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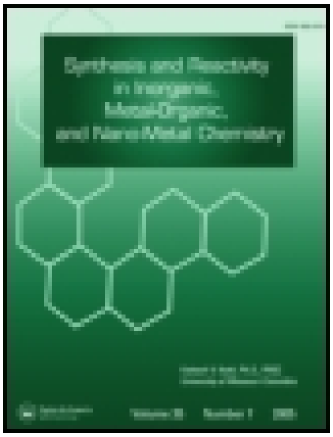

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Syntheses, Crystal Structures, and Characterizations of Nickel(II) Complexes with Schiff Bases and Thiocyanate Ligands

Xiao-Hui Li [a] & Gui-Mei Xu [b]

[a] College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China

[b] The Vocational School of Penglai, Penglai, P. R. China

Published online: 27 May 2010.

To cite this article: Xiao-Hui Li & Gui-Mei Xu (2010) Syntheses, Crystal Structures, and Characterizations of Nickel(II) Complexes with Schiff Bases and Thiocyanate Ligands, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 40:5, 355-358

To link to this article: http://dx.doi.org/10.1080/15533174.2010.487056

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ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2010.487056

Syntheses, Crystal Structures, and Characterizations of Nickel(II) Complexes with Schiff Bases and Thiocyanate Ligands

Xiao-Hui Li[1] **and Gui-Mei Xu**[2]
[1]*College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, P. R. China*
[2]*The Vocational School of Penglai, Penglai, P. R. China*

Self-assembly of Schiff base ligands 2,4-dibromo-6-[(3-dimethylaminopropylimino)methyl]phenol (BMP) and 2-[(3-cyclohexylaminopropylimino)methyl]-6-methoxyphenol (CMP) with nickel (II) acetate and ammonium thiocyanate forms two centrosymmetric mononuclear nickel(II) complexes, [Ni(BMP)$_2$] (1) and [Ni(CMP)$_2$(NCS)$_2$] (2), respectively. Complex 1 crystallizes in a monoclinic space group *C*2/*c*, while complex 2 crystallizes in a hexagonal space group *R*–3. Both crystal structures were characterized by X-ray diffraction analyses and IR spectra. Each Ni^{II} center in the complexes has NiN$_4$O$_2$ coordination environment, with the two imine N and two phenolate O atoms located in the base plane. The difference between the two coordinations is the axial donors, *viz.* amino N atoms for 1, and thiocyanate N atoms for 2.

Keywords crystal structure, nickel complex, synthesis, thiocyanate

INTRODUCTION

Schiff base complexes of transition metals have been widely investigated for many years. Their ready syntheses and versatile properties have received much attention.[1] Schiff base nickel(II) complexes have been regarded as models for enzymes such as urease.[2] Thiocyanate anions can coordinate to the metal atoms either through the bridging mode or through the terminal mode.[3] However, one can hardly possibly predict which coordination mode will be adopted by the thiocyanate groups. In this paper, two mononuclear nickel(II) complexes, [Ni(BMP)$_2$] (**1**) and [Ni(CMP)$_2$(NCS)$_2$] (**2**) (BMP = 2,4-dibromo-6-[(3-dimethylaminopropylimino)methyl]phenol, CMP = 2-[(3-cyclohexylaminopropylimino)methyl]-6-methoxyphenol), have been synthesized and structurally characterized to investigate the influence on the coordination mode of the thiocyanate groups.

EXPERIMENTAL

Materials and Methods

3,5-Dibromosalicylaldehyde, 3-methoxysalicylaldehyde, *N*,*N*-dimethylpropane-1,3-diamine and *N*-cyclohexylpropane-1,3-diamine were analytical pure grade from Aldrich Chemical Co., Milwaukee, Wisconsin, and used without further purification. Other reagents were also analytical pure grade and obtained from Beijing Reagent Factory, used without further purification. IR spectra were recorded on a Nicolet IR-470 spectrometer with KBr pellets in the range 4000–400 cm^{-1}. C, H, N analyses were carried out using a Perkin-Elmer model 240 analyzer. Crystallographic data were measured on a Bruker APEX-II CCD area-detector diffractometer with Mo-Kα radiation (λ = 0.71073 Å).

