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Synthesis, IR Spectrum, Thermal Analysis, and Crystal Structure of the Cyano-bridged Heteronuclear Polymeric Complex: $[Zn(teta)Ni(\mu\text{-}CN)_2(CN)_2]_n$

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Abstract. The heteronuclear polymeric complex, $[Zn(teta)Ni(\mu\text{-}CN)_2(CN)_2]_n$ (teta: triethylenetetramine), was synthesized and characterized by elementel analysis, FT-IR spectroscopy, thermal analysis and single crystal X−ray diffraction techniques. The complex crystallizes in the monoclinic system, space group $P2_1/c$ and in which the Zn^{II} ion exhibits a distorted octahedral coordination by one tetradentate teta ligand and two bridging cyano groups as a trans position, whereas the Ni^{II} ion has square planer coordination and is coordinated by four cyano ligands. The decomposition reaction takes places in the temperature range 30−600 °C in the static air atmosphere.

1 Introduction

Lattice inclusion complexes are the result of the supramolecular self-assembly of molecules in their crystal lattice with voids which are occupied by guest species [1]. The cyanide anion is able to behave as a bridging ligand at both ends, with the carbon and the nitrogen atom acting as Lewis bases between two coordination centers, which are generally metal cations acting as Lewis acids. The square-planar $Ni(CN)_4$ moiety may take a number of catenation modes to build up multidimensional structures [2]. Square planar $[M(CN)_4]^{2-}$ (M = Ni, Pd, Pt) have been extensively used as building blocks for the synthesis of extended cyano-bridged structures [3−32]. In particular, the Hofmann-type complexes, $[ML_2M'(CN)_4]$, where M is a divalent transition metal and L is a N-donor ligand molecule, have a structure consisting of polymeric two-dimensional networks formed $Ni(CN)_4{}^{2-}$ anions bridged by $ML_2{}^{2+}$ cations [33, 34].In one series of these studies [20, 22−26], the $\{Zn(L)[Ni(CN)_4]\}$ (L = ammine or diammine) systems have shown a wide range of complexation patterns involving two- or three-dimensional networks, and a wide variety in the shape or environment of the cavity where mainly aromatic organic compounds are accomodated.

We have recently reported the $[Cd(teta)Ni(\mu\text{-}CN)_2(CN)_2]\cdot 2H_2O$ which is the first example of tetracyanonickelate(II) complex with a triethylenetetramine ligand as blocking ligand [17]. As part of our on going research, in this study, we describe the synthesis, spectroscopic, thermal characterization and crystal structure of a heteronuclear polymeric complex, $[Zn(teta)Ni(\mu\text{-}CN)_2(CN)_2]_n$ (**1**).

2 Experimental Section

2.1 *Materials and Instrumentation*

Zinc(II) chloride, nickel(II) chloride hexahydrate, triethylenetetramine (teta), potassium cyanide were purchased from commercial sources and used as received. The infrared spectra were recorded on a IFS 66 v/S Brukeroptics FT-IR spectrometer using Nujol and KBr discs in the 4000-4000 cm^{-1} (4 cm^{-1} resolution). Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in the static air atmosphere at a heating rate of 10 $Kmin^{-1}$ in the temperature range 30−600 °C using platinum crucibles.

2.2 *X-ray Crystallography*

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structure was solved by direct methods and refined using the programs SHELXS97 and SHELXL97 [35]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods [SHELXL-97]. The hydrogen atoms were placed in geometrically idealized positions and refined as riding atoms. Data collection: X-Area, cell refinement: X-Area, data reduction: X-RED [36]; program(s) used for molecular graphics: ORTEP-3 for Windows [37]; software used to prepare material for publication: WinGX [38].

