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Solvent controlled nuclearity in Cu(II) complexes linked by the CO_3^{2-} ligand: synthesis, structure and magnetic properties †

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Two new carbonato-bridged copper complexes with different nuclearity have been synthesized and structurally characterized through X-ray diffraction analyses: the tetranuclear complex $[Cu^{II}_4(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2(dpt)_4](ClO_4)_4\cdot 3MeOH$, **2**·3MeOH and the trinuclear $[Cu^{II}_3(\mu_3\text{-}CO_3)(ClO_4)_2(dpt)_3(OH_2)](ClO_4)_2\cdot H_2O$, **3**·$H_2O$ (dpt is bis(3-aminopropyl)-amine). A rationalisation for the synthetic pathways that lead to the formation of tri- and tetra-nuclear complexes is described, proving that **2** is an intermediate to generate **3**. For the tetranuclear complex **2**·3MeOH, this report represents the first accurate and rigorous synthetic and structural description of this type of complex. For the trinuclear complex **3**·H_2O, it constitutes the first example of an asymmetric trinuclear μ_3-carbonato bridged complex. Magnetic susceptibility data were fitted according to the molecular structures using the following Hamiltonians: $H = -J_{12}S_1S_2 - J_{13}(S_1S_3 + S_2S_4) - J_{14}(S_1S_4 + S_2S_3) - J_{34}S_3S_4$, which corresponds to a rectangular array of spins for **2**·3MeOH, and $H = -J(S_1S_2 + S_2S_3 + S_1S_3)$, which corresponds to a triangular array of spins, corrected with a J' intertrimer coupling or ZFS parameter to fit low T data, for **3**·H_2O. The best fit parameters obtained were $J_{12} = -189.9\ cm^{-1}$, $J_{34} = -22.2\ cm^{-1}$, $J_{14} = -60.0\ cm^{-1}$, $J_{13} = 15.0\ cm^{-1}$, $g = 2.18$ and with $R = 1.2 \times 10^{-7}$ for **2**·3MeOH and $J = 13.89\ cm^{-1}$, $J' = -0.07\ cm^{-1}$ and $g = 2.1$ with $R = 5.3 \times 10^{-4}$ for **3**·H_2O.

Introduction

The coordination chemistry of the carbonato ligand to transition metal complexes is very rich, due to the capability of this ligand to act as a bridge in a large variety of coordination modes.[1–7] The resulting metal-carbonato complexes are of interest because of their relevance in bioinorganic[8,9] and environmental[10] fields.

Furthermore, from a magnetic point of view, the different coordination modes of the carbonato ligand are responsible for a wide diversity of magnetic behaviours. These range from diamagnetic complexes at room temperature in fully coupled metal centres, to moderate or weak antiferromagnetic compounds and even ferromagnetic systems.[5c] The possibility of generating carbonato complexes with a triangular arrangement is also of interest because this geometry might offer the possibility to study frustrated spin systems.[4f]

In spite of the general interest of these types of compound, no systematic procedure to prepare them is known and, furthermore, their magnetic properties for nuclearities higher than two have been scarcely described.[4f,5c]

In this work, we present a rationalisation of the synthetic procedures to obtain new tri- and tetra-nuclear carbonato complexes, together with their structural characterisation and magnetic properties.

Experimental

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Although we did not suffer any explosion, only a small amount of material should be prepared at a time, and it should be handled with great care.

Materials and reagents

Copper(II) chloride dihydrate (99.8%) was purchased from Probus, $NaClO_4\cdot H_2O$ (PA > 99%) from Fluka and bis(3-aminopropyl)amine (dpt, 98%) from Aldrich. All solvents were obtained from SDS as reagent grade and were used without further purification.

Synthesis

$[Cu_2(\mu\text{-}Cl)_2(dpt)_2]Cl_2$, 1. Was prepared according to literature procedures.[11]

$[Cu^{II}_4(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2(dpt)_4](ClO_4)_4\cdot 3MeOH$, 2·3MeOH. A sample of 500 mg (0.94 mmol) of $[Cu_2(\mu\text{-}Cl)_2(dpt)_2]Cl_2$ together with 400 mg (2.85 mmol) of $NaClO_4\cdot H_2O$ were placed in a 100 mL round bottomed flask. Then, 25 mL of methanol were added and the resulting solution kept under magnetic stirring for two minutes. A blue solid immediately precipitated out of the solution, which was filtered off in a Büchner funnel and washed with cold MeOH (10 mL) and ether (3 × 10 mL), and finally dried *in vacuo*. Yield: 125 mg (20%). Anal. calc. for $C_{28}H_{80}N_{12}O_{22}Cu_4Cl_6$: C, 23.9; H, 5.7; N, 12.0. Found: C, 23.7;

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† Electronic supplementary information (ESI) available: EPR spectrum at 4 K for complex **3**·H_2O, and its mathematical simulation. See http://www.rsc.org/suppdata/dt/b2/b203057h/

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Table 1 Crystal data for complexes **2**·3MeOH and **3**·H$_2$O

Formula	$C_{28}H_{80}N_{12}Cu_4Cl_6O_{22}$	$C_{19}H_{55}N_9Cu_3Cl_4O_{21}$
M	1403.90	1078.14
Crystal symmetry	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pbca$
a/Å	12.798(3)	22.664(5)
b/Å	17.105(3)	21.033(4)
c/Å	25.802(5)	17.550 (4)
β/°	96.02(3)	90.00
V/Å^3	5617(2)	8366(2)
Z	4	8
T/K	133(2)	293(2)
λ(Mo-Kα)/Å	0.71073	0.71073
ρ/g cm^{-3}	1.660	1.712
μ/mm^{-1}	1.859	1.852
$R1^a$	0.0472	0.0121
$wR2^b$	0.0991	0.0282

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma F_o$. [b] $wR2 = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(F_o)^2]\}^{1/2}$.

