Inorg. Chem. **1998,** *37,* 5693−5696 **5693**

Dimerized Nickel^{2+} Chain Compounds with Nitro−Nitrito Bridges and Unprecedented $[Ln(NO_3)_4(CH_3OH)_2]^-$ Anions (Ln = Lanthanide). Crystal Structure and Magnetic Properties

**T. M. Rajendiran,[†] Olivier Kahn,*,[†] Stéphane Golhen,[‡]
Lahcène Ouahab,[‡] Zentaro Honda,[§] and
Koichi Katsumata[§]**

Laboratoire des Sciences Moléculaires,
Institut de Chimie de la Matière Condensée de Bordeaux,
UPR CNRS No. 9048, 33608 Pessac, France,
Laboratoire de Chimie du Solide et Inorganique Moléculaire,
UMR CNRS No. 6511, Université de Rennes 1,
35042 Rennes, France, and The Institute of Physical and
Chemical Research (RIKEN), Wako, Saitama 351-01, Japan

Received April 22, 1998

Introduction

In 1982 we reported on the crystal structure and magnetic properties of a Ni^{2+} chain compound of formula $[Ni(en)_2(NO_2)](ClO_4)$, with en = ethylenediamine.[1] This compound was a good example of a one-dimensional $S = 1$ antiferromagnet. One year later Haldane suggested that the energy spectrum of such a chain with equally spaced integer spins would present an energy gap between a singlet ground state and the continuum of the excited states, such that, even in the absence of local anisotropy, the low-temperature limit of the zero-field magnetic susceptibility would be zero.[2] At a first glance Haldane's conjecture was quite surprising, and very rapidly the physicists looked for a real material allowing to confirm or refute this conjecture. It occurred that $[Ni(en)_2(NO_2)](ClO_4)$ was probably the best candidate, so that this compound became very famous in the condensed matter physics community,[3−5] where it is abbreviated as NENP.

Low-temperature magnetic susceptibility along with magnetization measurements allowed an estimate of the Haldane gap in $[Ni(en)_2(NO_2)](ClO_4)$, namely 13 cm^{-1}.[5] It was also found that a critical field of about 10 T breaks the gap.[5] Inelastic neutron scattering (INS) measurements have confirmed the existence of the gap. INS actually shows three gaps attributed to the splitting of the Haldane gap due to the Ni^{2+} local anisotropy.[3,4] The dispersion law of the magnetic excitations in the INS spectra also gave an estimate of the ratio between inter- and intrachain interaction parameters which is about 10^{-4}.[3,4]

Another way to create a gap between singlet ground state and low-lying excited states, valid for both integer and half-integer spins, is to dimerize the chain. There are then alternations of two interaction parameters, $J(1+\delta)$ and $J(1-\delta)$. Theoretically, an $S = 1$ Heisenberg antiferromagnet with bond alternation has an energy gap for all values of δ.[6] A phase transition from the Haldane to the dimerized state has been predicted to occur at about $\delta = 0.25$.[7] To our knowledge, the first dimerized Ni^{2+} chain with antiferromagnetic interaction was reported by Escuer et al.[8]

From a chemical viewpoint such a dimerization can be achieved by using a dianion, A^{2-}, instead of a monoanion as in $[Ni(en)_2(NO_2)](ClO_4)$. If the chain structure is retained, the formula will be $[Ni(en)_2(NO_2)]_2A$, and the repeat unit along the chain will contain two bridging networks $[Ni-(NO_2)]-Ni$ which cannot be crystallographically equivalent. Alternatively, the dimerization can be realized by involving in the structure two monoanions, A^- and B^-, which leads to the formula $[Ni(en)_2(NO_2)]_2AB$ with again two crystallographically nonequivalent bridging networks. This Note describes such compounds, of formulas $[Ni(en)_2(NO_2)]_2[Ln(NO_3)_4(CH_3OH)_2](NO_3)\cdot CH_3OH$ where Ln^{3+} is a lanthanide ion. The monoanions $[Ln(NO_3)_4(CH_3OH)_2]^-$ are unprecedented while the dianions $[Ln(NO_3)_5]^{2-}$ have already been reported.[9,10]

