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Two new tetranuclear μ_4-carbonato copper(II) complexes. Syntheses, crystal structure and magnetic behaviour of $[(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2\{Cu_4(bapa)_4\}]Br_4$ and $[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapma)_4\}]Cl_4\cdot 12H_2O$ [bapa = bis(aminopropyl)amine and bapma = bis(aminopropyl)methylamine]

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The syntheses, by fixation of atmospheric CO_2, and the crystal structures of the new tetranuclear μ_4-$CO_3{}^{2-}$ compounds $[(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2\{Cu_4(bapa)_4\}]Br_4$ **1** and $[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapma)_4\}]Cl_4\cdot 12H_2O$ **2**, [bapa and bapma are bis(3-aminopropyl)amine and bis(3-aminopropyl)methylamine respectively] are reported. Crystallographic data for **1** space group $C2/c$, $a = 14.928(5)$, $b = 19.010(3)$, $c = 17.337(4)$ Å, $\beta = 92.75(4)°$, $U = 4914(2)$ Å^3 and $Z = 4$, for **2** space group $P2_1/n$, $a = 14.947(6)$, $b = 13.047(4)$, $c = 16.084(5)$ Å, $\beta = 104.75(5)°$, $U = 3033(2)$ Å^3 and $Z = 2$. The analogous compound $[(\mu\text{-}CO_3)(\mu_4\text{-}Cl)_2\{Cu_4(bapa)_4\}]Cl_4$ **3** has been also prepared for comparative purposes; **1**–**3** show very strong antiferromagnetic coupling. According to the molecular structures, the experimental data were fitted to the expression derived from the Hamiltonian $H = -2J_{12}S_1\cdot S_2 - 2J_{13}(S_1\cdot S_3 + S_2S_4) - 2J_{14}(S_1\cdot S_4 + S_2\cdot S_3) - 2J_{34}S_3\cdot S_4$, which corresponds to a rectangular array of spins. The best fit parameters were for **1**–**3** respectively: $2J_{12} = -275(14), -390(12), -212(8)$; $2J_{34} = -31(4), -26(7), -26(3)$; $2J_{14} = -57(10), -10(12), -72(9)$; $2J_{13} = -8(8), 22(10), -20(7)$ cm^{-1}; $g = 2.03(1), 2.09(1)$ and $2.12(1)$.

The carbonate anion is a versatile bridging ligand,[1] able to generate compounds with different nuclearity including dimers,[2,3] trimers,[4] tetramers,[5] one-[6] or two-dimensional[7] systems. The co-ordination modes described to date for the carbonate ion when it acts as a bridge in polynuclear compounds with nuclearities greater than two are summarized in Fig. 1. In spite of this general interest, there has been no report of a systematic study of procedures for the synthesis of different nuclearities. From the magnetic point of view, the unusual range of magnetic behaviour than can be obtained as a function of the co-ordination of the bridging carbonato ligand should be pointed out: from strongly coupled,[8,9] to moderate[2a] or weak[4f,6] antiferromagnetic compounds and even ferromagnetic ones.[2e,4a,c,e] Furthermore, the magnetochemistry of the μ-carbonato ligand is poorly described for nuclearities greater than two.

We have recently published the syntheses, based on the carbonate ligand generated from fixation of atmospheric CO_2, and the magnetic behaviour of the trinuclear μ_3-$CO_3{}^{2-}$ systems $[(\mu_3\text{-}CO_3)\{Cu_3(bapma)_3(ClO_4)_3\}]ClO_4$,[4c] $[(\mu_3\text{-}CO_3)\{Ni_2(dmpn)_4(H_2O)\}Ni(dmpn)_2(H_2O)_2][ClO_4]_4\cdot H_2O$ and $[(\mu_3\text{-}CO_3)\{Ni_3(bapma)_3(NCS)_4\}]$[4d] [bapma = bis(3-aminopropyl)methylamine, dmpn = 2,2-dimethylpropane-1,3-diamine]. With the aim of continuing the study of the synthetic methods and the magnetochemistry of the polynuclear derivatives of the carbonato ligand for nuclearities greater than two, this work is devoted to the tetranuclear μ_4-$CO_3{}^{2-}$ systems $[(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2\{Cu_4(bapa)_4\}]Br_4$ **1** [bapa = bis(3-aminopropyl)amine] and $[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapma)_4\}]Cl_4\cdot 12H_2O$ **2**. Complexes **1** and **2** are prepared by the fixation of atmospheric CO_2 using copper(II) halides. The crystal structures of **1** and **2** reveal a rectangular arrangement of four copper(II) atoms with a central μ_4-carbonato bridge with Cl or Br atoms bridging the shorter sides of the rectangle. The tetranuclear nature of the product of the reaction between an aqueous solution of bapa with copper(II) chloride by fixation of atmospheric CO_2 was suggested by Curtis *et al.*[10] and structurally confirmed by Einstein and Willis[5a] for the analogous $[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapa)_4\}]Cl_4$ **3**, which has also been prepared by us in order to study its magnetic behaviour. The magnetic measurements for **1**–**3** show strong antiferromagnetic coupling due to the interaction of the copper atoms through four superexchange pathways. The experimental data were fitted to the expression derived from the Hamiltonian $H = -2J_{12}S_1\cdot S_2 - 2J_{13}(S_1\cdot S_3 + S_2\cdot S_4) - 2J_{14}(S_1\cdot S_4 + S_2\cdot S_3) - 2J_{34}S_3\cdot S_4$, which corresponds to a rectangular array of spins.

