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Synthesis and Crystal Structures of Two Dinuclear Nickel(II) Complexes Derived from 2-Ethoxy-6-[(2-phenylaminoethylimino)methyl]phenol

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Two nickel(II) complexes, $[Ni_2L_3(\mu_{1,1}\text{-NCS})]$ (1) and $2[Ni_2L_3(\mu_{1,1}\text{-}N_3)]\cdot H_2O$ (2), derived from the Schiff base 2-ethoxy-6-[(2-phenylaminoethylimino)methyl]phenol (HL) have been prepared and characterized by elemental analysis, IR spectra, and single crystal X-ray diffraction. Complex (1) is an end-on thiocyanato- and phenolate O-bridged dinuclear compound. Complex (2) consists of two end-on azido- and phenolate O-bridged dinuclear complex molecules and one water molecule of crystallization. The Ni atoms in the complexes are six-coordinated in octahedral geometries.

Keywords crystal structure, nickel, Schiff base, synthesis

INTRODUCTION

Schiff bases synthesized from the condensation reaction of salicylaldehydes and its derivatives with primary amines are an important class of versatile ligands.[1–4] Transition metal complexes derived from Schiff bases, especially for the polynuclear complexes, have received much attention due to their wide application.[5–7] The azide and thiocyanate ligands are interesting bridging groups in the construction of polynuclear complexes.[8–11] To the best of our knowledge, the metal complexes derived from the Schiff base 2-ethoxy-6-[(2-phenylaminoethylimino)methyl]phenol (HL) have never been reported. In the present paper, two new dinuclear nickel(II) complexes with the Schiff base HL have been prepared and characterized.

EXPERIMENTAL

Materials and Measurements

3-Ethoxysalicylaldehyde and *N*-phenylethane-1,2-diamine of AR grade were purchased from Aldrich. CHN elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. I.r. spectra (KBr disks) were recorded on a Perkin-Elmer 257 spectrophotometer.

Synthesis of HL

The Schiff base HL was prepared by the condensation reaction of equimolar quantities of 3-ethoxysalicylaldehyde with *N*-phenylethane-1,2-diamine in methanol at room temperature. Yield: 93%. Anal. calcd (%) for $C_{17}H_{20}N_2O_2$: C, 71.8; H, 7.1; N, 9.8. Found (%): C, 71.5; H, 7.2; N, 10.0.

Synthesis of $[Ni_2L_3(\mu_{1,1}\text{-NCS})]$ (1)

A methanol solution (5 mL) of $Ni(CH_3COO)_2\cdot 4H_2O$ (124.3 mg, 0.5 mmol) was added to a methanol solution (10 mL) of HL (142.2 mg, 0.5 mmol) and ammonium thiocyanate (38.0 mg, 0.5 mmol), and the mixture was stirred and heated under reflux (30 min). The solution was then cooled to room temperature and filtered. Green, X-ray quality crystals of the complex were obtained after five days by allowing the filtration to evaporate in air. Yield: 123 mg (72%) on the basis of HL. Anal. calcd. for $C_{52}H_{57}N_7Ni_2O_6S$: C, 60.9; H, 5.6; N, 9.6. Found: C, 60.2; H, 5.8; N, 9.9%.

Synthesis of $2[Ni_2L_3(\mu_{1,1}\text{-}N_3)]\cdot H_2O$ (2)

A methanol solution (5 mL) of $Ni(CH_3COO)_2\cdot 4H_2O$ (124.3 mg, 0.5 mmol) was added to a methanol solution (10 mL) of HL (142.2 mg, 0.5 mmol) and sodium azide (33.0 mg, 0.5 mmol), and the mixture was stirred and heated under reflux (30 min). The solution was then cooled to room temperature and filtered. Green, X-ray quality crystals of the complex were obtained after a week by allowing the filtration to evaporate in air. Yield: 97 mg (60%) on the basis of HL. Anal. calcd. for $C_{192}H_{208}N_{36}Ni_8O_{25}$: C, 59.3; H, 5.4; N, 13.0. Found: C, 59.8; H, 5.7; N, 12.5%.

