Crystal Structure and Magnetic Behavior of Two New Dinuclear Carbonato-Bridged Copper(II) Compounds. Superexchange Pathway for the Different Coordination Modes of the Carbonato Bridge in Polynuclear Copper(II) Compounds

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Four new μ-CO_3^{2-} copper(II) complexes with different coordination modes for the carbonato bridge have been obtained by fixation of atmospheric CO_2: $\{(\mu_3\text{-}CO_3)[Cu_3(ClO_4)_3(Et_3dien)_3]\}(ClO_4)$ (**1**), Et_3dien = *N*,*N*′,*N*″-triethylbis(2-aminoethane)amine; $\{(\mu\text{-}CO_3)[Cu_2(H_2O)(Et_4dien)_2]\}(ClO_4)_2\cdot H_2O$ (**2**), Et_4dien = *N*,*N*,*N*″,*N*″-tetraethylbis(2-aminoethane)amine; $\{(\mu\text{-}CO_3)[Cu_2(H_2O)_2(EtMe_4dien)_2]\}$ $(ClO_4)_2\cdot 2H_2O$ (**3**), $EtMe_4dien$ = *N*′-ethyl-*N*,*N*,*N*″,*N*″-tetramethylbis(2-aminoethane)amine; and $\{(\mu\text{-}CO_3)[Cu_2(H_2O)(Me_5dien)_2]\}(ClO_4)_2\cdot H_2O$ (**4**), Me_5dien = *N*,*N*,*N*′,*N*″,*N*″-pentamethylbis(2-aminoethane)amine. The crystal structures have been solved for **2**, monoclinic system, space group $P2_1/n$, formula $[C_{25}H_{62}Cl_2Cu_2N_6O_{13}]$ with $a = 12.763(6)$ Å, $b = 25.125(8)$ Å, $c = 13.261(4)$ Å, $\beta = 111.85(3)°$, $Z = 4$, and for **3**, triclinic system, space group $P\bar{1}$, formula $[C_{21}H_{58}Cl_2Cu_2N_6O_{15}]$ with $a = 8.412(3)$ Å, $b = 14.667(4)$ Å, $c = 16.555(5)$ Å, $\alpha = 99.66(2)°$, $\beta = 102.14(2)°$, $\gamma = 104.72(2)°$, $Z = 2$. Susceptibility measurements show ferromagnetic behavior ($J = +6.7(6)$ cm^{-1}) for the trinuclear compound **1** whereas **2**−**4** are antiferromagnetically coupled with $J = -17.8(8)$, $-125.5(9)$, and $-21.2(3)$ cm^{-1} respectively. Certain synthetic aspects that may be related to the nuclearity of the copper(II) μ-CO_3^{2-} compounds and the superexchange pathway for the different coordination modes of the carbonato bridge are discussed.

Introduction

The carbonate anion reacting with copper(II) salts and, generally, amminate ligands allows the syntheses of carbonato-bridged polynuclear compounds with varying nuclearity including dimers,[1−16] trimers,[17−20] tetramers,[21,22] and one-[23,24] and two-dimensional[25−27] systems in which the carbonato ligand presents different coordination modes. In function of the coordination mode of the carbonato ligand, the magnetic behavior of the complexes varies greatly: from strongly coupled[1,2,4] to moderate or weak[7,16,22,24] antiferromagnetic compounds and even ferromagnetic ones.[14,17−20]

Recently, in seeking to contribute to the establishment of a relationship between the different starting copper(II) salts and amminate ligands with the products obtained and also in studying the magnetochemistry of the μ-carbonato coordination compounds, we have reported the crystal structure and magnetic behavior of three new polynuclear copper(II) carbonato-bridged compounds: the trinuclear $\{(\mu_3\text{-}CO_3)[Cu_3(bapma)_3(ClO_4)_3]\}$-$ClO_4$[19] and the tetranuclear $\{(\mu_4\text{-}CO_3)(\mu\text{-}Br)_2[Cu_4(bapa)_4]\}Br_4$ and $\{(\mu_4\text{-}CO_3)(\mu\text{-}Cl)_2[Cu_4(bapma)_4]\}Cl_4\cdot 12H_2O$[22] [bapa = bis(aminopropyl)amine and bapma = bis(aminopropyl)methyl-

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amine]. As a continuation of our systematic research in this field, here we present four new carbonato-bridging copper(II) complexes with different coordination modes for the carbonato bridge: $\{(\mu_3\text{-CO}_3)[\text{Cu}_3(\text{ClO}_4)_3(\text{Et}_3\text{dien})_3]\}(\text{ClO}_4)$ (**1**), Et$_3$dien = *N*,*N*′,*N*″-triethyl-bis(2-aminoethane)amine; $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})(\text{Et}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (**2**), Et$_4$dien = *N*,*N*,*N*″,*N*″-tetraethylbis(2-aminoethane)amine; $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (**3**), EtMe$_4$dien = *N*′-ethyl-*N*,*N*,*N*″,*N*″-tetramethylbis(2-aminoethane)amine and $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{Me}_5\text{dien})_2]\}(\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (**4**), Me$_5$dien = *N*,*N*,*N*′,*N*″,*N*″-pentamethylbis(2-aminoethane)amine. All these complexes were obtained by fixation of atmospheric CO$_2$. The crystal structures for **2** and **3** were solved. The structure of **2** consists of $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})(\text{Et}_4\text{dien})_2]\}^{2+}$ dinuclear units, with different environments for each copper atom: one atom is linked to one water molecule and one oxygen atom of the carbonate and the other copper(II) is linked to the other two oxygen atoms of the carbonato bridge. The structure of **3** consists of $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}^{2+}$ dinuclear units in which the carbonato ligand acts as a bridge between the two copper atoms showing an anti−anti coordination mode. The susceptibility measurements showed ferromagnetic behavior ($J = +6.7(6)$ cm^{-1}) for the trinuclear compound **1**, whereas **2**−**4** are antiferromagnetically coupled with $J = -17.8(8)$, $-125.5(9)$, and $-21.2(3)$ cm^{-1}, respectively. The coupling constants are clearly related to the different coordination modes of the carbonato bridge as well as the coordination geometry of the Cu(II) ion and, therefore, with the different superexchange pathways found in the compounds.

