



Metal chelates of bioinorganic and catalytic relevance, magnetic and spectral studies

Jasbeer Singh and Sahadev

Department of Chemistry, Govt. Raza P.G. College, Rampur U.P, India

ABSTRACT

The ligand *N*-(4'-butyrylidene-3-methyl-1-phenyl-2-pyrazolin-5-one)-*p*-anisidine was prepared and characterised by M.P., elemental analyses & spectral studies. The transition metal complexes of the ligand using Mn(III), Co(III), Ti(III), V(III), Ru(III), VO(IV) and MoO(V) were prepared and characterised using elemental analyses, molar conductance, magnetic moments, electronic, i.e. and MNR spectral studies.

Key words: Bioinorganic, pyrazolin, spectral studies.

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and their complexing ability containing different donor atoms is widely reported (1,2). The chemistry of transition metal complexes containing Schiff bases of pyrazolone moiety is of considerable interest on account of their interesting structural features and also because of biological importance (3,4). A literature survey revealed that of the selected metals complexes derived from 4-butyryl-3-methyl-1-phenyl-2-pyrazolin-5-one are not reported. In view of the above the selected ligand and its transition metal complexes have been prepared and characterised. The probable structures have also been proposed.

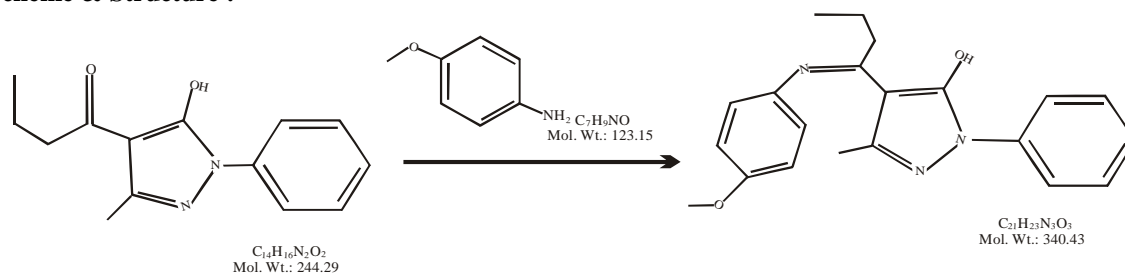
EXPERIMENTAL SECTION

All chemicals used were of AR grade (Alobrich, Lancaster, Sisco and E. merck). The Ligands as well as metal complexes were analysed by standard methods. Conductivity measurements were carried out on philips conductivity Bridge Model PR9500 using 10^{-3} M DMF solution. The IR spectra were recorded on perpin-Elmer spectro meter using KBr pelets. Electronic spectra were recorded on Beckman DU-2-spectrometer in the range of $750-350\text{ cm}^{-1}$, magnetic-susceptibility was measured on Gouy balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a calibrant. The analytical data, colour magnetic moment and important IR spectral bonds were recorded in KBr phase.

Preparation of the Ligand :

N-(4'-butyrylidene-3-methyl-1-phenyl-2 pyrazolin-5 -one)-*p*-anisidine :

Scheme & Structure :



PROCEDURE :

Ethanol solution of 4-butyryl-3-methyl-1-phenyl-2-pyrazoline-5-one (0.005 mol, 1.22g and p-anisidine (0.005 mol, 0.66g) were refluxed for 5 hrs. and then cooled it and charged 1N HCl solution 100 ml and extracted with ethyl acetate (100 ml), recovered that organic layer at 40°C under reduced pressure and washed with ethanol-water mixture (1:9) and dried under high vacuum for 4 hrs.

Sl. No.	Molecular formula weight	Colour	M.P. °C	Elemental Analyses			IR Spectra		
				C	H	N	ν (C=N)	ν (OH)	ν N ₂ (ring)
1.	(C ₂₁ H ₂₃ N ₃ O ₂)	Yellow	95	72.00 (72.30)	6.55 (6.59)	12.00 (12.03)	1624	3480	1585 cm ⁻¹

Preparation of Metal Complexes :

The solution of the respective metal salt and the ligand (1:2) in ethanol were allowed to react. The precipitate formed was filtered, washed and dried. The metals used were Mn (III), Co (III), Ti (III), V (III), Ru (III), VO (IV) & MoO(V).

