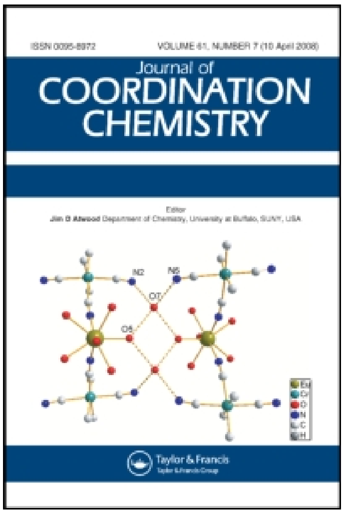

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Synthesis, structure and properties of a one-dimensional coordination polymer containing both dicyanamide and ethylenediamine

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SYNTHESIS, STRUCTURE AND PROPERTIES OF A ONE-DIMENSIONAL COORDINATION POLYMER CONTAINING BOTH DICYANAMIDE AND ETHYLENEDIAMINE

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The nickel(II) complex $[Ni(en)_2\{N(CN)_2\}]ClO_4$ **1** (en = ethylenediamine) has been synthesized and its structure determined. The complex forms a one-dimensional chain structure via the bidentate bridging ligand dicyanamide. A two-dimensional network is formed via interchain hydrogen-bond interactions. The magnetic properties of the compound (5–300 K) show the existence of weak antiferromagnetic exchange interactions between paramagnetic centers along chains.

Keywords: Crystal structure; Dicyanamide; Hydrogen bonding; Nickel complex

INTRODUCTION

Pronounced interest has recently been focused on crystal engineering of supramolecular architectures assembled by means of coordinated covalent bonding or supramolecular contacts (such as hydrogen bonds, π–π interactions, etc.) [1–4].

The ligand $[N(CN)_2]^-$ is a remarkably versatile building block for supramolecular architectures since it may act as a uni-, bi- or terdentate ligand. Additional ligands, such as coordinating amines (Lewis bases), in combination with dicyanamide have been shown to produce novel structural types [5–7]. Examples of unidentate $[N(CN)_2]^-$, where coordination occurs via a terminal N, have been reported for $[Cu(phen)_2\{N(CN)_2\}][C(CN)_3]$ [8], $[Cu(phen)_2\{N(CN)_2\}_2]$ (phen = phenanthroline) [9], $[Ni\{N(CN)_2\}_2(4\text{-miez})_4]$ (4-miez = 4-methylimidazole) [10] and $M\{N(CN)_2\}_2(bpym)\cdot H_2O$ (M = Fe, Mn, Co) (bpym = 2,2′-bipyrimidine) [11]. Many examples of bidentate $[N(CN)_2]^-$ have been reported, $[Cu\{N(CN)_2\}_2(phen)]$ [12], $[M\{N(CN)_2\}_2(pyr)_2]$ (M = Mn, Co) (pyr = 2-pyrrolidone) [13], $[Cu\{N(CN)_2\}_2(ampym)_2]$ (ampym = 2-aminopyrimidine) [14], $[Ni(tn)_2\{N(CN)_2\}]ClO_4$ (tn = trimethylenediamine) [15],

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$[Mn\{N(CN)_2\}_2(py)_2]$ (py = pyridine), $[Mn\{N(CN)_2\}_2(2,2'\text{-bipy})]$ (2,2′-bipy = 2,2′-bipyridine) and $[Mn\{N(CN)_2\}_2(4,4'\text{-bipy}) \cdot (3/2H)_2O]$ (4,4′-bipy = 4,4′-bipyridine) [16], which form one-dimensional chains or two-dimensional sheets, as in $[Co_2\{N(CN)_2\}_4(bpym)] \cdot H_2O$ [11]. In an attempt to prepare supramolecular architectures by using the dicyanamide ligand and ethylenediamine (en), we obtained a one-dimensional chain nickel complex, which forms a two-dimensional network by hydrogen-bonding interactions. Here we report the structure and properties of the dicyanamide complex $[Ni(en)_2\{N(CN)_2\}]ClO_4$.

