Synthesis and Magnetic Properties of Four New (Cu−Ni)$_2$ Tetranuclear Complexes of General Formula [Cu(oxpn)Ni(μ-NCS)(H$_2$O)(aa)]$_2$(X)$_2$ (oxpn = *N,N′*-Bis(3-aminopropyl)oxamide; aa = Bidentate Amine; X = ClO$_4^-$ or PF$_6^-$). Ferro- and Antiferromagnetic Alternation

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Received July 18, 1997

The reaction of ethanolic/water solutions of NiX$_2$·6H$_2$O (X = NO$_3^-$, ClO$_4^-$), bidentate amine *N,N,N′,N′*-tetramethylethylenediamine (tmen) and *N,N,N′*-trimethylethylenediamine (trimen) with [Cu(oxpn)] (oxpn = *N,N′*-bis(3-aminopropyloxamide) and ammonium thiocyanate, in the presence of ammonium hexafluorophosphate when X is NO$_3^-$, leads to the high-yield formation of new heterotetranuclear (Cu−Ni)$_2$ complexes of general formulation [Cu(oxpn)Ni(μ-NCS)(H$_2$O)(aa)]$_2$(X)$_2$ (**1**, X = PF$_6^-$, aa = tmen; **2**, X = ClO$_4^-$, aa = tmen; **3**, X = ClO$_4^-$; aa = trimen; **4** , X = PF$_6^-$, aa = trimen). The crystal structures of **1**, **2**, and **3** were determined. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$ with a = 9.059(8) Å, b = 12.604(2) Å, c = 12.743(4) Å, α = 95.27(6)°, β = 99.22(2)°, γ = 108.86(7)°, and Z = 2. Complex **2** crystallizes in the triclinic system, space group $P\bar{1}$ with a = 8.7586(7) Å, b = 12.580(4) Å, c = 12.6318(12) Å, α = 94.630(14)°, β = 98.486(8)°, γ = 107.963(13)°, and Z = 2. Complex **3** crystallizes in the triclinic system, space group $P\bar{1}$ with a = 8.407(7) Å, b = 12.779(4) Å, c = 14.081(3) Å, α = 63.25(2)°, β = 88.62(3)°, γ = 79.06(4)°, and Z = 2. The cationic parts of the three complexes are very similar, consisting of two [Cu(oxpn)Ni] moieties linked by two SCN$^-$ bridging ligands. The Cu^{II} ions have square-pyramidal geometry with the S atom of the thiocyanato ligand in the apical position at *ca.* 3 Å. The Ni^{II} ions are distorted octahedrally coordinated. Variable-temperature magnetic susceptibility studies were performed on **1**−**4** in the temperature range 2−300 K. Satisfactory fits to the observed susceptibility data were obtained by assuming isotropic magnetic exchange interactions and using the appropriate spin Hamiltonians considering the complexes first as two dinuclear entities and second as a single tetranuclear unit. In the former the susceptibility equation is easy to derive, but for the latter full-matrix diagonalization was needed. The J value for the Cu(oxpn)Ni entity is close to −110 cm^{-1} in all four cases. By using the full-matrix diagonalization method it was possible to derive both J_1, Cu(oxpn)Ni and J_2, Cu−SCN−Ni coupling constants. J_1 is very similar to that derived assuming a dinuclear entity (*ca.* −115 cm^{-1}) and J_2 is very small but positive, ~0.03 cm^{-1} (ferromagnetic coupling). Theoretical calculations were performed for different J_2 values (from 10 to −10 cm^{-1}) assuming a high J_1 coupling constant (J_1 = −115 cm^{-1}). Such calculations revealed the influence of this J_2 value on the susceptibility curves at low temperatures. The EPR spectra measured at different temperatures (from 4 to 300 K) on polycrystalline samples of **1**−**4** show the typical band centered at $g \approx 2.2$ due to the spin transition $|^1/_2, -^1/_2> \rightarrow |^1/_2, ^1/_2>$ of the spin ground-state $S_T = ^1/_2$.

Introduction

Molecules that contain two kinds of metal ion play an important role in molecular magnetism.[2] The factors that explain this situation are, firstly, the types of interaction between two spin carriers A and B within a molecular unit are much more diverse when A and B are different and, secondly, with several kinds of magnetic centers it is possible to design lattices showing quite peculiar spin topologies. Two reviews have been published about these heteropolymetallic systems.[2,3] Until now, only the intramolecular interactions within an A−B heterodinuclear molecule have been described in detail. For example, the mononuclear species [Cu(oxpn)] (Chart 1), where oxpn is the dianion of *N,N′*-bis(3-aminopropyl)oxamide, has been used extensively to synthesize new homo-[4] and heterodinuclear complexes.[5,6] The chelating properties of the oxamidato oxpn ligand are similar to those of oxalato. The simultaneous presence of nitrogen and oxygen donor atoms in the former facilitates the synthesis of heteropolymetallic complexes in contrast

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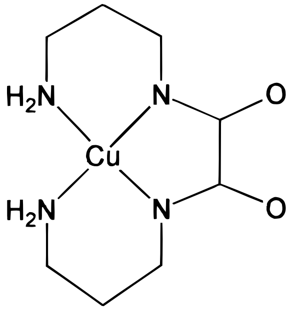
S0020-1669(97)00899-9 CCC: $15.00

