248 *Inorg. Chem.* **1996,** *35,* 248−251

Synthesis, Crystal Structure, and Magnetic Behavior of $(\mu_3\text{-}CO_3)[Cu_3(Medpt)_3(ClO_4)_3](ClO_4)$: A New Copper(II) Carbonato-Bridged Complex with a Triangular Array

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Introduction

The study of copper−carbonato coordination chemistry is a research field of growing interest because of the combination of several interesting characteristics of this ligand. From the point of view of coordination chemistry, the carbonato anion is an extremely versatile bridging ligand,[1] able to generate compounds with different nuclearity on not only whole dimers[2−3] but also trimers,[4] tetramers,[5] and 1D[6] or 2D[7] systems. In spite of this potential interest, no systematic study has been reported and the magnetochemistry of this ligand is poorly described for nuclearity greater than two. From the magnetic point of view, the unusual range of magnetic behavior that can be obtained as a function of the coordination of the bridging carbonato ligand should be pointed out, from fully coupled compounds (diamagnetic at room temperature[2d]) to moderate[2a] or weak[6] antiferromagnetic compounds and even ferromagnetic systems.[2e,4] Finally, the copper−carbonato models are a subject of interest because of the variety of bioinorganic roles of CO_2: coordinated carbonate or the nucleophilic fixation of atmospheric CO_2 is relevant in some metalloenzymes such as carbonic anhydrase, D-ribulose 1,5-bisphosphate carboxylase-oxygenase, non-heme iron in the photosynthetic system II, or copper complexes of the cyclic peptide ascidiacyclamide.

Table 1. Crystal Data for **1**

formula	$[C_{22}H_{57}Cl_4Cu_3N_9O_{19}]$
a, Å	16.849(5)
b, Å	20.907(4)
c, Å	13.501(7)
β, deg	109.69(4)
V, Å^3	4478(3)
Z	4
formula weight	1084.20
space group	*Cc*
T, K	293(2)
λ(Mo Kα), Å	0.710 69
d_{calc}, g/cm^{-3}	1.608
μ(Mo Kα), cm^{-1}	17.82
R[a]	0.0444
ϖR^2[b]	0.1191
$F_{(000)}$	2236

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

This work is devoted to the synthesis and magnetic study of the copper(II) trinuclear μ_3-CO_3^{2-} system $(\mu_3\text{-}CO_3)[Cu_3(Medpt)_3(ClO_4)_3](ClO_4)$ (**1**) (Medpt is bis(3-aminopropyl)methylamine). The resolution of the crystal structure of **1** reveals a practically equilateral triangle of copper(II) atoms with a central μ_3-carbonate bridge. The magnetic measurements show ferromagnetic coupling. The trinuclear nature of the product of the reaction between tridentate amines with copper in strongly basic medium and atmospheric CO_2 was suggested by Curtis[8] on the basis of the IR spectra for the analogous compound $(\mu_3\text{-}CO_3)[Cu_3(dpt)_3](ClO_4)_4$ (**2**) (dpt is bis(3-aminopropyl)amine), which has been also prepared by us to study its magnetic behavior. Triangular metal complexes are interesting in magnetochemistry because they offer the possibility to study frustrated spin systems. Thus, several antiferromagnetic μ_3-X (generally X = OH^-) complexes are well known,[9] whereas compounds with a triangular array of copper atoms without μ_3-L[9] (L = ligand) or ferromagnetic μ_3-L systems are extremely rare.[4]

Experimental Section

Synthesis: Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of compound should be prepared, and it should be handled with caution.

To a solution of 10 mmol of $Cu(ClO_4)_2 \cdot 6H_2O$ and 10 mmol of Medpt or dpt in 50 mL of water, 6 mmol of $NHEt_2$ was added and maintained for 1 h with vigorous stirring. After 2 weeks, slow reaction with atmospheric CO_2 yielded blue crystals of the corresponding compound, suitable for X-ray determination for **1**. Analytical data (C, H, N, and Cl) were in agreement with the proposed formula.