Experimental Section

CAUTION. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

Synthesis. $\{(\mu_3\text{-CO}_3)[\text{Cu}_3(\text{ClO}_4)_3(\text{Et}_3\text{dien})_3]\}(\text{ClO}_4)$ **(1).** To an aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O (5.4 mmol in 50 mL of water) we added 5.4 mmol of *N*,*N*′,*N*″-triethylbis(2-aminoethane)amine (Et$_3$dien) and 5.4 mmol of diethylamine in 5 mL of water, while stirring. The final blue solution was filtered and left in the air to fix atmospheric CO$_2$. Ten days later, small violet crystals of **1**, unsuitable for X-ray structural determination, were collected.

$\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})(\text{Et}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ **(2).** To an aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O (5.4 mmol in 60 mL of water) we added 5.4 mmol of *N*,*N*,*N*″,*N*″-tetraethylbis(2-aminoethane)amine (Et$_4$dien) and 5.4 mmol of diethylamine in 10 mL of water, while stirring. The final blue solution was filtered and left in the air to fix atmospheric CO$_2$. One week later, blue crystals of **2** were collected.

$\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ **(3).** To an aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O (5.4 mmol in 50 mL of water) we added 5.4 mmol of *N*′-ethyl-*N*,*N*,*N*″,*N*″-tetramethylbis(2-aminoethane)amine (EtMe$_4$dien) and 5.4 mmol of diethylamine in 10 mL of water, while stirring. The final blue solution was filtered and left in the air to fix atmospheric CO$_2$. Ten days later, blue crystals of **3** were collected.

$(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})(\text{Me}_5\text{dien})_2](\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ **(4).** To an aqueous solution of Cu(ClO$_4$)$_2$·6H$_2$O (5.4 mmol in 50 mL of water), we added 5.4 mmol of *N*,*N*,*N*′,*N*″,*N*″-pentamethylbis(2-aminoethane)amine (Me$_5$dien) and 5.4 mmol of diethylamine in 10 mL of water, while stirring. The final blue solution was filtered and left in the air to fix atmospheric CO$_2$. Ten days later, small blue violet crystals of **4**, unsuitable for X-ray structural determination, were collected.

Anal. Found (calcd): C, 30.6 (30.8); H, 6.1 (6.2); N, 10.5 (10.4) for **1**; C, 35.1 (35.2); H, 7.5 (7.3); N, 9.8 (9.8) for **2**; C, 31.0 (30.3); H, 6.8 (7.0); N, 10.4 (10.1) for **3**; C, 30.4 (30.4); H, 6.5 (6.5); N, 11.3 (11.2) for **4**.

Spectral and Magnetic Measurements. Magnetic measurements were carried out with a DSM8 pendulum type susceptometer for **2** and with a Quantum Design instrument with a SQUID detector, working in the temperature range 300−2 K and an applied external field of 0.3 T for **1**, **3**, and **4**. Diamagnetic corrections were estimated from Pascal tables.

Table 1. Crystallographic Data for $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})(\text{Et}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (**2**) and $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (**3**)

	2	**3**
empirical formula	$C_{25}H_{63}Cl_2Cu_2N_6O_{13}$	$C_{21}H_{58}Cl_2Cu_2N_6O_{15}$
fw	852.79	832.71
space group	$P2_1/n$	$P\bar{1}$
a, Å	12.763(6)	8.412(3)
b, Å	25.125(8)	14.667(4)
c, Å	13.261(4)	16.555(5)
α, deg	90.0	99.66(2)
β, deg	111.85(3)	102.14(2)
γ, deg	90.0	104.72(2)
V, Å^3	3947(3)	1877.7(10)
Z	4	2
T, °C	20(2)	23(2)
λ(Mo Kα), Å	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.435	1.473
μ, mm^{-1}	1.275	1.342
R^a	0.0769	0.0743
wR2 ^{b}	0.1530	0.1889

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

Crystallographic Data Collection and Refinement of the Structures. The X-ray single-crystal data for both compounds were collected on a modified STOE four-circle diffractometer. Crystal size: 0.70 × 0.20 × 0.12 mm for **2** and 0.65 × 0.55 × 0.13 mm for **3**. The crystallographic data, the conditions maintained during intensity data collection, and some features of the structural refinements are listed in Table 1. Graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,69$ Å) with the ω-scan technique was used to collect the data sets. The accurate unit-cell parameters were determined from automatic centering of 59 reflections ($7.08 < \theta < 13.79°$) for **2** and 27 reflections ($8.88 < \theta < 13.46°$), for **3** and refined by least-squares methods. 7409 reflections (6293 independent reflections, $R_{\text{int}} = 0.0518$) were collected in the range $2.80 < \theta < 25.00°$ for **2** and 7553 reflections (6773 independent reflections, R_{int} 0.0444) were collected in the range $2.93 < \theta < 26.07°$) for **3**. No significant intensity decay of control reflections (0, 2, 2; 0, 4, 0; 1, 1, 1) (compound **2**) and (2, −1, −2; −1, 4, −5) (compound **3**), measured after each block of 100 data, was observed. Corrections were applied for Lorentz−polarization effects and for absorption (range of normalized transmission coefficients: 0.438−1.000 (compound **2**); 0.187−1.000 (compound **3**) using the DIFABS[28] computer program. The structures were solved by heavy-atom procedures (compound **2**) and direct methods (compound **3**) using the SHELXS-86[29] computer program, and refined by full-matrix least-squares methods on F^2, using the SHELXL-93[30] program incorporated in SHELXTL/PC V 5.03[31] program library and the graphics program PLUTON.[32] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to C atoms were located on calculated positions and assigned with isotropic displacement parameters. The positions of the remaining hydrogen atoms were obtained from Δ*F* maps or from geometrical considerations, and included in final refinement cycles by use of O(N)−H and H−H distance restraints (8 for compound **2**; 20 for compound **3**). The final *R* factors were 0.0769 and 0.0743 for **2** and **3**, respectively, for all observed reflections. The number of refined