H, 6.0; N, 11.9%. IR (KBr pellet, cm^{-1}): 3336, 3255, 2951, 1597, 1531, 1365, 1103, 625. UV–Vis (MeOH) λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}): 619 (1014), 262 (26101).

[Cu$^{II}_3$(μ_3-CO$_3$)(ClO$_4$)$_2$(dpt)$_3$(OH$_2$)](ClO$_4$)$_2$·H$_2$O, 3·H$_2$O. A 200 mg (0.192 mmol) sample of **2**·3MeOH was placed in a 25 mL Erlenmeyer flask and dissolved with 4 mL of water. The volume of the solution was then allowed to reduce to 0.5 mL in an open atmosphere upon which small violet crystals were grew. The crystals were then filtered off in a Büchner funnel, washed with cold water (1 mL) and ether (3 × 5 mL), and dried *in vacuo*. Yield: 50 mg (25%). Anal. calc. for $C_{19}H_{55}N_9O_{21}Cu_3Cl_4$: C, 21.2; H, 5.1; N, 11.7. Found: C, 21.6; H, 5.4; N, 11.8%. IR (KBr pellet, cm^{-1}): 3336, 3248, 1091, 625. UV–Vis (MeOH) λ_{max}/nm (ε_{max}/M^{-1} cm^{-1}): 630 (357), 256 (21465).

Measurements

C, H and N elemental analyses were performed in a CHNS-O Fisons instrument. Infrared spectra were obtained on a Mattson Satellite FT-IR spectrophotometer using KBr pellets. Absorption spectra were recorded on a Cary 50 UV–Vis spectrophotometer. EPR spectra were monitored with a Bruker ESP 300E instrument. Samples were run at 9.4 GHz (X-band) in the temperature range 4–298 K. EPR simulations were performed using the WIN-EPR Simfonia program from Bruker. Variable-temperature magnetic susceptibility measurements in the polycrystalline state were carried out on a MANIC DSM8 equipped with a Bruker BE15 electromagnet and an Oxford CF 1200S cryogenic apparatus. Data were taken in the temperature range 4–300 K with an applied magnetic field of 15000 G. Diamagnetic corrections were estimated from Pascal tables.

Crystallographic measurements

A single crystal X-ray structure determination on compound **2**·3MeOH was carried out using a Stoe-Siemens-Huber four circle diffractometer fitted with a Siemens CCD area detector, with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). On standing the reaction mixture, single crystals were obtained; one was selected and rapidly cooled[12a] in a drop of perfluoropolyether, on top of a glass fiber. The crystal data, data collection and refinement parameters are summarised in Table 1. Direct methods[12b] were used to locate the four copper and the two bridging chlorine atoms of the asymmetric unit, while subsequent cycles of least-squares refinements and difference Fourier maps were used to locate the remaining non-hydrogen atoms.[12c] After the bulk of the cation (and even the four perchlorate anions, and the three crystallisation methanol molecules) had been located, the difference Fourier peaks showed a strong disorder of the heavier atoms around a pseudo-centre of symmetry (coincident with the position of the carbon atom of the carbonate bridge, C0, which does not lie on a crystallographic special position). In the crystal, packing is achieved thanks to the triamine ligands which wrap the metal atoms, so that the exact positions of the innermost atoms have little effect on the structure. Two different approaches were tested: a) The second component of the disordered molecule was generated by inversion about the C0 pseudo-centre, with a common, variable s.o.f., such that both components added to 1. Atomic displacement parameters were constrained to be equal to those of the equivalent atoms of the first component. Not surprisingly, although convergence was achieved and the residuals were small, the carbon and nitrogen atoms of the triamine ligands could not be modelled as anisotropic and this solution was abandoned; b) The Fourier peaks adjacent to the primary heavy atoms (copper and chlorine) were chosen as the "real" positions; of each pair, those corresponding to a higher electron density were assigned to one of the components of the disorder, while the others were assigned to the second component. The atomic displacement parameters of each pair were constrained to be equal. After successive full-matrix least-squares refinement cycles, the common site occupation factor of part 1 targeted to 0.66. The non-hydrogen atoms were stepwise included in anisotropic refinement, with almost no change in the multiplicity factors which were, therefore, finally fixed at 2/3 : 1/3, leaving then the thermal parameters free to refine. Hydrogen atoms were placed at geometrically calculated positions and refined "riding" on the corresponding carbon atom, with dependent isotropic displacement parameters. Finally, the donor N-atoms were modelled in each of the two components (on exactly equal coordinates, and constrained to equal thermal displacement parameters) so that riding H-atoms could be attached to them. The chemically equivalent bonds Cl1B–Cu1B, Cl1B–Cu2B, Cl2A–Cu3A and Cl2A–Cu4A were restrained to be of similar length; likewise, similarity restraints were imposed on the Cl1A–Cu1A, Cl1A–Cu2A, Cl2B–Cu3B and Cl2B–Cu4B distances. Two of the perchlorate anions showed disorder as well, accounting for the highest residual electronic density peaks (less than 1 e A^{-3}). Modelling of this disorder was tried and discarded, since the occupation factor of the second component refined to only 10%, which was thought to be no improvement. Disorder of the O and C atoms of the crystallisation methanol molecules can be discarded since there are no phantom hydrogen bonds to the carbon atoms.