Chart 1



to the latter case. By suitable choice of the terminal ligands bonded to the M ion in a Cu−M heterodinuclear complex, it can be used as a "complex as ligands",[4b,7] following a stepwise strategy to synthesize new large clusters with special spin topologies. Indeed, as pointed out by Kahn,[2] in molecular magnetism not only local spins associated with metal ions but also the molecular spins associated with molecular units as a whole are important. For the neutral molecule [Cu(oxpn)], the magnetic coupling in Cu−Cu, Cu−Ni, or Cu−Mn dinuclear entities is strongly antiferromagnetic, owing to the broad overlap between the magnetic orbitals of the two metal ions through the corresponding molecular orbital of the oxamidato bridge.[2−6] Thus, it would be interesting to attempt to link two of these molecules in a ferromagnetic way in order to study the spin topology of the final system. One ligand that allows the formation of small ferromagnetic coupling is the SCN^- anion. Indeed, the geometry of an M−NCS−M′ entity (M, M′ = Cu, Ni) is close to 180° for M−NCS and close to 90° for NCS−M′, which creates orthogonality of magnetic orbitals and, thus, small ferromagnetic coupling. Ginsberg *et al.*[8] and Duggan *et al.*[9] developed a valence bonding model applying the Goodenough−Kanamori rules[10] or Anderson's expanded orbital theory[11] to demonstrate the ferromagnetism of these pseudohalide complexes. The closer to those values (180 and 90°), the stronger the ferromagnetic coupling. This theory was used to evaluate the ferromagnetic coupling between Cu_3 trinuclear species through the same SCN^- bridging ligand.[12] Here we present the synthesis of the first $(Cu-Ni)_2$ tetranuclear complexes in which the antiferromagnetic coupling is given by the oxpn ligand and the ferromagnetic coupling is given by the thiocyanate anion. The structures of three of these complexes are shown to be tetranuclear by X-ray crystallography. The magnetic interactions were studied assuming, firstly, only the strong antiferromagnetic coupling within the dinuclear Cu−Ni moiety and, secondly, the whole tetranuclear system by full-matrix diagonalization method.

Experimental Section

Materials. Nickel(II) perchlorate, nickel(II) nitrate, ammonium thiocyanate, ammonium hexafluorophosphate, *N,N,N′,N′*-tetramethylethylenediamine (tmen), *N,N,N′*-trimethylethylenediamine (trimen), were purchased from Aldrich and used without purification. The [Cu(oxpn)], where oxpn is the dianion of *N,N′*-bis(3-aminopropyl)oxamide, was synthesized as previously described.[13] Ethanol was distilled before use.

Caution. Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. They should be prepared in small quantities and handled with care.

Syntheses. $[Cu(oxpn)Ni(\mu\text{-}NCS)(H_2O)(tmen)]_2(PF_6)_2$ (1). An ethanolic solution (5 mL) of $Ni(NO_3)_2 \cdot 6H_2O$ (0.397 g, 1.36 mmol) was added to a stirred solution of *N,N,N′,N′*-tetramethylethylenediamine (tmen) (0.159 g, 1.36 mmol) in ethanol (5 mL). Solutions of [Cu(oxpn)] (0.36 g, 1.36 mmol) in water (20 mL), NH_4SCN (0.104 g, 1.36 mmol) in water (5 mL), and NH_4PF_6 (0.220 g, 1.36 mmol) in water (10 mL) were then added consecutively. The resulting blue solution was filtered to remove any impurity and left to evaporate slowly at room temperature. Blue monocrystals suitable for X-ray determinations were collected after 1 week (yield *ca.* 70%). Anal. Calcd for $C_{15}H_{34}CuF_6N_7NiO_3PS$: C, 27.31; H, 5.19; N, 14.86; S, 4.85. Found: C, 27.3; H, 5.2; N, 14.8; S, 4.7.

$[Cu(oxpn)Ni(\mu\text{-}NCS)(H_2O)(tmen)]_2(ClO_4)_2$ (2). An ethanolic solution (5 mL) of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.5 g, 1.36 mmol) was added to a stirred solution of *N,N,N′,N′*-tetramethylethylenediamine (tmen) (0.159 g, 1.36 mmol) in ethanol (5 mL). Solutions of [Cu(oxpn)] (0.36 g, 1.36 mmol) in water (25 mL) and NH_4SCN (0.104 g, 1.36 mmol) in water (5 mL) were then added consecutively. The resulting blue solution was filtered to remove any impurity and left to evaporate slowly at room temperature. Blue monocrystals suitable for X-ray determinations were collected after 1 week (yield *ca.* 60%). Anal. Calcd for $C_{15}H_{34}ClCuN_7NiO_7S$: C, 29.33; H, 5.58; N, 15.96; Cl, 5.77; S, 5.22. Found: C, 29.6; H, 5.6; N, 16.0; Cl, 5.3; S, 5.3.

$[Cu(oxpn)(\mu\text{-}NCS)(H_2O)(trimen)]_2(ClO_4)_2$ (3). This was prepared like complex (**2**), using *N,N,N′*-trimethylethylenediamine (trimen) (0.139 g, 1.36 mmol) instead of *N,N,N′N′*-tetramethylethylenediamine (yield *ca.* 60%). Anal. Calcd for $C_{14}H_{32}ClCuN_7NiO_7S$: C, 28.02; H, 5.37; N, 16.33; Cl, 5.91; S, 5.34. Found: C, 27.7; H, 5.4; N, 16.1; Cl, 6.0; S, 5.3.

