New Dinuclear Penta- and Hexacoordinated Nickel(II) Complexes with μ-Azido Bridges. Crystal Structures of Ferromagnetically Coupled $(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2{\cdot}2H_2O$ and $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$

Ramon Vicente,*,† Albert Escuer,† Joan Ribas,† M. Salah el Fallah,† Xavier Solans,‡ and Mercé Font-Bardia‡

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

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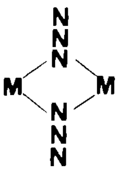
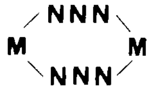
The synthesis, characterization, and properties of the dinuclear Ni(II) complexes $(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2{\cdot}2H_2O$ (**1**), $(\mu\text{-}N_3)_2[Ni(Me_4[12]N_3)]_2(ClO_4)_2{\cdot}H_2O$ (**2**), and $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**) are reported. $Me_3[12]N_3$ is 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, $Me_4[12]N_3$ is its 9-methyl derivative, and 232-N_4 is *N,N'*-bis(2-aminoethyl)-1,3-propanediamine. The crystal structure of **1** was solved by Patterson synthesis and refined to a discrepancy factor of 0.043. The crystals are monoclinic, space group $P2_1/n$, with lattice constants a = 10.151(2) Å, b = 15.478(3) Å, c = 12.317(2) Å, β = 106.60(2)°, and Z = 2. The dimer consists of two pentacoordinated nickel atoms coordinated to two 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene and two end-on azido bridging ligands. Each nickel(II) has a distorted trigonal bipyramidal environment. The crystal structure of **3** was solved by Patterson synthesis and refined to a discrepancy factor of 0.045. The crystals are monoclinic, space group $P2_1/n$, with lattice constants a = 11.892(2) Å, b = 13.611(3) Å, c = 9.340(1) Å, β = 106.03(1)°, and Z = 2. The dimer consists of two nickel atoms coordinated to two *N,N'*-bis(2-aminoethyl)-1,3-propanediamine and two end-on azido bridging ligands. Each nickel(II) has a distorted octahedral environment. Magnetic susceptibility data for the three compounds were recorded between 290 and 4 K, showing strong ferromagnetic coupling for **1** and **3** and strong antiferromagnetic coupling for **2**. These data were fitted giving the parameters J = 43.9 cm^{-1}, D = −13.4 cm^{-1}, and $z'J'$ = −1.0 cm^{-1} for **1**, J = −84.4 cm^{-1}, D = −15.7 cm^{-1}, and $z'J'$ = 0.9 cm^{-1} for **2**, and J = 33.8 cm^{-1}, D = −21.5 cm^{-1}, and $z'J'$ = −0.08 cm^{-1} for **3**. Magnetic interactions in these compounds are discussed in terms of bonding differences, and magneto–structural trends are given.

Introduction

It is well-known that the azide ion is a versatile anion which can act as a bridging ligand between two metal atoms in an end-to-end or an end-on fashion, both possibilities being structurally well characterized for nickel(II)[1–5] and copper(II)[6–9] cations. The general magnetic behavior for these two different coordination possibilities is well established in the literature: end-to-end coordination gives antiferromagnetically coupled compounds and end-on coordination gives ferromagnetically coupled compounds.[6]



end-on



end-to-end

In the case of the end-on coordination mode, the intensity of the ferromagnetic superexchange has been studied theoretically for (μ-1,1-azido) copper(II) compounds as a function of the Cu–N–Cu angle, and a maximum for 103° has been predicted.[8,9] In the case of copper(II) dinuclear derivatives, this rule agrees sufficiently well with the experimental data. On the other hand, Kahn and co-workers[10] have exhaustively studied the interaction between copper(II) ions through the azido bridge from a theoretical point of view (even with ab initio calculations on model systems), developing the new concept of spin polarization induced by the in-plane Π_g orbital of N_3^-. In the case of nickel(II) μ-azido dinuclear complexes only a qualitative theoretical approach was made by Hendrickson[4] on antiferromagnetically coupled complexes. To our knowledge, no theoretical study has been reported for ferromagnetically coupled μ-azido nickel(II) dinuclear complexes. On the other hand, only two examples of ferromagnetic bis(μ-1,1-azido) nickel(II) complexes, in which nickel(II) atoms are octahedrally coordinated, have been described,[1,2] and consequently the number of experimental data is clearly not sufficient to make magneto–structural correlations. Taking into account that the Ni–N–Ni angle cannot be controlled experimentally (at present it is not even possible to control the end-to-end or end-on coordination of the azido ligand), to extend the structural and magnetic examples we attempt to vary the Ni–N(azido) distances. According to the literature data[11] and our previous work,[12] a

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[†] Department of Inorganic Chemistry.

[‡] Department of Crystallography.

