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Syntheses and Structures of Schiff Base Condensed from PMBP with 1-Naphthylamine and Its Complexes

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Schiff base compounds are realatively easy to obtain and they frequently show high biological activities. Therefore, the studies of the Schiff bases and their metal complexes are the focus point of many research groups working in the fields of coordination chemistry, biomedicine and pharmaceutical chemistry [1].

4-Acyl-5-pyrazolones are enolizable β-diketones, which afford stable chelate complexes with several metals [2,3]. A number of compounds derived from 4-acyl-5-pyrazolones and aromatic amines have been synthesized by Wang *et al*. [4–6]. The Schiff base ligand (L) prepared by condensation of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) with 1-naphthylamine was used for the syntheses of the metal complexes. In this communication these structures are reported.

20 mL (0.01 mol) of 1-naphthylamine anhydrous ethanol solution was added into 20 mL (0.01 mol) of PMBP hot anhydrous ethanol solution. At 70~80°C stirring the solution for about 3~4 h, the yellow crude product was isolated when the solvent had been evaporated out (4-[(1-naphthylamino)phenylmethylene]-5-methyl-2-phenyl-2H-pyrazol-3(4H) one (L)). After washing with cold anhydrous ethanol solution several times, the material was dried in the vacuum desiccator over $CaCl_2$.

20 mL (0.01 mol) of $Cu(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_2 \cdot 6H_2O$ ethanol solutions were added into 20 mL (0.02 mol) of ligand ethanol solutions, respectively. After vigorously stirring for 6~8 h at 70~80°C, the products were precipitated, filtered and washed with cold anhydrous ethanol solution several times and dried in the vacuum desiccator over $CaCl_2$. The formula and physical properties of the ligand and its Cu(II), Co(II), Ni(II), Zn(II) and Fe(II) complexes are listed in Table 1.

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Table 1. The formula and physical properties of ligand and its complexes.

No.	Formula	Color	m.p. (°C)
L	$C_{27}H_{21}N_3O_1$	Yellow	175~176
$CuL_2 \cdot 2H_2O$	$[C_{27}H_{20}N_3O_1]_2Cu \cdot 2H_2O$	Dark brown	> 320
$CoL_2 \cdot 2H_2O$	$[C_{27}H_{19}N_3O_1]_2Co \cdot 2H_2O$	Dark green	> 320
$NiL_2 \cdot 2H_2O$	$[C_{27}H_{19}N_3O_1]_2Ni \cdot 2H_2O$	Blue-green	> 320
$ZnL_2 \cdot 2H_2O$	$[C_{27}H_{19}N_3O_1]_2Zn \cdot 2H_2O$	White	> 320
$FeL_2 \cdot 2H_2O$	$[C_{27}H_{19}N_3O_1]_2Fe \cdot 2H_2O$	Dark red	> 320

IR spectra in the region of 400~4000 cm^{-1} were determined with KBr pellets using AVATAR 360 (U.S.A) Infrared Spectrophotometer. The $\nu_{N\text{-}H}$ appearance in the ligand and disappearance in the complexes and broad $\nu_{O\text{-}H}$ band at 3364.7~3390.6 cm^{-1} in the complexes indicate that the N–H exists in the ligand and water molecules exist in the complexes. $\nu_{C=N}$ (ring) band appears at 1571.9 cm^{-1} in the ligand and change only slightly in the complexes ruling out the coordination through the nitrogen of the pyrazolinone ring. Absorption $\nu_{C=O}$, observed at 1637.0 cm^{-1} in PMBP, is shifted to 1624.0 cm^{-1} for the ligand, and to lower frequencies at 1587.9~1589.9 cm^{-1} in the complexes. New imine C=N absorption frequency is observed at 1506.3~1523.7 cm^{-1} in the complexes. These cases are in accordance with deprotonation of the ligand and involvement of carbonyls and imine nitrogen in bonding to metal in the complexes [7] (see Table 2).

Table 2. IR data of the ligand and its complexes (cm^{-1}).

No.	$\nu_{N\text{-}H}$	$\nu_{O\text{-}H}$	$\nu_{C=N}$ (ring)	$\nu_{C=O}$ (side)	$\nu_{C=N}$
PMBP			1589.2	1637.0	
L	3330		1571.9	1624.0	
$CuL_2 \cdot 2H_2O$		3390.6	1560.3	1589.9	1523.7
$CoL_2 \cdot 2H_2O$		3387.5	1554.5	1588.4	1516.3
$NiL_2 \cdot 2H_2O$		3384.8	1553.1	1588.6	1508.9
$ZnL_2 \cdot 2H_2O$		3364.7	1551.2	1587.9	1506.3
$FeL_2 \cdot 2H_2O$		3375.2	1556.3	1587.6	1518.6

UV spectra were collected on a SHIMADZU UV-2401 PC Spectrophotometer. Table 3 lists the UV data of the ligand and its complexes (95% ethanol solution). The K and B bands for $\pi \rightarrow \pi$ transitions, observed at 193.0 and 236.0 nm for PMBP, were shifted to 218.5 and 256.0 nm for the ligand and to 208.0~211.5 nm and 262.0~268.0 nm for these complexes, respectively. The R band for $n \rightarrow \pi$ transition, observed at 273.0 nm, was shifted to 305.5 nm for the ligand and to 281.5~296.5 nm for these complexes, respectively.