A blue plate of complex **3**·H$_2$O was mounted on a glass fibre with epoxy cement, at room temperature. Preliminary examination and data collection was performed on a Bruker P4 X-ray diffractometer (oriented graphite monochromator; Mo-Kα radiation, λ = 0.71073 Å). Data were collected using the θ–2θ scan mode for $4.0 \leq 2\theta \leq 50.0°$ at 293 K. The structure was solved by direct methods[12b] and full-matrix least-squares anisotropic refinement was used for all non-hydrogen atoms.[12c] The hydrogen atoms of the coordinated and crystal water molecules were also located by difference Fourier maps, and freely refined. The rest of the hydrogen atoms were placed in idealised positions on the corresponding carbon or nitrogen atoms, with dependent thermal parameters. Three of the four perchlorate counterions are disordered: they were first included in the model with equal atomic displacement parameters and common multiplicity for each of two orientations; finally, their site occupation factors were rounded to 2/3 : 1/3 or 1/2 : 1/2 and fixed, according to the result of the least-squares refinement, and the thermal parameters were then left free to refine. A summary of the data collection and structure solution is given in Table 1.

Neutral atom scattering factors and anomalous scattering correction terms were taken from *International Tables for X-Ray Crystallography*.[13] A summary of the data collection and structure solution is given in Table 1.

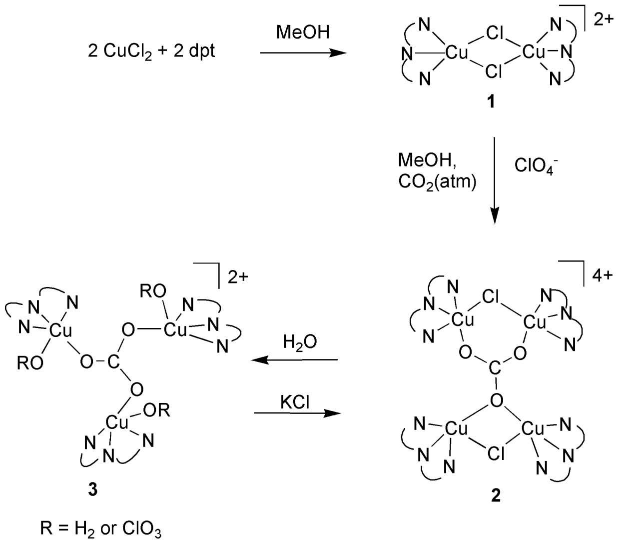
CCDC reference numbers 167772 and 167773.

See http://www.rsc.org/suppdata/dt/b2/b203057h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and structure

Addition of a stoichiometric amount of dpt to a $CuCl_2$ methanolic solution leads immediately to the formation of a dichloro-bridged dinuclear complex $[Cu^{II}_2(\mu\text{-}Cl)_2(dpt)_2]Cl_2$ **1** (see Scheme 1). This complex is then used as the starting material for the preparation of the carbonato-bridged tetranuclear complex $[Cu^{II}_4(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2(dpt)_4](ClO_4)_4\cdot3MeOH$, **2**·3MeOH. The latter is obtained by simply dissolving **1** in methanol and allowing it to react with atmospheric CO_2; thus, it constitutes an example of a model complex for atmospheric CO_2 fixation. Furthermore, it is the first accurately described synthesis for this type of complex, since in previous examples[5c,14] the yield was not even reported. The tetranuclear complex **2** was used as the starting material for the preparation of the trinuclear complex $[Cu^{II}_3(\mu_3\text{-}CO_3)(ClO_4)_2(dpt)_3(OH_2)](ClO_4)_2\cdot H_2O$, **3**·$H_2O$. Thus, complex **2** constitutes a synthetic intermediate which, when dissolved in water, is readily transformed into **3**, (see Scheme 1). This reaction also takes place in the absence of CO_2, under an argon atmosphere. The opposite reaction, the formation of the tetranuclear complex from the trinuclear one is observed in solution when adding an excess of KCl, or in the solid state when making a KBr pellet for IR measurements. These findings are in agreement with the fact that complex **2** can be regarded also as a structural intermediate between **1** and **3**. The methanolic solvent is the key factor that allows the reaction to stop at the formation of **2**, because the following reaction to form **3** is very slow and also because of the low solubility of **2** in this solvent.



Scheme 1 Synthetic strategy.

For the $CuCl_2$ or $CuBr_2$ salts reacting with non-substituted triamines in an open atmosphere, the experiments presented above together with previous results on related systems described in the literature,[4f,5c,11,14] agree well with the pathways proposed in Scheme 1. The equilibria involved in the processes outlined in that scheme are highly shifted to the formation of the trinuclear complex when using H_2O as the solvent. This explains why only very small amounts of the tetranuclear complexes had been previously obtained and, therefore, why their yields had never been reported.