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good way to shorten the Ni–N(azido) distances is to change the hexacoordination of nickel(II) to pentacoordination. Thus, the aim of this work is to synthesize the first dinuclear pentacoordinate nickel(II) systems with bridging azido ligands and to compare them with the analogous octahedrally coordinated Ni(II) dimers in order to determine the influence of the structural parameters (especially the Ni–N(azido) distances and the Ni–N–Ni angles) on the strength of the exchange coupling. To synthesize the pentacoordinate new compounds, we have used $[12]N_3$ macrocycles, which normally give distorted trigonal bipyramidal coordination when reacting with nickel(II),[11,12] and we present the magnetic properties of the two pentacoordinated nickel(II) compounds $(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2$ (**1**) and $(\mu\text{-}N_3)_2[Ni(Me_4[12]N_3)]_2(ClO_4)_2{\cdot}H_2O$ (**2**) and the crystal structure of **1**. On the other hand, to increase the number of ferromagnetically coupled dinuclear μ-azido nickel(II) complexes, we also present the synthesis, crystal structure, and magnetic behavior of the new $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**) compound, in which the central atom is octahedrally coordinated.

Table I. Crystallographic Data and Data Collection and Refinement Parameters for $(\mu\text{-}N_3)_2[Ni(Me_3[12])]_2(ClO_4)_2{\cdot}2H_2O$ (**1**) and $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**)

formula	$[C_{24}H_{50}N_{12}Ni_2]\text{-}(ClO_4)_2{\cdot}2H_2O$	$[C_{14}H_{40}N_{14}Ni_2]\text{-}(ClO_4)_2$
fw	858.93	720.89
space group	$P2_1/n$	$P2_1/n$
a, Å	10.151(2)	11.892(2)
b, Å	15.478(3)	13.611(3)
c, Å	12.317(2)	9.340(1)
β, deg	106.60(2)	106.03(1)
V, Å^3	1854.6(9)	1453.0(7)
Z	2	2
ρ_{calc}, g cm^{-3}	1.538	1.647
μ(Mo Kα), cm^{-1}	12.25	15.42
radiation λ(Mo Kα), Å	0.710 69	0.710 69
T, °C	25	25
$R(F_o)^a$	0.043	0.045
$R_w(F_o)^b$	0.046	0.049

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o) = \sum w||F_o| - |F_c||/\sum w|F_o|$.

Experimental Section

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

Reagents. The complexes $[Ni(Me_3[12]N_3)OH]_2(ClO_4)_2$[11] and $[Ni(Me_4[12]N_3)OH]_2(ClO_4)_2$[13] were synthesized by literature-described methods.

Synthesis. To 1 mmol of $[Ni(Me_3[12]N_3)(H_2O)_2]^{2+}$ or $[Ni(Me_4[12]N_3)(H_2O)_2]^{2+}$ in 20 mL of water, obtained by neutralization with 10% perchloric acid of the corresponding $[Ni(Me_n[12]N_3)(OH)_2](ClO_4)_2$ compounds (n = 3, 4) was added a concentrated solution of the stoichiometric amount of sodium azide with continuous stirring. After 5 min, complex **1** precipitated as a green powder. Complex **2** was obtained as a green microcrystalline powder by addition of a concentrated solution of $NaClO_4$ and slow evaporation of the resulting solution. Yield: 70% approximately. **1** and **2** are soluble in water and in common organic solvents. Crystals suitable for the structure determination of compound **1** were obtained by slow evaporation of a concentrated aqueous solution mantained at 5 °C. Anal. Calc for $C_{24}H_{54}Cl_2N_{12}Ni_2O_{10}$ (**1**): C, 33.6; H, 6.3; N, 19.6. Found: C, 33.7; H, 6.4; N, 19.5. Calc for $C_{26}H_{56}Cl_2N_{12}Ni_2O_9$ (**2**): C, 36.0; H, 6.5; N, 19.4. Found: C, 36.2; H, 6.4; N, 19.5.

Compound **3** was obtained by mixing *N,N'*-bis(2-aminoethyl)-1,3-propanediamine, sodium azide, and nickel(II) perchlorate in water in a 1:1:1 ratio. By slow evaporation, mauve crystals of *catena*-$(\mu\text{-}N_3)[Ni(232\text{-}N_4)](ClO_4)$[14] were obtained mixed with blue crystals of dinuclear $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**). By washing with water, the blue crystals of $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ were separated from the mauve crystals, since *catena*-$(\mu\text{-}N_3)[Ni(232\text{-}N_4)](ClO_4)$ is very soluble in water and **3** is slightly soluble. The recrystallization of $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**) is not possible because when this compound is dissolved in water, a mauve solution is formed and only the *catena*-$(\mu\text{-}N_3)[Ni(232\text{-}N_4)](ClO_4)$ is obtained by slow evaporation.

