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Magnetic coupling and spin topology in linear oxalato-bridged tetranuclear chromium(III)-copper(II) complexes with aromatic diimine ligands

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ABSTRACT

A novel heterotetranuclear chromium(III)-copper(II) complex of formula $\{[Cr^{III}(bpy)(ox)_2]_2Cu^{II}_2(b-c)\}$ $py_2(ox)$ BH_2O (1) has been synthesized by the ligand exchange reaction between $Ph_4P[Cr^{III}(b-c)]$ $py)(ox)_2$]·H₂O and $[Cu^{II}(bpy)_2(NO_3)]NO_3$ ·MeOH in methanol (bpy = 2,2'-bipyridine; $ox^{2-} = oxalate$ dianion). The X-ray crystal structure of **1** consists of neutral oxalato-bridged Cr^{III}₂Cu₂^{II} zigzag entities which are formed by the monodentate coordination of two $[Cr^{III}(bpy)(ox)_2]^-$ mononuclear anionic units through one of its two oxalato groups toward a $[Cu^{II}_2(bpy)_2(ox)]^{2+}$ dinuclear cationic moiety featuring relatively long axial bonds at the square pyramidal Cu^{II} ions. Variable temperature (2.0-300 K) magnetic susceptibility and variable-field (0-5.0 T) magnetization measurements for 1 have been interpreted on the basis of the linear tetranuclear topology of the $Cr^{III}_2Cu^{II}_2$ entities $[\mathbf{H} = -J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_3 \cdot \mathbf{S}_4) - J' \mathbf{S}_2 \cdot \mathbf{S}_3$ with $S_1 = S_4 = S_{Cr} = 3/2$ and $S_2 = S_3 = S_{Cu} = 1/2$]. A weak antiferromagnetic coupling occurs between the outer Cr^{III} and inner Cu^{II} ions through the peripheral bidentate/monodentate(outer) oxalates ($J = -8.7 \text{ cm}^{-1}$), while a strong antiferromagnetic coupling is operative between the inner Cu^{II} ions across the central bis-bidentate oxalate ($J' = -472.2 \text{ cm}^{-1}$), leading thus to a $S = (S_{Cr} - S_{Cu}) - (S_{Cr} - S_{Cu}) = 0$ ground spin state for the Cr^{III}₂Cu^{II}₂ entity of **1**. A simple orbital analysis of the electron exchange interaction in the oxalatobridged Cu^{II}_{2} and $Cr^{III}Cu^{II}$ fragments identify the σ -type pathways involving the $d_{x^2-y^2}(Cu)/d_{x^2-y^2}(Cu)$ and $d_{xy}(Cr)/d_{x^2-v^2}(Cu)$ pairs of magnetic orbitals as the two main contributions responsible for the different strength of the intramolecular magnetic coupling parameters for 1. A magneto-structural correlation between the nature and magnitude of the magnetic coupling and the bending angle at the axial carbonyl-oxygen to copper bond has been established for 1 and related oxalato-bridged chromium(III)-copper(II) dinuclear complexes.

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1. Introduction

Polynuclear complexes have long been recognized in coordination chemistry, playing an important role in the development of Werner's coordination theory [1]. This is well illustrated by the seminal work of Alfred Werner on 'hexol', a star-like hydroxobridged tetranuclear cobalt(III) complex of formula { $[Co^{III}(N-H_3)_4(OH)_2]_3Co^{III}$ }Br₆ which constitutes the first carbon-free species to be optically resolved into its two chiral isomers (enantiomers) [2a]. Ironically, Werner's famous hexol was first prepared by Jørgensen, Werner's primary scientific adversary and the foremost exponent of the rival Blomstrand chain theory, upon basic hydrolysis of a solution of the *fac*- or *mer*-isomers of $[Co^{III}(NH_3)_3(H_2O)_3]^{3+}$ [2b]. Since then, the search for the peculiar molecular and electronic structure of polynuclear transition metal complexes have largely evolved to become a well-established subject in modern coordination chemistry [3]. In particular, the studies on their magnetic properties have largely contributed to this renewed interest in the coordination chemistry of polynuclear complexes [3c,d], leading to the development of a new discipline in magnetochemistry which has been termed molecular magnetism [4].

Relevant concepts in molecular magnetism such as the strict orthogonality of the magnetic orbitals or the irregular spin-state structure appear historically associated with the study of dinuclear copper(II)–vanadium(IV) [5] and trinuclear copper(II)–manganese(II) complexes [6], respectively. Likewise, some general topics like spin frustration or spin topology issued from the studies on



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tetranuclear manganese(III) [7] and copper(II)-manganese(II) complexes [8] where the ground spin state is mainly dictated by their unique cubane and star-like molecular topologies, respectively. Along this line, it was reasonable to assume that new basic concepts and original phenomena would emerge from the study of the magnetic properties of higher nuclearity complexes. So, the first observation of magnetic hysteresis and magnetic quantum tunneling of pure molecular origin in a dodecanuclear manganese(III,IV) complex [9] two decades ago represents a further milestone in the field of molecular magnetism [10,11]. Since then, the design and synthesis of high-nuclearity complexes of paramagnetic transition metal ions continue to attract attention in the multidisciplinary field of molecular magnetism as potential candidates of molecular nanomagnets, so-called single molecule magnets (SMMs) [12–14].

Oxalate (ox) has a well-known ability to form discrete exchangecoupled, homo- [15,16] and heterometallic [17,18] polynuclear complexes containing blocking ligands that preclude the formation of undesired polymeric compounds. When acting as bidentate/ monodentate(outer) (I) and bis-bidentate (II) bridge between the same (M = M') or different (M \neq M') metal ions (Chart 1), oxalate affords weak to strong, either ferro- or antiferromagnetic couplings depending on the bridging mode and the nature of the blocking ligands [15a,16a,18e], as well as on the stereochemistry and electronic configuration of the metal ions [15a,17c,17f,17g,18d,18e]. For instance, the pair of oxalato-bridged linear trinuclear chromium(III)-cobalt(II) and chromium(III)-manganese(II) complexes $(Hampy)_4 \{ [Cr^{III}(ox)_3]_2 M^{II}(H_2O)_2 \} \cdot 3H_2O \quad (Hampy^+ = 4-aminopyridi$ nium cation and M = Co and Mn) reported by Pardo et al. show a weak ferromagnetic coupling between the outer Cr^{III} ions and the inner M^{II} ion across the bis-bidentate oxalate which results in high spin S = 9/2 (M = Co) and 11/2 (M = Mn) ground states [17g]. More interestingly, Martínez-Lillo et al. reported earlier the ferromagnetically coupled, star-like oxalato-bridged tetranuclear rhenium(IV)nickel(II) complex $(nBu_4N)_4\{[Re^{IV}Cl_4(ox)]_3Ni^{II}\}$ $(nBu_4N^+ = tetra$ *n*-butylammonium cation) possessing a highly anisotropic S = 11/2 ground state that exhibits slow magnetic relaxation effects at low temperatures [18c]. This constitutes one of the very few examples of SMMs belonging to the class of heterobimetallic oxalate complexes [3d].

Our research group is particularly interested in the use of stable, more or less inert, oxalato-containing heteroleptic chromium(III) complexes as ligands (metalloligands) because of its potential coordination capabilities toward other divalent 3d metal ions, from manganese(II) to copper(II), through the cis carbonyl-oxygen atoms of the oxalato groups [19]. Hence, a limited number of mononuclear bis(oxalato)chromate(III) complexes with aromatic α, α' -diimines as coligands [20] were able to produce a large variety of oxalatobridged di- [21], tri- [22], and tetranuclear [23] heterometallic species following the so-called "complex-as-ligand" approach. In particular, the anionic (2,2'-bipyridine)bis(oxalato)chromate(III) complex, $[Cr^{III}(bpy)(ox)_2]^-$, acts as bidentate ligand toward Cu^{II} ions having their coordination sites partially blocked with anionic tridentate ligands like bis(2-pyridylcarbonyl)amidate (bpca) or 3-[N-2-pyridylethyl)formidoyl]salicylate (Hfsaaep), yielding the corresponding dinuclear chromium(III)-copper(II) complexes {Cr^{III}(bpy)(ox)₂Cu^{II}(bpca)(H₂O)}·2.5H₂O [21a] and {Cr^{III}(bpy)(ox)₂-



Chart 1. Bidentate/monodentate(outer) (I) and bis-bidentate (II) coordination modes of the oxalato ligand.



Scheme 1. Chemical structures of (a) **1** and (b) **2** showing the different binding modes of the oxalato ligands. The dashed lines outline the Jahn–Teller elongated bonds to the copper atoms.

Cu^{II}(Hfsaaep)(H₂O)}·2H₂O [21b]. Surprisingly, when using bpy as blocking ligand of the Cu^{II} ions, we have obtained the novel tetranuclear chromium(III)-copper(II) complex { $[Cr(bpy)(ox)_2]_2Cu_2(bpy)_2(ox)$ }·6H₂O (1). Under somewhat different reaction conditions, Coronado et al. obtained instead the related tetranuclear chromium(III)-copper(II) complex { $[Cr(bpy)(ox)_2]_2Cu_2(bpy)_2(ox)$ }·2H₂O (2) [23b]. Complexes 1 and 2 have in common a central bis-bidentate oxalate but they differ in the bidentate/monodentate(outer)(1) and bis-bidentate (2) coordination mode of the peripheral oxalates (Scheme 1).

