The First 1D Nickel(II) Complex with a Single Azido Bridge: Structure and Magnetic Behavior of *catena*-(μ-N_3)[Ni(1,4,8,11-tetraazacyclotetradecane)](ClO_4)·H_2O

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Introduction

The azido group is a versatile bridging ligand which can coordinate two nickel(II) ions in end-on form[1-3] (ferromagnetic behavior) or end-to-end fashion[4,5] (antiferromagnetic behavior). Both kinds of complexes are structurally and magnetically well characterized, but the scarce compounds reported in the literature to date are only dinuclear systems. Very recently, we reported the first 1D nickel–azido compound,[6] in which double and single azido bridges alternate in the chain. This compound shows that the azido ligand can allow the synthesis of monodimensional nickel(II) compounds. Literature data show that when the blocking ligands (usually amines) permit cis coordination around the nickel(II) ion, dinuclear complexes are always obtained. Consequently, the reaction of the azido ligand with tetradentate amino-ligand complexes of nickel(II) in which the trans conformation is the more stable, seems a logical way to synthesize 1D compounds. Indeed, with [Ni(cyclam)](ClO_4)$_2$ as the starting material, in which cyclam is the 1,4,8,11-tetraazacyclotetradecane ligand, the solid compound obtained by reaction with the N_3^- anion corresponds to the desired 1D complex.

The counteranion is probably determinant in the stability of the chain in the solid state: in the previously reported[6] *catena*-[Ni_2(μ-N_3)$_3$(dpt)$_2$](ClO_4), in which dpt is bis(3-aminopropyl)amine, the synthesis is *only* possible with the perchlorate anion. Moreover, reaction of [Ni(tmcy)]$^{2+}$, in which tmcy is the very closely related ligand 1,4,8,11-tetramethylcyclam, using iodide as the counteranion, produces[1] the dinuclear compound (μ-N_3)-[Ni_2(N_3)$_2$(tmcy)$_2$]I, showing a single azido bridge and two nonbridging azido ligands in trans arrangement. A similar counteranion effect has also been reported[7] for other bridging ligands, such as NO_2^- in *catena*-(μ-ONO)[Ni(en)$_2$](ClO_4).

The magnetic behavior between 300 and 4 K indicates strong antiferromagnetic coupling. The χ_M values tend to zero at low temperatures, and this fact can be a consequence of the Haldane[8] prediction for homogeneous $S = 1$ chains.

The main goal of this work is to show a synthetic way to obtain 1D nickel(II)–azido systems, tailored from trans tetraamine complexes of the nickel(II) ion.

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.

A concentrated aqueous solution of 2 mmol of [Ni(cyclam)](ClO_4)$_2$[9] was mixed with 2 mmol of NaN_3 dissolved in 10 mL of water. Slow evaporation of the resulting solution (yellow; no changes were produced) gave violet crystals of the 1D compound. This complex was insoluble in the common organic solvents, but it was recrystallized in hot water, in which total dissociation was observed (a yellow solution of square-planar nickel(II) was obtained); the complex was regenerated by slow evaporation.

Spectral and Magnetic Measurements. IR spectra were recorded on a Perkin-Elmer 1330 IR spectrophotometer. Magnetic measurements were carried out on a polycrystalline sample with a pendulum type magnetometer (Manics DSM8) equipped with a helium continuous-flow cryostat working in the 4.2–300 K range and a Drusch EAF 16UE electromagnet. The magnetic field was approximately 15 000 G. Diamagnetic corrections were estimated from Pascal tables.

X-ray Crystallography. A prismatic violet crystal (0.1 mm × 0.1 mm × 0.2 mm) was selected and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12 \le \theta \le 18°$) 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 1955 reflections were measured in the range $2 < \theta < 25°$; 1764 reflections were assumed as observed by applying the conditions $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz–polarization but 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 I. The structure was solved by Patterson synthesis, using the SHELXS computer program[10] and refined by full-matrix least-squares methods, with the SHELX76 computer program.[11] The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.0044|F_o|^2)^{-1}$. f, f', and f'' were taken from ref 12. Twenty-six H atom positions were computed and refined with an overall isotropic factor, using a riding model. Maximum shift/esd = 0.1; maximum and minimum peaks in the final difference synthesis were 0.3 and –0.3 e·Å^{-3}, respectively. Final atomic coordinates are given in Table II.