X-ray Crystallography. A prismatic blue crystal (0.1 mm × 0.1 mm × 0.2 mm) of $(\mu_3\text{-}CO_3)[Cu_3(Medpt)_3(ClO_4)_3](ClO_4)$ (**1**) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12° < \theta < 21°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation using the $\varpi/2\theta$ scan technique. A total of 6769 reflections were measured in the range $1.61° < \theta < 30.02$. A total of 5049 reflections were assumed as observed, applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz polarization corrections, but not absorption corrections, were made. The crystallographic data, collection conditions, and relevant features of the structure refinement are listed in Table 1. The structure was solved by Patterson synthesis, using the SHELXS computer program,[10] and

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Table 2. Positional Parameters ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for **1**[a]

atom	x	y	z	U_{eq}	atom	x	y	z	U_{eq}
Cu(1)	7830(1)	1367(1)	5456(1)	41(1)	O(43)	4349(18)	1906(15)	3361(26)	164(10)
Cu(2)	6640(1)	2440(1)	7841(1)	41(1)	O(44)	4754(26)	2713(20)	2604(31)	200(14)
Cu(3)	7775(1)	3692(1)	5579(1)	41(1)	N(1)	7031(11)	1713(7)	4106(10)	69(4)
O(1)	7286(7)	1885(4)	6258(7)	48(2)	N(2)	8686(8)	1053(6)	4804(10)	55(3)
O(2)	7017(6)	2855(4)	6758(6)	45(2)	N(3)	8485(12)	1053(7)	6914(11)	80(5)
O(3)	7624(7)	2756(3)	5544(8)	49(2)	N(4)	5732(10)	2007(8)	6707(12)	71(3)
Cl(1)	6430(4)	247(2)	5669(5)	86(2)	N(5)	6580(9)	1838(5)	9010(9)	57(3)
O(11)	7060(10)	354(8)	5200(14)	99(5)	N(6)	7526(11)	3000(8)	8794(12)	75(4)
O(12)	5971(22)	−273(16)	5355(29)	104(10)	N(7)	6536(9)	3791(7)	5110(12)	65(3)
O(13)	5960(36)	817(23)	5580(54)	105(37)	N(8)	8024(9)	4615(5)	6114(11)	56(3)
O(14)	7001(22)	312(17)	6838(21)	90(9)	N(9)	8974(10)	3442(7)	5893(15)	77(4)
O(12′)	6340(17)	−428(11)	5796(23)	77(6)	C(1)	7304(8)	2507(4)	6178(9)	36(2)
O(13′)	5687(33)	549(30)	5084(52)	269(36)	C(2)	6880(15)	1380(9)	3112(13)	78(6)
O(14′)	6663(25)	504(18)	6680(26)	108(11)	C(3)	7773(18)	1260(12)	2945(19)	90(6)
Cl(2)	5477(4)	3805(2)	7561(5)	85(2)	C(4)	8275(18)	818(9)	3658(18)	94(7)
O(21)	5625(9)	3216(7)	8091(13)	88(4)	C(5)	9243(19)	493(13)	5361(25)	105(8)
O(22)	4781(21)	3954(18)	7333(34)	152(12)	C(6)	9678(15)	572(15)	6520(28)	104(9)
O(23)	6254(18)	4111(19)	7884(33)	113(10)	C(7)	9031(17)	494(10)	7137(20)	95(7)
O(24)	5189(14)	4258(11)	8181(19)	72(5)	C(8)	9223(13)	1611(10)	4823(17)	76(5)
O(22′)	5173(58)	3535(38)	6605(38)	274(48)	C(9)	4997(12)	1745(12)	6908(17)	80(6)
O(23′)	5598(26)	3792(24)	6591(43)	141(15)	C(10)	5302(18)	1283(11)	7898(28)	98(8)
O(24′)	5728(14)	4190(11)	8214(19)	72(5)	C(11)	5695(16)	1613(10)	8827(20)	90(6)
Cl(3)	7736(5)	3449(2)	3057(4)	87(2)	C(12)	6861(26)	2134(12)	10112(18)	123(11)
O(31)	7786(10)	3921(8)	3772(14)	103(5)	C(13)	7735(29)	2456(10)	10506(19)	98(9)
O(32)	8536(19)	3098(14)	3589(23)	91(8)	C(14)	7655(17)	3093(10)	9927(16)	91(7)
O(33)	7252(26)	3619(24)	2257(29)	212(18)	C(15)	7137(13)	1302(8)	8972(17)	75(5)
O(34)	8116(15)	3667(12)	2321(19)	142(7)	C(16)	6119(15)	4412(11)	4679(18)	86(6)
O(32′)	8204(21)	2972(15)	3622(27)	103(9)	C(17)	6503(16)	4944(10)	5380(21)	89(7)
O(33′)	6909(21)	3294(21)	3311(40)	168(14)	C(18)	7336(18)	5072(8)	5435(22)	99(7)
O(34′)	7319(28)	2876(20)	2810(45)	190(19)	C(19)	8826(23)	4880(11)	6088(26)	114(11)
Cl(4)	4716(3)	2496(2)	3592(5)	77(1)	C(20)	9625(18)	4497(14)	6617(25)	100(8)
O(41)	5500(18)	2503(10)	4371(25)	133(8)	C(21)	9628(17)	3897(14)	5934(22)	103(7)
O(42)	4150(24)	2898(22)	3765(36)	214(15)	C(22)	7997(13)	4573(9)	7218(14)	73(4)

