

Synthesis and Spectroscopic Investigation of Metal Chelates of Hydrazo Pyrazolone Derivative

M. ALAUDEEN[†], P.G. SUSHAMMA and A. MARY DOROTHY*

Department of Chemistry, Government College for Women, Trivandrum-695 004, India

E-mail: marytsn@rediffmail.com

A new series of Co(III) and Ni(II) complexes of N-(3-methyl-1-thiocarbamoyl-5-oxo-2-pyrazoline-4-ylene)-N'-(2'-hydroxyphenyl)hydrazine were synthesized. Metal chelates were characterized by elemental analysis, IR and electronic spectral data, molar conductance and magnetic moment measurements. In all the metal complexes the ligand acts as monoanionic tridentate. On the basis of physico-chemical studies, Ni(II) complexes have assigned tetrahedral structure while octahedral stereochemistry is assigned to Co(III) chelates.

Key Words: Ni(II), Co(III), *o*-Amino phenol, Pyrazolone derivative, Hydrazone.

INTRODUCTION

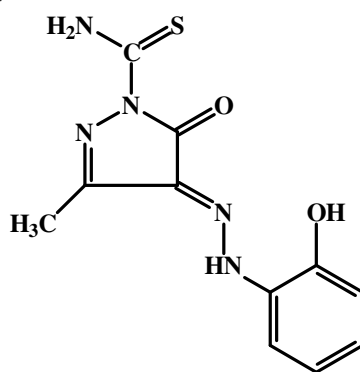
Chemistry of hydrazones especially those of heterocyclic compounds and their metal chelates are of current interest owing to the diverse applications in various fields such as antioxidants, polymerization inhibitors, stabilizers, as well as fungicides and pesticides¹⁻⁴. The hydrazone described in the present investigation is obtained by the coupling of the diazotized *o*-amino phenol with reactive methylene group of 3-methyl-1-thiocarbamoyl-2-pyrazoline-5-one (MTP). The product obtained was N-(3-methyl-1-thiocarbamoyl-5-oxo-2-pyrazoline-4-ylene)-N'-(2'-hydroxyphenyl)hydrazine (H₂PTP). Ni(II) and Co(III) complexes of the ligand H₂PTP were synthesized and characterized by analytical and physico-chemical studies.

EXPERIMENTAL

All the reagents used are of AR grade. Pentamine carbonato Co(III)-nitrate used for the preparation of Co(III) complexes was synthesized by reported method⁵.

[†]Department of Chemistry, University College, Trivandrum-695 034, India.

Synthesis of H₂PTP: The ligand N-(3-methyl-1-thiocarbamoyl-5-oxo-2-pyrazoline-4-ylene)-N'-(2'-hydroxyphenyl)hydrazine (H₂PTP) (**I**) was synthesized by diazotising 5.5 g (0.05 mol) *o*-amino phenol and coupling the diazotized compound with 3-methyl-1-thiocarbamoyl-2-pyrazoline-5-one. Brownish yellow crystals obtained were suction filtered, washed and recrystallized using ethanol and characterized on the basis of analytical and spectral data.



Structure of N-(3-methyl-1-thiocarbamoyl-5-oxo-2-pyrazoline-4-ylene)-N'-(2'-hydroxyphenyl)hydrazine (H₂PTP) (**I**)

Synthesis of complexes: Ni(II) complexes were synthesized by refluxing aqueous ethanolic solution of the ligand in 1:2 molar ratios for *ca.* 3 h. Solid complexes formed on slow evaporation of the solution were filtered and washed with benzene and dried over P₄O₁₀ under vacuum. Complexes of Co(III) were synthesized⁵ by adding ethanolic solutions of pentaminecarbonato Co(III) nitrate in small portion to an ethanolic solution of the ligand, refluxed and concentrated. The brown crystals of the complexes were suction filtered, washed with methanol and dried over vacuum. Complexes with counter anions chloride, bromide, acetate and perchlorate were synthesized by adding a saturated solution of the appropriate salt (KCl, KBr, NaOAc and NaClO₄) to the refluxing mixture of pentamine carbonate Co(II)nitrate and the ligand.

