxylic group) also participate in the energetic stability of the overall structure (see deposited CIF for details). The water molecule O24 is included in the hole of the lattice and seems to be free to rotate.

Spectral data

In the infrared spectrum of the complex, consistent with its bridging character,[10,11] $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ appear at 1576 and 1431 cm^{-1} respectively, while ν(C–OH) appears at 1067cm^{-1}.

The diffuse reflectance-electronic spectrum presents a charge-transfer band at 353 nm with a shoulder at 341 nm. This type of absorption has often been associated with dinuclear copper in systems such as $Cu_2(AcO)_4(H_2O)_2$. In the visible region of the spectrum, there is only one broad, skewed band with a maximum at 703 nm, characteristic of d–d transitions in C_{4v} copper complexes.[12]

The X-band EPR spectra of the powdered samples, both at room temperature and at 6.15 K, display an almost isotropic, featureless absorption for which $g = 2.12$ is assigned. At room temperature, the absorption features in the $\Delta H = 10^4$ G range exclude any significant detection of magnetic coupling in the solid product. However, at 6.15 K, a detachment of absorption from $dA/dH = 0$ (both in the low and high magnetic field sides, *ca.* 2000–5000 G range) and associated with the main absorption (centered at 3190.32 G) is observed. These features could be attributed to the existence of magnetic coupling in the sample.

Magnetic results

The experimental data of molar magnetization ($\bar{M}$,emu G mol^{-1} of mononuclear Cu(II) unit) as a function of temperature (K) and for 10, 100 and 1000 G, show an abrupt decrease in the $\bar{M}$ values when going from 2 K to higher temperature values (up to *ca.* 5 K for $H = 10$ G; *ca.* 10 K for $H = 100$ G; *ca.* 30 K for $H = 1000$ G). With a further temperature increase, the $\bar{M}$ values show a very smooth decrease. For the whole range of temperature explored, the $\bar{M}$ values show an increase with ascending the magnetic field. This increase is successively higher with descending temperature. This behaviour is also observed in the experimental $\bar{M}$–H plot for several T values. For the experimental range of the magnetic field explored, there is no evidence for magnetic saturation in the solid product. The same trends are also observed when the magnetic data are plotted in the $\bar{\chi}$ (emu mol^{-1} of mononuclear Cu(II) unit)–T fashion. From these data, 10^{-3} emu mol^{-1} values for $\bar{\chi}$ (at 300 K, and for the three magnetic fields) are obtained.

On the other hand, the $(\bar{\chi})^{-1}$–T curves for all the fields show increasing slopes (within the 50–300 K range) with a decrease in temperature. The inflection in the curves, shown in the low temperature region, suggests that the sample reaches a long range magnetic ordering. This type of behaviour is characteristic of a ferrimagnetic-type coupling.[13,14] The inflection is dependent on the magnetic field value, and it is observed at higher T values as the magnetic field is increased.

The existence of magnetic coupling in the solid product is also inferred from the fitting of the $\bar{\chi} = C/(T - \theta)$ equation to the experimental $(\bar{\chi})^{-1}$–T data for all the fields explored. For the $T > 100$ K region, the negative values of the θ parameter are suggestive of an antiferromagnetic coupling. For $T < 100$ K, the fitting of this same equation to the experimental data (2–100, 2–50 and 2–10 K ranges), gives positive values for θ. Thus, in this same approximation, the positive θ values for the low temperature region are suggestive of ferromagnetic coupling.

In order to perform a more detailed analysis of the magnetic response of the solid product under study, the experimental data were explored in the $(\bar{\chi}T)$–T fashion. Interestingly, and for the three magnetic fields, the $(\bar{\chi}T)$ values first show a decrease with descending temperature, reaching a minimum value at a finite T ($= T_c$) (<50 K, 10 G; ≈ 50 K, 100 G; > 50 K, 1000 G) and then increase at lower temperatures. This behaviour is associated with a ferrimagnetic-type coupling.[13–15] In other words, when going from 300 K to T_c, the $(\bar{\chi}T)$ values decrease is associated with an increase in the population of the electronic states with successively lower spin multiplicity. The $(\bar{\chi}T)$ minimum corresponds to a short range antiferromagnetically ordered state, for which pairs of first neighbour spins are antiparallel, with no correlation between such pairs. When the temperature decreases below T_c, the correlation range increases: the $(\bar{\chi}T)$ increases at those lower T values can be associated with the achievement of a long range paramagnetic-type ordering; for such lower T values, the magnetic behaviour is qualitatively equivalent to ferromagnetic coupling in an electronic spin chain. In fact, the $(\bar{\chi}T)$ features for $T \longrightarrow 0$ K follow an AT^{-x} behaviour, which has also been found for a ferromagnetic chain of $S = 1/2$ local spins.[15] For the whole temperature range explored, the $(\bar{\chi}T)$ values show an increase with the magnetic field intensity.

