A second source of abnormally high specific heat at low temperatures is the low frequency vibrations of the 4-bromopyridinium groups. These vibrations are thermally activated at relatively low temperatures, and their specific heat may be best described by Einstein functions. Thus two weighted Einstein frequencies were incorporated into the Komada-Westrum approximation for the lattice specific heat as internal branches at 38 and 72 cm^{-1}. We note that we have no spectroscopic evidence for these values, and their selection was arbitrary and served to achieve a fit between the sum of all contributions and the experimental results. However, thermal activation of low-frequency vibrations at low temperatures, although not very common, is known and has been reported for ammonium salts[21-23] and several silver compounds.[16] The apparent characteristic temperature Θ_{KW}, presented in Figure 2, was calculated by taking these internal modes into account. A constant Θ_{KW} equal to 31.1 K was established as the characteristic temperature for $[4\text{-Br(py)H}]_3Fe_2Cl_9$ and was used to calculate the lattice specific heat between 0 and 38 K. The resulting lattice contribution to the specific heat is also presented in Figure 1.

Once the lattice specific heat is calculated, the excess specific heat is readily obtained. This excess specific heat is also shown in Figure 1 and is believed to originate solely from magnetic ordering phenomena. The broad maximum at higher temperatures appears to agree well with the theoretical prediction for magnetic dimers and therefore may be interpreted as such. The λ-type transition at lower temperatures is associated with canted antiferromagnetic ordering of the Fe(III) ions.[2] The magnetic entropy between 0 and 9.0 K, $\Delta_{tr}S^0$, is found to be $(1.887 \pm 0.05)R$. The theoretical value for the entropy of disorder corresponding to two $S = {}^5/_2$ ions is $2R \ln (2S + 1) = 2R \ln 6 = 3.58R$. This value is about twice as large as the experimental entropy of transition. The rest of the entropy has to be included in the Schottky-like anomaly due to the stronger pair exchange constant. Less than half of the disorder process takes place below the peak temperature, 2.280 K. The tail of the transition extends up to 9.0 K with a corresponding post-transition entropy of 1.036*R*. This indicates that short-range interactions play an important role in the magnetic ordering process.

The transition temperature, 2.280 K, is lower than that previously reported, 2.34 K.[2] The origin of the shift in T_c may be attributed to mechanical stress afflicted on the samples prior to the calorimetric measurement.

The tail of the transition (i.e., the magnetic specific heat at temperatures higher than T_c) follows a T^{-2} behavior as expected.[24] However, the presence of a large degree of short-range order precludes the use of the T^{-2} dependence of the magnetic specific heat, according to Domb and Miedema,[24] for the evaluation of the exchange constant. Previously,[2] the compound has been interpreted as an Heisenberg antiferromagnet based upon its magnetic susceptibility and the exchange constant J/k_B was determined to be between −0.111 and −0.094 K. From the critical point determined here, 2.280 K, we find that $J/k_B = -0.114$ K, in good agreement with the previous report.

Acknowledgment. This research was supported by the Solid State Chemistry program of the Division of Materials Research of the National Science Foundation, through Grant DMR-8815798, as well as by the CICYT, Grant MAT 89-531. We wish to extend our gratitude to Mr. John Costa for invaluable assistance in the cryostat assembly.

Supplementary Material Available: Text giving a complete description of the calorimeter, a figure depicting the calorimeter, and a table of specific heats as a function of temperature (9 pages). Ordering information is given on any current masthead page.

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Contribution from the Departament de Química Inorgànica,
Universitat de Barcelona, Diagonal 647,
08028-Barcelona, Spain, and Departament de Cristal.lografia
i Mineralogia, Universitat de Barcelona, Martí Franquès s/n,
08028-Barcelona, Spain

The First Nickel(II) Alternating Chain with Two Different End-to-End Azido Bridges

Ramon Vicente,[*,†] Albert Escuer,[†] Joan Ribas,[†]
and Xavier Solans[‡]