[a] U_{eq} is defined as one-third the trace of the orthogonalized U_{ij} tensor.

refined by the full-matrix least-squares method, using the SHELX93 computer program.[11] The function minimized was $\sum \varpi ||F_o|^2 - |F_c|^2|^2$, where $\varpi = [\sigma^2(I) + (0.0820P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from *International Tables of X-ray Crystallography*.[12] Refinement indicates that the crystal was a twin with twin law (−1,0,0/0,1,0/0,0,−1). Refinement led to a proportion of every crystal of 0.92/0.08. The extinction coefficient was 0.000 43. The chirality of the structure was defined from the Flack coefficient, equal to 0.01(4). Twenty-four H atoms were computed and refined with an overall isotropic temperature factor using a riding model. The number of parameters refined was 468. Maximum shift (esd) = 3.9. Mean shift (esd) = 0.31. Maximum and minimum peaks in final difference synthesis were 1.138 and −0.916 e Å^{-3}, respectively. Final atomic coordinates are given in Table 2.

Results and Discussion

Description of the Structure of Compound 1. The structure consists of trinuclear (μ_3-CO_3)[Cu_3(Medpt)$_3$(ClO_4)$_3$]$^+$ units and one isolated perchlorate counteranion. A labeled diagram is shown in Figure 1. The main bond lengths and angles are gathered in Table 3. The structure of each trinuclear unit consists of three copper atoms in a square pyramidal environment, of which the apical position is occupied by one oxygen atom of a perchlorate anion at a large distance (Cu−O$_{av}$ = 2.45 Å) and the basal plane is formed by the three nitrogen atoms of the Medpt ligand and one oxygen atom of the carbonato ligand. Each oxygen atom of the carbonato group is bonded to a different copper atom, giving a triangular array of copper atoms. The copper atoms are slightly out of the carbonato plane, the average deviation being 0.189 Å. The CuN_3O planes are tilted with respect to the practically planar CO_3Cu_3 fragment with an average dihedral angle of 61.5°.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**

Copper Environment

Cu(1)−O(1)	1.963(9)	Cu(2)−O(2)	1.980(8)	Cu(3)−O(3)	1.973(7)
Cu(1)−N(1)	2.001(13)	Cu(2)−N(4)	1.98(2)	Cu(3)−N(7)	1.977(14)
Cu(1)−N(2)	2.035(11)	Cu(2)−N(5)	2.048(11)	Cu(3)−N(9)	1.99(2)
Cu(1)−N(3)	2.016(14)	Cu(2)−N(6)	1.991(14)	Cu(3)−N(8)	2.053(11)
Cu(1)−O(11)	2.45(2)	Cu(2)−O(21)	2.46(2)	Cu(3)−O(31)	2.49(2)

