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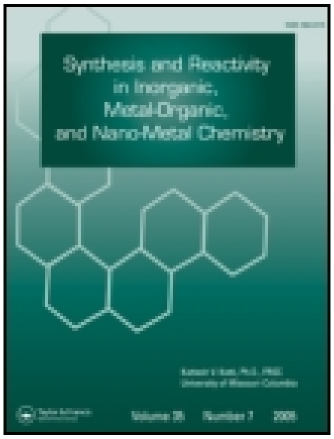

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Synthesis, Characterization, and Crystal Structures of Nickel Complexes Derived from N,N′-Bis(3,5-dichlorosalicylidene)-1,3-pentanediamine and N,N′-Bis(3-methylsalicylidene)-1,2-ethanediamine

Gui-Hua Sheng [a] , Xiao-Shan Cheng [b] , Xue Wang [b] , Di Huang [b] , Zhong-Lu You [b] & Hai-Liang Zhu [a]
[a] School of Life Sciences , Shandong University of Technology , ZiBo , P. R. China
[b] Department of Chemistry and Chemical Engineering , Liaoning Normal University , Dalian , 116029 , P. R. China

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Synthesis, Characterization, and Crystal Structures of Nickel Complexes Derived from *N,N′*-Bis(3,5-dichlorosalicylidene)-1,3-pentanediamine and *N,N′*-Bis(3-methylsalicylidene)-1,2-ethanediamine

Gui-Hua Sheng,[1] Xiao-Shan Cheng,[2] Xue Wang,[2] Di Huang,[2] Zhong-Lu You,[2] and Hai-Liang Zhu[1]

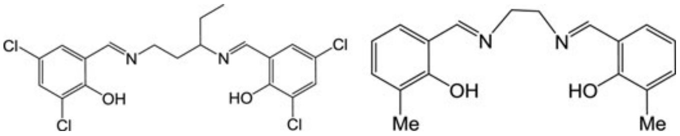
[1]*School of Life Sciences, Shandong University of Technology, ZiBo, P. R. China*
[2]*Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P. R. China*

Two new mononuclear Schiff base nickel(II) complexes, [Ni(ClSal)] (1) and [Ni(MeSal)] (2) (H_2ClSal = *N,N′*-bis(3,5-dichlorosalicylidene)-1,3-pentanediamine; H_2MeSal = *N,N′*-bis(3-methylsalicylidene)-1,2-ethanediamine), have been synthesized and characterized by elemental analyses, infrared spectra, and single-crystal X-ray diffraction. Complex 1 crystallizes in the orthorhombic space group $P2_12_12_1$, with unit cell dimensions a = 9.788(1) Å, b = 10.206(1) Å, c = 20.458(2) Å, V = 2043.7(4) Å^3, Z = 4, R_1 = 0.0814, and wR_2 = 0.1689. Complex 2 crystallizes in the monoclinic space group $P2_1/n$, with unit cell dimensions a = 11.6353(5) Å, b = 11.8807(6) Å, c = 12.8241(6) Å, β = 115.213(1)°, V = 1603.9(1) Å^3, Z = 4, R_1 = 0.0243, and wR_2 = 0.0675. The Ni atoms in the complexes are four-coordinated in square planar geometry by the N_2O_2 donor set of the ligands.

Keywords Crystal structure, mononuclear, nickel complex, Schiff base

INTRODUCTION

Schiff bases and their transition metal complexes have attracted much attention for their importance in the fields of coordination chemistry related to catalysis and enzymatic reactions, magnetism, and molecular architectures.[1–5] Nickel is an important element in biological systems, which functions as the active site of hydrolytic enzymes, such as urease.[6] Nickel complexes with Schiff bases have been proved to possess interesting biological activities.[7–10] Recently, we have reported some Schiff base complexes.[11–13] To our knowledge, no complexes have been reported from the Schiff base ligand *N,N′*-bis(3,5-dichlorosalicylidene)-1,3-pentanediamine (H_2ClSal; Scheme 1), and two complexes have been reported from the Schiff base ligand *N,N′*-bis(3-methylsalicylidene)-1,2-ethanediamine (H_2MeSal; Scheme 1).[14,15] As an extension of our work on Schiff base complexes, we report in this article the syntheses, characterization, and crystal structures of new mononuclear Schiff base nickel(II) complexes, [Ni(ClSal)] (**1**) and [Ni(MeSal)] (**2**).



