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Crystal Structures and Ferromagnetic Properties of Two New Dinuclear Complexes with Thiocyanato Bridging Ligands: [{Ni$_2$(1,2-diamino-2-methylpropane)$_3$(NCS)$_2$}(μ-NCS)$_2$]$_2$[Ni(1,2-diamino-2-methylpropane)$_2$(NCS)$_2$]·H$_2$O and [{Ni$_2$(1,2-diamino-2-methylpropane)$_4$}(μ-NCS)$_2$](PF$_6$)$_2$. Magneto−Structural Correlations

Montserrat Monfort,[*,†] Joan Ribas,[†] and Xavier Solans[‡]

Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028-Barcelona, Spain, and Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franqués s/n, 08028-Barcelona, Spain

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Two complexes of formulas [{Ni$_2$(1,2-diamino-2-methylpropane)$_3$(NCS)$_2$}(μ-NCS)$_2$]$_2$[Ni(1,2-diamino-2-methylpropane)$_2$(NCS)$_2$]·H$_2$O (**1**) and [{Ni$_2$(1,2-diamino-2-methylpropane)$_4$}(μ-NCS)$_2$](PF$_6$)$_2$ (**2**) have been synthesized, and their crystal structures have been determined by single-crystal X-ray diffraction methods at room temperature. Complex **1** crystallizes in the triclinic system, space group $P\bar{1}$, $Z = 1$, with $a = 11.400(3)$ Å, $b = 13.068(3)$ Å, $c = 14.381(3)$ Å, $\alpha = 77.37(2)°$, $\beta = 67.89(3)°$, $\gamma = 73.21(3)°$, and $V = 1886(1)$ Å^3. Complex **2** crystallizes in the monoclinic system, space group $P2_1/n$, $Z = 2$, with $a = 7.5937(8)$ Å, $b = 14.3627(9)$ Å, $c = 17.0895(12)$ Å, $\beta = 91.03(2)°$, and $V = 1863.4(4)$ Å^3. The crystal structures of **1** and **2** were determined from Patterson synthesis and refined by full-matrix least-squares techniques. The final values of the reliability factors R (R_w) were 0.050 (0.055) for **1** and 0.065 (0.076) for **2**, with 8558 and 3517 observed reflections, respectively. Their structures consist essentially of dinuclear Ni$_2$ entities in which the two Ni(II) atoms are linked by two NCS$^-$ bridges. In **1** this dinuclear entity is highly asymmetric: one Ni(II) atom has two bidentate 1,2-diamino-2-methylpropane molecules as blocking ligands whereas the second Ni(II) has only one amine and two terminal thiocyanate-*N* ions as blocking ligands. On the other hand, in crystal structure of **1** there are two of these dinuclear entities together with one mononuclear [Ni(amine)$_2$(NCS)$_2$] entity. The two entities are neutral, and all Ni(II) ions are octahedrally coordinated. In **2** there is only one dinuclear entity in which each Ni(II) is octahedrally coordinated by two thiocyanato bridging ligands and two amines as blocking ligands, giving a dicationic complex. Two PF$_6^-$ anions are present in the crystal lattice for each dinuclear entity. Magnetic susceptibility data, measured from 300 to 4 K, were fitted to the Ginsberg equation, giving the parameters $J = 4.3$ cm^{-1}, $g = 2.13$, $D = -20$ cm^{-1}, and $z'J' = 0.20$ cm^{-1} for **1** and $J = 6.3$ cm^{-1}, $g = 2.14$, $D = -2.0$ cm^{-1}, and $z'J' = -0.14$ cm^{-1} for **2**. The magnetic behavior of these and related complexes is discussed, and some magneto−structural trends are given.

Introduction

Exchange interactions propagated by pseudohalide bridging ligands (NCO$^-$, NCS$^-$, N$_3^-$) between paramagnetic centers have attracted great interest in the past few years. The most comprehensive literature refers to N$_3^-$ bridging ligands: when the ligand acts in the end-to-end mode,[1,2] antiferromagnetic coupling always occurs while the end-on coordination mode always exhibits ferromagnetic coupling.[3,4] Extended Hückel OM calculations[2ae,5] and spin-polarization phenomena[6] have been reported to explain this behavior. With cyanato bridging ligands, such behavior is not so clear and the number of reported complexes that have been fully characterized is too low to permit magneto−structural correlations.[7,8] In contrast, the literature on thiocyanato ligands is more abundant but its versatility is less pronounced than that of azido derivatives. Although bridging thiocyanato ligands are relatively common, the bridge mode usually involves both nitrogen and sulphur, and thus an M−NCS−M linkage occurs.[9,10] Bridging via sulfur has also been observed,[11] although, like bridging solely through nitrogen,[12] it is quite rare and normally occurs with other polynuclear bridging ligands. Focusing our attention on Ni(II) dinuclear complexes,[10] one experimental finding is observed: all dinuclear

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[†] Departament de Química Inorgànica.

[‡] Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals.

