

Full Length Research Paper

Preparation, characterization and kinetic study of metal complexes derived from N₅ acyclic ligand

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The complexes of a new pentadentate acyclic ligand derived from 1,2-diamino benzene and 2,6-diacetylpyridine with vanadium(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) have been synthesized. Metal to ligand ratio in all complexes has been found to be 1:1. The polydentate ligand behaves as N₅ system upon linkage with Cr (III), Fe (III), Mn(II), Co(II), and Cu(II) ions. All the complexes have been assigned octahedral stereo chemistry, while VO (IV) complex was square pyramid. The thermodynamic parameters such as ΔG^* , ΔH^* and ΔS^* are calculated from the curve of $\log K_s$ verse temperature. It is found that Ni (II) and Cu (II) are the most stable complexes from the data of formation constant and Gibbs free energy.

Key words: Preparation, characterization, kinetic study, metal complexes, acyclic ligand.

INTRODUCTION

The coordination complexes of the Schiff bases have been widely investigated due to their manifestation of novel structural features, unusual magnetic properties and relevance to biological processes (Tuba et Al, 2011.), (Poonam et Al, 2010.), (Munde et Al, 2012). The coordination compounds pentadentate Schiff bases have been reported to act as inhibitors for enzymes (Popov et Al, 2007.). Considerable interest has been shown in the synthesis of transition metal complexes of pentadentate Schiff bases (Cerchiaro et Al, 2004.), (Tubas, 2003.). Pyran-2-one derivatives containing hydroxyl, acetyl and phenylazo substituents have been employed as complexing agents (Kalshetty et Al, 2011.), (Majia et Al, 2011.), (Marie et Al, 2009.), (Skoog, 1998.). Literature survey reveals that very little work, however, have been reported on conductimetric studies of macro cyclic metal complexes involving pyridine moiety (Skoog, 1998). In the present article we reported the preparation of a new pentadentate ligand (L) derived from 2,6-diacetylpyridine and 1,2-diamino benzene and its complexes with VO(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II).

Experimental

Physical measurements and analysis

Melting points were recorded on a Gallen Kamp melting point apparatus and were corrected. The FTIR spectra were recorded using FTIR – 8300 Shimadzu in the range (4000-400) cm⁻¹ and samples of metal complexes were measured as CsI – disc, while the free ligand was done in KBr – disk. The U.V- Visible spectra of compounds were recorded on Shimadzu model Spectrophotometer. Metal estimations were carried out spectrophotometrically using atomic absorption Shimadzu AA-670 spectrophotometer. Molar conductance of the solutions of the complexes in DMF (10⁻³M) were measured on PW9526 digital conductivity meter. The contents of metals in complexes (C₁- C₆) were estimated in Ibn-Cina center via a Shimadzu AA680 G atomic absorption spectrophotometer.

MATERIALS AND PREPARATIONS

2, 6-diacetylpyridine, starting material for synthesis of N₅ ligand (L) was purchased from Fluka Company. All the other chemicals used were of AR grade. The metal salt

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Table 1. Physical and analytical data for the ligand and their complexes.

Compound	Symbol	Color	Yield (%)	M.P. C°	%M*
Ligand	L	Yellow	88	133– 135	-
[VO (L)]SO ₄	C ₁	Olive	77	288 ^d	11.33 (10.00)
[Cr(L) Cl ₂]	C ₂	Pale green	76	300	12.01 (13.87)
[Fe(L) Cl ₂]Cl	C ₃	Brown	78	288 ^d	12.44 (13.00)
[Mn(L) Cl ₂]	C ₄	Cream	65	312 ^d	11.43 (12.00)
[Co(L) Cl ₂]	C ₅	Pale green	90	325 ^d	11.46 (13.08)
[Ni (L) Cl ₂]	C ₆	Deep green	88	297 ^d	11.95 (10.95)
[Cu(L) Cl ₂]	C ₇	Bluish green	96	355 ^d	12.63 (11.89)

d = decomposed ,*=analysis of metal content via flame atomic absorption

solutions were standardized by the recommended procedure(Khedr, 2005). The metal salt solutions were normalized by the recommended procedure(Vogel ,1961.) .Dilute solutions of the metal ions and ligand (N₅) under study of 2.5×10^{-6} M, 1×10^{-6} M, 2.5×10^{-5} M, 1×10^{-5} M and 1×10^{-4} M were prepared with accurate dilution.

