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Synthesis and crystal structure of nickel complex of *N*,*N*-bis(benzimidazol-2-yl-methyl)amine

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Abstract

A new nickel(II) complex, [NiL$_2$]Cl$_2$ (L = *N*,*N*-bis(benzimidazol-2-yl-methyl)amine), was synthesized and its crystal structure was determined. According to X-ray crystallographic studies, each nickel(II) ion was six-coordinated with six nitrogen atoms of two L ligands. The complex crystallizes in triclinic system, space group $P\bar{1}$, $a = 9.764(3)$ Å, $b = 11.032(3)$ Å, $c = 16.402(5)$ Å, $\alpha = 80.529(6)°$, $\beta = 79.180(7)°$, $\gamma = 74.232(6)°$, and $Z = 2$. The title complex forms two-dimensional hydrogen bond network structures between the chlorine atoms and the nitrogens of L. The IR and UV spectroscopy were measured. The absorption bands of d–d electron transition are assigned, the values of Dq and B were calculated according to the electronic spectrum of the complex.

Keywords: Crystal structure; *N*,*N*-bis(benzimidazol-2-yl-methyl)amine; Nickel(II) complex; Hydrogen bond

1. Introduction

Histidine is known to be an important biological ligand present at the active site of superoxide dismutases (SOD) [1,2] and many metalloproteins [3]. It appears to play a crucial role in the coordination chemistry of numerous metalloproteins. The ligand of *N*,*N*-bis(benzimidazol-2-yl-methyl)amine (L) has proven to be an appropriate model compound of histidine [4,5]. This paper reports the synthesis and crystal structure of [NiL$_2$]Cl$_2$ complex which shows a potential coordination environment in biological system.

2. Experimental

2.1. General

Iminodiacetic acid and *o*-phenylenediamine were of analytical grade and used without further purification. All other starting materials were purchased from the Tianjin chemical company and were of reagent grade. C, H, N elemental analyses were carried out with a Perkin–Elmer analyzer model 240. The IR spectra were recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm^{-1} region. The electronic spectra were measured on a Perkin–Elmer Hitachi-240 spectrophotometer.

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Table 1
Experimental data

Empirical formula	$C_{32}H_{30}Cl_2N_{10}Ni$
Formula weight	684.27
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.764(3)$ Å, $\alpha = 80.529(6)°$ $b = 11.032(3)$ Å, $\beta = 79.180(7)°$ $c = 16.402(5)$ Å, $\gamma = 74.232(6)°$
Volume, Z	1658.0(9) Å^3, 2
Density (calculated)	1.371 g cm^{-3}
Absorption coefficient	0.785 mm^{-1}
$F(000)$	708
Crystal size	$0.30 \times 0.25 \times 0.20$ mm^3
θ Range for data collection	2.36–25.03°
Limiting indices	$-11 \leq h \leq 8$, $-12 \leq k \leq 13$, $-19 \leq l \leq 11$
Reflections collected	6820
Independent reflections	5770 [$R_{(int)} = 0.0422$]
Max. and min. transmission	0.8588 and 0.7986
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5770/0/406
Goodness-of-fit on F^2	0.950
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0544$, $wR2 = 0.0870$
R indices (all data)	$R1 = 0.1504$, $wR2 = 0.1037$
Largest diff. peak and hole	0.815 and -0.268 e Å^{-3}

2.2. Preparation of N,N-bis(benzimidazol-2-yl-methyl)amine (L)

The ligand L was prepared by using a literature procedure described earlier [5]. A mixture of *o*-phenylenediamine (0.2 mol) and iminodiacetic acid (0.1 mol) in 1,2-ethandiol was refluxed for 24 h. After cooling, 450 ml of water was added with stirring. The resulting pink precipitate was filtered and dried under vacuum. The obtained solid was recrystallised three times from the mixed solvent of water and propanone in volume 1:1 to give white powder of *N*,*N*-bis(benzimidazol-2-yl-methyl)amine. The yield was 19.24 g (70%) and mp 249–251 °C.

2.3. Preparation of the title complex

To 110.8 mg (0.4 mmol) of L stirred in 10 cm^3 of methanol, 95.2 mg (0.4 mmol) of $NiCl_2 \cdot 6H_2O$ in 10 cm^3 of methanol was added and the mixture was continuously stirred for about 2 h. Blue single crystals suitable for X-ray investigation were obtained by slowly evaporating the resulting solution in air. The C, H and N contents were determined by elemental analysis (calcd for C.56.16; H.4.42; N.20.47. Found: C.55.71; H.4.28; N.20.32).