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$[Ni_2(\mu\text{-}NCS)_2]$ cores have approximately the same angles and distances, and they all show low ferromagnetic behavior, which was explained by Ginsberg[13] and Hendrickson[10e] using a valence bonding model, according to Anderson's general theory of superexchange.[14] Continuing our interest in polynuclear Ni(II) complexes with pseudohalides as bridging ligands,[2,4,5,8c,10g] we now present the synthesis of two new dinuclear Ni(II) complexes with thiocyanato bridging ligands. We report their crystal structures and magnetic properties, and we compare the structural and magnetic properties of several octahedrally coordinated nickel(II) dimers with NCS^- as bridging ligands, to determine the influence of structural parameters on the strength of the exchange coupling.

Experimental Section

Synthesis of the Complexes. $[\{Ni_2(1,2\text{-diamino-2-methylpropane})_3(NCS)_2\}(\mu\text{-}NCS)_2]_2[Ni(1,2\text{-diamino-2-methylpropane})_2(NCS)_2]\cdot H_2O$ (1). An aqueous solution of 1,2-diamino-2-methylpropane (Aldrich, 99%) (0.44 g, 5 mmol) was added to an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ (1.45 g, 5 mmol). To this blue solution was added with constant stirring solid NH_4NCS (1.14 g, 15 mmol). A violet precipitate was immediately formed, which was isolated by filtration (analytical and spectroscopic measurements indicated a mononuclear complex). The blue solution was left to stand at room temperature for several days, and suitable blue crystals of **1** were obtained by slow evaporation.

$[\{Ni_2(1,2\text{-diamino-2-methylpropane})_4\}(\mu\text{-}NCS)_2](PF_6)_2$ (2). An aqueous solution of 1,2-diamino-2-methylpropane (Aldrich, 99%) (0.35 g, 4 mmol) was added to an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ (0.58 g, 2 mmol). To this blue solution was added with constant stirring solid NH_4NCS (0.15 g, 2 mmol). No precipitate was formed. Solid KPF_6 (0.40 g, 2.17 mmol) was added with constant stirring, and the solution was left to stand undisturbed for several days. Suitable blue crystals were obtained by this slow evaporation. Satisfactory analytical results (C, H, N, Ni) were obtained for the two complexes.

Physical Measurements. Infrared spectra (4000−200 cm^{-1}) were recorded from KBr pellets in a Nicolet 520 FTIR spectrophotometer. Susceptibility measurements were carried out with a pendulum-type magnetometer (MANICS DSM8), equipped with a TBT helium continuous-flow cryostat working in the temperature range 300−4 K, and a Bruker B E15 electromagnet. The magnetic field was approximately 15 000 G. The instrument was calibrated by magnetization measurements of a standard ferrite. Diamagnetic corrections were estimated from Pascal's tables. For **1** susceptibility measurements were also performed in an MPMS Quantum Design instrument (with a SQUID detector).

Table 1. Crystallographic Data (at Room Temperature) for $[\{Ni_2(1,2\text{-diamino-2-methylpropane})_3(NCS)_2\}(\mu\text{-}NCS)_2]_2[Ni(1,2\text{-diamino-2-methylpropane})_2(NCS)_2]\cdot H_2O$ (**1**) and $[\{Ni_2(amine)_4\}(\mu\text{-}NCS)_2](PF_6)_2$ (**2**)

	1	**2**
chem formula	$C_{42}H_{98}N_{26}Ni_5OS_{10}$	$C_{18}H_{48}F_{12}N_{10}Ni_2P_2S_2$
fw	1615.63	876.13
space group	$P\bar{1}$	$P2_1/n$
a, Å	11.400(3)	7.5937(8)
b, Å	13.068(3)	14.3627(9)
c, Å	14.381(3)	17.0895(12)
α, deg	77.37(2)	90.00
β, deg	67.89(3)	91.03(2)
γ, deg	73.21(3)	90.00
V, Å^3	1886(1)	1863.4(4)
Z	1	2
λ(Mo Kα), Å	0.710 69	0.710 69
d_{calc}, g·cm^{-3}	1.422	1.561
μ(Mo Kα), cm^{-1}	15.38	12.94
R^a	0.050	0.065
$R_w{}^b$	0.055	0.076

