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Synthes and Crystal Structure of Chiral Amin Alcohol-Nickel Complexes[1]

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Abstract—Two novel chiral amino alcohol-nickel complexes (**I**) and (**II**) have been first reported from the direct reaction of L-plenylglycinol with $Ni(OAc)_2 \cdot 4H_2O$ in anhydrous ethanol and L-phenylalaninol with $NiCl_2 \cdot 6H_2O$ in anhydrous methanol. The crystal structures of **I** and **II** were determined by X-ray diffraction and further characterized by elemental analysis and IR. For **I**: $C_{24}H_{31}N_3NiO_3$, monoclinic, $P2_1$, $a = 5.2581(12)$, $b = 23.683(5)$, $c = 13.744(3)$ Å, $\beta = 97.939(6)°$, $V = 1695.1(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 0.917$ g/cm^3, the final R factor was $R_1 = 0.0897$, 5315 for reflections were observed with $I_0 > 2\sigma(I_0)$; for **II**: $C_{27}H_{43}Cl_2N_3NiO_5$, orthorhombic, $P2_12_12_1$, $a = 9.844(3)$, $b = 12.373(3)$, $c = 26.158(7)$ Å, $V = 3186.3(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.291$ g/cm^3, the final R factor was $R_1 = 0.0371$, 6265 for reflections were observed with $I > 2\sigma(I)$.

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INTRODUCTION

Nickel complexes have been widely used in catalytic chemistry and biochemistry [1–6]. For example, as the catalysts, they have shown high activities in Norbornene polymerization, Hydroboration reaction, the Henry reaction, Heck reaction and etc. [7–9]. Recently, a variety of chiral amino alcohol such as ephedrine derivatives [10–12], chiral pyridine derivatives [13–15], borneol derivatives [16–18], pyrrolidine derivatives [19], and others [20–22] has been also used in nickel-catalyzed conjugate addition of diethylzinc to a chalcones with excellent enantioselectivity. Encouraged by the pioneer's research work, in this paper, we first synthesized and got the two novel crystal structures of the Ni(II) complexes **I** and **II** derived from chiral amino alcohol ligands, and prepare to use them as the catalysts in the Henry reaction, cyanosilylation, and allylation reaction.

EXPERIMENTAL

Infrared spectra are recorded on a Mattson Galaxy Series Spectrum-100 spectrometer. Elemental analysis was performed on a VARIO ELIII elemental analyzer. Crystal structure was determined by a Gemini S Ultra diffractometer.

Synthesis of complex I. 4.1156 g (30 mmol) L-phenylglycinol was added to a methanol solution (50 mL) of 2.4886 g (10 mmol) of $Ni(OAc)_2 \cdot 4H_2O$ in a dry 100 mL Schlenk flask. The reaction mixture was stirred vigorously while refluxing for 48 h and then the solvent was reduced under vacuum. Recrystallizing the blue oil with anhydrous etha-nol, blue crystals which were suitable for X-ray single-crystal analysis. The yield was 34%, m.p. 85–87°C, $[\alpha]_D^5 = -148.81°$ ($c = 0.0484$, CH_3OH).

IR (KBr; ν, cm^{-1}): 3321, 3276, 3151, 3064, 2823, 1552, 1498, 1461, 1406, 1341, 1146, 1028, 914, 833, 760, 700, 654, 541.

For $C_{24}H_{31}N_3O_3Ni$

anal. calcd., %:	C, 61.57;	H, 6.67;	N, 8.97.
Found, %:	C, 61.88;	H, 7.01;	N, 8.52.

Synthesis of complex II. 2.2630 g (10 mmol) L-phenylalaninol was added to a ethanol solution (45 mL of 1.2442 g (5 mmol)) of $NiCl_2 \cdot 6H_2O$ in a dry 100 mL Schlenk flask. The reaction mixture was stirred vigorously while refluxing for 24 h and then the solvent was reduced under vacuum. Recrystallizing the blue oil with $CHCl_3$ and anhydrous ethanol, blue crystals which were suitable for X-ray single-crystal analysis.

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[1] The article is published in the original.

