Two Ferromagnetic One-Dimensional Nickel(II) Complexes Containing the Diamagnetic $[Ni(CN)_4]^{2-}$ Group

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A cyano-bridged nickel(II) compound, $[NiL][Ni(CN)_4]\cdot 4H_2O$ (L = 3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane), was prepared and characterized. Single crystal X-ray analysis reveals that the compound assumes a cyano-bridged chain structure in which one nickel(II) ion is coordinated by four cyanide ligands and the other is coordinated by four nitrogen atoms of the macrocyclic ligand and two nitrogen atoms of the bridging cyanide ligands. The six-coordinate nickel(II) centres display an axially elongated octahedron, whereas the four-coordinate nickel(II) centres assume planar geometry. Magnetic investigations on $[NiL][Ni(CN)_4]\cdot 4H_2O$ and a similar chain-like compound $[Ni(TIM)][Ni(CN)_4]$ show the presence of weak intrachain ferromagnetic interactions between the paramagnetic nickel(II) ions through the diamagnetic $[Ni(CN)_4]^{2-}$ anions.

Introduction

During the last two decades, much attention has been directed to the synthesis of molecule-based magnets, especially to Prussian Blue analogues.[1] Prussian Blue, with the formula $Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot 15H_2O$ is a ferromagnet with T_c = 5.6 K, in which the paramagnetic iron(III) ions are bridged in three-dimensions by the diamagnetic hexacyanoferrate(II) anion, with a shortest intermetallic $Fe^{III}\cdots Fe^{III}$ separation of 10.6 Å.[2] Recently, a series of three-dimensional bimetallic compounds $[Ni(L)_2]_3[Fe^{II}(CN)_6]X_2$ (L = en or tn, X = PF_6^- or ClO_4^-) and one two-dimensional copper(II)-iron(II) compound $[Cu(dmen)_2]_2[Fe^{II}(CN)_6]$ (dmen = dimethylaminoethylamine) were prepared and found to exhibit ferromagnetic interactions between the nearest nickel(II) or copper(II) ions through the diamagnetic $[Fe(CN)_6]^{4-}$ anions.[3] Nevertheless, antiferromagnetic coupling between paramagnetic transition metal ions is more often operative via diamagnetic building blocks, such as $[Co(CN)_6]^{3-}$, $[Ni(CN)_4]^{2-}$, $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$.[4–6] In addition, the diamagnetic $[CrO_4]^{2-}$ group can mediate either ferromagnetic[7] or, in most cases, antiferromagnetic interactions.[8] We have been interested in magnetic interactions via cyanide-containing diamagnetic building blocks, and have found that the nitroprusside anion $[Fe(CN)_5(NO)]^{2-}$ can transmit weak antiferromagnetic interactions in $[Cu(en)][Fe(CN)_5(NO)]$,[9] as is also observed in $[Ni(en)_2][Fe(CN)_5(NO)]$.[10] Using the diamagnetic $[Ni(CN)_4]^{2-}$ building block, we prepared two one-dimensional chain complexes $[NiL][Ni(CN)_4]\cdot nH_2O$ [L = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene abbreviated as TIM, n = 0 (**1**);11 L = 3,10-diethyl-1,3,5,8,10,12-hexaazacyclotetradecane, n = 4 (**2**)]. Interestingly, a ferromagnetic interaction is observed in the two complexes. In the present paper, we report the synthesis, crystal structure and magnetic properties of **2** together with the magnetic behaviour of **1**.

Results and Discussion

The IR spectrum of **2** exhibits two strong bands at 2150 and 2120 cm^{-1}, which can be attributed to the C≡N stretching vibration. It is well-known that the formation of a cyanide bridge shifts ν(CN) towards higher frequencies.[1] The strong band at 2150 cm^{-1} may therefore be attributed to ν(CN) of the bridging cyanides and that at 2120 cm^{-1} to the terminal ones. The strong absorption at 1650 cm^{-1} indicates the presence of water in the molecule, which is consistent with the structural studies.

It has been shown that the four-coordinate nickel(II) macrocyclic complexes can accept donor atoms yielding six-coordinate nickel(II) geometries.[11,12] The cyano nitrogen

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atom is a strong donor and easily coordinates to the nickel(II) ion to give rise to cyano-bridged complexes.