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) were recorded from KBr pellets on a Perkin-Elmer 1330 IR spectrophotometer. Electronic spectra were obtained on a Shimadzu UV 160 A spectrophotometer, in the 1100–200-nm range. Magnetic measurements were carried out with a pendulum type magnetometer (MANICS DSM8) equipped with a 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. Calibration of the instrument was made by a magnetization measurement of a standard strontium ferrite. Diamagnetic corrections were estimated from Pascal's tables.

Crystallographic Structure Determination. Prismatic crystals (0.1 × 0.1 × 0.2 mm) of **1** and **3** were selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centring of 25 reflections ($8 < \theta < 12°$ for **1** and $12 < \theta < 16°$ for **3**) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique. For **1**, 3605 reflections were measured in the range $2 < \theta < 25°$, 2741 of which were assumed as observed by applying the condition $I < 2.5\sigma(I)$. For **3**, 2840 reflections were measured in the range $2 < \theta < 25°$, 2482 of which were assumed as observed by applying the condition $I > 2.5\sigma(I)$. For **1** and **3**, three reflections were measured every 2 h as orientation and intensity control. Significant intensity decay was not observed. Table I shows details of the data collection together with the structure refinement. Lorentz–polarization, but not absorption, corrections were made.

The structures of **1** and **3** 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 $w = (\sigma^2(F_o) + k|F_o|^2)^{-1}$ and k = 0.0011 for **1** and 0.0002 for **3**. f, f', and f'' were taken from ref 17. For **1**, two O atoms of the perchlorate ions were located in disordered positions. For **1** and **3**, all H atoms were determined from a difference synthesis. All H atoms were refined with an overall isotropic temperature factor, using a riding model for computed atoms. The final R factors were 0.043 (R_w = 0.046) (**1**) and 0.045 (R_w = 0.049) (**3**) for all observed reflections. The numbers of refined parameters were 326 (**1**) and 242 (**3**). For **1** and **3**, the maximum shift/esd = 0.1. Maximum and minimum peaks in the final difference syntheses were 0.3 and –0.3 e Å^{-3}, respectively. Final atomic coordinates are given in Tables II and III for **1** and **3**, respectively.

Results and Discussion

Synthesis. In the synthesis of these complexes, a small variation in the macrocyclic nonbridging ligand strongly influences the coordination mode of the bridging azido groups: magnetic measurements indicate end-to-end coordination for **2**, derived from $Me_4[12]N_3$, and the X-ray crystal structure shows end-on coordination for **1**, derived from $Me_3[12]N_3$. Comparison can be extended to two similar compounds synthesized by Wieghardt[5] et al., using the triaza macrocyclic ligands 1,5,9-triazacyclododecane and *N,N',N''*-trimethyl-1,4,7-triazacyclononane, which show double and triple end-to-end azido bridges, respectively. These results show that, for four published related complexes, three kinds of azido-bridged compounds are obtained, and very probably surprising new systems can be synthesized by modifying the nonbridging ligands. At the moment, it is not possible to control the result of a specific synthesis, and only a systematic study may lead to new results. The $232\text{-}N_4$ ligand provides us with another example of the low barrier that exists between both azido coordinations, since from the same solution crystallization of both end-on and end-to-end isomers occurs simultaneously.

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Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) with Their Estimated Standard Deviations for $(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2\cdot 2H_2O$ (**1**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{EQ}[a]
Ni	0.09799(4)	0.02299(3)	0.12714(3)	2.34(2)
Cl	0.24767(13)	0.19356(8)	0.59239(11)	5.26(6)
N(1)	0.0392(3)	0.0690(2)	–0.0395(3)	3.34(14)
N(2)	0.0420(3)	0.1444(2)	–0.0679(3)	3.66(15)
N(3)	0.0463(5)	0.2147(3)	–0.0949(4)	5.68(21)
N(4)	0.2894(3)	0.0753(2)	0.1631(3)	2.81(12)
N(5)	0.1477(3)	–0.0414(2)	0.2784(3)	2.86(12)
N(6)	0.0003(3)	0.1151(2)	0.1918(3)	3.35(13)
C(1)	0.3892(4)	0.0014(3)	0.1930(4)	3.50(17)
C(2)	0.3948(4)	–0.0359(3)	0.3092(4)	3.84(18)
C(3)	0.2667(4)	–0.0573(2)	0.3422(3)	3.10(14)
C(4)	0.0271(4)	–0.0604(3)	0.3171(4)	3.82(18)
C(5)	–0.0412(5)	0.0201(3)	0.3421(4)	4.49(21)
C(6)	–0.1024(4)	0.0782(3)	0.2421(4)	4.50(21)
C(7)	0.0914(5)	0.1790(3)	0.2672(4)	4.08(19)
C(8)	0.2054(5)	0.2116(3)	0.2228(4)	4.04(19)
C(9)	0.3232(5)	0.1502(3)	0.2410(5)	4.28(19)
C(10)	0.3421(5)	–0.0665(3)	0.1016(5)	4.30(21)
C(11)	0.5336(5)	0.0314(4)	0.1975(6)	5.31(26)
C(12)	0.3006(6)	–0.0955(3)	0.4588(4)	4.55(21)
O(1)	0.3074(14)	0.2588(8)	0.5407(11)	8.84(59)
O(2)	0.3029(12)	0.1876(8)	0.7113(11)	7.85(44)
O(3)	0.1077(6)	0.2085(5)	0.5518(5)	10.40(36)
O(4)	0.2640(6)	0.1100(3)	0.5498(5)	9.56(29)
O(1)′	0.3585(38)	0.2277(23)	0.5647(30)	7.84(186)
O(2)′	0.2436(41)	0.2237(26)	0.7081(33)	11.87(236)
OW(1)	0.3667(5)	0.1771(4)	–0.0255(5)	8.62(30)

