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Synthesis and Structure of Ni(II) Complex Derived from Phthalic Acid and 1,10-Phenanthroline

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A nickel(II) complex [Ni(TPHA)(Phen)$(H_2O)_3$]Cl·H_2O), where TPHA = phthalic acid and phen = 1,10-phenanthroline, has been synthesized and characterized by IR, elemental analysis, and single-crystal X-ray diffraction analysis. Crystal data: monoclinic, space group P2(1)/n with a = 7.5432(2) Å, b = 13.6549(3) Å, c = 20.1959(6) Å. β = 97.38°, v = 2062.98(9) $Å^3$, z = 4, Dc = 1.530 mg/m^3, Mr = 475.09, F(000) = 984 and μ = 3.092 mm^{-1}. The final R and wR are 0.0403 and 0.0904, respectively for 3645 observed reflections with $I > 2\sigma(I)$. The centre nickel(II) ion is coordinated by six atoms in a prolonged octahedron geometry.

Key Words: Nickel(II), Complex, Phthalic acid, 1,10-Phenanthroline, Crystal structure.

INTRODUCTION

Transition metal coordination compounds of multidentate nitrogen organic ligands have attracted wide interest due to their uses in industrial catalysis, biology and curative fields and so on, because of its novel conformation, multiple fashion of bond constitution and paramagnetic behaviour[1–2]. The construction of functional system compound lies on the character of mutual effect in reagents. The important headway of multidentate nitrogen organic cooperation is inducting organic compound as oriented reagent to inorganic framewok by self-assembly of covalent bond, assort bond and hydrogen bond in order to form compounds with novel conformation[3, 4]. Inorganic solids have been reported as useful catalysts for many reactions, resulting in higher selectivity, mild conditions and easier operation[5–9]. In this communication, the synthesis and the structure of a novel complex [Ni(TPHA)(Phen)$(H_2O)_3$]Cl·H_2O has been reported.

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EXPERIMENTAL

1,10-Phenanthroline, potassium hydrogen phthalate and $NiCl_2$ were of analytic grade. IR spectrum was recorded on a Nexus-870 spectrometer. Elemental analyses were determined on an Elementar Vario EL-III elemental analyzer.

Synthesis

A mixture of $NiCl_2$ (0.052 g, 0.4 mmol), 1,10-phenanthrolline (0.079 g, 0.4 mmol), potassium hydrogen phthalate (0.082 g, 0.4 mmol) and H_2O (20 mL) was sealed in a 25 mL cone bottle under normal atmospheric temperature and normal pressure for seven days. The pH value was about 8.0 before and after the reaction. The product was light blue pillar-shaped crystal. Elemental analysis (%) Calcd. for $C_{20}H_{20}N_2NiO_8$: C, 50.26; H, 4.00; N, 5.65; Found: C, 50.56; H, 4.20; N, 5.90. IR (KBr, cm^{-1}): 3400–3080, (broad, vs, $\nu(COO^-)$, $\nu(H_2O)$); 1550(vs, $\nu(C{=}O)$); 1490, 1410(vs, $\nu(C{=}N)$); 849(s, $\nu(C{=}O)$); 771, 725(vs, $\nu(=C{-}H)$).

Structure determination

A light blue crystal of the Ni(II) compound with approximate dimensions of 0.40 × 0.38 × 0.24 mm was selected and mounted on a glass fibre in a random orientation for X-ray diffraction study. The diffraction data were collected on a Siemens Smart CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) at 293(2) K, using ω scan technique in the range of $1.80° \le \theta \le 25.07°$. A total of 10462 reflections were collected with 3645 unique ones (R(int) = 0.0284) in the ranges of $-7 \le h \le 8$, $-12 \le k \le 16$, $-22 \le l \le 24$. LP effects and empirical absorption were applied in data corrections. The nickel atoms were located by direct methods and the others were derived from the successive difference Fourier synthesis. SHELXS-97 program system[10] was refined anisotropically. Hydrogen atoms were added according to the theoretical model. The final full-matrix least-squares refinement including 304 variable parameters for 3645 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.0403 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.0904 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.0314P)^2 + 2.4856P]$ and $P = (F_0^2 + 2F_c^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.280 and $-0.512 e/Å^3$ respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters are given in Table-1 and the selected bond angles are listed in Table-2. The molecular structure of $[Ni(TPHA)(Phen)(H_2O)_3]\cdot Cl\cdot H_2O$ is shown in Fig. 1 with the hydrogen atoms omitted for clarity. Molecular packing arrangement in the unit cell is shown in Fig. 2. The molecule consists of $[Ni(TPHA)(Phen)(H_2O)_3]^+$, counter-ions of Cl^- and one crystalline H_2O. The cation $[Ni(TPHA)(Phen)(H_2O)_3]^+$ has the prolonged asymmetric octahedron configuration, in which nickel cation has a slightly