$[Cu(oxpn)(\mu\text{-}NCS)(H_2O)(trimen)]_2(PF_6)_2$ (4). This was prepared like complex (**1**), using *N,N,N′*-trimethylethylenediamine (trimen) (0.139 g, 1.36 mmol) instead of *N,N,N′N′*-tetramethylethylenediamine (yield *ca.* 65%). Anal. Calcd for $C_{14}H_{32}CuF_6N_7NiO_3PS$: C, 26.04; H, 4.99; N, 15.18; S, 4.96. Found: C, 25.8; H, 5.1; N, 14.9; S, 4.7. In spite of all efforts no crystals suitable for X-ray determination were obtained.

Crystal Data Collection and Refinement. Crystallographic data for **1**, **2**, and **3** are shown in Table 1.

$[Cu(oxpn)Ni(\mu\text{-}NCS)(H_2O)(tmen)]_2(PF_6)_2$ (1). A purple platelike crystal (0.38 × 0.19 × 0.114 mm) was mounted on a StoeAED2-4-circle diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Unit cell parameters were determined by least-squares from the $\pm\omega$ values of 13 reflections in the range $14 < \theta < 16.6°$. In total, 3518 independent reflections were measured in the range $2.56 < \theta < 22.5°$ at 273(2) K; 3223 reflections $[I > 2\sigma(I)]$ were considered observed. Two standard reflections were measured every hour and showed a 2% intensity variation. An empirical absorption correction was applied using the routine DIFABS included in the program PLATON,[14] which gave transmission factors: min/max 0.502/1.000. Further crystallographic data are given in Table 1. The crystal structure was solved by direct methods and Fourier synthesis using the program SHELXS[15] and refined by the full-matrix least-squares

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Table 1. Crystallographic Data for [Cu(oxpn)Ni(μ-NCS)(H_2O)(tmen)]$_2$(PF_6)$_2$ (**1**), [Cu(oxpn)Ni(μ-NCS)(H_2O)(tmen)]$_2$(ClO_4)$_2$ (**2**), and [Cu(oxpn)Ni(μ-NCS)(H_2O)(trimen)]$_2$ (ClO_4)$_2$ (**3**)

	1	**2**	**3**
empirical formula	$C_{15}H_{34}CuF_6N_7NiO_3PS$	$C_{15}H_{34}ClCuN_7NiO_7S$	$C_{14}H_{32}ClCuN_7NiO_7S$
fw	659.77	614.25	600.23
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T (°C)	0(2)	25	25
λ (Å)	0.71073	0.71069	0.71069
a (Å)	9.059(8)	8.7586(7)	8.407(7)
b (Å)	12.604(2)	12.580(4)	12.779(4)
c (Å)	12.743(4)	12.6318(12)	14.081(3)
α (deg)	95.27(6)	94.630(14)	63.25(2)
β (deg)	99.22(2)	98.486(8)	88.62(3)
γ (deg)	108.86(7)	107.963(13)	79.06(4)
V (Å^3)	1342.9(13)	1297.6 (4)	1323.1(12)
Z	2	2	2
ρ_{obsd} (g cm^{-3})	1.632	1.572	1.507
μ (mm^{-1})	1.711	1.775	1.739
R^a	0.095	0.0398	0.0687
wR^b	0.167	0.1107	0.1820

[a] R (on F) $= \sum||F_o| - |F_c||/\sum|F_o|$. [b] w$R$ (on F^2) $= [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

method on F^2, using the program SHELXL-93.[16] The function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ where $w = [\sigma^2(I) + (12.16P)]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. Complex neutral atom scattering factors were taken from *International Tables for X-ray Crystallography*, Vol C.[17a] The water H atoms were located from difference maps and held fixed ($U_{iso} = 0.08$ Å^2). The remaining hydrogen atoms were included in calculated positions as riding atoms using SHELXL-93[16] default parameters. In all, 390 parameters were refined for 4611 reflections. Refinement converged at R (on F) 0.095, wR (on F^2) 0.167, for 3223 observed reflections. The maximum shift/esd and the min shift/esd were −0.001 and 0.000, respectively. Maximum and minimum peaks in the final difference maps were 0.593 and −0.522 e Å^{-3}, respectively.

[Cu(oxpn)Ni(μ-NCS)(H_2O)(tmen)]$_2$(ClO_4)$_2$ (2). A prismatic crystal (0.3 × 0.2 × 0.2 mm) was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by least-squares methods. Intensities were collected with graphite-monochromated Mo Kα radiation, using the ω/θ scan technique. In all, 7538 reflections were measured in the range $1.64 \leq \theta \leq 29.96°$, and 5139 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls, and no significant intensity decay was observed. Lorentz−polarization but not absorption corrections were made. The structure was solved by direct methods, using SHELXS[15] and refined by full-matrix least-squares method with SHELX93[16] using 7488 reflections (very negative intensities were not assumed). The function minimized was $\sum w|||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.1705P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$, f, f', and f'' were taken from *International Tables of X-ray Crystallography*.[17b] The extinction coefficient was 0.000(13). The oxygen atoms of perchlorate ion were located in disorder positions; an occupancy factor of 0.5 was assumed according to peaks of Fourier synthesis. In total, 33 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor, using a riding model for hydrogen atoms linked to N or C atoms. The final R (on F) factor was 0.039, wR (on $|F_o|^2$) = 0.110, and goodness of fit = 0.889 for all observed reflections. The number of parameters refined was 340; maximum shift/esd = 0.06. Maximum and minimum peaks in final difference synthesis were 0.755 and −0.800 eÅ^{-3}, respectively.

