Discrete trinuclear copper(II) compounds as building blocks: the influence of the peripheral substituents on the magnetic coupling in oxamato-bridged complexes†

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Two new trinuclear copper(II) complexes without end-capping ligands, (Bu4N)2[Cu(dmso)2{Cu(dnopba)(dmso)}2] (1) and (Bu4N)2[Cu(dmso)2{Cu(dcopba)(dmso)}2] (2) [dnopba = 4,5-dinitro-ortho-phenylenebis(oxamate), dcopba = 4,5-dichloro-ortho-phenylenebis(oxamate), Bu4N+ = tetra-n-butylammonium and dmso = dimethylsulfoxide], were synthesized and their structures were determined by single crystal X-ray diffraction. The crystal structures of 1 and 2 consist of two outer bis(oxamato)(dmso)cuprate(II) units which act as bidentate ligands toward a trans-bis(dmsos)coppper(II) inner entity leading to centrosymmetric tricopper(II) complexes with copper-copper separations across the oxamate bridges of 5.1916(3) Å (1) and 5.1776(3) Å (2). The peripheral copper(II) ions in 1 and 2 are five-coordinate in somewhat distorted square pyramidal environments with a dmso molecule filling the apical position whereas the inner copper(II) ion is six-coordinate in an elongated octahedral environment with two dmso molecules in the axial sites. The investigation of their magnetic properties in the temperature range 2.0–300 K shows the occurrence of a strong intramolecular antiferromagnetic coupling between the copper(II) ions through the oxamate bridges [J1 = −296(1) cm⁻¹ (1) and −334(1) cm⁻¹ (2), the Hamiltonian being defined as $\hat{H} = -J_1 \hat{S}_{Cu1} \hat{S}_{Cu2} + \hat{S}_{Cu2} \hat{S}_{Cu1}$], which leads to a low-lying spin doublet at low temperatures. Density functional theory calculations (DFT) have been used to substantiate these magnetic couplings and also to analyse the influence exerted on these interactions by the type of substituent at the 4,5-positions from the phenylene ring of the bis(oxamate) ligand.

1. Introduction

The control of the dimensionality of molecular architectures based on the manipulation of chemical bonds in the solid state is one of the major goals of synthetic chemists in the rational design of multifunctional magnetic compounds.1 Among several strategies employed, molecular-programmed self-assembly methods where specifically tailored multitopic ligands2 or metal complexes (complex-as-ligand)3 coordinate to fully solvated metal ions or metal complexes with partially blocked coordination sites have been proven to be effective toward the preparation of Single Molecule Magnets (SMMs). The better control of the degree of the nuclearity and dimensionality of the magnetic systems achieved through the complex-as-ligand strategy is well illustrated by the impressive magneto-structural studies carried out with oxalate-1,1d,e,A cyanide-5 and oxamate/oxamidate-containing precursors.6 The good donor properties, great stability and remarkable ability of these polyatomic ligands to mediate relatively strong magnetic interactions between the paramagnetic centres connected through them are the reasons for their intensive use in molecular magnetism.7–9

The easy functionalization of the amide nitrogen atom from the oxamate or oxamidate has allowed the programmed

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synthesis of multifunctional molecule-based magnetic materials such as Single Ion Magnets (SIMs), Single-Molecule Magnets (SMMs), chiral Single Chain Magnets (CSCMs), chiral three-dimensional metal-organic polymers (CMOPs), redox/photo-magnetic switches, magnetic nanowires, porous/luminescent magnets, magnetic sensors of small guest molecules, pH-triggered switches for the reversible formation of emulsions, enantioselective self-assembled hexacopper(II) rings together with theoretical calculations to analyse the influence of the x and y substituents on the intramolecular magnetic coupling.

2. Experimental

2.1. Materials

All reagents used were of analytical grade, purchased from commercial sources and used as received. The diethyl ester 4,5-dinitro-ortho-phenylenebis(oxamic acid) (Et2H2dnopba) and the Bu4N][Cu(dcopba)]-3H2O and (Bu4N)2[Cu-dnopba]-3H2O precursors were prepared as described previously.