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

X-ray Data and Crystal Structure Determinations. A blue rhomboidal crystal (0.08 × 0.08 × 0.18 mm^3) of **1** and a blue prismatic crystal (0.1 × 0.1 × 0.2 mm^3) of **2** were selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($16 < \theta < 22°$ for **1** and $12 < \theta < 22°$ for **2**) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo Kα radiation, using the ω-scan technique. For **1**, 11 064 reflections were measured in the range $2 \leq \theta \leq 30°$, 8558 of which were assumed as observed by applying the condition $I \geq 2.5\sigma(I)$. For **2**, 5781 reflections were measured in the range $2 \leq \theta \leq 30°$, 3517 of which were assumed as observed by applying the condition $I \geq 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz−polarization but no absorption corrections were made. The crystallographic data, conditions used for the intensity data collection, and some features of the structure are listed in Table 1. The structures were solved by Patterson syntheses, using the SHELXS computer program,[15] and refined by full-matrix least-squares methods, with the SHELX76 computer program.[16] The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.004|F_o|^2)^{-1}$; f, f', and f'' were taken from ref 17. For **1** the final R factor was 0.050 ($R_w = 0.055$) for all observed reflections. The Number of parameters refined was 388. Maximum shift/esd = 0.1; maximum and minimum peaks in the final difference synthesis were 0.3 and −0.3 e Å^{-3}, respectively. For **2**, N and S atoms of μ-NCS bridges and fluorine atoms of PF_6^- were located in disordered positions, and an occupancy factor of 0.5 was assigned, according to the height of Fourier synthesis. All H atoms were computed and refined with an overall isotropic temperature factor, using a riding model for computed atoms. The final R factor was 0.065 ($R_w = 0.076$) for all observed reflections. The number of parameters refined was 281. Maximum shift/esd = 0.08; maximum and minimum peaks in the final difference synthesis were 0.3 and −0.3 e Å^{-3}, respectively. Final atomic coordinates for **1** and **2** are given in Tables 2 and 3.

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Table 2. Final Atomic Coordinates (×10^4; Ni and S, ×10^5) for $C_{42}H_{98}N_{26}Ni_5OS_{10}$ (**1**)

	x/*a*	*y*/*b*	*z*/*c*	B_{eq},^{a} Å^2
Ni(1)	24910(2)	1927(2)	47883(2)	3.01(1)
Ni(2)	23216(2)	45487(2)	31044(2)	3.09(1)
Ni(3)	50000	0	0	4.29(2)
S(11)	15075(9)	−13500(6)	24756(6)	5.42(4)
S(12)	28888(12)	28864(6)	63716(7)	6.58(5)
S(13)	3363(6)	37881(4)	44226(5)	4.41(2)
S(21)	44077(5)	7708(4)	33533(4)	3.74(2)
S(31)	53728(10)	35479(6)	2167(6)	6.52(4)
N(11)	2281(2)	−639(2)	3803(2)	4.26(8)
N(12)	2717(2)	1143(2)	5653(2)	3.94(8)
N(13)	1118(2)	1544(1)	4442(2)	3.77(7)
N(14)	3824(2)	−1133(2)	5199(2)	4.13(8)
N(15)	1144(2)	−504(2)	6004(2)	4.01(8)
N(21)	3465(2)	3016(2)	3183(2)	4.12(8)
N(22)	2033(2)	4309(2)	1816(1)	3.83(7)
N(23)	987(2)	6024(1)	2910(1)	3.76(7)
N(24)	4020(2)	5124(2)	2272(2)	4.42(8)
N(25)	2719(2)	4870(2)	4294(2)	4.43(8)
N(31)	5018(3)	1509(2)	308(2)	5.41(10)
N(32)	2951(3)	431(2)	413(2)	5.56(11)
N(33)	5132(3)	−692(2)	1406(2)	5.51(10)
C(11)	1957(2)	−937(2)	3250(2)	3.93(8)
C(12)	2766(2)	1872(2)	5954(2)	3.62(8)
C(13)	788(2)	2481(2)	4433(2)	3.30(7)

^{a} $B_{eq} = (8\pi^2/3)U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 3. Final Atomic Coordinates (×10^4; Ni and P, ×10^5) for $C_{18}H_{48}F_{12}N_{10}Ni_2P_2S_2$ (**2**)

	x/*a*	*y*/*b*	*z*/*c*	B_{eq},^{a} Å^2
Ni	21415(7)	14468(4)	43235(3)	5.27(3)
P	74262(16)	36662(9)	28464(9)	6.39(6)
S	3163(2)	−385(1)	4599(1)	6.67(9)
S′	−1468(3)	1616(2)	4800(2)	6.04(13)
N(1)	−73(8)	1138(4)	4810(4)	5.55(26)
N(1)′	1931(11)	150(6)	4568(6)	5.91(41)
N(2)	4501(5)	1430(2)	3709(2)	5.44(16)
N(3)	1122(5)	1108(3)	3213(2)	6.04(17)
N(4)	3238(8)	1779(3)	5417(3)	8.38(25)
N(5)	1869(4)	2900(2)	4280(2)	5.08(14)
C(1)	−1511(6)	751(4)	5084(3)	6.39(22)
C(2)	4265(6)	902(3)	2984(3)	6.48(23)
C(3)	2486(6)	1148(3)	2594(2)	5.52(19)
C(4)	2515(6)	2145(4)	2274(2)	6.31(22)
C(5)	2087(10)	467(5)	1932(3)	9.34(36)
C(6)	3762(11)	2763(5)	5412(4)	9.40(36)
C(7)	2366(6)	3335(3)	5053(2)	5.78(20)
C(8)	734(10)	3314(6)	5577(4)	9.97(41)
C(9)	2969(11)	4320(4)	4949(4)	9.76(39)
F(1)	9390(16)	3717(9)	2612(11)	12.78(83)
F(1)′	8909(24)	3814(13)	2190(8)	7.70(79)
F(2)	5738(28)	3591(15)	3211(12)	8.64(67)
F(2)′	5410(48)	3489(24)	3337(16)	5.72(78)
F(3)	7684(19)	2594(6)	2891(14)	12.42(82)
F(3)′	7145(40)	2728(14)	2384(14)	11.40(127)
F(4)	8589(17)	3841(14)	3542(8)	13.53(87)
F(4)′	8130(25)	3046(29)	3526(20)	16.80(185)
F(5)	7123(14)	4741(6)	2836(10)	9.65(62)
F(5)′	7576(40)	4609(16)	3200(16)	14.78(172)
F(6)	6204(17)	3567(15)	2091(6)	13.09(87)
F(6)′	6897(38)	4122(16)	2100(10)	12.57(153)