RESULTS AND DISCUSSION

All the complexes are coloured and decompose at very high temperature. The elemental analyses of these metal complexes suggest 1:2 (M:L) stoichiometry. The solid complexes were found to be insoluble in water and common organic solvents but soluble in DMF and DMSO. The value of molar conductance in DMF at 25°C and 10⁻³M dilution suggested 1:1 electrolytic nature for all the synthesised complexes except that VO(IV), which is a non-electrolyte (Values are given in the table-1

Table-1 Elemental Analyses & Some Physical Props. of Complexes

Sl No	Compounds	Colour	M.P. °C	Elemental analyses					Magnetic Moment (B.M.)	Molar Conductance ohm ⁻¹ cm ² mole ⁻¹ DMF
				% C	% H	% N	% M	% Cl		
1.	[Mn(C ₂₁ H ₂₃ N ₃ O ₂) ₂ .2H ₂ O] Cl Mol.wt. = 824.5	Brown	275	60.96 (61.16)	5.96 (6.06)	9.98 (10.19)	6.46 (6.67)	4.06 (4.24)	4.96	70 (1:1 electrolyte)
2.	[Co(C ₂₁ H ₂₃ N ₃ O ₂) ₂ .2H ₂ O] Cl Mol.wt. = 828.5	Greenish	278	60.78 (60.86)	5.98 (6.03)	10.00 (10.14)	7.06 (7.12)	4.18 (4.22)	Dia magnetic	75 (1:1 electrolyte)
3.	[Ti(C ₂₁ H ₂₃ N ₃ O ₂) ₂ .2H ₂ O] Cl Mol.wt. = 813.5	Yellow	273	61.80 (61.99)	6.09 (6.15)	10.19 (10.33)	5.86 (5.90)	4.28 (4.30)	1.70	65 (1:1 electrolyte)
4.	[V(C ₂₁ H ₂₃ N ₃ O ₂) ₂ .2H ₂ O] Cl Mol.wt. = 816.5	Light Yellow	274	61.71 (61.76)	6.10 (6.12)	10.19 (10.29)	6.20 (6.25)	4.19 (4.28)	2.94	70 (1:1 electrolyte)
5.	[MoO(C ₂₁ H ₂₃ N ₃ O ₂) ₂ .H ₂ O] Cl Mol.wt. = 859.5	Light Yellow	310	58.60 (58.67)	5.56 (5.58)	9.72 (9.77)	11.09 (11.17)	4.00 (4.07)	1.78	75 (1:1 electrolyte)
6.	[Ru(C ₂₁ H ₂₃ N ₃ O ₂) ₂ .2H ₂ O] Cl Mol.wt. = 586.5	Green	315	58.00 (58.06)	5.74 (5.76)	9.62 (9.67)	11.59 (11.63)	4.00 (4.03)	1.88	70 (1:1 electrolyte)
7.	[VO(C ₂₁ H ₂₃ N ₃ O) ₂ .H ₂ O]	Greenish Yellow	276	64.48 (64.53)	6.00 (6.14)	10.69 (10.75)	6.50 (6.53)	-	1.76	Non-electrolyte

Cacl'd. Values are given in brackets.

The value of magnetic moment of the complex calculated from observed value of the magnetic susceptibility has been found to be 4.96 B.M. corresponding to four unpaired electrons and high spin state of the metal complex. This value also suggests the absence of any kind of exchange interaction (5) and octahedral geometry around Mn (III) ion in the complex.

The electronic spectrum of Mn (III) complex showed an intense and sharp charge transfer band at 20480 and a spin allowed d-d transition band ⁵E_g⁵T_{2g} at 18540 cm⁻¹. This broad band occurring at lower frequency with increased intensity indicates the lowering of symmetry from octahedral configuration. The electronic spectra of the complex shows an intense charge transfer band at 27000 cm⁻¹. Since the Mn (III) ion is easily reducible charge transfer will be from the ligand to the metal corresponding to $\pi\tau_2$ transition (6).

The study of magnetic properties suggested diamagnetic nature for the complex, as expected for a low spin d⁶ ion. The electronic spectrum of the chelate displays bands at 15110, 21095 and 23370 cm⁻¹ assignable to ¹A_{1g} → ³T_{2g},

${}^1A_{1g} \longrightarrow {}^1T_{1g}$ and ${}^1A_{1g} \longrightarrow {}^1T_{2g}$ transitions respectively. These are similar to those reported for other six coordinated low spin cobalt (III) complexes (7).