TABLE-1
ATOMIC COORDINATES (× 10^4) AND THERMAL PARAMETERS (× 10^3 Å^2)

Atom	X	Y	Z	U(eq)
Ni	2827(1)	3063(1)	389(1)	32(1)
N(1)	3137(3)	1837(2)	998(1)	34(1)
N(2)	2311(3)	1973(2)	–334(1)	37(1)
C(1)	3543(4)	1779(2)	1655(2)	43(1)
C(10)	1910(5)	2048(3)	–988(2)	53(1)
C(11)	2440(4)	1060(2)	–65(2)	38(1)
C(12)	2903(4)	981(2)	645(2)	37(1)
C(13)	4770(4)	4390(2)	1428(1)	37(1)
O(1)	5539(3)	2945(2)	315(1)	40(1)
O(2)	2519(3)	4204(2)	290(1)	39(1)
O(3)	176(3)	3087(2)	538(1)	39(1)
O(4)	3304(2)	4149(1)	1095(1)	36(1)
O(5)	6100(3)	3832(2)	1542(1)	52(1)
O(6)	2269(3)	6013(2)	390(1)	41(1)
O(7)	488(3)	5871(2)	1183(1)	42(1)
O(8)	9696(3)	4064(2)	1693(1)	50(1)

distorted square plane defined by N(1)-N(2)-O(4)-O(2), with Ni-N(1) 2.073(2), Ni-N(2) 2.086(2), Ni-O(1) 2.076(2), Ni-O(2) 2.067(2), Ni-O(3) 2.061(2), Ni-O(4) 2.0567(19) Å, O(4)-Ni-N(2) 179.17(9), O(2)-Ni-N(2) 94.52(9)°. Because the TPHA is an oxygen donor, the bond length of Ni-O(4) is shorter than that of Ni-O(2). In addition, the plane of N(1)-N(2)-O(4)-O(2) is nearly coplanar with the plane of phen. Hydrogen bonds are given in Table-3. O(8) from crystalline H_2O forms hydrogen bond with O(3), O(5), and O(7). Hydrogen bonds are given in Table-3.

TABLE-3
HYDROGEN BOND LENGTHS (Å) AND BOND ANGLES (°)
(A = ACCEPTOR, D = DONOR)

D-H...A	d(D–H)	d(H...A)	d(D...A)	< (DHA)
O(1)-H(1)...O(5)	0.915(18)	1.890(2)	2.741(3)	154(3)
O(2)-H(4)...O(6)	0.915(18)	1.935(19)	2.844(3)	173(3)
O(8)-H(8)...O(5)	0.906(18)	1.820(2)	2.709(3)	165(3)
O(1)-H(2)...O(6)#1	0.902(18)	1.850(2)	2.719(3)	161(3)
O(2)-H(3)...O(7)#2	0.922(18)	1.800(19)	2.713(3)	170(3)
O(3)-H(5)...O(8)#3	0.914(18)	1.836(19)	2.749(3)	177(3)
O(3)-H(6)...O(6)#2	0.904(18)	1.844(19)	2.745(3)	174(3)
O(8)-H(7)...O(7)#4	0.923(18)	1.848(19)	2.768(3)	174(3)

Symmetry transformations used to generate equivalent atoms:
#1 –x + 1, –y + 1, -z #2 –x, –y + 1, –z #3 x–1, y, z #4 x + 1, y, z