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Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{(\mu\text{-}CO_3)[Cu_2(H_2O)(Et_4dien)_2]\}(ClO_4)_2\cdot H_2O$ (**2**)

atom	x	y	z	U(eq) (Å^2)	atom	x	y	z	U(eq) (Å^2)
Cu(1)	0.17004(7)	0.03180(3)	0.17604(7)	0.0380(3)	C(13)	0.1271(8)	0.2328(4)	0.0651(7)	0.072(4)
Cu(2)	0.23907(8)	0.17839(4)	−0.07265(7)	0.0454(3)	C(14)	0.0718(11)	0.2783(5)	0.1062(9)	0.115(6)
O(1)	0.2305(4)	0.0886(2)	0.1091(4)	0.0435(17)	C(15)	0.0598(9)	0.2634(4)	−0.1260(8)	0.084(4)
O(2)	0.0713(4)	0.0535(2)	−0.0007(4)	0.0437(17)	C(16)	−0.0399(8)	0.2255(5)	−0.1601(8)	0.096(5)
O(3)	0.1416(4)	0.1222(2)	−0.0597(4)	0.0455(17)	C(17)	0.2504(9)	0.2856(4)	0.0034(9)	0.081(4)
O(4)	0.3621(5)	0.1701(2)	0.1010(5)	0.056(2)	C(18)	0.3037(8)	0.2882(3)	−0.0778(8)	0.073(4)
N(1)	0.2894(5)	−0.0294(2)	0.1983(5)	0.052(3)	C(19)	0.3278(9)	0.2282(4)	−0.2165(7)	0.078(4)
N(2)	0.0784(5)	−0.0239(2)	0.2118(5)	0.044(2)	C(20)	0.3388(8)	0.1709(4)	−0.2373(8)	0.076(4)
N(3)	0.1061(5)	0.0829(2)	0.2641(5)	0.051(2)	C(21)	0.2935(9)	0.0827(4)	−0.1859(8)	0.076(4)
N(4)	0.1551(6)	0.2437(2)	−0.0320(5)	0.055(3)	C(22)	0.3908(8)	0.0740(4)	−0.0798(8)	0.079(4)
N(5)	0.3328(6)	0.2343(3)	−0.1042(6)	0.059(3)	C(23)	0.1418(8)	0.1424(4)	−0.2918(6)	0.068(3)
N(6)	0.2571(6)	0.1388(3)	−0.2055(5)	0.054(3)	C(24)	0.1237(9)	0.1190(4)	−0.4021(7)	0.096(5)
C(1)	0.3470(8)	−0.0325(4)	0.1184(8)	0.079(4)	C(25)	0.1471(6)	0.0885(3)	0.0143(6)	0.035(2)
C(2)	0.2673(9)	−0.0418(4)	0.0026(8)	0.082(4)	Cl(1)	0.2715(3)	−0.04943(11)	0.6084(2)	0.0869(14)
C(3)	0.3778(7)	−0.0184(4)	0.3098(7)	0.073(3)	O(11)	0.2910(10)	−0.0027(4)	0.5681(8)	0.184(6)
C(4)	0.4625(9)	−0.0620(5)	0.3624(9)	0.122(5)	O(12)	0.3065(16)	−0.0480(5)	0.7172(8)	0.260(11)
C(5)	0.2261(7)	−0.0787(3)	0.1959(8)	0.064(4)	O(13)	0.1697(12)	−0.0663(10)	0.5573(14)	0.338(12)
C(6)	0.1509(7)	−0.0696(3)	0.2603(7)	0.058(3)	O(14)	0.3306(18)	−0.0851(6)	0.5863(15)	0.305(15)
C(7)	0.0179(7)	−0.0015(3)	0.2787(6)	0.057(3)	Cl(2)	0.1660(3)	0.27552(13)	0.4661(2)	0.0844(12)
C(8)	0.0813(7)	0.0466(3)	0.3401(7)	0.061(3)	O(21)	0.0897(9)	0.2516(5)	0.5073(12)	0.212(8)
C(9)	0.0030(8)	0.1084(4)	0.1840(8)	0.076(4)	O(22)	0.2642(10)	0.2498(6)	0.5166(11)	0.219(8)
C(10)	−0.0699(9)	0.1394(5)	0.2333(10)	0.113(6)	O(23)	0.1695(15)	0.3249(5)	0.4874(15)	0.266(10)
C(11)	0.1823(9)	0.1271(4)	0.3225(8)	0.082(4)	O(24)	0.1304(15)	0.2668(8)	0.3633(10)	0.320(12)
C(12)	0.2996(9)	0.1124(5)	0.3831(9)	0.106(5)	O(5)	0.5889(6)	0.1483(4)	0.1705(7)	0.111(4)

[a] U(eq) = 1/3 of the trace of the orthogonalized **U** tensor.

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $\{(\mu\text{-}CO_3)[Cu_2(H_2O)_2(EtMe_4dien)_2]\}(ClO_4)_2\cdot 2H_2O$ (**3**)