Herein we report the synthesis and spectroscopic characterization, the crystal structure and the magnetic properties of **1**. The distinct nature and magnitude of the intramolecular magnetic coupling in **1** and **2** are discussed in the light of their different structural features, and they are compared with those reported for related oxalato-bridged copper(II) and chromium(III)–copper(II) dinuclear complexes aiming at elucidating the possible magnetostructural correlations.

2. Experimental

2.1. Materials

All chemicals were of reagent grade quality. They were purchased from commercial sources and used as received. $Ph_4P[Cr^{III}(b-py)(ox)_2] \cdot H_2O$ was prepared by refluxing a 1:2:1 mixture of $Cr^{III}Cl_3 \cdot 6H_2O$, Na_2ox , and bpy in ethanol/water and it was isolated by addition of an excess of PPh_4Cl [21a]. $[Cu^{II}(bpy)_2(NO_3)]$ - $NO_3 \cdot MeOH$ was prepared *in situ* from the stoichiometric reaction of $Cu^{II}(NO_3)_2 \cdot 3H_2O$ and bpy (1:2 molar ratio) in methanol [24].

2.2. Preparation

2.2.1. { $[Cr(bpy)(ox)_2]_2Cu_2(bpy)_2(ox)\} \cdot 6H_2O(1)$

A methanolic solution (5 cm^3) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.06 g, 0.25 mmol) was added dropwise to a methanolic solution (20 cm^3) of bpy (0.08 g, 0.50 mmol) under continuous stirring. The resulting deep blue solution was then added dropwise to a methanolic solution (25 cm^3) of $\text{Ph}_4\text{P}[\text{Cr}(\text{bpy})(\text{ox})_2] \cdot \text{H}_2\text{O}$ (0.19 g, 0.25 mmol) under continuous stirring. The final deep purple solution was filtered off and allowed to evaporate at room temperature. X-ray quality violet prisms of **1** appeared after a few days, which were collected on filter paper and air-dried (0.07 g, yield

35%). *Anal.* Calc. (%) for C₅₀H₄₄Cr₂Cu₂N₈O₂₆: C, 42.77; H, 3.16; N, 7.98. Found: C, 41.70; H, 3.18; N, 7.93. Electron microscopy analysis (molar ratio): Cr/Cu, 1.05. IR (KBr): 1654(sh), 1663vs, 1680(sh), 1684vs, 1707vs, and 1718(sh) cm⁻¹ (CO).

2.3. Physical techniques

Elemental (C, H, N) and electron microscopy (Cr, Cu) analyses were performed at the Servei Central de Suport a la Investigació Experimental (SCSIE, Spain). FT-IR spectra were recorded on a Nicolet-5700 spectrophotometer as KBr pellets. Variable-temperature (2.0–300 K) magnetic susceptibility measurements under an applied field of 10 kOe ($T \ge 25$ K) and 100 Oe (T < 25 K) and variable-field (H = 0-50 kOe) magnetization measurements at 2.0 K were carried out on powdered samples with a Quantum Design SQUID magnetometer. The susceptibility data were corrected for the diamagnetism of the sample holder and the constituent atoms, as well as for the temperature independent paramagnetism (tip) of the metal atoms.

2.4. Crystal structure determination

The single-crystal X-ray diffraction data of 1 were collected at 293(2) K on a Nonius Kappa CCD diffractometer by using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Data collection and data reduction were done with the COLLECT and EVALCCD programs [25]. Empirical absorption corrections were carried out using sADABS [26]. The structures were solved by direct methods and refined with full-matrix least-squares technique on F^2 using the SHELXS-97 and SHELXL-97 programs [27]. All calculations for data reduction, structure solution, and refinement were done by standard procedures (WINGX) [28]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the bpy ligand were calculated and refined with an overall isotropic thermal parameter, whereas those of the crystallization water molecules were neither found nor calculated. The final geometrical calculations and the graphical manipulations were carried out with PARST97 and CRYSTAL MAKER programs, respectively [29].

3. Results and discussion

3.1. Synthesis and general spectroscopic characterization

The neutral tetranuclear chromium(III)–copper(II) complex of formula ${[Cr(bpy)(ox)_2]_2Cu_2(bpy)_2(ox)\} \cdot 6H_2O$ (**1**) was synthesized by the stoichiometric reaction (1:1 molar ratio) of the tetraphenyl-phosphonium salt of the anionic 2,2'-bipyridinebis(oxalato)chromate(III) complex, $[Cr^{III}(bpy)(ox)_2]^-$, and the nitrate salt of the cationic bis(2,2'-bipyridine)nitratocopper(II) complex, $[Cu^{II}(bpy)_2(-NO_3)]^+$, in methanol (Scheme 2). Complex **1** was isolated as violet crystals with moderate yields (35%) after a few days under slow evaporation at room temperature.

The formation of the neutral heterotetranuclear complex, $\{[Cr^{III}(bpy)(ox)_2]_2Cu^{II}_2(bpy)_2(ox)\}$, instead of the expected cationic heterodinuclear one, $[Cr^{III}(bpy)(ox)_2Cu^{II}(bpy)_2]^+$, would be likely explained by the ligand exchange reaction between the anionic 2,2'-bipyridinebis(oxalato)chromate(III) precursor, $[Cr^{III}(bpy)(ox)_2]^-$, and the cationic bis(2,2'-bipyridine)nitratocopper(II) complex, $[Cu^{II}(bpy)_2(NO_3)]^+$, to afford the cationic mononuclear bis(2,2'-bipyridine)oxalatochromate(III) complex, $[Cr^{III}(bpy)_2(ox)]^+$, and the neutral dinuclear oxalato-bridged bis(2,2'-bipyridine)bis(nitrato)dicopper(II) species, $[Cu^{II}_2(bpy)_2(ox)(NO_3)_2]$, together with the free oxalato dianion [Eqs. (1) and (2)]. In this regard, it deserves to be noted that the related bis(1,10-phenanthroline)oxalatocobaltate(III) complex of formula $[Co(phen)_2(ox)]BF_4$ was isolated by



Russell et al. upon ligand exchange reaction of the tris(oxalato)cobaltate(III) precursor of formula $K_3[Co(ox)_3]$ ·3H₂O with excess 1,10-phenanthroline (phen) in water [20h].

$$\begin{split} & 2[Cr^{III}(bpy)(ox)_2]^- + 2[Cu^{II}(bpy)_2(NO_3)]^+ \\ & \rightarrow 2[Cr^{III}(bpy)_2(ox)]^+ + [Cu^{II}_2(bpy)_2(ox)(NO_3)_2] + ox^{2-} \end{split} \tag{1}$$

$$\begin{split} & 2[Cr^{III}(bpy)(ox)_2]^- + [Cu_2^{II}(bpy)_2(ox)(NO_3)_2] \\ & \to [Cr^{III}(bpy)(ox)_2]_2 Cu_2^{II}(bpy)_2(ox) + 2NO_3^- \end{split} \tag{2}$$

The chemical identity of **1** was established by elemental (C, H, and N) and electron microscopy (Cr and Cu) analyses, together with FT-IR spectroscopy. $Ph_4P[Cr^{III}(bpy)(ox)_2]\cdot H_2O$ shows two intense IR bands at 1680 and 1704 cm⁻¹ corresponding to the asymmetric $v_{as}(CO)$ stretching vibrations from the terminal oxalato ligands. Instead, complex **1** exhibits three intense IR bands at 1663, 1684, and 1707 cm⁻¹ with three distinct shoulders at 1654, 1680, and 1718 cm⁻¹, which are attributed to the occurrence of both terminal and bridging oxalato ligands. By comparison, complex **2** shows three intense IR bands at 1653, 1678, and 1718 cm⁻¹ with no distinct shoulders [23b]. The additional splitting of the IR bands for **1** compared to **2** suggests thus the presence of different type of oxalato bridges.