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Introduction

In a uniform linear-chain system, the intrachain exchange constant has been assumed not to vary with position. That is, the Hamiltonian used is

$$H = -J(S_{i-1}S_i + \alpha S_i S_{i+1})$$

with $\alpha = 1$. An alternating chain is defined for $\alpha < 1$. When $\alpha = 0$, the model is reduced to the dimer model with pairwise interaction. The preparation and properties of $S = {}^1/_2$ alternating chains has been of continuous interest for some years,[1] and there is a large body of results. Some examples of the previously reported complexes are $[Cu(\gamma\text{-picoline})_2Cl_2]$,[2] $[Cu(N\text{-methylimidazole})_2Br_2]$,[3] $Cu(NO_3)_2{\cdot}2.5H_2O$,[4] and $[Cu(hfa)_2TEMPOL]$.[5] With $S > {}^1/_2$, alternating chains are very scarce. Some of these chains are only found with alternating *g* factors, but not with $\alpha < 1$.[6] To our knowledge, only one case has been fully characterized: *catena*-(μ-oxo)hemi(porphyrazinato)iron(IV).[7] Consequently, no Ni(II) alternating chain has been reported. In order to study alternating chains of Ni(II), one of the ligands which may give good results is the N_3^- anion, because it is well established that it can bridge metal ions in two modes (double-bridging end-on or end-to-end)[8] and when the blocking ligands for Ni(II) are tridentate, the sixth position of each nickel atom is occupied by a terminal azido group.[9] These can consequently be potentially considered as blocks which can be linked together in a 1D alternating system. By using this strategy, we report here the synthesis and crystal structure of the first Ni(II) alternating chain with the N_3^- entity acting as an end-to-end bridge in two different modes, double and simple bridges, respectively: *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$, where dpt is the tridentate amine ligand bis(3-aminopropyl)amine. We have also measured the magnetic susceptibility of this compound between room temperature and 4 K. The magnetic behavior confirms that this chain is the first magnetically alternating Ni(II) chain.

Experimental Section

Materials. Bis(3-aminopropyl)amine (Fluka) and nickel perchlorate (Fluka) were purchased and used without purification. The dinuclear μ-azido-bridged compound $[Ni_2(\mu\text{-}N_3)_2(Me_3[12]N_3)_2](ClO_4)_2$ ($Me_3[12]N_3$ = *2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene*) was previously prepared.[10]

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

If an aqueous solution of nickel perchlorate hexahydrate, bis(3-aminopropyl)amine (dpt), and sodium azide in the molar ratio 1:1:3 is left at room temperature for several days, water-soluble blue crystals of *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$ are obtained. On the other hand, when 0.5 g of the dinuclear azido-bridged compound $[Ni_2(\mu\text{-}N_3)_2(Me_3[12]N_3)_2](ClO_4)_2$[10] is dissolved in 100 mL of a 0.1 M solution of aqueous sodium azide, blue single crystals of the same compound *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$ are also obtained after very slow evaporation of the solvent. The two products were characterized to be the same using spectral measurements and elemental analysis. The second synthetic pathway implies the cleavage of the bonded macrocycle in basic medium, yielding acetone and dpt. This cleavage has been previously reported by Curtis et al.[11] for similar macrocyclic compounds.

[†] Departament de Química Inorgànica.

[‡] Departament de Cristal.lografia i Mineralogia.

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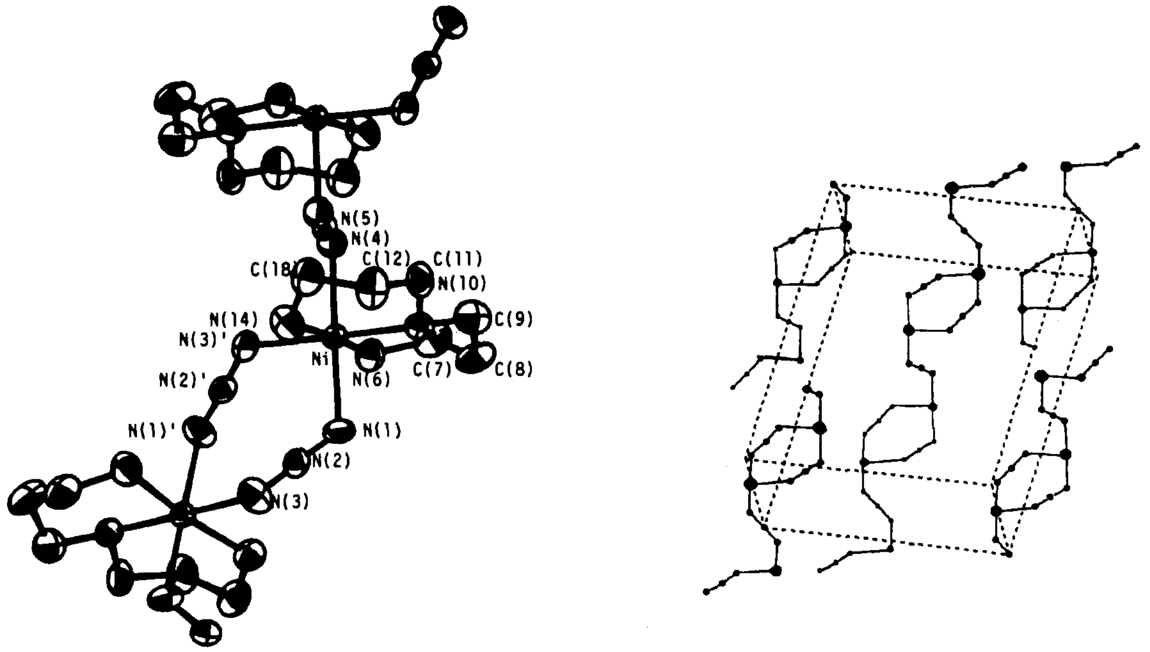