Caution! Although no problems were encountered in this work, care should be taken when using the potentially explosive perchlorate anion in the presence of organic matter.

2.2. Synthesis of (Bu4N)2[Cu(dmso)2{Cu(dnopba)(dmso)}2](1)

A dmso solution (17 cm3) of Cu(ClO4)2·6H2O (157 mg, 0.42 mmol) was added dropwise to another dmso solution (17 cm3) of Cu(ClO4)2·6H2O (157 mg, 0.42 mmol) under continuous stirring for half an hour. The resulting solution was filtered off to discard any small amount of solid particles and allowed to stand in a hood at room temperature. Greenish brown crystals of 1 were formed after a week. They were collected by filtration, washed with small amounts of dmso and dried under reduced pressure. Yield ca. 86%. Anal. Calcd for C60H100Cu3N6O16S4: C, 43.67; H, 6.50; N, 8.42; Cu, 11.50. Found: C, 43.40; H, 6.20; N, 8.39; Cu, 11.50. IR peaks (KBr/cm−1): 1681, 1624, 1599, 1568, 1026 and 793.

2.2. Synthesis of (Bu4N)2[Cu(dmso)2(Cu(dcopba)(dmso))]2 (2)

This compound was prepared by following the same procedure used for 1: Cu(ClO4)2·6H2O (50 mg, 0.13 mmol) and (Bu4N)2[Cu(dcopba)]-3H2O (157 mg, 0.49 mmol) each were dissolved in 10 cm3 of dmso. The green crystals formed after several days were filtered off, washed with dmso and dried under reduced pressure. Yield ca. 77%. Anal. Calcd for C60H100Cu3N6O16S4: C, 44.43; H, 6.21; N, 5.18; Cu, 11.75. Found: C, 43.67; H, 6.50; N, 4.99; Cu, 11.92. IR peaks (KBr/cm−1): 1681, 1624, 1599, 1568, 1026 and 793.

2.3. Physical measurements

Elemental analyses (C, H, N) were performed with a Perkin-Elmer 2400 analyser and the copper contents were determined by atomic absorption spectrometry. Infrared spectra were recorded with a Perkin-Elmer FTIR spectrometer as KBr pellets in the 400–400 cm−1 region. Magnetic susceptibility data were carried out on polycrystalline samples of 1 and 2 in the
temperature range 2.0–300 K with a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet and using applied dc fields of 0.1 T (T ≥ 100 K) and 500 G (2.0 ≤ T < 100 K). Corrections for the diamagnetism of the constituent atoms and the sample holder were done. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [60 × 10⁻⁶ cm³ mol⁻¹ per copper(u) ion].

### 2.4. Computational details

Calculations were performed through the Gaussian09 package using the B3LYP functional and the quadratic convergence approach. Triple-ζ and double-ζ all electron basis sets, as proposed by Ahlrichs et al., were used for the metal ions and for the rest of atoms, respectively. An approach based on the use of broken-symmetry (BS) functions built from localized orbitals was used to simulate the electronic effects of the surrounding molecules.

#### 2.5. X-ray crystallography

Diffraction data for 1 were collected at 120 K on an Oxford Diffraction GEMINI A-Ultra diffractometer equipped with an Atlas CCD detector using monochromatized Mo-Kα radiation. The CrysAlis CCD and CrysAlis RED (CrysAlis Pro, 2006) programs were used for data collection, cell refinement, absorption corrections and data reduction. Diffraction data for 2 were collected at 120 K on an Enraf-Nonius KappaCCD diffractometer with graphite monochromatized Mo-Kα. The final unit cell parameters were based on all reflections. Data collection was performed using the COLLECT software; integration and scaling of the reflections were carried out with the HKL Denzo-Scalepack software. Structures of 1 and 2 were solved using charge-flipping algorithm (SUPERFLIP) and direct methods (SIR92), respectively. The structures were refined by full-matrix least-squares through SHELXL-2013. All hydrogen atoms were modelled isotropically and assigned to idealized positions using the SHELXL riding model. The dmso molecule linked to the Cu(1) atom in 1 is disordered. Structural analysis and drawings were done using the ORTEP3 and MERCURY softwares. Data collection parameters, structure solution and refinement details are listed in Table 1 whereas selected bond lengths and angles are given in ESI Table S1. Crystallographic data for the structural analysis of the compounds discussed here have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, and are available on request quoting the deposition numbers CCDC 951150 and 951253, for 1 and 2, respectively.