Synthesis of BMP

A mixture of 3,5-dibromosalicylaldehyde (0.28 g, 10 mmol) and *N*,*N*-dimethylpropane-1,3-diamine (0.10 g, 10 mmol) in anhydrous methanol (50 mL) was stirred for 3 h under reflux. After the reaction mixture was cooled, the solvent was removed by vacuum distillation, and ice-water was added to the residue. The product was isolated by filtrating to obtain the straw yellow solid. Yield: 0.32 g, 89%. Anal. calcd. for $C_{12}H_{16}Br_2N_2O$: C, 39.6; H, 4.4; N, 7.7. Found: C, 39.3; H, 4.5; N, 7.9%.

Synthesis of CMP

A mixture of 3-methoxysalicylaldehyde (0.15 g, 10 mmol) and *N*-cyclohexylpropane-1,3-diamine (0.16 g, 10 mmol) in anhydrous methanol (50 mL) was stirred for 3 h under reflux. After the reaction mixture was cooled, the solvent was removed by vacuum distillation, and ice-water was added to the residue. The product was isolated by filtrating to obtain the straw yellow solid. Yield: 0.23 g, 79%. Anal. calcd. for

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Received 9 July 2009; accepted 16 April 2010.

Address correspondence to Gui-Mei Xu, The Vocational School of Penglai, Penglai 265600, P. R. China. E-mail: guimei_xu@126.com

TABLE 1
Crystallographic data and structure refinement for the complexes

Complex	**1**	**2**
Empirical formula	$C_{24}H_{30}Br_4N_4NiO_2$	$C_{36}H_{52}N_6NiO_4S_2$
Mr	784.87	755.67
Crystal system	monoclinic	hexagonal
Space group	$C2/c$	R–3
a/Å	19.461(6)	23.259(11)
b/Å	9.716(5)	23.259(11)
c/Å	17.959(8)	20.761(9)
α /°	90	90
β /°	122.81(3)	90
γ /°	90	120
V/Å^3	2854(2)	9727(8)
Z	4	9
D_c / g cm^{-3}	1.827	1.161
μ / mm^{-1}	6.308	0.586
T/K	298(2)	298(2)
Crystal size/mm^3	0.23 × 0.21 × 0.18	0.27 × 0.23 × 0.23
Independent Reflns	2434	4874
Reflns unique	1105	3947
Parameters	162	224
F(000)	1544	3618
R_{int}	0.0506	0.0273
$T_{\min}/T_{\max}$	0.325/0.396	0.858/0.877
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0403, 0.0597	0.0499, 0.1374
R_1, wR_2 (all data)^a	0.1002, 0.0677	0.0606, 0.1488

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

$C_{17}H_2N_2O_2$: C, 70.3; H, 9.0; N, 9.6. Found: C, 70.7; H, 9.2; N, 9.5%.

Synthesis of the Complex [Ni(BMP)$_2$]

At room temperature, a clear methanol solution (5 mL) of BMP (72.8 mg, 0.2 mmol) was slowly added to a methanol solution (10 mL) of $Ni(CH_3COO)_2{\cdot}4H_2O$ (24.9 mg, 0.1 mmol), then a methanol solution (5 mL) of ammonium thiocyanate (15.2 mg, 0.2 mmol) was added to the above mixture with continuous stirring for 30 min and filtered. The filtrate was allowed undisturbed evaporation at ambient temperature, and green block crystals suitable for X-ray diffraction were collected by filtration and washed with methanol. Yield: 27.3 mg, 70%.