3.2. Description of the structure

Compound **1** crystallizes in the triclinic $P\bar{1}$ space group, so does the related compound **2** but with completely different unit cell parameters [23b]. The crystal structure of **1** consists of centrosymmetric neutral oxalato-bridged chromium(III)–copper(II) tetranuclear complexes, {[$Cr^{III}(bpy)(ox)_2$]₂ $Cu^{II}_2(bpy)_2(ox)$ }, and crystallization water molecules (Figs. 1 and 2). The $Cr^{III}_2Cu^{II}_2$ entities of **1** arise from the monodentate coordination of two [$Cr^{III}(bpy)(ox)_2$]⁻ mononuclear anionic units through one of its two oxalato groups towards a [$Cu^{II}_2(bpy)_2(ox)$]²⁺ dinuclear cationic moiety (Fig. 1a). This situation clearly contrasts with that in **2**, whereby the two [$Cr^{III}(bpy)(ox)_2$]⁻ mononuclear anionic units coordinate to



Fig. 1. (a) Perspective view of the neutral heterotetranuclear unit of **1** with the atom-numbering scheme [*symmetry code*: (1) = 1 - x, 2 - y, 1 - z]. (b) Projection view of the oxalato-bridged heterotetranuclear zigzag skeleton of **1**. Selected intermetallic distances (Å) and angles (°): Cr(1)-Cu(1) = 5.410(2) and Cu(1)-Cu(1)¹ = 5.1400(12); Cr(1)-Cu(1)⁻¹ = 52.45(2) [*symmetry code*: (1) = 1 - x, 2 - y, 1 - z].

the $[Cu^{II}_{2}(bpy)_{2}(ox)]^{2+}$ dinuclear cationic moiety in a bidentate manner to give the corresponding $Cr^{III}_{2}Cu^{II}_{2}$ entities [23b]. The most noticeable feature of the molecular structure of **1** is, however, the occurrence of a $Cr^{III}_{2}Cu^{II}_{2}(ox)_{5}$ zigzag skeleton with up to three different types of oxalato ligands (Fig. 1b), which differs both stereo-chemically and conformationally from that earlier reported for **2**. A summary of the crystallographic data and selected bond distances and angles for **1** are given in Tables 1 and 2, respectively.

The two centrosymmetrically-related, outer Cr(1) and $Cr(1)^{I}$ atoms in 1 adopt a six-coordinated, trigonally compressed octahedral geometry (CrN₂O₄) similar to that found in 2, which is formed by two imine-nitrogen atoms from bpy and four carboxylate-oxygen atoms from the terminal and bridging oxalates (Fig. 1a). The values of the trigonal twist angle (ϕ) and the compression ratio (s/h) at the octahedral Cr^{III} ions in **1** are similar to those in **2** $[\phi = 49.74(22) (1) \text{ and } 52.69(20)^{\circ} (2) \text{ and } s/h = 1.32 (1) \text{ and } 1.36$ (2)] [23b]. The small distortion of the octahedral (O_h) environment towards trigonal prismatic (D_{3h}) , so-called Bailar twist, is due to the chelating coordination of the bpy and oxalato ligands ($\varphi = 60^{\circ}$ and $s/h = \sqrt{3}/2 = 1.22$ for an ideal octahedron) [30]. The Cr-N bond distances in 1 are somewhat longer than the Cr-O ones (Table 2), as previously found in 2 [23b]. This agrees with the stronger ligand field of the carboxylate-oxygen atoms from oxalate compared to the imine-nitrogen ones from bpy. The value of the N-Cr-N bite angle subtended by the chelating bpy in 1 is somewhat smaller than those of the O-Cr-O bite angle from the



Fig. 2. (a) Projection view of a fragment of the hydrogen-bonded layers of heterotetranuclear units of **1** along the [011] direction. Hydrogen bonds between the crystallization water molecules and the oxalato ligands are represented by dashed lines. (b) Crystal packing view of **1** along the crystallographic *a* axis showing the π - π stacking interlayer interactions between the bpy ligands. The adjacent hydrogen-bonded layers of heterotetranuclear units are shown in different colors. Selected intermetallic distances (Å): Cr(1)-Cr(1)^{II} = 9.822(2) and Cr(1)^I-Cr(1)^{VII} = 7.226(2) [symmetry code: (I) = 1 - x, 2 - y, 1 - z; (II) = 1 - x, 1 - y, 2 - z; (III) = 1 - x, 2 - y, 2 - z; (IV) = x, -1 + y, z; (V) = -x, 1 - y, 2 - z; (VI) = 1 + x, y, z; (VII) = x, y, -1 + z; (VIII) = 1 - x, 1 - y, 1 - z].

chelating oxalates (Table 2), all of them being smaller than that of 90° for an ideal octahedron.

The two centrosymmetrically-related, inner Cu(1) and $Cu(1)^{I}$ atoms in 1 exhibit a five-coordinated, axially elongated square pyramidal geometry (CuN₂O₃), whereas the corresponding ones of 2 have a six-coordinated, axially elongated octahedral surrounding (CuN₂O₄) [23b]. Two imine-nitrogen atoms from bpy and two carboxylate/carbonyl-oxygen atoms from the central bridging oxalate build the equatorial plane of the square pyramidal Cu^{II} ions in 1, the axial position being occupied by a carbonyl-oxygen atom from the peripheral bridging oxalate (Fig. 1a). In contrast, the equatorial plane of the octahedral Cu^{II} ions in 2 is formed by two iminenitrogen atoms from bpy and two carboxylate-oxygen atoms from the central and peripheral bridging oxalates, while their carbonyloxygen atoms occupy the two axial positions [23b]. The four equatorial donor atoms in **1** are nearly coplanar [maximum deviations of 0.116(4) and 0.127(5) Å at N(1) and N(2), respectively], the copper atom being slightly displaced from the mean basal plane toward the apical position [h' = 0.1596(8) Å]. The equatorial Cu–N bond distances in 1 (Table 2) are similar to those in 2 [23b]. The axial Cu–O bond distance in **1** is rather longer than the equatorial ones (Table 2), as previously found in 2 [23b]. This situation is as

Table 1	

Summary of crystallographic data for 1.

Formula	$C_{25}H_{22}CrCuN_4O_{13}$
M (g mol ⁻¹)	702.01
Crystal system	triclinic
Spatial group	$P\bar{1}$
a (Å)	9.2328(15)
b (Å)	10.2458(13)
c (Å)	14.886(3)
α (°)	83.765(13)
β(°)	86.504(13)
γ (°)	77.662(12)
V (Å ³)	1366.5(4)
Ζ	2
$ ho_{ m calc} ({ m g}{ m cm}^{-3})$	1.706
F(000)	714
μ (mm ⁻¹)	1.253
T (K)	293(2)
Reflections collected	14065
Independent reflections (R _{int})	6109 (0.0693)
Observed reflections $[I > 2\sigma(I)]$	3360
Data/restraints/parameters	6109/0/397
$R_1^a [I > 2\sigma(I)]$ (all)	0.0747 (0.1527)
$wR_2^{b} [I > 2\sigma(I)] (all)$	0.1467 (0.1783)
Goodness-of-fit	1.023
S ^c	1.023

 $R_1 = \sum (|F_0| - |F_c|) / \sum |F_0|.$

 $\begin{array}{l} & m_1 = \sum (|P_0| - |P_c|) \sum |P_0|. \\ & wR_2 = [\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}. \\ & c \quad S = [\sum w(|F_0| - |F_c|)^2 / (N_0 - N_p)]^{1/2}. \end{array}$

Table	2
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Cr(1)-N(3)	2.072(5)	Cr(1)-N(4)	2.076(5)
Cr(1)-O(5)	1.965(4)	Cr(1)-O(6)	1.961(4)
Cr(1)-O(7)	1.945(4)	Cr(1)-O(8)	1.954(4)
Cu(1)-N(1)	1.967(4)	Cu(1)-N(2)	1.978(5)
Cu(1) - O(1)	1.968(4)	Cu(1) - O(2)	1.969(4)
Cu(1)-O(3)	2.383(4)		
N(1)-Cu(1)-N(2)	82.5(2)	N(1)-Cu(1)-O(1)	164.09(18)
N(1)-Cu(1)-O(2)	95.15(18)	N(1)-Cu(1)-O(3)	103.50(17)
N(2)-Cu(1)-O(1)	96.98(18)	N(2)-Cu(1)-O(2)	176.87(19)
N(2)-Cu(1)-O(3)	89.39(17)	O(1)-Cu(1)-O(2)	84.70(15)
O(1)-Cu(1)-O(3)	92.39(15)	O(2)-Cu(1)-O(3)	93.19(16)
N(3)-Cr(1)-N(4)	78.1(2)	N(3)-Cr(1)-O(5)	95.91(18)
N(3)-Cr(1)-O(6)	95.58(18)	N(3)-Cr(1)-O(7)	89.85(18)
N(3)-Cr(1)-O(8)	167.44(18)	N(4)-Cr(1)-O(5)	97.09(18)
N(4)-Cr(1)-O(6)	173.5(2)	N(4)-Cr(1)-O(7)	90.31(17)
N(4)-Cr(1)-O(8)	91.2(2)	O(5)-Cr(1)-O(6)	81.96(16)
O(5)-Cr(1)-O(7)	171.41(18)	O(5)-Cr(1)-O(8)	91.91(18)
O(6)-Cr(1)-O(7)	91.16(16)	O(6)-Cr(1)-O(8)	95.24(17)
O(7)-Cr(1)-O(8)	83.55(17)		

^a Estimated standard deviations are given in parentheses.

expected because of the Jahn–Teller distortion typical of Cu^{II} ions. The value of the N–Cu–N bite angle subtended by the chelating bpy in 1 (Table 2) is similar to that in 2 but the value of the O-Cu-O bite angle from the chelating oxalate in 1 (Table 2) is greater than those in 2 [23b]. This situation reflects the distinct symmetric (1) or asymmetric (2) bis-bidentate bridging modes, with either two short (1) or one long and one short Cu-O bond distances (2). Interestingly, the values of the four *cis* axial O-Cu-O(N) and two *trans* equatorial N-Cu-O angles in 1 (Table 2) deviate slightly from those expected for an ideal square pyramid (90° and 180°, respectively). as a result of the small out-of-plane displacement of the copper atom from the mean basal plane.

