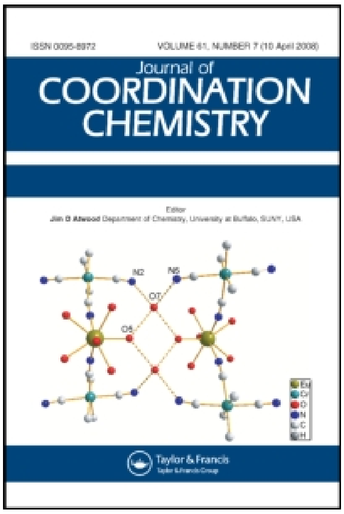

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Synthesis, characterization and crystal structure of a Ni(II) complex derived from heterocyclic acylpyrazolone

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Synthesis, characterization and crystal structure of a Ni(II) complex derived from heterocyclic acylpyrazolone

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A new complex, $[Ni(PMFP)_2(C_2H_5OH)_2]$ (HPMFP = 1-phenyl-3-methyl-4-(2-furoyl)-5-pyrazolone), has been synthesized and characterized by elemental analysis, IR, UV, and fluorescence spectra, thermal analysis, and X-ray single crystal diffraction. Its crystal structure is in an orthorhombic system, space group *Pbca* with cell parameters: $a = 15.2269(14)$ Å, $b = 9.3399(9)$ Å, $c = 22.794(2)$ Å, and $Z = 4$, $S = 1.019$. The Ni lies at an inversion center and has a slightly distorted octahedral coordination environment with four oxygens of the pyrazolone rings in the equatorial plane and two ethanols in axial positions. The compound displays O–H···N and weak C(6)–H(6)···O(4) hydrogen bonds. The fluorescent emission is at 539 nm.

Keywords: Acylpyrazolone; Complex; Crystal structure; Spectrum characterization

1. Introduction

Acylpyrazolones are β-diketones which exhibit keto-enol tautomerism [1] and can act as effective chelating and extracting reagents for many metal ions [2]. They play a key role in coordination chemistry [3] and are potential antifungal agrochemicals, antiviral, antipyretic analgesic, and anti-inflammatory in medicine [4, 5]. Furthermore, their metal complexes are used as NMR shift-reagents [6] and molecular precursors for supercritical fluid transport (SFT) CVD [7].

HPMFP is a 4-heterocyclic acylpyrazolone, previously reported [8–11], however, crystal structures and fluorescent properties have been limited. In this article, a complex of HPMFP with Ni(II) is synthesized and characterized by crystal structure and spectra (IR, UV, and fluorescence).

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2. Experimental

2.1. *Materials and physical measurements*

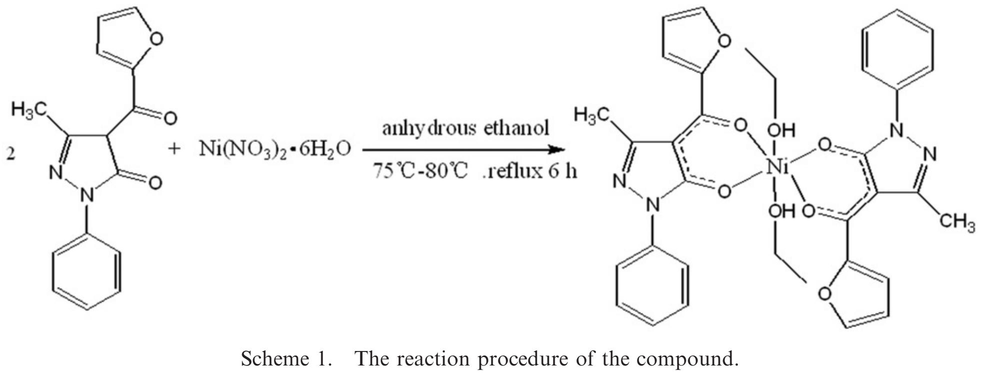
All reagents were obtained from commercial sources and used without purification. HPMFP was synthesized according to the method reported by Jensen [12] (yield: 73%, m.p.: 101–102°C). C, H and N analysis were carried out with a Thermo-Fiash EA1112 elemental analyzer. Infrared spectra were recorded using a Perkin–Elmer FTIR–1730 spectrophotometer (4000–400 cm^{-1}) with a crystalline sample in KBr pellets. Thermal analysis was performed on a Perkin–Elmer Diamond TG-DTA thermal analyzer. Fluorescence spectra were obtained with a Perkin Elmer LS55 luminescence spectrophotometer using a 150 W xenon lamp as excitation source. UV-Vis spectra were recorded on a Perkin Elmer LAMBDA45 spectrophotometer.