O(1)−Cu(1)−N(1)	90.4(5)	N(4)−Cu(2)−N(6)	169.8(7)
O(1)−Cu(1)−N(2)	161.3(5)	N(5)−Cu(2)−N(6)	94.8(6)
O(1)−Cu(1)−N(3)	81.0(5)	C(1)−O(2)−Cu(2)	119.1(6)
N(1)−Cu(1)−N(2)	94.6(6)	O(3)−Cu(3)−N(7)	89.0(5)
N(1)−Cu(1)−N(3)	170.6(7)	O(3)−Cu(3)−N(8)	161.9(5)
N(2)−Cu(1)−N(3)	94.8(6)	O(3)−Cu(3)−N(9)	81.8(5)
C(1)−O(1)−Cu(1)	118.4(7)	N(7)−Cu(3)−N(9)	169.2(7)
O(2)−Cu(2)−N(4)	89.2(5)	N(7)−Cu(3)−N(8)	94.8(6)
O(2)−Cu(2)−N(5)	161.8(5)	N(8)−Cu(3)−N(9)	95.7(6)
O(2)−Cu(2)−N(6)	82.1(5)	C(1)−O(3)−Cu(3)	118.1(7)
N(4)−Cu(2)−N(5)	95.1(6)		

Carbonato Group

O(1)−C(1)	1.306(11)	O(1)−C(1)−O(2)	119.5(9)
O(2)−C(1)	1.277(12)	O(1)−C(1)−O(3)	119.4(9)
O(3)−C(1)	1.267(13)	O(2)−C(1)−O(3)	121.1(8)

	dihedral angles (deg)[a]		deviation of Cu atoms from plane 1 (Å)
plane 1−plane 2	60.7	Cu(1)	0.160
plane 1−plane 3	62.0	Cu(2)	0.185
plane 1−plane 4	61.7	Cu(3)	0.224
plane 2−plane 3	80.9		
plane 2−plane 4	81.0		
plane 3−plane 4	80.8		

[a] Plane 1, C(1)−O(1)−O(2)−O(3); plane 2, Cu(1)−O(1)−N(1)−N(2)−N(3); plane 3, Cu(2)−O(2)−N(4)−N(5)−N(6); plane 4, Cu(3)−O(3)−N(7)−N(8)−N(9).

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(11) Sheldrick, G. M. Manuscript in preparation.

(12) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99−110 and 149.

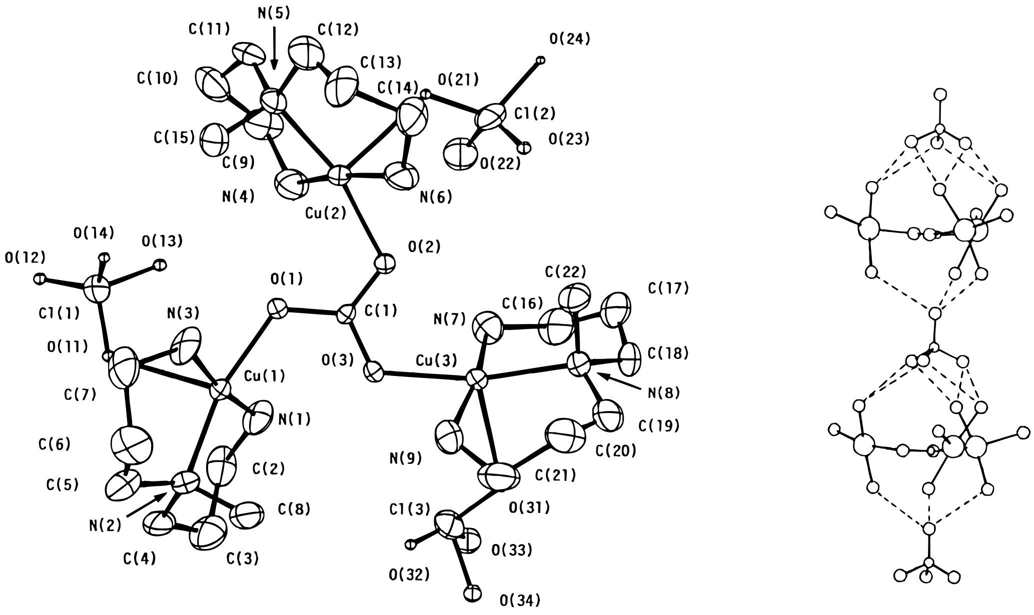

Figure 1. Ortep drawing of the cation **1** with atom-labeling scheme. On the right are hydrogen bonds involving the noncoordinated perchlorate anion.