atom	x	y	z	U(eq)^a (Å^2)	atom	x	y	z	U(eq)^a (Å^2)
Cu(1)	0.00682(8)	0.30733(5)	0.16834(4)	0.0393(2)	C(11)	0.3909(11)	0.7508(6)	0.2058(4)	0.074(3)
Cu(2)	0.52414(8)	0.68327(5)	0.35323(4)	0.0394(2)	C(12)	0.2130(8)	0.7419(6)	0.3030(6)	0.076(3)
O(1)	0.1885(5)	0.4289(3)	0.2021(2)	0.0524(12)	C(13)	0.4830(9)	0.8697(5)	0.3419(4)	0.057(2)
O(2)	0.3803(5)	0.5653(3)	0.2704(3)	0.0549(12)	C(14)	0.6714(8)	0.8829(4)	0.3679(4)	0.052(2)
O(3)	0.1846(6)	0.4979(3)	0.3326(3)	0.0694(17)	C(15)	0.6847(8)	0.8404(5)	0.5061(4)	0.0527(19)
O(4)	−0.0932(6)	0.3503(4)	0.2799(3)	0.0685(17)	C(16)	0.8063(10)	0.9381(5)	0.5605(5)	0.074(3)
O(5)	0.4029(6)	0.6409(3)	0.4550(3)	0.0621(17)	C(17)	0.8701(7)	0.7950(5)	0.4190(5)	0.056(2)
N(1)	−0.1349(7)	0.3588(4)	0.0810(3)	0.0526(17)	C(18)	0.8656(8)	0.6987(5)	0.4392(5)	0.061(2)
N(2)	−0.1675(7)	0.1740(3)	0.1098(3)	0.0492(16)	C(19)	0.6805(11)	0.5370(6)	0.4146(6)	0.088(4)
N(3)	0.1722(8)	0.2314(4)	0.2053(4)	0.066(2)	C(20)	0.7629(9)	0.5925(6)	0.2986(5)	0.079(3)
N(4)	0.3922(6)	0.7663(4)	0.2969(3)	0.0483(17)	C(21)	0.2499(7)	0.4979(4)	0.2704(4)	0.0456(17)
N(5)	0.7022(6)	0.8113(3)	0.4176(3)	0.0422(14)	Cl(1)	−0.2899(2)	0.17005(11)	0.39693(9)	0.0494(5)
N(6)	0.7194(7)	0.6212(4)	0.3798(4)	0.0549(17)	O(11)	−0.2889(7)	0.1457(5)	0.4767(3)	0.090(3)
C(1)	−0.1715(12)	0.4477(6)	0.1160(5)	0.085(3)	O(12)	−0.4392(7)	0.1140(5)	0.3355(4)	0.100(3)
C(2)	−0.0382(10)	0.3785(5)	0.0165(4)	0.069(3)	O(13)	−0.2807(10)	0.2682(4)	0.4039(5)	0.109(3)
C(3)	−0.2967(9)	0.2812(5)	0.0394(5)	0.065(3)	O(14)	−0.1423(7)	0.1562(6)	0.3725(4)	0.099(3)
C(4)	−0.2591(10)	0.1854(5)	0.0273(4)	0.066(2)	Cl(2)	0.8986(5)	0.8496(2)	0.1464(2)	0.1146(14)
C(5)	−0.2853(8)	0.1460(5)	0.1646(4)	0.055(2)	O(21)	0.778(2)	0.8476(8)	0.0724(7)	0.228(8)
C(6)	−0.4312(11)	0.0525(5)	0.1269(5)	0.084(3)	O(22)	0.8619(15)	0.7624(7)	0.1685(8)	0.215(7)
C(7)	−0.0633(10)	0.1068(5)	0.0998(5)	0.070(3)	O(23)	0.880(2)	0.9152(9)	0.2068(8)	0.239(9)
C(8)	0.0734(11)	0.1283(5)	0.1806(6)	0.080(3)	O(24)	1.043(2)	0.8729(10)	0.1294(12)	0.287(11)
C(9)	0.3058(11)	0.2502(8)	0.1607(7)	0.108(5)	O(6)	0.4096(15)	0.5031(11)	0.0957(6)	0.247(8)
C(10)	0.2538(12)	0.2603(7)	0.2985(6)	0.100(4)	O(7)	0.6089(17)	0.6257(10)	0.0387(10)	0.235(8)

[a] U(eq) = 1/3 of the trace of the orthogonalized **U** tensor.

parameters was 487 (**2**) and 452 (**3**). Maximum and minimum peaks in the final difference synthesis were 0.581 and −0.490 e Å^{-3} (**2**) and 1.130 and −1.020 e Å^{-3} (**3**) (0.90 Å for Cl(2)). Final atomic coordinates for **2** and **3** are reported in Tables 2 and 3, respectively, and significant bond parameters for **2** and **3** are given in Tables 4 and 5, respectively.

Results and Discussion

Description of the Structures. **$(\mu\text{-}CO_3)[Cu_2(H_2O)(Et_4dien)_2](ClO_4)_2\cdot H_2O$ (2).** The structure of **2** consists of $\{(\mu\text{-}CO_3)[Cu_2(H_2O)(Et_4dien)_2]\}^{2+}$ dinuclear units, two perchlorate counteranions and one molecule of water connected by hydrogen bonds. The labeled dinuclear unit is shown in Figure 1. This dinuclear unit is strongly asymmetric, with different environments for each copper atom. Cu(1) shows a highly distorted CuN_3O_2 trigonal bipyramid (tbp) coordination polyhedron as a consequence of the bidentate coordination of the carbonato ligand, which implies a O(1)−Cu(1)−O(2) bond angle of 61.7(2)°, within the typical range found for this coordination mode of the carbonato ligand.[3] Bond distances at the nitrogen atoms of the Et$_4$dien ligand are similar, Cu(1)−N(1) = 2.107(6) Å, Cu(1)−N(2) = 1.991(6) Å, and Cu(1)−N(3) = 2.094(6) Å, whereas the two bonds at the oxygen atoms of the bridging carbonato ligand show a short Cu(1)−O(1) = 1.983(5) Å distance and a large Cu(1)−O(2) = 2.276(5) Å distance. In contrast, Cu(2) is coordinated by one Et$_4$dien ligand, one of the oxygen atoms of the carbonato bridge, Cu(2)−O(3) = 1.932-

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})(\text{Et}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot\text{H}_2\text{O}$ (**2**)

