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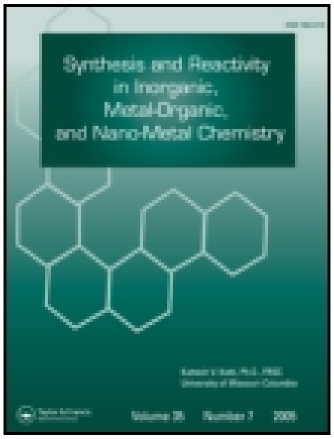

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information:
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Syntheses, Characterization, and Crystal Structures of Nickel Complexes Derived From Tridentate Schiff Bases and Thiocyanate Mixed Ligands

Chun-Lan Yuan [a]

[a] Department of Chemistry and Chemical Engineering , Baoji University of Arts and Sciences , Baoji , P. R. China

Accepted author version posted online: 23 Sep 2013.Published online: 21 Nov 2013.

To cite this article: Chun-Lan Yuan (2014) Syntheses, Characterization, and Crystal Structures of Nickel Complexes Derived From Tridentate Schiff Bases and Thiocyanate Mixed Ligands, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 44:4, 482-485, DOI: 10.1080/15533174.2013.776610

To link to this article: http://dx.doi.org/10.1080/15533174.2013.776610

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Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 44:482–485, 2014
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ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2013.776610

Syntheses, Characterization, and Crystal Structures of Nickel Complexes Derived From Tridentate Schiff Bases and Thiocyanate Mixed Ligands

Chun-Lan Yuan
Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji, P. R. China

The self-assembly and construction of specific Schiff base nickel complexes are important in the exploration of new functional materials. In the present work, in the presence of thiocyanate ligands, two mononuclear Schiff base nickel(II) complexes, [NiL1(NCS)] (1) and [Ni(L2)$_2$] (2) (L1 = 2-bromo-6-[(2-dimethylaminoethylimino)methyl]phenolate, L2 = 2-bromo-6-[(3-dimethylaminopropylimino)methyl]phenolate), with different coordination modes, have been synthesized and characterized by elemental analysis, IR spectra, and single-crystal X-ray diffraction. The Ni atom in (1) is four-coordinated in a square planar configuration, with three donor atoms of L1 and one nitrogen atom of thiocyanate ligand. The Ni atom in (2) is six-coordinated in an octahedral configuration, with six donor atoms from two L2 ligands. The relationship between the ligands and the final structures of the complexes is discussed.

Keywords crystal structure, mononuclear complex, nickel complex, Schiff base, self-assembly

INTRODUCTION

Schiff base ligands and their metal complexes are easily synthesized, and such complexes have been extensively used as catalyst in various organic reactions.[1–3] The study of nickel compounds attracts considerable attention in various aspects of chemistry, because these compounds are present in active sites of urease and widely used in the design and construction of novel biological, catalytic, and magnetic materials.[4–7] Nickel complexes derived from the tridentate Schiff base ligands bearing 2-[(2-dimethylaminoethylimino)methyl]phenolate and 2-[(3-dimethylaminopropylimino)methyl]phenolate moieties are not uncommon in the reported literature.[8–10] However, even though the above ligands are similar to each other, the final nickel complexes are much more different with respect to the coordination modes. In addition, owing to the versatile coordination modes of the thiocyanate ligand, this pseudohalide ligand was usually used in the preparation of metal complexes.[11–13] Previously, I have reported a few thiocyanate coordinated Schiff base complexes.[14] In order to explore the relationship between the ligands and the final structures of nickel complexes, especially in the presence of thiocyanate ligands, in the present work, two mononuclear Schiff base nickel(II) complexes, [NiL1(NCS)] (**1**) and [Ni(L2)$_2$] (**2**) (L1 = 2-bromo-6-[(2-dimethylaminoethylimino)methyl]phenolate, L2 = 2-bromo-6-[(3-dimethylaminopropylimino)methyl]phenolate), have been successfully synthesized and characterized.

EXPERIMENTAL

Materials and Measurements

Commercially available 3-bromosalicylaldehyde, *N*,*N*-dimethylethane-1,2-diamine, and *N*,*N*-dimethylpropane-1,3-diamine were purchased from Lancaster and used without further purification. Other solvents and reagents were made in China and used as obtained. C, H, and N elemental analyses were performed with a Perkin-Elmer 240 C elemental analyzer. IR spectra were measured with a FT-IR 170-SX (Nicolet) spectrophotometer.