Experimental Section

Synthesis. $Ni(en)_2(NO_2)_2$ was synthesized as described in the literature.[11] Single crystals of $[Ni(en)_2(NO_2)]_2$ $[Eu(NO_3)_4(CH_3OH)_2](NO_3)\cdot CH_3OH$ (abbreviated as Ni_2Ln) were obtained as follows: a solution of 1 mmol (0.270 g) of $Ni(en)_2(NO_2)_2$ dissolved in 40 mL of methanol was added to a solution of 1 mmol. (0451 g) of $Eu(NO_3)_3\cdot 6H_2O$ dissolved in 30 mL of methanol. The resulting solution was reduced to 10 mL. Slow diffusion of diethyl ether afforded red single crystals. Anal. Calcd for $C_{11}H_{44}N_{15}O_{22}EuNi_2$: C, 13.11; H, 4.40; N, 20.85; Eu, 15.08; Ni, 11.65. Found: C, 13.19; H, 4.17; N, 21.28; Eu, 15.21; Ni, 11.27. Replacing Eu(III) nitrate by another lanthanide(III) nitrate, $Ln(NO_3)_3\cdot 6H_2O$ (with Ln = La to Lu, and Y), resulted in related compounds $[Ni(en)_2(NO_2)]_2[Ln(NO_3)_4(CH_3OH)_2](NO_3)\cdot CH_3OH$. It may be noticed that in those syntheses only half of the used Ln^{3+} ions are recovered in the final compound. The Ln^{3+} nitrate plays also the role of a nitrate source.

Crystallographic Data Collection and Structure Determination. Data collection was performed at 233 K on a parallelipipedic crystal mounted on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (graphite monochromator), employing the $\theta-2\theta$ scan technique. A total of 4534 reflections (1.6. $\leq \theta \leq$ 28°) were collected, 3713 of them with $I > 2\sigma(I)$. The net intensity values of three standard reflections monitored after every 3600 s of X-ray exposure revealed no decay during the 72 h of exposure. Lorentz and polarization corrections as well as absorption corrections (DIFABS)[12] were applied

---

[†] Institut de Chimie de la Matière Condensée de Bordeaux.

[‡] Université de Rennes 1.

[§] RIKEN.

(1) Meyer, A.; Gleizes, A.; Girerd, J. J.; Verdaguer, M.; Kahn, O. *Inorg. Chem.* **1982**, *21*, 1729.

(2) Haldane, F. D. M. *Phys. Rev. Lett.* **1983**, *50*, 1153; *Phys. Lett. A* **1983**, *93*, 464.

(3) Renard, J. P.; Verdaguer, M.; Regnault, L. P.; Erkelens, W. A. C.; Rossat-Mignod, J.; Ribas, J.; Stirling, W. G.; Vettier, C. *J. Appl. Phys.* **1988**, *63*, 3538.

(4) Renard, J. P.; Regnault, L. P.; Verdaguer, M. *J. Phys. (Les Ulis)* **1988**, *C8-1425*, 49.

(5) Katsumata, K.; Hori, H.; Takeuchi, T.; Date, M.; Yamagishi, A.; Renard, J. P. *Phys. Rev. Lett.* **1989**, *63*, 86.

(6) Affleck I.; Haldane, F. D. M. *Phys. Rev. B* **1987**, *36*, 5291.

(7) Singh, R. R. P.; Gelfand, M. P. *Phys. Rev. Lett.* **1988**, *61*, 2133.

(8) Escuer, A.; Vicente, R.; Ribas, J.; Salah El Fallah, M.; Solans, X.; Font-Bardia, M. *Inorg. Chem.* **1994**, *33*, 1842.

(9) Al-Karaghouli, A. R.; Wood, J. S. *J. Chem. Soc., Chem. Commun.* **1970**, 135.

(10) Avecilla, F.; Bastida, R.; de Blas, A.; Fenton, D. E.; Macias, A.; Rodriguez, A.; Rodriguez-Blas, T.; Garcia-Granda, S.; Corzo- Suarez, R. *J. Chem. Soc., Dalton Trans.* **1997**, 409.

(11) *Jikken Kagaku Koza*; Inokuchi, Ed.; Maruzen Co.; Tokyo, 1991.

(12) Walker, N.; Stuart, D. *Acta Crystallogr. A* **1989**, *39*, 158.

