A Novel Pentadentate Coordination Mode for the Carbonato Bridge: Synthesis, Crystal Structure, and Magnetic Behavior of (μ_3-CO_3)[Ni_3(Medpt)$_3$(NCS)$_4$], a New Trinuclear Nickel(II) Carbonato-Bridged Complex with Strong Antiferromagnetic Coupling

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The trinuclear complex (μ_3-CO_3)[Ni_3(Medpt)$_3$(NCS)$_4$] was obtained by reaction of basic solutions of nickel(II), Medpt (bis(3aminopropyl)methylamine) and thiocyanate ligand with atmospheric CO_2 or by simple reaction with carbonate anion. (μ_3-CO_3)[Ni_3(Medpt)$_3$(NCS)$_4$] crystallizes in the triclinic system, space group $P\bar{1}$, with a = 12.107(5) Å, b = 12.535(7) Å, c = 16.169(9) Å, α = 102.69(5)°, β = 92.91(5)°, γ = 118.01(4)°, Z = 2, and R = 0.043. The three nickel atoms are asymmetrically bridged by one pentadentate carbonato ligand, which shows a novel coordination mode. The (μ_3-CO_3)[Ni_3(Medpt)$_3$(NCS)$_4$] compound shows a very strong antiferromagnetic coupling. Fit as irregular triangular arrangement gave $J_1 = -88.4$, $J_2 = -57.7$, and $J_3 = -9.6$ cm^{-1}, which is the strongest AF coupling observed to date for Ni_3 compounds. The magnetic behavior of the carbonato bridge is discussed.

Introduction

The coordination chemistry of the carbonate anion has received considerable attention in the past few years, mainly in polynuclear compounds of the first transition row. Extended copper−carbonato systems, such as the 3D natural azurite[1] [Cu_3(OH)$_2$(CO_3)], or the 1D [$Cu(NH_3)_2(CO_3)$] or 2D $Na_2[Cu(CO_3)_2]$ complexes[2,3] were the first studied. Together with a few dinuclear compounds of chromium,[4] copper also provides the first examples of di-, tri-, or tetranuclear complexes with a carbonato bridge,[5] which are generally obtained by using aminate ligands as blocking ligands. More recently however, a considerable number of polynuclear (μ-CO_3)−M systems, in which M = Ni, Co, Fe, Cr, Ti, V, or Mo, have been structurally characterized,[6,7] in relation to bioinorganic models and catalytic studies (or frequently, the accidental reaction of basic solutions with atmospheric CO_2). These latest carbonato complexes are generally dinuclear complexes involving one carbonato bridge, with only two exceptions[6d,8] [Ni_3(tmen)$_3$(hex-3)(CO_3)$_2$] and Na_6-[Fe_4(L)$_2$(O)$_2$(CO_3)$_2$] (tmen = tetramethylethylenediamine, hex-3 = hex-3-ene-3,4-dicarbonate) and LH_5 = (2-hydroxypropanediyl)-diiminotetraacetic acid). A common point in all these systems is the fact that when the bridging ligand is only carbonato (without oxo, hydroxo or other simultaneous bridges), the nuclearity is strictly 2.

From the magnetic point of view, the carbonato bridge is extremely versatile,[5] giving a range of compounds from those which present moderate or weak ferromagnetism to very strong antiferromagnetic coupling, which results in full coupling at room temperature (diamagnetism) in some cases. On the other hand the magnetic properties of some coordination modes are unexplored, and the compounds in which the magnetic properties of this ligand have been studied are scarce, taking into account that in the compounds in which there is a double or triple bridge (μ-carbonato/μ-oxo), the coupling through the oxo bridge masks the carbonate superexchange pathway.[7]

The aim of this work is to study the nickel(II)−triamine−carbonato system, in which triamines are dien, dpt or N-alkyl substituted derivatives. With dien = bis(2-aminoethyl)amine,

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Table 1. Crystal Data for (μ_3-CO$_3$)[Ni$_3$(Medpt)$_3$(SCN)$_4$]

chem formula	[$C_{26}H_{57}N_{13}Ni_3O_3S_4$]	fw	904.22
a, Å	12.107(5)	space group	$P\bar{1}$
b, Å	12.535(7)	*T*, K	293(2)
c, Å	16.169(9)	λ(Mo Kα), Å	0.71069
α, deg	102.69(5)	d_{calc},g/cm^{-3}	1.444
β, deg	92.91(5)	μ(Mo Kα), cm^{-1}	15.89
γ, deg	118.01(4)	R^a	0.0431
V, Å^3	2080(2)	$R_\omega{}^b$	0.0742
Z	2		

