

N-乙基-1,10-菲罗啉-2-甲胺镍(II)配合物的合成、晶体结构及性质研究

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Synthesis, Crystal Structure and Properties of Ni(II) Complex with N-ethyl-1,10-phenanthroline-2-methanamine

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A novel ligand N-ethyl-1,10-phenanthroline-2-methanamine and its Ni(II) complex have been synthesized. The crystal structure of the complex has been determined by X-ray diffraction method. The Ni(II) is five-coordinated by three nitrogen atoms from the ligand and two Cl⁻ anions in a distorted trigonal bipyramidal environment: the N(2), Cl(1) and Cl(2) in equatorial plane; the N(1) and N(3) in axial positions. The UV-spectra and IR-spectra of the ligand and its Ni(II) complex were recorded and discussed. The thermodynamic properties of the ligand with various bivalent metals were studied by potentiometric titrations and the order of the stability constants is in agreement with the Irving-Williams order in coordination chemistry. CCDC: 221750.

Keywords: crystal structure Ni(II) complex trigonal bipyramidal environment
N-ethyl-1,10-phenanthroline-2-methanamine

0 Introduction

Phenanthroline derivatives containing amine groups have both soft and hard sites and are good donors for metal ions. 1,10-phenanthroline and its derivatives have been extensively used as ligands in both analytical and preparative coordination chemistry^[1]. Most of these works have been prompted by the intense current interest in their catalytic, redox and photoredox properties, biological activity, complexation activity and their novel supermolecular chemis-

try^[2-4]. But most of these are focused on the derivatives of the parent compound and 2,9-dimethyl-1,10-phenanthroline^[5-10]. Only a few compounds containing mono-methyl-1,10-phenanthroline unit have been described in the literature^[11-14].

In order to extend the range of available chelating mono-methylphenanthroline-based ligands, we synthesized a new ligand N-ethyl-1,10-phenanthroline-2-methanamine (L) and its Ni(II) complex (Scheme 1). The crystal structure of the complex has been charac-

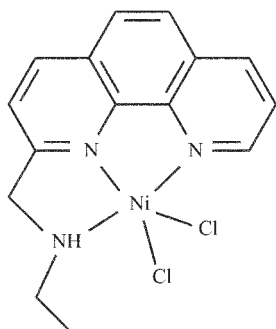
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terized by X-ray diffraction method and the spectroscopic and thermodynamic properties were studied.



Scheme 1

1 Experimental

1.1 Materials and Instruments

All the reagents used were of reagent grade. Redistilled water was used for all the solution. ^1H NMR spectra were recorded on a Varian UNITY-plus 400 MHz Spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer. The infrared spectra were carried out on a Equinox 55 FT spectrophotometer (Bruker), using KBr discs. The UV-spectra were recorded on Shimadzu UV-240 computer-controlled spectrometer, equipped with thermostated cell compartment. Stability constants of complexes were determined using a Beckman $\Phi 71$ pH instrument equipped with a 39 481 combined electrode.

1.2 Synthesis of L

The compound 2-carboxaldehyde-1,10-phenanthroline was synthesized according to literature^[14]. The synthesis of the ligand L was described as below.

To a stirred solution of ethylamine hydrochloride (1.63 g, 20 mmol) and sodium hydroxide (0.8 g, 20 mmol) in anhydrous methanol (50 mL), a solution of 2-carboxaldehyde-1,10-phenanthroline (1.04 g, 5 mmol) in methanol (50 mL) was added slowly. When the addition was completed, the mixed solution was stirred under room temperature unceasingly for 12 h. After filtration of the reaction mixture, NaBH_4 in situ was added in small quantities to the filtrate and the solution was stirred for another 12 h. After removing the

solvent, the residue was dissolved in water and then extracted with chloroform (3×80 mL). The organic fractions were combined, washed with distilled water (3×30 mL) and dried over MgSO_4 . The solution was filtered and the chloroform was removed on a rotary evaporator to give a yellow oil. The oil was dissolved in alcohol and concentrated HCl was then added. The pale yellow precipitate formed was collected and dried on P_2O_5 under vacuum to give product 0.83 g, yield 48%. ^1H NMR: (D_2O) δ 1.294 (t, 3H, CH_3); δ 3.225 (m, 2H, CH_2); δ 4.644 (s, 2H, phen- CH_2); δ 7.763~9.087 (m, 7H, phen $\text{H}_{3,9}$). Calculated for $\text{C}_{15}\text{H}_{15}\text{N}_3 \cdot 2\text{HCl} \cdot 2\text{H}_2\text{O}$ C: 52.02; H: 6.07; N: 12.14%; Found, C: 52.43; H: 5.96; N: 11.86%. IR (KBr pellet cm^{-1}): 3 448 ($\nu_{\text{N-H}}$), 1 535 (ν_{NH_2}), 1 507 ($\delta_{\text{N-H}}$), 1 602 ($\nu_{\text{C-C}}$, phen), 1 410 ($\nu_{\text{C-C}}$, phen), 869 ($\delta_{\text{C-H}}$, phen).