In the further magnetic study of the tetranuclear compound, several magnetic models were explored. Although the molecular structure of the title compound is known at room temperature, we decided to apply such methodology because the theoretical magnetic models have a noticeable selectivity for the description of magnetic reponses associated with systems which show both different structural arrangements and symmetries.

The first one was the pair of adjacent (first neighbour) $S = 1/2$ coupled spins, through the Bleaney–Bowers equation. The mean field approximation[16] was also considered in this case. The fitting of the corresponding equation to the experimental data ($H = 10$ G with $g = 2.12$, $\rho = 0.0$ and $\bar{\chi}_0 = 0.0022$ emu mol^{-1}) gave $J/k = -2.84 \pm 0.046$ K and $zJ'/k = +\ 4.68 \pm 0.072$ K. In this magnetic model the J parameter is associated with a very weak antiferromagnetic coupling between pairs of first neighbour spins; the J' parameter is interpreted as the exchange energy (of very weak ferromagnetic-type) between a pair of spins as a reference and the mean field generated by its neighbouring (*i.e.*, z) spin-pairs in the solid product. However, the equation belonging to this theoretical magnetic model does not successfully describe the experimental magnetic response of the solid product at both 100 and 1000 G.

The second model we explored was that corresponding to pairs of first neighbour $S = 1/2$ coupled spins in a linear chain, described by the Bonner–Fisher equation.[16] The fitting of this equation (including the mean field approximation) to the experimental data, yielded the following parameters (for $H =$ 10 G and $T =$ 5–200 K; $g = 2.12$, $\rho = 0.0$ and $\bar{\chi}_0 = 0.0011$ emu mol^{-1}): $J/k = -2.9 \pm 0.12$ K and $zJ'/k = +12.81 \pm 0.50$ K. From this model, a very weak antiferromagnetic coupling ($J < 0$) at the intramolecular level, and a weak ferromagnetic-type coupling ($J' > 0$) at the intermolecular level, can be suggested. In the same way as the previous case, this magnetic model is unable to describe the experimental data at both 100 and 1000 G. A closed chain ($N = 4$)[17] of $S = 1/2$ coupled spins with the mean field approximation was also considered. Again as for the two models described before, only the experimental data at $H = 10$ G are reasonably described by this model; for $g =$ 2.12, $\rho = 0.0$ and $\bar{\chi}_0 = 0.0012$ emu mol^{-1} the parameters $J/k =$ -3.16 ± 0.32 K and $zJ'/k = +2.92 \pm 0.16$ K were obtained. Here, $J < 0$ would be in concordance with the existence of a very weak antiferromagnetic coupling at the intramolecular level and $J' > 0$ would have the same meaning as before.

The next model we studied was that corresponding to tetranuclear units of $S = 1/2$ coupled spins, in several symmetries. First, a cubane-type model was explored, in which two pairs of $S = 1/2$ spins show both intrapair and interpair couplings within a T_d symmetry ($J_A = J = J_B = J'$) and in a mean field approximation. The fitting of the equation[15] to the experimental data (for $H = 10$ G, $g = 2.12$ and $\rho = 0.0$) gave $J/k = -3.43 \pm 0.06$ K, $zJ''/k = +2.55 \pm 0.05$ K and $\bar{\chi}_0 = 0.00498 \pm 0.00006$ emu mol^{-1}. This means that both a very weak antiferromagnetic coupling at the intramolecular level ($J < 0$) and a very weak ferromagnetic coupling at the mean field level ($J'' > 0$) can be proposed. Although this magnetic model predicts the existence of both a $\bar{\chi}T$ minimum (<50 K) and a $\bar{\chi}T$ inflection (2–10 K) in general agreement with the experimental data for $H = 10$ G, it is unable to describe the corresponding ones at 100 and 1000 G.