2.2. *Synthesis*

A mixture of a 10 mL HPMFP (2 mmol, 0.5365 g) anhydrous ethanol solution and 10 mL $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.2907 g) ethanol solution was refluxed for 6 h at 75–80°C; a green product which precipitated was filtered off, washed several times with anhydrous ethanol, and dried in air, yield: 70%. The green powder was recrystallized from ethanol and single crystals were obtained at room temperature after several days. The m.p.: 194.2–196.5°C. Calcd for $C_{34}H_{34}N_4O_8Ni$ (%): C, 59.59; H, 5.00; N, 8.18. Found: C, 59.75; H, 4.92; N, 8.05. The reaction procedure is shown in scheme 1.

2.3. *Crystal structure determination and refinement*

A crystal having approximate dimensions $0.22 \times 0.17 \times 0.09\ \mathrm{mm}^3$ was placed on a glass fiber and mounted on a Bruker SMART APEX CCD diffractometer. The data were collected with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensities were collected by the φ and ω scan technique. The structure was solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. The hydroxyl H was located in a difference Fourier map and refined as riding, with O–H distance



Scheme 1. The reaction procedure of the compound.

restraints of 0.85(1) Å and with $U_{iso}(H) = 1.5U_{eq}(O)$. Other hydrogen atoms were added at calculated positions and refined using a riding model. The structures were refined on F^2 using SHELXTL-97 [13]. The crystals used for diffraction showed no decomposition during data collection. The final R values (on F^2) were 0.0507 of the title compound. The parameters of the crystal data collection and refinement of the complex are given in table 1 and selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *IR spectra of the complex*

Infrared spectra of the title complex were compared with that of the ligand. A medium-intensity band at 3011 cm^{-1}, assigned to ν(OH) of β-diketones, is absent in the complex. A band at 1582 cm^{-1} in the free ligand from ν(C=O) of pyrazolone-ring shifts to 1566 cm^{-1} in the complex [14]. The absorbance at 779 cm^{-1} corresponds to phenyl characteristic absorption peak; 1013 cm^{-1} and 1227 cm^{-1} are assigned to ν(C–O–C) stretch. The band at 1462 cm^{-1} is assigned to ν(C=C=C) of pyrazolone. The weak band at 445 cm^{-1} is related to Ni–O stretch. From these observations, it is concluded that the enolic proton of ligand is replaced by Ni(II) in the complex.

Table 1. Crystal data and structure refinement for $[Ni(C_{15}H_{11}N_2O_3)_2(C_2H_5OH)_2]$.

CCDC No.	684921
Empirical formula	$C_{34}H_{34}N_4O_8Ni$
Formula weight	685.34
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, *Pbca*
Unit cell dimensions (Å, °)	
a	15.2269(14)
b	9.3399(9)
c	22.794(2)
α	90
β	90
γ	90
Volume (Å^3)	3241.7(5)
Z, Calcd density (mg m^{-3})	4, 1.404
Absorption coefficient (mm^{-1})	0.657
$F(000)$	1432.0
Crystal size (mm^3)	0.22 × 0.17 × 0.09
θ range for data collection (°)	2.68–28.34°
Limiting indices	$-15 \le h \le 20$, $-12 \le k \le 12$, $-28 \le l \le 30$
Reflections collected/unique	22027/4045 [$R_{(int)} = 0.0689$]
Completeness to $\theta = 28.34$	99.7%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4045/1/220
Goodness-of-fit on F^2	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0507$, $wR_2 = 0.1192$
R indices (all data)	$R_1 = 0.1023$, $wR_2 = 0.1416$
Largest difference peak and hole (eÅ^{-3})	0.457 and −0.276

Table 2. Selected bond lengths (Å) and angles (°).

Ni(1)–O(1)	1.990(2)	Ni(1)–O(2)	2.0359(19)
Ni(1)–O(4)	2.093(2)	C(10)–O(1)	1.264(3)
C(10)–N(1)	1.368(4)	N(1)–N(2)	1.394(3)
O(1#)–Ni(1)–O(1)	180.00(12)	O(4#)–Ni(1)–O(2#)	89.63(9)
O(2#)–Ni(1)–O(4)	90.37(9)	O(4)–Ni(1)–O(2)	89.63(9)
O(2)–Ni(1)–O(4#)	90.37(9)		

#1$-x$, $-y+1$, $-z+1$.

3.2. *Crystal structure of the complex*

The structure of the title compound is shown in figure 1. Coordination around Ni(II) is octahedral, coordinated by two oxygens of ethanol and four oxygens of two bidentate pyrazolonates. The Ni is located on an inversion center. Similar coordination is observed in other Cd [11], Zn [9, 15], and Co [16] complexes. The O(1A)–Ni(1)–O(1) angle is 180.00(12)°, while O(4A)–Ni(1)–O(2A), O(2A)–Ni(1)–O(4), O(4)–Ni(1)–O(2), and O(2)–Ni(1)–O(4A) angles are 89.63(9)°, 90.37(9)°, 89.63(9)°, and 90.37(9)°, respectively, adding to 360.00(36)°. We conclude that the coordination around the Ni is a slightly distorted octahedron.