1.3 Preparation of crystal NiLCl_2

A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (23.77 mg, 0.1 mmol) in methanol (10 mL) was added to a solution of L (34.6 mg, 0.1 mmol) in methanol (10 mL). The solution was adjusted to pH 8 with triethylamine. The resulting solution was stirred at room temperature for 1 h and then filtered. The filtrate was allowed to stand at room temperature for 2 weeks. Yellow crystals of the complex suitable for X-ray analysis were obtained by slow evaporation. Calculated for $\text{C}_{15}\text{H}_{15}\text{Cl}_2\text{N}_3\text{Ni}$: C, 49.05; H, 4.09; N, 11.44%; found: C, 49.38; H, 4.51; N, 11.63%. IR (KBr pellet cm^{-1}): 3 441 ($\nu_{\text{N-H}}$), 1 508 ($\delta_{\text{N-H}}$), 1 591 ($\nu_{\text{C-C}}$, phen), 1 394 ($\nu_{\text{C-C}}$, phen), 851 ($\delta_{\text{C-H}}$, phen), 381 ($\nu_{\text{N-N}}$, imine), 258 ($\nu_{\text{N-N}}$, phen).

1.4 Potentiometric Titrations

Potentiometric titrations were carried out at 298 ± 0.1 K according to the method reported^[15]. The concentrations of the ligand and the metal ions were $1 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ and the ionic strength was adjusted to $0.1 \text{ mol} \cdot \text{dm}^{-3}$ using KNO_3 . The calculations were carried out through the curve-fitting computer program (TITFIT)^[15].

2 Crystal Structure Determination

A single yellow crystal of the complex having the approximate dimensions $0.25 \times 0.20 \times 0.15 \text{ mm}^3$, was put

on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda=0.071\ 073$ nm). Data were collected at room temperature by θ - 2ω scan technique in the range $1.57^\circ \leq \theta \leq 26.45^\circ$ with index ranges $-4 \leq h \leq 8$, $-32 \leq k \leq 29$, $-11 \leq l \leq 8$. A total of 8 742 reflections were collected including 3 181 independent reflections [$R(\text{int})=0.026\ 3$]. A summary of the crystallographic data is given in Table 1. The structure was solved with direct methods using SHELXS-97. The H atoms were assigned with common isotropic displacement factors and included

Table 1 Crystal Data and Structure Refinement for NiLCl_2

empirical formula	$\text{C}_{15}\text{H}_{15}\text{Cl}_2\text{N}_3\text{Ni}$
formula weight	366.91
temperature / K	293(2)
wavelength / nm	0.071 073
crystal system	monoclinic
space group	$P2_1/n$
a / nm	0.664 9(2)
b / nm	2.587 3(9)
c / nm	0.918 8(3)
β / ($^\circ$)	102.146(6)
volume / nm^3	1.545 2(9)
Z	4
calculated density / ($\text{g}\cdot\text{cm}^{-3}$)	1.577
absorption coefficient / mm^{-1}	1.596
$F(000)$	752
crystal size / mm^3	$0.25 \times 0.20 \times 0.15$
θ range for data collection / ($^\circ$)	1.57~26.45
limiting indices	$-4 \leq h \leq 8$, $-32 \leq k \leq 29$, $-11 \leq l \leq 8$
reflections collected / unique	8 742 / 3 181 [$R(\text{int})=0.026\ 3$]
completeness to $\theta=26.45^\circ$	99.6%
absorption correction	semi-empirical from equivalents
max. and min. transmission	1.000 000 and 0.882 598
refinement method	full-matrix least-squares on F^2
data / restraints / parameters	3 181 / 0 / 191
goodness-of-fit on F^2	1.017
final R indices [$I > 2\sigma(I)$]	$R_1=0.042\ 7$, $wR_2=0.089\ 0$
R indices (all data)	$R_1=0.053\ 6$, $wR_2=0.094\ 8$
largest diff. peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	407 and -490

in the final refinement by use of geometrical restraints. Full-matrix least-squares refinement on F^2 was carried out using SHELXL-97. The final agreement factor values are $R_1=0.042\ 7$, $wR_2=0.089\ 0$ [$I > 2\sigma(I)$], $R_1=\sum(|F_o|-|F_c|)/\sum|F_o|$, $wR_2=[\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. Selected bond lengths and angles are presented in Table 2.