SCH. 1. The Schiff base ligands H_2ClSal (left) and H_2MeSal (right).

EXPERIMENTAL

Materials and Measurements

Commercially available 3,5-dichlorosalicylaldehyde, 3-methylsalicylaldehyde, pentane-1,3-diamine, and ethane-1,2-diamine were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. C, H, and N elemental analyses were performed with a Perkin-Elmer elemental analyzer. The infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region.

Synthesis of the Schiff Base H_2ClSal

3,5-Dichlorosalicylaldehyde (2.0 mmol, 0.382 g) and pentan-1,3-diamine (1.0 mmol, 0.102 g) were dissolved in EtOH (20 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a large quantity of yellow precipitate. The product was filtered, washed with cold ethanol, and

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Address correspondence to Zhong-Lu You, Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P. R. China. E-mail: youzhonglu@yahoo.com.cn and Hai-Liang Zhu, School of Life Sciences, Shandong University of Technology, ZiBo 255049, P. R. China. E-mail: hailiang_zhu@163.com

TABLE 1
Crystallographic and experimental data for the complexes

Complexes	**1**	**2**
Formula	$C_{19}H_{16}Cl_4N_2NiO_2$	$C_{18}H_{18}N_2NiO_2$
FW	504.8	353.0
Crystal shape/color	block/red	block/red
Crystal size/ mm	0.15 × 0.15 × 0.13	0.20 × 0.17 × 0.15
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a/Å	9.788(1)	11.635(1)
b/Å	10.206(1)	11.881(1)
c/Å	20.458(2)	12.824(1)
β/°		115.213(1)
V/Å^3	2043.7(4)	1603.9(1)
Z	4	4
T/K	298(2)	298(2)
μ/mm^{-1}(Mo Kα)	1.490	1.220
D_c/g cm^{-3}	1.641	1.462
Reflections/parameters	4181/254	2982/208
Restraints	0	0
Index ranges/h, k, l	−11, 12; −12, 12; −25, 25	−14, 12; −14, 9; −15, 15
Observed reflections [$I \geq 2\sigma(I)$]	2718	2578
F(000)	1024	736
$T_{\min}$	0.8074	0.7924
$T_{\max}$	0.8298	0.8381
Goodness of fit on F^2	1.041	1.056
R_1, wR_2 [$I \geq 2\sigma(I)$]^a	0.0814, 0.1689	0.0243, 0.0675
R_1, wR_2 (all data)^a	0.1276, 0.1904	0.0304, 0.0713
Largest diff. peak and hole/e Å^{-3}	1.232, −0.956	0.279, −0.186

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

TABLE 2
Selected bond lengths (Å) and angles (°)

1			
Ni(1)-O(1)	1.815(6)	Ni(1)-O(2)	1.830(6)
Ni(1)-N(1)	1.895(8)	Ni(1)-N(2)	1.877(7)
O(1)-Ni(1)-O(2)	82.2(3)	O(1)-Ni(1)-N(2)	94.4(3)
O(2)-Ni(1)-N(2)	166.8(3)	O(1)-Ni(1)-N(1)	165.4(3)
O(2)-Ni(1)-N(1)	93.9(3)	N(2)-Ni(1)-N(1)	92.4(3)
2			
Ni(1)-O(1)	1.842(1)	Ni(1)-O(2)	1.844(1)
Ni(1)-N(1)	1.847(1)	Ni(1)-N(2)	1.847(1)
O(1)-Ni(1)-O(2)	84.9(1)	O(1)-Ni(1)-N(2)	177.0(1)
O(2)-Ni(1)-N(2)	94.3(1)	O(1)-Ni(1)-N(1)	94.7(1)
O(2)-Ni(1)-N(1)	178.2(1)	N(2)-Ni(1)-N(1)	86.2(1)

dried in vacuum. Yield, 87%. Anal. Calcd. for $C_{19}H_{18}Cl_4N_2O_2$: C, 50.9; H, 4.0; N, 6.2. Found: C, 50.7; H, 4.1; N, 6.3%.