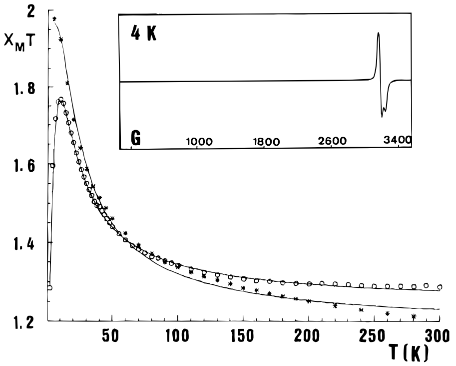

Figure 2. $\chi_M T$ experimental data for **1** (○) and **2** (*), (cm^3 K mol^{-1}). Solid lines show the best fit obtained (see text). The inset shows the EPR spectrum at 4 K for compound **1**.

The noncoordinated perchlorate counteranion plays an interesting role in the packing. The Cl(4)−O(41) direction is perpendicular to the carbonate plane and O(41) is placed in the center of the triangle determined by N(1), N(4), and N(7) at an average distance of 3.19 Å, which corresponds to weak hydrogen bonds (see Figure 1). The oxygen atoms O(42), O(43), and O(44) are placed in an alternated position with respect to the triangle determined by N(3)*, N(6)*, and N(9)*, giving six bond distances (average) of 3.29 Å. As a consequence of these hydrogen bonds, the trinuclear units form a chain-like arrangement along the [201] direction.

Magnetic Behavior. The molar $\chi_M{}^*T$ product *vs* T of **1** is shown in Figure 2. The $\chi_M{}^*T$ value of 1.28 cm^3 K mol^{-1} at room temperature increases continuously when the temperature decreases, giving a maximum value of 1.77 cm^3 K mol^{-1} at 10 K, indicating ferromagnetic coupling between the copper(II) ions. Compound **2** shows similar behavior: 1.21 cm^3 K mol^{-1} at room temperature and 1.98 cm^3 K mol^{-1} at 5 K. The experimental data were fitted to the expression derived from the Hamiltonian $H = -J(S_1S_2 + S_2S_3 + S_1S_3)$, which corresponds to a regular triangular array of spins corrected with a zJ' intertrimer coupling parameter in order to fit the low-temperature data.[13]

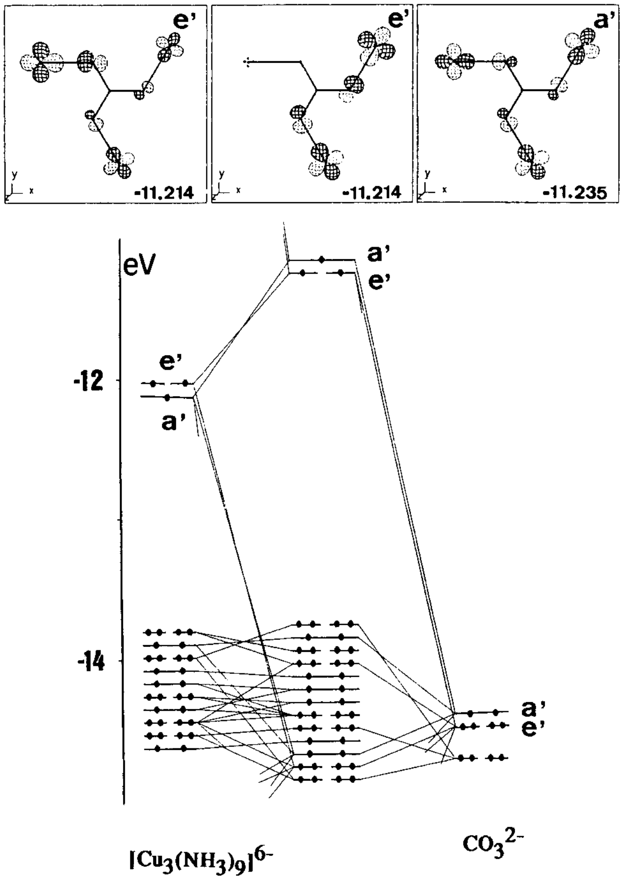

Figure 3. Interaction diagram between the [Cu$_3$(NH$_3$)$_9$]$^{6+}$ and CO$_3{}^{2-}$ fragments. At the top are drawings of the three active MOs that contain the unpaired electrons.