[Cu(oxpn)(μ-NCS)(H_2O)(trimen)]$_2$(ClO_4)$_2$ (3). A prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Enraf-Nonius CAD4 four-circle diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by least-squares methods. Intensities were collected with graphite-monochromated Mo Kα radiation, using the $\omega/2\theta$ scan technique. In total, 7787 reflections were measured in the range $2.47 \leq \theta \leq 29.97°$: 7688 were nonequivalent by symmetry (R_{int} (on I) = 0.009) and 4433 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 no absorption corrections were made. The structure was solved by Patterson synthesis, using SHELXS[15] and refined by full-matrix least-squares method with SHELX93[16] using 6786 reflections (very negative intensities were not assumed). The function minimized was $\sum w|||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.1303P)^2 + 0.9167P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$, f, f', and f'' were taken from *International Tables of X-ray Crystallography*.[17b] The extinction coefficient was 0.0010(14). In total, 30 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and using a riding model for hydrogen atoms linked to C atoms. The final R (on F) factor was 0.068, wR (on $|F_o|^2$) = 0.182, and goodness of fit = 1.094 for all observed reflections. The number of parameters refined was 315; maximum shift/esd = 0.0, mean shift/esd = 0.00. Maximum and minimum peaks in final difference synthesis were 1.388 and −0.922 e Å^{-3}, respectively.

Spectral and Magnetic Measurements. IR spectra (4000−400 cm^{-1}) were recorded on KBr pellets with a Nicolet 520 FT-IR spectrometer. Magnetic measurements were carried out on polycrystalline samples (30−40 mg) with a pendulum-type magnetometer−susceptometer (MANICS DSM.8) equipped with an Oxford helium continuous-flow cryostat, working in the 4.2−300 K range, and a Drusch EAF 16UE electromagnet. The applied magnetic field was ~1.2 T. The diamagnetic corrections were evaluated from Pascal's constants. To test the accuracy of results, especially in the low-temperature range, magnetic measurements were repeated with a Quantum Design MPMS SQUID susceptometer operating at a magnetic field of 0.5 T, between 2 and 300 K. The fit was carried out by using the MINUIT minimization program of the CERN program library (v. 92.1), CERN, Geneva, which ensures the accuracy of results so that the minimum can be calculated. EPR spectra were recorded on powder samples at X-band frequency with a Bruker 300E automatic spectrometer. Magnetic and EPR measurements were carried out in the "Servei de Magnetoquímica" (University of Barcelona).

Results and Discussion

Infrared Spectrum. At normal frequencies, the four new tetranuclear complexes show the strong bands corresponding to SCN$^-$ ligand (ν_a(CN) at 2100−2120 cm^{-1}), coordinate oxamidate group (ν_a(NCO) at 1620 cm^{-1}) and PF_6^- anion (ν_3-(T_{1u}) at 850 cm^{-1} and ν_4(T_{1u}) at 560 cm^{-1}) for complexes **1** and **4** or ClO_4^- anion (ν_3(T_2) at 1120 cm^{-1} and ν_4(T_2) at 630

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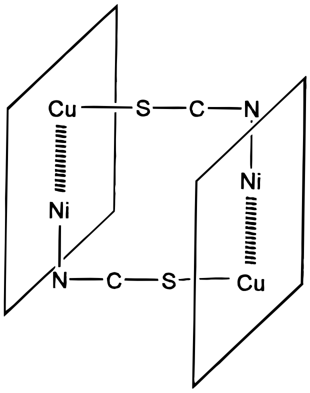

Figure 1. Perspective view of the tetranuclear (Cu−Ni)$_2$ complexes.

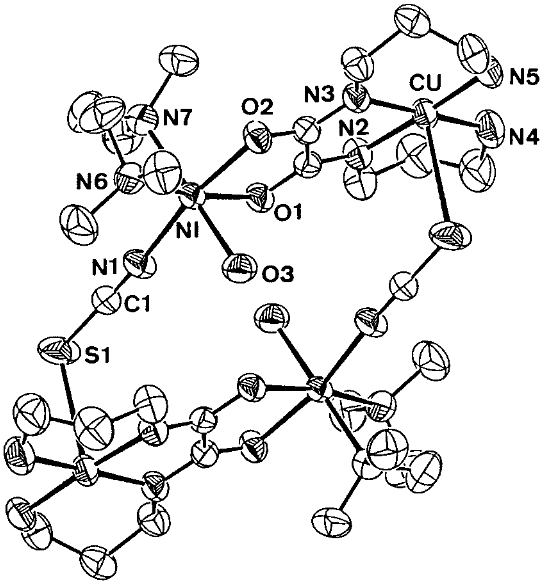

Figure 2. Drawing of the cationic part of [Cu(oxpn)Ni(μ-NCS)(H_2O)(tmen)]$_2$(ClO_4)$_2$ (**2**) with atom labeling scheme. The other two complexes show a very similar structure.

