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# عنوان مقاله

# ساختار کریستالی کمپلکس دی کلرو فنیل پیریدین فرماید نیکل(II) $[Ni(HphpyF)Cl_2]$

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## چکیده

کمپلکس جدید دی کلرو فنیل پیریدین فرماید نیکل(II) $Ni(HphpyF)Cl_2]$، سنتز شد و ساختار آن بوسیله پراش اشعه ایکس مشخص گردید. این کمپلکس دارای سیستم کریستالی مونوکلینیک ($Z=4$) و گروه فضایی $P\ 2_1/c$ با پارامترهای بلوری: $a$ = 13.304(2) Å, $b$ = 12.789(2) Å, $c$ = 7.767(13) Å, α=90(5)°, $\beta$ = 94.101(3)° و $V$= 1378.6(4)Å$^3$ می باشد. ساختار این کمپلکس تک هسته ای است که نیکل (II) در آرایش چهار وجهی به لیگاند های فنیل پیریدین فرماید و کلر کئوردینه شده است. طول پیوند Ni-N در محدوده .Å(4) 1.96-1.98 قرار دارد.

**واژه‌های کلیدی:** فنیل پیریدین فرماید، نیکل (II) کمپلکس، ساختار کریستالی.

# Crystal structure of $[Ni(HphpyF)Cl_2]$ complex

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## Abstract

A new complex of formula $[Ni(HphpyF)Cl_2]$ (HphpyF = phenylpyridylformamidine) has been synthesized and the crystal structure determined by X-ray diffraction methods. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a$ = 13.304(2) Å, $b$ = 12.789(2) Å, $c$ = 7.767(13) Å, α=90(5)°, $\beta$ = 94.101(3)°, $V$ = 1378.6(4)Å$^3$, and $Z$ = 4. The structure of this complex is mononuclear with the nickel(II) ion tetrahedrally coordinated and bound to the HphpyF through the nitrogen atoms. The Ni-N bond lengths are in the range of 1.96-1.98 (4)Å.

**Keywords:** Phenylpyridylformamidine, Ni (II) complex, Crystal structure.

**1. Introduction**

In coordination chemistry, Schiff bases have a significant role as ligands still a century after their discovery [Cozzi, et al]. Schiff base derived from the reaction of aromatic aldehydes and aliphatic or aromatic amines represent an important series of widely studied organic ligands. Schiff base and the relevant transition metal complexes are still found to be of great interest in inorganic chemistry although this subject has been studied extensively [Sallam, et al. Ali, et al]. The chelating abilities and analytical and biological applications of these compounds have attracted remarkable attention [Ren, et al]. The complexes containing O, N donor atoms are very important owing to their significant antibacterial and anticancer activity [Amer,et al. Thakor, et al]. The Schiff base complexes have been used in catalytic reactions and as models for biological systems and also have been used as fine chemicals and medical substrates [Olie and Olive].

**2. Experimental**

2.1. Materials

All solvents and chemicals were reagent grade or better and used as received.

2.2. Physical Measurements

UV-vis spectra were taken on a JASCO 7850 spectrophotometer. The IR spectra (KBr disks) were obtained on a Shimadzu 470 spectrophotometer. $^{1}H$ NMR data from DMSO-$d_6$ solutions were obtained by using a Bruker DRX-500 MHz AVANCE spectrometer. Heraeus CHN-O-Rapid elemental analyzer performed the elemental analysis.

2.3. X-ray crystallography and structural solution

Single-crystal X-ray diffraction measurements were carried out with a Bruker Apex II diffractometer equipped with a graphite monochoromator for data collection at 293(2)K. The determination of unit cell dimensions and data collection was performed with (Mo kα) radiation (λ= 0.71073Å). Data reduction processing was carried out by the use of the program SAINT, which applied Lorentz and polarization correction to three-dimensionally integrated diffraction spots. The space group was confirmed by XPREP routine in SHELXTL97 program. The structure was solved by direct method using SHELEXS97. All non-hydrogen atoms were anisotropic and hydrogen atoms were isotropic. Further details of the structural analyses are given in Table **1**. selected bond lengths and angles are listed in Table **2**.

**3. Preparation of [Ni(HphpyF)$Cl_2$]**

To a flask charged with HphpyF (210 mg, 1.10 mmol) and $NiCl_2$ (129.59 mg, 1.00 mmol) was added 20 ml of THF. After stirring for 2 h the mixture was dark yellow. The solid was collected by filtration, and it was washed with 2 × 20 ml of THF. This was dried under vacuum for 1 h. Yield: 80%.