10.1021/ic980458q CCC: \$15.00

Table 1. Crystallographic Data for $[Ni(en)_2(NO_2)][Eu(NO_3)(CH_3OH)_2]$ $[No_3]\cdot CH_3OH$

formula	$C_{11}H_{44}N_{15}O_{22}EuNi_2$
space group	*Pnma*
a, Å	15.791(7)
b, Å	10.465(5)
c, Å	21.716(2)
V, Å^3	3589(2)
Z	4
fw	1007.99
d_{calcd}, g cm^{-3}	1.854
T, K	233(2) K
μ, mm^{-1}	2.865
λ, Å	0.710 73
R indices	
R1[a]	0.0442
wR2[b]	0.1246

[a] $R1 = \sum||F_o| - |F_c||/\sum |F_o|$. [b] $wR2 = \{[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths in Å

	$[Eu(NO_3)_4(CH_3OH)_2]^-$		
Eu1−O1	2.520(4)	N1−O1	1.237(6)
Eu1−O3	2.565(4)	N1−O2	1.225(8)
Eu1−O5	2.491(4)	N2−O3	1.262(5)
Eu1−O7	2.489(5)	N2−O4	1.229(7)
Eu1−O8	2.490(5)	N3−O5	1.252(5)
Eu1−O10	2.428(4)	N3−O6	1.224(9)
Eu1−N1	2.938(6)	N4−O7	1.264(7)
Eu1−N2	2.980(6)	N4−O8	1.278(8)
Eu1−N3	2.903(7)	N4−O9	1.213(8)
Eu1−N4	2.927(6)	O10−C1	1.432(6)
	Free Nitrate		
N11−O15	1.243(5)	N11−O16	1.233(8)
	Dimerized Ni^{2+} Chain		
Ni1−N5	2.079(5)	Ni1−O12	2.245(7)
Ni1−N6	2.084(5)	Ni1−O14	2.229(7)
Ni1−N7	2.062(5)	N9−O11	1.245(9)
Ni1−N8	2.093(6)	N9−O12	1.304(10)
Ni1−N9	2.182(8)	N10−O13	1.259(10)
Ni1−N10	2.188(8)	N10−O14	1.275(9)
	Non-Coordinated Methanol Molecule		
C6−O17	1.413(11)		

Table 3. Lattice Parameters (Å) and Cell Volume (Å^3) for Some $[Ni(en)_2(NO_2)]_2[Ln(NO_3)_4(CH_3OH)_2][NO_3]\cdot CH_3OH$ Compounds at Room Temperature

Ln	*a*	*b*	*c*	*V*
Pr	15.901(3)	10.471(6)	21.829(3)	3636
Nd	15.896(1)	10.471(6)	21.817(3)	3631
Sm	15.868(4)	10.476(1)	21.850(13)	3632
Eu	15.852(21)	10.476(1)	21.827(3)	3624
Gd	15.865(3)	10.440(2)	21.739(8)	3600
Tb	15.890(1)	10.441(1)	21.791(4)	3615
Yb	15.785(6)	10.407(3)	21.677(10)	3561

on these data. The structure, including hydrogen atoms, was solved by direct methods in SHELXS-86[13] and refined by the full-matrix least-squares procedure based on F^2 in SHELXL-93.[14] All non-hydrogen atoms have been assigned anisotropic displacement parameters. Crystallographic and refinement parameters are given in Table 1. Selected bond lengths are given in Table 2. Single crystals were obtained for seven $[Ni(en)_2(NO_2)]_2[Ln(NO_3)_4(CH_3OH)_2](NO_3)\cdot CH_3OH$ compounds. They were all found to be isostructural. The lattice parameters and cell volumes are given in Table 3.

Magnetic Properties. These were carried out on powder samples of all Ni_2Ln compounds of the series (with Ln = La to Lu, and Y), using a Quantum Design SQUID magnetometer. In addition, the magnetic properties of Ni_2Y were measured on a sample consisting of several single crystals weighing together 35.1 mg, whose *b* axis directions were aligned along the external magnetic field.

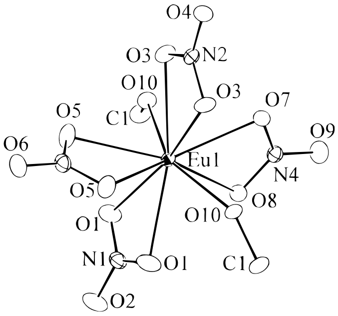

Figure 1. View of the $[Eu(NO_3)_4(CH_3OH)_2]^-$ anion in $[Ni(en)_2(NO_2)]_2[Eu(NO_3)_4(CH_3OH)_2][NO_3]\cdot CH_3OH$.