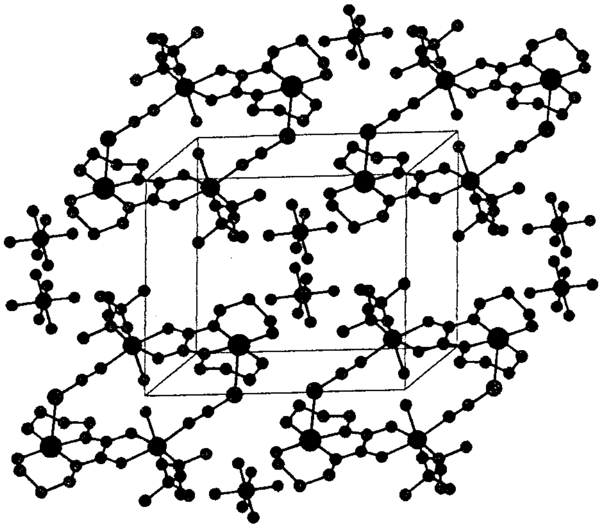

Figure 3. Unit cell for [Cu(oxpn)Ni(μ-NCS)(H_2O)(tmen)]$_2$(PF_6)$_2$ (**1**). The other two complexes show very similar unit cells.

cm^{-1}) for complexes **2** and **3**. Between 1599 and 400 cm^{-1} there are many bands attributable to the coordinated amines (tmen and trimen).

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for the Main Atoms of [Cu(oxpn)Ni(μ-NCS)(H_2O)(tmen)]$_2$(PF_6)$_2$ (**1**), [Cu(oxpn)Ni(μ-NCS)(H_2O)(tmen)]$_2$(ClO_4)$_2$ (**2**), and [Cu(oxpn)(μ-NCS)(H_2O) (trimen)]$_2$(ClO_4)$_2$ (**3**)

	x	*y*	*z*	*U*(eq)[a]
		Complex **1**		
Cu(1)	2767(2)	1721(1)	−3062(1)	39(1)
N(1)	3682(13)	674(8)	−3803(8)	64(3)
N(2)	3245(10)	1257(7)	−1641(7)	36(2)
N(3)	2039(10)	2770(7)	−2244(6)	37(2)
N(4)	2353(10)	2320(8)	−4442(7)	51(3)
Ni(1)	1027(2)	2148(1)	698(1)	36(1)
O(1)	2298(8)	1281(5)	−61(5)	38(2)
O(2)	1109(8)	2883(6)	−667(5)	39(2)
O(3)	−1213(9)	960(6)	−205(6)	48(2)
N(5)	3206(12)	3419(8)	1585(7)	53(3)
N(6)	−115(12)	3279(8)	1309(7)	52(3)
S(1)	601(5)	−67(3)	3580(3)	95(2)
C(15)	725(13)	663(9)	2590(8)	41(3)
N(7)	792(11)	1166(8)	1879(7)	50(2)
		Complex **2**		
Cu(1)	2158(1)	8231(1)	8113(1)	43(1)
Ni(1)	3926(1)	7869(1)	4288(1)	37(1)
S(1)	4367(2)	10100(1)	1376(1)	87(1)
O(1)	2624(3)	8724(2)	5080(2)	42(1)
O(2)	3881(3)	7125(2)	5661(2)	44(1)
O(3)	6222(3)	9023(2)	5154(2)	53(1)
N(1)	4143(4)	8872(2)	3110(2)	53(1)
N(2)	1682(3)	8741(2)	6694(2)	44(1)
N(3)	2969(3)	7218(2)	7267(2)	42(1)
N(4)	1176(4)	9250(3)	8882(2)	63(1)
N(5)	2640(4)	7625(3)	9504(2)	56(1)
N(6)	5118(4)	6768(2)	3649(2)	50(1)
N(7)	1698(3)	6633(2)	3413(2)	49(1)
C(1)	4230(4)	9390(2)	2394(2)	46(1)
		Complex **3**		
Cu(1)	2018(1)	2417(1)	1798(1)	46(1)
Ni(1)	404(1)	−1484(1)	1949(1)	35(1)
S(1)	672(2)	−3749(1)	−9(2)	70(1)
O(1)	−7(5)	−431(3)	2707(3)	48(1)
O(2)	1981(4)	−318(3)	1169(2)	39(1)
O(3)	−1621(5)	−254(4)	924(3)	49(1)
N(1)	701(6)	1242(4)	2641(3)	46(1)
N(2)	1112(7)	3558(5)	2388(5)	59(1)
N(3)	2831(5)	1254(4)	1255(3)	41(1)
N(4)	3566(7)	3512(5)	1005(5)	59(1)
N(5)	740(6)	−2285(4)	966(3)	46(1)
N(6)	2260(6)	−2755(4)	3057(4)	51(1)
N(7)	−1129(6)	−2633(4)	2955(4)	56(1)
C(9)	730(6)	−2877(4)	561(4)	41(1)

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

Description of the Structures. A schematic drawing of the three complexes is given in Figure 1, showing their peculiarity as two dinuclear [Cu(oxpn)Ni] complexes linked in an almost perpendicular way by two SCN$^-$ groups. Complexes **1, 2**, and **3** crystallize in triclinic space group $P\bar{1}$. The drawing of the cation for complex **2**, with atom labeling scheme is given in Figure 2. The drawings for complexes **1** and **3** are almost identical. As an example, a drawing of the unit cell of **1** is given in Figure 3. Fractional coordinates and isotropic thermal parameters as well as selected bond lengths and angles for **1**, **2**, and **3** are listed in Tables 2 and 3. The crystal structures consist of tetranuclear [Cu(oxpn)Ni(μ-NCS)(H_2O)(aa)]$_2^{2+}$ cations separated by hexafluorophosphate or perchlorate anions. The tetranuclear cations show two dinuclear [Cu(oxpn)Ni(H_2O)(aa)] entities linked by two (Cu)−SCN−(Ni) bridging ligands, related by an inversion center.