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Table 2 Bond Lengths(nm) and Angles($^\circ$)

Ni(1)-N(2)	0.207 5(3)
Ni(1)-Cl(2)	0.225 08(11)
Ni(1)-N(3)	0.225 3(3)
Ni(1)-Cl(1)	0.226 14(12)
Ni(1)-N(1)	0.229 0(3)
N(2)-Ni(1)-Cl(2)	128.48(9)
N(2)-Ni(1)-N(3)	76.51(11)
Cl(2)-Ni(1)-N(3)	102.45(8)
N(2)-Ni(1)-Cl(1)	115.15(9)
Cl(2)-Ni(1)-Cl(1)	116.08(5)
N(3)-Ni(1)-Cl(1)	96.79(9)
N(2)-Ni(1)-N(1)	75.00(11)
Cl(2)-Ni(1)-N(1)	92.86(8)
N(3)-Ni(1)-N(1)	151.34(11)
Cl(1)-Ni(1)-N(1)	97.99(9)

3 Results and Discussion

3.1 Description of NiLCl_2 Crystal Structure

The perspective view of NiLCl_2 with labeling scheme is given in Fig.1. The nickel ion is five-coordinated by three nitrogen atoms of the ligand and two Cl^- anions. It shows rather unsaturated coordination sphere and the coordination geometry can be described as a distorted trigonal bipyramidal arrangement: the N(2), Cl(1) and Cl(2) in equatorial plane [Cl(2)-Ni(1)-Cl(1) $116.08(5)^\circ$, N(2)-Ni(1)-Cl(1) $115.15(9)^\circ$ and N(2)-Ni(1)-Cl(2) $128.48(9)^\circ$]; the N(1) and N(3) in axial positions [N(3)-Ni(1)-N(1) $151.34(11)^\circ$]. The in-plane Ni(1)-N(2) bond distance is 0.207 5 (3) nm which is in the normal range^[16], while the axial Ni(1)-N(1) bond distance is 0.229 0(3) nm which is rather longer. The bond distances of Ni(1)-Cl(1), Ni(1)-Cl(2) and Ni(1)-N(3) are 0.226 14(12) nm, 0.225 08(11) nm and 0.225 3(3) nm respectively.

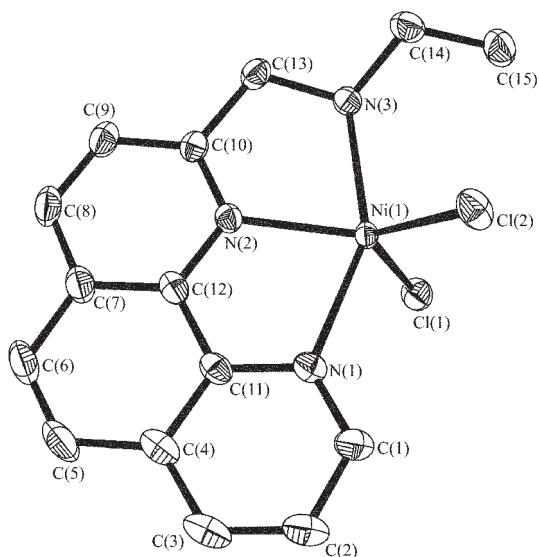


Fig.1 View of NiLCl_2 with the numbering scheme adopted

Fig.2 is a packing diagram of the complex. One Cl^- anion of the complex forms hydrogen bond with the phenanthroline hydrogen atom of one neighboring complex (0.283 8 nm) while the other Cl^- anion with the imine hydrogen atom of another neighboring complex (0.274 5 nm). The π - π stacking effects exist between two phenanthroline planes. Thus 2D network structure is formed.