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TABLE 1
Crystallographic and experimental data for the complexes

Complex	(**1**)	(**2**)
Formula	$C_{52}H_{57}N_7Ni_2O_6S$	$C_{192}H_{208}N_{36}Ni_8O_{25}$
FW	1025.5	3889.6
Crystal shape/colour	Block/green	Block/green
Crystal size/mm	0.20 × 0.20 × 0.18	0.23 × 0.20 × 0.20
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	*P*-1
a/Å	25.1941(9)	12.602(3)
b/Å	13.5637(4)	18.571(4)
c/Å	30.5575(8)	21.656(4)
α/°	90	107.98(3)
β/°	95.529(3)	90.50(3)
γ/°	90	96.94(3)
V/Å^3	10393.7(6)	4779.7(16)
Z	8	1
λ (Mo$K\alpha$) /Å	0.71073	0.71073
T/K	298(2)	298(2)
μ /mm^{-1} (Mo-K$_\alpha$)	0.819	0.846
$T_{\min}$	0.8534	0.8293
$T_{\max}$	0.8666	0.8491
Reflections/ parameters	10347/625	20053/1207
Independent reflections	4523	10501
F(000)	4304	2036
Goodness of fit on F^2	0.973	0.986
R_1, wR_2 [I $\geq 2\sigma$(I)]^a	0.0540, 0.1295	0.0586, 0.1246
R_1, wR_2 (all data)^a	0.1455, 0.1678	0.1316, 0.1580

[a] $R_1 = \sum ||Fo| - |Fc|| / \sum |Fo|$, $w\mathrm{R}_2 = [\sum w(Fo^2 - Fc^2)^2 / \sum w(Fo^2)^2]^{1/2}$.

Crystal Structure Determination

The single crystals of the two complexes were chosen and glued to thin glass fibers by epoxy glue in air for data collection. The diffraction data were collected on a Bruker SMART 1000 CCD with Mo $K\alpha$ radiation (λ = 0.71073 Å) at 298(2) K using the ω scan method. A multi-scan absorption correction was applied. The structures were solved by direct methods and difference Fourier synthesis. Crystal data collection, parameters, and refinement statistics for the two complexes are listed in Table 1. All of the non-H atoms were refined anisotropically. Amino and water H atoms of the two complexes were located from difference Fourier maps and refined isotropically, with N—H distances restrained to 0.90(1) Å. Other H atoms were included

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

(**1**)			
Ni1-O1	1.965(3)	Ni1-N1	1.969(4)
Ni1-O5	1.980(3)	Ni1-N7	2.116(4)
Ni1-N2	2.188(4)	Ni1-O6	2.324(3)
Ni2-O5	1.985(3)	Ni2-N3	1.993(5)
Ni2-O3	2.002(3)	Ni2-N5	2.067(5)
Ni2-N4	2.186(5)	Ni2-N7	2.272(4)
O1-Ni1-N1	93.50(17)	O1-Ni1-O5	94.16(14)
N1-Ni1-O5	171.59(15)	O1-Ni1-N7	91.00(14)
N1-Ni1-N7	92.28(16)	O5-Ni1-N7	84.14(15)
O1-Ni1-N2	176.29(15)	N1-Ni1-N2	82.81(16)
O5-Ni1-N2	89.51(13)	N7-Ni1-N2	88.86(15)
O1-Ni1-O6	86.21(12)	N1-Ni1-O6	110.62(13)
O5-Ni1-O6	73.37(12)	N7-Ni1-O6	157.05(14)
N2-Ni1-O6	95.36(14)	O5-Ni2-N3	165.80(18)
O5-Ni2-O3	93.06(13)	N3-Ni2-O3	92.96(19)
O5-Ni2-N5	88.65(17)	N3-Ni2-N5	103.9(2)
O3-Ni2-N5	92.34(16)	O5-Ni2-N4	89.87(15)
N3-Ni2-N4	82.1(2)	O3-Ni2-N4	169.87(18)
N5-Ni2-N4	97.43(19)	O5-Ni2-N7	80.06(14)
N3-Ni2-N7	87.47(18)	O3-Ni2-N7	86.58(14)
N5-Ni2-N7	168.57(18)	N4-Ni2-N7	84.38(17)
(**2**)			
Ni1-N1	1.96(4)	Ni1-O1	1.98(3)
Ni1-O5	1.98(3)	Ni1-N7	2.07(4)
Ni1-N2	2.20(4)	Ni1-O6	2.23(3)
Ni2-O5	1.98(3)	Ni2-O3	1.99(3)
Ni2-N3	1.99(4)	Ni2-N5	2.07(4)
Ni2-N7	2.23(4)	Ni2-N4	2.24(4)
Ni3-N10	1.97(4)	Ni3-O7	1.98(4)
Ni3-O11	1.98(3)	Ni3-N16	2.07(4)
Ni3-N11	2.19(5)	Ni3-O12	2.24(3)
Ni4-N12	1.99(4)	Ni4-O11	1.99(3)
Ni4-O9	2.01(3)	Ni4-N14	2.08(4)
Ni4-N13	2.19(4)	Ni4-N16	2.22(4)
N1-Ni1-O1	93.1(15)	N1-Ni1-O5	174.5(15)
O1-Ni1-O5	92.4(13)	N1-Ni1-N7	99.1(16)
O1-Ni1-N7	93.2(15)	O5-Ni1-N7	81.4(14)
N1-Ni1-N2	83.4(16)	O1-Ni1-N2	176.3(14)
O5-Ni1-N2	91.1(14)	N7-Ni1-N2	86.2(15)
N1-Ni1-O6	104.3(14)	O1-Ni1-O6	88.5(13)
O5-Ni1-O6	75.1(12)	N7-Ni1-O6	156.4(14)
N2-Ni1-O6	93.5(14)	O5-Ni2-O3	93.7(13)
O5-Ni2-N3	164.5(14)	O3-Ni2-N3	92.2(15)
O5-Ni2-N5	88.2(14)	O3-Ni2-N5	91.4(14)
N3-Ni2-N5	106.0(15)	O5-Ni2-N7	77.6(13)
O3-Ni2-N7	87.9(14)	N3-Ni2-N7	88.2(15)
N5-Ni2-N7	165.7(15)	O5-Ni2-N4	89.9(13)
O3-Ni2-N4	171.2(14)	N3-Ni2-N4	82.5(15)

