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Structural Studies of Vanadyl(II), Cobalt(II) and Nickel(II) Complexes of Schiff Bases

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The bidentate ligand complexes of VO(II), Co(II) and Ni(II) using Schiff bases have been prepared by refluxing—precipitation method at optimum pH. The compositions of these complexes were determined by elemental analysis. The magnetic measurements, electronic absorption data were used to provide an information about the bonding of metal ion with oxygen and nitrogen atom of the ligand while the magnetic data were in accordance with octahedral geometry for all these complexes.

INTRODUCTION

Schiff bases have been extensively used as analytical reagents[1, 2] and found to exhibit physiological activity. It is also found as a plant growth regulant and as an anti-coagulant[3, 4]. Because of such important commercial, medicinal and synthetic applications a wide variety of Schiff bases and their metal derivatives provide an interesting research problem. In the past, researchers have synthesised and characterised many transition metal complexes of Schiff bases. The present paper deals with the synthesis and structural diagnosis of VO(II), Co(II) and Ni(II) complexes derived from Schiff bases TIHT, PIHNT, PIHT and TIHNT, where

TIHT = 2′-Thiophenyl imino-3-hydroxo toluene.
PIHNT= Phenyl imino-2-hydroxo-5-nitro toluene.
PIHT = Phenyl imino-3-hydroxo toluene.
TIHNT= 2′-Thiophenyl-1-imino-2-hydroxo-5-nitro toluene.

EXPERIMENTAL

The Schiff's bases TIHT, PIHNT, PIHT and TIHNT were prepared by the method reported in literature[5]. The ligands were synthesised by mixing equimolar quantities of respective aldehydes in dry ethanol *viz.* 3-hydroxy benzaldehyde or 5-nitro salicylaldehyde with amines in dry ethanol namely aniline or *o*-amino thiophenol and stirred vigorously for 10 min. This reaction mixture was refluxed on water bath for 4–5 h. The Schiff base PIHNT separated on cooling while in the case of TINT and PIHT the solvent was evaporated to its half volume till the solution became thick and viscous, then it was poured on ice-cold water. After 24 h, the solid Schiff base was obtained. Similarly, in the case of TIHNT, the solvent was evaporated to more than half the volume and cooled. A solid precipitated out. The Schiff bases were recrystallised from dry ethanol. Eventually a crystalline product of each Schiff base was obtained. The Schiff bases TIHT (m.p. = 91°C), PIHNT (m.p. = 134°C), PIHT (m.p. = 104°C), and TIHNT (m.p. = 162°C) were yellow, brown and green in colour respectively..

The metal chelates were prepared by refluxing the aqueous-ethanolic solution of the respective metal(II) sulphates (1 mg/mL) and the ligand (10% ethanolic), for 2–3 h on water bath. The pH of the resulting solution was adjusted to optimum pH 7.0 by dropwise addition of dilute NaOH solution. The precipitated complexes were filtered, washed repeatedly with ethanol and dried in vacuum.

The Schiff bases and their metal complexes were characterised by elemental analysis and iso-thermal heating. The metal contents of Co(II) and Ni(II) in their respective complexes were determined by titration with 0.01 M EDTA[6], while vanadium in its complexes was determined[7] by redox titration with 0.01 N $KMnO_4$. The magnetic and spectral investigations were made as reported in the literature[8]. The molar conductance values of the complexes were measured in nitrobenzene (10^{-3} M), using Toshniwal conductometer. These findings of the complexes are tabulated in Table-1.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF METAL COMPLEXES

Complexes/ Colour	Analysis % Found (Calcd.)			μ_{eff} at 300 K (B.M.)	Molar conductance mhos cm^2 mole^{-1}
	N	S	M		
VO(TIHT)$_2$	5.09	13.11	9.89	1.45	11.130
(green)	(5.52)	(12.63)	(10.03)		
VO(PIHNT)$_2$	10.34	—	9.86	1.15	9.414
(green)	(10.50)	—	(9.55)		
VO(PIHT)$_2$	5.94	—	12.14	1.23	8.417
(green)	(6.32)	—	(11.49)		
VO(TIHNT)$_2$	9.78	10.56	8.34	1.46	10.749
(green)	(9.38)	(10.73)	(8.52)		
Co(TIHT)$_2$	4.88	11.98	11.15	4.97	6.129
(brown)	(5.43)	(12.44)	(11.43)		
Co(PIHNT)$_2$	10.69	—	11.12	4.82	6.758
(brown)	(10.35)	—	(10.88)		
Co(PIHT)$_2$	6.48	—	12.89	4.61	7.325
(brown)	(6.21)	—	(13.05)		
Co(TIHNT)$_2$	9.20	10.49	9.21	4.87	6.014
(brown)	(9.25)	(10.59)	(9.73)		
Ni(TIHT)$_2$	5.61	12.53	11.91	3.36	3.829
(green)	(5.44)	(12.44)	(11.39)		
Ni(PIHNT)$_2$	10.69	—	10.26	3.51	5.110
(brown)	(10.35)	—	(10.84)		
NI(PTIHT)$_2$	6.15	—	12.87	3.45	4.912
(green)	(6.21)	—	(13.01)		
Ni(TIHNT)$_2$	9.38	10.44	9.58	3.89	5.913
(brown)	(9.25)	(10.59)	(9.40)		