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Bond	Distance	Angles	(°)	Angles	(°)	Angles	(°)
Ni-O(4)	2.0567(19)	O(4)-Ni-O(3)	88.46(8)	O(2)-Ni-N(2)	94.52(9)	N(2)-C(11)-C(12)	117.60(2)
Ni-O(3)	2.061(2)	O(4)-Ni-O(2)	84.90(8)	N(1)-Ni-N(2)	80.57(9)	N(1)-C(12)-C(4)	122.80(3)
Ni-O(2)	2.067(2)	O(3)-Ni-O(2)	93.23(8)	O(1)-Ni-N(2)	89.51(9)	N(1)-C(12)-C(11)	117.10(2)
Ni-N(1)	2.073(2)	O(4)-Ni-N(1)	100.02(8)	C(1)-N(1)-C(12)	118.00(2)	O(5)-C(13)-O(4)	124.30(3)
Ni-O(1)	2.076(2)	O(3)-Ni-N(1)	87.91(8)	C(1)-N(1)-Ni	129.50(2)	O(5)-C(13)-C(14)	119.10(3)
Ni-N(2)	2.086(2)	O(2)-Ni-N(1)	174.99(9)	C(12)-N(1)-Ni	112.51(18)	O(4)-C(13)-C(14)	116.60(2)
N(1)-C(1)	1.325(4)	O(4)-Ni-O(1)	91.11(8)	C(10)-N(2)-C(11)	117.90(3)	O(7)-C(20)-O(6)	125.20(3)
N(1)-C(12)	1.368(4)	O(3)-Ni-O(1)	174.44(8)	C(10)-N(2)-Ni	130.00(2)	O(7)-C(20)-C(19)	117.20(2)
N(2)-C(10)	1.321(4)	O(2)-Ni-O(1)	92.25(8)	C(11)-N(2)-Ni	112.16(18)	O(6)-C(20)-C(19)	117.40(3)
N(2)-C(11)	1.359(4)	N(1)-Ni-O(1)	86.71(9)	N(1)-C(1)-C(2)	122.80(3)	C(13)-O(4)-Ni	128.38(18)
C(20)-O(7)	1.247(3)	O(4)-Ni-N(2)	179.17(9)	N(2)-C(10)-C(9)	123.00(3)	N(2)-C(11)-C(7)	122.60(3)
C(20)-O(6)	1.263(3)	O(3)-Ni-N(2)	90.97(9)				

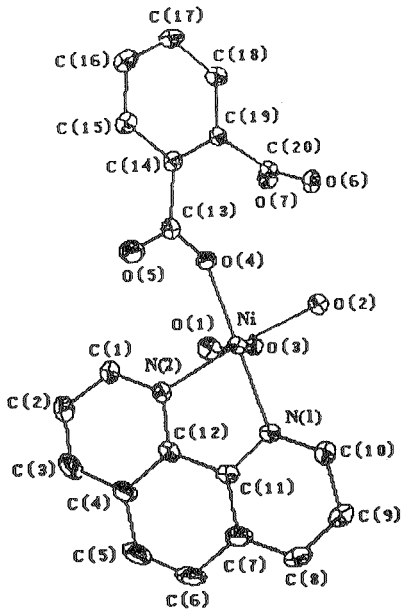

Fig. 1. Structure of the Ni(II) complex

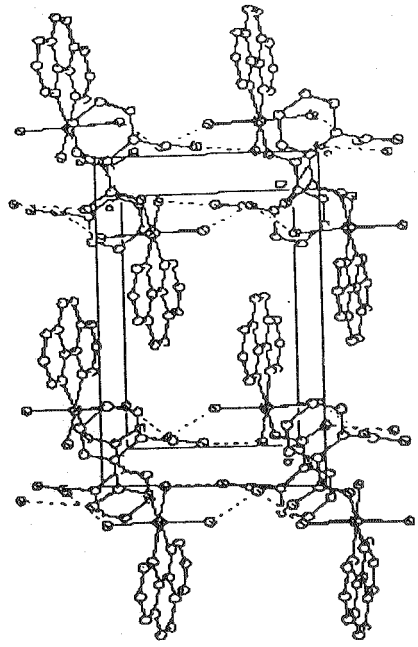

Fig. 2. Molecular packing arrangement in the unit cell

Conclusion

To summarize, we synthesized a novel nickel complex [Ni(TPHA)(Phen) $(H_2O)_3$·Cl·H_2O,the structure of which was confirmed by IR spectra, elemental analysis and single- crystal X-ray diffraction analysis.

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