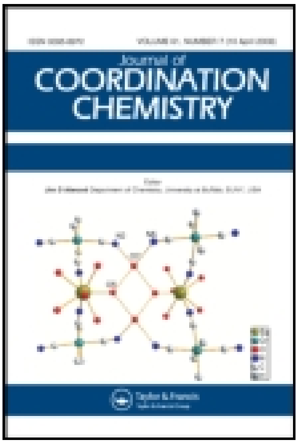

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Synthesis, characterization, and magnetic properties of a coordination polymer of nickel: poly[μ^4-dicyanamide-(2,9-dimethyl-1,10-phenanthroline-κ^2 N,N′)nickel(II)]

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Synthesis, characterization, and magnetic properties of a coordination polymer of nickel: poly[μ^4-dicyanamide-(2,9-dimethyl-1,10-phenanthroline-$\kappa^2 N,N'$)nickel(II)]

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A new coordination polymer of Ni^{2+}, $N(CN)_2^-$ (dicyanamide, herein denoted dca) and 2,9-dimethyl-1,10-phenanthroline (dmphen), has been synthesized, structurally and magnetically characterized. $\{[Ni_2(dmphen)_2[\mu\text{-dca}]_4\}_n$ (**1**), which crystallizes in the monoclinic space group $P2_1/n$, has a 2-D network that consists of double-bridged $[Ni_2(dca)_2(dmphen)_2]^{2+}$ "dimers" connected *via* single-bridging dca ligands and exhibits a typical (6, 3) topological network. Each NiN6 octahedron comprises a bidentate dmphen and four $\mu_{1,5}$-bridging dca anions. Magnetic susceptibility measurements indicate antiferromagnetic interactions between Ni(II) ions *via* the dca bridge.

Keywords: Nickel(II) compound; X-ray structure; Magnetic property; Dicyanamide; 2,9-Dimethyl-1,10-phenanthroline

1. Introduction

Coordination polymers have achieved considerable progress in supramolecular chemistry and magnetism [1]. Structures of products are dependent on many factors, such as the structure of chelating ligands, metal centers, anions, and solvents. The dicyanamide (dca) anion, $[N(CN)_2]^-$, is an important building block for the construction of supramolecular architectures because it has three N-donor sites showing versatility in coordination modes: monodentate bonding through a nitrile nitrogen, bidentate through two nitrile nitrogens of end-to-end bridging, tris-monodentate bridging of three metals as well as an unusual μ_4 coordination, where one nitrile nitrogen binds to two metals (scheme 1). Crystal structures with dca showing 1-D, 2-D, and 3-D compounds, especially $M(II)(dca)_2$ ($M = Ni$, Co, Cu and $dca = [N(CN)_2]^-$), have increased in the past few years [2–8]. Most compounds containing dca have dca as a bridging group and a second organic or inorganic ligand. The second ligand usually is 4,4′-bipyridine(4,4′-bipy), ethylenediamine (en), *N*,*N*-diethyl-ethylenediamine (et_2-en),

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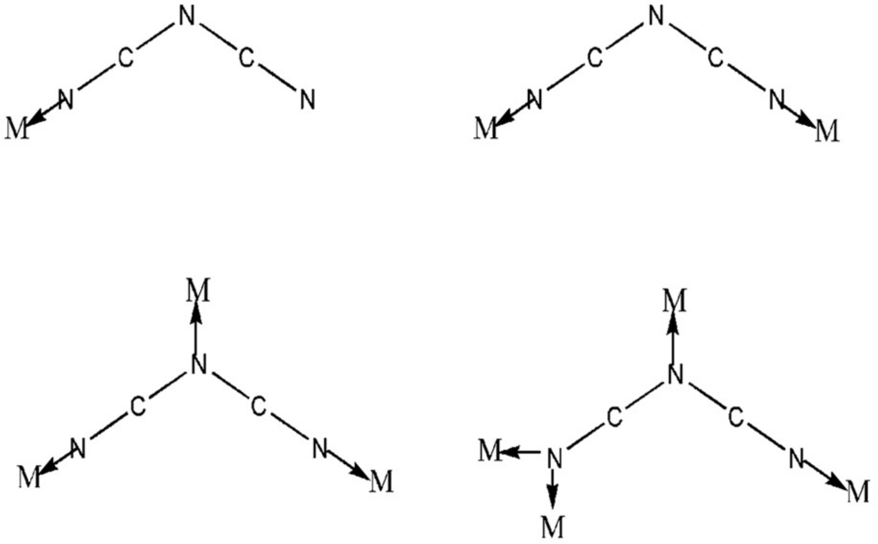