The coordination polyhedron of Cu(II) can be considered as a square pyramid with apical elongation (4 + 1). The four nitrogen atoms of the oxpn organic ligand are placed in the

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound $[Cu(oxpn)Ni(\mu\text{-}NCS)(H_2O)(tmen)]_2(ClO_4)_2$ (**2**)[a]

Cu−N(3)	1.957(2)	Ni−N(6)	2.149(3)
Cu−N(2)	1.982(2)	Ni−O(3)	2.154(3)
Cu−N(5)	2.010(3)	Ni−N(7)	2.159(3)
Cu−N(4)	2.013(3)	S(1)−C(1)	1.622(3)
Ni−N(1)	2.019(2)	N(1)−C(1)	1.155(4)
Ni−O(2)	2.036(2)	Cu−S(1)	3.058(2)
Ni−O(1)	2.092(2)		
N(3)−Cu−N(2)	82.74(9)	O(1)−Ni−O(3)	91.52(9)
N(3)−Cu−N(5)	94.05(11)	N(6)−Ni−O(3)	91.42(11)
N(2)−Cu−N(5)	176.54(11)	N(1)−Ni−N(7)	94.04(11)
N(3)−Cu−N(4)	175.40(12)	O(2)−Ni−N(7)	94.45(9)
N(2)−Cu−N(4)	93.70(11)	O(1)−Ni−N(7)	91.65(9)
N(5)−Cu−N(4)	89.45(12)	N(6)−Ni−N(7)	85.17(11)
N(1)−Ni−O(2)	169.61(10)	O(3)−Ni−N(7)	176.40(10)
N(1)−Ni−O(1)	92.98(9)	S(1)−Cu(1)−N(2)	92.80(7)
O(2)−Ni−O(1)	80.81(7)	S(1)−Cu(1)−N(3)	88.15(9)
N(1)−Ni−N(6)	96.67(11)	S(1)−Cu(1)−N(4)	94.95(11)
O(2)−Ni−N(6)	90.00(9)	S(1)−Cu(1)−N(5)	88.38(8)
O(1)−Ni−N(6)	170.03(9)	Cu(1)−S(1)−C(1)	104.38(11)
N(1)−Ni−O(3)	87.49(11)	Ni(1)−N(1)−C(1)	165.68(9)
O(2)−Ni−O(3)	84.38(10)		

[a] Bond distances and angles for complexes **1** and **3** are very similar.

basal positions. The Cu−N distances are close to 2.0 Å (Table 3). The coordination is completed by the S atom of the SCN^- bridge at 3.014 Å (**1**), 3.058 Å (**2**) and 3.051 Å (**3**). The N−Cu−S angles are between 88.6 and 95.0° for **1**, between 88.2 and 95.0° for **2**, and between 87.9 and 93.6° for **3** (Table 3). The Ni atoms are in a distorted octahedral environment. The four positions coplanar to the oxamidato bridge are occupied by the two oxygen atoms of this ligand at 2.04−2.1 Å (average), one nitrogen of the bidentate amine at 2.17 Å for **1**, 2.149 Å for **2**, and 2.141 Å for **3** and the nitrogen of the thiocyanato bridge, at 2.029 Å for **1**, 2.019 Å for **2**, and 2.046 Å for **3**. The two remaining positions are occupied by the oxygen of the water ligand at 2.151 Å for **1**, 2.154 Å for **2**, and 2.124 Å for **3** and one nitrogen of the bidentate amine at 2.156 Å for **1**, 2.159 Å for **2**, and 2.094 Å for **3**. The angles formed by the thiocyanato ligand and the Cu and Ni atoms, which determine the magnetic properties (see below), are Ni(1)−N(7)−C(15) = 175.9° and Cu(1)−S(1)−C(15) = 104.6° for **1**, Ni(1)−N(1)−C(1) = 165.7° and Cu(1)−S(1)−C(1) = 104.4° for **2**, and Ni(1)−N(5)−C(9) = 165.8° and Cu(1)−S(1)−C(9) = 106.1° for **3**. The Cu−Ni distances through the oxamidate bridge are 5.313 Å for **1**, 5.314 Å for **2**, and 5.323 Å for **3**, and those through the thiocyanate bridge are 6.313 Å for **1**, 6.335 Å for **2**, and 6.365 Å for **3**. Hydrogen bonding between dinuclear entities is observed through one of the hydrogen atoms of the water molecule and one oxygen atom of the oxamidate bridge of the neighboring entity at 2.00−2.21 Å.

Magnetic Studies. Variable temperature (2−300 K) magnetic susceptibility data were collected for microcrystalline samples of compounds **1**−**4**. In all four cases the magnetic measurements were taken at least twice from different samples with different magnetometers (see Experimental Section). Assuming a weak magnetic coupling between the two entities through the thiocyanate bridging ligand, the first fit was made from 300 to *ca.* 20 K to study *exclusively* the interaction within each Cu−Ni dinuclear moiety. The spin Hamiltonian that describes the isotropic magnetic exchange interaction in a Cu−Ni dinuclear complex is $H = -JS_{Cu}S_{Ni}$. There are two spin states, $S = {}^1/_2$ and ${}^3/_2$. Assuming antiferromagnetic coupling, the ground state is $S = {}^1/_2$ ($E = 0$) and the low-lying excited state is $S = {}^3/_2$ ($E = -3J/2$). The g values for each state are related to those of the ions: $g_{3/2} = ({}^1/_3 g_{Cu} + {}^2/_3 g_{Ni})$ and $g_{1/2} = (-{}^1/_3 g_{Cu} + {}^4/_3 g_{Ni})$.[18] By introducing these values to the Van Vleck equation, a typical expression of the molar susceptibility can be deduced. As an example, the experimental and theoretical curves of $\chi_M T$ of complex **2** are shown in Figure 4a. J and g values for the four new complexes are listed in Table 4. The J values for the four complexes (close to -110 cm^{-1}) agree with those reported in the literature for the Cu−Ni heterodinuclear complexes with the oxpn bridge.[5]

