1278 *Inorg. Chem.* **1995**, *34*, 1278−1281

X-ray Structure Determination and Magnetic Behavior of the New Uniform $S = 1$ Chain $[\{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$. Magneto−Structural Correlations

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Received July 12, 1994

Introduction

The azido ligand allows an efficient superexchange pathway between paramagnetic ions such as nickel(II), in dinuclear,[1−8] tetranuclear,[9] monodimensional[10−14] and bidimensional[15] compounds. In the monodimensional cases, several structurally different antiferromagnetically coupled 1D systems, derived from the end-to-end (EE) coordination of the bridging azido ligand, have been reported. These 1D systems can be classified, from the structural and magnetic point of view, as **alternating** or **uniform** chains. Focusing our attention on the **uniform** systems, we have reported a series of monobridged azido *trans*-$(-N_3-NiL-N_3-)_n$ 1D systems tailored from *trans* tetraammine complexes of nickel(II), with a generic formula $[\{Ni(L)(\mu\text{-}N_3)\}_n](ClO_4)_n$.[11−13] The J values have been correlated with structural parameters (mainly bond and torsion angles) by using MO extended Hückel calculations.[12−14]

We now present the full structural and magnetic characterization of another **uniform** monobridged μ-azido chain: the compound $[\{Ni((Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ (**1**), where $Me_2[14]$-1,3-dieneN$_4$ is the macrocycle 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene. For **1**, the magnetic behavior indicates the greatest antiferromagnetic $|J|$ parameter (−97.8 cm^{-1}) which has been found in this series of uniform *trans*-$(-N_3-NiL-N_3-)_n$ chains. The experimental J parameter correlates well with the structural parameters.

It has been established that Ni(III) and Ni(I) complexes of cyclam and cyclam-like ligands act as catalytic agents in some important chemical processes with different efficiencies,[16−19] and $[Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)](ClO_4)_2$ is a good nickel(II) catalyst for DNA oxidation.[16] The catalytic efficiency can be related to the cyclam-like structure of the ligands.[19] No structural complexes with the 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene ligand have been published to date; our study of $[\{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ provides the first structural description of the $[Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)]^{2+}$ fragment.

Experimental Section

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

$[\{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$. A solution of 2 mmol of $[Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)][ZnCl_4]$[20] in 30 mL of water was mixed with 2 mmol of NaN$_3$ in 20 mL of water and 4 mmol of $NaClO_4\cdot H_2O$ in 20 mL of water. Slow evaporation of the resulting solution gave dark red crystals of the corresponding 1D compound after several days. Elemental analysis (C, H, N, Cl) was in good agreement with the title compound.

Spectral and Magnetic Measurements. The IR spectrum was recorded on a Perkin-Elmer 1330 IR spectrophotometer. Magnetic measurements were carried out in the 300−4 K temperature range on polycrystalline samples with a pendulum type magnetometer (Manics DSM8) equipped with a helium continuous-flow cryostat and a Drusch EAF 16UE electromagnet. The magnetic field was approximately 1.5 T. Diamagnetic corrections were estimated from Pascal's tables.

X-ray Crystallography. A prismatic red crystal (0.1 mm × 0.1 mm × 0.2 mm) of $[\{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ (**1**) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12 \leq \theta \leq 21°$) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan technique. A total of 3200 reflections were measured in the range $1.19 \leq \theta \leq 31.94°$; 2515 reflections were assumed as observed by applying the condition $I \geq 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz−polarization but not absorption corrections were made. The crystallographic data, conditions used for the intensity data collection, and some features of the structure refinement are listed in Table 1. The structure was solved by a Patterson synthesis, using the SHELXS computer program,[21] and refined by the full-matrix least-squares method, with the SHELX93 computer program.[22] The function minimized was $\sum w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0983P)^2 + 0.0538P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f', and f'' were taken from ref 23. The extinction coefficient was 0.0000(1). Twenty-four H atoms were computed and refined with an overall isotropic temperature factor using a riding model. The number of refined parameters was 248. Maximum shift/esd = 0.30. Mean shift/esd = 0.08. Maximum and minimum peaks in final