Crystal Structure

The structure of **2** consists of one *trans*-$[NiL]^{2+}$ cation and one $[Ni(CN)_4]^{2-}$ anion as illustrated in Figure 1. Selected bond lengths and angles are listed in Table 1. The coordination geometry about Ni(1) is nearly octahedral, with four secondary amine nitrogen atoms of the macrocyclic ligand L [$Ni-N_{eq}$ = 2.072(4) Å] occupying the equatorial plane and two nitrogen atoms of two bridging cyanide ligands situated at the axial sites [$Ni-N_{ax}$ = 2.137(2) Å]. The bridging cyanides coordinate to Ni(1) in a linear fashion [Ni(1)−N(1)−C(1) = 175.0(5)°], significantly different from the situation found in **1**[158.0(2)°].[11] The bond lengths and angles of [NiL] are similar to those in $[NiL]_3[Fe(CN)_6]_2 \cdot 12H_2O$:[12a] each $[Ni(CN)_4]^{2-}$ unit uses two *tran*s C≡N groups to connect to two *trans*-$[NiL]^{2+}$ moieties giving rise to one-dimensional Ni−C≡N−Ni linkages, whereas the two remaining *trans* CN^- groups are monodentate. The adjacent Ni···Ni distance is 5.094 Å, and the nearest interchain Ni(1)···Ni(1) distance is 9.337 Å. The water molecules are positioned in the vicinity of the chain and hydrogen-bonded to the nitrogen atoms of the nonbridging cyanides within the chain and to each other (Figure 2 top and bottom). No hydrogen-bonded two- or three-dimensional network is formed.

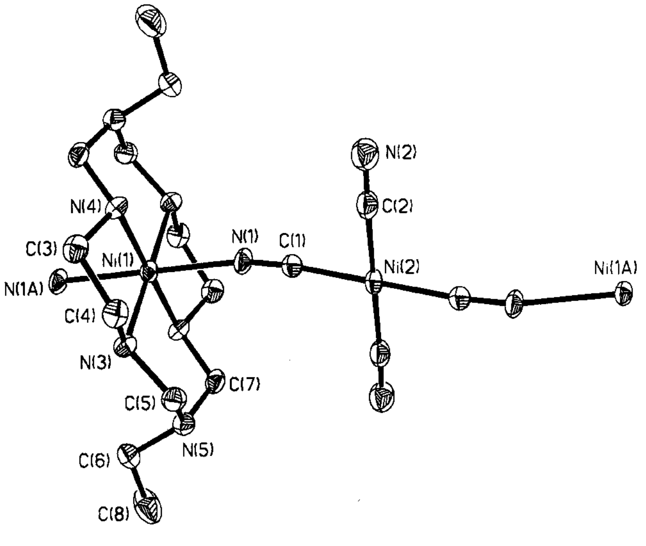

Figure 1.An ORTEP drawing of **2** with thermal ellipsoids drawn at the 30% probability level

Table 1. Bond lengths (Å) and angles (°) for **2**

Ni(1)−N(4)	2.070(4)	Ni(1)−N(3)	2.073(4)
Ni(1)−N(1)	2.137(5)	Ni(2)−C(2)	1.855(7)
Ni(2)−C(1)	1.871(6)	N(1)−C(1)	1.133(7)
N(2)−C(2)	1.148(7)		
C(1)−N(1)−Ni(1)	167.7(5)	C(4)−N(3)−Ni(1)	104.5(3)
N(1)−C(1)−Ni(2)	175.0(5)	N(2)−C(2)−Ni(2)	177.7(6)