Cu(1)−O(1)	1.983(5)	Cu(1)−N(2)	1.991(6)
Cu(1)−N(3)	2.094(6)	Cu(1)−N(1)	2.107(6)
Cu(1)−O(2)	2.276(5)	Cu(2)−O(3)	1.932(5)
Cu(2)−N(5)	1.987(6)	Cu(2)−N(6)	2.108(6)
Cu(2)−N(4)	2.135(6)	Cu(2)−O(4)	2.263(6)
O(1)−C(25)	1.310(8)	O(2)−C(25)	1.267(7)
O(3)−C(25)	1.279(8)	O(1)−O(4)	2.676(8)
O(1)−Cu(1)−N(2)	166.8(2)	O(1)−Cu(1)−N(3)	96.0(2)
N(2)−Cu(1)−N(3)	85.0(3)	O(1)−Cu(1)−N(1)	101.9(2)
N(2)−Cu(1)−N(1)	84.9(3)	N(3)−Cu(1)−N(1)	141.3(3)
O(1)−Cu(1)−O(2)	61.7(2)	N(2)−Cu(1)−O(2)	105.3(2)
N(3)−Cu(1)−O(2)	104.3(2)	N(1)−Cu(1)−O(2)	114.4(2)
O(3)−Cu(2)−N(5)	173.4(3)	O(3)−Cu(2)−N(6)	90.2(2)
N(5)−Cu(2)−N(6)	84.0(3)	O(3)−Cu(2)−N(4)	98.0(2)
N(6)−Cu(2)−O(4)	123.8(3)	N(4)−Cu(2)−O(4)	92.1(2)
N(5)−Cu(2)−N(4)	84.7(3)	N(6)−Cu(2)−N(4)	142.6(3)
O(3)−Cu(2)−O(4)	93.9(2)	N(5)−Cu(2)−O(4)	92.0(3))
O(2)−C(25)−O(3)	121.2(6)	O(2)−C(25)−O(1)	117.0(6)
O(3)−C(25)−O(1)	121.8(6)	C(25)−O(1)−Cu(1)	96.6(4)
C(25)−O(3)−Cu(2)	134.4(4)	C(25)−O(2)−Cu(1)	84.6(4)
O(1)−Cu(1)−O(2)	61.6(2)		

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (**3**)

Cu(1)−O(1)	1.936(4)	Cu(1)−O(4)	2.247(5)
Cu(1)−N(1)	2.045(6)	Cu(1)−N(2)	2.055(5)
Cu(1)−N(3)	2.051(7)	Cu(2)−O(2)	1.944(5)
Cu(2)−O(5)	2.240(5)	Cu(2)−N(4)	2.054(6)
Cu(2)−N(5)	2.033(5)	Cu(2)−N(6)	2.076(6)
O(1)−C(21)	1.294(7)	O(2)−C(21)	1.276(8)
O(3)−C(21)	1.265(8)	Cu(1)−Cu(2)	5.937(2)
O(1)−Cu(1)−O(4)	91.31(18)	O(1)−Cu(1)−N(1)	91.0(2)
O(1)−Cu(1)−N(2)	167.79(19)	O(1)−Cu(1)−N(3)	92.2(2)
O(4)−Cu(1)−N(1)	98.9(2)	O(4)−Cu(1)−N(2)	100.8(2)
O(4)−Cu(1)−N(3)	107.1(2)	N(1)−Cu(1)−N(2)	85.6(2)
N(1)−Cu(1)−N(3)	153.7(2)	Cu(1)−N(3)−C(10)	112.6(5)
N(2)−Cu(1)−N(3)	85.7(2)	O(2)−Cu(2)−O(5)	92.10(18)
O(2)−Cu(2)−N(4)	92.1(2)	O(2)−Cu(2)−N(5)	166.4(2)
O(2)−Cu(2)−N(6)	91.0(2)	O(5)−Cu(2)−N(4)	106.5(2)
O(5)−Cu(2)−N(5)	101.37(18)	O(5)−Cu(2)−N(6)	96.5(2)
N(4)−Cu(2)−N(5)	85.7(2)	N(4)−Cu(2)−N(6)	156.6(2)
N(5)−Cu(2)−N(6)	85.9(2)	Cu(1)−O(1)−C(21)	134.0(4)
Cu(2)−O(2)−C(21)	133.5(4)	O(2)−C(21)−O(3)	122.7(6)
O(1)−C(21)−O(2)	115.3(5)	O(1)−C(21)−O(3)	121.9(6)

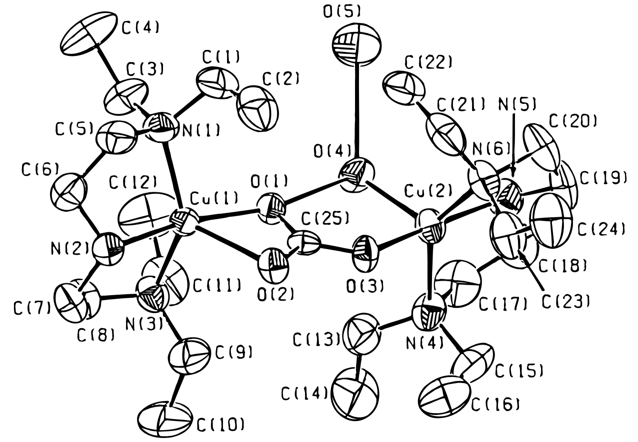

Figure 1. ORTEP drawing with atom labeling scheme and 50% thermal ellipsoids of the dinuclear unit $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})(\text{Et}_4\text{dien})_2]\}^{2+}$ of **2**.

(5) Å, and one water molecule, Cu(2)−O(4) = 2.263(6) Å, showing an CuN_3O_2 environment close to tbp. O(3)−Cu(2)−N(5) is apparently the main axis, bond angle 173.4(3)°, but the large bond distance corresponds to the coordinated water molecule. The intradimer Cu···Cu distance is 5.233(3) Å. The coordinated water molecule is related by hydrogen bonds to one oxygen atom of the carbonato ligand, O(1), and to the hydration water molecule: O(4)−O(1) = 2.676(8) Å, O(4)−O(5) = 2.746(11) Å.