The spin only value of magnetic moment of the complex has been found to be 1.70 B.M. which is slightly lower than the calculated value for d^1 system ($\mu=1.73$ B.M.) like Ti(III). The value suggested paramagnetic nature for the adduct. The value also indicated that Ti(III), which is very sensitive to oxidation, has not been oxidized to Ti(IV) during or after complexation.

The observed value of the effective magnetic moment of the complex is 2.94 B.M. This is very close to the calculated value of magnetic moment for two unpaired electrons expected for V(III) (d^2) system. The value also suggested paramagnetic nature and octahedral geometry for the complex. The electronic spectrum of the complex exhibits band at 17500 cm^{-1} with a shoulder at $21,300\text{ cm}^{-1}$. The low energy band has been assigned to ${}^2A_{1g} \longrightarrow {}^3T_{2g}$ while the high energy band may be due to ${}^2A_{1g} \longrightarrow {}^3T_{1g}$ (P) transition. These bands are characteristic of octahedral geometry.(8) This is also similar to bands reported for other octahedral V(III) complex.

The electronic spectrum of the complex suggested that the complex may be considered as octahedral with a strong tetragonal distortion resulting from Mo=O band. The spectrum exhibits three distinct absorption bands in the ligand field region. The low intensity band at 13550 cm^{-1} in the long wavelength region, is possibly due to first crystal field transition ${}^2B^2E$ (d_{xy}, d_{xz}, d_{yz}). The second transition at 19300 cm^{-1} is assignable to ${}^2B^2B_1$ ($d_{xy}, d_{x^2-y^2}$). The third peak at 29700 cm^{-1} may be due to ${}^2B_2 \longrightarrow {}^2A_1$ ($d_{xy} \longrightarrow dz^2$)(9).

The μ_{eff} for this complex was found to be 1.88 B.M. as expected for an octahedral Ru(III) complex with t_{2g}^5 configuration. This value shows paramagnetic character of the complex. Its electronic spectrum in CHCl_3 displayed bands at $17700, 21300, 27800$ and 33800 cm^{-1} , which may be assigned to ${}^1A_{2g} \longrightarrow {}^4T_{1g}, {}^2A_{2g} \longrightarrow {}^4T_{2g}, {}^2A_{2g} \longrightarrow {}^2A_{2g}, {}^2A_{1g}$ and charge transfer respectively. These are similar to those reported for other octahedral Ru (III) complexes(10).

The observed magnetic moment of the VO (IV) complex is 1.76 B.M., which indicated its paramagnetic nature. The electronic spectrum of the complex exhibits three bands at $10870, 19420$ and 26110 cm^{-1} assignable to $d_{xy} (b_2) \longrightarrow d_{xz} (e^*), d_{xy} (b_2) \longrightarrow dx^2y^2 (b)$ and $d_{xy} (b_2) \longrightarrow dz^2 (a_1^*)$ transitions respectively for octahedral stereochemistry.

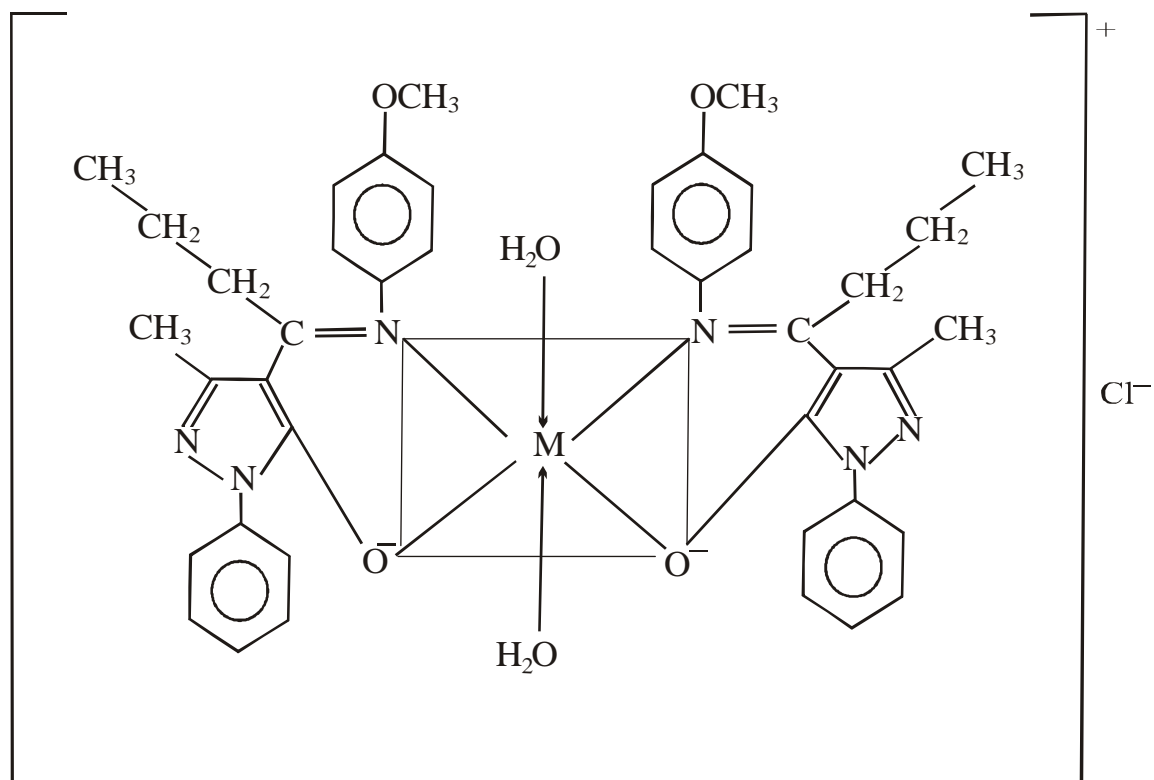
INFRA RED SPECTRA :