EXPERIMENTAL

Materials, Reagents and Physical Measurements

All reagents were of AR grade and were used without further purification. $NaN(CN)_2$ was purchased from Aldrich Company. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C instrument. IR spectra were obtained on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400 cm^{-1} region using KBr pellets. Variable-temperature (5–300 K) magnetic susceptibilities were determined on a CF-1 ESM magnetic balance.

Caution! Perchlorate compounds are potential explosives. Safety precautions should be taken in handling and using these materials.

Preparation

An aqueous (20 cm^3) solution of ethylenediamine (en) (0.060 g, 1.0 mmol) was added to a stirred aqueous solution (15 cm^3) of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.183 g, 0.5 mmol). The resulting solution was continuously stirred for 30 min and then a solution of $NaN(CN)_2$ (0.045 g, 0.5 mmol) in water (10 cm^3) was added. Well-shaped pink crystals of $[Ni(en)_2\{N(CN)_2\}]ClO_4$ were obtained from the mother liquor by slow evaporation at room temperature for two weeks. They were collected by filtration, washed with a small amount of water and dried in air. Yield: 81%. Elemental analysis confirmed the organic content (Found%: C, 20.78; H, 4.51; N, 28.25. Calcd. For $C_6H_{16}ClN_7NiO_4$: C, 20.92; H, 4.68; N, 28.47).

Crystal Structure Determination

A single crystal of Compound **1** with dimensions 0.44 × 0.29 × 0.16 mm was selected for data collection at 193.2 K, using a Rigaku Mercury CCD with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares analysis (SHELXTL-97) [17]. The positions of all remaining non-H atoms were obtained from successive Fourier syntheses. The positions of hydrogen atoms were calculated using idealized geometry. The final R_1 value is 0.0624 for 371 parameters and 5369 independent reflections $[I_{obs} > 2\sigma(I)]$ and wR_2 is 0.1312. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. A summary of the crystal data, experimental details and refinement results are listed in Table I. Atomic coordinates of non-hydrogen atoms are given in Table II.

TABLE I Crystal data and structure refinement for complex **1**

Empirical formula	$C_6H_{16}ClN_7NiO_4$
Temperature (K)	193.2
Formula weight	344.42
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	26.439(5)
b (Å)	15.7969(3)
c (Å)	13.794(3)
β (°)	102.37(3)
V (Å^3)	5627(2)
Z	16
$D_{\text{calcd.}}$ (g/cm^3)	1.626
Absorption coefficient (mm^{-1})	1.591
$F(000)$	2848
θ range for data collection (°)	3.02–27.48
Index ranges	$-34 \leq h \leq 34$, $-19 \leq k \leq 20$, $-14 \leq l \leq 17$
Reflections collections	20 745
Independent reflections	6158
Data/restraints/parameters	6158/0/371
Goodness-of-fit on F^2	1.069
Final R_1 and wR_2 [$I > 2\sigma(I)$] indices	$R_1 = 0.0624$, $wR_2 = 0.1312$
R_1 and wR_2 indices (all data)	$R_1 = 0.0767$, $wR_2 = 0.1389$
Largest diff. peak and hole (e Å^{-3})	0.605 and −0.468

$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 19.2130P]$.

Complete tables of atomic coordinates and thermal parameters excluding structure factors are available from the authors upon request.