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_\omega = \{\sum\omega[(F_o)^2 - (F_c)^2)^2]/[\sum\omega(F_o)^4]\}^{1/2}$.

or N-alkyl dien derivatives, the reaction with potassium carbonate or NHEt$_2$/CO$_2$ allows, in all cases, the slow precipitation in a few days of nickel hydroxide or the only thiocyanate derivative. With dpt = bis(3-aminopropyl)amine derivatives, extremely soluble compounds (oils or gums) were obtained; however, by blocking the remaining coordination sites of the nickel atoms with thiocyanate, it was possible to isolate the compound (μ_3-CO$_3$)[Ni$_3$(Medpt)$_3$(NCS)$_4$]. This compound shows several remarkable features: a nuclearity greater than two for carbonato-bridged compounds of the first transition row (except copper) is extremely rare and shows a new coordination mode for the carbonato bridge which acts as a **pentadentate** ligand.

From the magnetic point of view, this compound is strongly antiferromagnetically coupled and, to our knowledge, shows the strongest coupling reported to date for trinuclear nickel compounds.[9] The arrangement of the three nickel atoms is shown to be an extremely uncommon nonsymmetrical triangle. The magnetic behavior and superexchange pathway are also discussed.

Experimental Section

Synthesis. An aqueous solution of Medpt (3 mmol, 0.436 g) was treated with an aqueous solution of nickel nitrate hexahydrate (3 mmol, 0.872 g). After 10 min of stirring, the resulting blue solution was treated with an aqueous solution of potassium carbonate (3 mmol, 0.415 g) and finally with an aqueous solution of potassium thiocyanate (3.5 mmol, 0.340 g). After vigorous stirring, the solution was filtered off, and the filtrate was left undisturbed. Blue crystals, suitable for X-ray determination, were obtained by slow evaporation.

The same compounds may be obtained from other nickel(II) salts or by the following method: a slight excess of NHEt$_2$ was added to the aqueous solution formed by the nickel(II) salt, Medpt, and potassium thiocyanate. Slow reaction with atmospheric CO$_2$ and slow evaporation of the solution gave the blue crystals of the title compound.

Anal. Calcd for Ni$_3$C$_{26}$H$_{57}$N$_{13}$S$_4$O$_3$ (found): C, 34.52 (34.5); H, 6.36 (6.4); N, 20.14 (20.2); S, 14.16 (13.9).

Spectral and Magnetic Measurements. IR spectra were recorded on a Nicolet 520 FTIR spectrophotometer. Magnetic measurements were carried out on polycrystalline samples with a pendulum type magnetometer (Manics DSM8) equipped with a helium continuous-flow cryostat working in the 300−4 K range under a magnetic field of approximately 1.5 T. Diamagnetic corrections were estimated from Pascal tables.

X-ray Crystallography. A prismatic blue crystal (0.1 mm × 0.1 mm × 0.2 mm) of (μ_3-CO$_3$)[Ni$_3$(Medpt)$_3$(SCN)$_4$](**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 least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique. A total of 12 082 reflections were measured in the range $1.31 < \theta < 29.96$. A total of 7780 reflections were assumed as observed by applying the condition $I > 2\ \sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz−polarization 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 refined by the full-matrix least-squares method, with the SHELX93 computer program.[11] The function minimized was $\sum\omega||F_o|^2 - |F_c|^2|^2$, where $\omega = [\sigma^2(I) + (0.2031P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from ref 12. The extinction coefficient was 0.00007. A total of 55 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor. The number of parameters refined was 610. The final *R* (on *F*) factor was 0.043. Maximum shift/esd = 1.8. Mean shift/esd = 0.08. Maximum and minimum peaks in final difference synthesis were 0.887 and −1.397 e Å^{-3}, respectively. Final atomic coordinates are given in Table 2.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for (μ_3-CO$_3$)[Ni$_3$(Medpt)$_3$(SCN)$_4$]

