Synthesis and crystal structure of tris(1,10-phenanthroline)-nickel(II) diperchlorate

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ABSTRACT

A new complex $[Ni(phen)_3]^{2+} \cdot (ClO_4^-)_2$ has been synthesized by the reaction of $Ni(OAc)_2 \cdot (H_2O)_4$ with 1,10-phenanthroline in the CH_3CH_2OH/H_2O (v:v = 5:1). It was characterized by elemental analysis, IR and X-ray single crystal diffraction analysis. The crystal of the title complex $[Ni(phen)_3]^{2+} \cdot (ClO_4^-)_2$ belongs to monoclinic, space group C_2/c with a = 3.6602(7) nm, b = 1.5762(3) nm, c = 1.2230(2) nm, β = 102.75(3) º, V = 6.882(2) nm^3, Z = 8, Dc = 1.541 $\mu g \cdot m^{-3}$, μ = 0.783 mm^{-1}, F(000) = 3263, and final R_1 = 0.0985, wR_2 = 0.2872. The complex comprises a six-coordinated Ni (II) center, with a N_6 distorted octahedron coordination environment. The molecules are connected by π-π stacking to form one dimensional chain structure.

Key words: 1,10-Phenanthroline; Ni (II) complex; synthesis; crystal structure

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INTRODUCTION

The design and synthesis of metal complex materials have attracted intense attention in recent years owing to their potential practical applications, such as molecule-based magnets, luminescence, biological properties [1-3]. The Ni (II) complexes have gained considerable attention, which may bring both intriguing architectures and promising potential applications in such fields as catalysis, gas storage, magnetics, luminescence materials, and so on [4–11]. The phen ligand has been shown to be good building blocks in the design of metal-organic materials with its rich coordination modes [12, 13]. With considering the points mentioned above, 1,10-phenanthroline was chosen as the organic ligand to construct new Ni (II) complex under room temperature. We report here the synthesis, structure, and characterization of a new Ni (II) complex, $[Ni(phen)_3]^{2+} \cdot (ClO_4^-)_2$.

EXPERIMENTAL SECTION

All chemicals were obtained from commercial sources and were used without further purification. Elemental analyses (C, H and N) were carried out on a Elementar Vario EL III elemental analyzer. IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrophotometer in the 4000–400 cm^{-1} region. The crystal data was collected on a Bruker smart CCD Area Detector.

Synthesis of the Ni (II) complex

The 2.0 mmol (0.3964 g) of 1,10-phenanthroline was added to the 5 mL of CH_3CH_2OH/H_2O (v:v = 5:1) solution. After being dissolved, 1.0 mmol (0.2489 g) of $Ni(OAc)_2 \cdot (H_2O)_4$ was added to the solution. The mixture was continuously stirred for 4 h at refluxing temperature and then cooled to room temperature. The production was collected by filtration. The colourless crystals were obtained after the filtrate was kept in air for 2 weeks. Yield: 60%. Elementary analysis: calcd for $C_{36}H_{24}Cl_2N_6NiO_8$: C, 54.12; H, 3.01; N, 8.55 %; found: C, 54.58; H, 3.49; N, 8.72 %. IR ν_{max} (cm^{-1}): IR ν_{max} (cm^{-1}): 1556(m, C=N).

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X-ray Crystallography

A colourless block single crystal with dimensions of 0.30 mm×0.26 mm×0.22 mm was selected for measurement. Diffraction data of the single crystal were collected by $\varphi\sim\omega$ scan mode using a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 (2) K on a Bruker Smart Apex CCD diffractometer. A total of 31909 reflections were collected in the range 3.10-27.48°, of which 7800 were unique ($R_{int} = 0.0350$) and 5427 were observed with $I>2\sigma(I)$. The data were corrected for Lp factors. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. The structure was solved by direct methods [14] using SHELXL-97 and expanded using Fourier techniques. All of the non-hydrogen atoms and hydrogen atoms were refined anisotropically and isotropically, respectively. The final refinement by full-matrix least squares method was converged at $R = 0.0985$, and $wR = 0.2872$ ($w = 1/[\delta^2(Fo^2)+(0.1000P)^2+0.0000P]$, $P = (Fo^2+2Fc^2)/3$, $S = 2.160$, $(\Delta/\sigma)_{max} = 0.001$). The largest peak in the final difference fourier map is 0.163 e / Å^3 and the minimum peak is -0.175 e / Å^3. Molecular graphics were drawn with the program package SHELXTL-97 crystallographic software package [15]. The most relevant crystal data for complex are quoted in Table 1, and the selected bond distances and angles are listed in Table 2.