2.3 *Synthesis*

$Zn[Ni(CN)_4]$

A mixture of a solution of $NiCl_2\cdot 6H_2O$ (1.19 g, 5 mmol) in water (20 mL) and a solution of KCN (1.30 g, 20 mmol) in water (20 mL)

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Table 1. The details of crystal and experimental data of **1**

Empirical formula	$C_{10}H_{18}N_8NiZn$
Formula weight	374.40
Temperature /K	296
Wavelength /Å	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a, b, c /Å	13.2535 (4), 9.1250 (3), 14.5588(4)
β /°	120.477 (2)
V /Å^3	1517.44 (8)
Z	4
μ /mm^{-1}	2.82
D_{calc} /Mg m^{-3}	1.639
θ range /°	1.62-28.15
Measured reflections	33171
Independent reflections	3148
Absorption correction	integration
Refinement method	Full−matrix least−squares on F^2
Final R indices [$I>2\sigma(I)$]	$R_{int} = 0.052$
$R[F^2 > 2\sigma(F^2)]$	0.032
$wR(F^2)$	0.086
Goodness−of−fit on F^2	1.08
Largest difference peak and hole (eÅ^{-3})	0.48, −0.72

Table 2. Selected bond lengths/Å and bond angles/° of **1**

C7−Ni1	1.866 (3)	N2−Zn1	2.122 (3)
C8−Ni1	1.863 (3)	N3−Zn1	2.103 (2)
C9−Ni1	1.864 (3)	N4−Zn1	2.119 (3)
C10−Ni1	1.873 (3)	N5−Zn1	2.083 (3)
N1−Zn1	2.117 (3)	N7−Zn1^{i}	2.088 (2)
C8−Ni1−C9	90.52 (13)	N3−Zn1−N1	94.88 (12)
C8−Ni1−C7	87.95 (13)	N5−Zn1−N4	92.20 (13)
C9−Ni1−C7	176.98 (13)	N7^{ii}−Zn1−N4	94.22 (11)
C8−Ni1−C10	177.09 (14)	N3−Zn1−N4	82.65 (10)
C9−Ni1−C10	88.83 (13)	N1−Zn1−N4	176.27 (13)
C7−Ni1−C10	92.83 (14)	N5−Zn1−N2	169.65 (11)
N5−Zn1−N7^{ii}	92.61 (11)	N7^{ii}−Zn1−N2	93.78 (11)
N5−Zn1−N3	91.15 (11)	N3−Zn1−N2	82.93 (11)
N7^{ii}−Zn1−N3	175.20 (11)	N1−Zn1−N2	81.46 (11)
N5−Zn1−N1	90.63 (11)	N4−Zn1−N2	95.44 (12)
N7^{ii}−Zn1−N1	88.07 (12)		

Symmetry codes: (i) x, −y+1/2, z−1/2; (ii) x, −y+1/2, z+1/2.

was added dropwise with stirring at 50 °C to a solution of $ZnCl_2$ (0.681 g, 5 mmol) in water (10 mL). The mixture was refluxed with stirring for 2 h at 50 °C in a temperature-controlled bath and then the solution was cooled to room temperature.

$[Zn(teta)Ni(\mu\text{-}CN)_2(CN)_2]_n$

A solution of triethylenetetramine (0.73 g, 5 mmol) in ethanol (10 mL) was added dropwise upon stirring to a solution of $Zn[Ni(CN)_4]$ (1.14 g, 5 mmol) in water (30 mL). The solutions were refluxed with stirring for 4 h at 60 °C. The reaction mixture was cooled to room temperature. The violent crystals formed for $[Zn(teta)Ni(\mu\text{-}CN)_2(CN)_2]$ were filtered and washed with 10 mL of water and acetone and dried in air.

3 Results and Discussion

3.1 Crystal Structure of 1

The relevant crystal data and experimental conditions along with the final parameters are summarized in Table 1. The selected bond lengths, angles and hydrogen bond parameters are listed Table 2 and Table 3, respectively.

Table 3. Hydrogen bond parameters/Å, °

D-H	d(D-H)	d(H···A)	d(D···A)	<DHA
N1−H1D···N8^{iii}	0.70 (4)	2.53 (4)	3.137 (5)	147 (4)
N2−H2C···N6^{iv}	0.71 (4)	2.36 (4)	3.023 (4)	157 (4)
N3−H3C···N8^{iii}	0.77 (4)	2.52 (4)	3.180 (4)	144 (4)
N4−H4C···N6^{iv}	0.74 (5)	2.49 (5)	3.181 (5)	154 (4)

Symmetry codes: (iii) $-x+2, -y+1, -z+1$; (iv) $-x+1, -y+1, -z+1$.