After this, the $|J_A(=J)| \neq |J_B(=J')|$ case (S_4 symmetry[18]) was considered. Here, with the same methodology and for $H = 10$ G, the parameters $J/k = -7.42 \pm 0.55$ K, $J'/k = +11.30 \pm 1.18$ K, $zJ''/k = +0.54 \pm 0.05$ K and $\bar{\chi}_0 = 0.0049 \pm 0.00004$ emu mol^{-1} were obtained. Also, a better fitting than the fomer case (T_d symmetry) was achieved (for example, the $\bar{\chi}T$ minimum is at 37.4 K; the $\bar{\chi}T$ inflection at *ca.* 6.0 K). With these results, we can suggest that the cubane-type tetranuclear model within a S_4 symmetry predicts the existence of a very weak antiferromagnetic coupling ($J < 0$) between first neighbour pairs of $S =$ 1/2 spins and a weak ferromagnetic coupling ($J' > 0$) between second neighbour pairs. This model also predicts a negligible mean field coupling (*i.e.*, intertetranuclear, defined by the J'' parameter) in the solid product. However, this magnetic model is also unsuccessful in describing the experimental magnetic response of the product at both 100 and 1000 G.

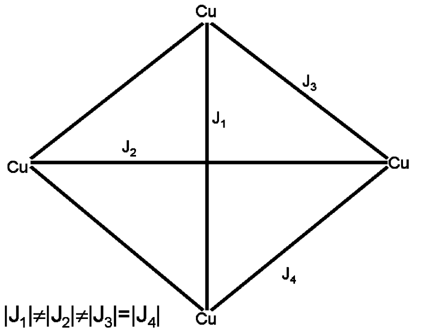

Fig. 3 Scheme of the magnetic model for a tetranuclear Cu system with C_{2v} symmetry.

A third tetranuclear model within a C_{2v} symmetry was considered, which is schematically represented in Fig. 3. The equation fitted to the $\bar{\chi}T$ *vs.* T experimental values was:[18]

$$\bar{\chi} = \frac{2N\beta^2 g^2}{kT} \left[\frac{5e^{-E_Q/kT} + e^{-E_{T1}/kT} + e^{-E_{T2}/kT} + e^{-E_{T3}/kT}}{5e^{-E_Q/kT} + 3e^{-E_{T1}/kT} + 3e^{-E_{T2}/kT} + 3e^{-E_{T3}/kT} + e^{-E_{S1}/kT} + e^{-E_{S2}/kT}} \right] (1-\rho) + \rho \frac{N\beta^2 g^2}{2kT} + \bar{\chi}_0 (1-\rho)$$

in which the E_i, are combinations of the different magnetic coupling parameters (J_i). ρ is the mole fraction of $S = 1/2$ non-coupled spins, $\bar{\chi}_0$ is the molar magnetic susceptibility (emu mol^{-1}) associated with the temperature independent paramagnetism, g is the g-tensor, β is the Bohr magneton, N the Avogadro number and k the Boltzmann constant. These symbols have the same meaning in all the models explored throughout this study.

The magnetic parameters obtained for $H = 10$ G, $g = 2.12$ and $\rho = 0.0$, were: $J_1/k = -2.47 \pm 1.60$ K, $J_2/k = -10.37 \pm 1.09$ K, $J_3/k = J_4/k = +11.36 \pm 0.58$ K, $zJ'/k = +0.46 \pm 0.01$ K and $\bar{\chi}_0 = 0.0074 \pm 0.00003$ emu mol^{-1}. From these results, the tetranuclear model within a C_{2v} symmetry and with the mean field approximation, allows us to suggest the existence of very weak antiferromagnetic couplings ($J_1, J_2 < 0$) between different first neighbour pairs of $S = 1/2$ spins; $J_3 = J_4$ is associated with the existence of weak ferromagnetic coupling ($J_3 = J_4 > 0$) between second neighbour pairs. J' is in agreement with the suggestion of a negligible ferromagnetic coupling ($J' > 0$) at the mean field level. A significant improvement on the theoretical description of both the $\bar{\chi}T$ minimum (*ca.* 45 K) and the $\bar{\chi}T$ inflection (*ca.* 3 K) is obtained when the 1.5–100 K range is considered. In such a fitting process, several parameters do not show significant changes.

In an attempt to prove the confidence of this last magnetic model, a C_2 symmetry model was also explored.[18] In this case, the fitting results were excellent, but the statistical errors in the magnetic parameters were significant.