### 3. Results and discussion

#### 3.1. Description of the structures of 1 and 2

The reactions between the fully solvated copper(u) ions and the [Cu(dnopba)]²⁻ or [Cu(dcopba)]²⁻ precursors in dmso solution afforded two new centrosymmetric trinuclear systems of formula (Bu₄N)₂[Cu(dmso)₂(Cu(dnopba)(dmso))]₂ (1) and (Bu₄N)₂[Cu(dmso)₂(Cu(dcopba)(dmso))]₂ (2). 1 and 2 crystallize in the P1 space group with very similar unit cell parameters (see Table 1). Interestingly, the crystals of 1 and 2 are isomorphous in spite of having different substituents in the aromatic ring. The charged entities in 1 and 2 are similarly self-assembled, generating crystal packings in which the anionic supramolecular synthons do not depend on the aromatic substituents (see Fig. 1). The structures of the tricopper(u) units of 1 and 2 exhibit a linear arrangement with the copper(u) ion connected by bis-bidentate oxamate groups (see Fig. 2).

Two crystallographically independent copper(u) ions [Cu(1) and Cu(2)] occur in 1 and 2. The outer Cu(1) atom in 1 and 2 is five-coordinate in a somewhat distorted CuN₅O₅ square pyramidal environment, the value of the trigonality parameter \( \tau \).
Fig. 1 Projections of the crystal packing of 1 (a) and 2 (b) onto the bc plane. All hydrogen and the disordered atoms were omitted for clarity. Colour code: copper(II) ions (red), tetra-n-butylammonium cations (blue) and the non-metallic part of the trinuclear units (green).

Fig. 2 Perspective drawings of the tricopper(II) units of 1 (a) and 2 (b). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown for the sake of clarity. Symmetry code: (i) = –x, –y, –z.

being 0.07 (1) and 0.09 (2) [τ = 0 and 1 for square pyramidal and trigonal bipyramidal surroundings, respectively]. The basal positions around Cu(1) are occupied by two amidate-nitrogen [N(1) and N(2)] and two carboxylate-oxygen [O(3) and O(4)] atoms from two oxamate ligands whereas the apical site is filled by an oxygen atom [O(7)] from a dmsm molecule. Cu(1) is shifted by 0.192(0) (1) and 0.169(2) Å (2) from the mean basal plane toward the apical site. The geometrical constraints caused by the occurrence of three-fused five-membered chelate rings subtended by the dcpoba (1) and dncopa (2) ligands at the Cu(1) account for severe distortion of the ideal basal plane at the metal environment: an opening at the less constrained O(3)–Cu(1)–O(4) angle [109.87(6) (1) and 108.58(7)° (2)] whereas the bite angles at the 5-5-5 fused chelate ring are smaller than 90° [values in the ranges 81.90(7)–83.97(7) (1) and 82.58(9)–84.50(8)° (2)]. The values of the Cu(1)–N(1) [1.913(2) (1) and 1.909(2) Å (2)] and Cu(1)–O(3) [1.942(1) (1) and 1.941(2) Å (2)] bond distances are slightly smaller than the corresponding distances Cu(1)–N(2) [1.940(2) (1) and 1.941(2) Å (2)] and Cu(1)–O(4) [2.044(2) (1) and 2.034(2) Å (2)] because of the different coordination modes of the two oxamate fragments, one of them being bidentate [through N(1) and O(3) toward Cu(1)] and the other being bis-bidentate [across N(2) and O(4) toward Cu(1) and O(6) and O(6) toward Cu(2)]. All these bond lengths in the basal plane are shorter than the apical Cu(1)–Odmso one [2.300(2) (1) and 2.343(2) Å (2)].