[a] $B_{EQ} = 8\Pi({}^2/_3\Sigma_i\Sigma_j U_{ij}\mathbf{a}^*_i\mathbf{a}^*_j\mathbf{a}_i\mathbf{a}_j)$.

Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) with Their Estimated Standard Deviations for $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{EQ}[a]
Ni	0.10182(3)	0.08744(2)	0.08097(4)	1.86(2)
Cl	0.30839(9)	0.83141(7)	0.77527(11)	3.81(4)
N(1)	0.0975(3)	0.2408(2)	0.0402(4)	2.50(12)
N(2)	0.0220(3)	0.1314(2)	0.2462(3)	2.67(12)
N(3)	0.2645(3)	0.0811(2)	0.2436(4)	2.95(13)
N(4)	0.2059(3)	0.0657(2)	–0.0636(4)	3.01(13)
N(5)	0.0616(3)	–0.0673(2)	0.0903(3)	2.47(11)
N(6)	0.1147(2)	–0.1339(2)	0.1598(3)	2.48(11)
N(7)	0.1660(3)	–0.1981(2)	0.2257(4)	4.45(15)
C(1)	0.0148(3)	0.2849(3)	0.1132(4)	3.13(15)
C(2)	0.0334(4)	0.2396(3)	0.2644(4)	3.08(16)
C(3)	0.0576(5)	0.0782(3)	0.3889(5)	4.33(22)
C(4)	0.1882(5)	0.0850(3)	0.4665(5)	4.57(21)
C(5)	0.2663(4)	0.0345(3)	0.3873(4)	3.78(17)
C(6)	0.3478(3)	0.0373(3)	0.1730(5)	3.76(18)
C(7)	0.3300(4)	0.0813(3)	0.0208(6)	3.96(20)
O(1)	0.2569(3)	0.8433(2)	0.8957(4)	5.70(18)
O(2)	0.2184(4)	0.8117(6)	0.6446(6)	13.20(41)
O(3)	0.3900(6)	0.7574(4)	0.7978(6)	10.38(32)
O(4)	0.3607(5)	0.9188(3)	0.7458(7)	9.74(35)

[a] $B_{EQ} = 8\Pi({}^2/_3\Sigma_i\Sigma_j U_{ij}\mathbf{a}^*_i\mathbf{a}^*_j\mathbf{a}_i\mathbf{a}_j)$.

On the other hand, Curtis et al.[11] have pointed out that the ligand $Me_3[12]N_3$ undergoes fast basic hydrolysis, giving acetone and 3,3′-dipropylamine (dpt).We observe that green fresh solutions of complex **1** maintained at room temperature and neutral pH become intensely blue in 3–4 days. Crystallization of these solutions gives a 1 D compound formulated as *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$ as the product of slow hydrolysis of $Me_3[12]N_3$.[18] For this reason, crystals suitable for the X-ray determination of compound **1** must be obtained from cold solutions with the aim of preventing the hydrolysis of the macrocycle. The complex derived from $Me_4[12]N_3$ does not hydrolyze at room temperature for at least 2 weeks, but all attempts to obtain good crystals were unsuccessful.