^{a} $B_{eq} = (8\pi^2/3)U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot a_j$.

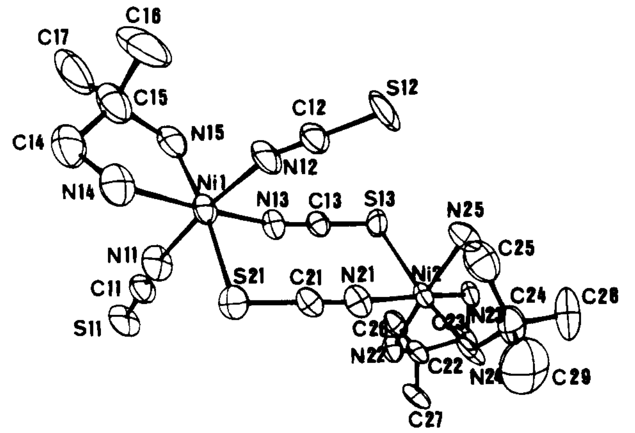

Figure 1. Molecular structure for [{Ni_2(amine)$_3$(NCS)$_2$}(μ-NCS)$_2$], the dimeric part of **1**, showing the atom-labeling scheme.

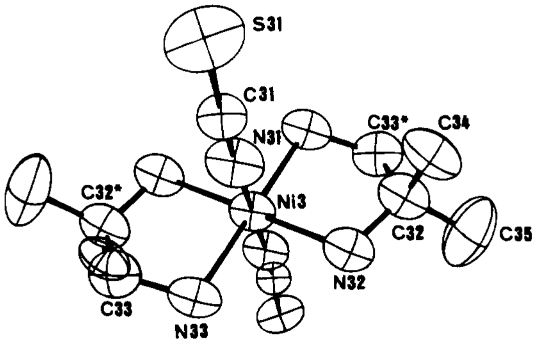

Figure 2. Molecular structure for [Ni(amine)$_2$(NCS)$_2$], the monomeric part of **1**, showing the atom-labeling scheme.

Table 4. Selected Bond Lengths (Å) and Angles (deg) For $C_{42}H_{98}N_{26}Ni_5OS_{10}$ (**1**)

S(21)—Ni(1)	2.546(1)	N(32)—Ni(3)	2.114(5)
N(11)—Ni(1)	2.079(3)	N(33)—Ni(3)	2.069(4)
N(12)—Ni(1)	2.063(3)	C(11)—S(11)	1.627(4)
N(13)—Ni(1)	2.103(3)	C(12)—S(12)	1.629(3)
N(14)—Ni(1)	2.089(3)	C(13)—S(13)	1.635(3)
N(15)—Ni(1)	2.082(3)	C(21)—S(21)	1.643(3)
S(13)—Ni(2)	2.636(1)	C(31)—S(31)	1.631(3)
N(21)—Ni(2)	2.056(3)	C(11)—N(11)	1.167(5)
N(22)—Ni(2)	2.101(3)	C(12)—N(12)	1.153(4)
N(23)—Ni(2)	2.121(3)	C(13)—N(13)	1.171(4)
N(24)—Ni(2)	2.109(3)	C(21)—N(21)	1.165(4)
N(25)—Ni(2)	2.077(3)	C(31)—N(31)	1.147(5)
N(31)—Ni(3)	2.121(3)		
N(13)—Ni(1)—S(21)	93.8(1)	C(13)—S(13)—Ni(2)	105.8(1)
N(21)—Ni(2)—S(13)	88.2(1)	C(21)—S(21)—Ni(1)	100.7(1)
N(21)—C(21)—S(21)	178.7(3)	C(13)—N(13)—Ni(1)	142.4(3)
N(13)—C(13)—S(13)	179.6(2)	C(21)—N(21)—Ni(2)	165.2(3)