The inner Cu(2) atom in 1 and 2 is six-coordinate in an CuO6 elongated octahedral surrounding. Two carbonyl(amidate)-oxygen [O(5) and O(5)\textsuperscript{a}] and two carboxylate-oxygen [O(6) and O(6)\textsuperscript{a}] atoms from two oxamate ligands build the equatorial plane whereas two dmsm molecules occupy the axial sites. The equatorial Cu(2)–O_{oxamate} distances [1.967(1) (1)/1.984(2) Å (2) for Cu(2)–O(5) and 1.996(1) (1)/1.981(1) Å (2) for Cu(2)–O(6)] are shorter than the axial Cu(2)–O_{oxamate} interactions [2.323(2) (1) and 2.367(2) Å (2) for Cu(2)–O(8)] illustrating the elongation of the octahedral surrounding around Cu(2). The values of the dihedral angle between the mean basal planes of Cu(1) and Cu(2) are 14.07(4) (1) and 16.18(5)° (2), and their shifts from the mean plane of the oxamato bridge are 0.143(1) (1)/0.115(9) (2) Å [Cu(1)] and 0.365(1) (1)/0.380(7) Å (2) [Cu(2)].

The tricopper(II) units are well isolated from each other by the bulky tetraethylammonium cations, the shortest inter-trinuclear copper–copper distances [values above 7.7 Å] being greater than the Cu(1)–Cu(2) separation through the oxamate bridge [5.1916 (1) and 5.1776 Å (2); see Fig. 3]. Supramolecular 2D networks are formed by trinuclear units parallel to the crystallographic (112) plane. These parallel planes are separated by 6.335(64) (1) and 6.429(54) Å (2). Fig. 4 illustrates that the closest stacked trinuclear units are more shifted away from each other along opposite [11–1] and [–1–11] directions in 1 than in 2. Consequently the distances of Cu\textsuperscript{ii}–Cu\textsuperscript{ii} [7.6610 Å] ≈ Cu\textsuperscript{ii}–Cu\textsuperscript{ii} [7.7000 Å] in 1, whereas Cu\textsuperscript{ii}–Cu\textsuperscript{ii} [8.6184 Å] > Cu\textsuperscript{ii}–Cu\textsuperscript{ii} [8.7124 Å] in 2 (see symmetry and labels in Fig. 3b).