Table 3. UV data (nm) of the ligand and its complexes (95% ethanol solution).

No.	λ_{max} nm (ε)		
	K	B	R
PMBP	193.0 (0.416)	236.0 (0.793)	273.0 (0.845)
L	218.5 (1.775)	256.0 (0.760)	305.5 (0.611)
$CuL_2 \cdot 2H_2O$	209.5 (1.329)	263.0 (0.511)	296.0 (0.700)
$CoL_2 \cdot 2H_2O$	209.0 (1.834)	262.0 (0.570)	296.5 (0.723)
$NiL_2 \cdot 2H_2O$	211.5 (1.681)	262.5 (0.431)	281.5 (0.701)
$ZnL_2 \cdot 2H_2O$	210.0 (2.449)	268.0 (0.578)	282.5 (0.725)
$FeL_2 \cdot 2H_2O$	208.0 (1.916)	266.5 (0.566)	285.5 (0.715)

^{1}H-NMR spectra data were recorded on a VARIAN 300 NMR instrument in $CDCL_3$ solvent [300 Hz, δ, (ppm)] and are listed in Table 4. The resonance signals of –NH, $-CH_3$, $-C_6H_5$,$-N(C_6H_5)$ and $-N(C_{10}H_7)$ observed in the spectra of the ligand, and the signal of –NH disappeared and the signals of methyl, phenyl and naphthyl rings were shifted upfield upon coordination [8] in the spectra of complexes, suggesting that the donors coordinate the metal atom in the deprotonated form [9].

Table 4. ^{1}H-NMR data in $CDCl_3$ of the ligand and its complexes (δ).

No.	N-H	$-CH_3$	$-C_6H_5$	$-N(C_6H_5)$	$-N(C_{10}H_7)$
L	4.66–5.22	1.30–2.12	7.24–7.41	7.46–7.57	7.88–8.18
$CuL_2 \cdot 2H_2O$		1.08–2.00	7.18–7.33	7.29–7.46	7.72–8.04
$CoL_2 \cdot 2H_2O$		1.02–1.88	7.15–7.31	7.26–7.43	7.71–8.01
$NiL_2 \cdot 2H_2O$		1.06–1.92	7.19–7.33	7.21–7.39	7.74–8.06
$ZnL_2 \cdot 2H_2O$		1.04–1.94	7.11–7.29	7.29–7.45	7.76–8.09
$FeL_2 \cdot 2H_2O$		1.01–1.85	7.16–7.32	7.24–7.41	7.73–8.05

Results of IR, UV and ^{1}H-NMR indicate that the enamine-keto and Schiff base forms exist both in the ligand and its complexes. It is confirmed by the X-ray analysis of the ligand, though the single crystals of the complexes have not been obtained. The structures of the ligand and tentative model of metal bonding in the complexes are presented in Fig. 1.

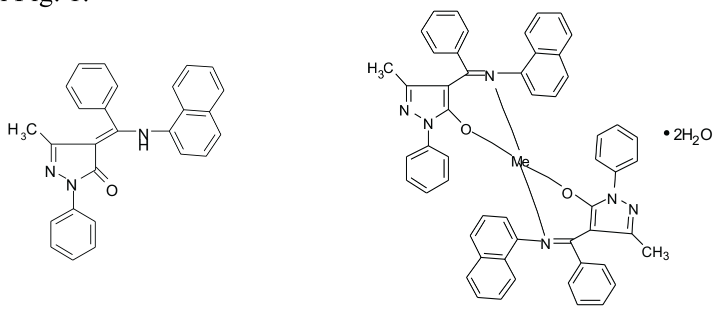

Figure 1. The structures of the ligand and tentative model of metal bonding in the complexes.

Yellow single crystal with dimensions of $0.20\times0.22\times0.25$ mm was selected for the X-ray analysis and mounted on a BRUKER SMART-1000 CCD diffractometer with a graphite monochromated MoKα radiation ($\lambda = 0.071073$ nm). A total of 3683 independent reflections were collected in the range of $2.10 \leq \theta \leq 25.02°$ by ω and ϕ scan technique at 293 K, in which 1943 reflections with $I \geq 2\sigma(I)$ were observed. The crystal data are as follows: monoclinic, $P2_1$, a = 1.0024(6), b = 1.8171 (11), c = 1.1982 (7) nm, $\beta = 106.682(11)°$, Z = 4, $D_{calc} = 1.282\ g\cdot cm^{-3}$, $\mu = 0.079\ mm^{-1}$, F(000) = 848, final $R_1 = 0.0532$ and $wR_2 = 0.1117$ ($w = 1/[\sigma^2(Fo^2) + (0.0442P)^2]$, where $P = (Fo^2 + 2Fc^2)/3$, S = 0.962. The maximum and minimum peaks in the final difference Fourier map were 144 and –136 $e\cdot nm^{-3}$, respectively. All calculations were performed on a PC computer using SHELXL-97 program [10] incorporated in WinGX system [11].