Synthesis of the Schiff base (L)

A methanolic solution (I) (1.56gm, 0.01 mol in 25ml) was added to a methanolic solution of 1, 2-diamino benzene (0.523gm, 0.02mol in 10ml), the mixture was refluxed on a water-bath for 2hr. The excess of solvent was partially evaporated under vacuum and the separated yellow precipitate was filtered under reduced pressure, washed with ethanol and crystallized from ethanol. The compound was dried in vacuum at room temperature over silica gel .The physical properties of ligand shown in table (1).

Preparation of the complexes

The metal complexes were prepared by refluxing hot methanolic solutions of metal chloride (0.01 mol) [except in case of Fe (III) and VO (IV) complexes where DMF solutions were used] and the ligand (0.01mol) for 5hr, in a water bath. The complexes separated by adjusting the (pH=6-8) and filtered, washed with methanol, diethyether and then left overnight to obtain colored crystals of the metal complexes.

Study of complex formation in solution

The complexes of the ligand (L) with the selected metal ions [Cr(III), Fe(III),VO(IV),Mn(II), Co(II),Ni(II) and Cu(II)] were studied in solution using ethanol as solvent, in order to determine (M:L) ratio in the prepared complexes, following molar ratio method (Skoog, 1998.).Series of solutions were prepared having a constant concentration (C) 10^{-3} M of the hydrated metal chlorides or vandil sulfate VOSO₄.5H₂O, and the ligand (L) at deferent concentration 10^{-3} - 10^{-5} M.

The [M: L] ratio was determined from the relationship between the absorption of the absorbed light and the mole ratio of [M: L]. The result of complexes formation in solution were listed in Table.1

Stability constant of the complexes (K_s)

The stability constant of the (1:1) [M: L] complex, was evaluated using the following equation (Skoog, 1998.):

$$K_s = 1 - \alpha / \alpha^2 c \quad \text{---- (1)}$$

Where α is the degree of the dissociation of ionization of (C₁-C₇) was determined by the equation (2):

$$\alpha = (A_s - A_m) / A_m \quad \text{----(2)}$$

Or conduct metrically by the equation (3):

$$\alpha = \Lambda_m / \Lambda^{\circ} \quad \text{---- (3)}$$

Λ_m : molar conductance of the complex solution in 10^{-3} M (DMF).

Table 2. U.V.- visible , I.R. spectra and other physical properties of the prepared compounds.

Compound	Electronic absorption bands	IR frequency peaks(cm ⁻¹)	Assignment (stretching)	Λ_m Ohm ⁻¹ .cm ² . mol ⁻¹ (DMF)
L	293	1660,3400,1615	C = N,-C=C, NH ₂	-
VO(IV)	330,499,655	3380,1588, 400, 600,990	NH,C=N V-N,V=O	95
Cr(III)	220,285 541,392,278	3370,1578, 350,415,515	NH, C = N Cr – Cl,Cr – N Cr–O	189
Fe(III)	345,467,566	3225,1566,533,405	-NH ₂ ,C=N, Fe-N	80
Mn(II)	265,362,415	3400,1585, 400 ,470,410	NH,C = N Mn-Cl, Mn-N Mn-O	76
Co(II)	475,500	3360,1600 295,415,480	NH,C=N Co-Cl, Co-O Co-N	79
Ni(II)	306,540	3244,1564 450,543 3170,1580	NH ,C = N Ni – O , Ni – N NH ,C = N	101
Cu(II)	250,566	323 ,400, 490	Cu-Cl ,Cu-O , Cu-N	112

Table 3. Stability constants, and molar absorptivities of the complexes (C₁-C₇).

Complex	A _s	A _m	A	λ_{max}	K _s (L.mol ⁻¹)	ϵ_{max}
C ₁	0.44	0.23	0.321	381	4 x 10 ⁴	6000
C ₂	0.57	0.470	0.144	521	12 x 10 ⁵	321
C ₃	0.55	0.23	0.300	265	3.5 x 10 ⁴	8900
C ₄	0.46	0.321	0.378	560	9.11 x 10 ⁴	289
C ₅	0.32	0.44	0.560	475	9.8 x 10 ⁴	5422
C ₆	0.334	0.321	0.205	474	24.5 x 10 ⁶	800
C ₇	0.551	0.40	0.301	600	7.5x 10 ⁴	333

Where is A_s the average of three measurements of the absorption of solution containing a stoichiometric amount of ligand and metal ion

Λ_m : molar conductance in infinite dilution(Khedr et Al, 2005.), and C is the concentration of the complex. The absorbance of the solutions was measured at (λ_{max}) of the maximum absorption, furthermore the molar absorptivity) for the complexes was calculated from absorptivity $A_m = \epsilon_{max} \cdot b \cdot C$ ---- (4)

where A_m is the average of three measurements of the absorption containing the same amount of metal ion and fivefold excess of ligand and b is the depth of the quartz cell, usually equal to 1cm . Λ_m = molar conductance were measured in units of ohm⁻¹.cm².mol⁻¹.