Table 1: Crystallographic data for Ni (II) complex

Formula	$C_{36}H_{24}Cl_2N_6NiO_8$
Formula weight	798.20
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	36.602(7)
b (Å)	15.762(3)
c (Å)	12.230(2)
β (°)	102.75(3)
Z	8
$F(000)$	3263
Temperature (K)	293(2)
V (Å^3)	6882(2)
Calculated density ($\mu g \cdot m^{-3}$)	1.541
Crystal size (mm^3)	0.30×0.26×0.22
μ (mm^{-1})	0.783
S	2.160
Limiting indices	$-43 \leq h \leq 47$, $-20 \leq k \leq 20$, $-15 \leq l \leq 15$
Reflections collected / unique	7800/5427
Parameters	479
Restraints	0
R_{int}	0.035
R_1, wR_2 [all data]	0.1211, 0.3067
R_1, wR_2 [$I>2\sigma(I)$]	0.0985, 0.2872
Largest diff. peak and hole (e·Å^{-3})	4.316, -0.780

Table 2: Selected bond lengths (Å) and angles (°) for Ni (II) complex

Bond	Distance	Bond	Distance
Ni1-N4	2.072(4)	C24-N3	1.332(6)
Ni1-N2	2.077(4)	N3-C18	1.361(7)
Ni1-N5	2.087(4)	C1-N1	1.348(6)
Ni1-N3	2.088(4)	N1-C5	1.349(6)
Ni1-N1	2.098(4)	N4-C13	1.322(6)
Ni1-N6	2.100(4)	N4-C17	1.393(6)
N2-C6	1.340(6)	N5-C25	1.330(6)
N2-C12	1.342(7)	N5-C29	1.359(6)
N6-C36	1.315(7)	N6-C30	1.368(7)
		Cl1-O1	1.203(9)
Angle	(°)	Angle	(°)
N4-Ni1-N2	92.80(16)	N4-Ni1-N6	170.48(17)
N4-Ni1-N5	93.81(15)	N6-Ni1-N2	94.03(18)
N5-Ni1-N2	170.94(16)	N5-Ni1-N6	80.16(18)
N4-Ni1-N3	79.91(16)	N3-Ni1-N6	92.71(16)
N3-Ni1-N2	96.60(15)	N1-Ni1-N6	88.73(15)
N5-Ni1-N3	90.66(14)	C1-N1-C5	117.5(4)
N4-Ni1-N1	99.09(14)	C18-N3-C24	117.1(5)
N1-Ni1-N2	79.05(15)	C25-N5-C29	117.6(4)
N5-Ni1-N1	93.78(15)	C13-N4-C17	117.4(4)
N3-Ni1-N1	175.51(15)	C30-N6-C36	120.4(5)

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RESULTS AND DISCUSSION

The result of elemental analysis indicated that the composition of Ni (II) complex conforms to a 1:3 metal-to-ligand stoichiometry, and is accorded with the result of single crystal X-ray diffraction analysis. The Ni (II) complex is soluble in DMF, DMSO, methanol, a little soluble in ethanol and acetone, insoluble in benzene, diethyl and THF. The molar conductance value of the Ni (II) complex measured in CH_3OH solution (1×10^{-3} mol L^{-1}) at 25 °C is 8.8 scm^2 mol^{-1}, showing the Ni (II) complex is non-electrolyte [16].

Infrared spectra
The IR spectrum of 1,10-phenanthroline ligand shows band at 1589 cm^{-1}, and it shifts to 1556 cm^{-1} in the complex, indicating that the nitrogen atoms of 1,10-phenanthroline take part in the coordination with Ni (II) ion [17]. The ClO_4^- anions do not take part in coordination with Ni (II) ion, which is in accordance with the results of X-ray single crystal diffraction analysis.

Structure Description
A single-crystal X-ray diffraction study reveals that the Ni (II) complex crystallizes in monoclinic system with C_2/c space group. The crystal structure of the title complex is revealed in Fig. 1. The molecular packing arrangement is shown in Fig. 2. As shown in Figure 1, we can see that the asymmetric unit consists of one Ni (II) ion and three phen ligands. The Ni (II) cation is coordinated by six nitrogen atoms from phen ligand (Ni1-N1 = 2.098(4) Å, Ni1-N2 = 2.077(4) Å, Ni1-N3 = 2.088(4) Å, Ni1-N4 = 2.072(4) Å, Ni1-N5 = 2.087(4) Å, Ni1-N6 = 2.100(4) Å) in a distorted octahedral geometry. Also, the distances of Ni-N are comparable with that observed in other Ni-based complexes [18, 19].