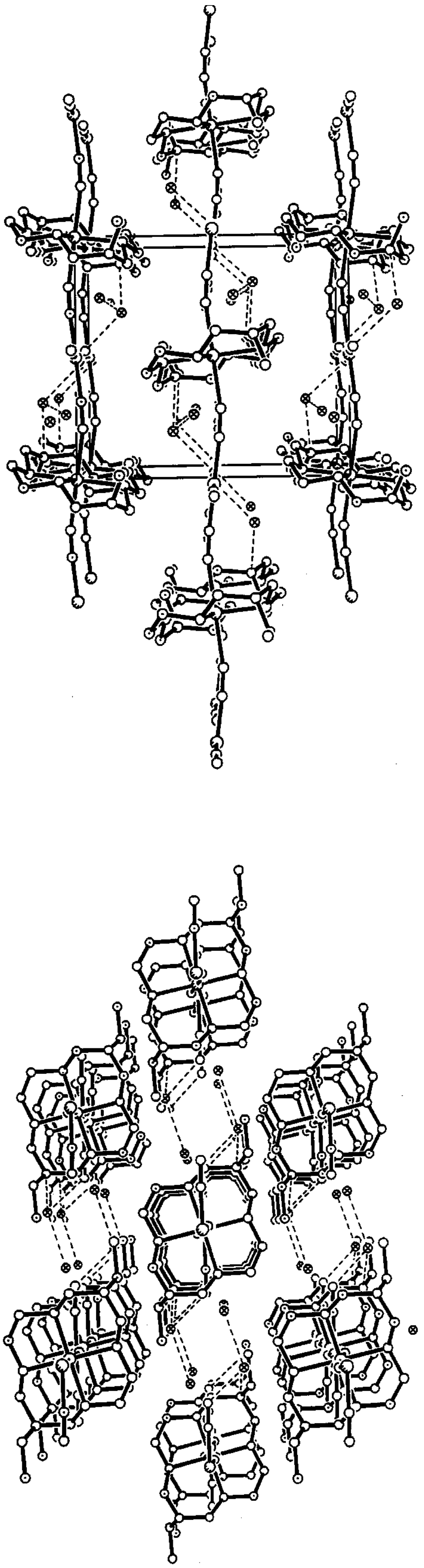

Figure 2. (top) Projection along the *c* axis, showing the polymeric chains including alternating nickel groups of **2**; (bottom) projection perpendicular to the *c* axis for **2**

Magnetic Properties

The magnetic susceptibilities of **1** and **2** have been measured in the temperature range 1.8−200 K. Plots of χ_mT and χ_m^{-1} vs. T for **1** and **2**, where χ_m is the magnetic susceptibility per Ni_2 unit, are shown below.

Complex 1

At 200 K, the χ_mT value is ca. 1.06 emu K mol^{-1} (2.91 μ_B), close to that (1.0 emu K mol^{-1}, 2.83 μ_B) of an isolated Ni^{II} ion (S = 1, g = 2.0) interacting with a diamagnetic Ni^{II} ion (S = 0). As the temperature decreases the χ_mT value increases slowly reaching a maximum value of 1.16 emu K mol^{-1} (3.05 μ_B) at 20.8 K and then decreases sharply reaching a minimum value of 0.53 emu K mol^{-1} (2.06 μ_B) at 1.8 K. Such a magnetic behaviour is characteristic of a dominant ferromagnetic interaction to which weak antiferromagnetic interactions are superimposed.[13] The lack of interchain intermolecular contacts in **1**[11] suggests the through-space magnetic coupling is weaker than that through the -NC−Ni−CN- pathway. Therefore, the dominant ferromagnetic interaction is due to the intrachain interaction, and the interchain interaction is antiferromagnetic. The magnetic susceptibility above 10 K obeys the Curie−Weiss law with a positive Weiss constant θ = +2.9 K (Figure 3); this also proves the presence of ferromagnetic coupling within the Ni_2 chain of **1**.

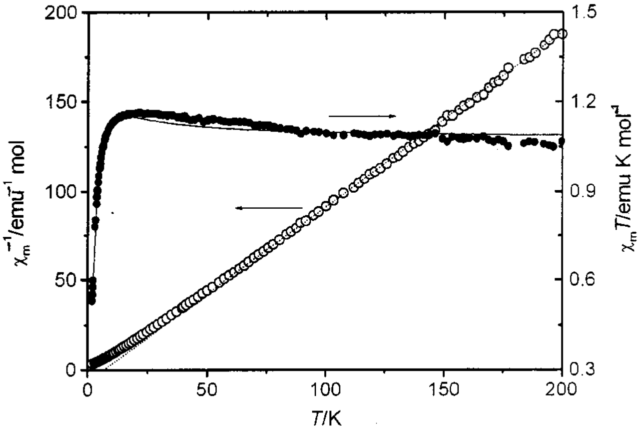

Figure 3. Temperature dependence of χ_mT and χ_m^{-1} for **1**; the solid line represents the theoretical values and the dotted line the fit to the Curie−Weiss law