**4. Results and discussions**

Orang crystals of [Ni(HphpyF)$Cl_2$] were grown by slow diffusion of diethyl ether into a solution of the complex in EDC at room temperature. [Ni(PhpyF)$Cl_2$] complex is air-stable and can be readily recrystallized. The elemental analysis of the complex is consistent with $C_{12}H_{10}Cl_2NiN_3$ formula, as are the following X-ray structure and spectroscopic characterizations. Fig. 1 and Fig. 2 show the coordination geometry of the ligands about the Ni (II) and unit cell of [Ni (PhpyF)$Cl_2$], respectively. In the complex [Ni(HphpyF)$Cl_2$], the Ni(1) center chelated to HphpyF and $Cl^-$ ligands. The HphpyF ligands is coordinated to the Ni(1) through its nitrogen atoms. The coordination geometry around the

Ni(1) is a distorted tetrahedron, with bite angles of 94.64−114.30° for ligands. The bond lengths of Ni - N are: Ni - N(1) 1.983(5 ) and Ni -N(3) 1.967(5) Å. The Ni - N bond lengths in the title complex are slightly different from the corresponding lengths reported for [Ni(Hdpc)$_2$ ]. 3$H_2O$ [Ni-N = 1.966(3) Å],[ Uçar, et al] [Ni(dpc) ($H_2$ O)$_2$ ] [Ni-N = 1.903(3) Å], [Ranjbar, et al] [Ni(bta)$_3$ (dpc)] [Ni-N = 1.992(5) Å][ Ramadevi, et al] [bta: benzo-trizole], [Ni(cyclam)($H_2O$)$_2$ ][Ni(dpc)$_2$ ]. 2.5$H_2O$ [Ni-N = 1.931(3) Å] [Park, et al]. The bond lengths of Ni - Cl are 2.202(4)- 2.214 Å , which is longer than the bond lengths of Ni- N. The bond lengths of N(2)- C(5) and N(2)-C(6) are 1.391(4), 1.333(4) Å respectively, which strongly suggest the existence of a delocalized system. The N-C-N bond angles are for N(2)-C(6) -N(3) 125.72 and N(1)-C(5) -N(2) 120.00.

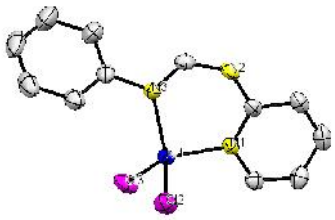

**Fig.1.** ORTEP of [Ni(HphpyF)$Cl_2$]

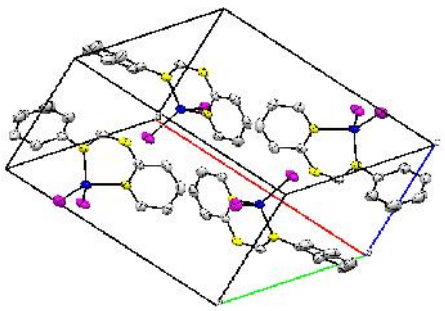

**Fig. 2.** Unit cell of [Ni(HphpyF)$Cl_2$]

**Table 1** Summary of crystal data and data collection parameters for [Ni(HphpyF)$Cl_2$]

| | |
|---|---|
| Empirical formula | $C_{12}H_{11}Cl_2NiN_3$ |
| Formula weight | 350.66 |
| Crystal system | monoclinic |
| Space group | *P* $2_1/c$ |
| *a* (Å) | 13.304(2) |
| *b* (Å) | 12.787(2) |
| *c* (Å) | 7.767(13) |
| α(°) | 90.00 |
| *β* (°) | 90.101(3) |
| Volume (Å$^3$) | 1318.15(4) |
| *Z* | 4 |
| Absorption Cofficient(mm$^{-1}$) | 0.436 |
| T (K) | 296(2) |
| $R_1$, $wR_2$ | 0.0360, 0.0934 |

| | |
|---|---|
| *R* indices (all data) | *R*2 =0.2016, wR2 = 0.1931 |
| Quality of fit [a] | 1.132 |

[a] Quality of fit = $[\sum[w(F^2_o - F^2_c)^2]/(N_{obs} - N_{params})$

**Table 2** Selected bond lengths (Å) and angles (°) for [Ni(HphpyF)$Cl_2$]

| Bond angles(°) | | Bond lengths(Å) | |
|---|---|---|---|
| N(1)-Ni(1)-N(3) | 94.6(1) | N(2)-C(5) | 1. 39(3) |
| N(1)- Ni(1)-Cl(3) | 108.02(8) | N(3)-C(6) | 1.35(2) |
| N(1)- Ni(1)-Cl(2) | 110.04(8) | N(1)- Ni(1) | 1.98(3) |
| N(3)- Ni(1)-Cl(2) | 116.62(8) | N(3)- Ni(1) | 1.96(3) |
| N(3)- Ni(1)-Cl(3) | 111.18(8) | Ni(1)-Cl(2) | 2.214(1) |
| Cl(2)- Ni(1)-Cl(3) | 114.30(3) | Ni(1)-Cl(3) | 2.201(9) |

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