Results and Discussion

IR and Analytical Data. The ν_{as} of the azide group appears at 2040 cm^{-1} (vs, broad), and the other two bands of the N_3^- group (ν_s and δ) are masked by the amine and perchlorate bands. Bands attributable to the cyclam ligand (3260–3200, 2940–2870, and a set of bands between 1500–800 cm^{-1}) and the perchlorate anion (1100, 630 cm^{-1}) appear at normal frequencies. The elemental analyses (C, H, N, Cl) are consistent with the product formulation (μ-N_3)[Ni(cyclam)](ClO_4)·H_2O.

Crystal Structure. The structure consists of 1D nickel–azido chains, isolated by ClO_4^- anions and water molecules, which are found in the interchain space. No hydrogen bonds between the chains or perchlorate groups are present. The structure of the chain is shown in Figure 1. The main bond lengths and angles are gathered in Table III. In the chain structure, each Ni(II) atom is coordinated by one cyclam ligand and two azido ligands in an octahedral trans arrangement. The four N atoms of the cyclam ligand and the nickel atom are in the same plane (maximum deviation from plane: 0.009 Å for N(6)). The coordination of the azido bridge is strongly asymmetrical; the two Ni–N–N angles are 140.7(3) and 128.2(3)°, respectively,

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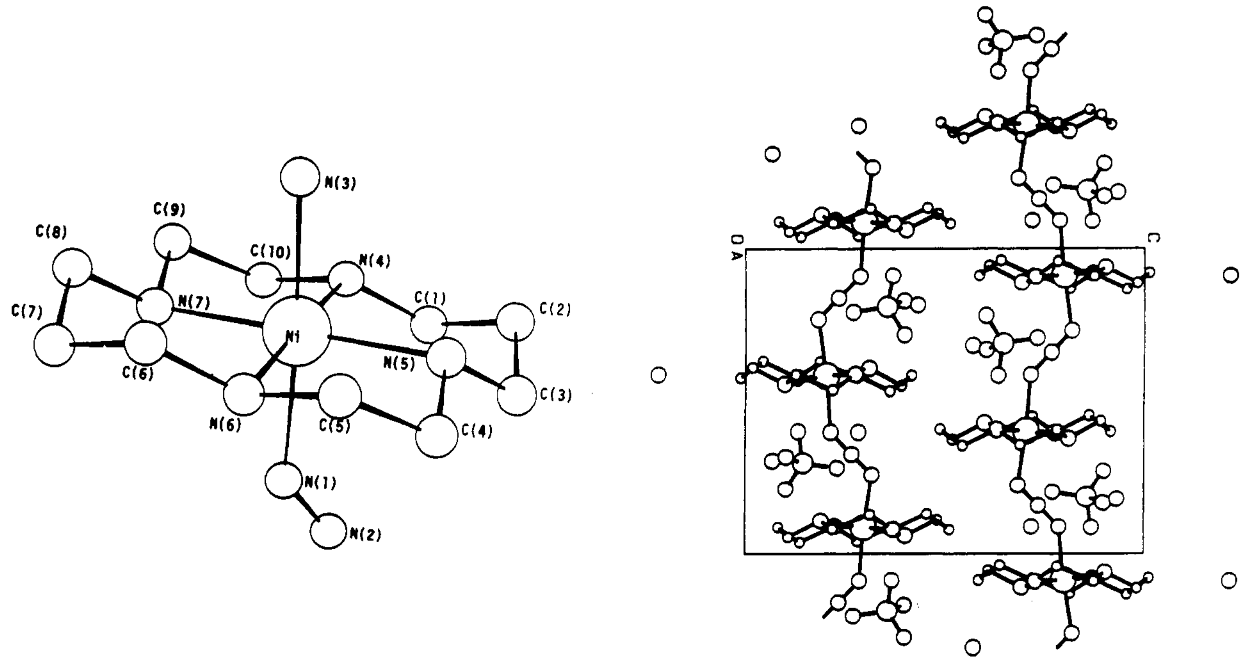

Figure 1. Atom-labeling scheme and cell packing for *catena*-(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O.