The IR spectra reveal that the pyrazolone based Schiff bases used in the present study can exist in keto and enol forms. All the Schiff base ligands under study exhibit a medium broad band (except the ligands (III), which exhibit two bands at 3480 and 3300 cm^{-1}) with fine structure in the region $3500-3150\text{ cm}^{-1}$. This suggests the involvement of 5-OH group of the pyrazolone moiety in the intramolecular or intermolecular hydrogen bonding with the lone pair of nitrogen. This also suggests the existence of the Schiff bases ligands in the enol form in the solid state. Thus, the ligands I, II and III contains four potential donor sites: (i) the ring nitrogen N_1 , (ii) the ring nitrogen N_2 (iii) the enolic oxygen and (iv) the azomethine nitrogen, while the Schiff base IV possess eight potential donor sites; (i) the two ring nitrogens N_1 , (ii) the two ring nitrogens N_2 , (iii) the two enolic oxygens and (iv) the two azomethine nitrogens.

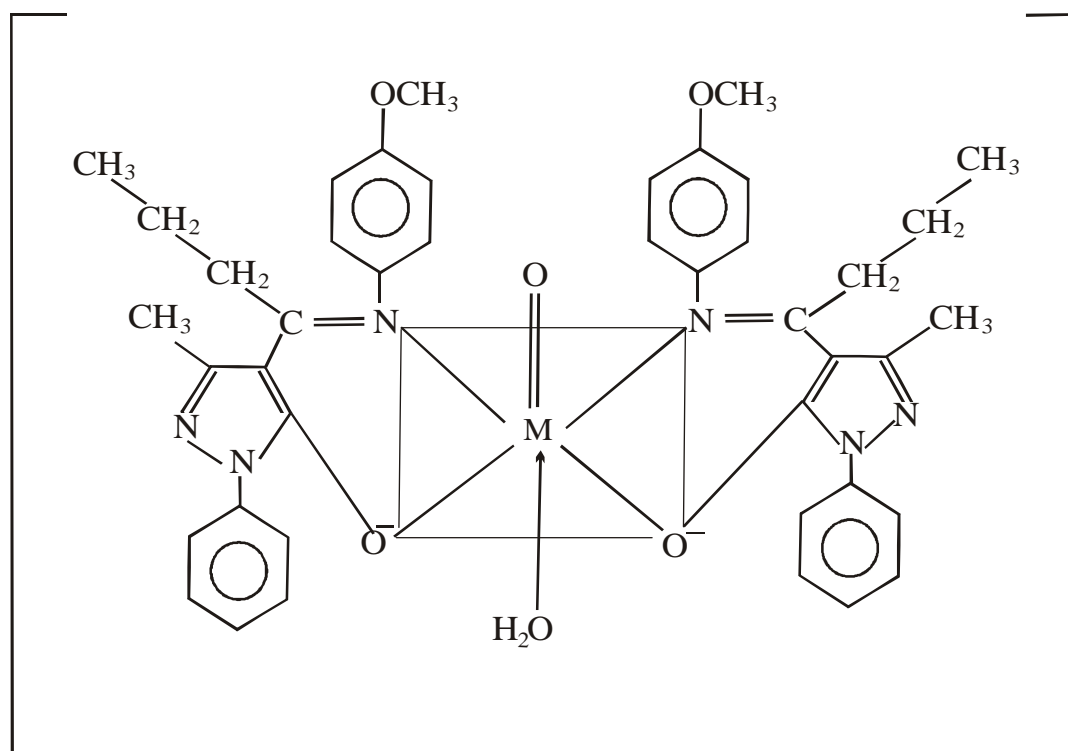
In the Schiff base ligands coordination of ring nitrogen N_1 is unfavourable due to the presence of bulky phenyl group attached to it. The ring nitrogen N_2 in these Schiff base ligand is found to be inert towards coordination as revealed by the unaltered positions of the $\nu(\text{C}=\text{N}_2)$ (1584 cm^{-1}) mode of the respective ligand after complexation. In fact, $\nu(\text{C}=\text{N}_2)$ mode of the free ligand appears to be merged with $\nu(\text{C}=\text{N})$ (azomethine) mode of respective complexes. The ligand show a strong band due to $\nu(\text{C}=\text{N})$ of the azomethine group at 1624 cm^{-1} . The observed low energy shift of this mode at $1610-1605\text{ cm}^{-1}$ in the complexes suggests coordination of azomethine nitrogen. The significant absorption band due to coordinated enolic oxygen the ligand is $\nu(\text{C}-\text{O})$. This band is observed at $1231-1250\text{ cm}^{-1}$ in these complexes. The overall infrared spectral results show that the ligand under discussion be have as monobasic bidentate manner (3).