3. Structure determination

Determination of the unit cell and data collection were performed on a Bruker Smart 1000 diffractometer using graphite monochromated Mo Kα radiation. The intensity data collected by ω-scan technique were corrected for Lorentz and polarisation factors. An absorption correction was performed using SADABS program [6]. Experimental data, methods and the procedures used to elucidate the structure and other related parameters are given in Table 1. The structure was solved by direct methods, SHELXS97 [7].

Since the difference synthesis did not clarify the position of the H atoms, they were placed in calculated positions at distances of 0.970, 0.930, 0.910 and 0.860 Å for CH_2, CH, NH (alkylamino) and NH (imidazolyl) bonds, respectively, from the

Table 2
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*(eq)
Ni(1)	7097(1)	7975(1)	6853(1)	33(1)
N(1)	5382(4)	7721(4)	6282(3)	38(1)
N(2)	8341(4)	6558(3)	4604(3)	38(1)
N(3)	8311(4)	7081(3)	5856(2)	32(1)
N(4)	6843(4)	6209(4)	7495(2)	34(1)
N(5)	5544(4)	4810(4)	7610(3)	44(1)
N(6)	8666(4)	8389(4)	7359(3)	37(1)
N(7)	10,212(5)	9547(4)	7256(3)	64(2)
N(8)	5646(4)	9184(4)	7620(3)	37(1)
N(9)	4487(5)	11,184(4)	7798(3)	51(1)
N(10)	7237(4)	9765(4)	6105(3)	42(1)
C(1)	5961(5)	7071(5)	5534(3)	41(1)
C(2)	7548(5)	6902(4)	5323(3)	30(1)
C(3)	9753(6)	6537(4)	4636(3)	31(1)
C(4)	10,976(6)	6306(4)	4066(3)	44(2)
C(5)	12,223(6)	6364(5)	4314(4)	49(2)
C(6)	12,235(6)	6639(5)	5108(4)	47(2)
C(7)	11,006(6)	6888(5)	5676(3)	43(1)
C(8)	9732(6)	6851(4)	5423(3)	34(1)
C(9)	4556(5)	7008(5)	6942(3)	47(2)
C(10)	5622(5)	6012(5)	7369(3)	40(1)
C(11)	7636(6)	5039(5)	7813(3)	34(1)
C(12)	9052(6)	4658(5)	7972(3)	49(2)
C(13)	9577(7)	3371(6)	8223(4)	68(2)
C(14)	8756(8)	2493(6)	8305(4)	66(2)
C(15)	7378(7)	2865(5)	8140(3)	60(2)
C(16)	6823(6)	4150(5)	7886(3)	41(1)
C(17)	8712(6)	9904(5)	6100(3)	52(2)
C(18)	9202(6)	9280(5)	6903(4)	45(2)
C(19)	10,319(6)	8785(6)	8011(4)	54(2)
C(20)	11,132(7)	8692(7)	8629(5)	87(2)
C(21)	10,915(8)	7857(8)	9323(5)	92(3)
C(22)	9885(7)	7164(6)	9416(4)	68(2)
C(23)	9074(6)	7242(5)	8804(3)	47(2)
C(24)	9317(5)	8078(5)	8080(4)	40(1)
C(25)	6026(6)	10,788(5)	6417(4)	52(2)
C(26)	5373(5)	10,370(6)	7279(4)	41(1)
C(27)	4139(6)	10,471(6)	8541(4)	45(2)
C(28)	3281(6)	10,803(7)	9287(5)	69(2)
C(29)	3201(7)	9829(8)	9924(5)	77(2)
C(30)	3952(7)	8603(8)	9822(4)	71(2)
C(31)	4804(5)	8253(6)	9074(4)	50(2)
C(32)	4874(5)	9240(5)	8418(4)	40(1)
Cl(1)	6665(2)	6100(1)	3142(1)	74(1)
Cl(2)	7160(1)	9827(1)	4137(1)	60(1)

$U(\text{eq}) = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

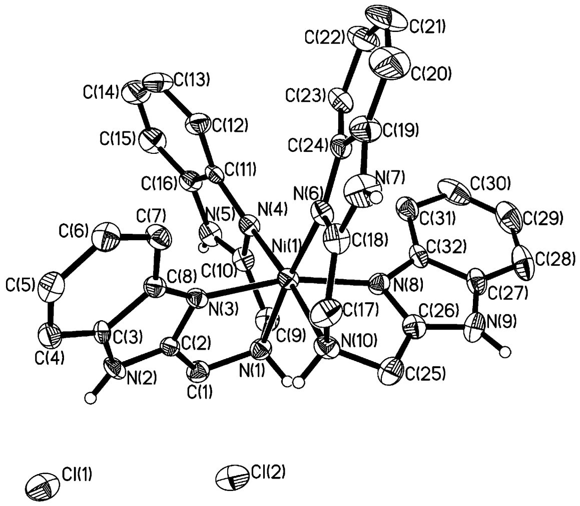

Fig. 1. An ORTEP [10] drawing of the title complex with the atom-numbering scheme. The displacement ellipsoids are drawn at 30% probability level.

corresponding atoms and a riding model was used during the refinement process by SHELXL97 [7]. Positional parameters and selected bond lengths and angles are presented in Tables 2 and 3, respectively.