The structure was solved by Fourier methods. The remaining non-hydrogen atoms were located from the subsequent Fourier difference syntheses. The hydrogen atoms were located from the difference maps. During the final cycles of the refinements, anisotropic and isotropic thermal parameters were assigned to the non-hydrogen and hydrogen atoms in the structure, respectively. An ORTEP [12] view of the Schiff base compound and the numbering scheme are shown in Fig. 2. The selected bond lengths and bond angles are listed in Table 5.

In the molecule, atoms O1, C1, C2 and C5 of the PMBP moiety and atom N3 of the naphthylamine form a basal plane with the largest deviation being 0.0064(2) nm for atom C5. The dihedral angles between the basal plane with pyrazoline and phenyl (C11–C16) ring is 4.08° and 9.07°, respectively, close to the value of 5.05(3)° in 4-[(2-hydroxy-phenylamino)-phenyl-methylene]-5-methyl-2-phenyl-2*H*-pyrazol-3(4H)-one [13]. The bond lengths within this part of the molecule [O1–C1 = 0.1247(3), C1–C2 = 0.1436(3), C2–C5 = 0.1383(3) and C5–N3 = 0.1336(4) nm] lie between the classical single- and double-bond lengths. This case clearly indicates that a big electronic conjugated system exists in this moiety. But the dihedral angles between the basal plane with C21–C26 phenyl and naphthyl rings are 64.58 and 136.26°, respectively, due to the steric hindrance effects.

A strong intramolecular N3-H3---O1 hydrogen bond [N---O 0.269(3) nm and N-H---O 145(2)°] is observed, leading to an enamine-keto tautomerism. This case is similar to that in the compound such as 1,5-dimethyl-4-{[E-3-oxo-3-(2-thienyl)-1-(trifluoromethyl)-1-propenyl]amino}-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one [0.2702(4) nm and 139(2)°] [14]. The interesting intermolecular C-H---O hydrogen bonds of [C15...O1_$1 0.338(4) nm, C15-H15---O_$1 172(2)° (symmetry code $1, 1-x, -y, -z)] and [C33...N2_$2 0.345(4) nm, C33-H33--- N2_$2 140.9(18)° (symmetry code $2, 2-x, -y, -z)] , respectively, are found.

Small torsion angles of O1–C1–C2–C5 [–4.6(4)°] and O2–C7–C6–N3 [11.4(4)°] show that atoms O1 and N3 are in a *cis* conformation and they can become the coordination atoms as a didentate ligand, same case was observed in compound of N-(1,5-dihydro-1-phenyl-3-methyl-4-benzoyl)-3-chloroaniline [15].

Table 5. Selected bond lengths (nm) and angles (°) with estimated standard deviations.

O1–C1	0.1247(3)	N2–C3	0.1305(3)	C2–C5	0.1383(3)
N1–C1	0.1372(3)	N3–C5	0.1336(4)	C2–C5	0.1430(3)
N1–N2	0.1401(3)	N3–C31	0.1416(3)	C3–C4	0.1496(4)
N1–C11	0.1412(3)	C1–C2	0.1436(3)	C5–C21	0.1474(3)
C1–N1–N2	111.27(19)	O1–C1–C2	129.0(2)	N2–C3–C4	118.5(2)
C1–N1–C11	129.9(2)	N1–C1–C2	105.3(2)	C2–C3–C4	129.7(2)
N2–N1–C11	118.8(2)	C5–C2–C3	132.2(2)	N3–C5–C2	117.4(2)
C3–N2–N1	106.7(2)	C5–C2–C1	122.7(2)	N3–C5–C21	120.8(2)
C5–N3–C31	132.1(2)	C3–C2–C1	105.1(2)	C2–C5–C21	121.8(2)
O1–C1–N1	125.8(2)	N2–C3–C2	111.5(2)		

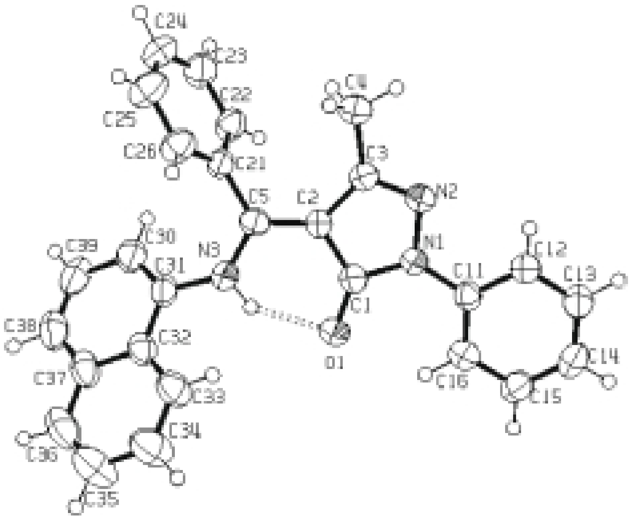

Figure 2. View of the title Schiff base compound (50% probability displacement ellipsoids).

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC - 204442. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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