Table 1. Selected bond lengths (Å) and angles (deg) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Ni(1)–N(1)	2.054(7)	O(1)–C(1)	1.396(9)
Ni(1)–N(2)	2.077(5)	O(2)–C(9)	1.398(10)
Ni(1)–O(2)	2.090(5)	O(3)–C(17)	1.474(10)
Ni(1)–N(3)	2.091(7)	N(1)–C(2)	1.446(11)
Ni(1)–O(3)	2.117(5)	N(2)–C(10)	1.497(10)
Ni(1)–O(1)	2.127(4)		
		II	
Ni(1)–N(1)	2.062(2)	Ni(1)–O(2)	2.1091(19)
Ni(1)–N(3)	2.067(2)	N(1)–C(2)	1.476(4)
Ni(1)–O(3)	2.077(2)	O(1)–C(1)	1.441(3)
Ni(1)–N(2)	2.094(2)	O(2)–C(10)	1.425(4)
Ni(1)–O(1)	2.100(2)		
Angel	ω, deg	Angel	ω, deg
		I	
N(1)Ni(1)N(2)	94.1(3)	O(2)Ni(1)O(1)	87.7(2)
N(1)Ni(1)O(2)	167.4(2)	N(3)Ni(1)O(1)	169.0(3)
N(2)Ni(1)O(2)	81.8(2)	O(3)Ni(1)O(1)	88.6(2)
N(1)Ni(1)N(3)	94.2(2)	C(1)O(1)Ni(1)	110.1(4)
N(2)Ni(1)N(3)	94.8(3)	C(9)O(2)Ni(1)	110.0(5)
O(2)Ni(1)N(3)	98.0(3)	C(17)O(3)Ni(1)	111.3(5)
N(1)Ni(1)O(3)	96.1(3)	C(2)N(1)Ni(1)	108.6(5)
N(2)Ni(1)O(3)	169.5(3)	C(10)N(2)Ni(1)	107.0(4)
O(2)Ni(1)O(3)	88.6(2)	C(18)N(3)Ni(1)	106.2(5)
N(3)Ni(1)O(3)	82.2(3)	O(1)C(1)C(2)	109.6(6)
N(1)Ni(1)O(1)	80.7(2)	N(1)C(2)C(1)	108.5(7)
N(2)Ni(1)O(1)	95.3(3)	N(1)C(2)C(3)	117.1(7)
		II	
N(1)Ni(1)N(3)	99.49(11)	O(3)Ni(1)O(2)	92.65(8)
N(1)Ni(1)O(3)	91.10(10)	N(2)Ni(1)O(2)	79.38(9)
N(3)Ni(1)O(3)	81.10(9)	O(1)Ni(1)O(2)	90.42(9)
N(1)Ni(1)N(2)	165.05(9)	C(2)N(1)Ni(1)	107.32(17)
N(3)Ni(1)N(2)	94.54(10)	C(11)N(2)Ni(1)	106.86(15)
O(3)i(1)N(2)	96.17(9)	C(20)N(3)Ni(1)	107.94(17)
N(1)Ni(1)O(1)	80.57(9)	C(1)O(1)Ni(1)	111.20(18)
N(3)Ni(1)O(1)	96.76(10)	C(10)O(2)Ni(1)	112.63(17)
O(3)Ni(1)O(1)	170.97(9)	C(19)O(3)Ni(1)	111.88(1
N(2)Ni(1)O(1)	92.74(8)	O(1)C(1)C(2)	107.6(2)
N(1)Ni(1)O(2)	87.26(9)	N(1)C(2)C(1)	107.1(2)
N(3)Ni(1)O(2)	170.83(10)	N(1)C(2)C(3)	114.3(2)

The yield was 30%, m.p. 142–144°C, $[\alpha]_D^5 = -25.6°$ ($c = 0.1948$, CH_3OH).

IR (KBr; ν, cm^{-1}): 3319, 3141, 2945, 2852, 1601, 1496, 1455, 1389, 1301, 1142, 1086, 1030, 842, 751, 702, 599, 568, 471.

For $C_{27}H_{43}N_3Cl_2O_5Ni$
anal. calcd., %: C, 52.37; H, 7.00; N, 6.79.
Found, %: C, 52.62; H, 6.77; N: 6.77.

X-ray structure determination. A green crystal of compound **I** with approximate dimensions of 0.30 × 0.32 × 0.24 mm was selected for data collection on a Bruker Smart diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.7103$ Å). Totally 1665 reflections were collected in a range of $1.72° < \theta < 25.49°$ by using ω-scan techniques at 293(2) K, $M = 468.23$, monoclinic, $P2_1$, $a = 5.2581$, $b = 23.683$, $c = 13.744$ Å, $\beta = 97.939°$, $V = 1695.1$ Å^3, $Z = 2$, $\rho_{calcd} = 0.917$ g/cm^3, the final R factor was $R_1 = 0.0897$, 5315 for reflections with $I > 2\sigma(I)$, $R_\omega = 0.2162$ for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL program [23–25].