RESULTS AND DISCUSSION

Crystal Structure

Selected bond lengths and angles are listed in Table III. The crystal structure of Complex **1** contains $[Ni(en)_2\{N(CN)_2\}]_n^{n+}$ cations and disordered ClO_4^- anions (Fig. 1). There are two kinds of Ni(II) coordination environment. Both Ni(II) atoms are coordinated by four nitrogen atoms from en ligands [Ni(1)–N(1), 2.109(3) Å; Ni(1)–N(2), 2.100(3) Å; Ni(1)–N(3), 2.110(4) Å; Ni(1)–N(4), 2.106(3) Å for Ni(1); Ni(2)–N(8), 2.101(4) Å; Ni(2)–N(9), 2.096(3) Å; Ni(2)–N(10), 2.114(3) Å; Ni(2)–N(11), 2.123(4) Å for Ni(2)], which occupy the equatorial positions, and two nitrile nitrogen atoms from two $[N(CN)_2]^-$ ligands [Ni(1)–N(5), 2.098(3) Å; Ni(1)–N(12), 2.081(3) Å; Ni(2)–N(14), 2.082(4) Å; Ni(2)–N(7)a (a: $x-1$, $y+1/2$, z), 2.082(3) Å], which occupy the axial positions. The Ni–N bond lengths lie in the range 2.081–2.110 Å for Ni(1) and 2.082–2.123 Å for Ni(2), respectively. These Ni–N bond lengths are similar to the Ni–N distances (2.095–2.124 Å) in $[Ni(tn)_2\{N(CN)_2\}]ClO_4$ [15]. Thus, the two kinds of Ni(II) atoms in the NiN_6 chromophore are present in similar slightly distorted octahedral coordination environments.

The Ni(II) atoms are bridged through two kinds of $[N(CN)_2]^-$ ligands. The complex forms a one-dimensional chain structure through $\mu_{1,5}$-$[N(CN)_2]^-$. This structure is similar to the one-dimensional chain in $[Ni(tn)_2\{N(CN)_2\}]ClO_4$ [15], with the obvious difference that two kinds of Ni(II) atoms [Ni(1) and Ni(2)] bridged by $[N(CN)_2]^-$

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement (Å $\times 10^3$) for Complex **1**

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Ni(1)	1181(1)	1314(1)	9658(1)	25(1)
Ni(2)	−1352(1)	3723(1)	9583(1)	29(1)
N(1)	1096(1)	1190(2)	8109(2)	36(1)
N(2)	1272(1)	−6(2)	9631(3)	35(1)
N(3)	1275(1)	1437(2)	11 209(3)	38(1)
N(4)	1094(1)	2638(2)	9701(3)	33(1)
N(5)	1983(1)	1468(2)	9822(3)	34(1)
N(6)	2919(1)	1246(2)	10 015(3)	40(1)
N(7)	3327(1)	−91(2)	9723(3)	41(1)
N(8)	−1525(2)	3846(3)	8030(3)	49(1)
N(9)	−2092(1)	3177(2)	9329(3)	35(1)
N(10)	−1181(1)	3589(2)	11 143(3)	37(1)
N(11)	−607(1)	4289(3)	9874(4)	51(1)
N(12)	385(1)	1168(2)	9492(3)	40(1)
N(13)	−556(1)	1219(2)	9375(3)	37(1)
N(14)	−1025(1)	2542(2)	9449(3)	41(1)
Cl(1)	2432(1)	752(1)	6821(1)	34(1)
Cl(2)	0	1766(1)	2500	42(1)
Cl(3)	5000	1558(1)	2500	43(1)
C(1)	983(2)	292(3)	7862(4)	48(1)
C(2)	1337(2)	−245(3)	8623(4)	43(1)
C(3)	1381(2)	2336(3)	11 463(4)	46(1)
C(4)	1022(2)	2866(3)	10 700(4)	43(1)
C(5)	2416(1)	1335(2)	9891(3)	27(1)
C(6)	3110(1)	515(2)	9846(3)	32(1)
C(7)	−1971(2)	3298(4)	7644(4)	59(1)
C(8)	−2356(2)	3373(4)	8306(4)	52(1)
C(9)	−746(2)	4159(4)	11 545(4)	57(1)
C(10)	−351(2)	4082(4)	10 905(4)	58(1)
C(11)	−55(1)	1218(2)	9446(3)	29(1)
C(12)	−785(1)	1938(2)	9424(3)	29(1)
O(1)	2178(2)	−42(3)	6731(4)	96(2)
O(2)	2978(1)	636(3)	7123(3)	76(1)
O(3)	2297(2)	1179(3)	5884(3)	68(1)
O(4)	2211(8)	1153(19)	7520(19)	88(8)
O(5)	2314(11)	1260(20)	7580(20)	105(8)
O(6)	89(3)	1242(5)	1740(4)	132(3)
O(7)	435(3)	2223(7)	2798(8)	213(5)
O(8)	4635(7)	2158(8)	2550(11)	133(7)
O(8A)	4537(4)	1880(16)	2495(12)	179(11)
O(9)	4849(3)	1238(9)	1408(8)	68(3)
O(9A)	4956(10)	959(12)	1847(14)	177(11)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ligands are located alternately in the one-dimensional chain of the title complex, but only one kind of Ni(II) atom is located in the tn complex. Each $[N(CN)_2]^-$ is coordinated to two metal atoms via the two nitrile nitrogen atoms. The dicyanamide ligand possesses *pseudo*-C_{2v} symmetry with CN bond distances ranging from 1.145 to 1.148 Å for one kind of $[N(CN)_2]^-$ and from 1.150 to 1.153 Å for the other. Bond angles related to the dicyanamide ligands, which occupy the axial positions of the octahedron, are 162.8(3) and 169.2(3)° for Ni(1)–N(5)–C(5) and Ni(1)–N(12)–C(11), respectively and 171.4(3) and 172.2(3)° for Ni(2)–N(14)–C(12) and Ni(2)–N(7)b–C(6)b (b: $x+1/2$, $y-1/2$, z), respectively. The two nickel atoms are bridged by $[N(CN)_2]^-$ separated by 7.686 and 7.718 Å for Ni(1)–Ni(2) and Ni(1)–Ni(2A), respectively.