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Table 1. Crystal Data for $[\{\mathrm{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)}\}_n](\mathrm{ClO_4})_n$

chem formula	$[\mathrm{C_{12}H_{26}N_7Ni}]_n(\mathrm{ClO_4})_n$	T, K	293(2)
a, Å	10.748(5)	λ(Mo Kα), Å	0.710 69
c, Å	34.360(5)	d_{calc}, g cm^{-3}	1.280
V, Å^3	3969(3)	μ(Mo Kα), cm^{-1}	11.31
Z	8	R^a	0.0233
fw	426.55	$R_w{}^b$	0.0605
space group	$I\bar{4}$		

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

Table 2. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $[\{\mathrm{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)}\}_n](\mathrm{ClO_4})_n$ (**1**)

atom	x	y	z	U(eq)^a
Ni	0.2501(1)	0.4023(1)	0.8750(1)	37(1)
Cl(1)	0.0	0.0	0.2026(1)	63(1)
Cl(2)	0.5	1.0	0.9524(1)	63(1)
N(1)	0.2443(2)	0.5464(3)	0.9126(1)	50(1)
N(2)	0.2677(3)	0.2628(3)	0.9147(1)	49(1)
N(3)	0.2319(3)	0.2630(3)	0.8354(1)	48(1)
N(4)	0.2551(2)	0.5477(3)	0.8378(1)	54(1)
N(5)	0.0487(2)	0.4009(2)	0.8793(1)	53(1)
N(6)	0.0	0.5	0.8790(1)	44(1)
N(7)	0.4513(2)	0.4030(2)	0.8712(1)	55(1)
N(8)	0.5	0.5	0.8714(1)	45(1)
C(1)	0.2170(4)	0.5297(4)	0.9541(1)	73(1)
C(2)	0.2678(5)	0.4064(5)	0.9698(1)	79(1)
C(3)	0.2125(4)	0.2894(4)	0.9524(1)	71(1)
C(4)	0.2239(3)	0.1493(3)	0.8954(1)	58(1)
C(5)	0.2769(3)	0.1494(3)	0.8553(1)	62(1)
C(6)	0.2869(4)	0.2907(4)	0.7967(1)	70(1)
C(7)	0.2318(5)	0.4067(5)	0.7795(1)	80(1)
C(8)	0.2850(4)	0.5306(5)	0.7960(1)	74(1)
C(9)	0.2637(3)	0.6522(3)	0.8541(2)	64(1)
C(10)	0.2367(3)	0.6537(3)	0.8962(1)	61(1)
C(11)	0.3002(6)	0.7723(4)	0.8337(2)	103(2)
C(12)	0.1993(5)	0.7713(4)	0.9158(2)	100(2)
O(1)	−0.0096(4)	0.1094(3)	0.2258(1)	93(1)
O(2)	0.1249(14)	0.0106(14)	0.1876(4)	91(4)
O(2′)	0.0878(16)	0.0111(18)	0.1724(5)	112(5)
O(3)	0.6109(4)	0.9898(4)	0.9752(1)	97(1)
O(4)	0.4956(20)	0.8714(13)	0.9363(5)	97(4)
O(4′)	0.4898(19)	0.9157(13)	0.9230(5)	107(5)

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

difference synthesis were 0.531 and −0.304 e Å^{-3}, respectively. Final atomic coordinates are given in Table 2. We have published[13] a communication describing the X-ray crystal structure determination of $[\{\mathrm{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)}\}_n](\mathrm{ClO_4})_n$ using a poor crystal (R = 0.035, R' = 0.037; 813 reflections, 227 refined parameters). The crystallographic data for this previous structure determination have some differences from the present ones due to the use of a very good crystal in the new X-ray structure determination.