We proceeded to complete the analysis by using the tetranuclear model in C_{2v} symmetry for the $H = 100$ G and 1000 G cases. For $H = 100$ G and $T = 2$–200 K, and considering $g = 2.12$, $\rho = 0.0$ and $\bar{\chi}_0 = 0.00649$ emu mol^{-1}, the magnetic parameters obtained were: $J_1/k = -1.36 \pm 4.22$ K, $J_2/k = -0.15 \pm 15.60$ K, $J_3/k = J_4/k = +7.62 \pm 1.39$ K and $zJ'/k = +0.013 \pm 0.00014$ K. Several fitting processes were performed in an attempt to reduce the statistical error in the magnetic parameters and to detect the interdependence between the different coupling parameters. For $H = 100$ G and $T = 5$–100 K, and considering $g = 2.12$, $\rho = 0.0$, $\bar{\chi}_0 = 0.00649$ emu mol^{-1}, $J_1/k = -1.00$ K, $J_3/k = J_4/k = +7.66$ K and $zJ'/k = 0$ K, we obtained $J_2/k = -0.68 \pm 0.08$ K. For the 2–100 K range, the fitting process predicts a $\bar{\chi}T$ minimum at *ca.* 48 K and a $\bar{\chi}T$ inflection at *ca.* 2.5 K, in agreement with the experimental data.

For $H = 1000$ G, the tetranuclear model with a C_{2v} symmetry also describes the experimental magnetic response of the sample. For $g = 2.12$, $\rho = 0.0$, $\bar{\chi}_0 = 0.0039$ emu mol^{-1} and $zJ'/k = +0.014$ K in the $T = 2$–250 K range, the resulting magnetic parameters were: $J_1/k = -1.39 \pm 5.92$ K, $J_2/k = -0.23 \pm 21.42$ K and $J_3/k = J_4/k = +7.89 \pm 1.85$ K. In the same way as for $H = 100$ G, we performed several fitting processes; for $T = 2$–100 K, $g = 2.12$, $\rho = 0.0$, $\bar{\chi}_0 = 0.0039$ emu mol^{-1}, $J_1/k = -1.57$ K, $J_3/k = J_4/k = +8.00$ K and $zJ'/k = +0.014$ K, we obtained $J_2/k = -0.14 \pm 0.11$ K. The theoretical $\bar{\chi}T$–T curve describes the $\bar{\chi}T$ minimum at *ca.* 63 K; the $\bar{\chi}T$ inflection is at a value below 2 K in agreement with the experimental data. Several attempts at the fitting process by considering various values for ρ and $\bar{\chi}_0$ within this symmetry were systematically performed, without positive results. Although the $\bar{\chi}_0$ values reported here for the C_{2v} symmetry show numeric differences with those from the $\bar{\chi}$–T data, both series of values are of the same order of magnitude (10^{-3} emu mol^{-1}).

When all the fittings performed with the equation in C_{2v} symmetry were compared, the most representative one is that corresponding to $H = 1000$ G. This is shown in Fig. 4.

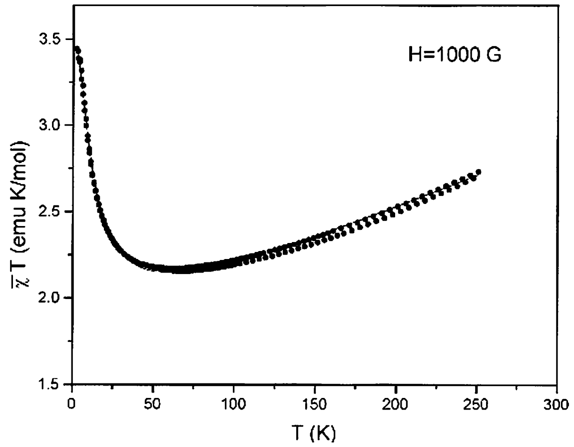

Fig. 4 Experimental (···) and theoretical (—, belonging to the C_{2v} tetranuclear magnetic model) $\bar{\chi}T$–T values for [Cu$_4$(phen)$_4$(glyOH)$_4$]-(NO$_3$)$_4$·2H$_2$O. $\bar{\chi}$ values are in emu mol^{-1} of tetranuclear Cu(II) system units.

When the whole set of magnetic studies is analyzed, we conclude that the tetranuclear model of $S = 1/2$ coupled spins in a C_{2v} symmetry, is the one that better describes the magnetic response of the Cu(II) compound for the experimental conditions investigated. This model allows us to suggest the existence of a very weak antiferromagnetic coupling for two different pairs of Cu(II) centers, and a weak ferromagnetic coupling between those pairs. Besides this, a negligible magnetic coupling at the mean field level is proposed. It is important to point out that nevertheless the system is homonuclear and with coordination spheres which are chemically equivalent for all the metallic centers at room temperature, different types of intramolecular magnetic coupling are inferred from the whole range ($T = 2$–300 K; $H = 10$, 100 and 1000 G) of the experimental conditions explored.