Table I. Crystal Data for *catena*-(μ-N_2)[Ni(cyclam)](ClO_4)·H_2O

formula	$[C_{10}H_{24}N_7Ni]_n(ClO_4)_n \cdot nH_2O$
fw	418.49
space group	$P2_12_12_1$
a, Å	9.932(2)
b, Å	11.940(2)
c, Å	15.443(3)
V, Å^3	1831(1)
Z	4
d_{calc}, g/cm^{-3}	1.503
μ(Mo Kα), cm^{-1}	12.39
λ(Mo Kα), Å	0.710 69
T, °C	25
scan method	$\omega/2\theta$
no. of params refined	227
R^a	0.048
$R_w{}^b$	0.047

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

and the torsion angle Ni–NNN–Ni is 13.1°. As a consequence of both factors, the angle between the normals to the two neighboring nickel–N_4(cyclam) planes is 17.3° (Figure 2). The four nickel–N(cyclam) distances are similar (2.060, 2.073, 2.059, 2.059 Å) and shorter than the two nickel–N(azido) distances (2.165 and 2.172 Å), giving an axially elongated octahedron in the chain direction. Taking into account the wide range of nickel(II)–azido bond parameters observed for related complexes,[2,3,6] Ni–N–N angles and Ni–N distances for *catena*-(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O are similar to these reported values. Between neighboring azido groups there exists also a torsion angle of 9.7°.

Magnetic Results. The magnetic susceptibility vs T of *catena*-(μ-N_3)[Ni(cyclam)]ClO_4·H_2O is plotted in Figure 3. The χ_M value (3.33×10^{-3} cm^3·mol^{-1} at room temperature) increases when the temperature decreases, reaching a broad maximum ca. 75 K, with a χ_M value of 5.81×10^{-3} cm^3·mol^{-1}. This maximum clearly indicates strong antiferromagnetic coupling between Ni(II) ions through the N_3^- bridge. The $\chi_M T$ curve vs T decreases continuously and tends to zero at low temperatures.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) and Their Estimated Standard Deviations for *catena*-(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O

atom	x	y	z	$B_{eq}{}^a$
Ni	–0.00947(5)	0.08826(3)	0.79724(3)	2.61(2)
N(1)	–0.0254(4)	–0.0920(2)	0.7858(3)	3.68(14)
N(2)	–0.9824(3)	–0.1637(2)	0.7336(2)	3.01(13)
N(3)	1.0031(5)	0.2681(3)	0.8169(3)	4.92(19)
N(4)	0.8692(4)	0.1120(3)	0.6907(3)	4.06(15)
N(5)	1.1671(4)	0.0933(3)	0.7257(3)	3.38(13)
N(6)	1.1154(4)	0.0618(3)	0.9017(2)	3.71(14)
N(7)	0.8170(4)	0.0825(3)	0.8700(3)	4.08(15)
C(1)	0.9080(6)	0.0561(4)	0.6090(3)	4.57(21)
C(2)	0.0456(8)	0.0896(4)	0.5844(3)	5.37(24)
C(3)	1.1599(7)	0.0387(5)	0.6385(3)	5.44(24)
C(4)	1.2692(5)	0.0427(4)	0.7812(4)	4.87(21)
C(5)	1.2526(4)	0.0922(4)	0.8739(4)	4.33(18)
C(6)	1.0750(7)	0.1148(4)	0.9814(3)	4.86(21)
C(7)	0.9360(9)	0.0817(6)	1.0122(3)	6.09(28)
C(8)	0.8149(7)	0.1347(5)	0.9549(3)	5.41(22)
C(9)	0.7073(5)	0.1332(4)	0.8125(5)	5.80(26)
C(10)	0.7322(5)	0.0830(6)	0.7194(4)	5.80(27)
Cl(1)	0.5776(1)	–0.1922(1)	0.8547(1)	4.73(5)
O(1)	0.5246(8)	–0.0899(5)	0.8669(5)	10.80(42)
O(2)	0.5198(10)	–0.2815(7)	0.8982(5)	11.59(47)
O(3)	0.5990(13)	–0.2093(6)	0.7693(4)	12.19(48)
O(4)	0.6977(7)	–0.1679(9)	0.8991(6)	13.24(55)
OW(1)	–0.2109(4)	0.3144(3)	0.5688(3)	6.05(19)

[a] $B_{eq} = 8\Pi^2/3\sum_i\sum_j U_{ij}\mathbf{a}^*_i\mathbf{a}^*_j\mathbf{a}_i\mathbf{a}_j$·pa.