Synthesis of the Complex [Ni(CMP)$_2$(NCS)$_2$]

At room temperature, a clear methanol solution (5 mL) of CMP (58.0 mg, 0.2 mmol) was slowly added to a methanol solution (10 mL) of $Ni(CH_3COO)_2{\cdot}4H_2O$ (24.9 mg, 0.1 mmol), then a methanol solution (5 mL) of ammonium thiocyanate (15.2 mg, 0.2 mmol) was added to the above mixture with continuous stirring for 30 min and filtered. The filtrate was allowed undisturbed evaporation at ambient temperature, and green block crystals suitable for X-ray diffraction were collected by filtration and washed with methanol. Yield: 21.2 mg, 56%.

X-Ray Structure Determination

Crystallographic data for the complexes were collected on a Bruker APEX-II CCD area detector diffractometer at 298(2) K with Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADSBS. The structures were solved with direct methods and refined with full-matrix least-squares techniques on F^2 using the SHELXTL program package.[4] All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. Crystal data are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

RESULTS AND DISCUSSION

Both complexes were synthesized according to the same method and similar materials, except for the minor difference of the Schiff base ligands. The thiocyanate ligands coordinate to the Ni atom of **2**, but do not coordinate to that of **1**, which might be caused by the large hindrance effects of the terminal cyclohexyl groups in **2** than those of the dimethyl groups in **1**.

IR Spectra

The IR spectra of the Schiff base ligands show the characteristic ν-OH absorption bands at *ca.* 3400 cm^{-1} which disappear after complexation, as a result of proton substitution by the

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

1			
Ni1–O1	2.024(3)	Ni1–N1	2.054(4)
Ni1–N2	2.311(4)		
O1–Ni1–O1$^{\#1}$	180.	O1–Ni1–N1	87.47(13)
O1–Ni1–N1$^{\#1}$	92.53(13)	N1–Ni1–N1$^{\#1}$	180
O1–Ni1–N2$^{\#1}$	87.49(13)	N1–Ni1–N2$^{\#1}$	97.86(15)
O1–Ni1–N2	92.51(13)	N1–Ni1–N2	82.14(15)
N2–Ni1–N2$^{\#1}$	180		
2			
Ni1–O1	2.0242(14)	Ni1–N1	2.0733(18)
Ni1–N3	2.123(2)		
O1–Ni1–O1$^{\#1}$	180	O1–Ni1–N1$^{\#1}$	91.28(6)
O1–Ni1–N1	88.72(7)	N1–Ni1–N1$^{\#1}$	180
O1–Ni1–N3	90.96(7)	N1–Ni1–N3	90.26(7)
O1–Ni1–N3$^{\#1}$	89.04(7)	N1–Ni1–N3$^{\#1}$	89.74(7)
N3–Ni1–N3$^{\#1}$	180		

Symmetry transformations used to generate equivalent atoms: #1 3/2 – x, 3/2 – y, – z; #2 1/3 – x, 2/3 – y, 2/3 – z.

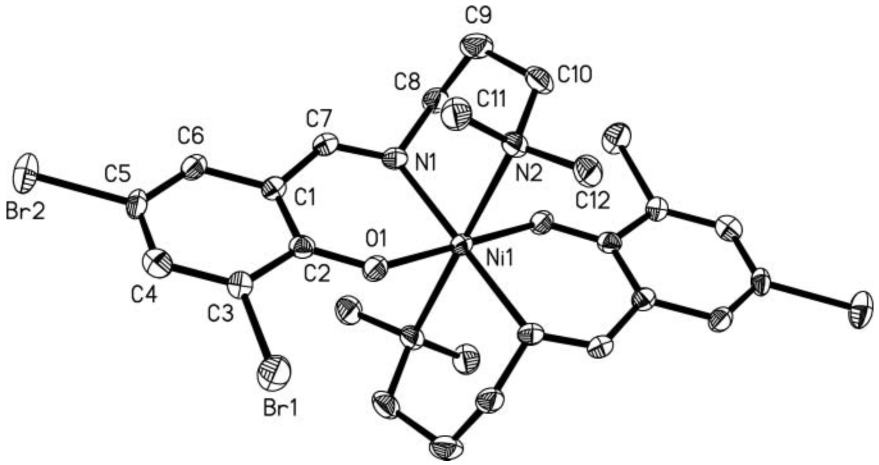

FIG. 1. Structure of **1** with the atom labeling scheme (ellipsoids at 30% probability). Unlabeled atoms are at the symmetry position 3/2 – *x*, 3/2 – *y*, – *z*. Hydrogen atoms have been omitted for clarity.