Results and Discussion

IR Data. The ν_{as} of the azide group appears at 2060 cm^{-1} (vs, broad), and the other two bands of the $\mathrm{N_3}^-$ group (ν_{s} and δ) are masked by the amine and perchlorate bands. Bands attributable to the ligand (3350−3270, 2960−2890, and a set of bands between 1600 and 800 cm^{-1}) and the perchlorate anion (1100, 620 cm^{-1}) appear at normal frequencies.

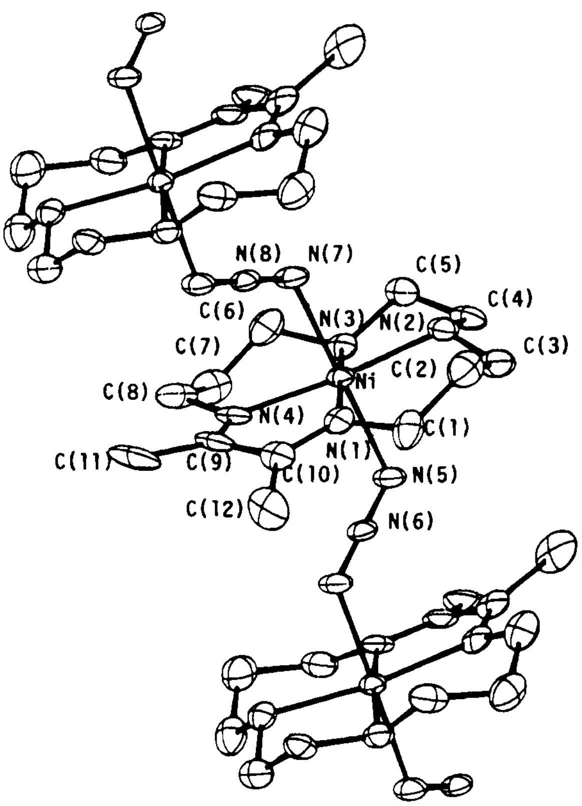

Figure 1. Labeled diagram of $[\{\mathrm{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)}\}_n]^{n+}$ in **1**.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\{\mathrm{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)}\}_n](\mathrm{ClO_4})_n$ (**1**)

	Distances		
N(1)−Ni	2.017(3)	N(2)−Ni	2.034(3)
N(4)−Ni	2.020(3)	N(7)−Ni	2.167(2)
N(3)−Ni	2.033(3)	N(5)−Ni	2.169(2)
N(5)−N(6)	1.187(2)	N(7)−N(8)	1.167(2)
N(6)−N(5)$^{\mathrm{iii}}$	1.187(2)	N(8)−N(7)$^{\mathrm{iv}}$	1.167(2)
Ni−Ni′	5.767	Ni−Ni″	5.771
N(1)−C(10)	1.286(6)	N(1)−C(1)	1.466(5)
N(2)−C(3)	1.456(5)	N(2)−C(4)	1.465(5)
N(3)−C(5)	1.480(5)	N(3)−C(6)	1.486(5)
N(4)−C(9)	1.258(6)	N(4)−C(8)	1.483(6)
C(1)−C(2)	1.532(7)	C(2)−C(3)	1.514(7)
C(4)−C(5)	1.490(5)	C(6)−C(7)	1.500(7)
C(7)−C(8)	1.556(7)	C(9)−C(10)	1.475(6)
C(9)−C(11)	1.520(5)	C(10)−C(12)	1.488(5)
	Angles		
N(4)−Ni−N(1)	79.11(11)	N(1)−Ni−N(5)	86.05(11)
N(1)−Ni−N(3)	172.33(12)	N(4)−Ni−N(5)	94.31(10)
N(4)−Ni−N(3)	98.6(2)	N(3)−Ni−N(5)	86.84(12)
N(1)−Ni−N(2)	98.10(14)	N(2)−Ni−N(5)	92.43(11)
N(4)−Ni−N(2)	172.5(12)	N(7)−Ni−N(5)	179.6(2)
N(3)−Ni−N(2)	85.09(10)	N(6)−N(5)−Ni	115.67(14)
N(1)−Ni−N(7)	93.83(11)	N(8)−N(7)−Ni	116.8(2)
N(3)−Ni−N(7)	93.29(12)	N(5)$^{\mathrm{iii}}$−N(6)−N(5)	179.0(5)
N(2)−Ni−N(7)	87.17(12)	N(7)−N(8)−N(7)$^{\mathrm{iv}}$	179.2(6)
N(4)−C(9)−C(10)	115.5(3)	N(4)−C(9)−C(11)	124.9(5)
C(10)−C(9)−C(11)	119.5(5)	N(1)−C(10)−C(9)	114.0(3)
N(1)−C(10)−C(12)	125.4(5)	C(9)−C(10)−C(12)	120.5(5)