3.2 Spectroscopic Properties

The IR-spectra of the title ligand and its Ni(II)

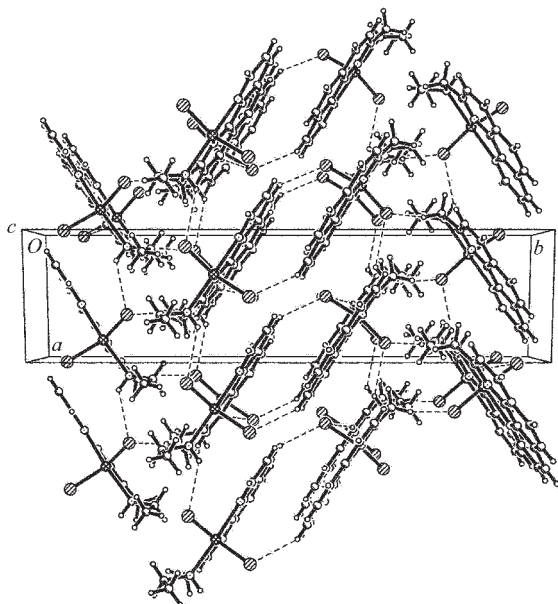


Fig.2 Packing diagram for complex NiLCl_2

complex suggest that Ni(II) ion is coordinated with all the three nitrogen atoms of the ligand, among which one comes from imine group and two from phenanthroline ring. Coordination of the nitrogen atoms from phenanthroline ring to Ni(II) ion is readily indicated by the red shift of the characteristic bands of phenanthroline ring from 1 602 cm^{-1} , 1 410 cm^{-1} , 868 cm^{-1} in the free ligand to 1 591 cm^{-1} , 1 394 cm^{-1} , 851 cm^{-1} in the complex and the appearance of the $\nu(\text{Ni-N}_{\text{phen}})$ stretching band at ca. 258 cm^{-1} . Coordination of the imine nitrogen atom to Ni(II) ion can be demonstrated by the fact that the NH_2^+ distorting vibration frequency of the free ligand (ca. 1 535 cm^{-1}) is absent in the IR-spectrum of the complex and the $\nu(\text{Ni-N}_{\text{imine}})$ stretching band appears at ca. 381 cm^{-1} . The stretching and distorting bands of N-H moiety of the ligand (at ca. 3 448 cm^{-1} and 1 507 cm^{-1}) change little after coordination (at ca. 3 441 cm^{-1} and 1 508 cm^{-1}).

The UV-spectra of methanol solution of the title ligand ($1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) and its Ni(II) complex ($1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) at pH 8.00 were recorded. The UV-spectrum of the ligand exhibits two bands with λ_{max} at 269 nm ($\epsilon = 26\,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 232 nm ($\epsilon = 32\,200 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) which are attributed to the $n-\pi^*$ transition and $\pi-\pi^*$ transition of the phenanthroline ring respectively, while the complex shows three bands with λ_{max} at 272 nm ($\epsilon = 51\,600 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 229 nm ($\epsilon = 113\,200 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 210 nm ($\epsilon = 163\,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). Except for the two bands at 272 nm and 210 nm attributable to the $n-\pi^*$ transition and $\pi-\pi^*$ transition of the phenanthroline ring, the complex also shows an additional shoulder around 229 nm attributed to a charge transfer transition from the nitrogen atom to Ni(II) ion (LMCT). Compared with the free ligand, the $n-\pi^*$ transition of the complex displays only a slight red shift from 269 nm to 272 nm, while the $\pi-\pi^*$ transition shows a evident blue shift from 232 nm to 210 nm probably because that the transferring of the electron cloud of nitrogen atom to Ni(II) ion induces the conjugation extent decreased and the electron excitation energy increased^[17].

3.3 Thermodynamic Properties

The protonation constants of the title ligand were determined in aqueous solution by potentiometric pH titration method according to literature^[15]. The experimental results suggest that this ligand has two step-wise protonation constants, which are 8.58, 4.84 respectively. The first protonation step involves the imine nitrogen atom while the second belongs to one of the two phenanthroline nitrogen atoms. The other phenanthroline nitrogen atom is not protonated in the pH range studied (2~11).

The ligand L with one imine nitrogen atom and two phenanthroline nitrogen atoms is a good donor for metal ions. The stability constants of its complexes with Co(II), Ni(II), Cu(II) and Zn(II) formed in 1:1 M(II)/L system in aqueous solution are determined as above and listed in Table 3. The distribution curves for species are shown in Fig.3.