Results and Discussion

Description of the Structures. [{Ni_2(1,2-diamino-2-methylpropane)$_3$(NCS)$_2$}(μ-NCS)$_2$]$_2$[Ni(1,2-diamino-2-methylpropane)$_2$(NCS)$_2$]·H_2O (1). Figures 1 and 2 show a view of the dimeric and monomeric entities of **1**. Final positional parameters for the non-hydrogen atoms are listed in Table 2; main bond distances and angles, in Table 4. The structure consists of two discrete neutral [{Ni_2(1,2-diamino-2-methylpropane)$_3$(NCS)$_2$}(μ-NCS)$_2$] dinuclear entities and one neutral mononuclear [Ni(amine)$_2$(NCS)$_2$] entity in the crystal lattice (Figure 3). The monomeric entity has an inversion center on the Ni(II) atom, giving an octahedral geometry with Ni—N(amine) = 2.11 and 2.07 Å and Ni—N(NCS) = 2.12 Å. From magnetic considerations (see above) it is important to discuss the most characteristic features of the dinuclear entity. In this dimeric entity, two nickel(II) atoms are bridged by two thiocyanate ions in an end-to-end fashion. One of the Ni(II) ions has two amines as blocking ligands, whereas the second Ni(II) center has two NCS^- ions in a trans arrangement and one amine as blocking ligands. According to the literature data,[10] this is the first case in which such an asymmetrical arrangement is reported.

Owing to this geometrical configuration, the whole molecule is highly asymmetrical: no symmetry elements are present

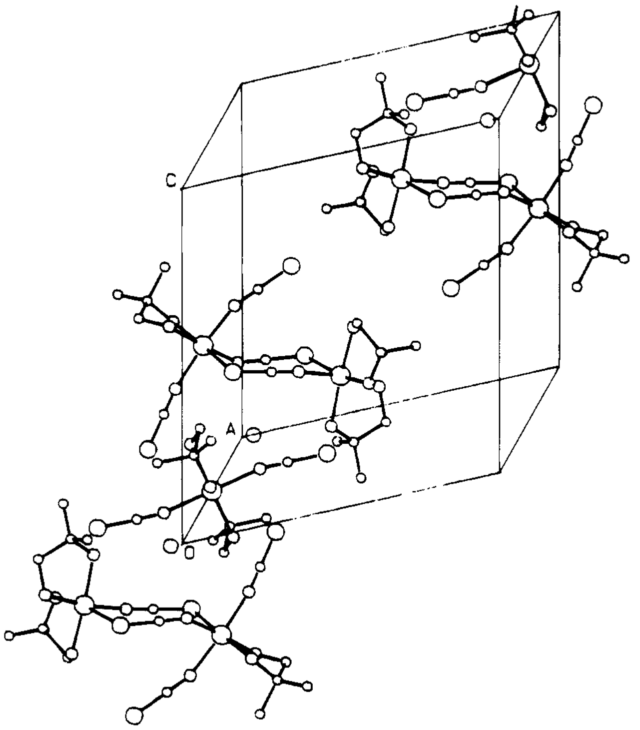

Figure 3. Crystal packing for $[\{Ni_2(amine)_3(NCS)_2\}(\mu\text{-}NCS)_2]_2[Ni(amine)_2(NCS)_2]\cdot H_2O$ (**1**).

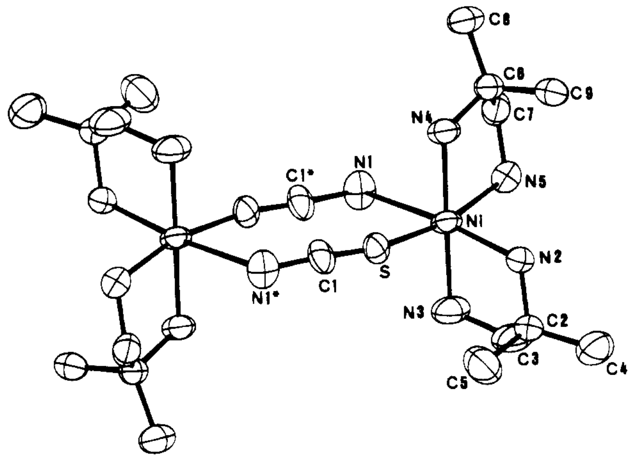

Figure 4. Molecular structure for $[\{Ni_2(amine)_4\}(\mu\text{-}NCS)_2]^{2+}$ (cation of **2**), showing the atom-labeling scheme.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $C_{18}H_{48}F_{12}N_{10}Ni_2P_2S_2$ (**2**)