Description of the Structure: $[\{\mathrm{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)}\}_n](\mathrm{ClO_4})_n$ (1). The structure consists of 1D nickel−azido chains, isolated by $\mathrm{ClO_4}^-$ anions which are found in the interchain space. No hydrogen bonds between the chains or perchlorate groups are present. A labeled diagram is shown in Figure 1. The main bond lengths and angles are gathered in Table 3. In the chain structure, each Ni(II) atom is coordinated by one $\mathrm{Me_2[14]\text{-}1,3\text{-}dieneN_4}$ ligand and two azido ligands in an octahedral *trans* arrangement elongated in the direction of the chain. The bond distances from the nickel atom to the nitrogen atoms of the azido bridge are Ni−N(5) 2.169(2) Å and Ni−N(7) 2.167(2) Å. The two bond angles related to the azido ligands are Ni−N(5)−N(6) 115.67(14)° and Ni−N(7)−N(8) 116.8(2)°, the larger angle corresponding to the shorter bond distance. The N(azido)−N(azido) bond distances are alternatively different: N(6)−N(5), 1.187(2) Å; N(7)−N(8),

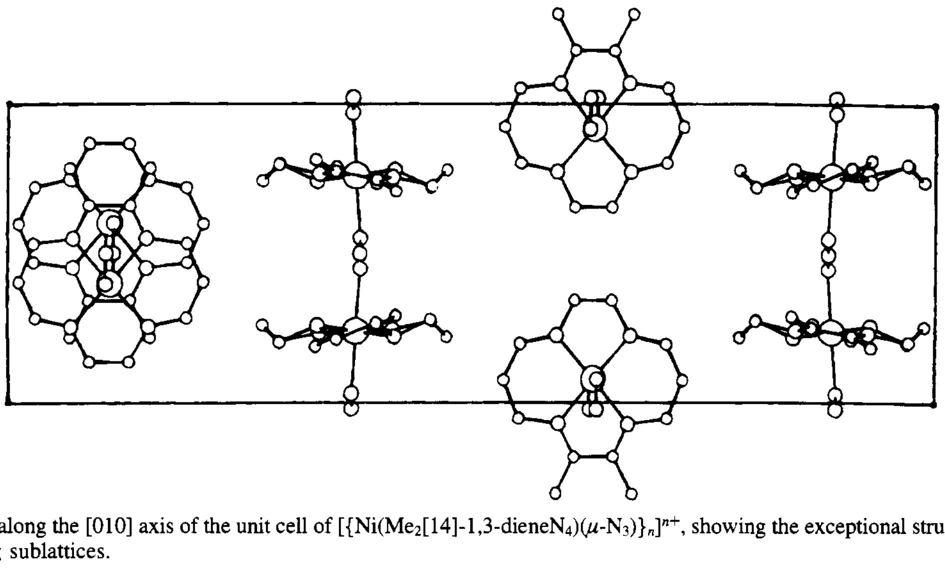

Figure 2. Projection along the [010] axis of the unit cell of $[\{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n]^{n+}$, showing the exceptional structure of perpendicular chains in neighboring sublattices.