4. Results and discussion

4.1. Crystal study

The title complex (Fig. 1) consists of one $[\text{NiL}_2]^{2+}$ cation and two Cl^- anions. Two alkylamino and four imidazolyls N atoms from two ligands are coordinated to nickel ion to form a slightly distorted octahedron. The two L ligands are tridentately bonded to Ni, forming five-membered chelate rings. Each ligand coordinated to Ni ion exhibits two distorted big planes whose dihedral angles are 91.2 and 85.8° for the two ligands, respectively. Each basal plane positions of the nickel atoms is occupied by seven carbon atoms and two nitrogen atoms of benzimidazol ring, one alkylamino N atom and one methene C atom from the L ligand. For the four planes of the $[\text{NiL}_2]^{2+}$ cation unit, the basal atoms deviate from their mean plane by ca. ± 0.0923, ± 0.1971, ± 0.0691 and ± 0.1117 Å, respectively, and the metal atom is displaced out of the plane by 0.1658, 0.0355, 0.0596 and 0.1702 Å,

Table 3
Selected bond lengths (Å) and angles (°)

Bond lengths		Bond angles		Bond angles	
Ni(1)–N(3)	2.054(4)	N(3)–Ni(1)–N(8)	165.65(16)	N(6)–Ni(1)–N(1)	174.78(17)
Ni(1)–N(8)	2.055(4)	N(3)–Ni(1)–N(6)	100.88(16)	N(4)–Ni(1)–N(1)	79.35(15)
Ni(1)–N(6)	2.056(4)	N(8)–Ni(1)–N(6)	86.22(15)	N(3)–Ni(1)–N(10)	87.76(16)
Ni(1)–N(4)	2.111(4)	N(3)–Ni(1)–N(4)	89.87(15)	N(8)–Ni(1)–N(10)	81.16(17)
Ni(1)–N(1)	2.165(4)	N(8)–Ni(1)–N(4)	100.32(17)	N(6)–Ni(1)–N(10)	79.95(16)
Ni(1)–N(10)	2.170(4)	N(6)–Ni(1)–N(4)	105.54(16)	N(4)–Ni(1)–N(10)	174.36(16)
		N(3)–Ni(1)–N(1)	80.77(16)	N(1)–Ni(1)–N(10)	95.21(15)
		N(8)–Ni(1)–N(1)	91.12(16)		

respectively. The Ni–N bonds of alkylamino (average 2.168(4) Å) are slightly longer than those of imidazolyls (average 2.069(4) Å), (Table 2). As can be seen from the packing diagram (Fig. 2) there are intermolecular hydrogen bonds between the Cl$^-$ anions and the N atoms of [NiL$_2$]$^{2+}$ cations of neighbouring molecules. Hydrogen bonding distances and angles are grouped in Table 4. For clarity the conventional description of hydrogen bonding structural parameters has been adopted: D(H)···A (D = N(1), N(2), N(5), N(7), N(9), N(10); A = Cl(1), Cl(2)) indicates the distance between a donor D atom and acceptor A atom, (D)H···A the distance between a donor hydrogen atom bound to D and acceptor, while D–H···A indicates the angle. The Cl(1) anion forms hydrogen bond network with N(2), N(5) and N(9) atoms from imidazolyls rings at 3.316, 3.125 and 3.149 Å of D(H)···A distances, and the Cl(2) anion with imidazolyls N(7) atom, and two alkylamino N atoms: N(1) and N(10) at 3.244, 3.214 and 3.232 Å, respectively. All these hydrogen bonds connect [NiL$_2$]$^{2+}$ and Cl$^-$ to form a two-dimensional network along *a* and *b* axes.

4.2. Spectroscopic properties

The infrared spectra of the title complex display the characteristic bands of the ligand. The ν(–C=N) absorption of the benzimidazole is observed at 1621s cm^{-1}, and ν(C–N) at 1450s cm^{-1}, and they are slightly shifted to higher wavenumbers than those of the free ligand. The ν(N–H) is at 3350s,b and 3100s,b cm^{-1}. The absorption bands, near 900w, 740m cm^{-1}, are due to out-of-plane bend vibration correlating with aryl ring, where s, b, m and w refer to strong, broad, medium and weak, respectively.