(Continued on next page)

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

N5-Ni2-N4	96.8(14)	N7-Ni2-N4	84.9(14)
N10-Ni3-O7	92.8(18)	N10-Ni3-O11	172.9(17)
O7-Ni3-O11	94.3(14)	N10-Ni3-N16	98.7(17)
O7-Ni3-N16	94.3(16)	O11-Ni3-N16	80.3(15)
N10-Ni3-N11	83.5(18)	O7-Ni3-N11	176.1(16)
O11-Ni3-N11	89.4(15)	N16-Ni3-N11	87.3(16)
N10-Ni3-O12	105.5(16)	O7-Ni3-O12	86.2(14)
O11-Ni3-O12	75.5(13)	N16-Ni3-O12	155.8(16)
N11-Ni3-O12	93.8(15)	N12-Ni4-O11	165.1(16)
N12-Ni4-O9	90.6(16)	O11-Ni4-O9	94.1(13)
N12-Ni4-N14	105.9(18)	O11-Ni4-N14	88.0(15)
O9-Ni4-N14	93.2(16)	N12-Ni4-N13	82.9(17)
O11-Ni4-N13	90.2(15)	O9-Ni4-N13	169.4(15)
N14-Ni4-N13	96.7(17)	N12-Ni4-N16	89.7(17)
O11-Ni4-N16	76.4(14)	O9-Ni4-N16	88.4(16)
N14-Ni4-N16	164.4(16)	N13-Ni4-N16	83.2(17)

in calculated positions, and assigned isotropic thermal parameters, which were set to ride on the parent atoms. All calculations were performed using the SHELXTL-97 package.[12]

RESULTS AND DISCUSSION

The condensation reactions of aldehydes with primary amines readily produce Schiff bases, with quantitative yields and high purity. The Schiff base HL is yellow oil, which can be diluted by methanol, ethanol, acetonitrile, acetone, and dichloroform. Both complexes are very stable in air at room temperature. The obvious difference between the structures is the bridging groups, thiocyanate for (**1**) and azide for (**2**).

I.R. Spectra

The I.R. spectra of HL shows the characteristic ν(O-H) and ν(N-H) absorption bands at 3415 and 3223 cm^{-1}, respectively. The ν(O-H) bands of HL were absent after complexation. The absorption attributed to the ν(C=N) vibrations are at 1627 cm^{-1}for HL; however, the corresponding vibrations in the two complexes are lower shifted about 12 cm^{-1}, as that described in similar Schiff base complexes.[13,14] The strong absorption band observed for HL at 1285 cm^{-1}can be attributed to the phenolic stretch. The bands are observed at higher wave numbers at 1303 cm^{-1} in both complexes, suggesting involvement of the oxygen atom of the Ar–O group in coordination. In (**1**), the very strong absorption band at 2073 cm^{-1}can be assigned to the vibration of the thiocyanate group, and that in (**2**) at 2035 cm^{-1}can be assigned to the vibration of the azide group. The close resemblance of the shape and the positions of the absorption bands in the I.R. spectra suggest similar coordination mode of the ligands.