S—Ni	2.781(2)	N(5)—Ni	2.099(4)
S′—Ni	2.884(3)	C(1)—S	1.473(6)
N(1)—Ni	1.941(6)	C(1)—S′	1.334(6)
N(1)′—Ni	1.915(9)	C(1)—N(1)	1.319(8)
N(2)—Ni	2.094(4)	C(1)—N(1)′	1.463(8)
N(3)—Ni	2.094(4)	C(2)—N(2)	1.460(6)
N(4)—Ni	2.087(4)		
N(1)—Ni—S	87.3(2)	Ni—N(1)—C(1)*	167.9(4)
N(1)′—Ni—S′	86.4(2)	Ni—N(1)′—C(1)	165.6(4)
Ni—S—C(1)	99.4(2)	S—C(1)—N(1)*	176.0(3)
Ni—S′—C(1)*	93.1(2)	S′*—C(1)—N(1)′	168.3(3)

which might relate one part of the molecule to another. For example, in the Ni(II) center linked to two amine ligands, the Ni—N(amine) distances are 2.08–2.12 Å and the Ni—N(NCS bridge) distance is the shortest (2.056 Å). The Ni(II) center linked to two SCN^- ligands and only one amine ligand is different: the Ni—N(NCS bridge) distance is the longest (2.103 Å), with 2.08 Å for Ni—N(amine) and 2.06 and 2.08 Å for Ni—N(NCS terminal). In both cases, the Ni—S(SCN bridge) distances are very long, 2.63 and 2.54 Å, respectively. The two thiocyanate ligands of this bridging unit are not coplanar (the SCN—SCN torsion angle is nearly 8°).

The most remarkable feature of this structure is 2-fold: (a) The angles corresponding to each Ni(II) center are very different. For Ni(1) the angle N—Ni—S is 93.8° while for Ni(2) it is 88.2°; the Ni—N—C angles are 142.4° for Ni(1) and 165.2° for Ni(2); the Ni—S—C angles are 100.7° for Ni(1) and 105.8° for Ni(2). In comparison, the Ni—N—C angles for terminal SCN^- groups are 162.9 and 166.6°, respectively, very similar to those found in the mononuclear entity (166.1°). (b) The dihedral angles formed by the mean-plane $(NCS)_2$ and the N—Ni—S planes are also quite different: 32.8° and 14.4°, respectively (this dihedral angle would be 0° if the structure were completely planar).

$[\{Ni_2(1,2\text{-diamino-2-methylpropane})_4\}(\mu\text{-}NCS)_2](PF_6)_2$ (2). Figure 4 shows a view of the dimeric entity of **2**. Final positional parameters for the non-hydrogen atoms are listed in Table 3, and main bond distances and angles are given in Table 5. The structure consists of discrete dicationic $[\{Ni_2(1,2\text{-diamino-2-methylpropane})_4\}(\mu\text{-}NCS)_2]^{2+}$ dinuclear entities and two hexafluorophosphate anions. In this dimeric entity, two nickel(II) atoms are bridged by two thiocyanate ions in an end-to-end fashion, having two amines as blocking ligands. Owing to this geometrical configuration, the whole molecule is highly symmetric: there is an inversion center in the middle of the Ni—Ni vector which relates one part of the molecule to another. The Ni—N(amine) distances are 2.09–2.10 Å; the average Ni—N(NCS) distance is 1.925 Å, and the average Ni—S(SCN) distance is 2.83 Å. The two thiocyanate bridging ligands are coplanar, showing the following average angles: N—Ni—S = 86.8°, C—N—Ni = 166.7°, and C—S—Ni = 96.2°. Taking into account the disorder in the N and S atoms of the thiocyanato bridging groups (see Experimental Section), we give the average of the two respective values reported in Table 5. Finally, the dihedral angle formed by the $(NCS)_2$ plane and the N—Ni—S planes is only 5.8°, much closer to that of the completely planar structure than to that of the previous compound (**1**).

Magnetic Properties. The $\chi_M T$ vs T plots for the dinuclear complexes **1** and **2** are shown in Figure 5. The $\chi_M T$ values first increase, clearly indicating ferromagnetic behavior. At ca. 15 K, a maximum is observed, followed by a continuous decrease down to 4 K, indicating the contribution of zero-field splitting, D, and antiferromagnetic coupling between the dinuclear entities. Variable-temperature susceptibility data (4–300 K) were analyzed using the isotropic Ginsberg[13] model from the Hamiltonian

$$\mathcal{H} = -2JS_1S_2 - D(S_{1z}^2 + S_{2z}^2) - g\beta H(S_1 + S_2) - z'J'S\langle S\rangle$$

in which J is the intradimer exchange parameter, D the single-ion zero-field splitting, and $z'J'$ the quantity for the effective interdimer exchange assuming that $g_x = g_y = g_z = g$. For **1**, we introduced in the final formula the correction due to the presence of one mononuclear Ni(II) complex for two dinuclear entities. Least-squares fitting of the magnetic data leads to the parameters reported in Table 6. The minimized function was $R = \sum(\chi_M T^{calc} - \chi_M T^{obs})^2/\sum(\chi_M T^{obs})^2$. As previously indicated by Ginsberg,[13] the parameters D and $z'J'$ are strongly correlated