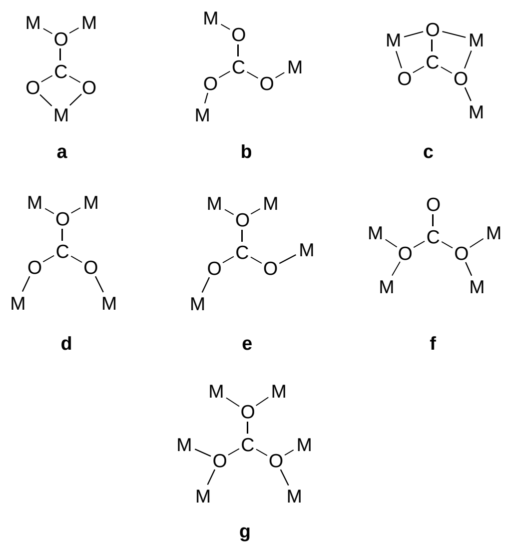


Fig. 1 Structurally characterized co-ordination modes of the carbonato bridge for nuclearities greater than two

Experimental

Synthesis

$[(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2\{Cu_4(bapa)_4\}]Br_4$ 1. To a solution of $CuBr_2$

Table 1 Crystallographic data for $[(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2\{Cu_4(bapa)_4\}]Br_4$ **1** and $[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapma)_4\}]Cl_4\cdot 12H_2O$ **2**

	1	**2**
Formula	$C_{25}H_{68}Br_6Cu_4N_{12}O_3$	$C_{29}H_{100}Cl_6Cu_4N_{12}O_{15}$
M	1318.53	1324.07
Crystal symmetry	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a/Å	14.928(5)	14.947(6)
b/Å	19.010(3)	13.047(4)
c/Å	17.337(4)	16.084(5)
β/°	92.75(4)	104.75(3)
U/Å^3	4914(2)	3033(2)
Z	4	2
T/K	239(1)	293(2)
D_c/g cm^{-3}	1.782	1.450
μ(Mo-Kα)/cm^{-1}	66.24	17.08
R^a	0.0445	0.0555
R'^b	0.1081	0.1347

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

(10 mmol) and bis(3-aminopropyl)amine (10 mmol) in water (50 cm^3), $NHEt_2$ (5 mmol) was added and maintained for 2 h with vigorous stirring. After three weeks blue crystals of **1**, unstable when taken out of the solution at room temperature, were obtained (Found: C, 21.6; H, 5.5; N, 12.1. Calc. for $C_{25}H_{68}Br_6Cu_4N_{12}O_3$: C, 22.8; H, 5.2; N, 12.7%). For this reason the structure was determined at 239 K.

$[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapma)_4\}]Cl_4\cdot 12H_2O$ 2. To a solution of $CuCl_2$ (10 mmol) and bis(3-aminopropyl)methylamine (10 mmol) in water (50 cm^3), $NHEt_2$ (5 mmol) was added and maintained for 2 h with vigorous stirring. After two weeks blue crystals of **2**, stable at room temperature, were obtained (Found: C, 26.1; H, 7.2; N, 12.6. Calc. for $C_{29}H_{100}Cl_6Cu_4N_{12}O_{15}$: C, 26.3; H, 7.6; N, 12.7%).

$[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapa)_4\}]Cl_4$ 3. This compound was prepared as previously described,[10] analytical data (C, H, N, Cl) were in agreement with the proposed formulae.

Magnetic measurements

Magnetic measurements were carried out on polycrystalline samples with a SQUID apparatus working in the range 2–300 K under a magnetic field of 0.3 T. Diamagnetic corrections were estimated from Pascal tables.