The ultraviolet and visible spectra were measured in the 200–900 nm range. The spectra show a very strong absorption band over 46,730 cm^{-1} ($\varepsilon = 3.00 \times 10^4$ L mol^{-1} cm^{-1}), and three strong absorptions at 41,152 cm^{-1} ($\varepsilon = 1.69 \times 10^4$ L mol^{-1} cm^{-1}), 36,630 cm^{-1} ($\varepsilon = 2.08 \times 10^4$ L mol^{-1} cm^{-1}) and 35,714 cm^{-1} ($\epsilon = 2.02 \times 10^4$ L mol^{-1} cm^{-1}), which may be attributed to charge transfer and the transition of the ligand itself. In addition, three very weak absorptions at 27,240 cm^{-1} (ν_1, $\varepsilon \approx 84$ L mol^{-1} cm^{-1}), 17,540 cm^{-1} (ν_2, $\varepsilon \approx 26$ L mol^{-1} cm^{-1}) and 11,792 cm^{-1} (ν_3, $\varepsilon \approx 12$ L mol^{-1} cm^{-1}) may be

Table 4
Relevant intermolecular hydrogen bonds parameters (distances in Å, angles in degrees)

D–H	(D)H···A	D–H···A	D(H)···A	A	Symm.
N(1)–H(1C)	2.328	164.45	3.214	Cl(2)	$[-x+1, -y+2, -z+1]$
N(2)–H(2A)	2.469	168.69	3.316	Cl(1)	
N(5)–H(5B)	2.343	151.34	3.125	Cl(1)	$[-x+1, -y+1, -z+1]$
N(7)–H(7B)	2.580	134.84	3.244	Cl(2)	$[-x+2, -y+2, -z+1]$
N(9)–H(9C)	2.345	155.84	3.149	Cl(1)	$[-x+1, -y+2, -z+1]$
N(10)–H(10A)	2.333	169.57	3.232	Cl(2)	

D: Donor; A: Acceptor; Symm.: Symmetry applied in acceptor.

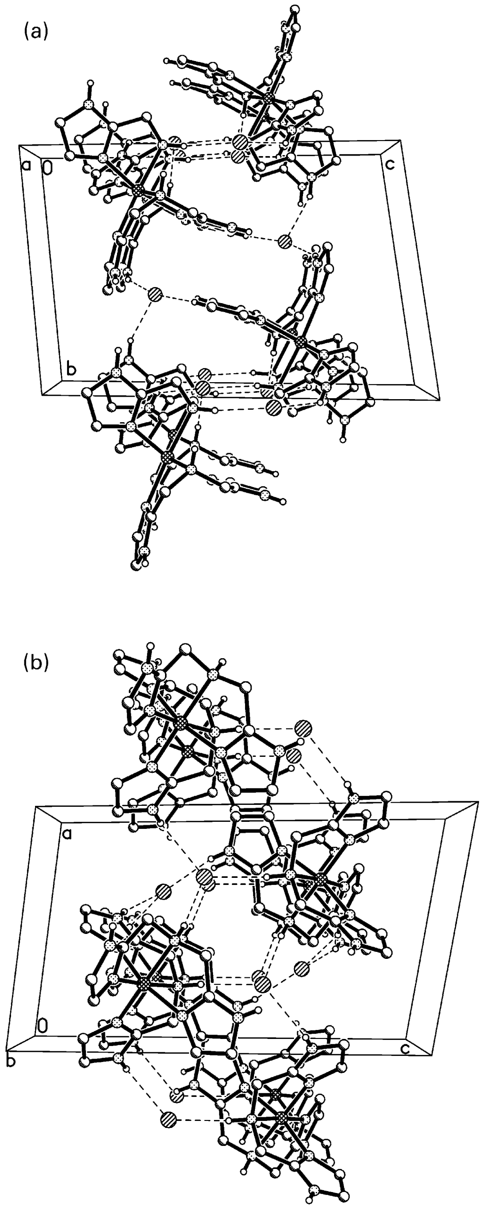

Fig. 2. The packing diagram of the title complex viewed along (a) *a*-axis and (b) *b*-axis. Hydrogen bonds are shown as dotted lines and H atoms not involved in hydrogen bonding and phenyl rings have been omitted for clarity.

observed in the concentrated solution. They are tentatively attributed to the electronic transitions $\nu_1 : {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$, $\nu_2 : {}^3A_{2g} \rightarrow {}^3T_{1g}$ and $\nu_3 : {}^3A_{2g} \rightarrow {}^3T_{2g}$. The values of the parameter Dq, B were 1179 and 626, respectively, and $\nu_2 = 17{,}526\ \mathrm{cm}^{-1}$, which calculated from the values of ν_1 and ν_3 according to the formula of electronic transitions energy [8], and the assignment was checked by comparing the predicted and observed positions of the second band. The agreement is very satisfactory. This spectrum is typical d–d charge-transfer bands in the octahedral Ni(II) surrounding [9].

Acknowledgments

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