It is important to point out, that for the global ferrimagnetic coupling shown by the Cu(II) compound under study, none of the cyclic tetranuclear Cu(II) systems reported to the present date[8b,18,19] shows this type of magnetic behaviour. Only a polynuclear Cu(II) system (linear chain)[14t] shows ferrimagnetism. This feature has been attributed to the existence of different magnetic couplings (ferromagnetic and antiferromagnetic-types) at the intramolecular level, produced by the alternation in the metallic coordination modes of the azide bridging ligands. One of the possible explanations for the ferrimagnetic behaviour shown by the tetranuclear compound [Cu(II)(1,10-phen)($OHCH_2CO_2^-$)]$_4$(NO_3^-)$_4$·$2H_2O$, is the one associated with the existence of spin polarization[15b] at the intramolecular level. A neutron diffraction study at variable T would undoubtedly contribute to the fine elucidation of this aspect.

Finally, it is also important to remark that despite the lack of analytical expressions of χT (T) for ferrimagnetic closed chains of S = 1/2 spins, the use of magnetic models for pairs of S = 1/2 coupled spins showing several structural arrangements and symmetries, has allowed us to study some of the magnetic properties of the solid product. The confidence of the tetranuclear model of S = 1/2 coupled spins within a C_{2v} symmetry in the global description of the magnetic response of the tetranuclear Cu(II) compound is remarkable, being better than the one of S_4 symmetry, which could be thought of as a more appropriate one due to the structural features (based in fixed symmetry considerations) from both the molecular and crystalline structure determinations at room temperature.

Experimental

Preparation of the complex

1 mmol of $Cu(NO_3)_2$·$2.5H_2O$ was dissolved in 15 mL of MeOH. To this solution, 1 mmol of 1,10-phenanthroline (previously dissolved in 10 mL of MeOH) was added with constant stirring. 1 mmol of glycolic acid was neutralized with 1 mmol of $NaHCO_3$ in the minimum necessary amount of water. The latter solution was added to the Cu(II)–phenanthroline mixture and the intense blue color dimmed to a light blue. The solution was left standing at room temperature, until pale blue crystals were formed, which were vacuum filtered and air dried. Elemental analysis was performed by Desert Analytics, Tucson, AZ. Calcd. for $C_{28}H_{24}Cu_2N_6O_{13}$: C, 43.13; H, 3.08; N, 10.78. Found: C, 43.95; H, 3.17; N, 10.56%.

Spectra

Pellet manufacture with all commonly used crystalline salts resulted in a clear decomposition of the sample, so mid IR vibrational spectrum was recorded on a single crystal using a 1600 Perkin-Elmer FT-IR spectrophotometer coupled with a Perkin-Elmer FT-IR microscope. Diffuse reflectance-electronic spectrum was obtained in a Cary 5E UV-VIS-NIR spectrophotometer in the 200–1000 nm range. X-Band EPR spectra for powdered samples were obtained at 293 K (9.7859 GHz) and at 6.15 K (9.4777 GHz) in an ER200D-SRC Bruker spectrophotometer.

X-Ray crystallography and structure solution

The diffraction data were collected[20] at 298 K on a Siemens P4 diffractometer, using graphite monochromatized Mo-K$_\alpha$ radiation (λ = 0.71073 Å) and the $\theta/2\theta$ scan mode at variable scan speed in ω (4–60° min^{-1}) in the 4–50° 2θ range. Because of the regular needle shape of the crystal, date were not corrected for absorption. The structure was solved by direct methods and Fourier difference maps.[21] The crystallization water molecule O24 was found to be disordered and was refined with a site occupation factor fixed to 1/2. H atoms were placed on idealized positions and refined isotropically using a riding model, except for the H atom of the hydroxyl group, H18, and H atoms of the water molecule O24, which were found on difference maps and refined as remaining H atoms. The complete model (227 parameters) was refined without constraints nor restraints with anisotropic thermal parameters for non-H atoms. The refinement of the Flack parameter indicated some twinning of the crystal, which was modeled using two components with opposite absolute configuration with a ratio 89 : 11.

CCDC reference number 182218.

See http://www.rsc.org/suppdata/dt/b1/b105735a/ for crystallographic data in CIF or other electronic format.

Magnetic measurements

Magnetization (M) of the polycrystalline solid was measured with a SQUID Quantum Design MPMS-5 system at 10, 100 and 1000 G in the 2–300 K range, in both an ascending and descending manner. Experimental M values were carefully corrected for the cell magnetic contribution, and molar magnetic susceptibilities were also meticulously corrected for the molar diamagnetic contribution of the product.

Acknowledgements

The authors are indebted to Dr Francisco Morales-Leal and Professor Roberto Escudero (IIM, UNAM) for the magnetic measurements carefully performed.

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