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Synthesis, Characterization, and Crystal Structure of a Dicyanamide-Bridged Polymeric Nickel(II) Complex With 4-Chloro-2-[(3dimethylaminopropylimino)methyl]phenol

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Synthesis, Characterization, and Crystal Structure of a Dicyanamide-Bridged Polymeric Nickel(II) Complex With 4-Chloro-2-[(3-dimethylaminopropylimino)methyl]phenol

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A dicyanamide-bridged polymeric nickel(II) complex, [NiL(MeOH)(μ_2 -N(CN)₂)]_n, where L is the anionic form of the Schiff base 4-chloro-2-[(3-dimethylaminopropylimino)methyl] phenol, was synthesized and characterized by elemental analysis, IR spectrum, and single-crystal X-ray diffraction. The crystal of the complex crystallizes in the monoclinic space group $P2_1/c$, with unit cell dimensions a = 9.860(1) Å, b = 20.234(2) Å, c =18.601(2) Å, $\beta = 103.127(2)^\circ$, V = 3614.0(6) Å³, Z = 4, $R_1 = 0.0368$, $wR_2 = 0.0702$. The Ni atom of the complex is in an octahedral coordination, with two N atoms of the Schiff base ligand, one methanol O atom, and one terminal N atom of the dicynamide ligand defining the equatorial plane, and with one phenolate O atom of the Schiff base ligand, and one terminal N atom of another dicyanate ligand occupying the two axial positions.

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Keywords crystal structure, nickel complex, polymeric complex, Schiff base, synthesis

INTRODUCTION

In the past few years there has been a burgeoning effort to study the polynuclear complexes containing bridging groups, due to their interesting magnetic properties,^[1–3] catalytic properties,^[4,5] and biological activities.^[6,7] Among the bridging groups, azide and thiocyanate anions proved to be the most favorable groups for the construction of polynuclear complexes.^[8–11] Schiff bases are a kind of versabile ligands in the coordination chemistry. To date, a large number of azide or thiocyanate-bridged polynuclear complexes with Schiff bases

have been reported. Dicyanamide, a pseudohalide anion, structurally similar to azide or thiocyanate, has also been widely used for the construction of polynuclear complexes.^[12–15] However, to the best of my knowledge, no dicyanamide-bridged nickel(II) complexes with Schiff bases have been reported so far. In the present study, a polymeric dicyanamide-bridged polymeric nickel(II) complex, [NiL(MeOH)(μ_2 -N(CN)₂)]_n, derived from the Schiff base 4-chloro-2-[(3-dimethylaminopropylimino) methyl]phenol (HL), was prepared and characterized.

EXPERIMENTAL

Materials and Measurements

5-Chlorosalicylaldehyde and *N*,*N*-dimethylpropane-1,3-diamine with AR grade were purchased from Lancaster (Beijing, China) and used as obtained. C, H, and N elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer (Baoji University of Arts and Sciences, Baoji, China). The IR spectrum was recorded with a Nicolet FT-IR 170-SX spectrophotometer (Baoji University of Arts and Sciences, Baoji, China).

Synthesis of the Schiff Base Ligand HL

5-Chlorosalicylaldehyde (1.0 mmol, 157 mg) and *N*,*N*-dimethylpropane-1,3-diamine (1.0 mmol, 102 mg) were mixed in a methanolic solution (30 mL). The mixture was stirred at room temperature for 30 min to give a clear yellow solution. The solvent was removed by distillation to give yellow oily product of the Schiff base. Anal. Calcd. for $C_{12}H_{17}ClN_2O$: C, 59.87; H, 7.12; N, 11.64. Found: C, 59.72; H, 7.23; N, 11.75%.

Synthesis of $[NiL(MeOH)(\mu_2-N(CN)_2)]_n$

A 5 ml methanolic solution containing HL (0.1 mmol, 24.0 mg) and sodium dicyanamide (0.1 mmol, 8.9 mg) was stirred to a 5 mL methanolic solution of Ni(NO₃)₂·6H₂O (0.1 mmol, 29.1 mg). The mixture was stirred at room temperature for one hour to give a clear green solution. The solution was kept still in air, green block-shaped crystals of the complex, suitable for X-ray single-crystal determination, were formed on slow evaporation of the solvents for several days. The crystals were isolated by filtration and washed with methanol.