Synthesis of L1 and L2

The ligands L1 and L2 were prepared by the condensation of 3-bromosalicylaldehyde (1.0 mmol, 201 mg) with *N*,*N*-dimethylethane-1,2-diamine (1.0 mmol, 88 mg) and *N*,*N*-dimethylpropane-1,3-diamine (1.0 mmol, 102 mg), respectively, in methanol (20 mL) at room temperature. Anal. Calcd. for $C_{11}H_{15}BrN_2O$ (L1, FW 271.2): C, 48.7; H, 5.6; N, 10.3. Found: C, 48.6; H, 5.7; N, 10.4%. Yield, 203 mg (75%). Anal. Calcd. for $C_{12}H_{17}BrN_2O$ (L2, FW 285.2): C, 50.5; H, 6.0; N, 9.8. Found: C, 50.3; H, 6.1; N, 9.8%. Yield: 226 mg (79%).

Synthesis of [NiL1(NCS)] (1) and [Ni(L2)$_2$] (2)

The complexes are synthesized by the similar method as described subsequently. To a stirred methanol solution (10 mL) of the Schiff base ligand (0.1 mmol) was added a methanol solution (5 mL) of NH_4NCS (0.1 mmol), and a methanol solution

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Received 28 January 2013; accepted 10 February 2013.

Address correspondence to Chun-Lan Yuan, Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji 721007, P. R. China. E-mail: chunlanyuan@163.com

(5 mL) of $NiCl_2.6H_2O$ (0.1 mmol). The mixtures were stirred for 30 min at room temperature to give a clear red solution for (**1**) and green solution for (**2**). Single crystals of the complexes, suitable for X-ray single-crystal analysis, were formed at the bottom of the vessel on slow evaporation of the solvents for several days. The isolated crystals were washed three times with cold methanol, and dried in a vacuum over anhydrous $CaCl_2$. Anal. Calcd. for $C_{12}H_{14}BrN_3NiOS$ (**1**, FW 386.9): C, 37.2; H, 3.6; N, 10.9. Found: C, 37.4; H, 3.6; N, 10.7%. Yield, 15.0 mg (39% on the basis of L1). Anal. Calcd. for $C_{24}H_{32}Br_2N_4NiO_2$ (**2**, FW 627.1): C, 46.0; H, 5.1; N, 8.9. Found: C, 46.2; H, 5.2; N, 8.8%. Yield: 14.5 mg (46% on the basis of L2).

Crystal Structure Determination

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker SMART APEX 1000 CCD area-detector with Mo*Kα* radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,[15] and multiscan absorption corrections were performed using the SADABS program.[16] The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL version 5.1.[17] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms in the two complexes were placed in calculated positions and constrained to ride on their parent atoms. Crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Crystallographic data for the two complexes have been deposited with the Cambridge Crystallographic Data Centre (CCDC 921134 and 921135).

TABLE 1
Crystallographic and experimental data for complexes (**1**) and (**2**)

	(**1**)	(**2**)
Formula	$C_{12}H_{14}BrN_3NiOS$	$C_{24}H_{32}Br_2N_4NiO_2$
FW	386.94	627.07
Crystal shape/color	Block/red	Block/green
Crystal size/mm	0.37 × 0.32 × 0.30	0.13 × 0.10 × 0.10
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
a/Å	33.082(2)	8.814(2)
b/Å	6.212(1)	7.677(1)
c/Å	14.323(1)	19.281(2)
β/°	97.569(2)	103.21(2)
V/Å^3	2918.0(3)	1270.1(3)
Z	8	2
λ (Mo$K\alpha$)/Å	0.71073	0.71073
T/K	298(2)	298(2)
μ/mm^{-1} (Mo-K$_\alpha$)	4.206	3.938
T_{min}	0.3052	0.6285
T_{max}	0.3651	0.6942
Reflections/parameters	3164/174	1644/153
Independent reflections	2464	994
F(000)	1552	636
Goodness of fit on F^2	1.055	1.119
R$_1$, wR$_2$ [I ≥ 2σ(I)]^a	0.0447, 0.1045	0.0557, 0.1437
R$_1$, wR$_2$ (all data)^a	0.0648, 0.1161	0.1227, 0.2087

$^a R_1 = \sum||Fo|\text{-}|Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2\text{-}Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$.