Table 3 Binary Stability Constants for Ligand L with Respect to Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} at I=0.1 mol·dm⁻³ KNO₃, 25±0.1 °C

	CoL	NiL	CuL	ZnL
lgβ ₁₁₁	11.52±0.05	12.24±0.01	14.78±0.03	11.01±0.04
lgβ ₁₁₀	4.03±0.08	4.64±0.09	7.47±0.07	5.04±0.08
lgβ ₁₁₋₁	-5.06±0.11	-4.23±0.12	-1.37±0.16	-4.38±0.20

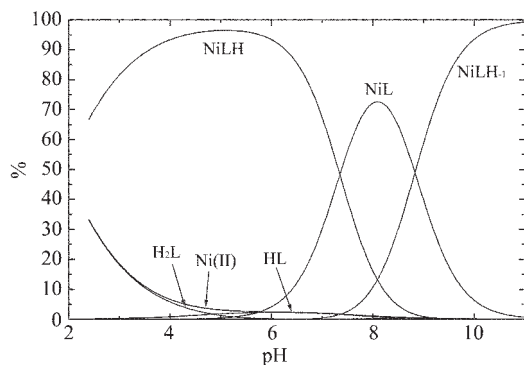


Fig.3 Species distribution diagram as a function of pH for Ni(II)-L complex at 25.0±0.1 °C

From the results, we can see that the ligand L can form three complexes in solution, which are 111, 110, 11-1 type mononuclear complexes respectively. The possible structures are shown in Fig.4. The species 111, 110 and 11-1 are formed in pH 2~8, 6~

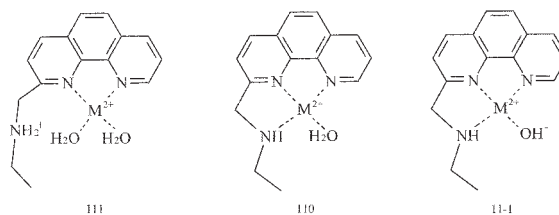


Fig.4 Possible structures of M(II)-L complex

10 and 7~11 respectively. In this paper preparation of the crystal is made in about pH 8, therefore, the crystal structure of NiLCl₂ corresponds with specie 110.

From Table 3, it is apparent that for all stability constants the order is: Co(II) < Ni(II) < Cu(II) > Zn(II), which is in agreement with the Irving-Williams order in coordination chemistry.

References

- [1] Wilkinson G., Gillard R. D., McCleverty J. A. (Eds.) *Comprehensive Coordination Chemistry*, Vol.2, Pergamon: Oxford, UK, 1987.
- [2] Palmer C. E. A., McMillin D. R., Kimaier C., Holten D. *Inorg. Chem.*, **1987**,**26**,3167.
- [3] Sakaki S., Koga G., Ohkubo K. *Inorg. Chem.*, **1986**,**25**, 2330.
- [4] Sammes P. G., Uahoglu G. *Chem. Soc. Rev.*, **1994**,**23**,327.
- [5] Zhao G., Sun H., Lin H., Zhu S., Su X. *J. Inorg. Biochem.*, **1998**,**72**,173.
- [6] Sun H., Lin H., Zhu S., Zhao G., Su X., Chen Y. *Polyhedron*, **1999**,**18**,1045.
- [7] Wang Z., Lin H., Zhou Z., Zhu S., Liu T., Chen Y. *J. Chem. Research(s)*, **2000**,170.
- [8] Krakowiak K. E., Bradshaw J. S., Jiang Weiming, Kent Dalley N., Wu Geng, Izatt R. M. *J. Org. Chem.*, **1991**,**56**, 2675.
- [9] Rodriguez-Ubis J. C., Alpha B., Plancherel D., Lehn J. M. *Helv. Chem. Acta*, **1984**,**67**,2264.
- [10] Guo Y., Ge Q., Lin H., Lin H., Zhu S. *Inorg. Chem. Com.*, **2003**,**6**,308.
- [11] Madeja V. K. *J. Prakt. Chem.*, **1962**,**17**,97.
- [12] Case F. H. *J. Am. Chem. Soc.*, **1948**,**70**,3994.
- [13] Eifert R. L., Hamilton C. S. *J. Am. Chem. Soc.*, **1955**,**77**, 1818.
- [14] Mlochowski J., Sliwa W. *Rocz. Chem.*, **1971**,**45**,803.
- [15] Sun H., Lin H., Zhou Z., Zhao G., Su X., Chen Y. *Indian J. Chem.*, **2001**,**40A**,763.
- [16] Liu T., Lin H., Zhu S., Wang Z., Wang H., Leng X., Chen Y. *J. Mol. Struct.*, **2001**,**597**,199.
- [17] Ma X., Wu J., Deng R. *J. Inorg. Chem.*, **1991**,**7**,229.