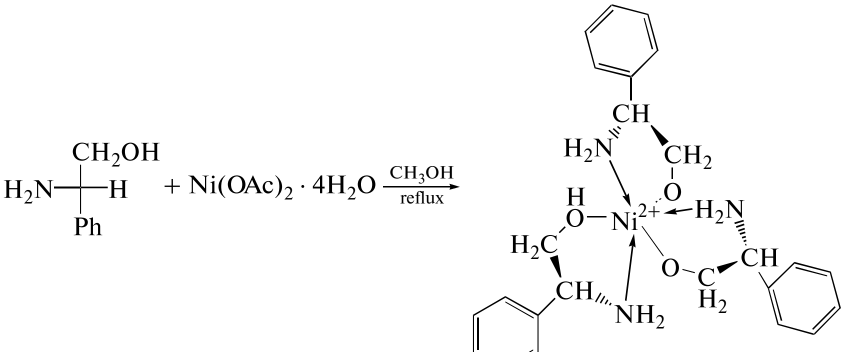
A colorless crystal of compound **II** with approximate dimensions of 0.211 × 0.175 × 0.101 mm was selected for data collection on a Bruker Smart diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.7103$ Å). Totally 19412 reflections were collected in a range of $1.82° < \theta < 26.00°$ by using ω-scan techniques at 293(2) K, $M = 619.25$, ortorombic, $P2_12_12_1$, $a = 9.8443$, $b = 12.3733$, $c = 26.1587$ Å, $V = 3186.3$ Å^3, $Z = 4$, $\rho_{calcd} = 1.291$ g/cm^3, the final R factor was $R_1 = 0.0824$, 1579 for reflections with $I > 2\sigma(I)$, $R_\omega = 0.2387$ for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL program [23–25].

The selected bond lengths and bond angles and hydrogen bond for complexes **I** and **II** are listed in Tables 1 and 2, respectively.

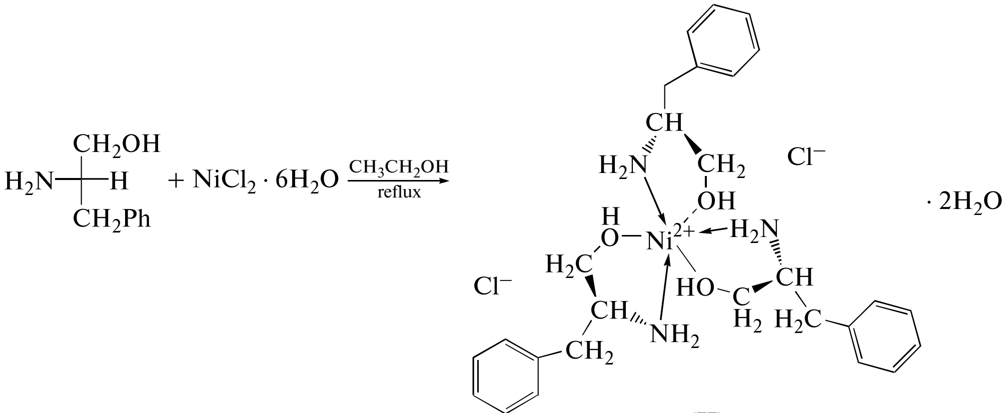
Supplementary material for structures **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 972729 (**II**) and 972730 (**I**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The synthetic route of compounds **I** and **II** can be summarized as follows:



(I)

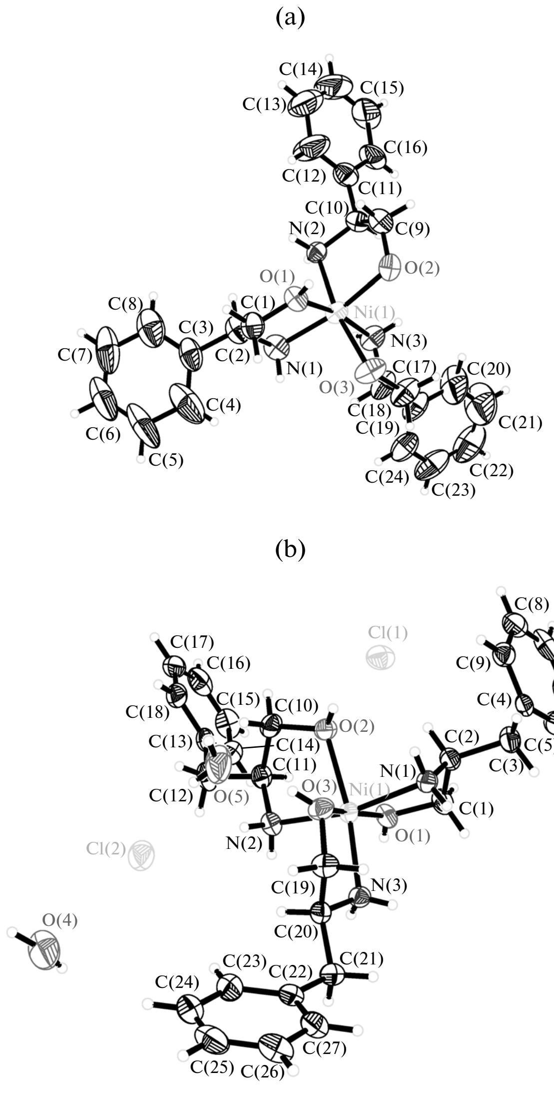


(II)