Crystal data collection and refinement

Analyses on single prismatic blue crystals of $[(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2\{Cu_4(bapa)_4\}]Br_4$ **1** (0.1 × 0.1 × 0.2 mm) and $[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapma)_4\}]Cl_4\cdot 12H_2O$ **2** (0.1 × 0.1 × 0.2 mm) were carried out on an Enraf-Nonius CAD4 X-ray diffractometer. Intensities were collected using the ω–2θ scan technique with graphite-monochromatized Mo-Kα radiation (λ = 0.710 69 Å). A summary of the crystallographic data is reported in Table 1. Unit-cell parameters for **1** and **2** were determined from automatic centring of 25 reflections (12 < θ < 21°) and refined by the least-squares method. For **1** 7053 reflections were measured in the range 1.74 < θ < 29.97°, 2895 of which were assumed observed applying the condition $I > 2\sigma(I)$. For **2** 9206 reflections were measured in the range 2.04 < θ < 29.97°, 5707 of which were assumed observed applying the condition $I > 2\sigma(I)$. For **1** and **2** three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz, polarization and absorption corrections (ψ scans, for compound **1** only)[11] were made.

The structures of **1** and **2** were solved by direct methods, using the SHELXS computer program[12] and refined by the full-matrix least-squares method, with SHELXL 93.[13] The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0639P)^2]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$ for **1** and $w = [\sigma^2(I) + (0.0797P)^2 + 3.1803P]^{-1}$, $P = (|F_o|^2 + 2|F_c|^2)/3$ for **2**. Values of f, f' and f'' were taken from ref. 14. The extinction coefficient was 0.0000(7) for **1** and 0.0043(4) for **2**. For **1** the three O atoms of the carbonato group and for **2** the three O atoms of the carbonato group and the Cl(1) atom are disordered: an occupancy factor of 0.5 was assigned in accordance with the height of Fourier synthesis and the symmetry conditions. For **1** all the H atoms were computed and refined with an overall isotropic temperature factor using a riding model. The number of parameters refined was 237. Maximum shift/e.s.d. = 7.96, mean shift/e.s.d. = 0.92. Maximum and minimum peaks in the final difference synthesis were 0.722 and −0.616 e Å^{-3}, respectively. For **2** 46 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. The number of parameters refined was 516. Maximum shift/e.s.d. = 0.57, mean shift/e.s.d. = 0.04. Maximum and minimum peaks in final difference synthesis were 0.658 and −0.428 e Å^{-3}, respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/523.

Results and Discussion

Syntheses

As mentioned above, we have recently published the synthesis and crystal structure of the trinuclear μ_3-carbonato system $[(\mu_3\text{-}CO_3)\{Cu_3(bapma)_3(ClO_4)_3\}]ClO_4$.[4c] The synthetic procedure, previously described by Curtis *et al.*[10] for the analogous $[(\mu_3\text{-}CO_3)\{Cu_3(bapa)_3(ClO_4)_3\}]ClO_4$, is very similar to the one described here for the syntheses of the μ_4-carbonato complexes **1**–**3**, but the starting copper(II) salt used to prepare the trinuclear compounds is the perchlorate instead of the copper(II) halide used in the preparation of the tetranuclear ones. Using the potentially tridentate base 2-[2-(2-pyridyl)ethyliminomethyl]pyridine (pip) and copper(II) nitrate, it is possible to obtain[4a] another trinuclear μ_3-carbonato compound $[(\mu_3\text{-}CO_3)\{Cu_3(pip)_3(H_2O)_3\}][NO_3]_4$. Consequently, the synthesis of copper(II)–carbonato derivatives with different nuclearities can be placed into two categories: using tridentate amine ligands (like bapa, bapma or pip), atmospheric CO_2 or K_2CO_3 and copper(II) salts of poorly co-ordinative anions like nitrate or perchlorate leads to $\mu_3\text{-}CO_3^{2-}$ trinuclear copper(II) derivatives. In contrast, if copper(II) halides (chloride or bromide) are used the resulting compound is a μ_4-carbonato tetranuclear copper(II) derivative with two bridging halide ligands. There are two published exceptions to this rule: using the bulky tridentate ligands *N,N,N′,N″N″*-pentaethyldiethylenetriamine (pedien) and 2,4,4,7-tetramethyl-1,5,9-triazyclododec-1-ene (L) and copper(II) perchlorate, the dinuclear $\mu_2\text{-}CO_3^{2-}$ compounds. $[(\mu_2\text{-}CO_3)\{Cu_2(pedien)_2\}][ClO_4]_2$[2a] and $[(\mu_2\text{-}CO_3)\{Cu_2(L)_2\}][ClO_4]_2\cdot$dmf (dmf = dimethylformamide)[8] are obtained rather than trinuclear μ_3-carbonato compounds. The bulky character of pedien and L could be the reason for this anomalous results.