Within the $Cr^{III}_{2}Cu^{II}_{2}(ox)_{5}$ zigzag skeleton of **1**, the outer Cr(1)and inner Cu(1) atoms are bridged through a bidentate/monodentate(outer) oxalate that coordinates toward the copper atom with one long axial bond (Fig. 1b). This situation contrasts with that of **2**, whereby the peripheral oxalate coordinates in a bis-bidentate bridging mode toward the copper atom with a short equatorial and a long axial bonds [23b]. The value of the axial Cu-O bond distance in **1** is slightly longer than that in **2** $[R_{ax} = 2.383(4)$ (**1**) and 2.357(5) Å (2)], both of them being much longer than the equatorial Cu–O bond distance in **2** $[R_{eq} = 2.080(5) \text{ Å}]$ [23b]. The axially coordinated carboxylate group from the peripheral oxalate exhibits the anti-syn configuration in 1, whereas it adopts the anti-anti one in **2** [23b]. The values of the axial Cu–O–C bending angle (α) are 124.0(4) (1) and 108.2(4)° (2), while those of the axial Cu-O-C–O torsion angle (β) are 25.5(8) (**1**) and 173.2(7)° (**2**) [23b]. The resulting Cr(1)(ox)Cu(1) bridging moieties of both 1 and 2 exhibit a noncoplanar, almost perpendicular disposition of the mean basal plane of the square pyramidal (1) and octahedral (2) Cu^{II} ions with respect to the mean plane of the peripheral oxalato bridge. The value of the dihedral angle between the copper basal plane and the peripheral oxalato plane in **1** deviates further from 90° than that in **2** [γ = 62.59(12) (**1**) and 86.5(2)° (**2**)] [23b].

The inner Cu(1) and $Cu(1)^{I}$ atoms of **1** are bridged through a bisbidentate oxalate that coordinates in a symmetric binding mode toward each copper atom, with two short equatorial bonds (Fig. 1b). In contrast, the central bis-bidentate oxalate in 2 adopts an asymmetric binding mode with one short equatorial and one long axial bond at each copper atom [23b]. The values of the equatorial Cu-O bond distances in 1 are similar than that in 2 $[R'_{eq} = 1.968(4) - 1.969(4)$ (1) and 1.964(5) Å (2)], all of them being much shorter than the axial Cu-O bond distance in 2 $[R'_{ax} = 2.245(5) \text{ Å}]$ [23b]. The values of the axial Cu–O–C bending angle (α') and the axial Cu–O–C–O torsion angle (β') in **2** are 108.8(4) and 178.0(6)°, respectively [23b]. The mean basal planes of the two square pyramidal Cu^{II} ions in **1** are parallel for symmetry reasons but they have a slightly bent, coplanar disposition with respect to the mean plane of the central oxalato bridge, leading thus to an overall chair conformation for the resulting $Cu(1)(ox)Cu(1)^{I}$ bridging moiety. Instead, it exhibits a parallel noncoplanar disposition of the mean basal planes of the two octahedral Cu^{II} ions in **2**. with a perpendicular orientation with respect to the mean plane of the central oxalato bridge [23b]. The values of the dihedral angle between the copper basal plane and the central oxalato plane (γ') are 6.28(11) (1) and 81.69(19)° (2) [23b].

In the crystal lattice of 1, there is an extensive network of hydrogen bonds involving the free carbonyl group from the peripheral bidentate/monodentate(outer) oxalate and/or the crystallization water molecules [0...Ow = 2.883(2) Å and Ow...Ow = 2.737(2)-2.97(11) Å]. These intermolecular hydrogen-bonding interactions lead to layers of water-bridged tetranuclear Cr^{III}₂Cu^{II}₂ zigzag entities perpendicular to the [011] direction (Fig. 2a). In addition, there are very weak intermolecular π - π stacking interactions between the bpy ligands of the outer Cr^{III} ions from tetranuclear Cr^{III}₂Cu^{II}₂ zigzag entities of adjacent layers along the crystallographic *c* axis [inter-ring centroid–centroid distance of 3.8355(7) Å] (Fig. 2b).

3.3. *Magnetic properties*

The magnetic properties of **1** in the form of the $\chi_{\rm M}T$ versus T plot $(\chi_M$ being the molar magnetic susceptibility per tetranuclear unit and T the absolute temperature) are typical of overall antiferromagnetically coupled Cr^{III}₂Cu^{II}₂ linear entities (Fig. 3a). Upon cooling, $\gamma_{\rm M}T$ for **1** decreases smoothtly from room temperature down to *ca*. 100 K to reach a sort of plateau of $3.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (Fig. 3a), a value which corresponds to that expected for the sum of two d³ Cr^{III} ($S_{Cr} = 3/2$) ions magnetically isolated. Below 10 K, $\chi_{\rm M}T$ for **1** decreases abruptly down to 3.47 K cm³ mol⁻¹ K at 2.0 K. The distinct decrease of $\chi_{\rm M}T$ at high and low temperatures for 1 conform with the occurrence of strong and weak intramolecular antiferromagnetic interactions between the two inner Cu^{II} ions and among the inner Cu^{II} and outer Cr^{III} ions through the



Fig. 3. (a) Temperature dependence of $\chi_M T$ for $\mathbf{1}$ (\triangle). The solid line is the best-fit curve for a tetranuclear model with J < 0 and J' < 0 (see text). (b) Field dependence of M for $\mathbf{1}$ (\blacktriangle) at T = 2.0 K. The solid line is the Brillouin curve for two $S_{CT} = 3/2$ states.

central bis-bidentate and peripheral bidentate/monodentate(outer) oxalates, respectively. In fact, the *M* versus *H* plot for **1** at 2.0 K (*M* being the molar magnetization per tetranuclear unit and *H* the applied field) agrees with the presence of strong antiferromagnetically coupled Cu^{II}₂ pairs and weakly coupled Cr^{III} ions within the Cr^{III}₂Cu^{II}₂ linear entities (Fig. 3b). Thus, the *M* value of 5.86 N β for **1** at 50 kOe is close to the saturation magnetization for two quartet spin states ($M_s = 2 \times g_{Cr}S_{Cr} = 6.0 \ N\beta$ with $g_{Cr} = 2.0$). Moreover, the isothermal magnetization curve for **1** is very close to the Brillouin curve of two $S_{Cr} = 3/2$ states [solid line in Fig. 3b], supporting thus the absence of significant zero-field splitting (ZFS) effects due to the small single-ion magnetic anisotropy of the Cr^{III} ions in a trigonal distorted octahedral geometry (⁴B₁ ground term in the D_3 point group) [17e].

The magnetic susceptibility data of **1** was then analyzed through a spin Hamiltonian for a linear tetranuclear chromium(III)–copper(II) model [Eq. (3) with $S_1 = S_4 = S_{Cr} = 3/2$ and $S_2 = S_3 = S_{Cu} = 1/2$], where *J* and *J'* are the intramolecular magnetic coupling parameters between the outer Cr^{III} and inner Cu^{II} ions ($J = J_{12} = J_{34}$) and the two inner Cu^{II} ions ($J' = J_{23}$) (Scheme 3), and g_{Cr} and g_{Cu} are the Landé factors of the Cr^{III} and Cu^{II} ions.

$$\mathbf{H} = -J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_3 \cdot \mathbf{S}_4) - J'\mathbf{S}_2 \cdot \mathbf{S}_3 + gCr(\mathbf{S}_1 + \mathbf{S}_4)\beta H + g_{Cu}(\mathbf{S}_2 + \mathbf{S}_3)\beta H$$
(3)

The least-squares fit of the experimental data of **1** by full-matrix diagonalization techniques [31] gave $J = -8.7 \text{ cm}^{-1}$, $J' = -472 \text{ cm}^{-1}$, $g_{Cr} = 2.001$, and $g_{Cu} = 2.102$ with $F = 1.0 \times 10^{-5}$, where F is the



Scheme 3. Spin topologies and ground spin states for a $Cr^{II_2}Cu^{II_2}$ linear complex with (a) J' < 0 and J < 0, (b) J' < 0 and J > 0, (c) J' > 0 and J < 0, or (d) J' > 0 and J > 0. The boxed structure shows the magnetic coupling scheme.

agreement factor defined as $F = \sum [(\chi_M T)_{exp} - (\chi_M T)_{calcd}]^2 /$ $\sum [(\chi_{\rm M} T)_{\rm exp}]^2$. The theoretical curve closely matches the experimental data of **1** with J < 0 and J' < 0 (solid line in Fig. 3a). This situation contrasts with that found for 2, where a good fit of the magnetic susceptibility data was obtained for J < 0 and J' > 0 (J = -1.3 cm⁻¹ and J' = +4.0 cm⁻¹) [23b]. So, a ground S = 0 Cr^{III}₂Cu^{II}₂ spin state would result from the intramolecular antiferromagnetic coupling (J' < 0) between the two inner Cu^{II} ions, whatever the nature of the intramolecular coupling between the inner Cu^{II} and outer Cr^{III} ions is, either antiferro- (J < 0) as in **1** or ferromagnetic (J > 0)(Schemes 3a and b, respectively). In contrast, the intramolecular ferromagnetic coupling (J' > 0) between the two inner Cu^{II} ions leads to ground S = 2 or S = 4 $Cr^{III}_{2}Cu^{II}_{2}$ spin states depending on the nature of the coupling between the inner Cu^{II} and outer Cr^{III} ions, either antiferro- (J < 0) as in **2** or ferromagnetic (J > 0)(Scheme 3c and d, respectively).