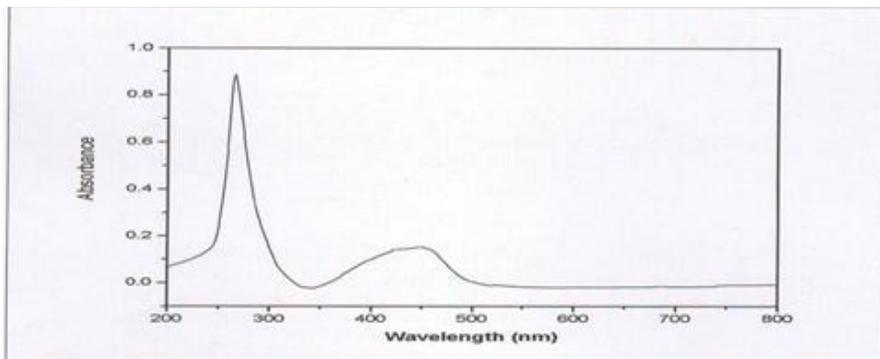


Figure 1. UV-Visible of ligand in methanol ($10^{-3}M$).

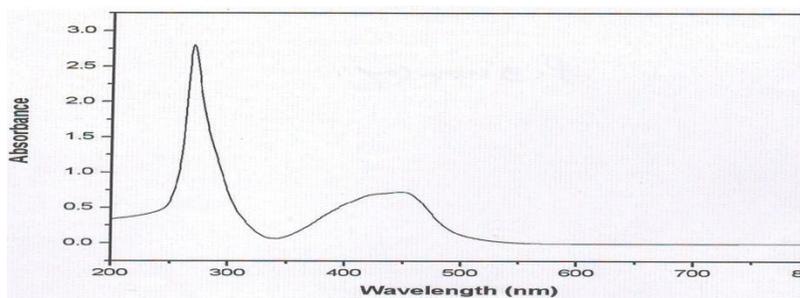


Figure 2. UV-Visible of Co(II) complex in DMF solution($10^{-3}M$).

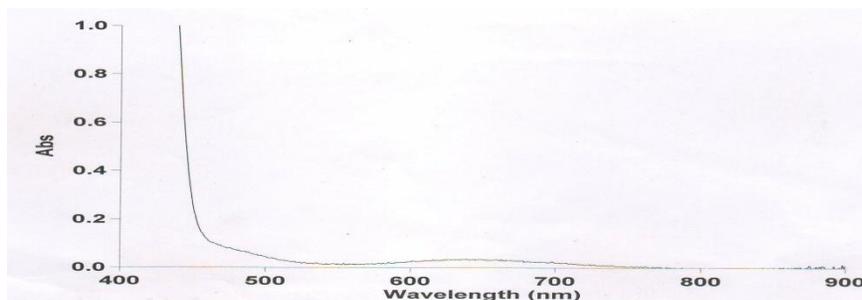


Figure 3. UV-Visible of Cu(II) complex in DMF solution($10^{-2}M$).

SD = standard deviation which is estimated after carrying out three data of experiments.

As evident in Table.3 that stability constant K_s for Ni (II) complex is (24.5×10^6), compared with Cr (III) complex (12×10^5) $L.mol^{-1}$ which investigates the presence of d^8 configuration and agrees with Irving Williamson(Cotton et Al, 1981.) .

A: molar absorptivity have been measured in $L^{-1}.mole^{-1}.cm$

B: formation constant of complexes were determined by spectroscopic method.

The stability constant (K_s) was evaluated using the following equations:

$$K_s = (1-\alpha)/\alpha^2c \quad \text{----(5)}$$

$$A = A_m - A_s / A_m \quad \text{---- (6)}$$

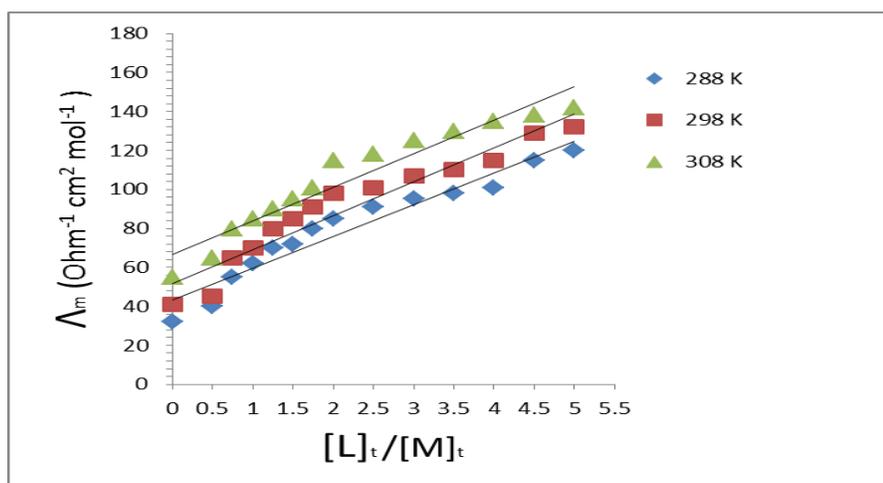
(α) Is the degree of the dissociation (c) is the concentration of the complex in (mole/L) units, (A_s and A_m) are the absorbance values of the solution were measured at (λ_{max}) of the maximum absorption.The molar absorptivity (ϵ_{max}) (eq.7) has been calculated using equation:

$$A = \epsilon_{max} . b.C \quad \text{---- (7)}$$

(A) Is the average of three measurements of the absorp-

Table 4. Thermodynamic parameters for metal complexes in DMF solutions.

complex	Λ_m $\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$	$-\Delta G^\ddagger_{C \pm SD}$ KJ/mole	$\Delta H^\ddagger_{C \pm SD}$ KJ/mole	$\Delta S^\ddagger_{C \pm SD}$ KJ/mole
Cr (III)	177	15.85 ± 2.80 (13.263)	-55.5 ± 6.4	-333 ± 18.9
VO(IV)	95	18.95 ± 0.44 (14.50)	23.66 ± 8.00	342.5 ± 30.1
Ni(II)	68	20.51 ± 0.56 ($25.3 \cdot 10^3$)	92.71 ± 7.8	671.5 ± 2.500

**Figure 4.** Molar conductance mole-ratio for Cu(II) complex in pure DMF at different temperature.

tion containing the same amount of metal ion and three fold excess of ligand, (b) is the depth of the quartz cell usually equal 1cm(Skoog, 1998.).

RESULTS AND DISCUSSION

The free pentadentate ligand (L) has been prepared by condensation reaction of two moles of dactyl pyridine and two moles of 2, 6-diamino propane. The ligand was stable in atmosphere, and insoluble in common organic solvents except DMF and DMSO.

Elemental analysis

The physical and analytical data of the pentadentate ligand (L) and its metal complexes are given in Table.1, which are in a satisfactory agreement with the calculated values. The suggested molecular formulas are supported by the subsequent spectral, and molar ratio, as well as magnetic moment and molar conductivity in 10^{-3}M solution of DMF. The values of Λ_m (table 2) show that C_1 and C_2 complexes are electrolytes in ratio 1:1, whereas

C_6 complex is conductive in 2:1(Geary, 1970.).

Infra- red spectra

Table.2, lists the most useful infrared assignments for those bands most diagnostic of the mode of coordination of ligand (L).The infrared spectra of all metal complexes a decrease in the frequency by $(15-20) \text{ cm}^{-1}$ on complication for $\nu(\text{C}=\text{N})$ and $\nu(\text{NH}_2)$ and are constant with coordination carbonyl oxygen and azomethan nitrogen atoms, moreover the presence of bands at range. $415 - 610$ and $395 - 415\text{cm}^{-1}$ are assigned to $\nu(\text{M}-\text{N})$ (Yamanaka et Al, 1975.), (Ain et Al, 1970.), and $\nu(\text{M}-\text{O})$ respectively. The infrared spectra of chloro complexes show one new band at $295 - 350\text{cm}^{-1}$ as assigned to $\nu(\text{M}-\text{Cl})$ of trans - isomer (Rama et Al, 1981.). A strong band in the VO (IV) complex was observed at 990cm^{-1} which is assigned to $\nu(\text{V}=\text{O})$ (Nakamoto , 1986.), (Pasto et Al, 1969.).