Table 2. Geometric parameters of hydrogen bonds for complexes **I** and **II***

Contact D–H···A	Distance, Å			Angel D–H···A, deg
	D–H	H···A	D···A	
		I		
N(1)–H(1*A*)···O(1)$^{\#1}$	0.90	2.45	3.254(9)	149.0
N(2)–H(2*A*)···O(2)$^{\#1}$	0.90	2.38	3.209(7)	152.4
N(3)–H(3*A*)···O(3)$^{\#1}$	0.90	2.39	3.201(7)	150.0
		II		
O(4)–H(4*B*)···Cl(1)$^{\#1}$	0.85	2.74	3.227(3)	118
N(3)–H(3*E*)···Cl(1)$^{\#2}$	0.83(3)	2.69(3)	3.501(3)	163(3)
N(1)–H(1*E*)···Cl(1)	0.87(3)	2.51(3)	3.349(3)	162(3)
O(3)–H(3*D*)···O(5)	0.769(19)	1.85(2)	2.604(4)	165(4)
N(1)–H(1*D*)···Cl(1)$^{\#2}$	0.821(17)	2.530(19)	3.339(3)	169(3)
N(3)–H(3*C*)···Cl(2)$^{\#1}$	0.802(17)	2.70(2)	3.442(3)	155(3)
O(2)–H(2*C*)···Cl(1)	0.830(18)	2.225(19)	3.067(2)	166(3)
O(5)–H(5*B*)···Cl(2)	0.789(18)	2.37(3)	3.085(4)	152(4)
O(5)–H(5*A*)···Cl(2)$^{\#3}$	0.792(19)	2.40(2)	3.160(4)	163(4)
O(1)–H(1)···O(4)$^{\#1}$	0.785(18)	1.858(19)	2.639(4)	173(3)
N(2)–H(2*B*)···Cl(2)	0.90	2.87	3.744(3)	165.0
N(2)–H(2*A*)···Cl(2)$^{\#1}$	0.90	2.96	3.744(3)	152

* Symmetry transformations used to generate equivalent atoms: **I**; $^{\#1}$ $x - 1, y, z$. **II** ; $^{\#1}$ $x - 1/2, -y + 5/2, -z + 2$; $^{\#2}$ $x - 1/2, -y + 3/2, -z + 2$; $^{\#3}$ $x + 1/2, -y + 5/2, -z + 2$.



Crystal structure of complexes **I** (a) and **II** (b).

The synthesis of complex **I** was carried out in anhydrous methanol, using a ratio of 3 : 1 of the L-phenylglycinol to the nickel acetate tetrahydrate. After refluxing for 48 h, blue ioly solution appeared. The blue crystals were recrystallizd from anhydrous methanol and hexane.

The synthesis of complex **II** was carried out in anhydrous ethanol using a ratio of 3 : 1 of the L-phenylalaninol to nickel(II) chloride hexahydrate. The reaction mixture was stirred vigorously, while refluxing for 48 h. The solvent was reduced under vacuum. A blue crystals were precipitated after recrystallization from anhydrous ethanol and hexane.

From figure, several interesting observations can be made about the structure. Complex **I** was a Ni–N complex that nickel atom is octahedrally coordinated three L-phenylglycinol molecules. The Ni atom was complexed with one oxygen atoms O(1) and three nitrogen atoms N(1), N(2), N(3). The two amino groups of the bridging $OCH_2CHNHPh$ ligand do not coordinate to the nickel atom. The Ni–O and Ni–N bond lengths of the L-phenylglycinolate ligand were 2.127(4)/2.090(5)/2.117(5) and 2.054(7)/2.077(5)/2.091(7) Å, respectively. The aforementioned components were held together through hydrogen bonding interactions.

Complex **II** is a mononuclear compound with three chelating amino L-phenylalaninolate ligands. Three oxygen atom O(1), O(2), and O(3) and three nitrogen atoms N(1), N(2), and N(3) are coordinated to the nickel atom, thus, the complex was six-coordinate. The uncoordinated two chloride ions and water molecure form a three dimensional hydrogen-bond network.

Thus, the two complexes **I** ($C_{24}H_{31}N_3O_3Ni$) and **II** ($C_{27}H_{43}N_3O_{54}Cl_2Ni$) were first reported with a simple, directly method. Research is going towards the application to organic reactions such as the Henry reaction, cyanosilylation reaction.

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