The largest deviation from the mean planes of the bis(oxamate) ligands (the chloro and nitro substituents being excluded) are 0.139(5) [O(6)] and 0.139(9) Å [O(2)] (dnopa) and 0.191(3) [O(6)] and 0.152(2) Å [O(3)] (dcpoba). The outer carbon–oxygen bond lengths of the dcpoba and dncopa ligands are somewhat shorter [values in the narrow range 1.209(3)–1.236(3) Å] than the inner ones [1.249(3)–1.266(2) Å], in agreement with their greater double bond character. The C(1)–C(2) and C(9)–C(10) bond lengths of the oxamate fragments [values in the range 1.539(2)–1.565(3) Å] agree with those expected for a single carbon–carbon bond. The values of the dihedral angle between the mean plane of the phenylene ring of the dcpoba ligand and the planes of the two nitro substituents are 16.36(13)[N(4)]/68.81(11)° [N(3)], the deviations from the coplanarity of these fragments being due to the steric hindrance caused by the two cis-positioned nitro substituents.
Fig. 3 Partial packing representations of 1 and 2 showing the intra (a) and inter (b) metal–metal separations. Hydrogen, dms and aromatic substituent atoms are omitted for best visualization. The crystal structure of 2 was used to prepare the representation. Copper–copper separations: 5.1916 (1)/5.178 Å (2) for Cu1⋯Cu2; 10.383 (1)/10.355 Å (2) for Cu1⋯Cu1; 13.515 (1)/13.280 Å (2) for Cu1⋯Cu1; 14.165 (1)/14.358 Å (2) for Cu1⋯Cu2; 16.509 (1)/17.016 Å (2) for Cu1⋯Cu1; 14.784 (1)/14.150 Å (2) for Cu1⋯Cu2; 17.561 (1)/16.663 Å (2) for Cu1⋯Cu1; 13.133 (1)/13.029 Å (2) for Cu1⋯Cu1; 13.385 (1)/12.789 Å (2) for Cu1⋯Cu1; 23.046 (1)/22.993 Å (2) for Cu1⋯Cu1; 11.625 (1)/11.448 Å (2) for Cu1⋯Cu1; 11.259 (1)/11.032 Å (2) for Cu1⋯Cu2; 13.127 (1)/12.847 Å (2) for Cu1⋯Cu1; 7.6610 (1)/8.6184 Å (2) for Cu1⋯Cu1; 7.7000 (1)/7.8124 Å (2) for Cu1⋯Cu2; 10.667 (1)/10.070 Å (2) for Cu1⋯Cu1; 8.3777 (1)/8.3088 Å (2) for Cu1⋯Cu2; 13.669 (1)/13.710 Å (2) for Cu1⋯Cu1; [Symmetry codes: (i) = −x, −y, z; (ii) = x − 1, y + 1, z; (iii) = −x − 1, −y + 1, −z; (iv) = x + 1, y + 1, z − 1; (v) = −x + 1, −y + 1, −z − 1; (vi) = x, y + 2, z − 1; (vii) = −x, −y + 2, −z − 1; (vii) = x, y + 2, z − 1; (vii) = x, y + 2, −z − 1; (vii) = x, y + 2, −z − 1].

3.2. Magnetic properties of 1 and 2

The magnetic properties of 1 and 2 under the form of $\chi_M T$ versus $T$ plots [$\chi_M$ being the magnetic susceptibility per tricopper(II) unit] are shown in Fig. 5.

The values of $\chi_M T$ at room temperature are 0.68 (1) and 0.62 cm$^3$ K mol$^{-1}$ (2). These values are well below the expected one for three magnetically isolated spin doublets [$\chi_M T = 1.24$ cm$^3$ mol$^{-1}$ K with $S_{Cu} = 1/2$ and $g = 2.1$]. Upon cooling, $\chi_M T$ for 1 and 2 continuously decreases to reach a plateau below ca. 100 K with $\chi_M T$ equal to 0.41 cm$^3$ mol$^{-1}$ K, as a value which is as expected for a spin doublet state [$\chi_M T = 0.41$ cm$^3$ K mol$^{-1}$ with $g = 2.1$]. A slight decrease of $\chi_M T$ occurs for 1 below 10 K whereas the plateau is kept in the case of 2 until 2.0 K.

These features are indicative of a strong intramolecular antiferromagnetic coupling leading to a low lying spin doublet in both compounds, the small decrease of $\chi_M T$ for 1 at very low temperatures being most likely due to very weak intermolecular antiferromagnetic interactions.

The isotropic spin Hamiltonian to analyse the magnetic data of 1 and 2 is given by eqn (1)

$$\hat{H} = -J_1(\hat{S}_{Cu1} \cdot \hat{S}_{Cu1A} + \hat{S}_{Cu2} \cdot \hat{S}_{Cu1B}) - J_2(\hat{S}_{Cu1A} \cdot \hat{S}_{Cu1B})$$ (1)

where $J_1$ denotes the exchange coupling parameter between the central [Cu(2)] and peripheral [Cu(1A) and Cu(1B)] copper(II) ions, and $J_2$ is the coupling parameter between the two peripheral copper(n) ions, the tricopper(II) unit being centrosymmetric. The expression of the magnetic susceptibility derived through this Hamiltonian is given by eqn (2)

$$\chi_M = \frac{N\beta^2 g^2}{4k(T-\theta)} \left[1 + \exp(-J_1/kT) + 10 \exp(J_1/2kT) + 2 \exp(J_2/kT)\right]$$ (2)