TABLE III Selected bond lengths (Å) and angles (°) for Complex **1**

Ni(1)–N(1)	2.109(3)	Ni(1)–N(2)	2.100(3)
Ni(1)–N(3)	2.110(4)	Ni(1)–N(4)	2.106(3)
Ni(1)–N(5)	2.098(3)	Ni(1)–N(12)	2.081(3)
Ni(2)–N(8)	2.101(4)	Ni(2)–N(9)	2.096(3)
Ni(2)–N(10)	2.114(3)	Ni(2)–N(11)	2.123(4)
Ni(2)–N(14)	2.082(4)	Ni(2)–N(7)^{a}	2.082(3)
N(5)–C(5)	1.145(5)	N(6)–C(5)	1.313(5)
N(6)–C(6)	1.301(5)	N(7)–C(6)	1.148(5)
N(12)–C(11)	1.153(5)	N(13)–C(11)	1.308(5)
N(13)–C(12)	1.295(5)	N(14)–C(12)	1.150(5)
N(1)–Ni(1)–N(2)	82.96(14)	N(1)–Ni(1)–N(3)	179.43(13)
N(1)–Ni(1)–N(4)	97.63(13)	N(2)–Ni(1)–N(3)	96.90(14)
N(2)–Ni(1)–N(4)	179.37(15)	N(3)–Ni(1)–N(4)	82.51(14)
N(1)–Ni(1)–N(5)	90.37(14)	N(2)–Ni(1)–N(5)	90.00(13)
N(3)–Ni(1)–N(5)	89.08(14)	N(4)–Ni(1)–N(5)	89.77(13)
N(1)–Ni(1)–N(12)	89.54(15)	N(2)–Ni(1)–N(12)	90.27(13)
N(3)–Ni(1)–N(12)	91.01(15)	N(4)–Ni(1)–N(12)	89.96(13)
N(8)–Ni(2)–N(9)	82.96(16)	N(8)–Ni(2)–N(10)	179.53(16)
N(8)–Ni(2)–N(11)	98.27(18)	N(9)–Ni(2)–N(10)	96.76(14)
N(9)–Ni(2)–N(11)	178.53(16)	N(10)–Ni(2)–N(11)	82.02(16)
N(8)–Ni(2)–N(14)	89.79(15)	N(9)–Ni(2)–N(14)	90.39(14)
N(10)–Ni(2)–N(14)	89.84(14)	N(11)–Ni(2)–N(14)	90.41(15)
N(8)–Ni(2)–N(7)^{a}	90.46(15)	N(9)–Ni(2)–N(7)^{a}	90.15(14)
N(10)–Ni(2)–N(7)^{a}	89.92(15)	N(11)–Ni(2)–N(7)^{a}	89.04(15)
Ni(1)–N(5)–C(5)	162.8(3)	Ni(1)–N(12)–C(11)	169.2(3)
Ni(2)–N(14)–C(12)	171.4(3)	Ni(2)–N(7)B-C(6)^{b}	172.2(3)