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Ni(1)	2082(1)	375(1)	2354(1)	31(1)
Ni(2)	3817(1)	4008(1)	2133(1)	32(1)
Ni(3)	5986(1)	1545(1)	3363(1)	35(1)
S(1)	−1862(1)	−1331(1)	562(1)	49(1)
S(2)	2595(2)	4034(1)	4859(1)	80(1)
S(3)	5670(1)	1988(1)	338(1)	74(1)
S(4)	6724(1)	−1419(1)	4371(1)	61(1)
O(1)	3518(2)	2352(2)	2528(1)	36(1)
O(2)	3969(2)	993(2)	2929(1)	35(1)
O(3)	5555(2)	2843(2)	2955(2)	39(1)
N(1)	423(3)	163(3)	1731(2)	44(1)
N(2)	1736(3)	941(3)	3564(2)	43(1)
N(3)	1264(2)	−1539(2)	2403(2)	38(1)
N(4)	2577(3)	76(3)	1133(2)	41(1)
N(5)	3109(3)	4476(3)	3251(2)	53(1)
N(6)	1926(3)	2933(3)	1481(2)	41(1)
N(7)	4073(3)	5557(2)	1584(2)	40(1)
N(8)	5607(3)	5124(3)	2881(2)	46(1)
N(9)	4472(3)	3267(3)	1102(2)	45(1)
N(10)	5873(3)	21(3)	3718(2)	57(1)
N(11)	5925(3)	2428(3)	4587(2)	49(1)
N(12)	5823(3)	687(3)	2070(2)	48(1)
N(13)	8034(3)	2560(3)	3603(2)	47(1)
C(1)	−514(3)	−446(3)	1240(2)	37(1)
C(2)	513(4)	159(4)	3800(3)	52(1)
C(3)	317(4)	−1138(4)	3747(3)	60(1)
C(4)	131(4)	−1929(3)	2847(3)	50(1)
C(5)	787(4)	−2459(3)	1529(3)	48(1)
C(6)	1696(5)	−2212(4)	898(3)	56(1)
C(7)	1832(4)	−1175(4)	490(2)	49(1)
C(8)	2243(4)	−1674(4)	2885(3)	53(1)
C(9)	2904(4)	4299(3)	3924(2)	48(1)
C(10)	1265(4)	3660(4)	1447(3)	53(1)
C(11)	1752(4)	4488(4)	841(4)	64(1)
C(12)	3156(4)	5002(4)	751(3)	53(1)
C(13)	5360(4)	6135(4)	1345(3)	53(1)
C(14)	6488(4)	6738(4)	2085(3)	62(1)
C(15)	6677(3)	5828(4)	2487(3)	56(1)
C(16)	3920(5)	6550(4)	2161(3)	62(1)
C(17)	4968(3)	2754(3)	789(2)	41(1)
C(18)	6217(3)	−578(3)	3992(2)	44(1)
C(19)	6804(4)	372(4)	1783(3)	58(1)
C(20)	8099(5)	1512(5)	2063(4)	66(1)
C(21)	8592(4)	1908(4)	3035(3)	62(1)
C(22)	8586(4)	2723(4)	4500(4)	67(1)
C(23)	8159(5)	3322(5)	5222(3)	66(1)
C(24)	6794(4)	2568(4)	5338(3)	58(1)
C(25)	8415(4)	3804(4)	3452(4)	58(1)
C(26)	4362(3)	2104(3)	2809(2)	33(1)

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

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Table 3. Selected Bond Lengths (Å) for (μ_3-CO_3)[$Ni_3(Medpt)_3(SCN)_4$]

Nickel Environment			
Ni(1)−N(2)	2.064(3)	Ni(2)−N(5)	2.124(3)
Ni(1)−N(1)	2.072(3)	Ni(2)−O(1)	2.179(2)
Ni(1)−N(4)	2.098(3)	Ni(2)−N(7)	2.208(3)
Ni(1)−O(2)	2.120(2)	Ni(3)−N(10)	2.060(3)
Ni(1)−N(3)	2.146(3)	Ni(3)−N(11)	2.068(4)
Ni(1)−O(1)	2.200(3)	Ni(3)−N(12)	2.082(4)
Ni(2)−N(8)	2.064(3)	Ni(3)−O(3)	2.142(2)
Ni(2)−N(6)	2.098(3)	Ni(3)−N(13)	2.153(3)
Ni(2)−N(9)	2.102(3)	Ni(3)−O(2)	2.227(2)
Carbonato Ligand			
O(1)−C(26)	1.289(3)	O(3)−C(26)	1.270(4)
O(2)−C(26)	1.307(3)		
Thiocyanato Ligands			
S(1)−C(1)	1.638(4)	C(1)−N(1)	1.152(4)
S(2)−C(9)	1.642(4)	C(9)−N(5)	1.173(5)
S(3)−C(17)	1.642(3)	C(17)−N(9)	1.132(4)
S(4)−C(18)	1.648(4)	C(18)−N(10)	1.164(5)