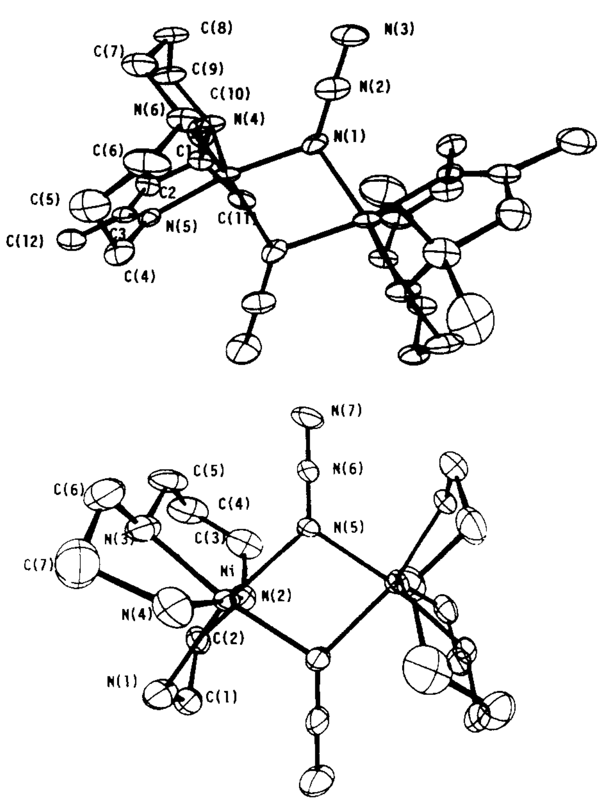

Figure 1. Molecular structures showing the atom-labeling schemes for $(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2\cdot 2H_2O$ (**1**) and for $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**).

Table IV. Main Bond Lengths (Å) and Angles (deg) for $(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2\cdot 2H_2O$ (**1**)

N(1)–Ni	2.092(3)	N(6)–Ni	2.025(3)
N(1)′–Ni	2.067(3)	N(1)–N(2)	1.221(4)
N(4)–Ni	2.034(3)	N(2)–N(3)	1.142(5)
N(5)–Ni	2.045(3)	Ni–Ni′	3.273(1)
N(1)–Ni–N(1)′	76.2(1)	N(5)–Ni–N(6)	90.3(1)
Ni–N(1)–Ni	103.8(3)	N(4)–Ni–N(1)′	147.9(1)
N(4)–Ni–N(1)	93.7(1)	N(5)–Ni–N(1)′	95.4(1)
N(5)–Ni–N(1)	170.7(1)	N(6)–Ni–N(1)′	111.0(1)
N(6)–Ni–N(1)	96.4(1)	N(2)–N(1)–Ni	125.7(3)
N(4)–Ni–N(5)	91.4(1)	N(3)–N(2)–N(1)	179.0(5)
N(4)–Ni–N(6)	100.3(1)		

Description of the Structures. $(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2\cdot 2H_2O$ (1). The unit cell contains two dinuclear [NiNi] dications, two perchlorate anions and two water molecules. Selected bond lengths and angles are listed in Table IV. Other distances and angles may be found in the supplementary material. The molecular structure consists of isolated $[Ni_2(Me_3[12]N_3)_2(N_3)_2]^{2+}$ dinuclear units, in which the two metallic centers are linked only at the N-ends of two azido bridging groups. The structure of the complex molecule is shown in Figure 1. The Ni_2N_2 unit has a crystallographic inversion center. The nickel atoms occupy an intermediate environment between square pyramidal and trigonal bipyramidal. We have quantified the distortion of the coordination polyhedron around the nickel(II) cation by using the Muetterties and Guggenberger[19] description and by considering the regular square pyramid (SP) and the ideal trigonal bipyramid (TBP) as the limiting geometries. From the observed dihedral angles the parameter δ (0 for tbp and 1 for sp) is found to be 0.09. Consequently, we can consider the nickel(II) environment a TBP. The axial TBP positions are occupied by the N(1) and the N(5) atoms and the equatorial ones by the N(4), N(6), and N(1)′ atoms. The nickel(II)–N(azido) distances

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[18] Vicente, R.; Escuer, A.; Ribas, J.; Solans, X. *Inorg. Chem.* **1992**, *31*, 1726.

[19] Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

Table V. Main Bond Lengths (Å) and Angles (deg) for $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**)

N(1)-Ni	2.119(3)	N(5)'-Ni	2.166(2)
N(2)-Ni	2.109(3)	N(6)-N(5)	1.190(4)
N(3)-Ni	2.106(3)	N(7)-N(6)	1.144(4)
N(4)-Ni	2.090(3)	Ni-Ni'	3.434(1)
N(5)-Ni-N(5)'	75.1(1)	N(5)-Ni-N(1)	165.8(1)
Ni'-N(5)-Ni	104.9(2)	N(5)-Ni-N(2)	95.6(1)
N(2)-Ni-N(1)	81.9(1)	N(5)-Ni-N(3)	95.8(1)
N(3)-Ni-N(1)	98.1(1)	N(5)-Ni-N(4)	93.7(1)
N(3)-Ni-N(2)	89.6(1)	N(5)'-Ni-N(1)	91.1(1)
N(4)-Ni-N(1)	90.7(1)	N(5)'-Ni-N(2)	94.8(1)
N(4)-Ni-N(2)	168.4(1)	N(5)'-Ni-N(3)	170.2(1)
N(4)-Ni-N(3)	82.5(1)	N(5)'-Ni-N(4)	94.3(1)

are slightly different, 2.092(3) and 2.067(3) Å, respectively, giving a quasi-symmetrical and planar $Ni(N_3)_2Ni$ entity. The Ni–N(1)–Ni angle is 103.8°(3). As expected, the Ni–N distances (N(azido) and N(macrocycle)) are shorter than those observed in similar octahedral compounds of nickel(II) by ca. 0.1 Å.