Structures of compounds 1 and 2

The structure of these compounds is basically the same and consists of tetranuclear $[(\mu_4\text{-}CO_3)(\mu\text{-}X)_2\{Cu_4(triamine)_4\}]^{4+}$ units, X = Cl or Br for compounds **2** and **1** respectively, and four isolated halide counter anions. In **2** there also exist 12 water molecules. Labelled diagrams are shown in Figs. 2 and 3 for compounds **1** and **2** respectively. The main bond lengths and angles are presented in Table 2. The structure of each tetranuclear unit consists of four copper atoms placed at the corners of a rectangle with a μ_4-carbonate ligand in the centre (disordered

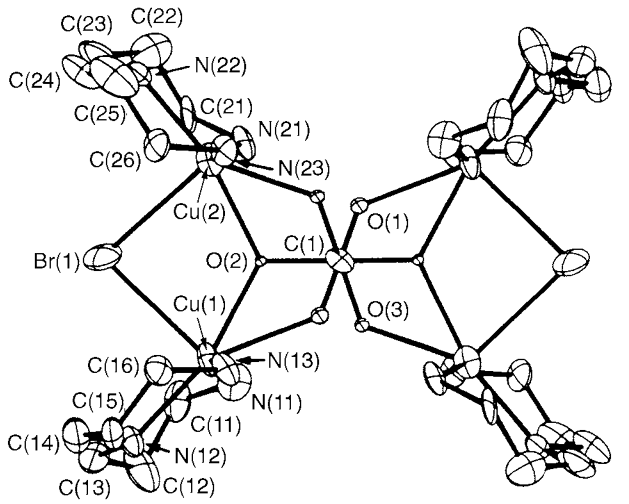


Fig. 2 An ORTEP[15] drawing of the cation $[(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2\{Cu_4(bapa)_4\}]^{4+}$ of compound **1** with atom labelling scheme

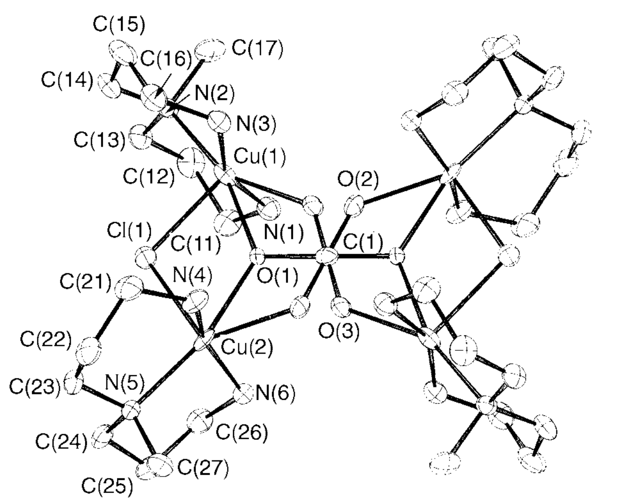


Fig. 3 An ORTEP drawing of the cation $[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapma)_4\}]^{4+}$ of compound **2** with atom labelling scheme

in **1** and **2**). The bridging halides are placed on the plane of the rectangle and perpendicular to the short edges. The carbonate acts as a tetradentate ligand: one oxygen atom bridges a pair of halide-bridged Cu atoms, forming a four-membered Cu–X– Cu–O ring, while the other two oxygen atoms are linked to each of the remaining two Cu atoms, forming a six-membered Cu–X–Cu–O–C–O ring. One bapa or bapma ligand is *mer* co-ordinated to each copper atom making them five-co-ordinate.

There are two different average C–O distances in the μ_4-carbonate ligand depending on whether the O atom bridges two Cu atoms or links to one Cu atom. In the first case the average C–O distances are 1.416(8) and 1.472(4) Å for **1** and **2** respectively. In the second case, the average C–O distances are 1.195(11) and 1.211(5) Å for **1** and **2** respectively. These values compare well with similar average C–O distances in the analogous compound $[(\mu_4CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapa)_4\}]Cl_4$ **3**[5a] which are 1.412(10) Å for the four- and 1.224(10) Å for the six-membered rings.

As in the case of the C–O distances, the related distances and angles for **1**–**3** compare well, with the obvious exception of the structural parameters involving the different halides. In **1**, the Cu–Br–Cu average angle is 88.32(4)° and the average Cu–Br distance is 2.712(1) Å. In **2**, the Cu–Cl–Cu average angle is 94.3(1)° and the Cu–Cl average distance is 2.578(3) Å. In **3**,[5a] the average Cu–Cl–Cu angle is 93.1(1)° and the average Cu–Cl distance is 2.532(2) Å.