Symmetry code: $^{a}x-1,\ y+1/2,\ z$; $^{b}x+1/2,\ y-1/2,\ z$.

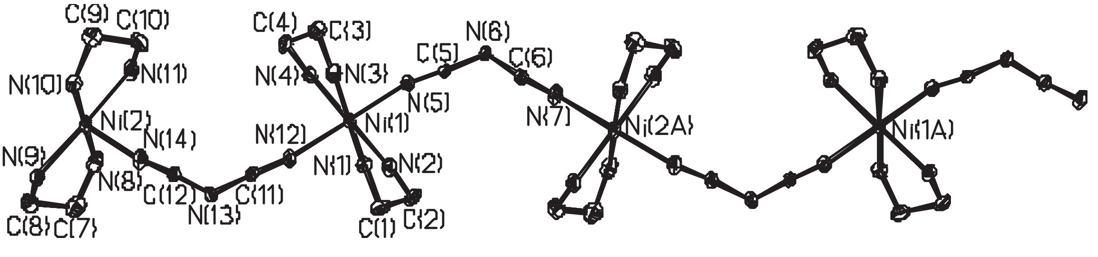

FIGURE 1 The local coordination of Ni(1) and Ni(2) in Complex **1** with 30% thermal ellipsoids.

Hydrogen bonding occurs between the uncoordinated amide nitrogen atom N(6) and N(13) from dicyanamide and amine hydrogen atoms from ethylenediamine (en): N(6)···N(4) ($1/2-x$, $1/2-y$, $2-z$), 3.103 Å and N(6)···H–N(4) ($1/2-x$, $1/2-y$, $2-z$) 153.3°; N(13)···N(2) ($-x$, $-y$, $2-z$), 3.202 Å and N(13)···H–N(2) ($-x$, $-y$, $2-z$) 154.9°. A two-dimensional network is formed via hydrogen-bonding interactions (Fig. 2). The shorter Ni···Ni interchain distances are 7.725 and 7.793 Å for Ni(1)–Ni(1D) and Ni(1)–Ni(1J), respectively. The perchlorate anions are located between the chains. Hydrogen bonding also occurs between amine hydrogen atoms from ethylenediamine (en) and oxygen atoms from disordered ClO_4^-.

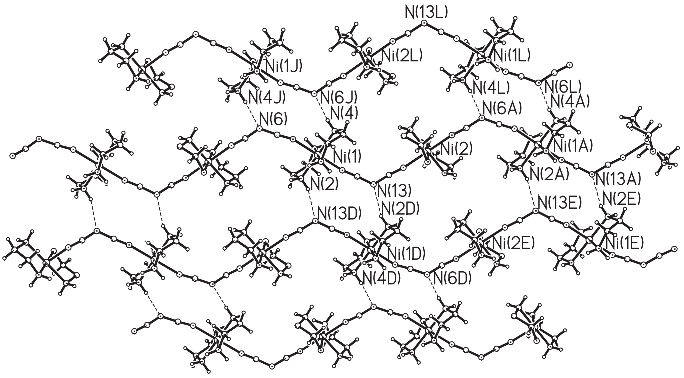

FIGURE 2 Two-dimensional network formed via hydrogen-bonding interactions in Complex **1**.