Table 4. Selected Bond Angles (deg) for (μ_3-CO_3)[$Ni_3(Medpt)_3(SCN)_4$]

Nickel Environment			
N(2)−Ni(1)−N(1)	93.4(1)	N(9)−Ni(2)−O(1)	83.7(1)
N(2)−Ni(1)−N(4)	171.8(1)	N(5)−Ni(2)−O(1)	86.1(1)
N(1)−Ni(1)−N(4)	86.9(1)	N(8)−Ni(2)−N(7)	90.3(1)
N(2)−Ni(1)−O(2)	88.4(1)	N(6)−Ni(2)−N(7)	90.1(1)
N(1)−Ni(1)−O(2)	167.0(1)	N(9)−Ni(2)−N(7)	90.9(1)
N(4)−Ni(1)−O(2)	89.5(1)	N(5)−Ni(2)−N(7)	99.3(1)
N(2)−Ni(1)−N(3)	92.0(1)	O(1)−Ni(2)−N(7)	173.61(9)
N(1)−Ni(1)−N(3)	95.3(1)	N(10)−Ni(3)−N(11)	93.4(2)
N(4)−Ni(1)−N(3)	96.2(1)	N(10)−Ni(3)−N(12)	91.5(2)
O(2)−Ni(1)−N(3)	97.5(1)	N(11)−Ni(3)−N(12)	171.6(1)
N(2)−Ni(1)−O(1)	87.3(1)	N(10)−Ni(3)−O(3)	164.4(1)
N(1)−Ni(1)−O(1)	105.2(1)	N(11)−Ni(3)−O(3)	85.3(1)
N(4)−Ni(1)−O(1)	84.7(1)	N(12)−Ni(3)−O(3)	88.1(1)
O(2)−Ni(1)−O(1)	61.93(9)	N(10)−Ni(3)−N(13)	94.0(1)
N(3)−Ni(1)−O(1)	159.47(9)	N(11)−Ni(3)−N(13)	91.9(2)
N(8)−Ni(2)−N(6)	174.2(1)	N(12)−Ni(3)−N(13)	94.6(1)
N(8)−Ni(2)−N(9)	93.7(1)	O(3)−Ni(3)−N(13)	101.6(1)
N(6)−Ni(2)−N(9)	92.1(1)	N(10)−Ni(3)−O(2)	104.2(1)
N(8)−Ni(2)−N(5)	86.6(2)	N(11)−Ni(3)−O(2)	90.2(1)
N(6)−Ni(2)−N(5)	87.6(1)	N(12)−Ni(3)−O(2)	82.0(1)
N(9)−Ni(2)−N(5)	169.7(1)	O(3)−Ni(3)−O(2)	60.38(8)
N(8)−Ni(2)−O(1)	93.3(1)	N(13)−Ni(3)−O(2)	161.6(1)
N(6)−Ni(2)−O(1)	86.8(1)		
Carbonato bridge			
O(3)−C(26)−O(1)	125.0(3)	C(26)−O(1)−Ni(1)	88.3(2)
O(3)−C(26)−O(2)	117.1(2)	C(26)−O(2)−Ni(1)	91.3(2)
O(1)−C(26)−O(2)	117.9(2)	C(26)−O(1)−Ni(2)	128.2(2)
Ni(2)−O(1)−Ni(1)	141.4(1)	C(26)−O(2)−Ni(3)	88.8(2)
Ni(1)−O(2)−Ni(3)	172.5(1)	C(26)−O(3)−Ni(3)	93.7(2)
Thiocyanato ligands			
N(1)−C(1)−S(1)	178.5(3)	N(9)−C(17)−S(3)	179.0(3)
N(5)−C(9)−S(2)	179.1(4)	N(10)−C(18)−S(4)	179.0(4)
Ni(1)−N(1)−C(1)	149.8(3)	Ni(2)−N(5)−C(9)	145.3(3)
Ni(2)−N(9)−C(17)	154.7(3)	Ni(3)−N(10)−C(18)	158.4(3)