Scheme 1. Several different coordinative modes of dca.

imidazole (im), oxazoline, or phenanthroline (phen) [9–15]. dca may induce a large variety of topologies and magnetic properties due to its versatile coordination [16–19]. Herein, we report the synthesis, crystal structure, and magnetic properties of a 2-D compound, $\{[Ni_2(C_{14}H_{12}N_2)_2[\mu\text{-}N(CN)_2]_4\}x_n$ (**1**), using dmphen ligands linked by dca. Compound **1** shows antiferromagnetic coupling between Ni(II) ions with no long-range ordering above 2 K.

2. Experimental

2.1. *Materials and instrumentation*

All chemicals and solvents were commercially available reagents of analytical grade and used as received. The preparations and manipulations were performed under aerobic conditions. Infrared spectra were recorded as pure crystals on a Nicolet 170SXTF/IR spectrometer in the range 4000–400 cm^{-1}. Magnetic data were recorded using a Quantum Design SQUID magnetometer.

2.2. *Preparation of compound* 1

Compound **1** was synthesized by mixing a solution of dmphen (2,9-dimethyl-1,10-phenanthroline) (0.104 g, 0.5 mmol) in methanol (5 mL) with a solution of $NiCl_2 \cdot 6H_2O$ (0.119 g, 0.5 mmol) in methanol (5 mL), followed by dropwise addition of an aqueous solution $NaN(CN)_2$ (0.178 g, 0.6 mmol, 2 mL) without stirring. The green mixture was allowed to stand for several days until good quality green block crystals of **1** were obtained in a yield of 68.3%. Anal. Calcd for $C_{18}H_{12}N_8Ni$ (%): C, 54.2; H, 3.0; N, 28.1. Found (%): C, 54.4; H, 3.1; N, 27.9. IR spectrum (KBr pellet, cm^{-1}): 2319ms, 2293ms, 2269ms, 2247m, 2212s, 2189s, 1600m.

Table 1. Crystal data and details of the structure determination.

Compound	**1**
Empirical formula	$C_{18}H_{12}N_8Ni$
Formula weight ($g\,mol^{-1}$)	399.07
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	8.868(2)
b	15.282(3)
c	12.793(3)
β	93.99(3)
Volume ($Å^3$), Z	1729.6(6), 4
Calculated density, ρ_{Calcd} ($g\,cm^{-3}$)	1.532
Absorption coefficient, μ (mm^{-1})	1.143
$F(000)$	816
Crystal size (mm^3)	$0.45 \times 0.35 \times 0.15$
θ range for data collection (°)	3.52–28.30
Reflections collected	8341
Independent reflection	4279 [$R(\text{int}) = 0.0163$]
Completeness to θ (%)	99.4
Data/restraints/parameters	4279/0/246
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0314$, $wR_2 = 0.0800$
R indices (all data)	$R_1 = 0.0530$, $wR_2 = 0.0860$
Largest difference peak and hole ($e\,Å^{-3}$)	0.25 and −0.38

2.3. *X-ray crystallography*

Determination of the unit cell and data collection was performed on a Nonius KappaCCD (Nonius, 1998) diffractometer using graphite-monochromated Mo-Kα radiation. The structure was solved by direct methods in SHELXS-97 [20] and refined using full-matrix least-squares on F^2 in SHELXL97 [20]. Hydrogens were assigned with isotropic displacement factors and included in the final refinement cycles by the use of geometrical restraints (C_{ar}–H = 0.93 Å; C_{Me}–H = 0.96 Å; N–H = 0.86 Å).