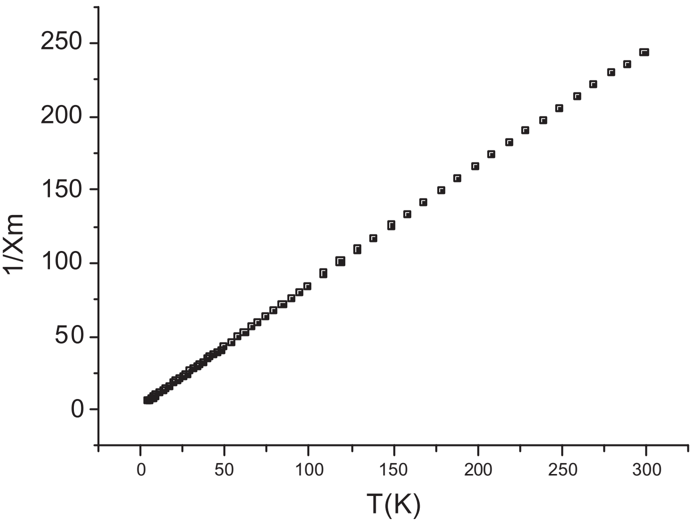

FIGURE 3 Plot of $1/\chi_m$ *vs.* T for Complex **1**.

IR and Magnetic Measurements

The IR spectrum of **1** shows the following absorptions: 3599m, 3368s, 3302s, 3175w, 2943m, 2886m, 2303vs, 2261s, 2187vs, 1605s, 1458w, 1385w, 1346s, 1096vs, 999s, 949m, 671s, 621s and 517s cm^{-1}. The absorption bands at 3599, 3368 and 3302 cm^{-1} are attributed to NH of the NH_2 groups; the 2303 cm^{-1} band is a $\nu_s + \nu_{as}$(C–N) vibration. 2261 and 2187 cm^{-1} bands are due to C≡N stretching vibrations; the 1096 cm^{-1} band is attributed to ClO_4^-.

The magnetic moment of **1** is 2.78–2.98 BM for one Ni(II) in the temperature range 5–300 K. The value corresponds to the spin-only value (2.83 BM) for $S = 1$. Variable temperature magnetic susceptibility studies in the temperature range 5–300 K, showed that **1** obeys the Curie–Weiss law, $\chi_m = C/(T - \theta)$, with $\theta = -1.67$ K and $C = 1.221\ \text{cm}^3\ \text{K}\ \text{mol}^{-1}$ (Fig. 3). This value of θ for **1** is consistent with values of θ for other $\mu_{1,5}$-$[N(CN)_2]^-$ bridging compounds, such as −5.15 K for $[Ni(tn)_2\{N(CN)_2\}]$

ClO_4 [15], -1.90 K for $Mn[N(CN)_2]_2(py)_2$, -3.5 K for $Mn[N(CN)_2]_2$(2,2′-bipy), -4.7 K for $Mn[N(CN)_2]_2$(4,4′-bipy) [16], -0.76 K for $Mn[N(CN)_2]_2(bpym)\cdot H_2O$, -7.6 K for $Fe[N(CN)_2]_2(bpym)\cdot H_2O$ and -5.4 K for $Co[N(CN)_2]_2(bpym)\cdot H_2O$ [11], indicating very weak antiferromagnetic coupling. Weak antiferromagnetic coupling is typical for bridging dicyanamide compounds.

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