Results and Discussion

Description of the Structure of (μ_3-CO_3)[$Ni_3(Medpt)_3$-$(NCS)_4$]. The structure consists of well-isolated trimeric units of the neutral compound (μ_3-CO_3)[$Ni_3(Medpt)_3(NCS)_4$]. The main bond lengths and angles are gathered in Tables 3 and 4, respectively. A labeled diagram is shown in Figure 1. The three nickel atoms are bridged by one carbonato ligand, forming an isosceles triangle (Ni(1)−Ni(2) 4.133(1) Å, Ni(1)−Ni(3) 4.337(1) Å, Ni(2)−Ni(3) 5.492(1) Å). The carbonato bridge and the three nickel atoms are roughly coplanar, defining the mean plane of the molecule. The carbonate is bonded to Ni(1) by means of O(1) and O(2) and to Ni(3) by means of O(2) and O(3) whereas Ni(2) is only coordinated to O(1), acting as a pentadentate ligand in this new coordination mode. The carbonato ligand is strictly planar, showing the bond angle O(1)-C(26)-O(3) to be 125.0(3)° whereas the two remaining angles are close to 117.5°. The C−O bond lengths (Å) are C(26)−O(2) = 1.307(3), C(26)−O(1) = 1.289(3), and C(26)−O(3) = 1.270(4).

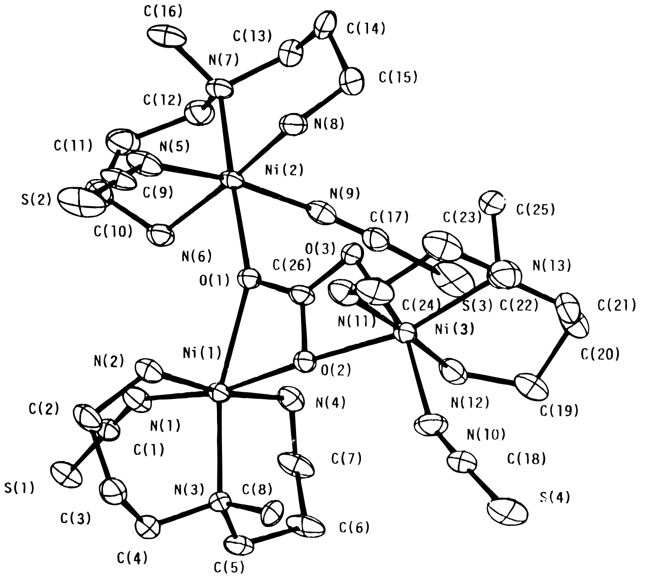

Figure 1. Ortep drawing of the (μ_3-CO_3)[$Ni_3(Medpt)_3(NCS)_4$] compound with atom labeling scheme.

The three nickel atoms are octahedrally coordinated, but the environment of Ni(1) and Ni(3) is strongly distorted due to the coordination to the carbonate bridge. These two atoms coordinate two oxygen atoms (carbonate) and four nitrogen atoms from a tridentate Medpt and one thiocyanate ligand, showing very similar bond parameters: the bond angles O(1)−Ni(1)−O(2) and O(2)−Ni(3)−O(3) are 61.93(9) and 60.38(8)° respectively and the two octahedrons are elongated along the O(1)−Ni(1)−N(3) and O(2)−Ni(3)−N(13) axes respectively. In contrast, Ni(2) is coordinated to one oxygen atom (carbonate), five nitrogen atoms from one Medpt ligand, and two thiocyanate ligands, showing a more regular octahedron, elongated along the O(1)−Ni(2)−N(7) axis. The two Ni−O−Ni bond angles are different: whereas Ni(2)−O(1)−Ni(1) is 141.4(1)°, Ni(1)−O(2)−Ni(3) is 172.6(1)°.

The three Medpt are coordinated in a *mer* arrangement; Medpt coordinated to Ni(2) lies approximately in the main plane of the molecule, (dihedral angle between the carbonato plane and the NiN_3 plane is 22.5°), whereas the two Medpt ligands coordinated to Ni(1) and Ni(3) are placed perpendicular to the main molecular plane, (dihedral angles between the carbonato plane and the NiN_3 planes of 83.1 and 86.5°, respectively). The three nickel atoms are −0.311, −0.187, and 0.033 Å out of the carbonato plane. The four thiocyanate ligands acts as monodentate (−N) ligands showing bond Ni−N−C angles in the range 145.3(3)−158.4(3)°.

The most remarkable feature observed in this structure is the asymmetric coordination of the carbonato ligand to three metallic centers, which is a new coordination mode for this ligand.