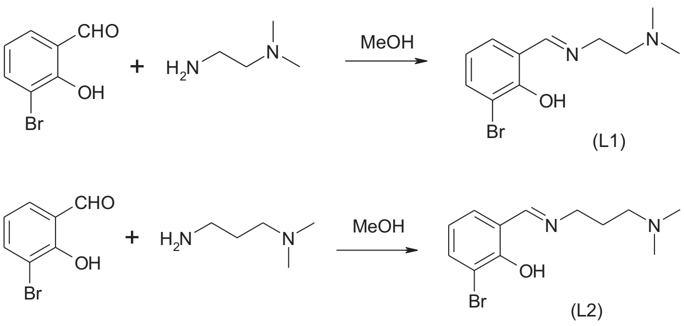
TABLE 2
Selected bond lengths (Å) and bond angles (°) for complexes (**1**) and (**2**)

(**1**)			
Ni1-N1	1.842(4)	Ni1-N2	1.958(3)
Ni1-N3	1.874(4)	Ni1-O1	1.848(3)
N1-Ni1-O1	94.0(1)	N1-Ni1-N3	172.3(2)
O1-Ni1-N3	88.5(1)	N1-Ni1-N2	87.0(2)
O1-Ni1-N2	179.0(1)	N3-Ni1-N2	90.5(2)
(**2**)			
Ni1-O1	2.028(7)	Ni1-N1	2.056(7)
Ni1-N2	2.266(7)		
O1-Ni1-O1A	180	O1-Ni1-N1A	93.3(3)
O1-Ni1-N1	86.7(3)	N1-Ni1-N1A	180
O1-Ni1-N2	91.2(3)	O1-Ni1-N2A	88.8(3)
N1-Ni1-N2A	98.3(3)	N1-Ni1-N2	81.7(3)
N2-Ni1-N2A	180		

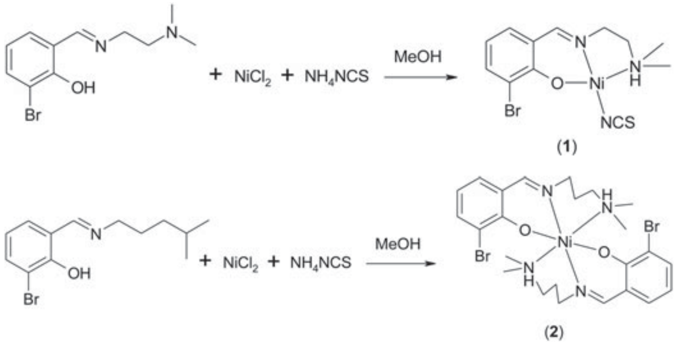
RESULTS AND DISCUSSION

Preparation of the Ligands and the Complexes

The tridentate Schiff base ligands were synthesized by 1:1 condensation reaction of 3-bromosalicylaldehyde with *N,N*-dimethylethane-1,2-diamine and *N,N*-dimethylpropane-1,3-diamine, respectively, in methanol according to Scheme 1. The nickel(II) complexes were prepared by treatment of the ligands H2L with nickel chloride and ammonium thiocyanate in molar ratio 1:1:1 in methanol according to Scheme 2.



SCH. 1.



SCH. 2.

From the results of X-ray determination and infrared spectra, it can be observed that the thiocyanate anion coordinates to the Ni atom in (**1**). However, as for complex (**2**), the thiocyanate anion was not participating in coordinating. This phenomenon is in agreement with the similar complexes reported previously.[9,10] Detailed comparison on the relationship between the Schiff base ligands and the final structures can observe that the flexibility of the former might contribute to the difference. There form a rigid five-membered chelate ring for (**1**) with the Schiff base L1, while a flexible six-membered chelate ring for (**2**) with the Schiff base L2. Thus, the slightly difference, for example, the flexibility, of the Schiff base ligands used in the preparation of the complexes with nickel chloride and ammonium thiocyanate can result in different structures of the final complexes.

Stability in Air and Solubility in General Solvents

The yellow gummy products of the Schiff base ligands L1 and L2 are stable in air at room temperature and soluble in polar organic solvents, such as MeOH, EtOH, MeCN, and Me_2CO, but insoluble in water and Et_2O. The two complexes are also stable in air at room temperature; soluble in DMF, DMSO, MeOH, EtOH, and MeCN; and insoluble in water and Et_2O.