Structure Description of the Complexes

Selected bond lengths and angles are listed in Table 2. The molecular structures of the complexes (**1**) and (**2**) are shown in Figures 1, 2a and 2b, respectively. The two complexes are very

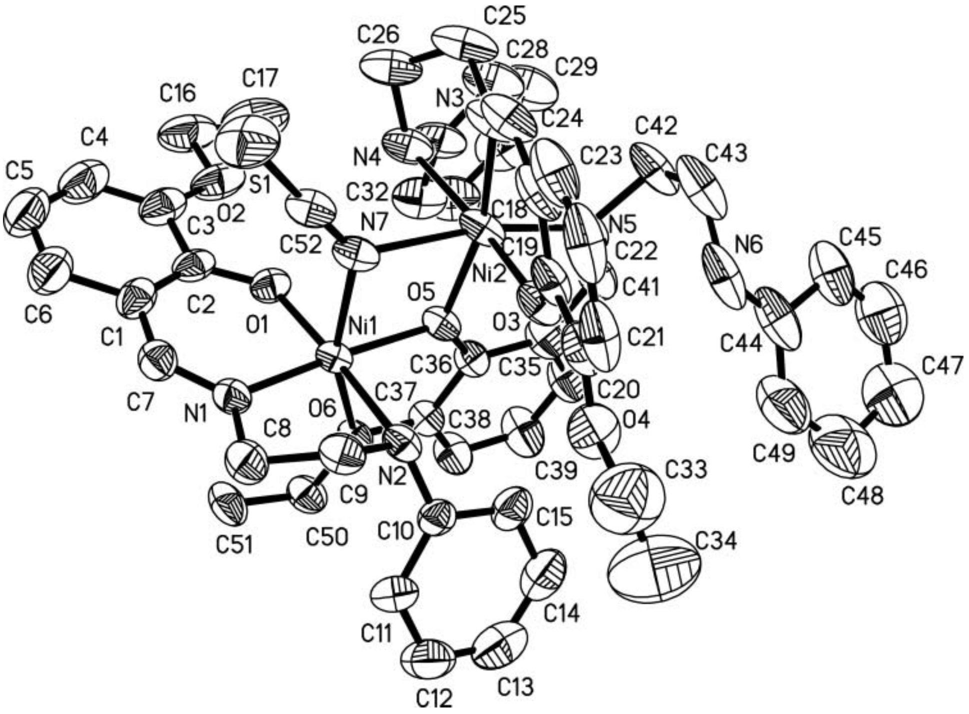

FIG. 1. Molecular structure of the complex (**1**) at the 30% ellipsoid. H atoms have been omitted for clarity.