Experimental data have been fitted to the Weng equation,[13] based upon the spin Hamiltonian $H = -JS_1S_2$, where the nickel ion is assumed to be magnetically isotropic:

$$\chi_M = (N\beta^2g^2/kT)(2 + A\alpha + B\alpha^2)/(3 + C\alpha + D\alpha^2 + E\alpha^3)$$

in which $A = 0.019$, $B = 0.777$, $C = 4.346$, $D = 3.232$, $E = 5.834$, and $\alpha = |J|/kT$. Fit is only possible up to near the maximum (in our case up to 50 K) because neither zero-field splitting nor the Haldane gap is taken into account in the equation. The J value has been obtained by minimizing the function $R = \sum(\chi_M{}^{calcd} - \chi_M{}^{obs})^2/\sum(\chi_M{}^{obs})^2$. The best fitting parameters obtained are $J = -39.2$ cm^{-1}, $g = 2.22$, and $R = 1.14 \times 10^{-4}$.

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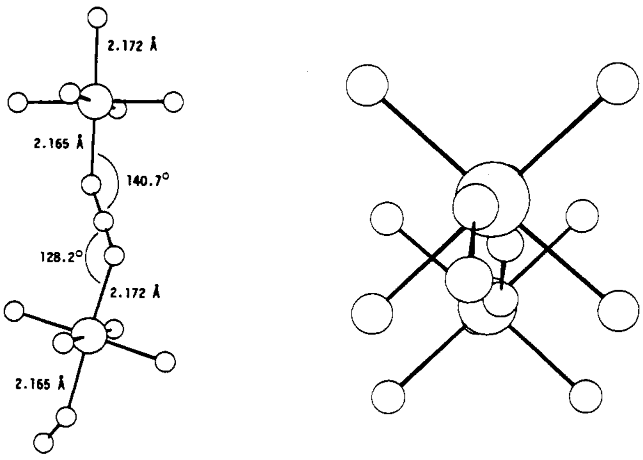

Figure 2. (a) Left: Fragment of *catena*-(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O showing the bond parameters related with the azido bridge. The torsion between neighboring Ni–cyclam planes is clearly shown. (b) Right: Axial view of the same fragment of *catena*-(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O showing the relative position of cyclam and the azido bridges. Only the nickel(II)–nitrogen skeleton is shown for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) for *catena*-(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O

Distances			
N(1)–Ni	2.165(3)	N(3)–Ni	2.172(4)
N(4)–Ni	2.060(4)	N(5)–Ni	2.073(4)
N(6)–Ni	2.059(3)	N(7)–Ni	2.059(4)
N(2)–N(1)	1.178(5)	N(3)–N(2)	1.138(5)
Ni–Ni′	6.149(1)		
Angles			
N(3)–Ni–N(1)	176.5(2)	N(4)–Ni–N(1)	91.6(2)
N(4)–Ni–N(3)	90.5(2)	N(5)–Ni–N(1)	92.7(1)
N(5)–Ni–N(3)	89.8(2)	N(5)–Ni–N(4)	93.7(2)
N(6)–Ni–N(1)	87.5(1)	N(6)–Ni–N(3)	90.4(2)
N(6)–Ni–N(4)	178.4(2)	N(6)–Ni–N(5)	85.0(2)
N(7)–Ni–N(1)	87.2(2)	N(7)–Ni–N(3)	90.3(2)
N(7)–Ni–N(4)	87.2(2)	N(7)–Ni–N(5)	179.1(1)
N(7)–Ni–N(6)	94.1(2)	N(2)–N(1)–Ni	140.7(3)
N(2)–N(3)–Ni	128.2(3)	N(1)–N(2)–N(3)	176.4(5)