metal atoms coordination to the oxygen atoms. The absorption attributed to the *ν*-C=N vibration is at *ca.* 1625 cm^{-1} in the ligands, the corresponding vibrations in the complexes, are shifted approximately 8 cm^{-1} for **1** and 11 cm^{-1} for **2** to lower wave number as described in similar complexes.[5] The medium intensity bands observed for the Schiff base ligands at about 1280 cm^{-1} can be attributed to the phenolic stretch. These bands are observed at lower wave numbers by *ca.* 10 cm^{-1} relative to the free ligands for the complexes suggesting involvement of the oxygen atom of the phenolate moiety in coordination. The strong absorption band indicates the existence of the thiocyanate groups in **2** is at 2093 cm^{-1}, which is absent in **1**.

Description of the Crystal Structure of the Complexes

The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Both compounds are centrosymmetric mononuclear nickel(II) complexes, with the Ni atoms lying on the inversion centers. Both the coordination polyhedra can be described as distorted octahedra. In **1**, the Ni atom is coordinated by six donor atoms of two BMP Schiff base ligands, with the two imine N atoms and two phenolate O atoms defining the base plane, and the two amine N atoms occupying the axial positions. While in **2**, the Ni atom is coordinated by four donor atoms of CMP Schiff base ligands at the base plane, and two N atoms of two thiocyanate ligands at the axial positions. The amino N atoms in **2** are prononated, and not coordinate to the metal atom. It is obvious that the axial coordinate bonds are much longer than those of the basal bonds. Besides the non-equivalence of the bond lengths, the values of the bond angles also show some deviations from regularity, the four base bond angles of each octahedron being 2.53(13)° for **1** and 1.28(6)° for **2** from the ideal 90^o. The distortion of the

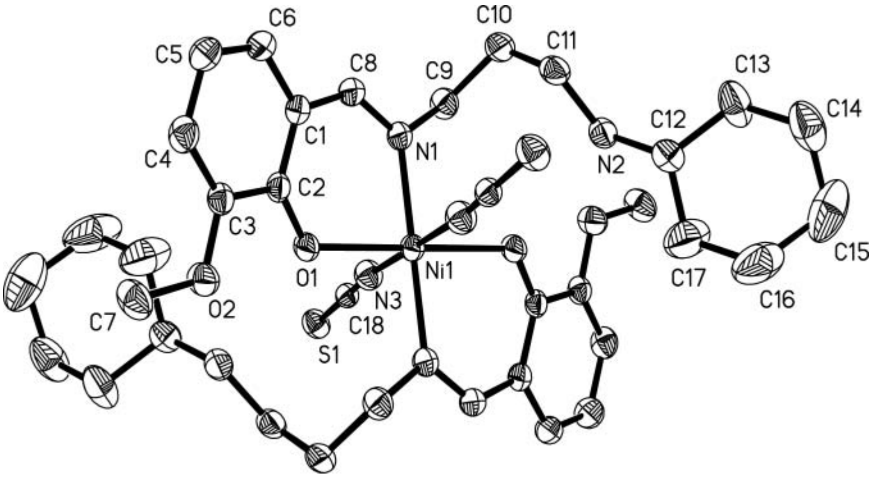

FIG. 2. Structure of **2** with the atom labeling scheme (ellipsoids at 30% probability). Unlabeled atoms are at the symmetry position 1/3 – *x*, 2/3 – *y*, 2/3 – *z*. Hydrogen atoms have been omitted for clarity.

octahedral coordinations can also be observed in other similar complexes.[6]

CONCLUSIONS

Two mononuclear nickel(II) complexes have been synthesized and structurally characterized. The amino N atoms of such Schiff base ligands can coordinate to the metal atoms. However, the bulky terminal groups such as cyclohexyl may prevent the coordination, which give a chance for the thiocyanate ligands to coordinate to the metal atoms.