3. Results and discussion

Single-crystal X-ray diffraction of **1** reveals that it crystallizes in the monoclinic space group $P2_1/n$; details are presented in table 1. The structure of the molecular unit is shown in figure 1. Selected bond lengths and angles of **1** are given in table 2. In $\{[Ni_2(C_{14}H_{12}N_2)_2[\mu\text{-}N(CN)_2]_4\}_n$, each nickel(II) is in an octahedral environment, coordinated by six nitrogens, two from 2,9-dimethyl-1,10-phenanthroline and four from dca anions. Two nitrogens from dca are in axial sites. Bond distances and angles around nickel fall in the range 2.053(2)–2.132(2) Å and 78.90(6)–177.91(6)°, respectively. The shortest Ni $\cdots$ Ni distance is 7.384(2) Å.

The structure is a 2-D coordination network with $Ni(C_{14}H_{12}N_2)$ bridged into chains by dca anions along the b-axis (figure 2), with Ni $\cdots$ Ni distance of 7.702(2) Å; between chains, two kinds of $Ni(C_{14}H_{12}N_2)$ components with Ni $\cdots$ Ni distances of 8.857(2) and

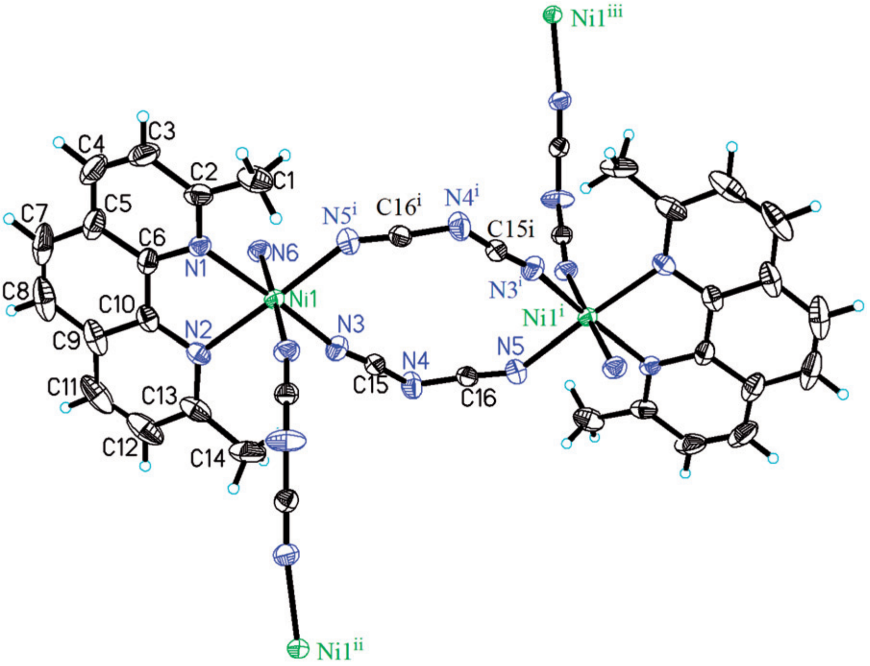

Figure 1. The centrosymmetric repeat unit of **1** showing the coordination of metal ions and ligands. Displacement ellipsoids are drawn at the 30% probability level (Symmetry codes: $^{i}-x+1/2,\ y+1/2,\ -z+3/2$; $^{ii}-x+1,\ -y+2,\ -z+1$).

Table 2. Selected bond lengths (Å) of **1**.

Ni1–N8^{i}	2.0535(16)	Ni1–N6	2.1071(16)
Ni1–N3	2.0721(18)	Ni1–N1	2.1230(15)
Ni1–N5^{ii}	2.0926(18)	Ni1–N2	2.1318(16)

Symmetry codes: $^{i}-x+1/2,\ y+1/2,\ -z+3/2$; $^{ii}-x+1,\ -y+2,\ -z+1$.

7.384(2) Å and the nearer Ni($C_{14}H_{12}N_2$) groups are double bridged by dca anions to form a 2-D framework (figure 3a). This network is a typical example of a (6, 3) topology (figure 3b). Intercalation of phenanthroline units in the structure are attributed to π–π stacking, from the mean distance between coordinated and intercalated phenanthroline units (around 3.66 Å).