Description of the Crystal Structure of $[Ni(en)_2(NO_2)][Eu(NO_3)_4(CH_3OH)_2][NO_3]\cdot CH_3OH$. The crystal structure of the Ni_2Eu compound was solved at 233 K. This structure is rather complicated and must to be described carefully. It comprises four different entities, namely, (i) an unprecedented $[Eu(NO_3)_4(CH_3OH)_2]^-$ monoanion; (ii) an isolated nitrate anion; (iii) a slightly dimerized cationic Ni^{2+} chain with nitro−nitrito bridges, of formula $\{[Ni(en)_2(NO_2)]_2\}_n^{2n+}$; and (iv) finally, a noncoordinated methanol molecule.

The structure of $[Eu(NO_3)_4(CH_3OH)_2]^-$ is represented in Figure 1. The europium atom is surrounded by eight oxygen atoms, six of them arising from three bidentate nitrato ligands, and the last two arising from two methanol molecules. The europium atom together with the N1, O2, N2, O4, N3, O6, N4, O7, O8, and O9 atoms are located on a mirror plane. The Eu−O(CH_3OH) bond length (2.428(4) Å) is significantly shorter than the Eu−O(NO_3) bond lengths, from 2.489(5) to 2.565(4) Å. The Eu···N separations involving the nitrogen atoms of the nitrato groups are rather short, from 2.903(7) to 2.980(6) Å. Concerning the four nitrato ligands, the N−O bond lengths involving terminal oxygen atoms (mean value: 1.222 Å) are slightly but significantly shorter than the N−O bond lengths involving coordinated oxygen atoms (mean value: 1.258 Å).

The unit cell contains another monoanion, a nitrate. Its nitrogen atom as well as one of its oxygen atoms are situated on a mirror plane. The mean value of the N−O bond lengths is equal to 1.239 Å.

The structure of the cationic Ni^{2+} chain is somewhat subtle. The chain runs along the *b* axis direction. All the nickel sites are crystallographically equivalent. They are in a strongly distorted octahedral environment with two en ligands in the basal plane and two NO_2^- groups occupying the apical positions. The two NO_2^- groups are crystallographically independent, in contrast with what has been found in $[Ni(en)_2(NO_2)](ClO_4)$. The nitrogen atoms of the nitro−nitrito ligands are disordered on two general positions with occupancy factors of 1/2. The oxygen atoms of these nitro−nitrito groups are also disordered with occupancy factors of 1/2, but occupy particular positions. This disorder of the nitro−nitrito oxygen atoms has already been observed in $[Ni(en)_2(NO_2)](ClO_4)$.[1] From a purely crystallographic viewpoint the Ni chromophores along the chain direction may be either all $Ni(en)_2(NOO)(ONO)$, with both a nitro and a nitrito ligand, or alternatively $Ni(en)_2(NOO)_2$ with two nitro ligands and $Ni(en)_2(ONO)_2$ with two nitrito ligands. The magnetic properties arising from the Ni^{2+} chains in Ni_2Ln compounds and $[Ni(en)_2(NO_2)](ClO_4)$ are very similar (see below). Therefore, the structures of these Ni^{2+} chains in the two types of compounds should be similar, and the former structural hypothesis is by far the most likely. The related chain structure is represented in Figure 2.

Let us compare this chain structure of Figure 2 with that found in $[Ni(en)_2(NO_2)](ClO_4)$. The mean values of the Ni−N bond lengths involving the en ligands are much the same, 2.079 Å in Ni_2Eu and 2.080 Å in $[Ni(en)_2(NO_2)](ClO_4)$. The Ni−N bond lengths involving the nitro ligands are also very similar, 2.182(8) and 2.188(8) Å in Ni_2Eu and 2.163(4) in $[Ni(en)_2(NO_2)](ClO_4)$. On the other hand, the Ni−O bond lengths involving the nitrito ligands are significantly longer in

---

(13) Sheldrick, G. M. *SHELXS-86*: *Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1986.

(14) Sheldrick, G. M *SHELXL 93*: *Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1993.