The Zn^{II} ion adopts a distorted octahedral coordination and is coordinated by four N atoms [N(1)-N(4)] from tetradentate teta ligand and two N atoms of the cyano groups, whereas the Ni^{II} ion is coordinated by four C atoms [C(1)-C(4)] of four cyano ligands in a square-plane fashion (Fig. 1). The crystallographic analyses reveal that the crystal structure of **1** is a one dimensional zigzag chain polymer (2,2-CT type) along the c axis (Fig. 2). Two of the CN groups are in *trans* positions bridge, other two CN groups are terminal. The bond distances of Ni−C [range of 1.863(3)-1866(3) Å] in the $Ni(CN)_4$ moiety are in accordance with the reported values for similar complexes [22−24]. The Zn1−N1/N2/N3/N4 average bond distance of 2.115(3) Å is similar to the corresponding values found in $[Zn(hydeten)_2Pd(CN)_4]_n$ (2.178(2) and 2.138(2) Å) [20], $[Zn(en)_2Ni(CN)_4]_n$ (2.107(5) and 2.138(5) Å) [23], but shorter that found in the $[Zn(hydeten)_2Pt(CN)_4]_n$ (2.39(1) and 2.36(1) Å) [22], $[Cd(hydeten)_2Pd(CN)_4]_n$ (2.360(3) and 2.398(2) Å) [20] and $[Cd(en)_2Ni(CN)_4]_n$ (2.313(5) and 2.345(5) Å) [23]. The Zn1−N5 and Zn1−N7 bond distances of 2.083(3) and 2.088(2) Å are somewhat shorter that found in the $[Zn(hydeten)_2Pt(CN)_4]_n$ (2.33(1) Å), $[Cd(hydeten)_2Pt(CN)_4]_n$ (2.38(3) Å) [22], $[Zn(hydeten)_2Pd(CN)_4]_n$ (2.215(2) Å), $[Cd(hydeten)_2Pd(CN)_4]_n$ (2.328(2) Å) [20].

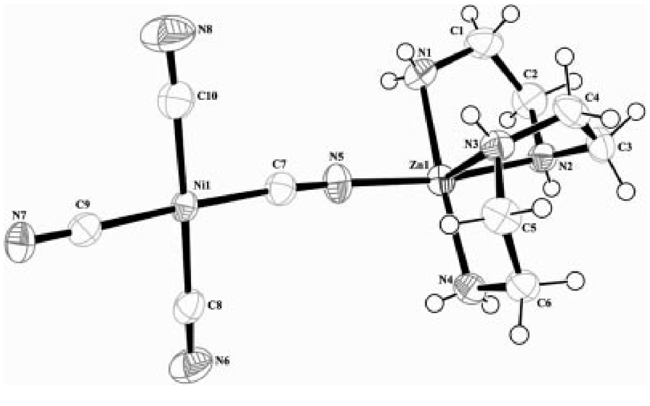

Figure 1. An *ORTEP-3* drawing of 1 with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level

The Zn1-N5≡C7 bond angle is 174.8(3)°, resulting in a one-dimensional zigzag chain being formed, whereas the Ni1-C7≡N5 and Ni1-C9≡N7 bond angles [175.6(3) and 178.1(3)°, respectively] are essentially linear. The crystal packing was formed by intermolecular hydrogen bonding between the one-dimensional zigzag chain. This weak hydrogen bond is observed between N1/N2/N3/N4-H of teta ligand and N6, N8 atom of cyano groups [$N1\cdots N8^{iii}$ = 3.137(5), $N2\cdots N6^{iv}$ = 3.023(4), $N3\cdots N8^{iii}$ = 3.180(4) and $N4\cdots N6^{iv}$ = 3.181 (5)°, (iii) $-x+2$, $-y+1$, $-z+1$; (iv) $-x+1$, $-y+1$, $-z+1$] (Fig. 3). The intramolecular $Zn\cdots Zn^{i}$ distance is 10.087 Å, whereas the shortest interchain $Zn\cdots Zn^{ii}$ and $Zn\cdots Zn^{iii}$ distances are 5.890 and 7.588 Å, respectively [symmetry codes (i) x, 1/2−y−1, −1/2+z, (ii) 1−x, 1−y, 1−z, (iii) 1−x, 1/2+y, 3/2−z].

