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Synthesis and Spectroscopic Studies of Novel Transition Metal Complexes with 5-Phenyl-2-[2-Hydroxy pyridylacethydrazide]-1,3,4-Oxadiazole

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ABSTRACT

A new Schiff base 5-Phenyl-2-[2-hydroxy benzylhydrizido]-1,2,4-oxadiazole (HL) and its complexes with (Cr(III), Mn (II), Ni (II), Co(II) and Cu (II) were synthesized. The ligand was prepared in two steps, in the first step a solution of 2- mercapto -5-phenyl-1,3,4–oxadiazole in methanol reacts with 98% hydrated hydrazine under reflux to give an intermediate compound 2-hydrazion-5-phenyl-1,3,4-oxadiazole which reacts in the second step with o-hydroxybenzaldehyde to give the mentioned ligand (HL). The complexes were synthesized by addition the corresponding metal chloride solution to solution of ligand in methanol under reflux (1:2) metal to ligand ratio. On the basis of molar conductance, magnetic susceptibility, I.R, UV–visible spectra and elemental analysis (C.H.N) the complexes may be formulated as $[CrL_2(H_2O_2]Cl$ *and* $[ML_2]$*, where M: (Mn(II), Co(II), Ni(II) and Cu(II). The data suggested an octahedral geometry for Cr(III) complex and a square planar for Co(II), Ni(II) and Cu(II), while the Mn(II) complex was tetrahedral.*

Keywords: Novel transition, 1,3,4-oxadiazole, Metal complexes

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INTRODUCTION

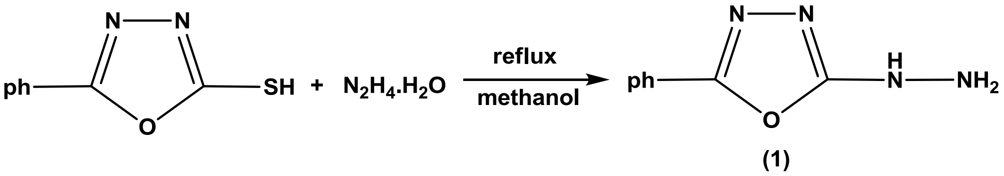
Transition metals play a central role in the construction of molecular materials, which display magnetic properties and find application and supra molecular chemistry and biochemistry [1-4]. Transition metal complexes of 1,3,4-oxadiazole derivatives are well known for their biological importance as well as their anticarcinogenic antibacterial and antifungal properties [5]. There are numerous M(II) complexes, which have been well characterized, providing a fertile set of model small molecule oxidant for inquiry. Cr(II), Mn (II) and V (IV) complexes with Schiff base of 1,3,4-oxadiazole ligands can increase the activity of insulin by binding to a small chromium, manganese and vanadyl binding protein [6] the amino group in Schiff bases can from stable complexes with transition metal ion Co (II), Ni(II) and Cu(II) when benzene ring carries an electron donating groups as CH_2OH,-OH in the ortho position. In this paper the synthesis and characterization of new ligand 5-phenyl-2-[2-pyridylacethydrizido]-1,3,4-oxadiazole and its complexes with Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) metal ions is reported.

MATERIALS AND INSTRUMENTATION

All chemicals used in the present investigation were of AR grade, purchased from Sigma chemical Co., USA. Elemental analysis (CHN) of these complexes was carried out on a Carlo-Erba 1106 Elemental Analyzer. Infra-red spectrophotometer, the electronic spectra of complexes solution in DMF were done on Variu-100C UV-Visible spectrophotometer. Magnetic susceptibility measurements were per formed on Gouy-Balance at 30°C using $CuSO_4.5H_2O$ as calibrant. Molar conductance was measured on ELICO conductivity bridge (Type CM82T).

Preparation of the Schiff base (HL)

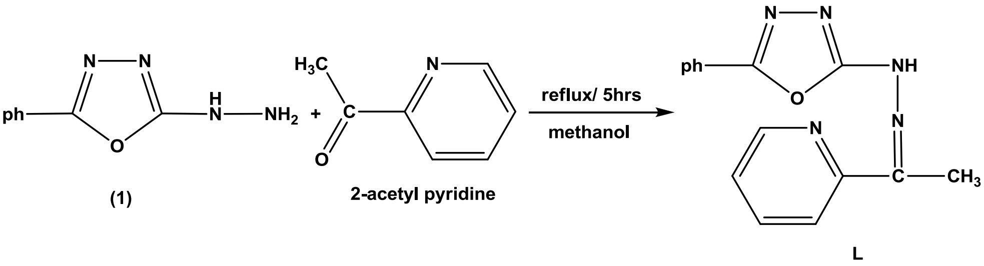
Preparation 2-hydrazion-5-phenyl-1,3,4-oxadiazole this derivative is prepared by the method reported earlier, this is shown in Scheme 1.