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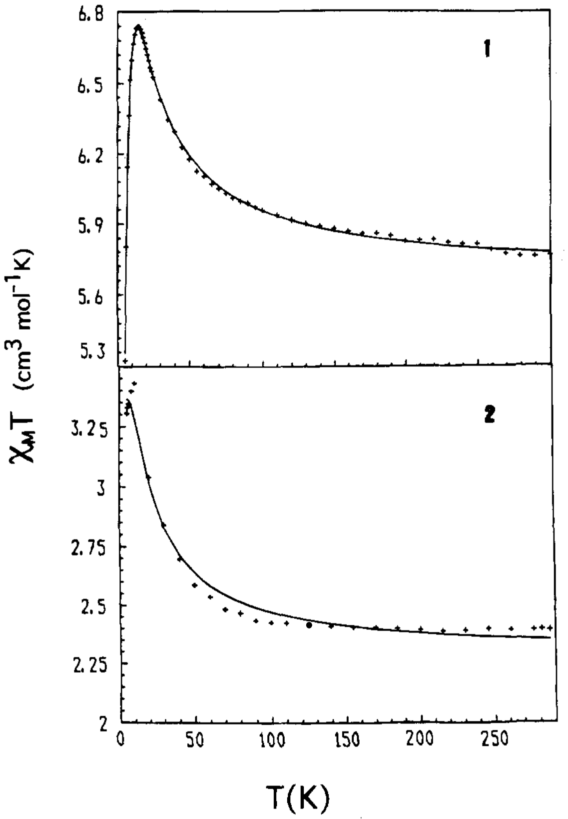


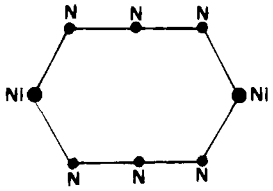
Figure 5. Experimental and calculated temperature dependence of $\chi_M T$ (cm^3 mol^{-1} K) for the dinuclear complexes **1** and **2**.

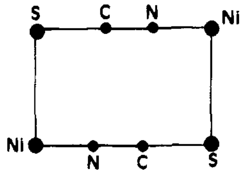
Table 6. Best Fitted Magnetic Parameters for $[\{Ni_2(1,2\text{-diamino-2-methylpropane})_3(NCS)_2\}(\mu\text{-}NCS)_2]_2[Ni(1,2\text{-diamino-2-methylpropane})_2(NCS)_2]\cdot H_2O$ (**1**) and $[\{Ni_2(1,2\text{-diamino-2-methylpropane})_4\}(\mu\text{-}NCS)_2](PF_6)_2$ (**2**)

compd	J, cm^{-1}	g	D, cm^{-1}	$z'J'$, cm^{-1}	R
1	4.30	2.13	−20.0	0.20	0.41×10^{-5}
	5.07	2.12		−0.42	0.14×10^{-3}
2	6.33	2.14	−2.0	−0.14	0.28×10^{-3}
	5.86	2.14		−0.22	0.38×10^{-3}

with each other but are only weakly correlated with g and J. Thus, it is impossible to calculate D and $z'J'$ accurately. For this reason, we have attempted to fit experimental results with the same Ginsberg formula but by assuming $D = 0$, as indicated by this author: the magnetic parameters J and g are very similar, but the R factor (defined above) is worse, and they are also reported in Table 6. Thus, for (**1**), if one takes into account the great asymmetry of the dinuclear complex, the D parameter could be high but the fitted −20 cm^{-1} makes no chemical sense. On the other hand, the best fitted $z'J'$ parameter is positive (0.2 cm^{-1}) when this intermolecular exchange is normally negative (antiferromagnetic). In consequence, we must assume that the two effects (D and $z'J'$) are present but that the values are strongly correlated and do not influence the J or g parameter. For **2**, with or without D, the magnetic parameters J, g, and $z'J'$ are similar but the R factor is worse (Table 6). For this reason, we have carried out magnetic susceptibility measurements at different fields[18] but without noticeable variations (supplementary Figure S1). The fit was not improved with these different fields. Taking into account the symmetry of each Ni(II), the fitted D value (−2.0 cm^{-1}) seems to be only a little greater. Consequently, as in the previous case, the two effects (D and $z'J'$) are correlated but do not influence the J or g value.

Interpretation of the Magnetic Results. In the classical work of Ginsberg[13] to interpret the ferromagnetic coupling in $[\{Ni_2(en)_4\}(\mu\text{-}NCS)_2]I_2$, assuming that the Ni—N—C and Ni—S—C angles are 180 and 90°, respectively (the real values are 167 and 100°), the author follows the valence-bond theory applying the Goodenough–Kanamori[19] rules or Anderson's expanded orbital theory.[14] With this theory, the antiferromagnetism in the idealized structures can be explained in terms of $e_g||\sigma$, $\pi||e'_g$ pathways. With these idealized angles (180 and 90°), the overlap is zero and the orthogonality of the orbitals creates the possibility of ferromagnetism. Hendrickson,[10e] by comparing the few structures reported in 1974 for azido, cyanato, and thiocyanato derivatives, assumes that there are two factors which can explain the difference in magnetic behavior: the deviation in planarity of the nickel(II) dimers and the symmetry of the dimeric species. Hendrickson argued that the first factor is less important, since the most important are the symmetry and energy of bridged molecular orbitals: for a symmetric bridging situation (a mirror plane perpendicular to the metal–metal vector), the antiferromagnetic coupling is enhanced





In Table 7 we report the magnetic parameters for SCN^- and $SeCN^-$ dinuclear complexes characterized structurally. We observe that all thiocyanato and selenocyanoto complexes are weakly ferromagnetically coupled and that this ferromagnetism is enhanced when the asymmetrization is more pronounced: selenocyanato is the case in which Ni—Se—C and Ni—N—C angles are the closest to those of the idealized geometry (90 and 180°).