The ligand is changed in $[Ni(C_{15}H_{11}N_2O_3)_2(C_2H_5OH)_2]$. The C(10)–O(1) bond length is 1.264(3) Å, shorter than 1.43 Å for a C–O single bond and longer than 1.22 Å for a C=O double bond. Moreover, the C(10)–N(1) bond length is close to the C=N double bond, confirming that the keto form of the ligand isomerizes to the enol form. The N(1)–N(2) bond length is 1.394(3) Å, shorter than 1.401 Å for the N(1)–N(2) bond length in the free ligand. These changes indicate a delocalized pyrazolone-ring, averaging the bond length.

The chelate ring, Ni(1)–O(1)–C(10)–C(9)–C(11)–O(2), has a boat configuration with Ni(1) and O(2) deviating from the plane by 0.184 Å and 0.228 Å, respectively. The pyrazolone ring C7–C9–C10–N1–N2 is originally planar with deviation less than 0.008 Å, which indicates that coordination does not influence conjugation. Furthermore, the slight deviation observed in the endocyclic angle is almost 4° compared with 108° in the orthopentatomic-ring. The dihedral angle formed by the chelate ring and the mean pyrazolone ring plane is 14.38°. Due to steric hindrance, dihedral angles of the pyrazolone ring plane with phenyl C(1)–C(2) and furan rings are 24.09° and 25.11°, respectively. As a result, the compound is not planar.

Crystal packing is illustrated in figure 2. The two Ni–O bond lengths in the equatorial plane differ by *ca* 0.103 Å (table 2) from O–H···N hydrogen bonds (table 3) involving the pyrazolonate nitrogens linking adjacent molecules to form chains in approximately orthogonal directions. The molecules are well ordered through two intermolecular hydrogen bonds, O(4)–H(18)···N(2) and weak C(6)–H(6)···O(4). The compound also has C(6)–H(6)···π interactions. The distance between H atom and the mean C(9)–C(10)–N(1)–N(2)–C(7) is 2.871 Å.

3.3. *Thermal decomposition process of the complex*

TG-DTA curves of the complex presented in "Supplementary material" show that there are three main stages in decomposition. The first from 113–172°C with mass loss 13.1% arise from loss of two ethanols (theoretical, 13.4%). The DTA curve shows an

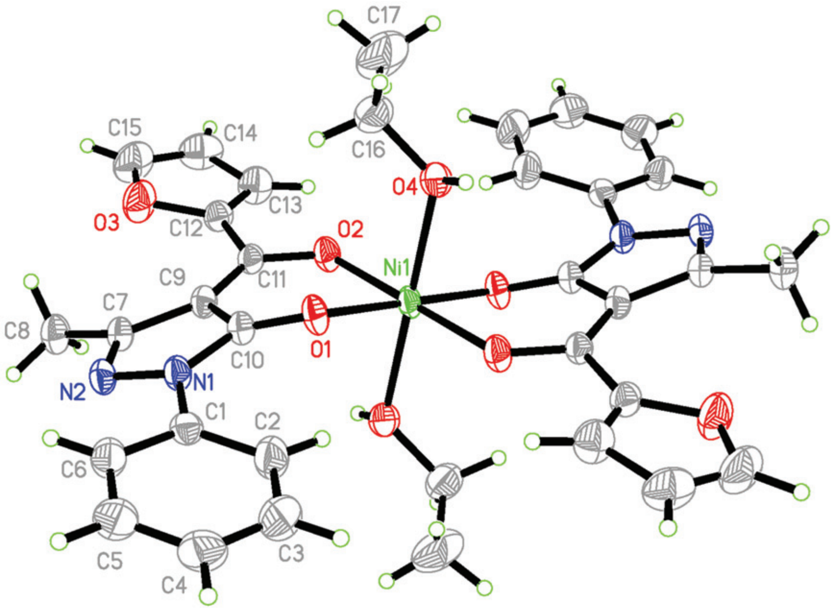


Figure 1. The molecule structure of the title complex (30% probability ellipsoids).

endothermic peak. The second decomposition from 172–324°C with a mass loss of 5.2% is close to the theoretical mass loss of two methyls (4.4%). The last step occurs in the range 324–513°C, accompanied by two exothermic peaks in the DTA curve from decomposition of acylpyrazolone. The final material is NiO (10.1%), corresponding to theoretical (10.9%) of NiO.