Scheme 1: Schiff base (HL)

Preparation of the ligand (L)

A solution of 2-hydrezion-5-phenyl-1,3,4-oxadiazole (1) 1.76 g (0.01 mol) in 35 ml methanol was added to a stirred solution of 2-acetyl pyridine 1.35 g (0.01 mol) in dry benzene (20 ml). The resultant solution was refluxed for about 5 h and then left undisturbed at room temperature. Upon standing pale yellow crystals of (L) formed over a period of 30 h. The crystals of the ligand were collected by filtration, washed with diethyl ether, toluene and dried in desiccator over $MgSO_4$ (Scheme 2).



Scheme 2: Preparation of ligand

Preparation of metal complexes

Absolution of $CrCl_3.6H_2O$, 0.267 g (1 mmol) in 20 ml ethanol was refluxed with an ethanolic solution of the Schiff base (L) 0.558 g (2 mmol) in 20 ml ethanol for 3 h. The solution was then reduced to on third on a water bath. The green solid complex precipitated was filtered washed thoroughly with ethanol and dried in vacuum. The Co(11), Ni(11), Mn(11) and Cu(11) complexes was prepared by the same procedure but in the ration of 1:1 for Mn(11) complexes and in presence of 5 ml of 5% aqueous sodium acetate solution (Scheme 3).

$$2L \quad + \quad CrCl_3 . H_2O \xrightarrow[EtOH]{reflux} [Cr(L)_2Cl_2]Cl \quad + \quad H_2O$$

$$2L \quad + \quad MCl_2 . H_2O \xrightarrow[\substack{CH_3CO_2Na \\ (5\%\ W/V)}]{reflux} [ML_2]Cl_2 \quad + \quad XH_2O$$

M = Co , Ni and Cu(II) , X = $6H_2O$ for Co(III) and Ni(II) , $2H_2O$ for Cu(II)

$$2L \quad + \quad MnCl_2 . 4H_2O \xrightarrow[\substack{CH_3CO_2Na \\ (5\%\ W/V)}]{reflux} [MnL_2Cl_2] \quad + \quad 4H_2O$$

Scheme 3: Preparation of metal chelates

Table 1: Elemental analysis and physical properties of the ligand (L) and its metal complexes

Compound	Formula	Colour/mp Co	M*%	C%	H%	N%
L	$C_{15}H_{13}N_5O$	Pale yellow 270-272^d	-	64.5 (64.21)	4.70 (4.11)	20.20 (24.81)
CrL	$[Cr(C_{30}H_{26}N_{10}O_2]Cl_2$	Deep green 315^d	7.45 (6.95)	50.13 (50.05)	3.62 (3.21)	19,40 (19.11)
MnL	$[Mn(C_{15}H_{13}N_5O]Cl_2.2H_2O$	Pink 318^d	13.58 (12.91)	44.44 (43.88)	3.20 (3.01)	17.2 (16.91)
CoL	$[Co(C_{30}H_{26}N_{10}O_2)]Cl_2$	Olive 360-362^d	8.30 (7.39)	52.47 (51.81)	3.90 (2.91)	20.4 (19.91)
NiL	$[Ni(C_{30}H_{26}N_{10}O_2)]Cl_2$	Orange 365^d	8.44 (8.21)	51.95 (50.91)	3.50 (2.81)	20.3 (19.51)
CuL	$[Cu(C_{30}H_{26}N_{10}O_2)]Cl_2$	Reddish brown 364-366^d	9.18 (9.00)	52.02 (51.11)	3.42 (2.66)	20.23 (20.00)

d: Decomposed, *The percentage of metal content in solid complex were carried via flame atomic absorption spectroscopy (F.A.A.S)

Table 2: FTIR spectral assignments of the ligand (L) and its complex (ν cm^{-1})