In a procedure similar to that reported in our previous study of $[Ni_2(\mu\text{-}N_3)_2]$ complexes with end-to-end azido bridges,[2a] we have carried out extended Hückel calculations[20] for an idealized rectangular $[\{Ni_2(NH_3)_8\}(\mu\text{-}NCS)_2]^{2+}$ species. In the thiocyanato complexes, the behavior is very different from that observed with an azido bridging ligand.[2a] Assuming a movement from planarity to chairlike geometry, the molecular orbitals are always practically degenerate, indicating the possibility of ferromagnetism: the nonplanarity of the structure does not change the magnetic behavior, as in the azido case.[2a] This

Table 7. Main Structural and Magnetic Parameters for Dinuclear Nickel(II) Complexes with End-to-End NCS^- or $SeCN^-$ Bridging Ligands

compd	Ni—X—C, deg	Ni—N—C, deg	Ni—N, Å	Ni—X, Å	J, cm^{-1}	D, cm^{-1}	d,[a] Å	ref
$[\{Ni_2(en)_4\}(\mu\text{-}NCS)_2]I_2$	100.0	167.0	2.04	2.61	4.5	−3.3	0.05	10f
$[\{Ni_2(tren)_2\}(\mu\text{-}NCS)_2](BPh_4)_2$	100	167	2.04	2.61	2.4	−0.4	0.05	10e[b]
$[\{Ni_2(terpy)_2(NCS)_2\}(\mu\text{-}NCS)_2]\cdot 2H_2O$	100.0	159.0	2.04	2.62	4.9	−4.3	0.56	10a
$[\{Ni_2(2\text{-methyl})_3(NCS)_2\}(\mu\text{-}NCS)_2]$	100.7	165.2	2.06	2.55	4.3	−20	0.84	*c*
	105.8	142.4	2.10	2.64			0.42	
$[\{Ni_2(2\text{-methyl})_4\}(\mu\text{-}NCS)_2](PF_6)_2$	96.2	166.7	1.93	2.83	6.3	−2.0	0.16	*c*
$[\{Ni_2(Medpt)_2(NCSe)_2\}(\mu\text{-}NCSe)_2]$	97.4	169.1	2.04	2.82	8.8	1.5	0.25	21

[a] d = Ni—mean $(NSC)_2$ plane distance. [b] Not fully characterized. [c] This work.

agrees with the above mentioned Hendrickson theory. On the other hand, we have also carried out extended Hückel calculations passing from rectangular geometry to trapezoidal (azido-like) geometry. A change in the overlap of magnetic orbitals is calculated: for rectangular geometry, orthogonality between magnetic orbitals is observed, allowing ferromagnetic coupling. When the symmetry moves from rectangular to trapezoidal, a strong mixing in the wave functions ($d_{z^2} \pm d_{z^2}$; $d_{xy} \pm d_{xy}$) is observed, which hinders the calculation of the possible overlaps. In any case, overlap among the magnetic orbitals becomes more pronounced, creating the possibility of antiferromagnetic coupling. Unfortunately, thiocyanato complexes with this trapezoidal geometry, which would corroborate this theory, have not been reported to date.

From these semiempirical calculations, it is possible to realize that it is not necessary to have Ni—N—C and Ni—S—C angles very close to 180 and 90°, respectively, for a quasi-orthogonality of the molecular orbitals and, consequently, for an experimental ferromagnetism.

In conclusion, the main qualitative factors by which to interpret the ferromagnetism in the XCN^- (X = S, Se) derivatives are the values of the Ni—N—C and Ni—X—C angles. The more rectangular the geometry, the greater the orthogonality of the orbitals and, then, the greater the possibility of ferromagnetic coupling. The deviation from planarity is less important.

Thus, we can interpret, at least qualitatively, the new values shown in Table 7: complex **1**, which presents the greatest deviation from the planarity but with less pronounced rectangular geometry, has a J value of ca. 4 cm^{-1}, while the two complexes with the more pronounced rectangular geometry (**2** and the $SeCN^-$ derivative) present the strongest J parameters (6 and 9 cm^{-1}, respectively).

Obviously, with these qualitative molecular orbital methods, it is possible to evaluate only the possibility of the orthogonality of the orbitals, not the strength of the ferromagnetic term of the J parameter. New XCN^- dinuclear complexes are necessary to demonstrate the reliability of the theory and to interpret it accurately. Efforts in this respect are currently underway in our laboratory.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lenghts, bond angles, anisotropic thermal parameters, and hydrogen atom locations and a plot of $\chi_M T$ vs T for complex **2** at different fields (14 pages). Ordering information is given on any current masthead page.

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