1.167(2) Å. Each $Ni-N_3-Ni$ fragment is practically coplanar (the torsion angle is 171.3°). The torsion angle between neighboring azido groups is close to 0° (4.3°), giving an almost planar chain. The dihedral angle between two neighboring $[Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)]$ planes is 6.2°. From the structural parameters $[\{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ is, strictly, an alternating chain, but due to the little difference found in these parameters, we can consider this 1D product as a **uniform** chain with a mean Ni−N(azido) distance of 2.168 Å and a mean Ni−N−N angle of 116.2°.

In the $[Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)]^{2+}$ fragment, the NiN_4 atoms form a plane (maximum deviation of the mean plane −0.128 Å for N(1)). The double bond C−N distances (N(1)−C(10) and N(4)−C(9) distances are respectively 1.286(6) and 1.258(6) Å) are clearly less than the single bond C−N distances. The torsion C(11)−C(9)−C(10)−C(12) angle is 22.5°. The N(4), C(9), C(10), and N(1) atoms are placed in the same plane (maximum deviation of the mean plane 0.086 Å for C(9)). The angle between this plane and the NiN_4 plane is 7.83°. The N−Ni−N angles in the NiN_2C_3 rings are, as expected, greater than the same angles in the NiN_2C_2 rings (98.10(14) and 98.6(2)°; 85.09(10) and 79.11(11)° respectively). The $N_{imine}-Ni-N_{imine}$ angle (79.11(11)°) is less than the $N_{amine}-Ni-N_{amine}$ angle (85.09(10)°) in the NiC_2N_2 rings. It is interesting to point out the tetrahedral distortion in the NiN_4 central plane: the N(1)−N(2)−N(3)−N(4) torsion angle is 8.9°.

All the reported uniform or alternating $(-N_3-NiL-N_3-)_n$ 1D compounds can be described as a packing of isolated parallel 1D entities,[10-12,14] but as can be seen in Figure 2, $[\{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ presents the exceptional structure of perpendicular chains in neighboring sublattices.

Magnetic Results. The molar magnetic susceptibility *vs* *T* per nickel atom of $[\{Ni((Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ is shown in Figure 3. The χ_M value (2.26×10^{-3} cm^3 mol^{-1} at room temperature) increases when the temperature decreases, reaching a broad maximum ca 180 K with a χ_M value of 2.43×10^{-3} cm^3 mol^{-1}. Below this temperature, the curve decreases continuously and reaches the minimum value of 8.24×10^{-4} cm^3 mol^{-1} at 12 K, after which it increases due to paramagnetic impurities. The position of the maximum clearly indicates strong antiferromagnetic coupling between Ni(II) ions through the N_3^- bridge. The χ_MT *vs* *T* curve is also shown in Figure 3. The χ_MT value (0.68 cm^3 K mol^{-1} at room temperature) decreases when the temperature decreases, tending to 0 at 0 K. The experimental data for **1** were fitted to the formula deduced from Weng's results,[24] based upon the spin Hamiltonian $-J\sum S_iS_{i+1}$. Fit is only possible up to near the maximum (in our case up to 165 K), because neither zero field splitting, Haldane gap effects, nor weak interchain interactions are taken into account in the equation. The best fitted parameters ($J = -97.8$ cm^{-1}, $g = 2.29$) were obtained by minimizing the function $R = \sum(\chi_M\text{calcd} - \chi_M\text{obs})^2/\sum(\chi_M\text{obs})^2$ up to 8.5×10^{-4}.