We attempted to interpret the magnetic data using Fisher's model[14] for the classical spin chain system (S = 1 and $\boldsymbol{H}_{chain} = -J\Sigma S_iS_{i+1}$) neglecting zero-field splitting and the Haldane gap effect[15] and taking into consideration a mean-field correlation term.[7a,16] The magnetic susceptibility can be expressed by Equation (1), where N is Avogadro's number, β is the Bohr magneton, k is the Boltzmann constant and z is the number of nearest neighbours (two in this case). The least-squares fitting to the experimental data led to J = +2.88 cm^{-1}, J' = −0.94 cm^{-1} and g = 2.08. This result (J = +2.88 cm^{-1}) shows the presence of weak ferromagnetic interaction between the paramagnetic nickel ions within each chain through the diamagnetic $[Ni(CN)_4]^{2-}$ ions.

$$\chi_{chain} = \frac{Ng^2\beta^2}{3kT}\frac{1+u}{1-u}\times S(S+1)$$
$$u = \coth K - 1/K \text{ and } K = JS(S+1)/kT \qquad (1)$$
$$\chi_m = \chi_{chain}/[1-\chi_{chain}(zJ'/Ng^2\beta^2)]$$

Complex 2

Complex **2** has a magnetic behaviour similar to that of **1** (Figure 4). At 200 K, the χ_mT value is ca. 1.25 emu K mol^{-1} (3.16 μ_B), larger than that (1.0 emu K mol^{-1}, 2.83 μ_B) of an isolated Ni^{II} ion (S = 1, g = 2.0) interacting with a diamagnetic Ni^{II} ion (S = 0). As the temperature decreases, the χ_mT value increases slightly reaching a maximum value of 1.29 emu K mol^{-1} (3.21 μ_B) at 16.6 K and then decreases sharply reaching a minimum value of 0.60 emu K mol^{-1} (2.2 μ_B) at 1.6 K. The magnetic susceptibility above 11 K obeys the Curie−Weiss law with a positive Weiss constant θ = +1.5 K (Figure 4), which confirms the presence of ferromagnetic coupling within the Ni_2 chain of **2**. Similarly, the magnetic data can be analysed by Equation (1) giving the parameters J = +2.19 cm^{-1}, J' = −0.92 cm^{-1} and g = 2.23.

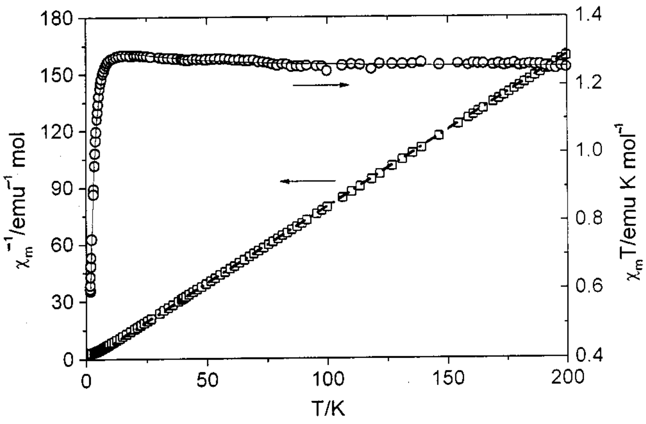

Figure 4. Plot of χ_mT and χ_m^{-1} vs. temperature for **2**; the solid line represents the theoretical values and the dashed line the fit to the Curie−Weiss law