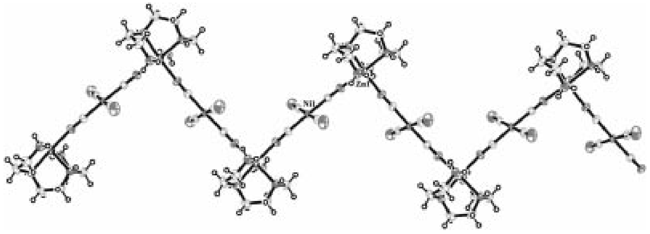

Figure 2. A view of the one-dimensional zigzag chain of **1**

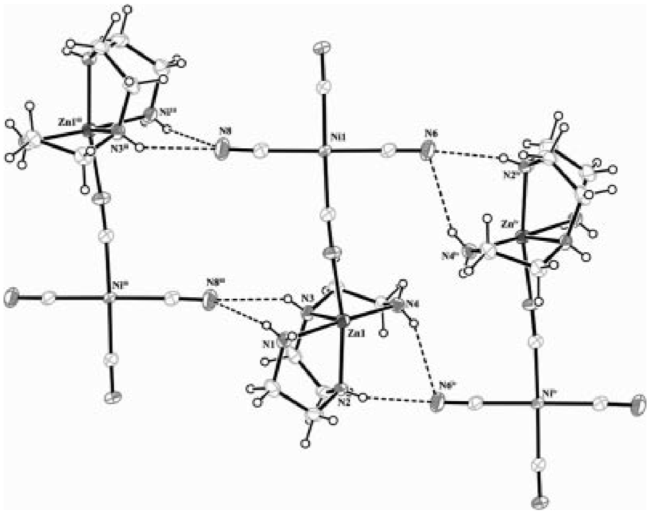

Figure 3. The hydrogen-bonding interactions of **1**

3.2 *FT-IR Spectrum*

The bands observed in the 3350-3276 cm^{-1} spectral region are assigned to the NH_2 symmetric and antisymmetric stretching frequencies which are lower than the corresponding values of the teta molecule and characteristic of bond $Zn\text{-}NH_2$ groups [39]. The splitting of these bands indicates that the teta ligand is coordinated in a tetradentate manner. The N-H stretching frequencies should decrease, while the C-H frequencies should increase due to the consecutive inductive effects.

The most important aspects of the infrared spectra of the title complex **1** involve the characteristic vibration of the CN groups. The formation of a cyanide bridge in the polymeric complex was evidenced by infrared spectra in the region of stretching vibration of the cyanide ligands. It shows two sharp bands at 2151 and 2166 cm^{-1} in the IR spectrum. In order to assign the bands attributable to the $Ni(CN)_4$ ion in the spectrum, we refer to the work of *McCullough* et al. who presented vibrational data for the salt $Na_2Ni(CN)_4$ in the solid state [40]. The assigned wavenumbers of the $Ni(CN)_4$ units of the complex appear to be much higher than those for isolated $Ni(CN)_4$ ion. Such frequency shifts have been observed for Hofmann-type host frameworks [41−44] and are attributed to the mechanical coupling of the internal modes of $Ni(CN)_4$ group are bound to a Zn^{II} atom in the complexes.

3.3 *Thermal Analysis*

The $[Zn(teta)Ni(\mu\text{-}CN)_2(CN)_2]$ complex is thermally stable up to 322 °C. Thermal decomposition of the complex proceeds in three exothermic stages. The first stage between 314 and 420 °C is related to the release of the 0.5 mole teta ligand (found = 19.09, calcd. = 19.53 %, DTA_{max} = 351 °C). In the following stages, remaining organic part and cyano groups decomposes between 363 and 458 °C and to calculate mass loss value is impossible due to overlapping decomposition processes (DTA_{max} = 382 and 445 °C). The total mass loss of all decomposition process is 59.26 % (calcd. 58.30 %) suggest that ZnO and NiO is the end product at 458 °C.

Supplementary material. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 682040 for **1**. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: 44-1223-336-033; e-mail for deposition: **deposit@ccdc.cam.ac.uk**)

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