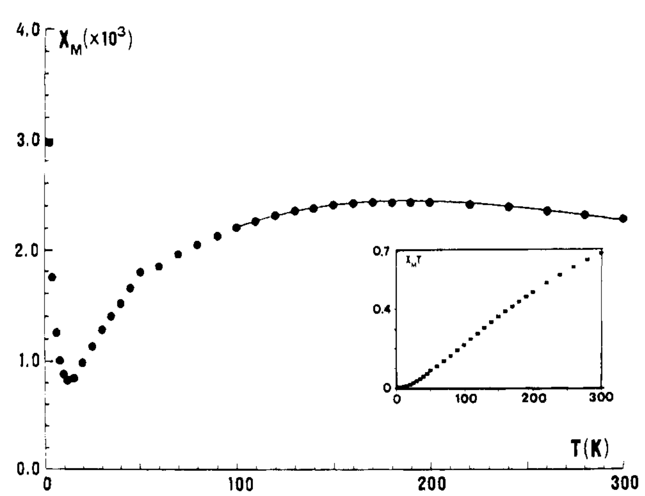

Figure 3. Molar magnetic susceptibility vs *T* plot of polycrystalline sample of $[\{Ni(Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ (χ_M in cm^3 mol^{-1}). Solid lines show the best fit obtained with the Weng's results (see text). In the lower figure, variation with χ_MT (in cm^3 K mol^{-1}) is shown.

In previous studies, the exchange interaction through a single azido bridge in uniform[12] and alternating[14] 1D nickel(II) systems was analyzed by means of MO extended Hückel calculations[25] showing that the $\sum\Delta^2(xy,z^2)$ value defined as[26] $|E(\Phi xy(s)) - |E(\Phi xy(a))|^2 + |E(\Phi z^2(s)) - |E(\Phi z^2(a))|^2$ depends, principally, on the Ni−N−N angle and the $Ni-N_3-Ni$ torsion angle. The maximum $\sum\Delta^2(xy,z^2)$ ($\sum\Delta^2$ henceforth) is found for a Ni−N−N angle of 108°, with the $Ni-N_3-Ni$ torsion angle of 180° and, consequently, the maximum $|J|$ value should be obtained for these structural parameters.[12,14] There is good correlation

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Table 4. Calculated $\Sigma\Delta^2$ and Experimental J Values for All Reported **Uniform** Monodimensional Antiferromagnetic Ni(II) Azido Complexes

compd	$\Sigma\Delta^2$	J (cm^{-1})	ref
$[\{Ni(cyclam)(\mu\text{-}N_3)\}_n](ClO_4)_n$	0.133	−39.2	11
$[\{Ni(232)(\mu\text{-}N_3)\}_n](ClO_4)_n$	0.130	−26.9	12
$[\{Ni(323)(\mu\text{-}N_3)\}_n](ClO_4)_n$	0.207	−62.7	12
$[\{Ni(L)(\mu\text{-}N_3)\}_n](ClO_4)_n$	0.306	−97.8	*b*

[a] L = Me_2[14]-1,3-dieneN_4. [b] This work.

between the calculated $\Sigma\Delta^2$ and $|J|$ values found in the published uniform 1D nickel(II) systems (Table 4). The $\Sigma\Delta^2$ calculated from the structural parameters of $[\{Ni((Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$, using the same model as in refs 12 and 14, is 0.306, the highest $\Sigma\Delta^2$ found to date (Table 4). According to the $\Sigma\Delta^2$ value, the $|J|$ parameter expected for $[\{Ni((Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ is very high. As indicated above, the experimental value of J is −97.8 cm^{-1}, the highest $|J|$ found for a single azido bridge and it correlates with the structural parameters of **1**: the lowest Ni−N−N angle reported to date, 116.2°, and the Ni−N_3−Ni torsion angle close to 180°. In fact, this mean angle of 116.2° is the nearest experimentally found for the angle for which a maximum $\Sigma\Delta^2$ is expected (108°).[14]

Acknowledgment. This work was financially supported by the Comisión Interministerial de Ciencia y Tecnologia PB93-0772. We are very grateful to Dr. C. Mealli for supplying the CACAO program.

Supplementary Material Available: A description of the experimental crystallographic details and tables of complete crystal data, anisotropic thermal parameters, hydrogen coordinates, and angles and distances for $[\{Ni((Me_2[14]\text{-}1,3\text{-}dieneN_4)(\mu\text{-}N_3)\}_n](ClO_4)_n$ (6 pages). Ordering information is given on any current masthead page.

IC940820A