Figure 1. ORTEP plot and labeling scheme (left) and simplified cell-packing diagram (right) of *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2]^+$. In the cell-packing diagram, only the Ni and the N_3^- groups are shown for clarity.

Table I. Crystal Data for *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$

formula	$[C_{12}H_{34}N_{15}Ni_2]_n(ClO_4)_n$	d_{calc}, g/cm^{-3}	1.570
fw	605.36	μ(Mo Kα), cm^{-1}	16.93
space group	C2/c	λ(Mo Kα), Å	0.7106
a, Å	13.578 (2)	*T*, °C	25
b, Å	9.873 (1)	scan method	ω
c, Å	19.175 (2)	no. of params refined	223
β, deg	95.18 (1)	R^a	0.046
V, Å^3	2560.0 (9)	R_w^b	0.049
Z	4		

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

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) and Their Estimated Standard Deviations for *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$

atom	*x*	*y*	*z*	B_{EQ}^a
Ni	0.10027 (4)	0.2946 (6)	0.13921 (2)	2.31 (3)
N(1)	−0.0548 (3)	0.0623 (5)	0.1584 (2)	4.11 (21)
N(2)	−0.0958 (3)	0.0255 (4)	0.2056 (2)	2.88 (16)
N(3)	−0.1406 (3)	−0.0122 (5)	0.2517 (2)	3.84 (19)
N(4)	0.0620 (3)	0.0654 (5)	0.0299 (2)	3.63 (18)
N(5)	0	0	0	2.82 (22)
N(6)	0.0617 (3)	−0.1731 (5)	0.1263 (3)	3.68 (18)
C(7)	0.1227 (5)	−0.2661 (6)	0.0890 (3)	4.53 (27)
C(8)	0.2311 (5)	−0.2482 (6)	0.1140 (3)	4.70 (27)
C(9)	0.2765 (4)	−0.1214 (6)	0.0861 (3)	4.37 (26)
N(10)	0.2504 (3)	0.0056 (4)	0.1201 (2)	3.02 (16)
C(11)	0.2928 (4)	0.1198 (6)	0.0828 (3)	4.10 (24)
C(12)	0.2847 (4)	0.2567 (6)	0.1182 (4)	4.86 (28)
C(13)	0.1819 (5)	0.3156 (6)	0.1158 (3)	4.46 (26)
N(14)	0.1189 (4)	0.2334 (5)	0.1588 (3)	4.36 (23)
Cl(1)	0	0.4749 (2)	0.7500	3.82 (8)
O(1)	0.0500 (6)	0.5762 (9)	0.7856 (5)	5.32 (41)
O(2)	−0.1020 (7)	0.4659 (14)	0.7654 (6)	7.73 (62)
O(1)′	−0.0063 (7)	−0.5052 (9)	0.1732 (5)	5.10 (40)
O(2)′	−0.0437 (9)	−0.3488 (9)	0.2428 (5)	7.35 (57)

[a] $B_{EQ} = 8\Pi(^2/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j)$.

Spectral and Magnetic Measurements. IR spectra were recorded on a Perkin-Elmer 1330 IR spectrophotometer. Magnetic measurements were carried out on a polycrystalline specimen with a Faraday type magnetometer (Manics DSM8) equipped with an Oxford 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's tables.