The temperature dependence of the magnetic susceptibility of **1** was measured on polycrystalline sample from 1.8 to 300 K under 1 kOe. $\chi_M T$ *versus* T plots of **1** are shown in figure 4. At room temperature $\chi_M T$ is 1.19(2) $cm^3\,mol^{-1}$ K (per Ni(II) ion), and above 10 K χ_M obeys the Curie–Weiss law with a Weiss constant, $\theta = -1.32(1)$ K, and the Curie constant, $C = 1.20(1)\ cm^3\,mol^{-1}$ K. The negative Weiss constant indicates antiferromagnetic interaction between Ni(II) ions. No susceptibility maximum is observed over the studied temperature range, indicating a very small antiferromagnetic coupling, typical in this kind of compound with $\mu_{1,5}$-dca bridges or ZFS of Ni^{II} ions. The plot of the reduced magnetization (M) for **1** is also shown in figure 4 (inset). The $N\beta$ expected value for two unpaired electrons at saturation would be 2.42 (assuming $g = 2.20$). The experimental value for **1** tends to 2.24 $N\beta$ at 2 K and 70 kOe.

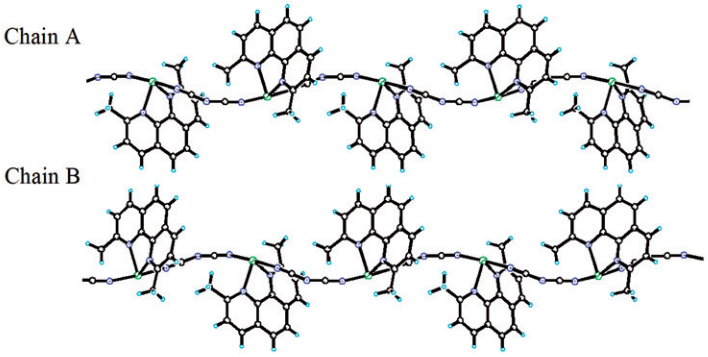

Figure 2. Fragment of the structure of **1** showing a dca-bridged chain extended along the *b*-axis.

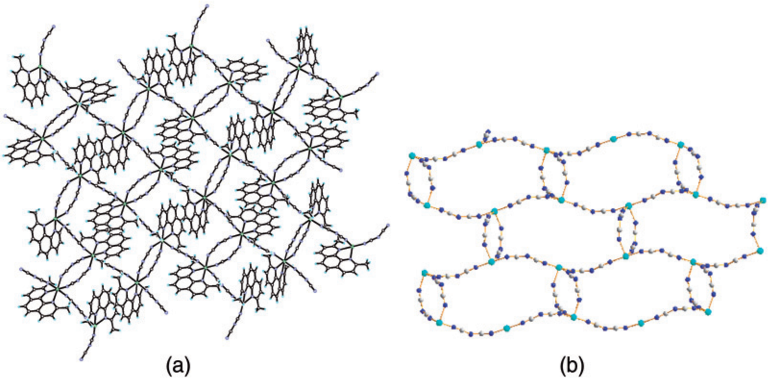

Figure 3. (a) The 2-D network viewed along the *a*-axis. (b) The (6, 3) network topology omitting dmphen.

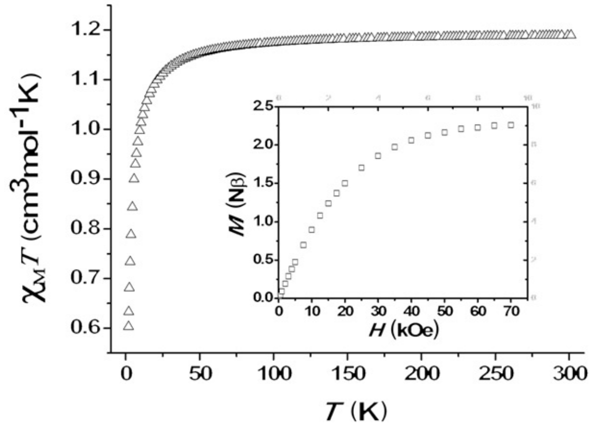

Figure 4. Plots of the $\chi_M T$ *vs*. T and M vs. H (inset, 2 K) for **1**.

4. Conclusion

X-ray structural analysis reveals a 2-D sheet structure of **1** with alternate single and double $\mu_{1,5}$ dca bridges. Such a small value of θ with this kind of structure is very difficult to fit. According to the shape of the plot (figure 4), in a first approach, it is concluded that the long dca-bridging ligand does not create any noticeable coupling.

Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC 784675 for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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