IR Spectrum. The infrared spectrum of (μ_3-CO_3)[Ni_3-$(Medpt)_3(NCS)_4$] shows two strong bands at 2088 and 2069 cm^{-1} corresponding to the ν(CN) of the thiocyanato ligands and a set of bands in the 3500−2900 and 1600−400 cm^{-1} regions. The bands due to the carbonato bridge can be assigned by comparison with the infrared spectra of the {(μ-SCN)[Ni-

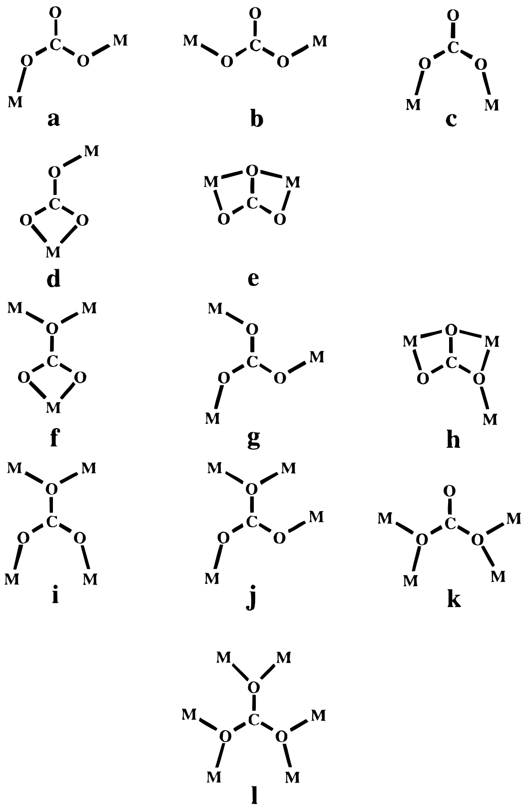

Figure 2. Structurally characterized coordination modes of the carbonato bridge.

(Medpt)(NCS)]}$_n$ compound,[13] which also presents the Medpt ligand coordinated in a *mer* arrangement. The spectra of the two complexes are very similar, except four strong and sharp bands at 1520, 1384, 839, and 745 cm^{-1}. The local symmetry of the carbonato ligand in the present coordination mode may be assumed to be C_s, and by comparison with copper and cobalt carbonato compounds,[14,15] the band at 745 cm^{-1} may be assigned to the in-plane deformation ν_4, the band at 839 cm^{-1} to the out-of-plane deformation ν_2, which is very close to the ionic carbonate, and the bands at 1520 and 1384 cm^{-1} to the asymmetric stretching ν_3. The splitting of ν_3 (136 cm^{-1}) is commonly attributed to the presence of at least bidentate coordination.

Magnetochemistry of the Carbonate Bridge. The coordination modes described to date for the carbonate ion when it acts as a bridge in polynuclear compounds are summarized in Figure 2. Modes **a** and **b** are very similar to the *syn*−*anti* and *anti*−*anti* coordination modes of the carboxylate bridge, and magnetically, allow weak ferro or antiferromagnetic coupling.[3,5d] The **b** coordination mode has also been observed for one chromium compound.[16] Mode **c**, equivalent to the *syn*−*syn* coordination mode of the carboxylate bridge, has been observed in chromium(II) compounds analogous to the chromium(II) acetate[4] and it is frequently observed for cobalt, iron and chromium(III) dinuclear compounds, almost always with an additional oxo or hydroxo bridge.[7,17] The coupling through the oxo bridge is always very strong, but magnetic data for the isolated coordination mode **c** are not available. Mode **d** is analogous to the combined **a** and **b** modes and shows weak antiferromagnetic behavior.[2,18] The **e** mode, found in some copper[5a] and cobalt[7] compounds and all the nickel derivatives[6] characterized to date, shows very strong antiferromagnetic coupling in all cases, giving diamagnetic complexes for the copper compounds. Interaction between the magnetic orbitals of the paramagnetic centers, which in all cases show an M−O−M bond angle close to 180°, through the a$_2'$ MO of the bridge (under the D_{3h} point group), gives a very efficient superexchange pathway, which has been compared with the interaction through a single oxo bridge. Finally, mode **g** shows weak or moderate ferromagnetic coupling and the superexchange pathway has recently been discussed by the authors.[19] The remaining coordination modes **f**, **i**, **j**, **k**, and **l** have not been studied from a magnetic point of view.