X-ray Crystallography. Crystals suitable for X-ray structural determination were grown from $[Ni_2(\mu\text{-}N_3)_2(Me_3[12]N_3)_2](ClO_4)_2$[10] by using the synthetic pathway (see Synthesis). A prismatic blue crystal (0.1 mm × 0.1 mm × 0.2 mm) was selected and mounted on a Philips Pw-1100 diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($8 \le \theta \le 12°$) and refined by least-squares methods. Intensities were collected with graphite-monochromatized Mo Kα radiation, using the ω-scan technique. A total of 1929 reflections were measured in the range $2 < \theta < 25°$, and 1686 reflections were assumed as observed by applying the condition $I > 2.5\sigma(I)$. R_{int} of *F* was 0.014. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz and polarization but no absorption corrections were made. The crystallographic data, conditions employed for the intensity data collection, and some features of the structure refinement are listed in Table I. The structure was solved by direct methods, using the SHELX86 computer program,[12] and refined by the full-matrix least-squares method, with the

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Table III. Selected Bond Distances (Å) and Angles (deg) for *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$

	Distances		
N(1)–Ni	2.194 (4)	C(8)–C(7)	1.517 (9)
N(3)′–Ni	2.153 (4)	C(9)–C(8)	1.514 (9)
N(4)–Ni	2.143 (4)	N(10)–C(9)	1.471 (7)
N(6)–Ni	2.076 (4)	C(11)–N(10)	1.479 (7)
N(10)–Ni	2.117 (4)	C(12)–C(11)	1.521 (9)
N(14)–Ni	2.059 (5)	C(13)–C(12)	1.509 (9)
N(2)–N(1)	1.162 (6)	N(14)–C(13)	1.482 (7)
N(5)–N(4)	1.169 (4)	N(3)–N(2)	1.179 (6)
C(7)–N(6)	1.465 (7)		
	Angles		
N(4)–Ni–N(1)	98.3 (2)	N(2)′–N(3)′–Ni	124.4 (3)
N(6)–Ni–N(1)	85.8 (2)	N(5)–N(4)–Ni	119.2 (3)
N(6)–Ni–N(4)	90.4 (2)	N(4)–N(5)–N(4)′	180.0
N(10)–Ni–N(1)	177.9 (2)	C(7)–N(6)–Ni	120.9 (4)
N(10)–Ni–N(4)	90.1 (2)	C(8)–C(7)–N(6)	110.4 (5)
N(10)–Ni–N(6)	96.2 (2)	C(9)–C(8)–C(7)	113.6 (5)
N(14)–Ni–N(1)	85.9 (2)	N(10)–C(9)–C(8)	115.2 (5)
N(14)–Ni–N(4)	91.8 (2)	C(9)–N(10)–Ni	116.5 (3)
N(14)–Ni–N(6)	171.4 (2)	C(11)–N(10)–Ni	115.0 (3)
N(14)–Ni–N(10)	92.1 (2)	C(11)–N(10)–C(9)	108.4 (4)
N(3)′–Ni–N(1)	91.7 (2)	C(12)–C(11)–N(10)	114.5 (5)
N(3)′–Ni–N(4)	178.3 (2)	C(13)–C(12)–C(11)	115.7 (5)
N(3)′–Ni–N(6)	88.3 (2)	N(14)–C(13)–C(12)	110.5 (5)
N(3)′–Ni–N(10)	89.0 (2)	C(13)–N(14)–Ni	120.1 (3)
N(3)′–Ni–N(14)	89.6 (2)	N(3)–N(2)–N(1)	177.4 (4)

SHELX76 computer program.[13] The function minimized was $w\|F_o| - |F_c\|^2$, where $w = (\sigma^2(F_o) + 0.0057|F_o|^2)^{-1}$. f, f', and f'' were taken from ref 14. The coordinates of 16 H atoms were located from a difference synthesis and refined with an overall isotropic factor. Maximum shift/esd = 0.1, and maximum and minimum peaks in the final difference synthesis were 0.4 and –0.4 e Å^{-3}, respectively. Final atomic coordinates are given in Table II.

Results and Discussion

IR and Analytical Data. The most characteristic band for the linear amine ligand is that found at 1600 cm^{-1} (s), in contrast to the analogous band when the ligand is the N_3 macrocycle (1650 cm^{-1}). The ν_{as} azide at 2040 cm^{-1} (s, broad) and the perchlorate bands at 1100 (s) and 610 cm^{-1} (m) are also found. The other two bands of the N_3^- group (ν_s and δ) are masked by the amine and perchlorate bands. The elemental analyses for the two different syntheses are consistent with the product formulation $[Ni_2(N_3)_3(dpt)_2](ClO_4)$.