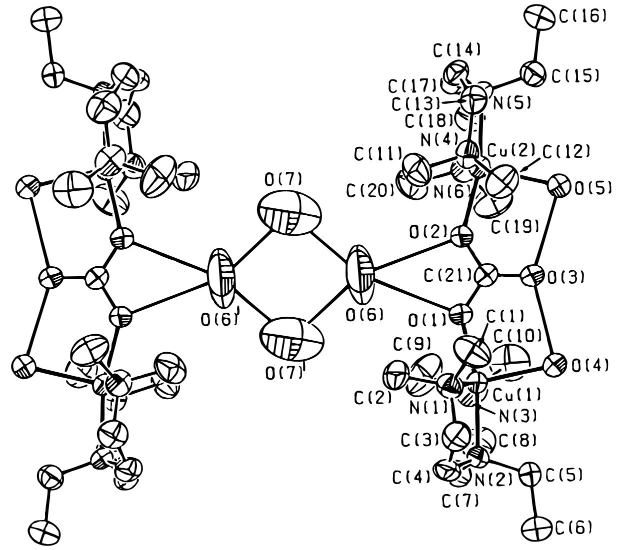

Figure 2. ORTEP drawing with atom labeling scheme and 50% thermal ellipsoids of the tetranuclear unit $\{\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}\cdot 2\text{H}_2\text{O}\}_2{}^{4+}$ of **3**.

$\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}(\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ (3). The labeling scheme for **3** without perchlorate anions is shown in Figure 2. In this structure the hydrogen bonds play an important structural role: around a square ring of four water molecules linked by hydrogen bonds (O(7)−O(6) = 2.576(16) Å, O(7)−O(6)$^{\text{ii}}$ = 2.615(16) Å), are placed two $\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}^{2+}$ dinuclear units and two perchlorate counteranions, each of them linked to one water molecule from the central water ring by hydrogen bonds: O(7)−O(22) = 2.761(17) Å, O(6)−O(1) = 2.956(10) Å, O(6)−O(2) = 2.964(9) Å, forming a tetranuclear copper(II) unit. In the dinuclear $\mu\text{-CO}_3{}^{2-}$ units, the two copper atoms show the same $[\text{N}_3\text{O}_2]$ coordination environment formed by one EtMe_4dien ligand, one water molecule and one oxygen atom of the carbonato bridge in a square pyramidal arrangement in which the apical site is occupied by the H_2O ligand: Cu(1)−O(4) = 2.247(5) Å, Cu(2)−O(5) = 2.240(5) Å. The carbonato ligand acts as a bridge between the two copper atoms showing an anti−anti coordination mode with Cu(1)−O(1) = 1.936(4) Å and Cu(2)−O(2) = 1.944(5) Å, remaining uncoordinated O(3), which is related to the apical coordinated water molecules by strong hydrogen bonds: O(3)···O(4) = 2.616(6) Å and O(3)···O(5) = 2.632(6) Å. The Cu−O−C bond angles are similar: Cu(1)−O(1)−C(21) = 134.0(4)° and Cu(2)−O(2)−C(21) = 133.5(4)°, the interdimeric Cu···Cu distance being 5.937(2) Å larger than the related distance in **2**.

Magnetic Measurements. The magnetic behavior of compounds **1**−**4** show a wide variety of superexchange interactions. For the trinuclear compound **1**, the $\chi_M T$ value increases continuously when cooling ($\chi_M T$ at 160 K, 1.26 $\text{cm}^3\ \text{K mol}^{-1}$; $\chi_M T$ at 2.0 K, 2.05 $\text{cm}^3\ \text{K mol}^{-1}$), indicating a ferromagnetic interaction, Figure 3a. Fit by means of the expression derived from $H = -J(S_1S_2 + S_1S_3 + S_2S_3)$[19,33] allows the best fit parameters $J = +6.7(6)\ \text{cm}^{-1}$, $g = 2.10(1)$. These results are

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(33) Kahn, O. *Molecular Magnetism;* VCH Publishers: New York, 1993.

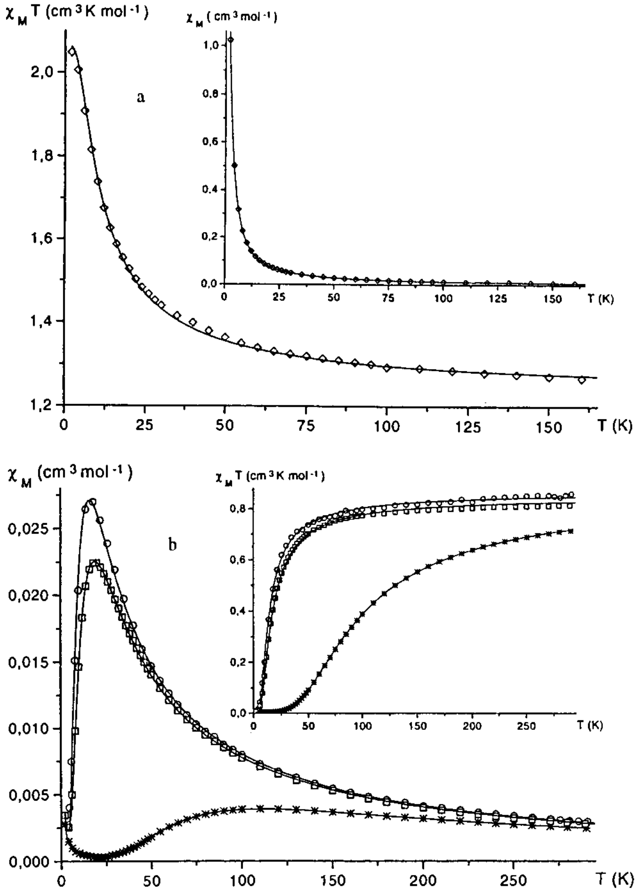


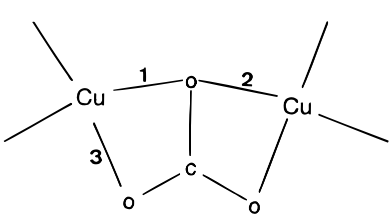
Figure 3. (a) $\chi_M T$ vs T plot in the 2−160 K range of temperatures for **1**. The inset shows χ_M vs T plot in the 2−160 K range of temperatures for **1**. Solid lines show the best fit indicated in the text. (b) χ_M vs T plot in the 2−300 K range of temperatures for **2** (○), **3** (*), and **4** (□). The inset shows $\chi_M T$ vs T plot in the 2−300 K range of temperatures for **2** (○), **3** (*), and **4** (□). Solid lines show the best fit indicated in the text.