3.4. *Photochromism and fluorescent properties*

The complex changes to yellow under irradiation of 312 nm ultraviolet light indicating photochromic properties in the solid state.

All complexes were dissolved in anhydrous ethanol ($1 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) and surveyed from 200–700 nm at room temperature; the best excitation wavelength (λ_{ex}) and maximum emission bands (λ_{em}) are shown in "Supplementary material". On excitation at 408 nm, the complex gives an emission band at 454 nm assigned to intramolecular fluorescent emission. There is a slightly purple shift with respect to free HPMFP at 539 nm from coordination of Ni [17] affecting energy levels. The fluorescent emission of $[\mathrm{Ni(PMFP)_2(C_2H_5OH)_2}]$ suggests that it may be used as a luminescent material.

3.5. *Ultraviolet-Vis absorption spectra*

Ultraviolet-Vis absorption spectra (provided in Supplementary material) of ethanolic solutions were recorded in the wavelength range 190–900 nm and the values of $\lambda_{\max}$ (nm) and $\varepsilon_{\max}$ are given in table 4. The three absorptions of the complex at 205, 232, and 297 nm are assigned to π–π^* transitions of aryl ring, carbonyl, and n–π^* transition

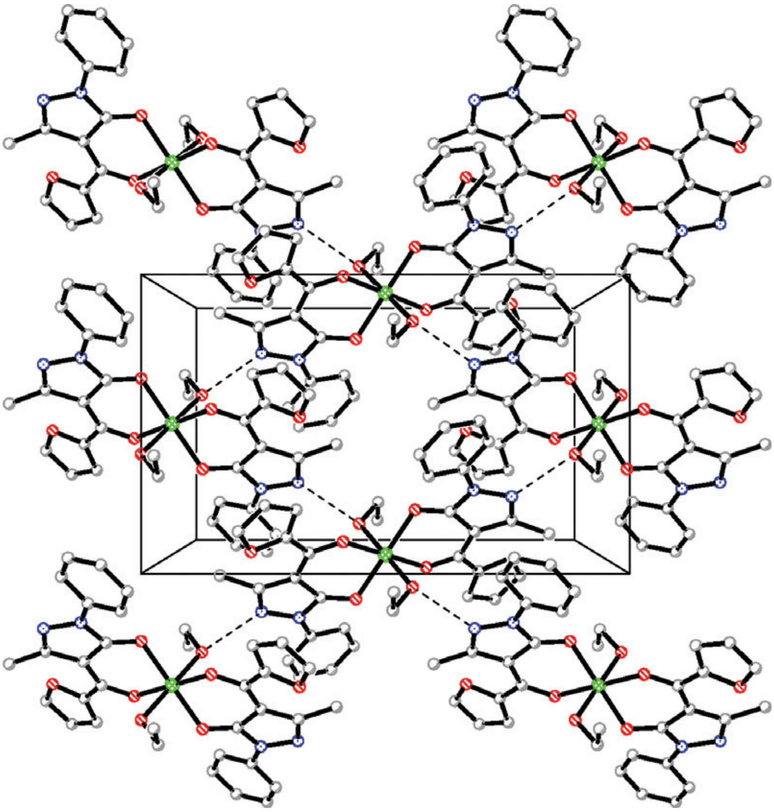


Figure 2. The crystal packing of the complex, viewed along the *c* axis. Hydrogen atoms have been omitted for clarity.

Table 3. Hydrogen bond geometry (Å).

D–H···A	D–H	H···A	D···A	D–H···A
O(4)–H(18)···N(2)#2	0.852(10)	1.91(2)	2.733(3)	162(6)
C(6)–H(6)···O(4)	0.93	2.52	3.3894	155

Note: Symmetry transformations used to generate equivalent atoms: #2 $-x+1/2$, $y+1/2$, z.

of carbonyl [18]. Compared with the electronic spectral data of the free ligand, the absorption peaks of emerge shifting bands. In the visible region, very weak absorptions near 684 and 741 nm for the Ni(II) complex are assigned as $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ d–d transitions [19], consistent with nickel in an octahedral environment.

4. Conclusions

A new 4-heterocyclic acylpyrazolone nickel(II) compound has been synthesized. The Ni lies at an inversion center with a slightly distorted octahedral

Table 4. UV-Vis spectral data in anhydrous ethanol.

Compound	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)	λ_5 (nm)
$[Ni(PMFP)_2(C_2H_5OH)_2]$	205(2.21)	232(1.26)	297(1.53)	684(0.19)	741(0.22)

coordination environment. Two intermolecular hydrogen bonds and C(6)–H(6)$\cdots\pi$ interactions provide further stability.

Supplementary material

CCDC-684921 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgments

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