The structures of the carbonato-bridged tetranuclear $[Cu^{II}_4(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2(dpt)_4](ClO_4)_4\cdot3MeOH$, **2**·3MeOH, and the trinuclear $[Cu^{II}_3(\mu_3\text{-}CO_3)(ClO_4)_2(dpt)_3(OH_2)](ClO_4)_2\cdot H_2O$, **3**·$H_2O$, complexes, have been established by means of X-ray diffraction analyses. ORTEP views of their cations at 50 and 40% probability, together with the atom labelling schemes are displayed in Figs. 1A and 1B, respectively. Selected bond distances (Å) and angles (°) can be found in Tables 2 and 3.

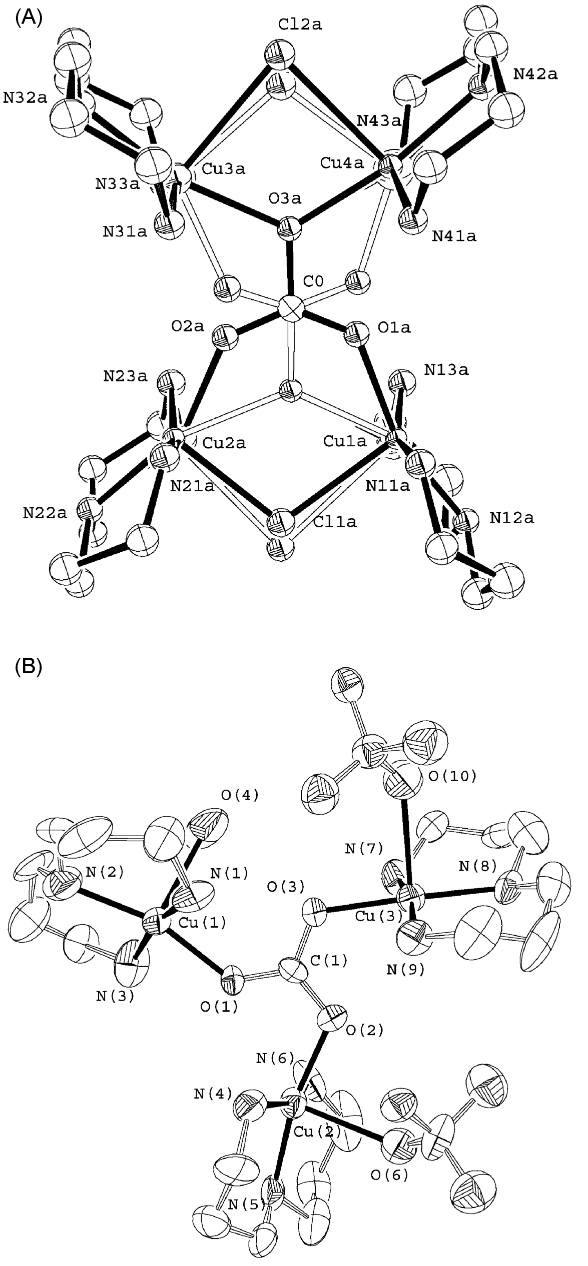


Fig. 1 (A) ORTEP[18] view of the molecular structure of the cation of $[Cu_4(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2(dpt)_4](ClO_4)_4\cdot3MeOH$ (**2**·3MeOH) (ellipsoids at 50% probability). (B) ORTEP view of the molecular structure of the cation of $[Cu_3(\mu_3\text{-}CO_3)(ClO_4)_2(dpt)_3(OH_2)](ClO_4)_2\cdot H_2O$ (**3**·H_2O) (ellipsoids at 40% probability).

X-Ray diffraction analysis indicates that the atoms of the tetranuclear complex **2**·3MeOH are disordered, giving rise to two limiting structures with 67 and 33% occupancy. This disorder is strongly manifested in the oxygen atoms of the carbonato and in the chloride bridging ligands, and to a lesser extent in the positions of the copper metal centres. The rest of the atoms are practically unaffected by this disorder. Unless explicitly mentioned, the distances and angles reported hereafter are the weighted averages, taking into consideration the corresponding occupancies.

The structure of the $[Cu^{II}_4(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2(dpt)_4]^{4+}$ cation consists of four copper atoms arranged in the corners of a distorted rectangle, with the following distances and angles, respectively: Cu1–Cu2 = 3.763, Cu2–Cu3 = 4.904, Cu3–Cu4 = 3.577, Cu4–Cu1 = 4.637 Å; Cu1–Cu2–Cu3 = 86.71, Cu2–Cu3–Cu4 = 89.10, Cu3–Cu4–Cu1 = 93.12, Cu4–Cu1–Cu2 = 91.05°.

The copper atoms are approximately coplanar (see Table 4). The disordered μ_4-carbonato ligand lies in the centre of the rectangle formed by the four copper atoms, so that one oxygen bridges a pair of chloride-bridged copper centres, forming a four-membered ring Cu–Cl–Cu–O, whereas the other two oxygens are linked each one to only one copper atom, forming a six-membered Cu–Cl–Cu–O–C–O ring. As might be expected, there are two significantly different average C–O distances to the μ_4-carbonato ligand, depending on whether the oxygen atom is bonded to one or two copper centres. In the first case, the average C–O distance is 1.224 Å, while in the second the average distance is 1.426 Å. The disorder of the CO_3^{2-} ligand consists of an inversion of its oxygen atoms with regard to the carbon atom of the carbonato ligand. The chloride bridging ligands are also situated very close to the plane defined by the copper atoms with the maximum deviation being 0.1073 Å for Cl2b.