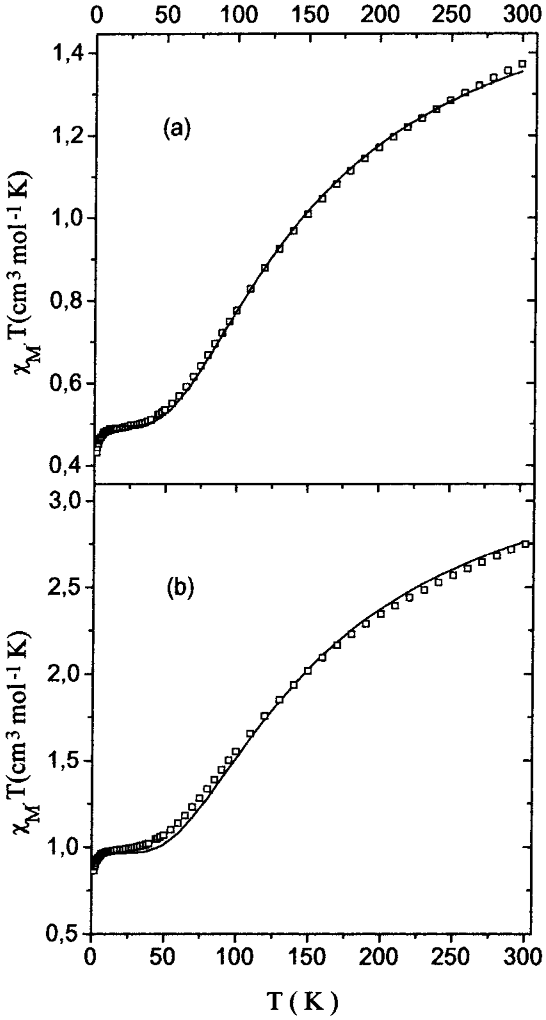

Figure 4. Plot of $\chi_M T$ vs temperature for $[Cu(oxpn)Ni(\mu\text{-}NCS)(H_2O)(tmen)]_2(ClO_4)_2$ (**2**) as an example of the four complexes. The solid lines result from a fit of the data to the appropriate theoretical equation for a [Cu−Ni] complex (a) and by full-matrix diagonalization method for the whole tetranuclear complex (b).

Table 4. Best-Fit J and g Parameters for **1**−**4** from the Hamiltonian Given in the Text

compound	J (cm^{-1})	g_{Cu}	g_{Ni}	R[a]
1	−110	2.07	2.25	8×10^{-6}
2	−111	2.15	2.26	5×10^{-5}
3	−106	2.09	2.18	2×10^{-5}
4	−107	2.06	2.29	1×10^{-5}

[a] $R = \sum_i(\chi_{Mcalcd}T - \chi_{Mobsd}T)^2/\sum_i(\chi_{Mobsd}T)^2$.

Study of the Exchange of the Whole Tetranuclear Entity. As shown in the crystallographic part, the tetranuclear complexes are formed by two dinuclear entities linked by the SCN^- bridging ligand (Figures 1 and 2). The two cases represented

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(18) Bencini, A.; Gatteschi, D. *EPR of Exchange Coupled Systems*; Springer: Berlin, 1990; p 182.

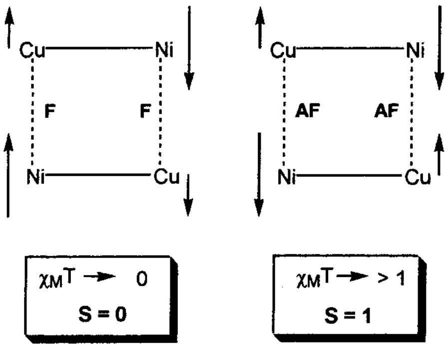


Figure 5. Scheme of the spin topology assuming ferro- or antiferromagnetic coupling between the two heterodinuclear [Cu−Ni] entities.

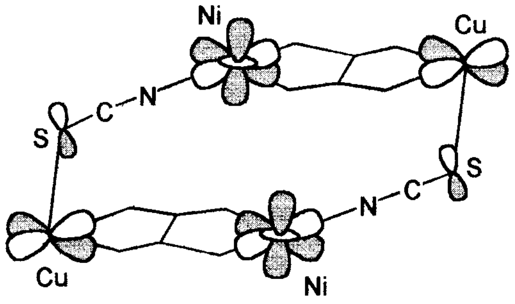
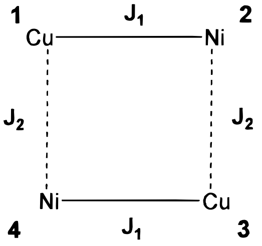


Figure 6. Scheme of the magnetic molecular orbitals for the tetranuclear $[Cu-Ni]_2$ complexes, showing the orthogonality of the magnetic orbitals centered on the metal ions.