The increase in χ_mT is due to a substantial contribution of ferromagnetic coupling, although the origin of this is not clear at this stage. Apparently, the ferromagnetic nature is not due to the orthogonality of the magnetic orbitals. One possibility is that it is due to a long-range interaction mediated through the empty d_σ orbital of the diamagnetic Ni^{II} ion. According to the Goodenogh−Kanamori rules for magnetic superexchange,[17] if a magnetic orbital overlaps an empty orbital the interaction between the two ions is ferromagnetic. This mechanism has recently been used to explain the ferromagnetic interaction between the nearest paramagnetic metal ions through the diamagnetic $[Fe(CN)_6]^{4-}$ or $[Co(CN)_6]^{3-}$ anions in $[Ni(en)]_3[Fe(CN)_6]PF_6$, $[NiL_2]_3[Fe(CN)_6]X_2$ (X = PF_6^- or ClO_4^-) and $[Ni(tn)_2]_2[Co(CN)_6]NO_3\cdot 2H_2O$.[3a,18] For the present complexes, an electron spin of the same sign as that of the unpaired electron in the $d_{x^2-y^2}$ (paramagnetic Ni^{II}) orbital (x axis is taken along the Ni−C≡N−Ni linkage) is polarized on the empty $d_{x^2-y^2}$ (diamagnetic Ni^{II}) orbital (x axis is taken perpendicular to the NiC_4 plane) through the filled orbital of the cyanide bridges, giving rise to a ferromagnetic coupling between the nearest intrachain paramagnetic nickel(II) ions.

If we compare the θ and J values of the two complexes, we see that the values for **1** are slightly larger indicating a stronger magnetic coupling in **1**. This is in good agreement with the increasing order of the Ni(2)−C(1) and Ni(1)−N(1) bond lengths (1.858, 2.123 Å for **1**, 1.871, 2.137 Å for **2**). Such an elongation indicates a decreasing overlap of the d_σ orbitals and is unfavourable for the magnetic interaction between paramagnetic Ni^{II} ions.

Experimental Section

Physical Measurements: Elemental analyses of carbon, hydrogen and nitrogen were carried out with a Perkin−Elmer analyzer model 240. Infrared spectroscopy on KBr pellets was performed on a Shimadzu IR-408 infrared spectrophotometer in the 4000−600 cm^{-1} region. Variable-temperature magnetic susceptibility measurements (1.8−200 K) of powder samples were performed in a field of 1 T on a model Maglab System^{2000} magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's Tables).

Preparations: All reagents used in the syntheses were of analytical grade and were used without further purification. $[Ni(TIM)][Ni(CN)_4]$ (**1**),[11] $[Ni(TIM)](ClO_4)_2$,[19] and $[NiL](ClO_4)_2$,[20] were prepared as described previously.

$[NiL][Ni(CN)_4]\cdot 4H_2O$ (2): Two aqueous solutions of $[NiL](ClO_4)_2$ (0.25 mmol) and $K_2[Ni(CN)_4]$ (0.25 mmol) were mixed to produce immediately a brown fine powder which was collected by suction filtration, washed with water and dried under vacuum over P_2O_5. Yield 125 mg (90%). $C_{16}H_{42}N_{10}Ni_2O_4$ (556.0): calcd. C 34.71, H 6.66, N 28.92; found C 34.87, H 6.48, N 28.95. IR: $\tilde{\nu}_{max}$ = 2150, 2130 and 2110 (C≡N) cm^{-1}. Well-shaped light-grey crystals suitable for an X-ray structure analysis were grown at room temperature by the slow mixing of an orange acetonitrile solution of $[NiL](ClO_4)_2$ and a colourless aqueous solution of $K_2[Ni(CN)_4]$ in an H-tube.

Crystal Data for 2: $C_{16}H_{42}N_{10}Ni_2O_4$, $M = 556.02$, monoclinic, $P2_1/n$, $a = 11.0104(8)$, $b = 10.1878(4)$, $c = 11.5099(10)$ Å, $\beta = 91.980(10)°$, $U = 1290.3(2)$ Å^3, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 1.500$ mm^{-1}. $F(000) = 592$, 2263 unique reflections, 1265 observations [$I > 2.00\sigma(I)$] considered unique ($R_{int} = 0.0295$). The final R_{wF} was 0.129, with conventional $R_F = 0.0401$ for 148 parameters.
Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152642. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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