3.4. Magneto-structural correlations: orbital mechanism of the magnetic coupling

In order to account for the different magnetic properties of **1** and **2**, we may refer to simple dinuclear complexes with common structural features to those of these tetranuclear chromium(III)–copper(II) complexes. Selected magneto-structural data for **1** and **2** and related oxalato-bridged copper(II) and chromium(III)–copper(II) dinuclear complexes are listed in Tables 3 and 4, respectively.

The change from strong antiferro- (1) to weak ferromagnetic (2) coupling between the two inner Cu^{II} ions for 1 and 2 can be explained in terms of the well-known orbital reversal phenomenon

Table 3
Selected magneto-structural data for ${\bf 1}$ and ${\bf 2}$ and related oxalato-bridged dinuclear copper(II) complexes

Entry	Complex ^a	Bridge ^b	$R'_{ax}^{c}(Å)$	${\alpha'}^d$ (°)	${\beta'}^{e}(^{\circ})$	$h'^{\mathbf{f}}(\mathbf{A})$	$\gamma'^{g}(^{\circ})$	$J'^{h}(cm^{-1})$	Ref.
1	1	IIa				0.16	6.3	-472	This work
2	2	IIb	2.245	108.8	178.0	0.03	81.7	+4.0	[23b]
3	$[Cu_2(bpy)_2Cl_2(ox)] \cdot H_2O$	IIa				0.37	15.0	-330	[15a]
4	$[Cu_2(bpy)_2(PF_6)_2(ox)]$	IIa				0.08	3.2	-385	[15a]
5	$[Cu_2(bpy)_2(H_2O)_2(ox)](ClO_4)_2 \cdot [Cu(bpy)(ox)]$	IIa				0.18	12.0	-376	[15a]
6	$[Cu_2(bpy)_2(H_2O)_2(ox)](BF_4)_2\cdot [Cu(bpy)(ox)]$	IIa				0.16	10.4	-378	[15a]
7	$[Cu_2(bpy)_2(H_2O)_2(ox)](NO_3)_2 \cdot [Cu(bpy)(ox)]$	IIa				0.16	3.2	-386	[15a]
8	$[Cu_2(phen)_2(NO_3)_2(ox)]$	IIa				0.27	16.9	-330	[15a]
9	$[Cu_2(mpz)_2(NO_3)_2(H_2O)(ox)]_2[Cu_2(mpz)_2(NO_3)_2(ox)]$	IIa				0.06	2.1	-312	[15a]
10	$[Cu_2(mpz)_2(H_2O)_2(ox)](PF_6)_2 \cdot mpz \cdot 3H_2O$	IIa				0.24	13.9	-402	[15a]
11	$[Cu_2(mpz)_2(H_2O)_2(ox)](ClO_4)_2$	IIa				n.a.	n.a.	-350	[15a]
12	$[Cu_2(bzpm)_2(H_2O)_2(ox)](PF_6)_{1.5}(ClO_4)_{0.5} \cdot 1.5H_2O$	IIa				0.19	8.9	-349	[15a]
13	$[Cu_2(tmen)_2(H_2O)_2(ox)](ClO_4)_2 \cdot 1.25H_2O$	IIa				0.18	8.4	-385	[15a]
14	$[Cu_2(bpca)_2(ox)]$	IIb	2.26	107.5	171.4	0.16	92.0	+1.1	[15b]
15	$[Cu_2(bpca)_2(H_2O)_2(ox)]\cdot 2H_2O$	IIb	2.41	106.9	174.3	0.05	80.7	+1.0	[15c]
16	$[Cu_2(bpcam)_2(H_2O)_2(ox)]$	IIb	2.44	106.6	175.7	0.00	101.8	+0.75	[15d]

^a Abbreviations: $ox^{2-} = oxalate$; byy = 2,2'-bipyridine; phen = 1,10-phenanthroline; mpz = 4-methoxy-2-(5-methoxy-3-methyl-pyrazol-l-yl)-6-methylpyrimidine; bzpm = 7-bromo-1,3-dihydro-(2-pyridyl)-2H-1,4-benzodiazepine-2-one; tmen = N, N, N', N'-tetramethylethylenediamine; bpca⁻ = bis(2-pyridylcarbonyl)amidate; bpcam⁻ = bis(2-pyrimidylcarbonyl)amidate.

^b Bridging modes of the oxalato ligand: (IIa) symmetric bis-bidentate; (IIb) asymmetric bis-bidentate.

^c Axial Cu–O distance.

^d Axial Cu–O–C bending angle.

^e Axial Cu–O–C–O torsion angle.

^f Out-of-plane displacement of the Cu atom from the metal basal plane.

^g Bending angle between the metal basal plane and the oxalato plane.

^h Intramolecular magnetic coupling parameter ($\mathbf{H} = -J'\mathbf{S_1} \cdot \mathbf{S_2}$ with $S_1 = S_2 = S_{Cu} = 1/2$).

Table 4

Selected magneto-structural data for 1 and 2 and related oxalato-bridged dinuclear chromium(III)-copper(II) complexes.

Entry	Complex ^a	Bridge ^b	$R_{ax}^{c}(Å)$	α^{d} (°)	β^{e} (°)	$h^{\mathrm{f}}(\mathrm{\AA})$	γ^{g} (°)	$J^{h}(cm^{-1})$	References
1	1	Ι	2.383	124.1	25.5	0.16	62.59	-8.7	This work
2	2	II	2.357	108.2	173.2	0.03	86.02	-1.3	[23b]
3	$[Cu(bpy)_2(CH_3CO_2)][Cr(ox)_3Cu(bpy)_2] \cdot 10.5H_2O$	I	2.078	118.1	1.7	0.36	88.44	-0.05	[17e]
4	[Cr(bpy)(ox) ₂ Cu(bpca)(H ₂ O)]·2.5H ₂ O	I	2.253	124.7	6.8	0.19	86.70	0	[21a]
5	[Cr(phen)(ox) ₂ Cu(bpca)(H ₂ O)]·2H ₂ O	I	2.325	125.6	22.0	0.12	70.32	0	[21a]
6	[Cr(bpy)(ox) ₂ Cu(Hfsaaep)(H ₂ O)]·2H ₂ O	II	2.504	105.9	177.7	0.06	87.22	+1.4	[21b]
7	[Cr(salen)(ox)Cu(salpy)]·0.5H ₂ O	II	n.a.	n.a.	n.a.	n.a.	n.a.	+4.4	[17b]
8	[Cr(salen)(ox)Cu(saleten)]·0.5H ₂ O	II	n.a.	n.a.	n.a.	n.a.	n.a.	+5.4	[17b]
9	[Cr(salen)(ox)Cu(acpy)]·1.5H ₂ O	II	2.378	107.0	174.3	0.15	80.46	+5.6	[17c]

^a Abbreviations: $ox^{2-} = oxalate$; bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline; bpca⁻ = bis(2-pyridylcarbonyl)amidate; Hfsaaep⁻ = 3-[N-2-pyridylethyl)formidoyl]salicylate; salen²⁻ = N,N'-ethylenediaminebis(salicylate); salpy⁻ = N-salicylate-N-(2-pyridylethyl)amine; saleten⁻ = N-salicylate-N',N'-diethylethylenediamine; acpy⁻ = N-acetylacetonate-N-(2-pyridylethyl)amine.

^b Bridging modes of the oxalato ligand: (I) bidentate/monodentate(outer); (II) bis-bidentate.

^c Axial Cu-O distance.

^d Axial Cu-O-C bending angle.

^e Axial Cu-O-C-O torsion angle.

^f Out-of-plane displacement of the Cu atom from the metal basal plane.

^g Bending angle between the metal basal plane and the oxalato plane.