$(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (3). The unit cell contains two dinuclear [NiNi] dications and two perchlorate anions. The molecular structure consists of isolated $[Ni_2(232\text{-}N_4)_2(N_3)_2]^{2+}$ dinuclear units, in which the two metallic centers are linked only at the N-ends of two azido bridging groups. Selected bond lengths and angles are listed in Table V. A view of the dinuclear unit with the atom-labeling scheme and the unit cell are presented in Figure 1.

The nickel atoms occupy an asymmetrical octahedral environment consisting of two N-end atoms of the azide bridging ligand and four N atoms of the amine ligand. The Ni–N(azido) distances are 2.167(2) and 2.166(2) Å. The Ni–N(5)–Ni' angle is 104.9(2)°, and the compound also shows a crystallographic inversion center in the planar and symmetrical Ni_2N_2 unit.

Infrared Spectroscopy and Electronic Spectra. The ν_{as} azide band is found at 2040 cm^{-1} for **1**, 2040–2100 cm^{-1} for **2**, and 2060 cm^{-1} for **3**. The remaining bands of this group are masked by the macrocyclic and perchlorate bands, which appear at normal frequences. Electronic spectra of fresh aqueous solutions of **1** and **2** are typical of pentacoordinated nickel(II) systems, showing two absorptions centered at 381–616 nm for **1** and at 388–626 nm for **2**. This shift of ca. 10–12 nm between $Me_3[12]N_3$ and $Me_4[12]N_3$ is in good agreement with the literature data.[12] For **3**, the electronic spectrum of a fresh mauve aqueous solution shows three absorptions centered at 346, 554, and 907 nm. After 1 h at room temperature, the electronic spectrum evolves to the *catena*-$(\mu\text{-}N_3)[Ni(232\text{-}N_4)](ClO_4)$ aqueous solution absorption spectrum.

Magnetic Behavior. The variable-temperature magnetic susceptibility data were recorded for the compounds between 290 and 4 K. Compounds **1** and **3** are strongly ferromagnetically coupled, and compound **2** shows a strong antiferromagnetic behavior. Plots of $\chi_M T$ vs T for **1** and **3** (Figure 2) show a typical ferromagnetic behavior: an increase in the effective magnetic moment with decreasing temperature. At 290 K they show $\chi_M T$ values of 2.91 and 2.76 cm^3 K mol^{-1} for **1** and **3**, respectively. This quantity increases up to maximum values of 3.69 cm^3 K mol^{-1} at 35 K for **1** and 3.77 cm^3 K mol^{-1} at 25 K for **3**. Below this temperature, $\chi_M T$ decreases gradually due to intermolecular interactions and ZFS of ground state ($S = 2$), reaching values of 2.43 cm^3 K mol^{-1} for **1** at 4 K and 2.99 cm^3 K mol^{-1} for **3** at 4 K. A plot of $\chi_M T$ vs T for **2** (Figure 2) shows behavior corresponding to a very strong antiferromagnetic coupling: the $\chi_M T$ value at 290 K is 2.18 cm^3 K mol^{-1} and decreases to 0 at low temperature; the χ_M vs T plot shows a maximum for χ_M of 9.79×10^{-3} cm^3 mol^{-1} at 119 K.

The $\chi_M T$ vs temperature curves for **1** and for **3** and the χ_M vs temperature curve for **2** were least-squares fitted to the theoretical expression of the magnetic susceptibility of Ginsberg et al.,[20] from the Hamiltonian