Table 2 Selected bond lengths (Å) and angles (°) for $[(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2\{Cu_4(bapa)_4\}]Br_4$ **1** and $[(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2\{Cu_4(bapma)_4\}]Cl_4\cdot 12H_2O$ **2**

Compound **1**			
Cu(1)–N(13)	2.015(5)	Cu(1)–N(11)	2.030(5)
Cu(1)–N(12)	2.043(5)	Cu(1)–O(1)	2.032(10)
Cu(1)–O(2)	2.125(7)	Cu(1)–Br(1)	2.6994(14)
Cu(2)–N(21)	2.001(4)	Cu(2)–N(23)	2.025(5)
Cu(2)–N(22)	2.065(5)	Cu(2)–O(2)	2.072(5)
Cu(2)–O(3)	2.158(12)	Cu(2)–Br(1)	2.7250(13)
C(1)–O(3)	1.102(11)	C(1)–O(1)	1.288(10)
C(1)–O(2)	1.416(8)		
N(13)–Cu(1)–N(11)	152.5(2)	N(13)–Cu(1)–N(12)	90.0(2)
N(11)–Cu(1)–N(12)	94.9(2)	N(13)–Cu(1)–O(1)	82.9(3)
N(11)–Cu(1)–O(1)	79.2(3)	N(12)–Cu(1)–O(1)	149.4(3)
N(13)–Cu(1)–O(2)	89.3(3)	N(11)–Cu(1)–O(2)	92.7(3)
N(12)–Cu(1)–O(2)	164.8(2)	O(1)–Cu(1)–O(2)	45.3(3)
N(13)–Cu(1)–Br(1)	103.7(2)	N(11)–Cu(1)–Br(1)	102.89(13)
N(12)–Cu(1)–Br(1)	94.05(12)	O(1)–Cu(1)–Br(1)	116.5(3)
O(2)–Cu(1)–Br(1)	71.4(2)	N(21)–Cu(2)–N(23)	151.8(2)
N(21)–Cu(2)–N(22)	92.8(2)	N(23)–Cu(2)–N(22)	89.1(2)
N(21)–Cu(2)–O(2)	94.3(3)	N(23)–Cu(2)–O(2)	91.2(3)
N(22)–Cu(2)–O(2)	164.4(3)	N(21)–Cu(2)–O(3)	81.8(3)
N(23)–Cu(2)–O(3)	84.5(3)	N(22)–Cu(2)–O(3)	154.4(3)
O(2)–Cu(2)–O(3)	40.9(4)	N(21)–Cu(2)–Br(1)	100.8(2)
N(23)–Cu(2)–Br(1)	107.14(14)	N(22)–Cu(2)–Br(1)	93.5(2)
O(2)–Cu(2)–Br(1)	71.5(2)	O(3)–Cu(2)–Br(1)	112.1(3)
Cu(1)–Br(1)–Cu(2)	88.32(4)	O(3^i)–C(1)–O(1^i)	143.3(6)
O(3)–C(1)–O(1)	143.3(6)	O(3)–C(1)–O(2^i)	109.3(7)
O(1)–C(1)–O(2^i)	107.4(5)	O(3^i)–C(1)–O(2)	109.3(7)
O(1^i)–C(1)–O(2)	107.4(5)	C(1)–O(1)–Cu(1)	127.7(7)
C(1)–O(2)–Cu(2)	117.3(4)	C(1)–O(2)–Cu(1)	114.2(4)
Cu(2)–O(2)–Cu(1)	128.4(4)	C(1)–O(3)–Cu(2)	131.1(9)
Compound **2**			
Cu(1)–N(3)	1.987(4)	Cu(1)–N(2)	2.067(3)
Cu(1)–N(1)	1.996(3)	Cu(1)–O(3′)	2.080(5)
Cu(1)–O(1)	2.047(4)	Cu(1)–Cl(1)	2.376(2)
Cu(2)–N(6)	1.980(2)	Cu(2)–N(5)	2.078(3)
Cu(2)–N(4)	1.992(4)	Cu(2)–O(1)	2.089(4)
Cu(2)–O(2′)	2.065(6)	Cu(2)–Cl(1)	2.342(3)
C(1)–O(1)	1.472(4)	C(1)–O(2)	1.232(5)
C(1)–O(3)	1.190(5)		
N(3)–Cu(1)–N(1)	155.5(2)	N(3)–Cu(1)–O(1)	92.6(2)
N(1)–Cu(1)–O(1)	89.7(2)	N(3)–Cu(1)–N(2)	91.71(13)
N(1)–Cu(1)–N(2)	92.98(13)	O(1)–Cu(1)–N(2)	163.34(14)
N(3)–Cu(1)–O(3′)	82.1(2)	N(1)–Cu(1)–O(3′)	82.9(2)
N(2)–Cu(1)–O(3′)	153.2(2)	N(3)–Cu(1)–Cl(1)	99.69(14)
N(1)–Cu(1)–Cl(1)	103.10(14)	O(1)–Cu(1)–Cl(1)	62.88(13)
N(2)–Cu(1)–Cl(1)	100.53(11)	O(3′)–Cu(1)–Cl(1)	106.2(2)
N(6)–Cu(2)–N(4)	157.4(4)	N(6)–Cu(2)–O(2′)	82.8(2)
N(4)–Cu(2)–O(2′)	82.1(2)	N(6)–Cu(2)–N(5)	92.22(13)
N(4)–Cu(2)–N(5)	92.68(14)	O(2′)–Cu(2)–N(5)	150.8(2)
N(6)–Cu(2)–O(1)	90.3(2)	N(4)–Cu(2)–O(1)	90.7(2)
N(5)–Cu(2)–O(1)	164.64(14)	N(6)–Cu(2)–Cl(1)	102.77(14)
N(4)–Cu(2)–Cl(1)	97.8(2)	O(2′)–Cu(2)–Cl(1)	107.4(2)
N(5)–Cu(2)–Cl(1)	101.72(11)	O(1)–Cu(2)–Cl(1)	62.96(13)
Cu(2)–Cl(1)–Cu(1)	104.82(11)	C(11)–N(1)–Cu(1)	119.3(3)
C(1)–O(1)–Cu(1)	116.1(2)	C(1)–O(1)–Cu(2)	114.5(2)
Cu(1)–O(1)–Cu(2)	129.3(2)	C(1)–O(2)–Cu(2′)	130.4(4)
C(1)–O(3)–Cu(1′)	131.3(4)	O(3′)–C(1)–O(2′)	139.3(3)
O(3)–C(1)–O(2)	139.3(3)	O(3′)–C(1)–O(1′)	110.9(3)
O(2′)–C(1)–O(1′)	109.4(3)	O(3)–C(1)–O(1)	110.9(3)
O(2)–C(1)–O(1)	109.4(3)		