^h Intramolecular magnetic coupling parameter ($\mathbf{H} = -J\mathbf{S_1} \cdot \mathbf{S_2}$ with $S_1 = S_{Cr} = 3/2$ and $S_2 = S_{Cu} = 1/2$).

found for related oxalato-bridged dinuclear copper(II) complexes with a "coplanar" or "parallel" configuration of the copper basal planes [4]. In a previous theoretical work, Cano et al. established a magneto-structural correlation between the magnitude of the magnetic coupling and the dihedral angle between the copper basal planes and the bridging oxalato plane (γ') and/or the height of the copper atom from the metal basal plane (h') for antiferromagnetically coupled, "coplanar" oxalato-bridged dicopper(II) complexes [15a]. In this series, the -J' values decrease with the outof-plane displacement of the Cu atom and/or the bending of the $Cu(C_2O_4)Cu$ framework leading to a chair conformation, parameters which are in turn related so that the larger the bending angle is, the more important the out-of-plane displacement distance (Table 3). A similar magneto-structural correlation can be found between the magnitude of the magnetic coupling and the axial carbonyl-oxygen to copper bond angles (α') and bond distances (R'_{ax}) for ferromagnetically coupled, "parallel" oxalato-bridged

dicopper(II) complexes, as observed earlier by Castillo and García-Couceiro for related copper(II) chains [32,33]. In this other series, the J' values decrease with the bending of the axial Cu–O–C angle, a feature which is directly related to the lengthening of the axial Cu–O bond in such a way that the larger the axial distance is, the more bent the angle (Table 3).

So, the $d_{x^2-y^2}$ -type magnetic orbitals of each square-pyramidal Cu^{II} ion in **1** are coplanar and they are parallel to the mean plane of the central oxalate such that a good overlap with its σ -type antibonding orbital of appropriate symmetry occurs (Scheme 4a). The overlap between the $d_{x^2-y^2}$ (Cu) and $p_x(O)/p_y(O)$ orbitals from the equatorial carboxylate groups would be maximum for a coplanar disposition (h' = 0 Å and $\gamma' = 0^\circ$), when the antiferromagnetic exchange interaction would be the strongest one [4]. As h' increases when increasing γ' , the overlap decreases and consequently, the – J' values become smaller with the out-of-plane Cu displacement [15a]. Complex **1** has one of the smallest deviations from



Scheme 4. Orbital pathways of the exchange coupling for 1 and 2.

coplanarity (h' = 0.16 Å and $\gamma' = 6.3^\circ$; Table 3, entry 1) among those found in the related dicopper(II) complexes of general formula $[Cu^{II}_2(bpy)_2X_2(ox)]$ (X = Cl⁻ and PF₆⁻) and $[Cu^{II}_2(bpy)_2(H_2O)_2$ (ox)](X)₂·[Cu^{II}(bpy)(ox)] (X = ClO₄⁻, BF₄⁻, and NO₃⁻) possessing a symmetric bis-bidentate oxalato bridge (h' = 0.08-0.37 Å and $\gamma' = 3.2-15.0^\circ$; Table 3, entries 3-7) [15a]. Hence, the antiferromagnetic coupling for **1** (J' = -472 cm⁻¹; Table 3, entry 1) is the largest one among those reported previously for the aforementioned series of antiferromagnetically coupled, "coplanar" oxalato-bridged dicopper(II) complexes (-J' = 330-386 cm⁻¹; Table 3, entries 3-7) [15a].

Instead, the $d_{x^2-y^2}$ -type magnetic orbitals of each octahedral Cu^{II} ion in **2** are parallel to each other in two different planes and they are perpendicular to the mean plane of the central oxalate leading thus to a small, if not zero, overlap with its σ -type antibonding orbital of appropriate symmetry (Scheme 4b). The overlap between the $d_{x^2-y^2}(Cu)$ and $p_x(O)/p_y(O)$ orbitals from the axial carbonyl groups would be strictly zero for an α' value close to 120° and, consequently, the exchange interaction would reduce only to the ferromagnetic contribution [4]. As α' decreases when increasing $R'_{\alpha\nu}$, the overlap increases and so the antiferromagnetic contribution in such a way that an overall decrease of the *I* values is observed with the bending of the axial Cu–O–C angle [33]. Because of the rather small axial Cu-O distance, complex 2 has the less bent axial Cu–O–C angle (α' = 108.8° and R'_{ax} = 2.245 Å; Table 3, entry 2) [23b] among those found in the related dicopper(II) complexes of formula $[Cu^{II}_{2}(bpca)_{2}(ox)]$, $[Cu^{II}_{2}(bpca)_{2}(H_{2}O)_{2}(ox)]\cdot 2H_{2}O$, and [Cu^{II}₂(bpcam)₂(H₂O)₂(ox)] possessing an asymmetric bis-bidentate oxalato bridge (α' = 106.6–107.5° and $R'_{\alpha x}$ = 2.26–2.44 Å; Table 3, entries 14–16) [15b–d]. Hence, the ferromagnetic coupling for 2 $(J' = +4.0 \text{ cm}^{-1}; \text{ Table 3, entry 2})$ is greater than that previously reported for the aforementioned series of ferromagnetically coupled, "parallel" oxalato-bridged dicopper(II) complexes (J' = 0.75-1.1 cm⁻¹; Table 3, entries 14–16) [15b–d].

On the other hand, the change from moderate (**1**) to weak (**2**) antiferromagnetic coupling between the inner Cu^{II} and outer Cr^{III} ions for **1** and **2** with the bending of the axial Cu–O–C angle conforms with the trend observed for related oxalato-bridged dinuclear chromium(III)–copper(II) complexes with an "*anti–syn*" or "*anti–anti*" configuration of the oxalato bridge. So, a weak to moderate ferromagnetic coupling is found for the series of "*anti–anti*" bis-bidentate oxalato-bridged dinuclear chromium(III)–copper(II) complexes having rather bent Cu–O–C angles (J = +1.4 and +5.6 cm⁻¹ with $\alpha = 105.9$ and 107.0° ; Table 4, entries 6 and 9)



Fig. 4. (a) Dependence of the magnetic coupling parameter (*J*) on the axial Cu–O–C bond angle (α) for **1** and **2** and related dinuclear chromium(III)–copper(II) complexes with "*anti–syn*" bidentate/monodentate(outer) (**■**) and "*anti–anti*" bisbidentate (\bullet) oxalate, respectively (data from Table 4). The solid line corresponds to the best fit through a simple second–order polynomial equation. (b) Dependence of the axial Cu–O–C bond angle (α) on the axial Cu–O bond distance (R_{ax}) for **1** and **2** and related dinuclear chromium(III)–copper(II) complexes with "*anti–syn*" bidentate/monodentate(outer) (**□**) and "*anti–anti*" bisbidentate (σ) oxalate, respectively (data from Table 4). The solid line correspond to the linear fits.

(Fig. 4a). In this series, the α values decrease with the lengthening of the axial Cu–O bond ($R_{ax} = 2.378$ and 2.504 Å; Table 4, entries 6 and 9) (Fig. 4b). Instead, a very weak, if not negligible, antiferromagnetic coupling is found for the series of "*anti–syn*" bidentate/ monodentate(outer) oxalato-bridged dinuclear chromium(III)– copper(II) complexes which possess less bent axial Cu–O–C angles (-J < 0.05 cm⁻¹ with $\alpha = 118.1-125.6^{\circ}$; Table 4, entries 3–5) (Fig. 4a). In this other series, the α values increase with the lengthening of the axial Cu–O bond ($R_{ax} = 2.078-2.325$ Å; Table 4, entries 3–5) (Fig. 4b).

In fact, as is usually the case for extended bridging ligands like oxalate, the mixed σ/π -type orbital contributions involving the $d_{xz}(Cr)/d_{x^2-y^2}(Cu)$ and $d_{yz}(Cr)/d_{x^2-y^2}(Cu)$ pairs of orthogonal magnetic orbitals are always positive for symmetry considerations $(J_{xz,x^2-y^2}, J_{yz,x^2-y^2} > 0)$ [4]. However, the purely σ -type orbital contribution involving the $d_{xy}(Cr)/d_{x^2-y^2}(Cu)$ pair of nonorthogonal magnetic orbitals can be either positive $(J_{xy,x^2-y^2} > 0)$ or negative $(J_{xy,x^2-y^2} < 0)$, depending on some structural parameters like the axial Cu–O bond distance (R_{ax}) , the axial Cu–O–C bond angle (α) , and/ or the axial Cu–O–C–O torsion angle (β) .