The fit was performed by minimizing the function $R = \sum(\chi_M{}^*T_{calc} - \chi_M{}^*T_{obs})^2/\sum(\chi_M{}^*T_{obs})^2$, the best fit parameters being $J = 12.6$ cm^{-1}, $g = 2.103$, $zJ' = -0.68$ cm^{-1}, and $R = 8.7 \times 10^{-6}$ for **1** and $J = 15.8$ cm^{-1}, $g = 2.060$, $zJ' = -0.015$ cm^{-1}, and $R = 9.0 \times 10^{-5}$ for **2**. Consequently, the gap between the $|{}^3/_2,1\rangle$ ground state and the degenerate $|{}^1/_2,1\rangle$ and $|{}^1/_2,0\rangle$ excited states is 18.9 cm^{-1} for **1** and 23.7 cm^{-1} for **2**. Magnetization measurements at 2 K up to a field of 5 T confirms the $S = {}^3/_2$

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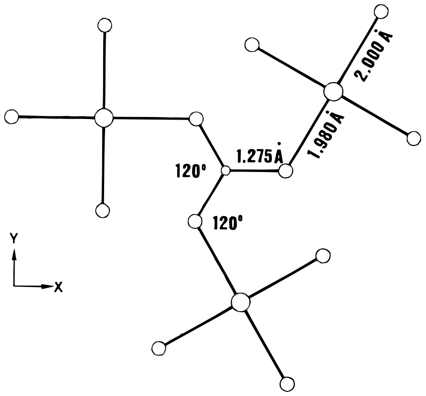
(13) Kahn, O. *Molecular Magnetism*; VCH Publishers, Inc.: New York, 1993.

Scheme 1



ground state. The shape of the plot at low temperatures might be indicative of weak intertrimer interactions or zero-field splitting (ZFS) in the ground state. Moreover, the electron paramagnetic resonance (EPR) spectrum at 4 K shows three signals, $g_1 = 2.130$, $g_2 = 2.116$, and $g_3 = 2.089$, for **1** whereas at higher temperatures the spectra consist of a sharp band centered at $g = 2.114$ for the two compounds (Figure 2), which suggests a negligible ZFS. The ferromagnetic character of these trimeric compounds is consistent with previously reported data.[4]

Superexchange through a carbonato bridge has been analyzed satisfactorily for different environments of the copper atoms for dimeric compounds in which one of the oxygen atoms of the carbonato ligand acts as a direct bridge between the two copper atoms.[2a] In that case, the a2′ MO of the carbonato bridge acts as a superexchange pathway, similar to an oxo or hydroxo bridge, allowing a very strong antiferromagnetic coupling, as can be expected taking into account the large Cu−O−Cu bond angle. In our case, this immediate explanation cannot be applied, and a new analysis has been performed by using MO extended Hückel calculations[14] on the trimeric model (μ-CO_3)-$[Cu_3(NH_3)_9]^{4+}$ shown in Scheme 1.

The parameters used are the standard values of the program, and the angles and distances were the schematized values. For clarity in the drawings, the CuN_3O planes have been placed in the same plane as that of the carbonato after checking that the orientation of the basal planes of the copper atoms with respect to the carbonato plane is not relevant to the result of the calculations.

The interaction diagram between the CO_3^{2-} ligand and the $[Cu_3(NH_3)_9]^{6+}$ fragment is shown in Figure 3. For this trimeric array, the combinations of the three d_{xy} copper atomic orbitals show the same symmetry as the a2′ and e′ MOs of the carbonato group, and consequently, the antibonding interactions are comparable, giving a set of three MOs with the same energy. From this kind of calculation, we can explain that the J_{AF} component of the superexchange parameter J should be close to zero, whereas information about the magnitude of J_F cannot be obtained although the low J value is consistent with the large Cu−Cu (average) separation of 4.87 Å.

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Supporting Information Available: Tables of complete crystal data, anisotropic thermal parameters, atom coordinates, angles, and distances, main planes, and magnetization measurements for compound **1** (11 pages). Ordering information is given on any current masthead page.

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