Supplementary Material

Crystallographic data for the complexes have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 727599 for (**1**) and 727600 for (**2**). Copies of these information may be obtained free of charge from: the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

REFERENCES

1. (a) Biswas, C., Drew, M.G.B., and Ghosh, A. Stabilization of a helical water chain in a metal-organic host of a trinuclear Schiff base complex, *Inorg. Chem.*, **2008**, 47, 4513–4519; (b) Roth, A., Buchhoz, A., Rudolph, M., Schuetze, E., Kothe, E., and Plass, W. Directed synthesis of a heterobimetallic complex based on a novel unsymmetric double-Schiff-base ligand: Preparation, characterization, reactivity and structures of hetero- and homobimetallic nickel(II) and zinc(II) complexes, *Chem. Eur. J.*, **2008**, 14, 1571–1583; (c) Chen, Z.H., Morimoto, H., Matsunaga, S., and Shibasaki, M. A bench-stable homodinuclear Ni Schiff base complex for catalytic asymmetric synthesis of α-tetrasubstituted anti-α, β-diamino acid surrogates, *J. Am. Chem. Soc.*, **2008**, 130, 2170–2173.
2. (a) Horn, A., Firn, L., Bortoluzzi, A.J., Szpoganicz, B., Silva, M.D., Novak, M.A., Neto, M.B., Eberlin, L.S., Catharino, R.R., Eberlin, M.N., and Fernandes, C. Solid state and solution characterization of a new dinuclear nickel(II) complex: The search for synthetic models for urease, *J. Mol. Struct.*, **2006**, 797, 1–3; (b) Carlsson, H., Haukka, M., Bousseksou, A., Latour, J.-M., and Nordlander, E. Nickel complexes of carboxylate-containing polydentate ligands as models for the active site of urease, *Inorg. Chem.*, **2004**, 43, 8252–8262.
3. (a) Addison, A.W., Butcher, R.J., Homonnay, Z., Pavlishchuk, V.V., Prushan, M.J., and Thompson, L.K. The hexakis(thiocyanate)ferrate(III) ion: A coordination chemistry classic reveals an interesting geometry pattern for the thiocyanate ligands, *Eur. J. Inorg. Chem.*, **2005**, 2404–2408; (b) Sharma, S.B., and Tiwari, I.N., Studies on tris[thiocyanato-μ-thiocyanato-copper(I)] tris(pyridyl)molybdenum(III) and related complexes, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **1996**, 26, 1255–1266.
4. Sheldrick, G.M. *SHELXTL-97*, University of Göttingen, Germany, 1997.
5. (a) Tümer, M., Köksal, H., and Serin, S. Antimicrobial activity studies of mononuclear and binuclear mixed-ligand copper(II) complexes derived from Schiff base ligands and 1,10-phenanthroline, *Transition Met. Chem.*, **1999**, 24, 13–17; (b) Fernández-G., J.M., Acevedo-Arauz, E., Cetina-Rosado, R., and Toscano, R.A. Electrochemical studies of copper(II) complexes derived from bulky Schiff bases. The crystal structure of bis[N-(1-adamantyl)salicylaldiminato]copper(II), *Transition Met. Chem.*, **1999**, 24, 18–24.
6. (a) Di Vaira, M., and Orioli, P.L. Molecular and crystal structure of the octahedral nickel(II) complex with N-γ-dimethylaminopropylsalicylaldimine. *Inorg. Chem.*, **1967**, 6, 490–495; (b) Choudhury, C.R., Dey, S.K., Mondal, N., Mitra, S., Mahalli, S.O.G., and Malik, K.M.A. Synthesis and structural characterization of [$Ni(Me_2NCH_2CH_2CH_2N{=}CHC_6H_4O)_2$], *J. Chem. Cryst.*, **2001**, 31, 57–62.