Table 2 Selected bond distances (Å) and angles (°) for complex **2**·3MeOH

O1a–C0	1.238(6)	Cu2a–N22a	2.026(6)
O2a–C0	1.226(6)	Cu2a–N21a	2.029(7)
O3a–C0	1.398(6)	Cu2a–O2a	2.110(7)
Cl1a–Cu1a	2.315(6)	Cu3a–N33a	2.002(5)
Cl1a–Cu2a	2.419(5)	Cu3a–O3a	2.008(5)
Cl2a–Cu4a	2.644(4)	Cu3a–N31a	2.022(6)
Cl2a–Cu3a	2.649(4)	Cu3a–N32a	2.037(5)
Cu1a–N13a	1.980(7)	Cu4a–Cl2a	2.644(4)
Cu1a–O1a	2.026(8)	Cu4a–N43a	1.994(5)
Cu1a–N11a	2.050(8)	Cu4a–N41a	2.029(5)
Cu1a–N12a	2.059(7)	Cu4a–O3a	2.036(6)
Cu2a–N23a	2.003(6)	Cu4a–N42a	2.071(6)
Cu1a–Cl1a–Cu2a	103.1(2)	O1a–C0–O3a	111.7(4)
Cu3a–O3a–Cu4a	121.6(2)	O1a–Cu1a–N12a	151.4(3)
Cu4a–Cl2a–Cu3a	83.64(15)	O2a–C0–O1a	133.3(5)
N13a–Cu1a–N11a	154.5(3)	O2a–C0–O3a	114.9(4)
N22a–Cu2a–O2a	157.7(3)	O3a–Cu3a–N32a	169.9(3)
N23a–Cu2a–N21a	151.9(3)	O3a–Cu4a–N42a	169.2(2)
N33a–Cu3a–N31a	150.3(2)	C0–O1a–Cu1a	135.4(4)
N43a–Cu4a–N41a	152.0(2)	C0–O2a–Cu2a	131.9(4)

Only the data for the major component (67%) are given here.

Table 3 Selected bond distances (Å) and angles (°) for complex **3**·H_2O

Cu(1)–O(1)	1.9914(7)	Cu(2)–O(6)	2.4360(10)
Cu(1)–N(1)	1.9832(13)	Cu(3)–O(3)	2.0006(7)
Cu(1)–N(2)	2.0660(12)	Cu(3)–N(7)	1.9791(10)
Cu(1)–N(3)	1.9870(11)	Cu(3)–N(8)	2.0223(9)
Cu(1)–O(4)	2.3051(12)	Cu(3)–N(9)	1.9857(10)
Cu(2)–O(2)	1.9729(8)	Cu(3)–O(10)	2.4676(10)
Cu(2)–N(4)	2.0104(11)	C(1)–O(1)	1.2720(11)
Cu(2)–N(5)	2.0025(11)	C(1)–O(2)	1.2872(11)
Cu(2)–N(6)	2.0025(11)	C(1)–O(3)	1.2842(11)
Cu(1)–O(1)–C(1)	130.35(6)	N(5)–Cu(2)–O(2)	168.50(3)
Cu(2)–O(2)–C(1)	117.53(6)	N(7)–Cu(3)–N(9)	167.50(4)
Cu(3)–O(3)–C(1)	118.41(6)	N(8)–Cu(3)–O(3)	175.19(3)
N(1)–Cu(1)–N(3)	166.72(5)	O(1)–C(1)–O(2)	118.47(8)
N(2)–Cu(1)–O(1)	164.06(4)	O(1)–C(1)–O(3)	119.90(9)
N(4)–Cu(2)–N(6)	160.57(5)	O(2)–C(1)–O(3)	121.49(8)

The Cu–Cl bonding parameters are significantly distinct in the two different rings. For the six-membered ring an average Cu–Cl distance of 2.369 Å and a Cu–Cl–Cu bond angle of 102.55° are found, while for the four-membered ring the averages are 2.710 Å and 84.46°, respectively. The latter values clearly show that the degree of strain generated in this particular four-membered ring is primarily manifested in a substantial decrease of bonding between the bridging chloride ligand and the copper metal centre, with regard to the six-membered ring case.

Each copper metal atom is pentacoordinated by three nitrogen atoms from the dpt ligand, a bridging Cl atom and, finally, a donor oxygen atom from the bridging carbonato ligand. In all four cases, the geometry around the copper centre can be regarded as a distorted square pyramid, with an oxygen atom and the three nitrogen atoms from the dpt ligand forming the base of the pyramid and with the chlorine atom occupying the apical position. This type of geometry can be assigned based on the τ factor defined by Reedijk *et al.*,[15] ($\tau = 0$, for a perfect square pyramid, and $\tau = 1$, for an ideal trigonal bipyramid), which in all cases are lower than 0.5 ($\tau_{Cu1a} = 0.05$, $\tau_{Cu2a} = 0.10$, $\tau_{Cu3a} = 0.33$, $\tau_{Cu4a} = 0.29$). In the present structure, the τ factors also reveal the presence of two distinct geometrical arrangements within the square pyramidal geometry: one concerning Cu1a and Cu2a, while the second involves Cu3a and Cu4a. In the former case, the copper centres are bonded to different oxygen atoms of the carbonato ligand, and their coordination geometry is close to the square pyramid. In sharp contrast for the latter, the copper centres do share an oxygen from the carbonato ligand, resulting in a higher degree of distortion towards a trigonal bipyramid, due to the constraints imposed by the formation of a four-membered (Cu–Cl–Cu–O) ring. The degree of distortion of the bond angles is exemplified by an averaged difference of 30.32° in the O–Cu–Cl bonds between the two different geometrical arrangements.