$J_2$ was assumed to be negligible and $g$ is the average Landé factor. $\theta$ is the Weiss factor introduced to take into account the weak intermolecular magnetic interactions ($j$) within the mean-field approximation and which is defined as $\theta = \frac{\nu S(S+1)/3k}{\nu = 1/2}$. Least-squares best-fit parameters are: $J_1 = -296(1)$ cm$^{-1}$, $g = 2.10(1)$, and $\theta = -0.39(1)$ K for 1, and $J_1 = -334(1)$ cm$^{-1}$, $g = 2.10(1)$, $\theta = -0.06(1)$ K for 2. The theoretical curves (solid lines in Fig. 5) closely reproduce the experimental data in the whole temperature range investigated.

Two points deserve to be discussed in the light of these magneto-structural data: (i) firstly, the strong intramolecular magnetic couplings in 1 and 2 [$J_1 = -296(1)$ (1) and $-334(1)$ cm$^{-1}$ (2)] and (ii) secondly, their different magnitude. Dealing with the first point, the large antiferromagnetic coupling in both complexes is due to the good overlap between the molecular orbitals that define the unpaired electrons of the
interacting copper(n) ions (magnetic orbitals). These orbitals are of the $d(x^2 - y^2)$-type and they are located in the basal planes of the peripheral and central copper(n) ions. The good σ in-plane overlap between the outer magnetic orbitals and the inner one through the NCO and OCO arms in the quasi coplanar Cu(1)-μ-(oxamato)-Cu(2)-μ-(oxamato)-Cu(1) motif accounts for the strong antiferromagnetic coupling observed in 1 and 2. In fact, values of $J$ ranging from $-320$ to $-386.5$ cm$^{-1}$ are reported for magneto-structurally characterized linear tricopper(n) complexes where the magnetic orbitals are practically coplanar. As far as the second point is concerned, given that 1 and 2 present practically identical Cu(1)-μ-(oxamato)-Cu(2)-μ-(oxamato)-Cu(1) skeletons, the different coupling observed is most likely due to the influence of the substituents on the phenylene ring (nitro in 1 and chloro in 2). As a matter of fact, the same trend is found in a related series of oxamato-bridged Co$^{II}$-Cu$^{II}$ chains of general formula CoCu(opba-xy)-m-dmso-nH$_2$O [$J = -24.2$ (x = y = NO$_2$) and $-32.9$ cm$^{-1}$ (x = y = Cl) and $-35.0$ cm$^{-1}$ (x = y = Me)]. This is why we decided to investigate this influence by DFT type calculations on a series of linear tricopper(n) compounds like 1 and 2 but varying the x and y substituents of the opba-xy ligand (see below).