Crystal Structure. The structure consists of the 1D $-Ni(N_3)_2Ni(N_3)-$system, isolated by ClO_4^- anions. The structure of the chain and the packing diagram are shown in Figure 1. The bond lengths and angles are gathered in Table III. In the packing diagram, only the Ni and azide N atoms are indicated for clarity. In the chain structure, each Ni(II) atom is coordinated by one dpt ligand and three azido ligands in a *mer* arrangement. Two of the azido bridges are shared with one Ni(II) atom (double bridge) and the third is shared with another Ni(II) atom (single bridge) (Figure 1). This structure corresponds to the first fully characterized alternating Ni(II) chain.

Magnetic Results. As has been previously reported by Carlin,[1] in the susceptibility curves of alternating chains, broad maxima are observed for all values of the alternating parameter α. These susceptibility curves vanish exponentially when temperature tends to 0 for all $\alpha < 1$; on the contrary, the uniform ($\alpha = 1$) chain reaches a finite value at $T = 0$ K, depending on the value of S. The case with $\alpha = 0$ is of course simply the isolated curve for a dimer. The magnetic susceptibility of a crystalline sample of *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$ is plotted in Figure 2 as a function of the temperature. The χ_M value increases when the temperature decreases, reaching a broad maximum ca. 120 K. This maximum clearly indicates strong antiferromagnetic coupling between the Ni(II) ions through the N_3^- bridge. The $\chi_M T$ curve vs T decreases continuously, corroborating this hypothesis. The most important feature is what happens when the temperature is lowered: the molar magnetic susceptibility value tends to zero when T tends to zero, indicating the existence of a nonuniform chain. On the other hand, the shape of the curve does not correspond to an antiferromagnetically coupled nickel(II) binuclear complex such as a structural alternating chain with one of the J parameters equal to zero,[15] because in this case the maximum should be more pronounced. The attempts made to fit this curve with the dimer model[16] were obviously unsuccessful, clearly indicating that this chain is the first true magnetically alternating Ni(II) chain. Further theoretical studies on this kind of alternating Ni(II) chain are in progress in order to account for their magnetic behavior.

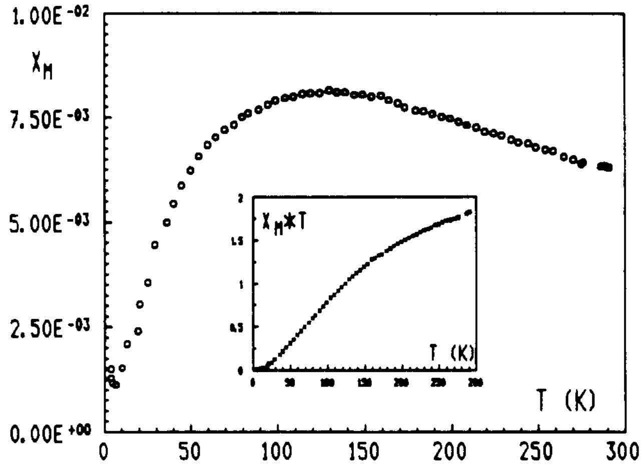

Figure 2. Magnetic susceptibility plots for a polycrystalline specimen for *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$ (χ_M in cm^3 mol^{-1} and $\chi_M T$ in cm^3 K mol^{-1}).

Acknowledgment. This work was undertaken with the financial support of CICYT Grant MAT88-0545.

Supplementary Material Available: For *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$, tables of complete crystal data, anisotropic thermal parameters, hydrogen atom coordinates, and distances and angles (3 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry
and Biochemistry, University of Colorado,
Boulder, Colorado 80309

Structural Characterization of $[((Hexamethylbenzene)Ru)_2(\mu\text{-}SPh)_3]Cl\cdot 2CHCl_3$

Hans T. Schacht, R. C. Haltiwanger, and M. Rakowski DuBois*

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In recent years there has been an increased interest in ruthenium complexes with sulfur donor ligands, in part because of the high catalytic activity of RuS_2 in various hydrotreating processes.[1,2] As a part of this development, many examples of ruthenium thiolate complexes have been reported.[3-14] During the course

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