Infrared Spectra

In the infrared spectra of the complexes, weak absorption bands at about 2930 and 2860 cm^{-1} are due to the coordinated NMe_2 groups. The strong absorption appeared at 1623 cm^{-1} for (**1**) and 1625 cm^{-1} for (**2**) are due to the azomethine groups. The C–O stretching vibrations in free ligands are observed at about 1220 cm^{-1}. The frequencies shift in the complexes toward higher values as a result of coordination of the oxygen to the metal ion [1231 cm^{-1} for (**1**) and 1228 cm^{-1} for (**2**)]. Complex (**1**) shows an intense peak due to the thiocyanate ligand at 2101 cm^{-1}.

Structure Description of (1)

The molecular structure of (**1**) is shown in Figure 1. The complex is a Schiff base and thiocyanate mixed ligands coordinated mononuclear nickel species. The Ni atom in the complex is in a square planar coordination configuration and is four-coordinated by the phenolate O, imine N, and amine N atoms of L1, and the N atom of the thiocyanate ligand. The significant distortion of the coordination is revealed by the bond lengths and angles related to the nickel center. The bond lengths are range from 1.842(4) to 1.958(3) Å. The perpendicular and *trans* bond angles are range from 87.0(2) to 94.0(1)°, and 172.3(2) to 179.0(1)°, respectively, as a result from the strain created by the five-membered chelate ring Ni1/N1/C8/C9/N2. The Ni—N and Ni—O bond lengths are in agreement with those found previously in similar nickel(II) complexes[9,18,19] and, as expected, the bond involving amine N atom is longer than that involving imine N atom. The thiocyanate ligand is nearly linear and show bent coordination mode with the metal atom.

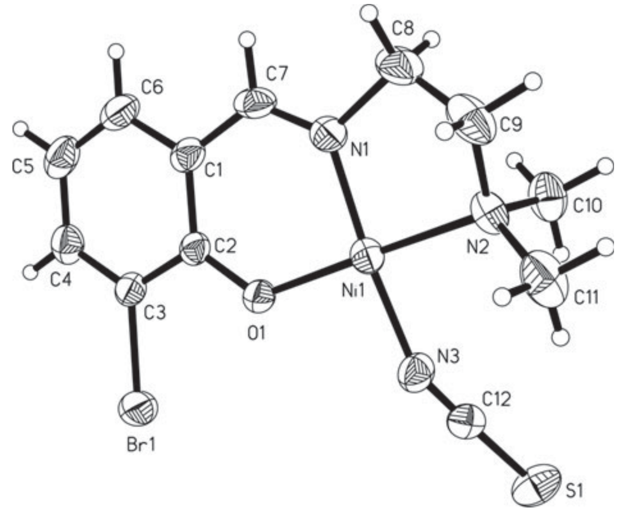


FIG. 1. The structure of (**1**), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

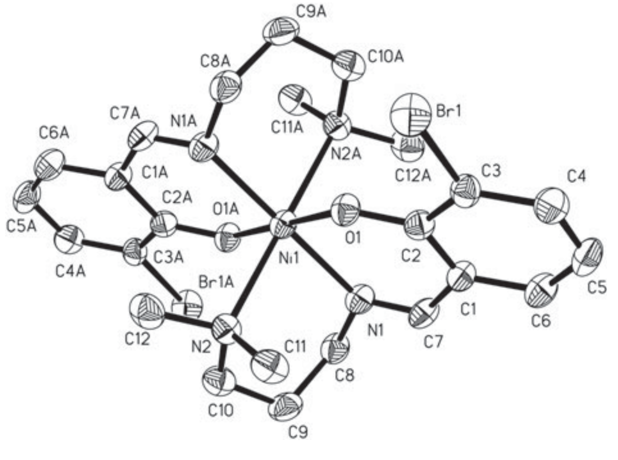


FIG. 2. The structure of (**2**), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Atoms labeled with the suffix A are at the symmetry positions –*x*, 1 – *y*, –*z*.

Structure Description of (2)

The molecular structure of (**2**) is shown in Figure 2. The complex is a centrosymmetric mononuclear nickel species, with the inversion center located at the metal atom. The Ni atom in the complex is in an octahedral coordination configuration and is six-coordinated by two phenolate O and two imine N atoms at the equatorial plane, and two amine N atoms at the axial positions, from two Schiff base ligands L2. The significant distortion of the coordination is revealed by the bond lengths and angles related to the nickel center. The bond lengths are range from 2.028(7) to 2.266(7) Å, which are much longer than those in (**1**). The perpendicular bond angles are range from 81.7(3) to 98.3(3)°. The Ni—N and Ni—O bond lengths are in agreement with those found previously in similar nickel(II) complexes[10,20] and, just as described for (**1**), the bonds involving amine N atoms are longer than those involving imine N atoms.

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