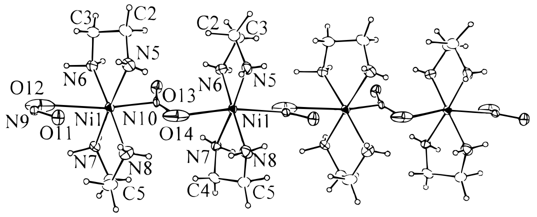

Figure 2. View of the dimerized Ni^{2+} chain in $[Ni(en)_2(NO_2)]_2[Eu(NO_3)_4(CH_3OH)_2][NO_3]\cdot CH_3OH$.

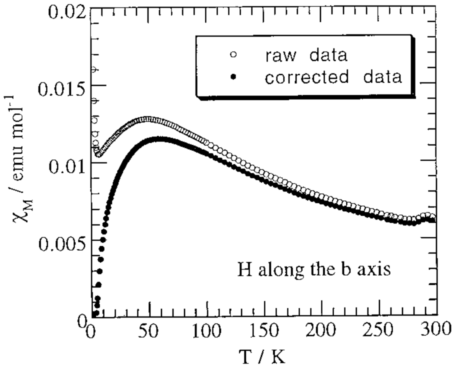

Figure 3. Temperature dependence of the molar magnetic susceptibility for $[Ni(en)_2(NO_2)]_2[Y(NO_3)_4(CH_3OH)_2][NO_3]\cdot CH_3OH$ (see text).

Ni_2Eu (2.245(7) and 2.229(7)) Å) than in $[Ni(en)_2(NO_2)](ClO_4)$ (2.183(4) Å). As a consequence of the differences of Ni−O bond lengths, the Ni···Ni separations along the chain are larger in Ni_2Eu, 5.221(3) and 5.244(3) Å, than in $[Ni(en)_2(NO_2)](ClO_4)$, 5.100(1) Å. To sum up the differences between the two chain compounds, Ni_2Eu and $[Ni(en)_2(NO_2)](ClO_4)$, we can say that the former is slightly dimerized, as a consequence of the presence of two monoanions in the lattice instead of only one. Furthermore, the Ni−O(NO) bond lengths and the Ni···Ni intrachain separations are significantly longer in the new compound.

The Ni^{2+} chains are strongly isolated from each other, due to the presence of bulky Ln-containing anions between them. The shortest interchain Ni···Ni separation is equal to 7.895(4) Å. The shortest Eu···Eu and Eu···Ni separations are 8.599(2) and 6.347(1) Å, respectively.

Magnetic Susceptibility Data. The magnetic properties of Ni_2Y were investigated in more details. In this compound the Y^{3+} ion is diamagnetic, so that only the dimerized Ni^{2+} chain contributes to the magnetic behavior. In other respects, this compound gives rather large needle-shaped single crystals, the needle axis being collinear with the *b* axis direction of the orthorhombic lattice.

The temperature (T) dependence of the molar magnetic susceptibility (χ_M) for Ni_2Y is represented in Figure 3, the magnetic field of 100 Oe being applied along the chain axis. Open circle show the raw data. The susceptibility exhibits a broad maximum around 55 K and then a Curie (or Curie−Weiss) tail as T is lowered further. These raw data were assigned to the superposition of the intrinsic susceptibility of the Ni^{2+} chain and an extrinsic susceptibility due to an uncoupled paramagnetic impurity. The low-temperature part of the susceptibility, assumed to follow a Curie−Weiss law $\chi_M^{impurity} = C/(T + \Theta)$, was subtracted from the raw data. C and Θ were found as 0.0723 emu K mol^{-1} and 2.58 K, respectively. The C value may correspond to a small amount of Gd^{3+} impurity present in the Y^{3+} salt used for the synthesis. Filled circles in Figure 3 show the corrected susceptibility data. The intrinsic susceptibility of the dimerized Ni^{2+} chain compound decreases steeply with decreasing temperature below 55 K and tends to zero as the temperature approaches the absolute zero. This is consistent with the theoretical prediction that the ground state of an $S = 1$ one-dimensional antiferromagnet with bond alternation is a singlet.

The temperature dependences of the magnetic susceptibility for the other Ni_2Ln compounds were measured on powder samples. In all the cases the raw data can be analyzed as resulting from two uncorrelated contributions, one arising from the $[Ln(NO_3)_4(CH_3OH)_2]^-$ anion, the other one arising from the Ni^{2+} chain. Within the experimental uncertainties the Ni^{2+} chain contributions are very close to what is shown in Figure 3.