### 3.3. Theoretical study

Electronic calculations based on density functional theory (DFT) were carried out in order to substantiate the observed intramolecular magnetic interaction in 1 and 2 and also to analyse the influence on this interaction of the x and y substituents of the opba-xy ligand. In so doing, the experimental molecular geometries were considered in both compounds. Although the magnetic coupling between the central and peripheral copper(n) ions ($J_{1}$) is the dominant magnetic interaction and that between the two peripheral copper(n) ions ($J_{2}$) from the tricopper(n) units is most likely very weak, both of them were considered in our calculations. In this respect, it deserves to be noted that this coupling between second-neighbours was found to be weak but non-negligible. The calculated $J$ values are: $J_{1} = -257.4$ cm$^{-1}$ and $J_{2} = -3.6$ cm$^{-1}$ for 1 and $J_{1} = -271.0$ cm$^{-1}$ and $J_{2} = -4.6$ cm$^{-1}$ for 2. The calculations confirmed the presence of a strong antiferromagnetic coupling through the oxamate ligand, as expected. Although the computed values of $J_{2}$ are not zero, they are very small with respect to those of $J_{1}$; moreover, their weight in the fit of the magnetic data is negligible. In this respect, a weak antiferromagnetic coupling (ca. $-1.6$ cm$^{-1}$) was found for $J_{2}$ in the trinuclear [Cu$_{3}$(Zn(oxpn))$_{2}$(H$_{2}$O)$_{2}$]$_{2}$ X = ClO$_{4}^{-}$ and BPH$_{4}^{-}$; H$_{2}$oxpn = N,N'-bis(3-aminopropyl)oxamidate]$^{-}$. The calculated values of $J_{1}$ [257.4 (1) and $-271.0$ cm$^{-1}$ (2)] are smaller than the results from the experimental data [-296(1) (1) and $-334(1)$ cm$^{-1}$ (2)], but the trend is retained (the antiferromagnetic interaction in 2 being stronger than that in 1). Most likely, subtle modifications in the electronic structure induced by the different substituents on the phenyl groups would be at the origin of this trend.

To get a clear-cut answer to this assumption and evaluate the magnitude of this indirect electronic influence on the size of $J_{1}$, DFT calculations were performed on a planar model that was built from the experimental geometries of 1 and 2 where the x and y substituents are MeO, Me, H, F, Cl, Br, I or NO$_2$ (see Scheme 1). Although in general both positions are filled by the same substituents, we have also considered the models with $x \neq y$ in order to explore the different electronic effects of each position. In the same way, two models were built for the case where $x = y =$ NO$_2$, one with two NO$_2$ groups perpendicular to the phenyl plane, [90, 90], and another with geometry very close to that experimentally observed, [70, 20]. The models with NO$_2$ groups coplanar to the phenyl ring [0, 0] were not considered to avoid non-real atomic interactions between the NO$_2$ groups that would be too close. Incidentally, an optimization of the relative geometry of the NO$_2$ groups in the oxamate ligand gives a conformational close to the experimental with dihedral angles equal to 73.6° and 22.9°.

The results of the calculations for the models which are shown in Table 2 reveal a clear influence of the electronic nature of the phenyl derivative on the magnetic coupling. Thus, models with electron-withdrawing groups presented weaker antiferromagnetic couplings. On the other hand, the relative positions of the NO$_2$ substituent to the phenyl plane had a much smaller effect on the magnetic coupling than that imposed by the electronic factors. A different impact on the

![Scheme 1](image-url)

**Table 2** Values of $J_{1}$ (in cm$^{-1}$) and Hammett constants for the groups in positions x and y, $H_{x}$ and $H_{y}$. The models are labelled with the groups in x and y positions. In the models with NO$_2$ groups, the values of dihedral angle between the planes of the NO$_2$ group and phenyl ring are joined to the labels.

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<th>Model</th>
<th>$H_{x}$</th>
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<th>$H_{z}$</th>
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</tbody>
</table>
magnetic coupling was observed in models with only one hydrogen atom on the positions \( x \) or \( y \) replaced by a chloro atom ([H, Cl] (−462.5 cm\(^{-1}\)) and [Cl, H] (−458.5 cm\(^{-1}\)) models). But, both models provided magnetic interactions that were between those corresponding to the furthest cases [H, H] (−468.1 cm\(^{-1}\)) and [Cl, Cl] (−455.2 cm\(^{-1}\)). In any case, the trend observed from the experimental data and from the DFT calculations on the experimental molecular geometries is observed also here with ideal models.

The use of the Hammett constants for the groups that are placed on \( x \) and \( y \) positions could allow the addition of their different electronic effects on the magnetic coupling even when \( x \neq y \). This is why different Hammett constants were used for the same groups as a function of their position.