Symmetry transformations used to generate equivalent atoms: i $-x + \frac{3}{2}, -y + \frac{1}{2}, -z$. (′) $-x + 1, -y + 1, -z$.

Magnetic results

Plots of χ_m *vs. T* (where χ_m is the molar susceptibility) for compounds **1**–**3** are shown in Fig. 4. For **1** the χ_m value of 4.0×10^{-3} $cm^3\ mol^{-1}$ at room temperature increases continuously when the temperature decreases, giving a maximum of 12.9×10^{-3} $cm^3\ mol^{-1}$ at 30 K, decreasing quickly close to zero at 4 K, and then increasing slightly due to the presence of a small quantity

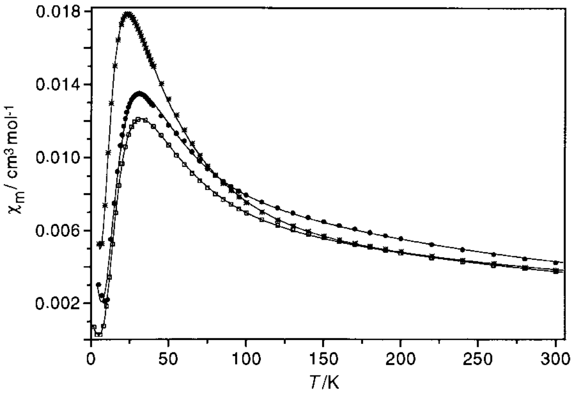
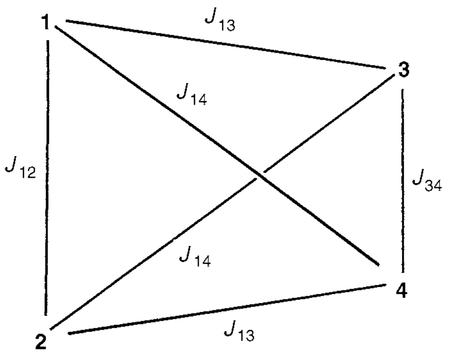


Fig. 4 A plot of χ_m *vs.* T for compounds **1**(□), **2**(*) and **3**(●). Solid lines show the best fit obtained (see text)



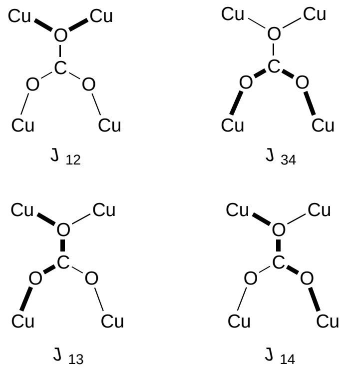
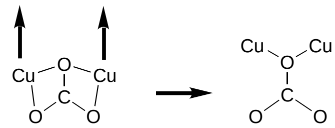


Fig. 5 Exchange interactions and atom labelling scheme for the four operative exchange pathways in compounds **1–3**



of paramagnetic impurities. This behaviour indicates a global antiferromagnetic coupling between the copper(II) ions. Compounds **2** and **3** show similar behaviour: 3.8×10^{-3} and 4.2×10^{-3} cm³ mol⁻¹ at room temperature for **2** and **3** respectively, a maximum of 17.8×10^{-3} cm³ mol⁻¹ at 23 K and 13.5×10^{-3} cm³ mol⁻¹ at 31 K for **2** and **3** respectively, a minimum at 5 K for **2** (9 K for **3**) and a slight increase due to the presence of a small quantity of paramagnetic impurities.