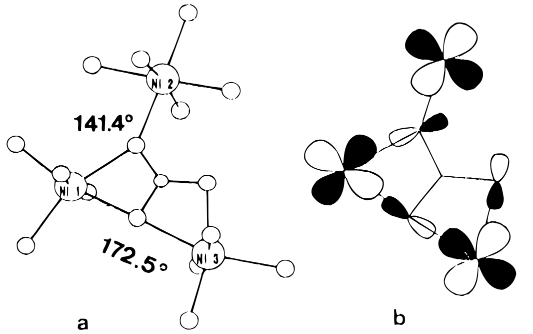

Figure 3. (a) Significant bond parameters in the bridge fragment for (μ_3-CO$_3$)[Ni$_3$(Medpt)$_3$(NCS)$_4$]. (b) Schematic representation of the singly occupied $d_{x^2-y^2}$ orbitals for (μ_3-CO$_3$)[Ni$_3$(Medpt)$_3$(NCS)$_4$] together with the main interaction pathway of the carbonato bridge.

The **h** mode, described in this paper, may be considered as derived from mode **e**, by the addition of a new paramagnetic center to one of the oxygen atoms of the bridge. As shown in Figure 3a, the two moieties Ni(1)/Ni(2) and Ni(1)/Ni(3) of the title compound are strongly asymmetrical, and the presence of two Ni−O−Ni large bond angles is particularly important. Consequently, the interaction between Ni(1) and the two terminal Ni(2) and Ni(3) atoms, should be strongly antiferromagnetic (but not necessary equal). The main superexchange pathway may be schematized as shown in Figure 3b, in which the a$_2'$ MO of the bridge gives a suitable antibonding interaction with the $x^2 - y^2$ atomic orbitals of the nickel atoms. The remaining MOs of adequate energy for the bridge are largely irrelevant, in a similar fashion to the studies reported for the **c** mode.[5a] The interaction between Ni(2) and Ni(3) related by a *syn-anti* pathway should be very weak, as occurs in mode **d**.

Magnetic Data and Coupling Constants Evaluation. The $\chi_M T$ product plotted *vs* temperature is shown in Figure 4. The plot is characteristic of a strongly coupled trimer with local $S = 1$. At room temperature, the $\chi_M T$ value is 2.89 cm^3·K·mol^{-1}, whereas at low temperatures, show a weakly marked minimum at 35 K with a $\chi_M T$ value of 1.34 cm^3·K·mol^{-1}. Near 4 K, $\chi_M T$ decreases slightly, due to the local zero field splitting or weak intertrimer interactions.

Evaluation of the coupling constants is not trivial for this compound (structural parameters of the carbonato−Ni$_3$ core are summarized in Figure 3a). According to these data and taking into account that for the carbonato bridge (or the formally analogous[5a] monoatomic hydroxo bridge, for which extensive

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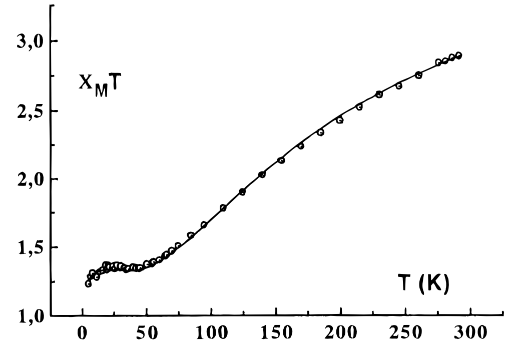
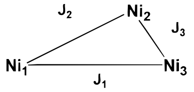


Figure 4. $\chi_M T$ *vs* T experimental data for (μ_3-CO_3)[Ni_3(Medpt)$_3$-(NCS)$_4$]. Solid line shows the best fit obtained by using the Hamiltonian in eq 3.

magnetostructural data are available[20]), some degrees of difference in the Ni−X−Ni bond angle are extremely important in the vicinity of 90°, whereas some degrees of difference in the 140−170° range do not lead to a dramatic loss of overlap. However, the different Ni−O−Ni bond angles imply that the J_1 value should be greater than J_2. As a first approach we have fitted the experimental data to the coupling constants ratio $J_1 = J_2$ (named $J_{1,2}$) > J_3; from the above considerations, the $J_{1,2}$ coupling constant should be only assumed as indicative of the J superexchange range of values, and the real J values should be $J_1 > J_{1,2} > J_2 > J_3$, which corresponds to an nonsymmetrical triangular array of local $S = 1$.