The total Hammett constant was calculated on the \( N_2 \) nitrogen atom (\( N_2 \) in Scheme 1) which belongs to the NCO magnetic pathway. A roughly good correlation between the value of \( J_1 \) and the total Hammett constant was found. However, the correlation is not perfect and some small inconsistencies cannot be satisfactorily explained. A possible cause may be related to the fact that the electronic effects concern not only \( N_2 \) but also the peripheral \( N_1 \) which belongs to the outer oxamato ligand. Considering this last donor atom, in spite of being not involved in the exchange pathway, the electronic density influences the p–d hybridization on the d metal orbital sending more or less electron density of the metal ion on the pathway (see Scheme 2) and modifying then the magnetic coupling. It is hard to think that both effects contribute in equal terms to the changes on the magnetic coupling. However, an inspection of the data shows that the points which deviate from correlation correspond to the models with the methoxy substituents (white circles in Fig. 6). In any case, the use of Hammett constants to account for the electronic effects mainly has a qualitative feature, and some deviation can be expected. It can be more remarkable in some cases like in these models with methoxy groups that act as donors or acceptors depending on the positions occupied (\( y \) or \( x \), respectively). The electronic density induced on the \( N_2 \) atom is responsible for the changes of the magnitude of the magnetic coupling, and the energy of the ligand orbitals should not be obviated, because it is modified for a donor feature as much by the MeO group in \( x \) and \( y \) positions. Thus, a modification of the Hammett constants for this group (0.050 and 0.030 for \( x \) and \( y \) positions, respectively) largely improves the correlation between the value of \( J \) and the total Hammett constant [see data displayed as grey circles in Fig. 6, \( J = -466.6 + 19.77 (H_x + H_y) \), with \( R \)-squared = 0.995].

In the light of the results from the theoretical calculations, it is possible to understand the above correlations. Therefore, the use of the electron-withdrawing groups like NO\(_2\) reduces the electronic density on the oxamato skeleton leading to: (i) a reduction of the contribution of the oxamato-nitrogen atom to the HOMO of the ligand, and (ii) a stabilization of this HOMO caused by a decrease of the antibonding interactions. A smaller overlap and a large energy gap between the ligand HOMO and magnetic d orbital of the copper(\( n\)) ion are expected from the first and second inferences, respectively. Then, poorer interactions between these orbitals should be envisaged and weak magnetic couplings should be presumed with more electron-withdrawing substituents through the Hay–Thiebaut–Hoffman (HTH) model.\(^{51}\) In such cases, larger spin densities will be sent to the magnetic exchange pathway. Consequently, a good correlation is found between the magnetic coupling (\( J \)) and the spin densities on the peripheral copper(\( n\)) ion (Fig. 7a) and on the \( N_2 \) atom (Fig. 7b). A similar correlation
is found by using the spin densities on the N₂ atom, proving that electron-withdrawing groups favour the interaction between the d orbital from the metal ion and the ligand orbitals. Finally, one can also see the correlation found between J and the energy of the HOMO of the ligand (Fig. 7). In summary, stronger magnetic interactions are predicted when larger delocalization of the spin densities from the d orbital of the copper(II) ion onto the exchange pathway occur. This is due to a larger orbital interaction between the metal and ligand orbitals mainly because they overlap extensively and less importantly, because they are closer in energy.

4. Conclusions

In this work, the first examples of oxamato-based trinuclear copper(II) complex without terminal ligands are described. The crystal structures determined by X-ray single-crystal diffraction consist of linear centrosymmetric dianionic complexes with tetrabutylammonium as counterions. The magnetic studies of trinuclear compounds (1 and 2) show a moderately strong intramolecular antiferromagnetic coupling through the σ in-plane exchange pathway. Theoretical calculations have shown that the size of the magnetic coupling between the copper(II) ions through the oxamato bridge in this type of complexes varies with the electron accepting or electron donating strength of the phenylene substituents on the opba ligand. Since the linear trinuclear complexes 1 and 2 present external free carbonyl groups to further coordination, their use as building blocks to prepare heterometallic polynuclear compounds has been investigated by our group.

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Notes and references