Synthesis of H_2MeSal

3-Methylsalicylaldehyde (2.0 mmol, 0.272 g) and ethane-1,2-diamine (1.0 mmol, 0.060 g) were dissolved in EtOH (20 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a large quantity of yellow precipitate. The product was filtered, washed with cold ethanol, and dried in vacuum. Yield, 81%. Anal. Calcd. for $C_{18}H_{20}N_2O_2$: C, 73.0; H, 6.8; N, 9.4. Found: C, 73.1; H, 6.8; N, 9.5%.

Synthesis of [Ni(ClSal)]

An MeOH solution (5 mL) of Ni(MeCOO)$_2$·4H$_2$O (0.1 mmol, 24.9 mg) was added to an MeOH solution (10 mL) of H_2Salpa (0.1 mmol, 44.8 mg) with stirring. The mixture was stirred for 30 min at room temperature to give a red solution. The resulting solution was allowed to stand in air for a week. Red block-shaped crystals suitable for X-ray single-crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold EtOH, and dried in a vacuum over anhydrous $CaCl_2$. Yield, 63%. Anal. Calcd. for $C_{19}H_{16}Cl_4N_2NiO_2$: C, 45.2; H, 3.2; N, 5.5. Found: C, 45.1; H, 3.2; N, 5.4%.

Synthesis of [Ni(MeSal)]

An MeOH solution (5 mL) of Ni(MeCOO)$_2$·4H$_2$O (0.1 mmol, 24.9 mg) was added to an MeOH solution (10 mL) of H_2MeSal (0.1 mmol, 29.6 mg) with stirring. The mixture was stirred for 30 min at room temperature to give a red solution. The resulting solution was allowed to stand in air for a week. Red block-shaped crystals suitable for X-ray single-crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold EtOH, and dried in a vacuum over anhydrous $CaCl_2$. Yield, 55%. Anal. Calcd. for $C_{18}H_{18}N_2NiO_2$: C, 61.2; H, 5.1; N, 7.9. Found: C, 61.1; H, 5.2; N, 8.1%.

Data Collection, Structural Determination, and Refinement

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with Mo Kα radiation (λ = 0.71073 Å). The collected data were reduced using the SAINT[16] and multi-scan absorption corrections were performed using the SADABS.[17] The

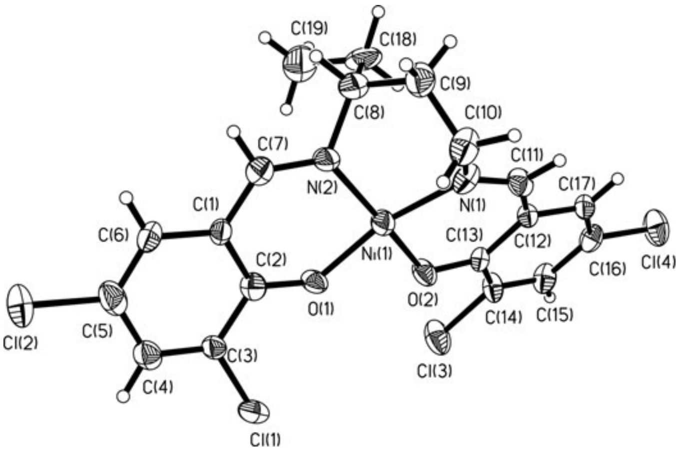

FIG. 1. Molecular structure of **1** at 30% probability displacement.

structures were solved by direct methods and refined against F^2 by full-matrix least-square methods using SHELXTL.[18] All of the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2. Crystallographic data for the complexes have been deposited with the Cambridge Crystallographic Data Centre (CCDC 891286 for **1** and 891284 for **2**).