The experimental data were fitted to the expression derived from the Hamiltonian $H = -2J_{12}\ S_1{\cdot}S_2 - 2J_{13}\ (S_1{\cdot}S_3 + S_2{\cdot}S_4) - 2J_{14}\ (S_1{\cdot}S_4 + S_2{\cdot}S_3) - 2J_{34}\ S_3{\cdot}S_4$, which corresponds to a tetrameric array of spins.[16] The expression was also corrected with a ρ paramagnetic impurity parameter in order to fit the low-temperature data resulting in equation (1).

$$\chi_m = \frac{0.37515\,g^2}{T}\left[(1-\rho)\left(10e^{\frac{(J_{12}+J_{34})/2+(J_{14}+J_{13})}{0.69504\,T}} + 2e^{\frac{(J_{12}+J_{34})/2-(J_{14}+J_{13})}{0.69504\,T}} + 2e^{\frac{-(J_{12}+J_{34})/2+\sqrt{(J_{12}-J_{34})^2+(J_{14}-J_{13})^2}}{0.69504\,T}} + 2e^{\frac{-(J_{12}+J_{34})/2-\sqrt{(J_{12}-J_{34})^2+(J_{14}-J_{13})^2}}{0.69504\,T}}\right)\Bigg/\left(5e^{\frac{(J_{12}+J_{34})/2+(J_{14}+J_{13})}{0.69504\,T}} + 3e^{\frac{(J_{12}+J_{34})/2-(J_{14}+J_{13})}{0.69504\,T}} + 3e^{\frac{-(J_{12}+J_{34})/2+\sqrt{(J_{12}-J_{34})^2+(J_{14}-J_{13})^2}}{0.69504\,T}} + 3e^{\frac{-(J_{12}+J_{34})/2-\sqrt{(J_{12}-J_{34})^2+(J_{14}-J_{13})^2}}{0.69504\,T}} + e^{\frac{-(J_{12}+J_{34})/2-(J_{14}+J_{13})+\sqrt{(J_{12}+J_{34}-J_{14}-J_{13})^2+3(J_{14}-J_{13})^2}}{0.69504\,T}} + e^{\frac{-(J_{12}+J_{34})/2-(J_{14}+J_{13})-\sqrt{(J_{12}+J_{34}-J_{14}-J_{13})^2+3(J_{14}-J_{13})^2}}{0.69504\,T}}\right) + \rho\right] \quad (1)$$

The exchange interactions and the atom labelling scheme are illustrated in Fig. 5. The best fit parameters, using as a criterion of best fit the minimum value of $R = \Sigma(\chi_m^{calc} - \chi_m^{obs})^2/\Sigma(\chi_m^{obs})^2$, were: $2J_{12} = -275(14)$, $2J_{34} = -31(4)$, $2J_{14} = -57(10)$, $2J_{13} = -8(8)$ cm⁻¹, $g = 2.03(1)$, $\rho = 5(8) \times 10^{-4}$ with $R = 1.7 \times 10^{-5}$ for **1**; $2J_{12} = -390(12)$, $2J_{34} = -26(7)$, $2J_{14} = -10(12)$, $2J_{13} = 22(10)$ cm⁻¹, $g = 2.09(1)$, $\rho = 1.4(5) \times 10^{-2}$ with $R = 2 \times 10^{-5}$ for **2**; and $2J_{12} = -212(8)$, $2J_{34} = -26(3)$, $2J_{14} = -72(9)$, $2J_{13} = -20(7)$ cm⁻¹, $g = 2.12(1)$, $\rho = 5(7) \times 10^{-3}$ with $R = 5.9 \times 10^{-4}$ for **3**. The $2J_{12}$ and $2J_{34}$ values are reliable because they are determined by the shape of the χ_m *vs.* T curve, mainly in the high-temperature region, and the maximum of the curve respectively whereas the $2J_{14}$ and $2J_{13}$ values are slightly sensitive to the shape or the maximum of the curve and their values are poorly determined, reflecting the difficulty of including six parameters in the regression analysis.