comparable to those obtained for the structurally characterized μ_3-carbonato copper(II) compounds.[17−20]

The compounds **2** and **4** show a very similar weak antiferromagnetic behavior as is shown in Figure 3b. The $\chi_M T$ values for **2** (○) and **4** (□) decrease continuously when cooling, tending to a zero value at low temperatures, whereas the χ_M values increase up to a maximum value of 0.027 cm^3 mol^{-1} at 18 K for **2** and 0.0224 cm^3 mol^{-1} at 20 K for **4.** Fits with the classical expression[33] for a copper dimer with paramagnetic impurities derived from the Hamiltonian $\mathbf{H} = -\mathbf{J}\mathbf{S}_1\mathbf{S}_2$ gave the best fit parameters $J = -17.8(8)$ cm^{-1} and $g = 2.14(2)$ for **2** and $J = -21.2(3)$ cm^{-1}, $g = 2.12(2)$, and $\rho = 0.009(2)$ for **4**. The practically identical magnetic properties together with the result of the elemental analysis for **2** and **4** seem to indicate a similar superexchange for the two compounds.

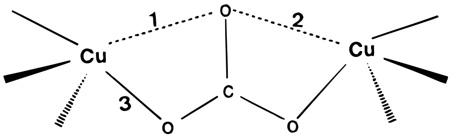
From the magnetic point of view, we will consider **3** as a dimer. **3** shows the typical χ_M vs T plot for a moderately strong antiferromagnet, Figure 3b. The $\chi_M T$ values (*) decay continuously to reach a zero value at low temperatures and the χ_M values increase gradually up to a maximum of 0.039 cm^3 mol^{-1} at 110 K. Subsequently, the χ_M value decreases practically to 0 at 25 K before increasing due to the presence of a small amount of paramagnetic impurities ρ. The best fit parameters obtained by using the above indicated expression for a dinuclear copper compound are $J = -125.5(9)$ cm^{-1}, $g = 2.15(1)$, and $\rho = 0.0066(7)$.

Superexchange Mechanism. The carbonato bridge is one of the most versatile ligands, both from the structural and the magnetic point of view. Its extraordinary ability to bridge from two up to six metallic centers in a variety of coordination modes (see ref 34) allows to strongly antiferromagnetically coupled compounds ($J < -1000$ cm^{-1} in some dinuclear copper compounds),[1,2,4] moderate or weak antiferromagnets[7,16,22,24] or even ferromagnetic coupling[14,17−20] for some coordination modes. Strong antiferromagnetic coupling is achieved in the case in which one of the oxygen atoms of the carbonato acts as a direct bridge between two metallic centers, giving a Cu−O−Cu quasilinear pathway with short Cu−O bond distances. This antiferromagnetic coupling is modulated by the arrangement of the magnetically active atomic orbitals of the metallic ion. A square planar arrangement maximizes of the overlap between the $d_{x^2-y^2}$ atomic orbitals with the a2′ MO of the carbonato bridge[7] in a situation similar to a single oxo bridge, giving the strongest AF coupling.[1,2,4]



A

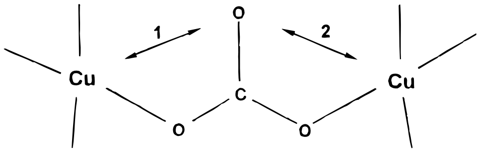
When the coordination around the copper atoms tends to trigonal bipyramid, and the 1 and 2 bond distances increase as in the compound (μ-CO$_3$)[Cu$_2$(Et$_5$dien)$_2$](ClO$_4$)$_2$,[7] Et$_5$dien = *N,N,N′,N″,N″*-pentaethyldiethylenetriamine,



B

the mixing of the AO $d_{x^2-y^2}$ with the d_{z^2} AO, which has a low unpaired electronic density, reduces the superexchange via the pseudo-oxo pathway and the J value found is −207(1) cm^{-1}.

The compound **3** may be considered as being derived from B by breaking the 1 and 2 bonds. The pseudo-oxo superexchange pathway is definitively lost and the only active magnetic coupling is through an anti−anti superexchange pathway.



C

Consequently the J value found in **3** of −125.5 cm^{-1} is smaller in absolute terms than the J value found in {(μ-CO$_3$)[Cu$_2$(Et$_5$dien)$_2$]}(ClO$_4$)$_2$.[7] The compound {(μ-CO$_3$)[Cu$_2$(bpy)$_2$]}(PF$_6$)$_2$, bpy = 2,2′-bipyridine, which has the same anti−anti superexchange pathway C, has previously been reported.[16] The found J value for this compound is similar: $J = -140.4$ cm^{-1}.

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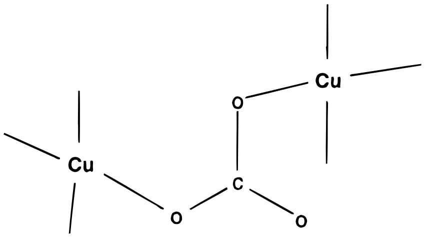
(34) Escuer, A.; Vicente, R.; Kumar, S. B.; Solans, X.; Font-Bardía, M. *J. Chem. Soc., Dalton Trans.* **1997**, 403.