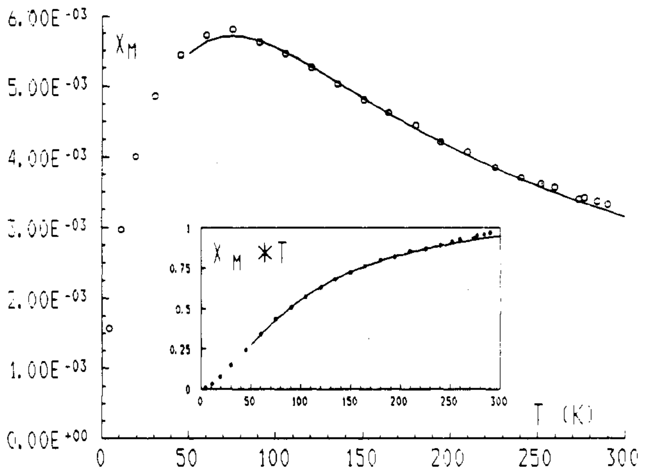

Figure 3. Magnetic susceptibility plots of a polycrystalline sample of *catena*-(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O. χ_M in $cm^3 \cdot mol^{-1}$ and $\chi_M T$ in $cm^3 \cdot K \cdot mol^{-1}$. Solid lines show the best fit obtained with the Weng equation (see text).

Table IV. J Values and Ni–N(1)–N(3)–Ni′ Torsion Angles for the Antiferromagnetic Reported Nickel(II) Azido-Bridged Compounds[a]

compound	J, cm^{-1}	torsion, deg	ref
(μ-N_3)[$Ni_2(tmcy)_2(N_3)_2$]I	−24.6	0.0	2
(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O	−39.2	13.1	*b*
(μ-N_3)$_2$[$Ni_2(tren)_2$](BPh_4)$_2$	−70.0	38.4	2
(μ-N_3)$_2$[$Ni_2(L)_2(N_3)_2$]	−90.0	*c*	3
(μ-N_3)$_3$[$Ni_2(L')_2$](ClO_4)	−71.0	*c*	3

[a] tmcy = 1,4,8,11-tetramethylcyclam; tren = 2,2′,2″-triaminotriethylamine; L = 1,5,9-triazacyclododecane; L′ = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane. [b] This work. [c] Non reported.

The most significant feature of the magnetic behavior of this compound is the high value of J, greater than $J = -24\ cm^{-1}$ reported[2] for the dinuclear complex (μ-N_3)[$Ni_2(tmcy)_2(N_3)_2$]I, also containing a single azido bridge. The J value is, in our case, lower than those reported when nickel(II) dinuclear complexes contain double or triple azido bridges (Table IV). The high efficiency of single azido bridges as a superexchange pathway is also evidenced when comparison is made with other nickel(II) chains in which the bridging ligand is oxalate[14] ($J = -24\ cm^{-1}$), nitrite[7] ($J = -33.0\ cm^{-1}$), or halogen[15,16] ($-J = 18$–$35\ cm^{-1}$).

Ab-initio magneto–structural correlations have been proposed for copper(II)–azido systems,[17] but to our knowledge, for nickel(II)–azido complexes only some qualitative symmetry-based suggestions have been made by Hendrickson.[2] According to this author, for the tetraamine ligands tmcy, cyclam, and tren, a correlation between the torsion angle Ni–N(1)–N(3)–Ni′ and J(antiferromagnetic) seems reasonable (Table IV), but must it be pointed out that this comparison is made between one trans single azido bridge dinuclear complex, one cis double azido bridge dinuclear complex, and one trans single bridge 1D compound. Using this nonhomogeneous set of compounds, correlations must be carefully assumed. Moreover, other factors may influence the overlap of the magnetic orbitals and the parameter J: Ni–N(azido) distances and, consequently, the magnetic nickel(II) orbitals in the direction of the bridges; values and asymmetry of the Ni–N–N angles, torsion angles of the azido bridging ligands, and dihedral angles between nearest Ni–N_4(amine) planes.

New structures and magnetic results are needed to delimit the most significant factors that influence the superexchange mechanism in nickel(II)–azido 1D systems, and current efforts in this direction are in progress in our group in order to obtain more magneto–structural information as a prior step to the theoretical study.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, anisotropic thermal parameters, atom coordinates, and bond angles and distances for *catena*-(μ-N_3)[Ni(cyclam)](ClO_4)·H_2O (4 pages). Ordering information is given on any current masthead page.