From the best fit parameters, the most efficient superexchange pathway in **1–3** is that corresponding to J_{12}: two copper(II) atoms bridged by one O (carbonate) and one halide. The participation of the bridging halide in the superexchange pathway should be negligible because it is placed on the apical position of the square pyramidal polyhedron around the copper(II) atoms. The J_{12} superexchange pathway may be related to the diamagnetic dinuclear μ_2-carbonate compounds $[(\mu_2\text{-}CO_3)\{Cu_2(L)_2\}][ClO_4]_2{\cdot}dmf$[8] and $[(\mu_2\text{-}CO_3)\{Cu_2(tmpn)_2Cl_2\}]$[9] (tmpn = *N,N,N′,N′*-tetramethylpropane-1,3-diamine), in which the two copper atoms are bridged by a doubly bidentate carbonato group: when the two copper atoms in the Cu,(carbonate),Cu plane are moved further away from the non-bridging O atoms of the carbonate, and the Cu–O–Cu angle is opened, the $2J_{12}$ coordination mode is reached. In the diamagnetic dinuclear compounds, the Cu–O distances are short and the Cu–O–Cu angles are close to 180°: 176.6(2)° for $[(\mu_2\text{-}CO_3)\{Cu_2(L)_2\}][ClO_4]_2{\cdot}dmf$[8] and 170.26° for $[(\mu_2\text{-}CO_3)\{Cu_2(tmpn)_2Cl_2\}]$,[9] adequate for a good Cu–O–Cu orbital overlap.[2a]

In compounds **1**, **2** and **3** the Cu–O distances are also short, but the Cu(1)–O(2)–Cu(2) angles are 128.4(4)°, 129.3(2)° and 124.0(4)° respectively, and the overlap should diminish. For this reason, an antiferromagnetic coupling may be predicted, but with a $2J$ value lower than that found in $[(\mu_2\text{-}CO_3)\{Cu_2(L)_2\}][ClO_4]_2{\cdot}dmf$[8] or $[(\mu_2\text{-}CO_3)\{Cu_2(tmpn)_2Cl_2\}]$.[9] The $2J_{12}$ values of −275(14), −390(12) and −212(8) cm⁻¹ for **1**, **2** and **3** respectively are as expected. The superexchange pathway corresponding to J_{34}, two copper(II) atoms bridged by a *syn–syn* carboxylato group, may also be predicted to be antiferromagnetic by analogy with copper acetate derivatives and related complexes,[17–19] but the value of the coupling constant should be lower due to the decreasing number of carboxylate bridges from four to one.[20] The $2J_{34}$ values are −31(4), −26(7) and −26(3) cm⁻¹ for **1**, **2** and **3** respectively. The sign of the superexchange pathway corresponding to J_{13}, two copper(II) atoms bridged by a *syn–anti* carboxylato group, is difficult to predict but the value should be low:[21,22] $2J_{13} = -8(8)$ for **1**, +22(10) for **2** and −20(7) cm^{-1} for **3**. The superexchange pathway corresponding to J_{14}, two copper(II) atoms bridged by an *anti–anti* carboxylato group, has been measured for the dinuclear carbonato compound $[(\mu_2\text{-}CO_3)\{Cu_2(bipy)_4\}][PF_6]_2\cdot 2dmf$ (bipy = 4,4′-bipyridine),[2g] which displays antiferromagnetic coupling with a $2J$ value of −140.5 cm^{-1}. The $2J_{14}$ values of −57(10), −10(12) and −72(9) cm^{-1} for **1**, **2** and **3** respectively, taking into account the structural differences and the certain indeterminacy of $2J_{14}$, are in accordance with this value.

Conclusion

From the synthetic point of view, the strategy to achieve trinuclear μ_3-carbonato–copper(II) derivates is to use copper(II) salts of poorly co-ordinative anions such as nitrate or perchlorate, tridentate amines (*e.g.* bapa, bapma or pip) and atmospheric CO_2 or K_2CO_3. In contrast, if the starting salt is a copper(II) halide (chloride or bromide), with the same reagents and method, the resulting compound is a μ_4-carbonato tetranuclear copper(II) derivative with two bridging halides.

In this work we have shown two examples of μ_4-carbonato tetranuclear copper(II) compounds. The magnetic behaviour of these compounds has been magnetically studied by using the expression derived from the Hamiltonian $H = -2J_{12} S_1\cdot S_2 - 2J_{13} (S_1\cdot S_3 + S_2\cdot S_4) - 2J_{14} (S_1\cdot S_4 + S_2\cdot S_3) - 2J_{34} S_3\cdot S_4$, which corresponds to a tetrameric array of spins. The values of $2J_{12}$ and $2J_{34}$ can be determined with precision but $2J_{14}$ and $2J_{13}$ are sensitive to the shape or the maximum of the curve (χ_m *vs.* T) and their values are poorly determined.

Acknowledgements

This work was supported financially by the Comisión Interministerial de Ciencia y Tecnología (PB93/0772 grant). E. P. thanks Comissió Interdepartamental de Recerca i Tecnologia (Generalitat de Catalunya) for a doctoral fellowship.

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Received 18*th February* 1997; *Paper* 7/01138E