RESULTS AND DISCUSSION

Structure Description of the Complexes

The molecular structures of the complexes **1** and **2** are shown in Figures 1 and 2, respectively. The Ni atoms in the complexes are coordinated by two phenolate O and two imine N atoms, forming distorted square planar geometry. The distortion of the coordination can be observed from the bond angles, ranging from 82.2(3)° to 94.4(3)° (**1**) and 84.9(1)° to 94.7(1)° (**2**) for the perpendicular angles, and from 165.4(3)° to 166.8(3)° (**1**) and 177.0(1)° to 178.2(1)° (**2**) for the *trans* angles. It can be seen that the distortion of the coordination geometry in **1** is much more severe than that in **2**. The different degree of the distortion can also be observed from the dihedral angles between the planes defined by N(1)-Ni(1)-O(2) and O(1)-Ni(1)-N(2) in **1** (17.7(2)°) and N(1)-Ni(1)-O(1) and O(2)-Ni(1)-N(2) in **2** (3.3(2)°). The Ni-N and Ni-O bond lengths in both complexes are similar to each other, and within normal values.[19,20] As for the Schiff base ligands themselves, the dihedral angles between the two benzene rings are 31.3(3)° for **1** and 5.9(3)° for **2**.

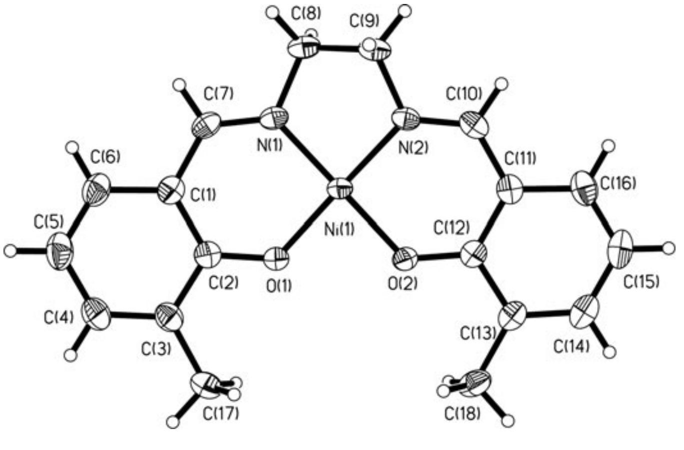

FIG. 2. Molecular structure of **2** at 30% probability displacement.

IR Spectra

The IR spectra of the free Schiff bases and the complexes provide information about the metal–ligand bonding. The bands in the range of 2870–2960 $\mathrm{cm^{-1}}$ are characteristic of aliphatic ν(C–H) vibrations for the complexes and the bands observed at about 3050 $\mathrm{cm^{-1}}$ are attributed to the aromatic ν(C–H) vibrations. The strong absorption bands at 1631 $\mathrm{cm^{-1}}$ for H_2ClSal and 1626 $\mathrm{cm^{-1}}$ for H_2MeSal are assigned to the azomethine groups, ν(C=N).[21] The bands shift to lower wave numbers of 1608 and 1605 $\mathrm{cm^{-1}}$ for the complexes **1** and **2**, respectively, which can be attributed to the coordination of the nitrogen atoms of the azomethine groups to the Ni atoms.[21] The phenolic ν(Ar–O) in the free Schiff base ligands exhibits strong bands at about 1205 $\mathrm{cm^{-1}}$. However, in the complexes, the bands appear at about 1180 $\mathrm{cm^{-1}}$, which may be assigned to the skeletal vibrations related to the phenolic oxygen of the Schiff base ligands.[22] The weak bands located at the low wave numbers, from 450–550 $\mathrm{cm^{-1}}$, may be assigned to the ν(Ni–O) and ν(Ni–N).

SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website.

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