Finally, long contacts are found between all the copper centres and two of the perchlorate counteranions that would complete an irregular octahedral coordination (Cu1b–O43 = 3.141, Cu4b–O43 = 3.259, Cu2b–O34 = 2.988, Cu3b–O32 = 3.155 Å). As a result, those ClO_4^- counteranions bridge the two adjacent copper centres that are not bridged by the chloride bridging ligands.

To the best of our knowledge, and leaving apart a bromine analogue,[5c] there are only two other fully characterised

Table 4 Least-squares planes (x, y, z in crystal coordinates), and deviations from them, for complex **2**[a]

$4.2218\ (0.0081)\ x + 15.9223\ (0.0101)\ y + 3.1383\ (0.0321)\ z = 6.9028\ (0.0120)$	$4.0297\ (0.0148)\ x + 16.0813\ (0.0127)\ y + 2.4902\ (0.0621)\ z = 6.6611\ (0.0223)$[b]
0.0706 (0.0045) Cu1a	0.0000 (0.0083) Cu1b
0.0704 (0.0038) Cu2a	−0.0443 (0.0073) Cu2b
−0.0566 (0.0036) Cu3a	−0.0608 (0.0083) Cu3b
−0.0088 (0.0035) Cu4a	0.0279 (0.0063) Cu4b
−0.0445 (0.0036) Cl1a	0.0917 (0.0066) Cl1b
0.0751 (0.0035) Cl2a	0.1073 (0.0073) Cl2b
−0.0710 (0.0042) O1a	0.0808 (0.0082) O1b
0.0102 (0.0041) O2a	−0.1643 (0.0085) O2b
−0.0203 (0.0039) O3a	−0.0026 (0.0076) O3b
−0.0250 (0.0037) C0	−0.0357 (0.0045) C0
Rms (dfa)[c] = 0.0520	Rms (dfa)[c] = 0.0782

[a] All the atoms shown in the table have been used to define the plane. [b] Dihedral angle between planes (with approximate esd) = 1.84 (0.12)°. [c] dfa means deviation of fitted atoms.

complexes described in the literature possessing a similar structure to the one reported here: $[Cu^{II}_4(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2(dpt)_4]Cl_4\cdot 7.5H_2O$,[16] and $[Cu^{II}_4(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2(Medpt)_4]Cl_4\cdot 12H_2O$[5c] (Medpt is bis(3-aminopropyl)methylamine). In the former case, the replacement of Cl^- by ClO_4^- counteranions produces a distortion of the Cu_4 spatial arrangement. The different crystallisation medium is also reflected by a different crystal symmetry, and by the long contacts established for only two of the copper centres and one oxygen atom of a water molecule. In the latter case, the replacement of the Medpt ligand by dpt also produces a distortion of the Cu_4 spatial arrangement, and no long contacts are observed between water molecules of crystallisation and the copper centres. In both cases the disorder has been considered to affect only the oxygen atoms of the carbonato and the chloride bridging ligands and not the metal centres, giving an occupancy of 50%/50%, in contrast to our result which converges to 67%/33%.

The trinuclear $[Cu^{II}_3(\mu_3\text{-}CO_3)(ClO_4)_2(dpt)_3(OH_2)]^{2+}$ cation consists of a triangular array of copper metal centres linked by the oxygen atoms of a bridging μ_3-carbonato ligand (see Fig. 1B). The atoms of the carbonato ligand and the three metal centres are almost coplanar (rms deviation, 0.029 Å); the secondary nitrogen atoms of the triamine ligands also lie in this plane: the dihedral angle between the plane defined by N2, N5 and N8 and the best plane for the Cu_3CO_3 moiety is only 2.47(2)°. Cu1, Cu2 and Cu3 are pentacoordinated, in a slightly distorted square pyramidal arrangement, with τ factors of 0.04, 0.13 and 0.13, respectively. One oxygen from the carbonato and three nitrogen atoms from the dpt ligand form the base of the pyramid, while the apical positions are occupied by oxygen atoms from perchlorato anions in the Cu2 and Cu3 centres (Cu2–O6 = 2.436(1), Cu3–O10 = 2.468(1) Å), whereas in Cu1 the apical position is occupied by an aquo ligand (Cu1–O4 = 2.305(1) Å). This asymmetric occupancy produces a markedly different arrangement of the CuN_3O planes, which are tilted by 52.16(3), 72.50(3) and 80.35(3)° for Cu1, Cu2 and Cu3, respectively, with regard to the plane formed by the carbonato bridging ligand.

There are six other fully characterised complexes in the literature with a relatively similar structure,[4] but the present case is the first example where the apical positions are occupied by different ligands, thus decreasing its symmetry. The most remarkable consequence of this structurally differentiating feature with regard to the six previous examples, is that in the previously described cases the maximum difference in the tilting angles (CuN_3O *vs.* CO_3^{2-}) was not higher than 2° whereas in the present compound it is 28.19°!