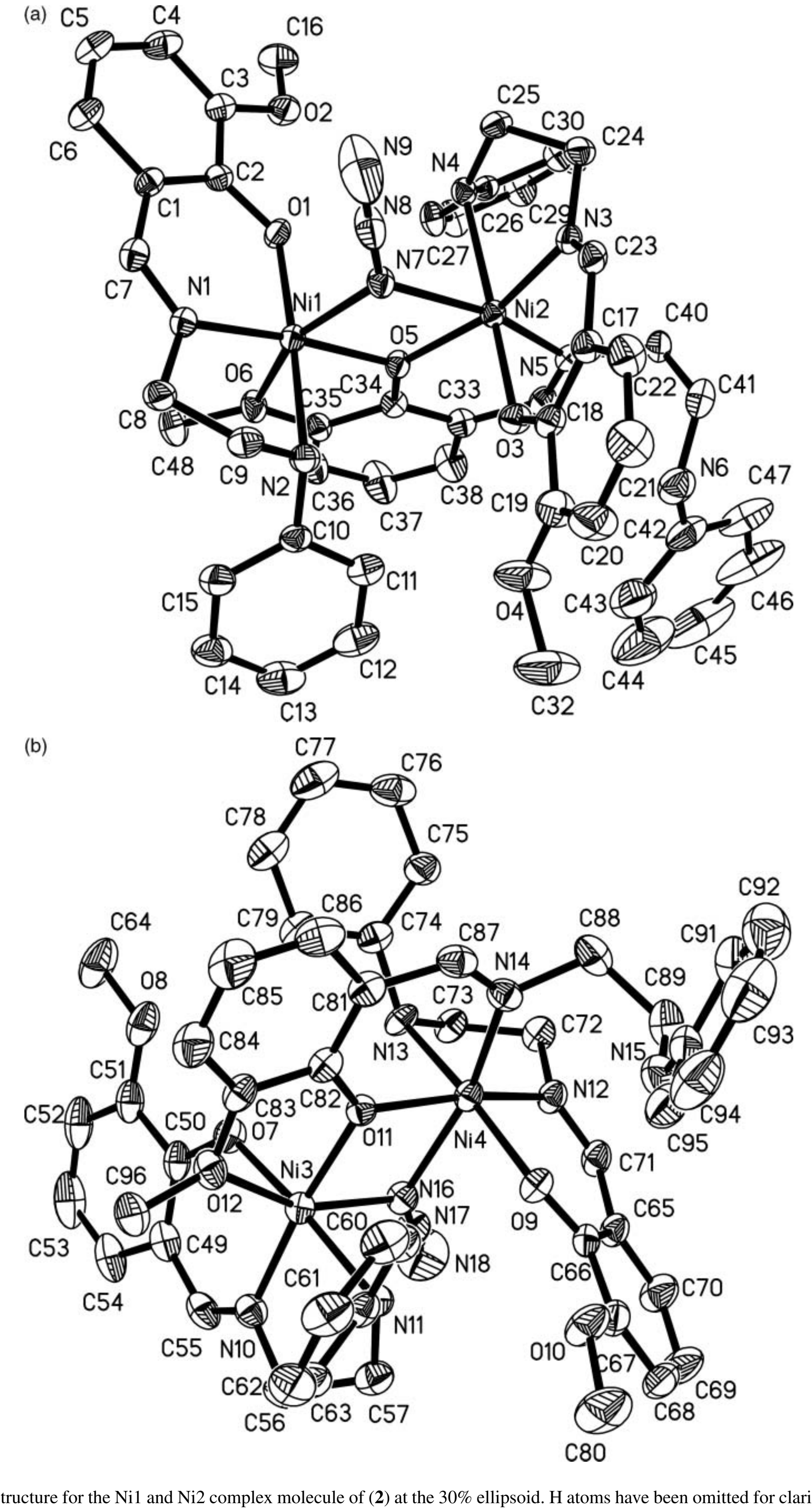

FIG. 2. (a) Molecular structure for the Ni1 and Ni2 complex molecule of (**2**) at the 30% ellipsoid. H atoms have been omitted for clarity. (b) Molecular structure for the Ni3 and Ni4 complex molecule of (**2**) at the 30% ellipsoid. H atoms have been omitted for clarity.

similar to each other. Complex (**1**) is an end-on thiocyanato- and phenolate O-bridged dinuclear compound. Complex (**2**) consists of two end-on azido- and phenolate O-bridged dinuclear complex molecules and one water molecule of crystallization. There are three Schiff base ligands in each dinuclear complex molecule, one of which acts as a bridging ligand.

The Ni atoms in the complexes are six-coordinated in octahedral geometries. The Ni1 atom in (**1**), Ni1, and Ni3 atoms in (**2**) are coordinated by one phenolate O, one imine N, and one amine N atoms of one Schiff base ligand, by one phenolate O and one ether O atoms of another Schiff base ligand, and by one N atom of a bridging ligand, *viz.* thiocyanate for (**1**) and azide for (**2**). The Ni2 atom in (**1**), Ni2 and Ni4 atoms in (**2**) are coordinated by one phenolate O, one imine N and one amine N atoms of one Schiff base ligand, by one phenolate O and one imine N atoms of another Schiff base ligand, and by one N atom of a bridging ligand, *viz.* thiocyanate for (**1**) and azide for (**2**). The Ni$\cdots$Ni distances are 3.137(2) Å for (**1**), 3.166(3) and 3.195(3) Å for (**2**), respectively.

In both complexes, the bond lengths and angles are comparable to each other, and are also comparable to those in other Schiff base copper(II) complexes.[15–17]The distortion of each octahedral coordination can be observed from the *trans* coordinate bond angles, which are caused by the strain created by the four- and five-membered chelate rings.

CONCLUSION

In the present work, two new structurally similar nickel(II) complexes with the Schiff base 2-ethoxy-6-[(2-phenylaminoethylimino)methyl]phenol and thiocyanate or azide groups have been prepared and structural characterized. The Schiff base coordinates to the nickel atoms through the phenolate O, imine N, amine N, and ether O atoms. The thiocyanate and azide groups play the same role in the coordination, both adopt end-on bridging mode.

SUPPLEMENTARY MATERIAL

CCDC 764940 and 764941 contain the supplementary crystallographic data for the two complexes. These data can be obtained free of charge *via* http://www.ccdc.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or email: deposit@ccdc.cam.ac.uk.

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