RESULTS AND DISCUSSION

All the complexes behave as non-electrolytes[9] (λ m = 3×10^{-7} to 12×10^{-7} mho cm^2 mole^{-1}). Elemental analysis confirms the monomeric nature of the metal complexes. The isothermal heating experiments indicate that all the complexes are precipitated without any co-ordinated water.

The weakening of ν(OH) phenolic (which occurs at 3400 cm^{-1} in the spectra of ligand) in the spectra of all the complexes suggests the cleavage of intramolecular hydrogen bonding[10] of OH due to coordination of phenolic oxygen to the metal ion with deprotonation of phenolic group. This is further confirmed[11] by an upward shift of ν(C—O) (phenolic) in the region 1190–1130 cm^{-1} in the complexes. The ν(C═N) (azomethine) band occurs in the region 1645–1580 cm^{-1} in the complexes indicating coordination of metal with azomethine nitrogen atom[12–15]. This is further supported by the appearance of ν(M—N) (664 to 615 cm^{-1}), ν(M—O) (600 to 500 cm^{-1}) bands in the spectra of all the complexes. The characteristic ν(V═O) band was pointed at 940 cm^{-1}. The ν(V═O) frequencies are normal[16] for five co-ordinate VO^{2+} complexes and are not affected by the ring substituents. The thiophenolic 'SH' donor group does not participate in the complexation as the peaks due to the 'SH' stretching vibrations do not change its positions in the complexes as well as in the ligand.

The room temperature (300 K) magnetic moment (μ_{eff}) for VO(II), Co(II) and Ni(II) are tabulated in Table-1. The magnetic moments for vanadyl complexes in the solid state fall in the range 1.15–1.46 B.M. which is close to the spin only value expected for oxovanadium complexes with normal magnetic properties[17] It is seen from magnetic susceptibility of cobalt complexes that they are paramagnetic in nature. The Co(TIHT)$_2$, Co(PIHNT)$_2$, Co(PIHT)$_2$ and Co(TIHNT)$_2$ complexes show normal magnetic susceptibility in the range 4.61–4.97 B.M. at room temperature, suggesting[18] octahedral geometry. The magnetic moment study at room temperature of Ni(II) complexes derived from TIHT, PIHNT, PIHT and TIHNT shows susceptibilities in between 3.36–3.89 B.M. It is reported that the octahedral complexes of Ni(II) exhibit magnetic moment in the range 3.08 to 3.45 B.M.[19, 20]

All the electronic spectra for VO(II), Co(II) and Ni(II) were carried out in spectroscopic grade DMSO.

The electronic absorpotion spectra of Co(II) complexes exhibit three bands which are assigned[19] to d-d transition:

$$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)\ 10{,}440\text{–}10{,}200\ \text{cm}^{-1}$$

$$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)\ 18{,}600\text{–}18{,}000\ \text{cm}^{-1}$$

and

$$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)\ 25{,}650\text{–}19{,}230\ \text{cm}^{-1}.$$

The charge transfer transition is assigned to band pointed 10,440–10,220 cm^{-1}.

Nickel(II) complexes exhibit three d-d transition bands in the reflectance mode which are assigned to

$^3A_{2g} \rightarrow {}^3T_{2g}(F)(\nu_1)$ 12,190 cm^{-1},

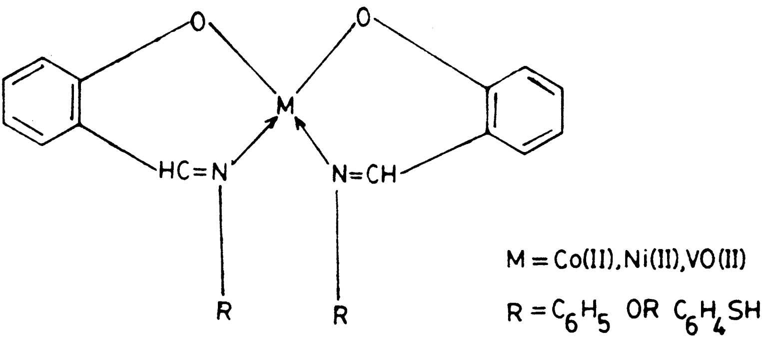
$^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ 17,240 cm^{-1}