Both coordinated perchlorato ligands, as well as one of the free ClO_4^- counterions, present disordered oxygen atoms; in contrast, the other ClO_4^- counteranion is not disordered. Finally, the crystal water molecule forms a moderate hydrogen bond to an oxygen of a perchlorato ligand.

Magnetic properties

Plots of χ_M *vs.* T and $\chi_M T$ *vs.* T (where χ_M is the molar magnetic susceptibility) for the tetranuclear complex **2**·3MeOH and a plot of $\chi_M T$ *vs.* T for the trinuclear complex **3**·H_2O are depicted in Fig. 2. EPR measurements for **3**·H_2O at different temperatures were also carried out, and the spectrum at 4 K together with its mathematical simulation is available as ESI.

At room temperature the χ_M for **2**·3MeOH is 5.13×10^{-3} cm^3 mol^{-1}; it increases continuously as the temperature decreases, and reaches a maximum value of 1.38×10^{-2} cm^3 mol^{-1} at 35.9 K. Then, it rapidly decreases to a value of 2.47×10^{-3} cm^3 mol^{-1} at 6.52 K. The shape of the $\chi_M T$ *vs.* T plot below approximately 50 K is characteristic for this type of tetranuclear complexes. Such magnetic behaviour is characteristic of a global *antiferromagnetic* interaction among Cu(II) centers, for both curves.

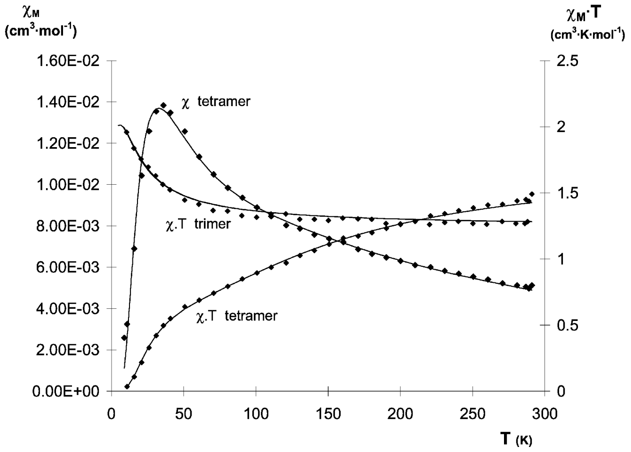
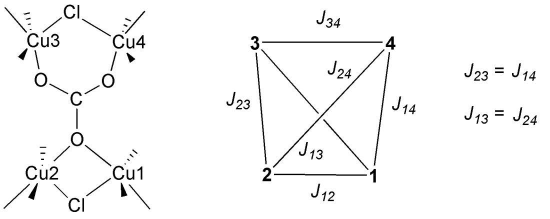


Fig. 2 χ_M *vs.* T experimental data for **2**·3MeOH (cm^3 mol^{-1}) and $\chi_M T$ *vs.* T experimental data for **2**·3MeOH and **3**·H_2O (cm^3 K mol^{-1}). Solid lines show the best fit obtained (see text).

The experimental data were fitted to the expression derived from the Hamiltonian $H = -J_{12}S_1S_2 - J_{13}(S_1S_3 + S_2S_4) - J_{14}(S_1S_4 + S_2S_3) - J_{34}S_3S_4$, which corresponds to a rectangular arrangement of spins.[17a] The exchange interaction scheme for the four operative exchange pathways is shown in Scheme 2. The most efficient superexchange pathway should be J_{12}: two Cu(II) atoms bridged by one O atom (from carbonate) and one Cl atom. The participation of the chloride bridge in the magnetic interaction between both Cu(II) centres should be negligible because it is located on the apical position of the square pyramid. J_{34} corresponds to the interaction through a *syn–syn* carboxylate group. Both J_{12} and J_{34} are expected to be antiferromagnetic based on related literature available,[5c–f] but J_{12} should be larger than J_{34} due to the higher superexchange efficiency of the "oxo" bridge. J_{14} is the superexchange pathway through a carboxylate bridge in *anti–anti* fashion, and is expected to be again antiferromagnetic.[3d,5c] The superexchange pathway termed J_{13} takes place across a *syn–anti* configuration and is analogous to the one described for complex **3**·H_2O. This complex displays ferromagnetic behaviour (*vide infra*) and thus a positive value for J_{13} can be forseen in the tetranuclear complex.



Scheme 2 Spin system in the tetranuclear complex **2**.