Ligand/Complex	νNH/ νOH	νC=N	νC-O	νC-H	νM-N/ νM-Cl
L	3310-3186 (br)	1635 (s)	1288 (s)	2985 2692^*	-
$[CrL_2Cl_2]cL$	3386 (br)	1612 (s)	1280 (s)	2939 2684^*	470-555(w) 354 (Cr-Cl)
$[MnLCl_2]$	3425^{**}(νNH/ νOH)	1620 (s)	1280 (s)	2985 2638^*	455-570 δO-H** 1519 (s) 295
$[CoL_2]Cl_2$	3348 (br)	1620 (s)	1280	2939 (m) 2677^*	470-555 (m)
$[NiL_2]Cl_2$	3180 (br)	1615 (s)	1280 (s)	2962 (m) 2710^*	480 (m)
$[CuL_2]Cl_2$	3250 (br)	1610 (s)	1275 (m)	2992-2890 (m) (2960-2710^*)	560 (m)

br: Broad, m: Medium, s: Strong, δO-H: Rocking of water molecules hydrated to Mn(II) complex, *Asymmetric vibration of C-H for pyridine ring. **Overlapping of O-H (H_2O) and (N-H) groups in Mn(II) complex

Table 3: Electronic spectral data, magnetic moment and molar conductance of the prepared metal chelates

Ligand/Complex	λ_{nm} (Σ*max) max	Assignment	μ_{eff}(B.M)	$\Lambda ohm^{-1}/cm^2$	Proposed geometry
L	203 254(7650)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
$[CrL_2Cl_2]cL$	297(13500) 407(120) 480(90)	MLCT $A_2g^4 \rightarrow T_2g^4$ $A_2g^4 \rightarrow T_1g^4$	3.21	102	Regular octahedral
$[MnLCl_2]$	372(20500) 881(88) 898(75)	LMCT $A_2^6 \rightarrow E^4(G)$ $A_2^6 \rightarrow T^4(G)$	5.40	15	Tetrahedral
$[CoL_2]Cl_2$	250 490(102) 498(18900)	LMCT $A_1g^1 \rightarrow B_1g^1$ INCT	1.80	142	Square plananr
$[NiL_2]Cl_2$	377(28750) 555(180)	$A_1g^1 \rightarrow A_2g^1$ $A_1g^1 \rightarrow B_2g^1$	0	162	Square plannar
$[CuL_2]Cl_2$	250(40000) 384(28500) 487(80)	C.T ($\pi \rightarrow \pi^*$) INCT $B_1g^2 \rightarrow A_1g^2$	1.42	133	Square plannar

*Extinction coefficient in M^{-1}. cm^{-1} units, INCT: Interchange transfer of the ligand, LMCT: Ligand to metal charge transfer and MLCT: Metal to ligand charge transfer

RESULTS AND DISCUSSION

Physical characteristic and micro analytical data of the complexes are given in Table 1. The analytical data of the complexes correspond to the suggested formula $[CrL_2Cl_2]$ Cl and $[ML_2]Cl_2$ M=Co(II), Ni(II) and Cu(II) and $[MnLCl_2].2H_2O$. The molar conductance measured in DMF of 10^{-3} M solutions of these complexes, indicates the electrolytic behavior in 1:2 ratio for Co(II), Ni(II) and Cu(II) complex, 1:1 for Cr(III) complex, while Mn(II) complex shows no appreciable electrolytic behavior (Tables 2 and 3) [7-11].

FTIR spectra

The important features for the shift base and its complexes may be summarized as follows: The broad band that appeared in the IR spectrum of the ligand (Figure 1), at 3310-3186 cm^{-1} is assigned to the stretching vibration of the intermolecular hydrogen bonded (N-H) in the molecule [12]. The ligand exhibits strong absorption at 1635 cm^{-1} which indicates the overlapping of new imino group (terminal) C=N with C=N of pyridine ring [13]. In all metal complexes, the azomethine group is shifted to lower frequency in the region 1600-1620 cm^{-1} which indicates that chelation takes place through nitrogen atoms of C=N of pyridine ring and acethydrizido (CH_3-C=N=N) [14]. The metal complexes show new bands in the region [15] 560-470 cm^{-1} which is due to the formation of M-N bond and (295-354) [15] cm^{-1} as week absorption due to Mn-Cl and Cr-Cl bonds (Figures 2 and 3).