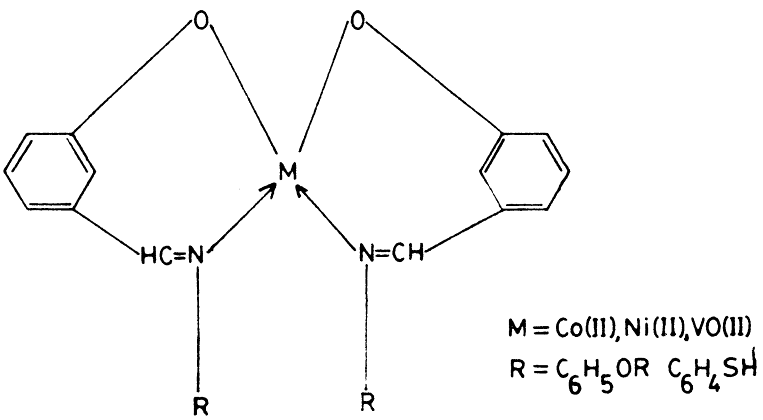
and $^3A_{2g} \rightarrow {}^3T_{2g}(P)(\nu_3)$ 24,390 cm^{-1}.

The absorption spectra in DMSO of the some complexes reproduce these bands around 12,000 cm^{-1} (ν_1), 16,500 cm^{-1} (ν_2) and 26,300 cm^{-1} (ν_3) which proves that the solvent does not interfere in the structural moiety, *i.e.*, the phenomenon of solvolysis is absent. The values of ν_1, ν_2 and ν_3 are very well in accordance with the values obtained for octahedral Ni(II) complexes[21, 22].

The electronic absorption spectra of all VO(II) complexes exhibit bands at 11,620, 17,240 and 24,390 cm^{-1} which are assigned to $d_{xy} \rightarrow d_{yz}$, $d_{xy} \rightarrow d_{y^2-x^2}$, $d_{xy} \rightarrow d_{z^2}$ respectively. These values are in close resemblance with the value given by Vanquickenborne and McGlynn[22, 23].

On the basis of foregoing studies the following structures are suggested for these complexes.





REFERENCES

1. T.R. Seashadri and Vardarajan, *Proc. Indian Acad. Sci.*, **35A**, 75 (1952).
2. P. Singh, R.L. Goel and B.P. Singh, *J. Indian Chem. Soc.*, **52**, 958 (1975).
3. R.B. Arora and G.N. Malhar, *Brit. J. Pharmaco.*, **20**, 39 (1963).
4. C.R. Hamcock, H.B. Barloq and H.J. Lacey, *J. Eseplt. Bolt.*, **12**, 401 (1981).
5. E.M. Kathal, "Studies on Co(II), Ni(II) and Zn(II) complexes of Schiff bases", Ph.D. Thesis, University of Bombay (1989).
6. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 1st edition, Longman Green, London (1978).
7. Wilfred W. Scott, in N. Howell Furman (Ed.), Standard Method of Chemical Analysis, 5th Edition, D. Van Nostrand Company Inc., Vol. 1, pp. 1037–1038 (1939).
8. A.A. Gupte, V.V. Dixit and B.H. Mehta, *J. Univ. of Bom.*, **53**, 102 (1984).
9. W.J. Geary, *Coord. Chem. Rev.*, **81** (1971).
10. A.K. Rama and J.R. Shah, *J. Indian Chem. Soc.*, **58**, 1100 (1981).
11. N.S. Biradar, V.B. Mahale and B.R. Havinale, *J. Indian Chem. Soc.*, **46**, 6 (1976).
12. J. Csaazar and L. Kiss, *Acta Chim. Acad. Sci. Hung.*, **78**, 73 (1973).
13. K. Burger, Coordination Chemistry Experimental, 1st Edition, Butterworths, London, p. 73 (1973).
14. V.B. Rodrigues and B.H. Mehta, *Nat. Acad. Sci. Letters (India)*, **13**, 337 (1990).
15. E.M. Kathal and B.H. Mehta, *Nat. Acad. Sci. Letters (India)*, **14**, 17 (1991).
16. J. Selbin, L.H. Holmes and S.P. McGlynn, *J. Inorg. Nucl. Chem.*, **25**, 1359 (1963).
17. J. Selbin, *Coord. Chem. Rev.*, **I**, 293 (1966).
18. B.N. Figgis and Lewis, Progressive Inorganic Chemistry, First Edition, Interscience, New York (1964).
19. G. Narain, P.R. Shukla, V.K. Singh and A.M. Jaiswal, *J. Indian Chem. Soc.*, **60**, 321 (1983).
20. S.M. Mahapatra, B.B. Mahapatra and S.K. Pujar, *J. Indian Chem. Soc.*, **59**, 988 (1982).
21. K.K. Narang and R.A. Lal, *Curr. Sci. (India)*, **47**, 793 (1978).
22. K.K. Rey and S.K. Sen, *J. Indian Chem. Soc.*, **52**, 261 (1975).
23. L.G. Vanquickenborne and S.P. McGlynn, *Theort. Chim. Acta*, **9**, 390 (1968).

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