RESULTS AND DISCUSSION

The analytical data of the synthesized complexes is given in Table-1. The molar conductance values measured for both Ni(II) and Co(III) complexes were very low corresponding to non-electrolytes (Table-1). Room temperature magnetic moment measurement show that Co(III) complexes are diamagnetic. Ni(II) complex exhibited values from 3.72 to 3.85 BM which fall in the range of tetrahedral geometry (Table-1).

TABLE-1
ANALYTICAL DATA AND OTHER DETAILS OF Co(III) AND Ni(II) CHELATES OF H₂PTP

Complexes	Yield (%)	Analysis (%) Found (Calcd.)					Molar conductance ohm ⁻¹ cm ² mol ⁻¹	μ_{eff} (B.M.)
		M	C	H	N	S		
[Co(HPTP)(H ₂ O)Cl ₂]	81	13.85 (13.89)	31.10 (31.14)	2.85 (2.83)	16.50 (16.51)	7.50 (7.55)	8.30	Diamagnetic
[Co(HPTP)(H ₂ O)Br ₂]	78	11.45 (11.49)	25.70 (25.75)	2.36 (2.34)	13.61 (13.65)	6.30 (6.24)	8.50	Diamagnetic
[Co(HPTP)(H ₂ O)(OAc) ₂]	75	12.48 (12.50)	38.20 (38.22)	3.85 (3.82)	14.90 (14.87)	6.78 (6.80)	15.20	Diamagnetic
[Co(HPTP)(H ₂ O)(NO ₃) ₂]	76	12.38 (12.35)	27.65 (27.65)	2.55 (2.52)	20.58 (20.55)	6.73 (6.71)	10.50	Diamagnetic
[Co(HPTP)(H ₂ O)(ClO ₄) ₂]	81	10.70 (10.67)	23.90 (23.92)	2.15 (2.17)	12.70 (12.68)	5.82 (5.80)	8.50	Diamagnetic
[Ni(HPTP)Cl]	75	15.79 (15.87)	35.09 (35.67)	2.62 (2.70)	18.88 (18.64)	8.98 (8.64)	5.24	3.85
[Ni(HPTP)Br]	75	14.16 (13.98)	31.82 (31.05)	2.41 (2.78)	16.87 (16.98)	7.72 (7.70)	9.20	3.82
[Ni(HPTP)NO ₃]	70	14.70 (14.79)	32.89 (33.24)	2.48 (2.51)	20.48 (21.15)	7.99 (8.06)	4.60	3.76
[Ni(HPTP)OAc]	70	14.99 (14.91)	38.95 (39.62)	3.25 (3.30)	17.68 (17.77)	8.00 (8.12)	5.24	3.80

Electronic spectral transitions for Ni(II) complexes were observed in the region 15000 cm^{-1} due to ${}^3T_1(F) \rightarrow {}^3T_1(P)$ expected for tetrahedral Ni(II)⁶. Co(III) complexes showed absorption in the region $28000\text{--}25000$, $23000\text{--}20000$ and $18000\text{--}16000\text{ cm}^{-1}$ which can be assigned to ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and due to split components of ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition suggesting octahedral geometry for Co(III) complexes⁷.

The IR spectra of the ligand showing absorption in the region 3355 and 1660 cm^{-1} are assignable to $\nu(\text{N-H})$ of NH_2 and $\nu(\text{C=O})$ vibrational modes of the thiocarbamoyl pyrazolone part of the ligand⁸⁻¹¹. The azomethine stretching frequency has appeared¹² in the region 1610 cm^{-1} . The band at 3410 cm^{-1} is due to the stretching vibration of phenolic OH group¹³. Phenolic $\nu(\text{C-O})$ was found¹⁴ at 1300 cm^{-1} .