The next step of this work is to interpret quantitatively the magnetic data of Figure 3. A theoretical model for the magnetic susceptibility of alternating $S = 1$ chains has been proposed by Borras.[15] However, in the present case, the dimerization, or bond alternation, is very weak. Let us remind that the Ni···Ni separations are alternatively 5.221(3) and 5.244(2) Å. It turns out that the two interaction parameters may be assumed to be very close to each other and that it makes sense to consider the law appropriate for a uniform $S = 1$ one-dimensional antiferromagnet and to look for an average value of the interaction parameter between adjacent Ni^{2+} ions. Numerical values of the susceptibility of $S = 1$ chains have been derived by Weng,[16] using the ring chain techniques.[17,18] Subsequently, an analytical expression was proposed, valid for antiferromagnetic coupling.[1] This expression is:

$$\chi_M = (Ng^2\beta^2/kT)(2 + 0.0194x + 0.777x^2)/(3 + 4.346x + 3.232x^2 + 5.834x^3) \quad (1)$$

with

$$x = |J|/kT \quad (2)$$

the spin Hamiltonian in zero field being written as

$$\mathbf{H} = -J\sum_i \mathbf{S}_i\cdot\mathbf{S}_{i+1} \quad (3)$$

Let us emphasize that eq 1 does not take into account the gap between the ground singlet state and the continuum, and therefore is not valid as T tends to zero. Equation 1 closely reproduces the experimental data (which are expressed for two Ni^{2+} ions in Figure 3) down to 10 K, with $J = -30.5\ cm^{-1}$ and $g = 2.12$. The Weng approach together with the analytical expression (1) may seem rather crude. That is why we also interpreted the magnetic data with a more accurate calculation based on a quantum transfer matrix method. This led to $J = -31.3\ cm^{-1}$. The J value for $[Ni(en)_2(NO_2)](ClO_4)$ was found to be $-33\ cm^{-1}$, using the Weng approach. The antiferromagnetic interaction is slightly weaker in the title compounds, which is in line with the slightly larger Ni···Ni separations. An attempt to use Borras' model for alternating Ni^{2+} chains results in no improvement of the fitting of the experimental data.

Conclusion

The compounds $[Ni(en)_2(NO_2)]_2[Ln(NO_3)_4(CH_3OH)_2](NO_3)\cdot CH_3OH$ contain dimerized Ni^{2+} chains with nitro−nitrito bridges. This dimerization is the consequence of the presence of two kinds of monoanions in the lattice, one of them being unprecedented. This novel anion is $[Ln(NO_3)_4(CH_3OH)]^-$ where Ln may be any lanthanide element as well as yttrium. Due to the large separation between Ni^{2+} chains and Ln-containing anions, the magnetic properties of the compounds have been interpreted as the sum of two contributions. In the case where Ln = Y, the anions are diamagnetic, and the magnetic behavior is that of the dimerized Ni^{2+} chain. As T tends to the absolute zero, the magnetic susceptibility tends to zero, which reveals the existence of an energy gap between singlet ground state and low-lying excited states. It would be very interesting to compare the magnitude of this gap to that observed in the equally spaced chain compound $[Ni(en)_2(NO_2)](ClO_4)$. INS could provide this information. In the title compounds the gap arises from both the specificity of the integer

---

(15) Borras, J. J. Ph.D. Thesis, University of Valencia, Spain, 1991.
(16) Weng, C. Y. Ph.D. Thesis, Carnegie Institute of Technology, Pittsburgh, PA, 1968.
(17) Bonner, J. C.; Fisher, M. E. *Phys. Rev. A* **1964**, *135*, 640.
(18) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

spin chains (Haldane gap) and the dimerization. It might be also worthwhile to examine whether the magnitude of the gap is influenced by the presence of isotropic (Ln = Gd) or anisotropic (Ln = Dy) magnetic centers between the Ni^{2+} chains.

The work described in this Note points out, if it was still necessary, how molecular chemistry can provide interesting new objects to condensed matter physicists.

Acknowledgment. We express our gratitude to Dr. Hitoshi Asakawa who performed the calculation of the magnetic susceptibility for an $S = 1$ chain using a quantum transfer matrix method.

Supporting Information Available: An X-ray crystallographic file for Ni_2Eu, in CIF format, is available. Access information is given on any current masthead page.

IC980458Q