Electronic absorption spectra

The electronic absorption of the Schiff base and its Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) complexes were recorded at room temperature using DMF as the solvent. The electronic spectrum of the free ligand in absolute ethanol shows two peaks at 49260 cm^{-1} and 38610 cm^{-1} which are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [16]. The Cr(III) complex solution exhibited a high intensity band at 33670 cm^{-1} in the UV-region, which is due to $\pi \rightarrow \pi^*$ transition associated with the azomethine linkage and ligand to metal charge transfer transition [17], as well as the spectrum of Cr(III) complex in the visible region at 24570 cm^{-1} and 20883 cm^{-1} referred to $A_2g^4 \rightarrow T_2g^4$ and $A_2g^4 \rightarrow T_1g^4$ transitions, this is well agree with electronic transitions of octahedral symmetry around Cr(III) ion [18]. The pink solution of Mn(II) complex in DMF shows absorption of low energy at 11350 cm^{-1} and 11248 cm^{-1} which are attributed to $A_2^6 \rightarrow E^4(G)$ and $A_2^6 \rightarrow T_1^4(G)$, this confirms the tetrahedral configuration around the Mn(II) ion [18], the Co(II) complex solution exhibits a two bands at 20408 cm^{-1} and 20,000 cm^{-1} referred to $A_1g^1 \rightarrow B_1g^1$ and inter charge transfer transitions of square planar Co(II) complexes. As well as the Ni(II) and Cu(II) complexes give ad-d transition of high intensity bands due to INCT and week intensity bands in the region 25000-20,000 cm^{-1} due to $A_1g^1 \rightarrow A_2g^1$ and $B_1g^2 \rightarrow A_1g^2$ for low spin square planar of d^{8+} and d^{9+} respectively [19].

Magnetic susceptibility measurement

The observed magnetic moment of Cr(III) complex was 3.21 BM [19]. This value suggested octahedral stereochemistry of the complex. The observed magnetic of Mn(II) complex was 5.40 BM, which investigates high spin tetrahedral stereochemistry of the complex. Cu(II) complex of the ligand (L) showed a magnetic moment of 1.42 BM which considerably lower than the spin only value of Cu(II) complex. The low value of the magnetic moment is attributed for spin-orbital contribution of d-p orbitals of this confirms the square planar geometry around Cu(II) ion [20]. Moreover, Co(II) complex observed magnetic moment lower than expected for d^7 low spin configuration which suggests square planar stereochemistry of Co(II) complex [21].

CONCLUSION

We have synthesized Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) complexes using Schiff base formed by the condensation of 5-phenyl-2-hydrazino-1,3,4-oxadiazole and 2-acetyl pyridine. The ligand 5-phenyl-2-[2-pyridylacetylhydrazido]-1,3,4-oxadiazole behaved as neutral bidentate reagent to establish six-coordinated Cr(III) complex, and four –coordinated Mn(II), Co(II), Ni(II) and Cu(II) complex.

According to the results obtained from elemental analysis, spectroscopic measurements and magnetic susceptibilities, the proposed structures of the prepared complexes were shown as follows:

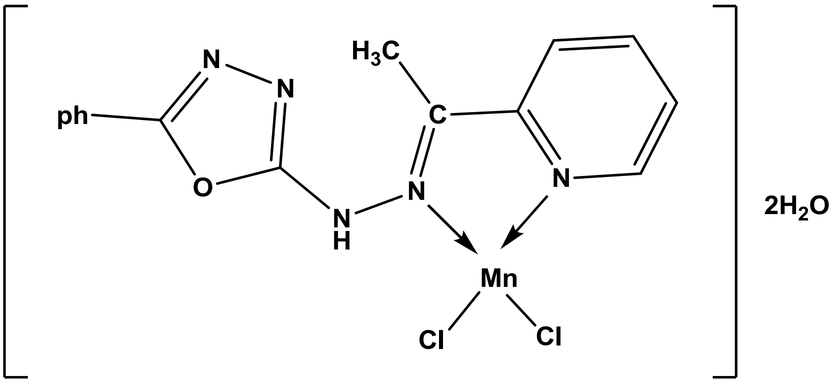


Figure 1: Suggested tetrahedral conifguration of Mn(II) complex

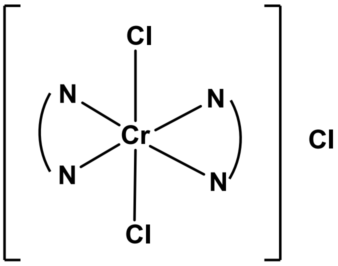
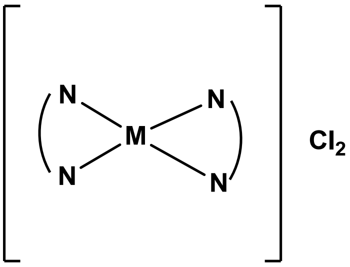


Figure 2: Suggested octahedral configuration of Cr(III) complex



M = Co(II) , Ni(II) and Cu(II)

Figure 3: Suggested square planar configuration of Co(II), Ni(II) and Cu(II) complexes

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