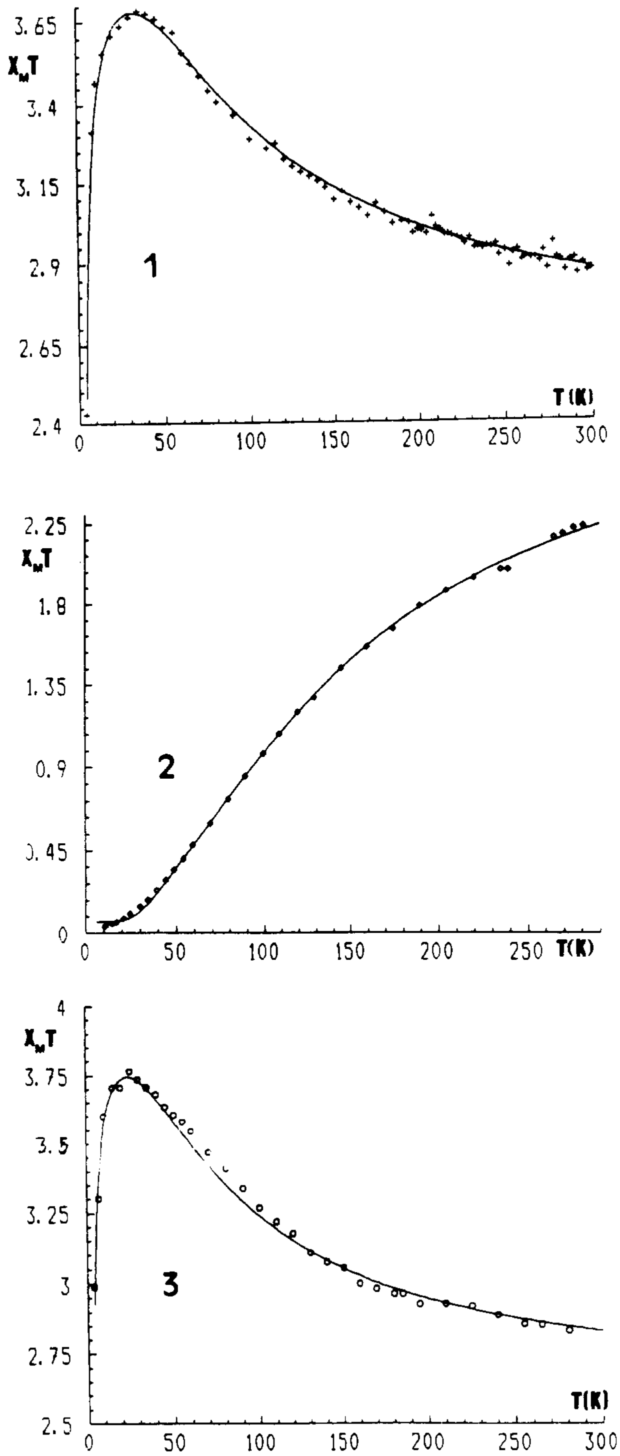

Figure 2. Experimental and calculated (solid line) temperature dependence of $\chi_M T$ for $(\mu\text{-}N_3)_2[Ni(Me_3[12]N_3)]_2(ClO_4)_2\cdot 2H_2O$ (**1**), $(\mu\text{-}N_3)_2[Ni(Me_4[12]N_3)]_2(ClO_4)_2\cdot H_2O$ (**2**), and $(\mu\text{-}N_3)_2[Ni(232\text{-}N_4)]_2(ClO_4)_2$ (**3**).

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

in which J is the intradimer exchange parameter, D the single-ion zero-field splitting, and $Z'J'$ the quantity for effective interdimer exchange; it is assumed that $g_x = g_y = g_z \equiv g$. The resulting χ_M expression is

$$\chi_M = 2Ng^2\beta^2/3k[F_1/(T - 4Z'J'F_1) + 2F'/(1 - 4Z'J'F')]$$

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[20] Ginsberg, A. P. *Inorg. Chim. Acta Rev.* **1971**, *5*, 45.

Table VI. Main Superexchange Parameters for the Reported Ferromagnetic Nickel(II) Dinuclear Complexes[a]

compound	Ni–Ni, Å	Ni–N, Å	Ni–N′, Å	Ni–N–Ni, deg	J, cm^{-1}	ref
$(\mu\text{-N}_3)_2[\text{Ni}(\text{Me}_3[12]\text{N}_3)]_2(\text{ClO}_4)_2$	3.273	2.068	2.092	103.8	43.9	*b*
$(\mu\text{-N}_3)_2[\text{Ni}(\text{Medpt})(\text{N}_3)]_2$	3.448	2.217	2.169	103.7	49.1	2
$(\mu\text{-N}_3)_2[\text{Ni}(\text{terpy})(\text{N}_3)]_2$	3.276	2.038	2.198	101.3	20.1	1
$(\mu\text{-OCN})_2[\text{Ni}(\text{terpy})(\text{H}_2\text{O})]_2(\text{PF}_6)_2$	3.193	2.044	2.195	97.7	4.6	24
$(\mu\text{-N}_3)_2[\text{Ni}(232\text{-N}_4)]_2(\text{ClO}_4)_2$	3.423	2.167	2.167	104.9	33.8	*b*

[a] All compounds are centrosymmetric, and the Ni_2N_2 central ring is planar. Ni–N and Ni–N′ are the distances between the nickel and the N(1,1-azido) atoms. [b] This work.