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 TABLE 1

 Crystallographic and experimental data for the complex

 TABLE 2

 Selected bond lengths (Å) and bond angles (°) for the complex

	Ĩ	
Parameter Value		
Formula	C ₃₀ H ₄₀ Cl ₂ N ₁₀ Ni ₂ O ₄	
Fw	793.0	
Crystal shape/color	Block/green	
Crystal size, mm	$0.27\times0.23\times0.22$	
Crystal system	monoclinic	
Space group	$P2_1/c$	
<i>a</i> , Å	9.860(1)	
<i>b</i> , Å	20.234(2)	
<i>c</i> , Å	18.601(2)	
$eta,^{\circ}$	103.127(2)	
$V, Å^3$	3614.0(6)	
Ζ	4	
λ (MoK α), Å	0.71073	
<i>Т</i> , К	298(2)	
μ , mm ⁻¹ (Mo-K α)	1.239	
T_{\min}	0.7309	
$T_{\rm max}$	0.7723	
Measured reflections	16177	
Unique reflections (R_{int})	5535 (0.0415)	
Observed reflections $[I \ge 2\sigma(I)]$ 4105		
Parameters 445		
Restraints	2	
<i>F</i> (000)	1648	
Goodness of fit on F^2	1.011	
$R_1, wR_2 [I \ge 2\sigma(I)]^a$	0.0368, 0.0702	
R_1 , wR_2 (all data) ^a	0.0584, 0.0791	
Largest diff. peak and hole, $e/Å^3$	0.361, -0.289	

		0	1
Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Ni(1)-O(1)	2.007(2)	Ni(1)-N(1)	2.026(2)
Ni(1)-N(2)	2.215(3)	Ni(1)-O(3)	2.129(2)
Ni(1)-N(5)	2.105(3)	Ni(1)-N(8)	2.064(3)
Ni(2)-N(3)	2.022(3)	Ni(2)-O(2)	2.025(2)
Ni(2)-O(4)	2.096(2)	Ni(2)-N(7)	2.060(3)
Ni(2)-N(9)	2.122(3)	Ni(2)-N(4)	2.201(3)
Angle	$\omega, ^{\circ}$	Angle	$\omega,^{\circ}$
O(1)-Ni(1)-N(1)	88.6(1)	O(1)-Ni(1)-N(8)	172.7(1)
N(1)-Ni(1)-N(8)	97.0(1)	O(1)-Ni(1)-N(5)	89.2(1)
N(1)-Ni(1)-N(5)	92.6(1)	N(8)-Ni(1)-N(5)	85.8(1)
O(1)-Ni(1)-O(3)	82.3(1)	N(1)-Ni(1)-O(3)	170.7(1)
N(8)-Ni(1)-O(3)	92.3(1)	N(5)-Ni(1)-O(3)	89.4(1)
O(1)-Ni(1)-N(2)	97.7(1)	N(1)-Ni(1)-N(2)	87.1(1)
N(8)-Ni(1)-N(2)	87.3(1)	N(5)-Ni(1)-N(2)	173.0(1)
O(3)-Ni(1)-N(2)	92.0(1)	N(3)-Ni(2)-O(2)	88.6(1)
N(3)-Ni(2)-N(7)	97.3(1)	O(2)-Ni(2)-N(7)	171.4(1)
N(3)-Ni(2)-O(4)	173.2(1)	O(2)-Ni(2)-O(4)	84.6(1)
N(7)-Ni(2)-O(4)	89.5(1)	N(3)-Ni(2)-N(9)	90.1(1)
O(2)-Ni(2)-N(9)	86.0(1)	N(7)-Ni(2)-N(9)	87.6(1)
O(4)-Ni(2)-N(9)	89.7(1)	N(3)-Ni(2)-N(4)	87.1(1)
O(2)-Ni(2)-N(4)	96.1(1)	N(7)-Ni(2)-N(4)	90.5(1)
O(4)-Ni(2)-N(4)	93.4(1)	N(9)-Ni(2)-N(4)	176.4(1)

 ${}^{a}R_{1} = \sum ||Fo| - |Fc|| / \sum |Fo|, wR_{2} = [\sum w(Fo^{2} - Fc^{2})^{2} / \sum w(Fo^{2})^{2}]^{1/2}.$

Yield, 25.0 mg (63%). Anal. Calcd. for $C_{30}H_{40}Cl_2N_{10}Ni_2O_4$: C, 45.44; H, 5.08; N, 17.66. Found: C, 45.27; H, 5.21; N, 17.60%.

Crystal Structure Determination

The diffraction intensities for the complex were collected on a Bruker Smart Apex CCD diffractometer (MoK α , $\lambda = 0.71073$ Å) at 298(2) K. Absorption corrections were applied using SAD-ABS.^[16] The crystal structure was solved with direct method and refined with a full-matrix least-squares technique using SHELXTL.^[17] Anisotropic thermal parameters were applied to all non-hydrogen atoms. The methanolic hydrogen atoms were located from a difference Fourier map and refined with isotropic temperature factors, and with O–H distances restrained to 0.85(1) Å. All other hydrogen atoms on carbon atoms were generated geometrically (C–H = 0.93–0.97 Å). The crystallographic data as well as details of data collection and refinement for the complex are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Drawings were produced with SHELXTL^[17].