Table 6. Magnetic Exchange Coupling Constants of Dinuclear Copper(II) Carbonato Bridge Compounds as a Function of the Coordination Mode (See Text)[a]

compound	mode	1	2	J (cm^{-1})	ref
$\{(\mu\text{-CO}_3)[\text{Cu(L1)}]_2\}^{2+}$	A	2.041	2.041	< -1000	1
$\{(\mu\text{-CO}_3)[\text{Cu(L2)Cl}]_2\}^{2+}$	A	2.153	2.153	< -1000	2
$\{(\mu\text{-CO}_3)[\text{Cu(Et}_5\text{dien)}]_2\}^{2+}$	B	2.305	2.346	−207	7
$\{(\mu\text{-CO}_3)[\text{Cu(bpy)}_2]_2\}^{2+}$	C	2.792	2.792	−140.4	16
$\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})_2(\text{EtMe}_4\text{dien})_2]\}^{2+}$	C	3.316	3.325	−125.5	this work
$\{(\mu\text{-CO}_3)[\text{Cu(NH}_3)_2]\}_n$	F			−6.2	24
$\{(\mu\text{-CO}_3)[\text{Cu}_2(\text{H}_2\text{O})(\text{Et}_4\text{dien})_2]\}^{2+}$	F			−17.8	this work
$\{(\mu\text{-CO}_3)[\text{Cu(ascidH}_2)(\text{H}_2\text{O})]_2\}$	D			+1.6	14

[a] L1 = 2,4,4,7-tetramethyl-1,5,9-triazacyclododec-1-ene; L2 = *N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine; ascidH$_4$ = ascidiacyclamide.

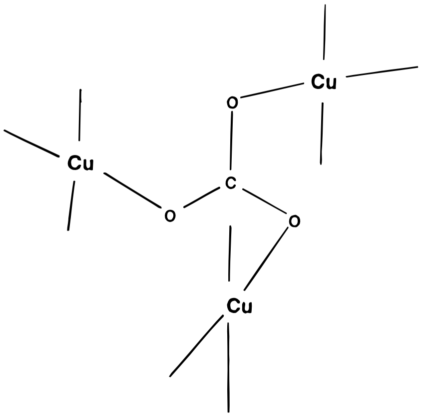
Another superexchange pathway for the carbonato bridge is that derived from the syn−anti coordination mode D



D

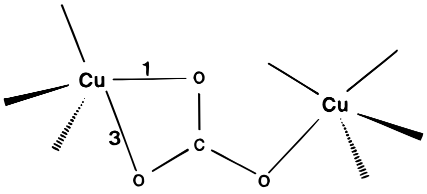
which has been found in several dinuclear[14] and trinuclear[17−20] carbonato-bridged copper(II) complexes and for which the *J* parameter is always positive. The superexchange mechanism has been analyzed by using MO extended Hückel calculations.[19]

The analytical and magnetic data found for **1** permit us to assign the coordination mode E of the next schema to this compound, as was the case for the previously studied analogous compounds with the bapa and bapma ligands (obtained starting from the copper(II) perchlorate salt).[19]



E

The other structurally characterized dimer, **2**, may be understood as derived being from A by breaking the bond 2 and enlarging the bond 3:



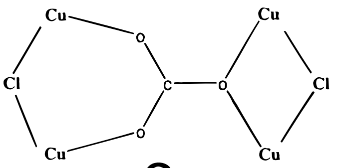
F

In this coordination mode F, the compound **2** simultaneously shows the syn−anti (D) and anti−anti (C) superexchange pathways which have opposite J signs. The resulting experimental coupling is antiferromagnetic but with a low *J* value, $J = -17.8(8)$ cm^{-1}. The analytical data and the practically equal magnetic behavior of **2** and **4** suggest the same coordination for the carbonato bridge and, lacking into structural data, the coordination mode F may also be assigned to **4**. It is interesting to note that this coordination mode was previously found in 1-D octahedral copper compounds involving one of the axial sites and consequently the *J* parameter was close to zero.[24] **2** is the first case in which this coordination mode has been found between two coordination sites considered adequate for the superexchange coupling, and, as was expected, actually allows weak coupling. Recently, this coordination mode has also been found between two nickel ions, also giving a weak AF coupling.[34] In Table 6 the reported dinuclear copper(II) μ-CO$_3^{2-}$ compounds with their different coordination modes and coupling constants are described.

Table 7. Nuclearity of Polynuclear Copper(II) Carbonato Bridge Compounds as a Function of the Starting Copper(II) Salt and the Triamine

L	counteranion	nucl.	ref
bapa	ClO_4^-	Cu-3	19
bapa	Cl^-	Cu-4	21
bapa	Br^-	Cu-4	22
bapma	ClO_4^-	Cu-3	19
bapma	Cl^-	Cu-4	22
bapma	Br^-	Cu-4	22
Et$_5$dien	ClO_4^-	Cu-2	7
Me$_5$dien	ClO_4^-	Cu-2	this work
EtMe$_4$dien	ClO_4^-	Cu-2	this work
Et$_4$dien	ClO_4^-	Cu-2	this work
Et$_3$dien	ClO_4^-	Cu-3	this work

By using triamines as a starting reagent in order to obtain comparative results, it becomes evident that the structural (and consequently the magnetic) properties for the system copper−tridentate ligand−carbonato bridge may be tuned in several ways as function of two parameters: the counteranion and the number of N−pendant groups of the aminated ligand, Table 7. The counteranion plays a structural role for bapa, bapma and Et$_3$dien in which the perchlorate anion generates, in all the cases, trinuclear systems, probably stabilized in all cases by means of a hydrogen bond superstructure as was reported for bapa.[19] For the same ligands, by using chloride or bromide counterions, the compounds obtained were tetranuclear with the halide ions also having a structural function:



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When the aminated ligands have at least four N,N,N″,N″ methyl or ethyl groups, the reaction yields in each reported case to dinuclear compounds, in which the coordination polyhedra around the copper atom is always close to trigonal bipyramid. Thus, we can conclude that ligands which produce planar environments around the copper atom tend to Cu_3 or Cu_4 compounds, whereas ligands which have pendant groups produce the most voluminous trigonal bipyramid environment around the copper atoms and prefer the Cu_2 nuclearity.

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Supporting Information Available: A complete listing of full data collection and processing parameters, bond lengths and bond angles, atomic coordinates, equivalent isotropic and anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients for **2** and **3** (24 pages). Ordering information is given on any current masthead page.

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