The IR spectra of the VO(IV) complex shows an additional band due to VO(IV) band at 955 cm^{-1} assignable to $\nu\text{V}=\text{O}$ moiety. The MoO(V) complex also show an additional band at 995 cm^{-1} due to $\nu\text{Mo}=\text{O}$ moiety.

All the complexes contain water molecules. Their coordinated nature is suggested by the IR bands in region of $3480-3510\text{ cm}^{-1}$ due to $\nu\text{O}-\text{H}$, wagging modes in the region of $840-855\text{ cm}^{-1}$ and rocking modes in the region of $735-755\text{ cm}^{-1}$. The TGA curves show the loss of water molecules above 150°C .



M= Mn(III), Co(III), Ti(III), V(III) or Ru (III)



M= VO (IV) or MoO (V)

CONCLUSION

On the basis of studies performed and discussed octahedral geometry has been proposed for all the prepared complexes.

REFERENCES

- [1] Kajdan T.N., Squattrito P.J., & Dubey S. N., *Bull Chem. Acta*, 300, 1082 (2000).
- [2] Vinod K Sharma & Shipra Srivastava, *Indian Journal of Chemistry*, 45A, pp. 1368-74 (2006).
- [3] Rahul K Rastogi & S. Ahmad, *Indian Journal of Applied Research*, 4, pp. 3-5 (2014).
- [4] R.C. Maurya, B. Hukla & T. Singh, A. Padey, *Indian Journal of Chemistry*, 41A, pp. 554-59 (2002).
- [5] R.C. Maurya, H. Singh, A.Padey & T.Singh, *Indian Journal of Chemistry*, 40A, pp. 1053-63 (2001).
- [6] Ruchi Agrawal, Mohd. Asif Khan & Shamim Ahmad, *Indian Journal of Applied Research*, 4, pp. 62-665 (2014).
- [7] Ledon H, Bonnet M & Lallemand J Y *J Chem. Soc Chem. Commun*, 702 (1979).
- [8] S.R. Aswale, P.R.Mandlik, S.S.Aswale, A.S.Aswale, *Indian Journal of Chemistry*, 42A, pp. 322-26 (2003).
- [9] Alok K. Parekh Josheph, P.E. and Daya S.Seth, *Oriental Journal of Chemistry*, 26(3), pp. 1195-97 (2010).
- [10] Raj D S, Shah Pe, Shah J R, *Sejnth react inorg met org Chem*, 22,321(1992).
- [11] Kamalender Dey and Kartick Chakrabarty, *Indian Journal of Chemistry*, 38A, pp. 381-84(1999).
- [12] A.K.Singh, B.K.Puri and R.K.rowlley, *Indian Journal of Chemistry*, 28A, pp. 59-62 (1989).