The relative effect of J_{13} on the shape of the curves is small, while the shape of the $\chi_M T$ *vs.* T plot is very sensitive to the value of J_{34}. On the other hand, J_{12} has an important effect on the shape of the χ_M *vs.* T curve in the region between 50 and 150 K. Keeping all these considerations in mind, the fit is obtained by minimising the function $R = \Sigma(\chi_M^{calc} - \chi_M^{obs})^2/\Sigma(\chi_M^{obs})^2$. The best fit parameters obtained are: $J_{12} = -189.9$ cm^{-1}, $J_{34} = -22.2$ cm^{-1}, $J_{14} = -60.0$ cm^{-1}, $J_{13} = +15.0$ cm^{-1} with $g = 2.18$ and $R = 1.2 \times 10^{-7}$. A superimposable curve can be obtained with $J_{12} = -189.9$ cm^{-1}, $J_{34} = -23.9$ cm^{-1}, $J_{14} = -58.1$ cm^{-1}, $J_{13} = +13.0$ cm^{-1}, $g = 2.18$ and $R = 2.70 \times 10^{-7}$. These two sets of values illustrate the intrinsic degree of accuracy for such a complex array of spin interactions. The results presented here are compatible with previous magnetic results obtained for analogous carbonato complexes described in the literature.[5c] In particular, the trend followed by J_{12} increasing as the CuOCu angle decreases, is also maintained in our case {for [Cu_4(μ_4-CO_3)(μ-Cl)$_2$(Medpt)$_4$]Cl_4 (Cu–O–Cu angle is 129.3°, J_{12} = −390 cm^{-1}); [Cu_4(μ_4-CO_3)(μ-Br)$_2$(dpt)$_4$]Br_4 (128.4°, −275 cm^{-1}); [Cu_4(μ_4-CO_3)(μ-Cl)$_2$(dpt)$_4$]Cl_4 (124.0°, −212 cm^{-1}); [Cu_4(μ_4-CO_3)(μ-Cl)$_2$(dpt)$_4$](ClO_4)$_4$, **2**·3MeOH, (121.0°, −189 cm^{-1})}.

In the particular case of **2**·3MeOH, the presence of the voluminous ClO_4^- counteranions generates the smallest Cu–O–Cu angle together with a slight disruption of the Cu_4 planarity and a major distortion of its rectangle with regard to the previous tetranuclear complexes cited above. These structural distortions are in turn responsible for the inherent magnetic properties displayed by **2**·3MeOH.

The $\chi_M T$ *vs.* T plot for the trimeric complex **3** is depicted in Fig. 2B. At room temperature the $\chi_M T$ value is 1.26 cm^3 K mol^{-1} and slightly increases when the temperature is decreased, giving a maximum value of 1.96 cm^3 K mol^{-1} at 10.6 K which is indicative of global *ferromagnetic* coupling among the three Cu(II) centres. The experimental data were fitted with the expression derived from the Hamiltonian $H = -J(S_1S_2 + S_2S_3 + S_1S_3)$, which corresponds to a triangular array of spins. The fit was performed by minimising the function $R = \Sigma(\chi_M T^{\mathrm{calc}} - \chi_M T^{\mathrm{obs}})^2/\Sigma(\chi_M T^{\mathrm{obs}})^2$. The best fit parameters, for the data from 10.6 K up to room temperature, being J = 15.32 cm^{-1} and g = 2.07 with $R = 3.4 \times 10^{-4}$. If the g value is fixed at g = 2.1, close to the g value obtained from the EPR spectrum, the best fit obtained is J = 12.57 cm^{-1}, with $R = 5.6 \times 10^{-4}$. In order to fit the low temperature data, a J' parameter was included in the fit.[17b] This parameter includes inter-trimer interactions and zero field splitting. The best fit with g = 2.1 is J = 13.89 cm^{-1}, J' = −0.07 cm^{-1} with $R = 5.3 \times 10^{-4}$. These values are in good agreement with previous magnetic measurements performed on related carbonato-bridged trinuclear complexes.[4] In the present case, the structural distortion produced by replacing a ClO_4^- by an H_2O in the trinuclear complex does not significantly affect the magnetic properties since the apical ligands are practically not involved in the spin exchange pathways.

The EPR spectrum of complex **3**·H_2O at 4 K (available as ESI) consists of a symmetric band centred at g = 2.11, with a width of 75 G. No band is detected in the half field zone. The ferromagnetic nature of complex **3**·H_2O implies that its ground state is a quartet (S = 3/2) with two low lying degenerate doublet states (S = 1/2) situated at 24.75 cm^{-1} ($\Delta E = 12J/8$). The spectrum at 4 K was successfully simulated yielding the following parameters: g_x = 2.13, g_y = 2.12, g_z = 2.10, D = 40 G. The low anisotropy presented by this system is attributed to the fact that the different $d_{x^2-y^2}$ Cu orbitals, which have the higher contribution to the magnetic molecular orbitals responsible for the spin coupling,[4] are not coplanar but rather tilted.

Conclusions

Two new carbonato bridged copper complexes with different nuclearity have been prepared and characterised: the tetranuclear [Cu^{II}_4(μ_4-CO_3)(μ-Cl)$_2$(dpt)$_4$](ClO_4)$_4$·3MeOH, **2**·3MeOH and the trinuclear [Cu^{II}_3(μ_3-CO_3)(ClO_4)$_2$(dpt)$_3$(OH_2)](ClO_4)$_2$·H_2O, **3**·H_2O. A rationalisation for the synthetic pathways that lead to the formation of tri- and tetra-nuclear complexes is proposed, proving that the tetranuclear complex **2** is an intermediate to generate the trinuclear complex **3**. Furthermore, an accurate synthetic and structural description of a μ_4-carbonato bridged tetranuclear copper complex is presented. Comparison of the tetranuclear complex **2** with similar complexes having related structures, indicates that slight structural distortions caused by the counterions (Cl^- *vs.* ClO_4^-) and solvation molecules bring about considerable perturbations in their magnetic properties.

The first asymmetric trinuclear carbonato bridged complex is described here, where the apical coordination positions are occupied by oxygens from two perchlorates and a water molecule. This produces structural distortions, chiefly manifested in the tilting of the CuN_3O planes with regard to the carbonato plane. However, since the structural differences affect mainly the apical positions of the square pyramid, the magnetic properties are not substantially influenced.

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