For the approximation with $J_{1,2}$ different to J_3 and taking into account the behavior of $\chi_M T$ at low temperature, experimental data have been fitted to the expression

$$\chi_M T = N\beta g^2 T(f(J,T)/kT - zJ'f(J,T)) \qquad (1)$$

in which zJ' is the intertrimer exchange parameter and $f(J,T)$ is

$$f(J,T) = \{6 + 6\exp(E2) + 30\exp(E3) + 6\exp(E4) + 30\exp(E5) + 84\exp(E6)\}/\{3 + \exp(E1) + 3\exp(E2) + 5\exp(E3) + 3\exp(E4) + 5\exp(E5) + 7\exp(E6)\}$$

In this case, the *En* values can be obtained using the Kambe method[21] from the Hamiltonian

$$H = -J_{1,2}(S_1S_2 + S_1S_3) - J_3(S_2S_3) \qquad (2)$$

and

$$E1 = J_{1,2} - 2J_3,\ E2 = 2J_{1,2},\ E3 = 2J_{1,2} - 2J_3$$

$$E4 = 3J_{1,2} - 3J_3,\ E5 = 4J_{1,2} - 2J_3,\ E6 = 5J_{1,2}$$

For the case in which the three J values are different, analytical expression is not available and the eigenvalues for the seven spin states were obtained in numerical form from a full-matrix diagonalization[22] of the Hamiltonian

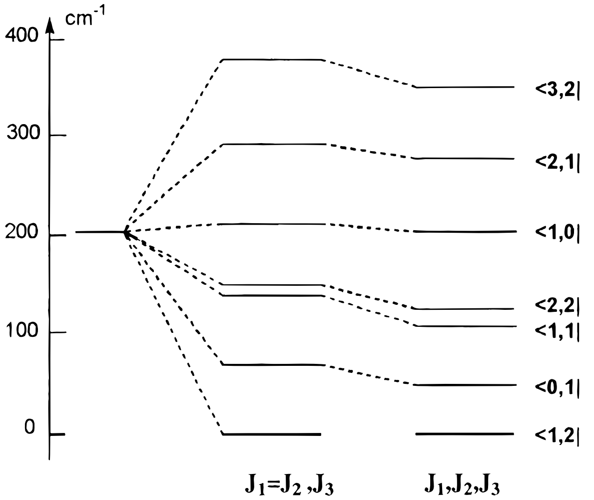


Figure 5. Energy level scheme for the nonsymmetric (μ_3-CO_3)[Ni_3-(Medpt)$_3$(NCS)$_4$] compound: left, energy values obtained from the approximation $J_1 = J_2 \gg J_3$; right, energy values obtained from CLUMAG results for $J_1 > J_2 \gg J_3$.

$$H = -J_1(S_1S_3) - J_2(S_1S_2) - J_3(S_2S_3) \qquad (3)$$

The best fit parameters obtained from (2) by minimizing the R factor $= \sum(\chi_M T^{calc} - \chi_M T^{obs})^2/\sum(\chi_M T^{obs})^2$, were $J_{1,2} = -76.3(5)$ cm^{-1}, $J_3 = -4.6(22)$ cm^{-1}, $g = 2.36$, $zJ' = -0.23(5)$ cm^{-1}, and $R = 4.8 \cdot 10^{-5}$. The low J_3 value is in good agreement with the *anti*−*anti* μ-CO_3 superexchange pathway that relates Ni(2) with Ni(3). The energy level scheme is shown in Figure 5.

Calculations performed from (3), allows to the same relative order of the spin states that was found from (2), Figure 5. The ground state was always found to be ⟨1,2|, followed at 57.0 cm^{-1} for ⟨0,1|, which produces the slight minimum of $\chi_M T$ close to 35 K. The coupling constant values were evaluated as $J_1 = -88.4$ cm^{-1}, $J_2 = -57.7$ cm^{-1}, and $J_3 = -9.6$ cm^{-1} for $g = 2.34$ and $zJ' = -0.15$ cm^{-1}. The J values are in good agreement with the structural parameters and may be unambiguously assigned as J_1 to the Ni(1)−Ni(3), J_2 to the Ni(1)−Ni(2) and J_3 to the Ni(2)−Ni(3) interactions. J_1 is also in very good agreement with the J value of −94.6 cm^{-1} obtained for the carbonato dinuclear compound[6b] (μ-CO_3)[Ni(HL)(NCS)]$_2$-(ClO_4)$_2$·3H_2O, (HL = 1-(3-(dimethylamino)propyl)-1,5,9-triazacyclododecane), which shows the bridge in the **e** coordination mode with an Ni−O−Ni bond angle of 174.1(2)°, (172.6(1)° for the title compound).

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Supporting Information Available: Text discussing the structure determination and tables of complete crystal data, anisotropic thermal parameters, atom coordinates and angles and distances (14 pages) for the complex (μ_3-CO_3)[Ni_3(Medpt)$_3$(NCS)$_4$]. Ordering information is given on any current masthead page.

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