In the spectra of the complexes, the peaks assigned to azomethine (1610 cm^{-1}) and carbonyl group (1660 cm^{-1}) in the ligand has undergone a downward shift by 50 cm^{-1} . The disappearance of a broad band at 3410 cm^{-1} [$\nu(\text{OH})$ in the ligand] and upward shift of $\nu(\text{C-O})$ 1300 cm^{-1} by 20 cm^{-1} indicates the coordination of the phenolic oxygen after deprotonation¹⁵. Hence H_2PTP is monobasic and tridentate coordinating through the azomethine-N, carbonyl and phenolic oxygen, coordinated as HPTP^- . Additional bands observed around $3500\text{--}3400$ and $830\text{--}800\text{ cm}^{-1}$ in the spectra of Co(III) complexes reveal the coordinated water molecules^{15,16}. The non-ligand bands observed around 550 , 440 , 330 and 270 cm^{-1} in the spectra of the complexes may be due to $\nu(\text{M-N})$, $\nu(\text{M-O})$, $\nu(\text{M-Cl})$ and $\nu(\text{M-Br})$, respectively^{17,18}. From the foregoing studies, monomeric distorted octahedral structure and distorted tetrahedral geometry can be assigned to Co(III) and Ni(II) complexes, respectively. Tentative structures of the complexes are shown in Fig. 1.

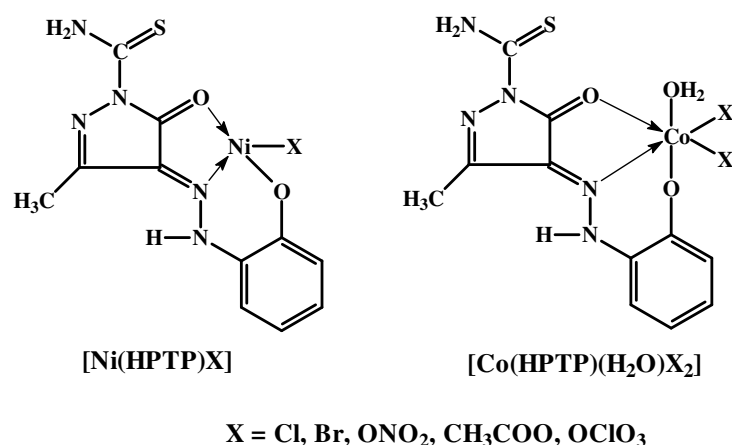


Fig. 1

REFERENCES

1. E.A. French and E.J. Blang, *Cancer Res.*, **26**, 1638 (1966).
2. V.M. Naik and N.B. Mallur, *Indian J. Chem.*, **41A**, 780 (2002).
3. R.C. Sharma, J. Ambwani and V.K. Varshney, *J. Indian Chem. Soc.*, **69**, 770 (1992).
4. S.K. Sahini, S.K. Gupta, S.K. Sanyal and V.B. Rana, *J. Inorg. Nucl. Chem.*, **39**, 1098 (1977).
5. J.C. Bailar Jr., *Inorganic Synthesis*, McGraw Hill, New York, Vol. 4 (1993).
6. C. Preti and G. Tosi, *J. Chem. Soc., Dalton Trans.*, 685 (1976).
7. N.S. Bhave, P.J. Bahad, P.M. Sonaparote and A.S. Aswar, *J. Indian Chem. Soc.*, **79**, 342 (2002).
8. S.N. Poddar, S. Ghosh and A.K. Das, *J. Indian Chem. Soc.*, **53**, 988 (1976).
9. H.G. Garg and C. Prakash, *J. Indian Chem. Soc.*, **53**, 1168 (1976).
10. R.K. Agarwal, A. Kumar, B. Bhushan and R. Prasad, *J. Indian Chem. Soc.*, **72**, 537 (1995).
11. M. Amir, S.A. Khan and S.A. Drabu, *J. Indian Chem. Soc.*, **79**, 280 (2002).
12. M. Alaudeen, P.G. Sushama and A.M. Dorothy, *Indian J. Chem.*, **42A**, 1617 (2003).
13. R.K. Agarwal, *J. Indian Chem. Soc.*, **72**, 263 (1995).
14. H.S. Yokoyama, *Metal Ions Biol. Syst.*, **10**, 313 (1980).
15. R.C. Maurya, B. Shukla and A. Pandey, *Indian J. Chem.*, **41A**, 554, (2002).
16. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley, INC, New York (1963).
17. M. Alaudeen and C.P. Prabhakaran, *Indian J. Chem.*, **33A**, 516 (1996).
18. P. Indrasenan and K.R. Sarojini, *J. Indian Chem. Soc.*, **30A**, 382 (1991).

(Received: 2 February 2006;

Accepted: 19 February 2007)

AJC-5420