Chart 2



in Figure 5 are two extremes used for the analysis of experimental magnetic measurements and treatment of data. If the magnetic interactions *between* these two entities were weakly ferromagnetic, the resulting S_T value would tend to zero at low temperatures, so the $\chi_M T$ curve would decrease and tend to zero at these temperatures. In contrast, if the coupling was weakly antiferromagnetic the resulting S_T value would tend to 1 and the $\chi_M T$ curve would increase and tend to a value greater than 1 (taking into account that $g > 2.00$). The fit of the experimental data for complex **2** as an example of the four new complexes, was performed according to the following Hamiltonian:

$$H = -J_1(S_1S_2 + S_3S_4) - J_2(S_1S_4 + S_2S_3) + g\beta M_s H$$

where J_1 corresponds to the coupling through the oxamidato bridge and J_2 to the coupling through the thiocyanato bridge (Chart 2).

The free parameters were J_1, J_2, and g (average). The fit made by the full-matrix diagonalization method using CLUMAG[19] gave the following results: $J_1 = -115$ cm^{-1}; $J_2 = 0.03$ cm^{-1}, $g = 2.26$, and $R = 4 \times 10^{-4}$ ($R = \sum_i(\chi_{Mcalcd} - \chi_{Mobsd})^2/\sum_i(\chi_{Mobsd})^2$ (Figure 4b).

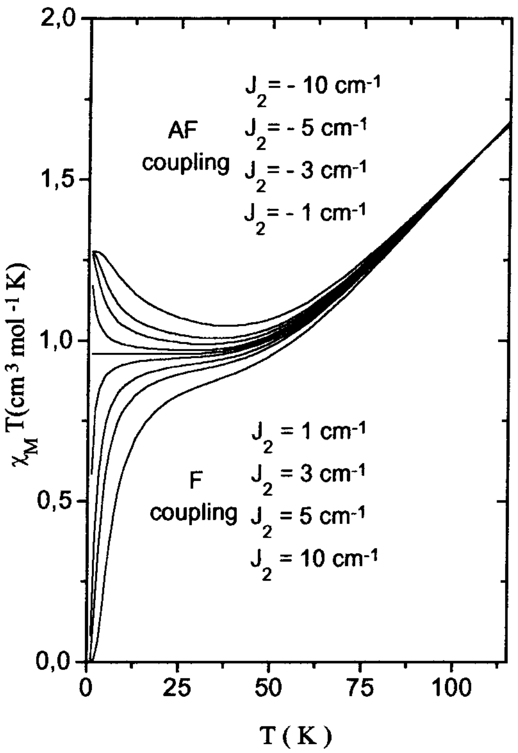


Figure 7. Theoretical curves obtained by CLUMAG program (see text) for different J_2 values. In all cases, J_1 and g were maintained constant and equal to the values obtained by fitting the complexes as dinuclear entities (see text): $J_1 = -115$ cm^{-1} and $g = 2.25$.

From these data, the coupling through the thiocyanate ligand is small but positive (ferromagnetism). This feature is consistent with the experimental data discussed above for this kind of ligand.[8,9,12] A schematic representation of the magnetic orbitals for the tetranuclear cation is shown in Figure 6. A clear orthogonality of the magnetic orbitals centered in the metal ions through the p orbitals of the SCN^- bridge is shown. This orthogonality of the magnetic molecular orbitals thus creates ferromagnetic coupling.

Finally, in order to compare the theoretical magnetic behavior for the two extreme cases represented in Figure 5, a simulation of the $\chi_M T$ *vs* T, using CLUMAG, was performed, fixing the J_1 value as -115 cm^{-1} and $g = 2.26$ and varying the values of J_2 (coupling through the thiocyanate bridging ligand) between -10 and 10 cm^{-1}. As expected, with these small J_2 values the variation of $\chi_M T$ *vs* T is manifested only at low temperatures. These theoretical $\chi_M T$ *vs* T curves are shown in Figure 7. When the J_2 coupling is antiferromagnetic, $\chi_M T$ increases with lower temperature for an isolated Ni−Cu complex; when the J_2 coupling is ferromagnetic, $\chi_M T$ decreases with lower temperature, tending to zero. These theoretical results are consistent with the qualitative proposal explained above in Figure 5.

Conclusions

The assembling process of the tetranuclear structure is another example of molecular boxes formed spontaneously by mixing bridging ligands and transition metals. From magnetic point of view, all aspects commented above indicate that in these new tetranuclear complexes the antiferromagnetic coupling through the oxamidato bridge is dominant. The coupling through the thiocyanato bridge is very small, but positive (ferromagnetic coupling). As further evidence of these results, the EPR spectra

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(19) The series of calculations were made using the computer program CLUMAG, which uses the irreducible tensor operator formalism (ITO): Gatteschi, D.; Pardi, L. *Gazz. Chim. Ital.* **1993**, *123*, 231.

of the four tetranuclear complexes show only one band centered at $g = 2.23$. This band is sharp at low temperature (4 K) and becomes broader at higher temperature (77 and 298 K). This band can be assigned to a transition between $|^1/_2, -^1/_2> \rightarrow |^1/_2, ^1/_2>$ of the $S = {}^1/_2$ ground state of the dinuclear entity.

Acknowledgment. We are very grateful for the financial support given by the Dirección General de Investigación Científica y Técnica (Spain) (Grant PB93/0772) and the Swiss National Science Foundation (Grant 20.45315.95). We also acknowledge the help given by Dr. M. S. el Fallah and the group of Dr. D. Gatteschi (University of Firenze) for the use of the CLUMAG program. We also thank to Dr. Núria Clos for recording the magnetic and EPR measurements.

Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available on the Internet. Access information is given on any current masthead page.

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