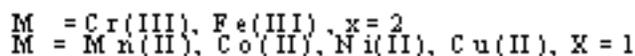
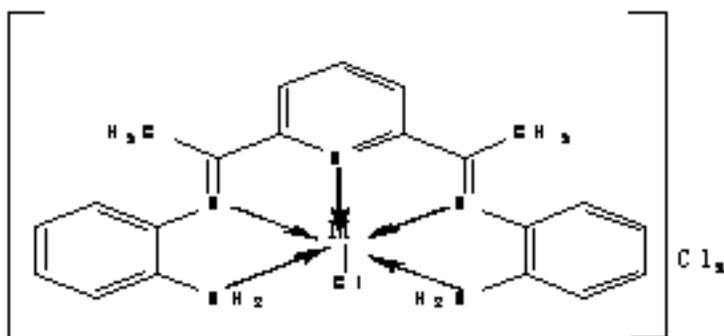
Electronic spectra and magnetic moment studies

The UV-Visible spectra of the ligand and their metal com-

Table 5. Parameters for evaluation of K_s of Cr^{III} , Co^{II} , Ni^{II} and Cu^{II} complexes.

Complex	A_s	A_m	A	K_s^b	ϵ_{max}^a	$\lambda_{\text{max}} \text{ nm}$
Cr(III)	1.4	1.22	0.044	$6.9 \cdot 10^5$	4590	380
Co(II)	2.11	0.77	0.06	$4.3 \cdot 10^5$	1450	395
Ni(II)	1.7	1.00	0.08	$5.71 \cdot 10^5$	3570	480
Cu(II)	2.01	1.05	0.045	$19.51 \cdot 10^5$	520	600

The vales of K_{eq} of the electrolytic complexes $\text{VO}(\text{IV})$, $\text{Cr}(\text{III})$ and $\text{Ni}(\text{II})$, were determined by using Ostwald dilution equation (Zahid et Al, 2006), (Pandeya et Al, 1983), after estimation the infinite conductance Λ° .

**Figure 5.** General structure of complexes (C₂-C₇).

plexes were recorded for their solutions in ethanol and DMSO as a solvents in the range (200 – 1000) nm Figures (1-3). In the case of all complexes, the assignments agree with the proposed stereo chemistry. The results shown in Table. 2, indicate that the molar ratio of (1:1) for complexes yielded high stability. Furthermore the molar absorptivities for all complexes is rather high, this probably was investigated on the presence of pentadental ligand of N₅ system which was stable kinetically due to the formation of Five-members ring with the central metal ion (Data et Al, 1993.), (Satish et Al, 2007.).

On the bases of magnetic data and spectral studies, $\text{VO}(\text{IV})$, $\text{Cr}(\text{III})$, $\text{Mn}(\text{II})$, $\text{Co}(\text{III})$, and $\text{Cu}(\text{II})$ complexes. According to previous above data have been assigned octahedral geometries (structures I and IV) while square – planer geometry is proposed for the $\text{Ni}(\text{II})$ complex (structure III) (Figgis, 1976).

Molar Conductance of complex

By using the relation $\Lambda_m = K/C$ the molar conductance of the complex (Λ_m) can be calculated where is the molar concentration of 10^{-3} molar of their solutions at $(25 \pm 2^\circ\text{C})$ were measured. it is calculated from the results that $\text{Cr}(\text{III})$

, $\text{V}(\text{IV})$, $\text{Ni}(\text{II})$ are electrolytes in 1:1 and 1:2 ratio respectively (Geary, 1970.). The thermodynamic of new metal complex have been measured Table.4, conductometrically that $\Delta G^\circ = -12500 \text{ KJ/mole}$ for $\text{V}(\text{IV})$ complex. In addition the stability constant of $\text{VO}(\text{IV})$ complex in DMF various temperature was obtained from variation of molar conduction as a function of ligand/metal cation mole ratios using a Gen plot computer program (Gen, 1989.). Table.5. Sufficiently, large value of ΔG° for $\text{VO}(\text{IV})$ complex showed that spontaneous formation of the complexes (Atalay, 2000.), (Kham, 2007.).

The thermodynamic parameters Table.4, Figure (4), free energy ΔG° , enthalpy change ΔH° and entropy change ΔS° were calculated by the following relationships : (Malovikova et Al, 1984.).

$$\Delta G^\circ = -RT \ln K_{\text{eq}} \quad \text{---- (8)}$$

And from changing the values K_{eq} with $1/T$

$$\left(\frac{d \log K_{\text{eq}}}{dt} \right) = \left(\frac{\Delta H^\circ}{2.303RT^2} \right) \quad \text{---- (9)}$$

The value of ΔH° were estimated. Finally ΔS° value was calculated from Gibbs equation: $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ --- (10)

General suggested stereo chemistry structures of complexes ($C_2 - C_7$)

According to the results obtained from the elemental and spectral analysis, the general structures of the above mentioned complexes are shown in Figure. 5.

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