So, the $d_{xy}(Cr)$ and $d_{x^2-y^2}(Cu)$ magnetic orbitals in **1** and **2** are perpendicular to each other with the $d_{x^2-y^2}(Cu)$ magnetic orbital being perpendicular to the mean plane of the peripheral oxalate leading thus to a small, but not zero, overlap with its σ -type

antibonding orbital of appropriate symmetry (Schemes 4a and b). Indeed, the overlap between the $d_{x^2-y^2}(Cu)$ and $p_x(O)/p_y(O)$ orbitals from the axial carbonyl group would be strictly zero for an α value close to 90° and, consequently, the exchange interaction would reduce only to the ferromagnetic contribution [4]. As α increases, the overlap increases and so, the antiferromagnetic contribution, in such a way that a net antiferromagnetic coupling is found for α values above 108.0° (Fig. 4a). Complex 2 has an axial Cu–O–C angle slightly larger than this limit value ($\alpha = 108.2^{\circ}$; Table 4, entry 2), while that of the related "anti-anti" bis-bidentate oxalato-bridged dinuclear chromium(III)-copper(II) complex of formula {Cr^{III}(bpy)(ox)₂Cu^{II}(Hfsaaep)(H₂O)·2H₂O is clearly smaller ($\alpha = 105.9^{\circ}$; Table 4, entry 6), in agreement with the experimentally observed antiferro- and ferromagnetic couplings, respectively (I = -1.3 and+1.4 cm⁻¹; Table 4, entries 2 and 6). Complex **1** has an axial Cu-O-C angle larger than that of **2**, so that the antiferromagnetic coupling for **1** is stronger than for **2** $[I = -8.7 (1) \text{ and } -1.3 \text{ cm}^{-1} (2) \text{ with}$ α = 124.1 (**1**) and 108.2° (**2**); Table 4, entries 1 and 2]. However, this situation contrasts with that reported for the related pair of magnetically uncoupled, "anti-syn" bidentate/monodentate(outer) oxalato-bridged dinuclear chromium(III)-copper(II) complexes of formula $\{Cr^{III}(bpy)(ox)_2Cu^{II}(bpca)(H_2O)\}$ 2.5H₂O and $\{Cr^{III}(phe$ n)(ox)₂Cu^{II}(bpca)(H₂O) \cdot 2H₂O [21a], which possess even larger axial Cu-O-C angles but smaller axial Cu-O-C-O torsion angles and axial Cu–O distances (α = 124.7 and 125.6°, β = 6.8 and 22.0°, and R_{ax} = 2.253 and 2.325 Å; Table 4, entries 4 and 5, respectively) than those of **1** (α = 124.1°, β = 25.5°, and R_{ax} = 2.383 Å; Table 4, entry 1). It thus appears that further magnetic and structural data are required to check the validity of this magneto-structural correlation and to further evaluate the influence of each structural parameter on the variation of the magnetic coupling along this series of "antisyn" bidentate/monodentate(outer) oxalato-bridged dinuclear chromium(III)-copper(II) complexes.

4. Conclusions

In the present work, we provide a comparative magneto-structural study of two linear heterotetranuclear chromium(III)-copper(II) complexes of general formula {[Cr^{III}(bpy)(ox)₂]₂ $Cu^{II}_{2}(bpy)_{2}(ox)$ $\cdot nH_{2}O$ [*n* = 6 (1) and 2 (2)] with 2,2'-bipyridine (bpy) as blocking ligand, where oxalate acts as bridge between two identical or distinct transition metal ions in a variety of ways, leading thus to different magnetic properties. So, this unique pair of complexes show different spin topologies and ground spin states $[S = (S_{Cr} - S_{Cu}) - (S_{Cr} - S_{Cu}) = 0$ (1) and $S = (S_{Cr} - S_{Cu}) + (S_{Cr} - S_{Cu}) = 2$ (2)] as a result of the change from strong antiferro-(1) to weak ferromagnetic (2) coupling between the two inner Cu^{II} ions with either a "coplanar" or "parallel" configuration across the central symmetric (1) or asymmetric (2) bis-bidentate oxalate, the magnetic interactions between the outer $Cr^{III}\xspace$ and inner $Cu^{II}\xspace$ ions through the peripheral bidentate/monodentate(outer) (1) or bis-bidentate (2) oxalates with either an "anti-syn" or "anti-anti" configuration changing from moderate (1) to weak (2) antiferromagnetic coupling. Extension of the present work to related oxalato-bridged heterotetranuclear chromium(III)-cobalt(II) complexes with higher values of the spin ground state and the magnetic anisotropy as potential candidates of SMMs is in progress.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for 1 have been deposited with the Cambridge Crystallographic Data Centre, CSD No. CCDC-879902. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html. or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] (a) G.B. Kauffman, Alfred Werner, Founder of Coordination Chemistry, Springer-Verlag, Berlin, Heidelberg, New York, 1966;
 - (b) G.B. Kauffman, Classics in Coordination Chemistry, Part 1, Dover Publications Inc., New York, 1968;
 - (c) G.B. Kauffman, Inorganic Coordination Compounds, Heyden & Son Ltd., London, Philadelphia, Rheine, 1981:
 - (d) K.-H. Ernst, F.R.W.P. Wild, O. Blacque, H. Berke, Angew. Chem., Int. Ed. 50 (2011) 10780. and references therein.
- [2] (a) A. Werner, Ber. Dtsch. Chem. Ges. 47 (1914) 3087;
- (b) S.M. Jørgensen, Z. Anorg. Chem. 16 (1898) 184.
- [3] (a) L. Cronin, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II: From Biology to Nanotechnology, vol. 7, Elsevier, Oxford, USA, 2004, p. 1; (b) M.W. Degroot, J.F. Corrigan, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II: From Biology to Nanotechnology,

vol. 7. Elsevier, Oxford, USA, 2004, p. 57: (c) R.E.P. Winpenny, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II: From Biology to Nanotechnology, vol. 7, Elsevier,

Oxford, USA, 2004, p. 125; (d) M. Pilkington, S. Decurtins, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II: From Biology to Nanotechnology,

- vol. 7, Elsevier, Oxford, USA, 2004, p. 177, O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.
- O. Kahn, P. Tola, J. Galy, H. Coudanne, J. Am. Chem. Soc. 100 (1978) 3931. [6] (a) Y. Pei, Y. Journaux, O. Kahn, A. Dei, D. Gatteschi, J. Chem. Soc., Chem. Commun. (1986) 1300;
- (b) Y. Pei, Y. Journaux, O. Kahn, Inorg. Chem. 27 (1988) 399.
- [7] D.N. Hendrickson, G. Christou, E.A. Schmitt, E. Libby, J.S. Bashkin, S. Wang, H.L. Tsai, J.B. Vincent, P.D.W. Boyd, J.C. Huffman, K. Folting, Q. Li, E. Streib, J. Am. Chem. Soc. 114 (1992) 2455.
- F. Lloret, Y. Journaux, M. Julve, Inorg. Chem. 29 (1990) 3967.
- [9] (a) R. Sessoli, D. Gatteschi, A. Caneschi, M.A. Novak, Nature 365 (1993) 141; (b) J.R. Friedman, M.P. Sarachik, J. Tejada, R. Ziolo, Phys. Rev. Lett. 76 (1996) 3830.
- [10] D. Gatteschi, R. Sessoli, Angew. Chem., Int. Ed. 42 (2003) 268. and references therein.
- [11] D. Gatteschi, R. Sessoli, J. Villain, Molecular Nanomagnets, Oxford University Press. 2006.
- [12] (a) D. Gatteschi, A. Caneschi, R. Sessoli, A. Cornia, Chem. Soc. Rev. 25 (1996) 101:
 - (b) D. Gatteschi, R. Sessoli, A. Cornia, Chem. Commun. (2000) 725;
 - (c) R.E.P. Winpenny, Adv. Inorg. Chem. 52 (2001) 1;
 - (d) E.K. Brechin, Chem. Commun. (2005) 5141;
 - (e) G. Aromi, E.K. Brechin, Struct. Bond. 122 (2006) 1;
 - (f) T.C. Stamatatos, G. Christou, Inorg. Chem. 48 (2009) 3308.
- [13] (a) L.K. Thompson, Coord. Chem. Rev. 233-234 (2002) 193; (b) J.M. Lehn, Angew. Chem., Int. Ed. Engl. 43 (2004) 3644; (c) L.K. Thompson, O. Waldman, Coord. Chem. Rev. 249 (2005) 2677.
- [14] (a) V. Marvaud, J.M. Herrera, T. Barilero, F. Tuyèras, R. Garde, A. Scuiller, C. Decroix, M. Cantuel, C. Desplanches, Monatsh. Chem. 134 (2003) 149; (b) L.M.C. Beltran, J.R. Long, Acc. Chem. Res. 38 (2005) 325; (c) E. Pardo, R. Ruiz-García, J. Cano, X. Ottenwaelder, R. Lescouëzec, Y.
- Journaux, F. Lloret, M. Julve, Dalton Trans. (2008) 2780; (d) M.-C. Dul, E. Pardo, R. Lescouëzec, Y. Journaux, J. Ferrando-Soria, R. Ruiz-
- García, J. Cano, M. Julve, F. Lloret, D. Cangussu, C.L.M. Pereira, H.O. Stumpf, J. Pasán, C. Ruiz-Pérez, Coord. Chem. Rev. 254 (2010) 2281.
- [15] (a) J. Cano, P. Alemany, S. Alvarez, M. Verdaguer, E. Ruiz, Chem. Eur. J. 4 (1998) 476. and references therein; (b) I. Castro, J. Faus, M. Mollar, A. Monge, E. Gutiérrez-Puebla, Inorg. Chim.

Acta 161 (1989) 97;

(c) M.L. Calatayud, I. Castro, J. Sletten, F. Lloret, M. Julve, Inorg. Chim. Acta 300-302 (2000) 846:

(d) D. Cangussu, H.O. Stumpf, H. Adams, J.A. Thomas, F. Lloret, M. Julve, Inorg. Chim. Acta 358 (2005) 2292.