F_1 and F' being complicated functions of temperature, zero-field splitting, and the intradimer exchange parameter J. This expression gives accurate values of J and g, but parameters D and $Z'J'$ are not well determined from magnetic susceptibility data.[21,22] The best-fitting parameters obtained are $J = 43.9$ cm^{-1}, $g = 2.31$, $D = -13.4$ cm^{-1}, and $Z'J' = -1.0$ cm^{-1} for **1**, $J = 33.8$ cm^{-1}, $g = 2.27$, $D = -21.5$ cm^{-1}, and $Z'J' = -0.08$ cm^{-1} for **3**, and $J = -84.4$ cm^{-1}, $g = 2.47$, $D = -15.7$ cm^{-1}, and $Z'J' = 0.9$ cm^{-1} for **2**. The high values of g can be considered normal for pentacoordinate nickel(II) systems according to the literature data.[12,23] The J values indicate that the superexchange interaction is extremely effective, and comparison with literature data for nickel(II) dinuclear complexes with μ-azido bridges shows that these compounds are placed between the most ferromagnetic, **1** and **3**, and antiferromagnetic, **2**, μ-azido complexes of nickel(II) reported up to now.

Discussion

For **2** the J value (-84.4 cm^{-1}) is similar to the J values reported in the literature for analogous end-to-end azido compounds: -70 and -90 cm^{-1} for the double-bridged μ-azido compounds $(\mu\text{-N}_3)_2[\text{Ni}(\text{tren})]_2(\text{BPh}_4)_2$[4] and $(\mu\text{-N}_3)_2[\text{Ni}(1,5,9\text{-triazacyclododecane})(\text{N}_3)]_2$,[5] respectively. For single-[4] and triple-bridged[5] μ-1,3-azido compounds, the literature values are -24.6 and -71 cm^{-1}, respectively. Since structural data for **2** are not available, no magneto–structural correlation can be made.

In order to discuss the magnetic data for the ferromagnetically coupled complexes **1** and **3**, we have tried to compare their structural and magnetic parameters with those reported for two ferromagnetically structurally characterized analogous $(\mu\text{-N}_3)_2$ complexes: $(\mu\text{-N}_3)_2[\text{Ni}(\text{terpy})(\text{N}_3)]_2$[1] and $(\mu\text{-N}_3)_2[\text{Ni}(\text{Medpt})(\text{N}_3)]_2$.[2] For comparative purposes, we can add the very similar μ-1,1-cyanato complex $(\mu\text{-OCN})_2[\text{Ni}(\text{terpy})(\text{H}_2\text{O})]_2(\text{PF}_6)_2$,[24] which also possesses the Ni_2N_2 cyclic entity. These data are gathered in Table VI.

From Table VI, we can see that **1** has the shorter (ca. 0.1 Å) average Ni–N(azido) distance. This agrees with the above mentioned assumption that pentacoordinate complexes have shorter Ni–N distances. From Table VI, no correlation can be seen between Ni–N(azido) average distance and the J value: the longest Ni–N(azido) distance in $(\mu\text{-N}_3)_2[\text{Ni}(\text{Medpt})(\text{N}_3)]_2$ corresponds to the highest J value, and a plot of J vs Ni–N(azido) average distance presents a random distribution.

We can try to find a correlation between the Ni–N–Ni angle and the J values. From the data of Table VI, the parameter J could be correlated only with the Ni–N–Ni value in the sense that greater Ni–N–Ni angles correspond to a most effective ferromagnetic superexchange. This result is placed in the same context as the study performed by Kahn et al.,[8] which found that for comparable copper(II) dinuclear complexes the main structural parameter related to the superexchange pathway is the Cu–N–Cu angle. Extended Hückel calculations on Cu_2O_2 and Cu_2N_2 rings show that orthogonality occurs for an angle around 90° for hydroxo bridges, and for a less electronegative bridge, such as a nitrogen of an azido group, orthogonality is displaced toward larger values of the Cu–N–Cu angle and is found at 103°. In the case of nickel(II) complexes, experimental data indicate the same correlation, and extended Huckel OM calculations on a model penta- or hexacoordinate nickel-end-on azido dimer by means of the CACAO[25] program also show a minimum of antiferromagnetic contribution around 110° for both geometries. More structural data, particularly involving Ni–N–Ni angles with values $<95°$ and values $>104°$ (if it is experimentally possible), will be interesting to test this assumption properly.

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Supplementary Material Available: Text giving experimental details of the structure determinations for **1** and **3**, tables of complete crystallographic data, anisotropic thermal parameters, hydrogen atom coordinates, and all the angles and distances for **1** and **3**, and OM Walsh diagrams for penta- and hexacoordinate nickel(II)-end-on $(\mu\text{-N}_3)_2$ molecules (16 pages). Ordering information is given on any current masthead page.

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