RESULTS AND DISCUSSION

Synthesis

The synthesis of the Schiff base ligand HL is shown in Scheme 1. The synthesis of the nickel(II) complex is shown in Scheme 2. The reactions were carried out at room temperature. It should be pointed out that the complex is the first sample of the dicynamide-bridged nickel(II) complex with Schiff base ligand.



HL + NaN(CN)₂ + Ni(NO₃)₂ $\xrightarrow{\text{MeOH}}$ the complex sch. 2.



FIG. 1. The structure of the complex, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

IR Spectra

The IR spectrum of the complex was analyzed and compared with that of the free ligand HL in the region 4000–400 cm⁻¹. The weak and broad bands at 3513 cm⁻¹ for HL and 3427 cm⁻¹ for the complex are assigned to the O–H stretching vibrations. A strong sharp absorption band around 1637 cm⁻¹ in the spectrum of the Schiff base ligand can be assigned to the C=N stretching. Upon complexation with the metal, this band is shifted to 1615 cm⁻¹ in the complex as a result of the coordination of the imine nitrogen to the Ni atom. The typical phenolic C–O absorption band at 1212 cm⁻¹ observed in the spectrum of HL is shifted to lower frequencies (1178 cm⁻¹ in the complex), supporting the deprotonation and the coordination of the phenolic oxygen atom to the Ni atom. The complex showed sharp absorption bands in the region 2150–2390 cm⁻¹, which indicate the

presence of the dicyanamide ligand. The dicyanamide anion in NaN(CN)₂ showed three sharp and strong characteristic bands in the frequency region 2290–2170 cm⁻¹, which are attributed to $v_{as} + v_s$ (C \equiv N) combination modes (2286 cm⁻¹), v_{as} (C \equiv N) (2232 cm⁻¹), and v_s (C \equiv N) (2179 cm⁻¹).^[18] Upon complexation, these bands shift towards higher frequencies along with further splitting. In the complex, the doubly splitted $v_{as} + v_s$ (C \equiv N) bands were located at 2375 and 2311 cm⁻¹. The v_{as} (C \equiv N) band appeared at 2245 cm⁻¹ and the bifurcated v_s (C \equiv N) bands were detected at 2170 and 2166 (s) cm⁻¹. The splitting and displacement of the bands towards higher frequencies clearly show the bidentate bridging mode of the dicynamide ligand in the complex. The weak bands in the region 400–600 cm⁻¹ can be attributed to the vibration of the Ni-O and Ni-N bonds.

Structure Description of the Complex

The molecular structure of the complex is shown in Figure 1. The complex is a dicynamide-bridged polymeric nickel(II) complex. The smallest repeat unit of the complex is [NiL(MeOH)(N(CN)₂)]. Each Ni atom of the complex is in an octahedral coordination, with two N atoms of the Schiff base ligand, one methanol O atom, and one teminal N atom of the dicynamide ligand defining the equatorial plane, and with one phenolate O atom of the Schiff base ligand, and one terminal N atom of another dicyanate ligand occupying the two axial positions. The Ni(1) and Ni(2) atoms displaced out of the planes defined by the four equatorial donor atoms by 0.027(2) and 0.057(2) Å, respectively. The distance between Ni(1) and Ni(2) is 8.011(2) Å. The chelate rings formed by the atoms Ni(1), N(1), C(8)-C(10), N(2) (Ring 1), and by the atoms Ni(2), N(3), C(20)-C(22), N4 (Ring 2) have chair conformations. In Ring 1, the diagonally positioned atoms, Ni(1) and C(9), are shifted from the least-squares plane defined by the atoms N(1), N(2), C(8), and C(10) by 1.036(2) and 0.693(3) Å, respectively. In



FIG. 2. The 1D packing diagram of the complex, viewed along the x axis. Hydrogen bonds are shown as dashed lines. H atoms not related to the hydrogen bonding have been omitted for clarity.

Ring 2, the distances of the two diagonally positioned atoms, Ni(2) and C(21), from the least-squares plane defined by the atoms N(3), N(4), C(20), and C(22) are 1.078(2) and 0.690(3) Å, respectively.

In the crystal structure of the complex, the [NiL(MeOH)] moieties are bridged by dicynamide ligands, as well as intermolecular O(3)-H(3)···O(2) and O(4)-H(4)···O(1) hydrogen bonds, to form 1D chains running along the *c* axis, as shown in Figure 2.

SUPPLEMENTARY MATERIALS

Crystallographic data for the complex have been deposited with the Cambridge Crystallographic Data Centre (CCDC 871991).

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