[16] (a) J. Glerup, P.A. Goodson, D.J. Hodgson, K. Michelsen, Inorg. Chem. 34 (1995) 6255;

(b) P. Román, C. Guzmán-Miralles, A. Luque, J.I. Beitia, J. Cano, F. Lloret, M. Julve, S. Alvarez, Inorg. Chem. 35 (1996) 3741. and references therein.

- [17] (a) Y. Pei, Y. Journaux, O. Kahn, Inorg. Chem. 28 (1989) 100;
 - (b) M. Ohba, H. Tamaki, N. Matsumoto, H. Okawa, S. Kida, Chem. Lett. (1991) 1157:
 - (c) M. Ohba, H. Tamaki, N. Matsumoto, H. Okawa, Inorg. Chem. 32 (1993) 5385;
 - (d) E. Coronado, J.R. Galán-Mascarós, C. Giménez-Saiz, C.J. Gómez-García, C. Ruiz-Pérez, S. Triki, Adv. Mater. 8 (1996) 737;
 - (e) O. Costisor, K. Mereiter, M. Julve, F. Lloret, Y. Journaux, W. Linert, M. Andruh, Inorg. Chim. Acta 324 (2001) 352;
 - (f) E. Coronado, J.R. Galán-Mascarós, C. Giménez-Saiz, C.J. Gómez-García, C. Ruiz-Pérez, Eur. J. Inorg. Chem. (2003) 2290;
 - (g) E. Pardo, C. Train, R. Lescouëzec, K. Boubekeur, E. Ruiz, F. Lloret, M. Verdaguer, Dalton Trans. 39 (2010) 4951.
- [18] (a) R. Chiozzone, R. González, C. Kremer, G. De Munno, J. Cano, F. Lloret, M. Julve, J. Faus, Inorg. Chem. 38 (1999) 4745;
 - (b) R. Chiozzone, R. González, C. Kremer, G. De Munno, D. Armentano, J. Cano, F. Lloret, M. Julve, J. Faus, Inorg. Chem. 40 (2001) 4242;
 - (c) J. Martínez-Lillo, D. Armentano, G. De Munno, W. Wernsdorfer, M. Julve, F. Lloret, J. Faus, J. Am. Chem. Soc. 128 (2006) 14218;
 - (d) J. Martínez-Lillo, D. Armentano, G. De Munno, W. Wernsdorfer, M. Julve, F. Lloret, J. Faus, Inorg. Chem. 48 (2009) 3027;
 - (e) J. Martínez-Lillo, D. Armentano, G. De Munno, W. Wernsdorfer, M. Julve, F. Lloret, J. Faus, Inorg. Chem. 50 (2011) 5731.
- [19] G. Marinescu, M. Andruh, F. Lloret, M. Julve, Coord. Chem. Rev. 255 (2011) 161.
- [20] (a) J.A. Broomhead, Aust. J. Chem. 15 (1962) 228;
 - (b) M.C. Muñoz, M. Julve, F. Lloret, J. Faus, M. Andruh, J. Chem. Soc., Dalton Trans. (1998) 3125;
 - (c) F.D. Rochon, G. Massarweh, Can. J. Chem. 77 (1999) 2059;
 - (d) G. De Munno, D. Armentano, M. Julve, F. Lloret, R. Lescouëzec, J. Faus, Inorg. Chem. 38 (1999) 2234;
 - (e) F. Bérézovsky, A.A. Hajem, S. Triki, J.S. Pala, P. Molinié, Inorg. Chim. Acta 284 (1999) 8;
 - (f) N. Sakagami, E. Kita, P. Kita, J. Wisniewska, S. Kaizaki, Polyhedron 18 (1999) 2001;
 - (g) R. Lescouëzec, G. Marinescu, M.C. Muñoz, D. Luneau, M. Andruh, F. Lloret, J. Faus, M. Julve, J.A. Mata, R. Llusar, J. Cano, New J. Chem. 25 (2001) 1224;
 - (h) V. Russell, D. Craig, M. Scudder, I. Dance, CrystEngComm 3 (2001) 96;
 - (i) G. Marinescu, R. Lescouëzec, D. Armentano, G. De Munno, M. Andruh, S.
 - Uriel, R. Llusar, F. Lloret, M. Julve, Inorg. Chim. Acta 336 (2002) 46;
 - (j) C. Yuste-Vivas, F.S. Delgado, C. Ruiz-Pérez, M. Julve, CrystEngComm 6 (2004) 11;
 - (k) G. Marinescu, M. Andruh, M. Julve, F. Lloret, R. Llusar, S. Uriel, J. Vaissermann, Cryst. Growth Des. 5 (2005) 261;
 - (I) M. Viciano-Chumillas, N. Marino, I. Sorribes, C. Vicent, F. Lloret, M. Julve, CrystEngComm 12 (2010) 122.

- [21] (a) R. Lescouëzec, G. Marinescu, J. Vaissermann, F. Lloret, J. Faus, M. Andruh, M. Julve, Inorg. Chim. Acta 350 (2003) 131;
 (b) G. Marinescu, D. Visinescu, A. Cucos, M. Andruh, Y. Journaux, V. Kravtsov, Y.A. Simonov, J. Lipkowski, Eur. J. Inorg. Chem. (2004) 2914;
 (c) S. Nastase, C. Maxim, F. Yuna, C. Duhayon, J.P. Sutter, M. Andruh, Polyhedron 28 (2009) 1688;
 (d) J. Vallejo, I. Castro, J. Ferrando-Soria, M.P. Déniz-Hernández, C. Ruiz-Pérez, F. Lloret, M. Julve, R. Ruiz-García, J. Cano, Inorg. Chem. 50 (2011) 2073;
 - (e) J. Vallejo, I. Castro, J. Ferrando-Soria, M.P. Déniz-Hernández, C. Ruiz-Pérez,
- F. Lloret, M. Julve, R. Ruiz-García, J. Cano, Inorg. Chem. 51 (2012) 3289. [22] (a) F.D. Rochon, R. Melanson, M. Andruh, Inorg. Chem. 35 (1996) 6086;
- (b) M. Andruh, R. Melanson, C.V. Stager, F.D. Rochon, Inorg. Chim. Acta 251 (1996) 309;
 (c) N. Stanica, C.V. Stager, M. Cimpoesu, M. Andruh, Polyhedron 17 (1998)
 - 1787; (d) D. Visinescu, J.P. Sutter, C. Ruiz-Pérez, M. Andruh, Inorg. Chim. Acta 359
 - (2006) 433; (e) J. Vallejo, I. Castro, L. Cañadillas-Delgado, C. Ruiz-Pérez, J. Ferrando-Soria,
- R. Ruiz-García, J. Cano, F. Lloret, M. Julve, Dalton Trans. 39 (2010) 2350.
 [23] (a) G. Marinescu, M. Andruh, R. Lescouëzec, M.C. Muñoz, J. Cano, F. Lloret, M. Julve, New J. Chem. 24 (2000) 527;
- (b) E. Coronado, M.C. Giménez, C.J. Gómez-García, F.M. Romero, Polyhedron 22 (2003) 3115.
- [24] P.Y. Zavalik, B.L. Burton, W.E. Jones Jr., Acta Crystallogr., Sect. C 58 (2002) m330.
- [25] (a) R.W.W. Hooft, COLLECT, Nonius BV, Delft, The Netherlands, 1999.;
 (b) A.J.M. Duisenberg, L.M.J. Kroon-Batenburg, A.M.M. Schreurs, J. Appl. Crystallogr. 36 (2003) 220 (EVALCCD).
- [26] SADABS, VERSION 2.03, Bruker AXS Inc., Madison, WI, 2000.
- [27] G.M. Sheldrick, SHELX97, Programs for Crystal Structure Analysis (Release 97-2), Institüt für Anorganische Chemie der Universität, Göttingen, Germany, 1998.
- [28] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837 (WINGX).
- [29] (a) M. Nardelli, J. Appl. Crystallogr. 28 (1995) 659;
 (b) D. Palmer, CRYSTAL MAKER, Cambridge University Technical Services, Cambridge, UK, 1996.
- [30] E.I. Stiefel, G.F. Brown, Inorg. Chem. 11 (1972) 434.
- [31] J. Cano, VPMAG package, University of Valencia, Valencia, Spain, 2003.
- [32] (a) H. Oshio, U. Nagashima, Inorg. Chem. 31 (1992) 3295;
 (b) J. Suárez-Varela, J.M. Domínguez-Vera, E. Colacio, J.C. Avila-Rosón, M.A. Hidalgo, D. Martín-Ramos, J. Chem. Soc., Dalton Trans. (1995) 2143;
 (c) O. Castillo, A. Luque, P. Román, F. Lloret, M. Julve, Inorg. Chem. 40 (2001) 5526;
- (d) O. Castillo, A. Luque, F. Lloret, P. Román, Inorg. Chim. Acta 324 (2001) 141. [33] (a) O. Castillo, Ph.D. Thesis, Bilbao, 2001.;
 - (b) U. García-Couceiro, Degree Thesis, Bilbao, 2002.