The molecules stack with each other via π-π interaction in arrays to form a 1D chained structure (Fig. 3). Obviously, the π-π interactions increase the stability of the crystal structure. The phen rings in the molecules are not coplanar and do not show any unusual features, and the bond lengths and bond angles are within the range of normal values.
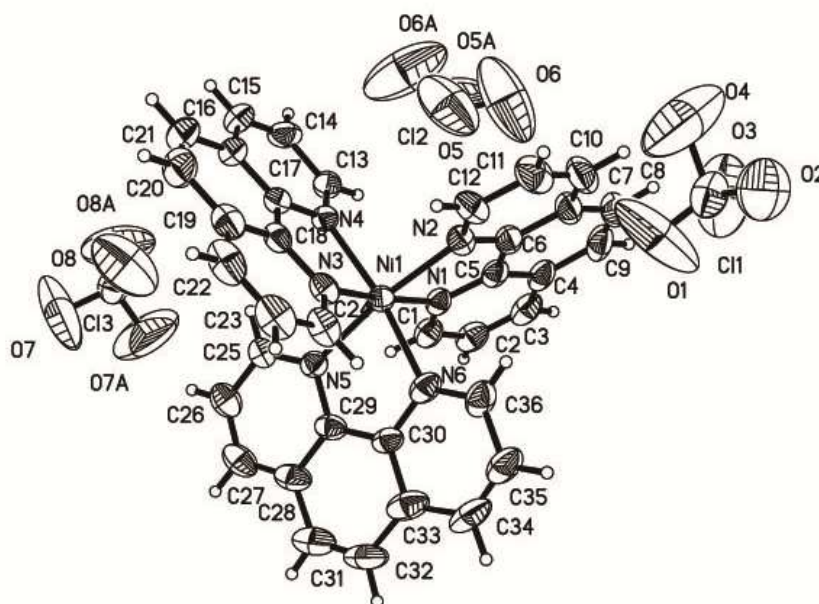

Fig 1: Molecular structure of the Ni (II) complex, where the thermal ellipsoids were drawn at 30% possibility
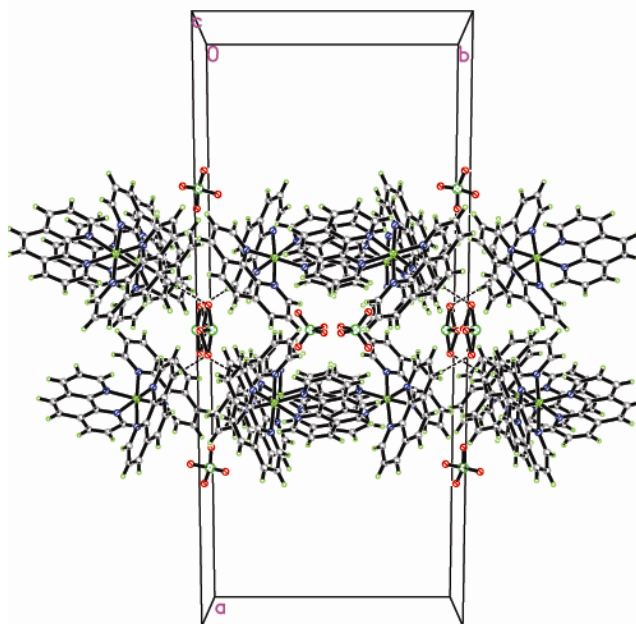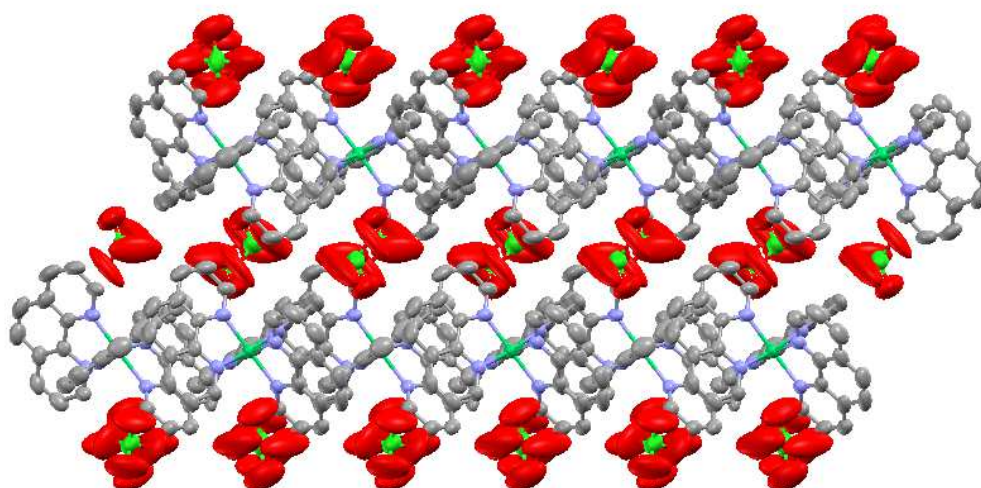
Fig 2: Packing of the Ni (II) complex

Fig 3: One dimensional chain structure of the Ni (II) complex by π-π stacking

CONCLUSION

In summary, a new complex $[Ni(phen)_3]^{2+} \cdot (ClO_4^-)_2$ has been synthesized and structurally characterized. The results show that the phen ligand coordinated to the Ni (II) ion by six nitrogen atoms and the complex molecule formed a distorted octahedron coordination environment. The molecules are connected by π-π stacking to form one dimensional chain structure.

Supplementary Material

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No.CCDC 975303. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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