

Synthesis and Characterization of Schiff Base Complexes of Mn(II), Co(II) and Zn(II)

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In the present paper, we describe the synthesis and characterization of eight metal complexes of Mn^{2+} , Co^{2+} and Zn^{2+} using Schiff base ligand salicylendene triethylenetetramine with some neutral ligands such as pyridine, quinoline, isoquinoline and γ -picoline.

INTRODUCTION

In the last few years, much interest has been generated in the field of inorganic coordination chemistry especially in the metal complexes with Schiff bases¹⁻³ because of various applications in different fields⁴⁻⁵. In this present work we have synthesised eight metal complexes of Mn^{2+} , Co^{2+} and Zn^{2+} using Schiff base ligand salicylendene triethylenetetramine (Sal_2trien) with some neutral ligands such as pyridine, quinoline, isoquinoline or γ -picoline.

EXPERIMENTAL

All chemicals are AR grade. The γ -picoline, pyridine, quinoline and isoquinoline were used as such without further purification.

Preparation of ligands: Schiff base ligand salicylendene triethylenetetramine were synthesised by refluxing salicylaldehyde and triethylenetetramine in ethanolic solution with 2 : 1 molar ratio for 1 h. On cooling pale yellow crystalline solid was isolated which was washed with alcohol, ether and dried in vacuum.

Preparation of complexes: A solution of metal salt MLL'_2 where $M = Mn(II)$, $Co(II)$ and $Zn(II)$ in ethanol was mixed with the ligand in 1 : 1 : 2 ratio ($M : L : L'_2$) (where $M =$ metal salt, $L = sal_2trien$ and $L' = \gamma$ -picoline, pyridine, quinoline and isoquinoline) and the contents were refluxed for 1 h with constant stirring. The refluxed solution was kept overnight when a coloured solid separated out which was isolated by filtration and washed with ether and dried in vacuum at room temperature. The metal complexes were analysed for metal contents by standard procedure; carbon, hydrogen and nitrogen were determined by the CE-440 elemental analyzer. IR spectra were recorded in nujol using a Unicom SP-200 double beam spectrophotometer. The electronic spectra were recorded using a Unicom SP-500 spectrophotometer. The magnetic moments were determined at room temperature by Gouy method. Diamagnetic corrections were made

using Pascal's constant. The conductance measurements were done in a Systronics direct reading conductivity meter-303 using 10⁻³ M DMF solutions. The physical data and magnetic moments are given in Table-1. The molecular weight measurements were measured by Rast's camphor method.

RESULTS AND DISCUSSION

The elemental analysis suggested the MLL₂ stoichiometrically (Table-1). The m.p.t.s. of all the complexes were above 180°C. The molecular weight measurements indicate the monomeric nature of all the complexes. The complexes are non-electrolytic in nature as indicated from their low molar conductance values (20–30 mhos).

TABLE-1

Complexes/Compounds	Colour	M.W. found (calcd.)	% Analysis, found (calcd.)				μ_{eff} (BM)
			M	C	H	N	
Ligand (Sal ₂ trien) C ₂₀ H ₂₆ O ₂ N ₄	Pale yellow	354	—	(67.41) 67.82	(7.86) 8.23	(15.73) 15.98	—
[Mn(Sal ₂ trien)ypic ₂]	Dark brown	(593.20) 600	(9.26) 9.54	(64.70) 64.91	(6.40) 7.12	(14.15) 14.56	5.78
[Mn(Sal ₂ trien)Py ₂]	Dirty brown	(565.14) 583	(9.72) 10.66	(63.68) 63.52	(6.01) 6.66	(14.86) 15.2	5.83
[Mn(Sal ₂ trien)IQn ₂]	Dirty yellow	(665.26) 690	(8.25) 8.53	(68.53) 68.61	(5.71) 6.24	(12.62) 13.01	5.98
[Co(Sal ₂ trien)IQn ₂]	Dirty pink	(669.25) 700	(8.80) 9.0	(68.12) 68.50	(5.67) 5.93	(12.55) 13.00	3.30
[Co(Sal ₂ trien)Qn ₂]	Dirty green	(669.25) 700	(8.78) 9.1	(68.12) 68.50	(5.67) 5.93	(12.55) 13.00	3.90
[Zn(Sal ₂ trien)IQn ₂]	Yellowish brown	(675.69) 700	(9.67) 10.01	(79.20) 80.00	(6.60) 6.75	(14.59) 14.80	Diamag
[Zn(Sal ₂ trien)Py ₂]	Orange yellow	(575.57) 600	(11.35) 11.74	(62.53) 62.61	(5.90) 6.8	(14.59) 14.9	Diamag
[Zn(Sal ₂ trien)Qn ₂]	Golden yellow	(675.69) 700	(9.67) 10.01	(79.20) 80.00	(6.60) 6.75	(14.59) 14.80	Diamag

The IR spectrum of salicylendene-triethylenetetramine complex however showing the bands which are important for the elucidation of structure, is given in the present work. It shows a broad band in the region 3400–3000 cm⁻¹ which represents a series of overlapping stretching vibrations corresponding to $\nu(\text{OH})$ and $\nu(-\text{NH})$ groups. The C—H stretching vibration seems to have been enveloped in the above band. A strong band observed at 1500 cm⁻¹ seems to be due to (C—N) vibration⁶ of the ligand. It undergoes a blue shift in the metal complexes and appears at 1560 cm⁻¹ indicating the coordination through N-atom of Sal₂trien. The band at ca. 1400 cm⁻¹ due to plane bending vibrations of OH in free ligand is absent in the complexes indicating the deprotonation of —OH group⁷. Again the $\nu(\text{C—O})$ band

of the free ligand shifts from *ca.* 1320 cm^{-1} to the lower wave number by 10–20 cm^{-1} indicating the co-ordination through O-atom. The appearance of the $\nu(\text{M—O})$ and $\nu(\text{M—N})$ bands at 460–440 cm^{-1} and 530–510 cm^{-1} respectively, in all the complexes, indicates that the Schiff base is coordinated through oxygen and nitrogen atoms to the metal ion^{8,9}. The presence of nitrogen coordination from the neutral ligands, *i.e.*, γ -picoline, pyridine, quinoline and isoquinoline in the complexes was ascertained from their $\nu(\text{C=C})$ and $\nu(\text{C=N})$ bands found at 1540–1530 cm^{-1} ¹⁰.

Electronic spectra: The Mn(II) complexes show bands at 18000 cm^{-1} , 25100 cm^{-1} and 27500 cm^{-1} which may be assigned to the transition $A_{1g}(\text{S}) \rightarrow {}^4T_{1g}(\text{G}) \rightarrow {}^4E_g + {}^4A_{1g}(\text{G})$ and $\rightarrow {}^4T_{2g}(\text{D})$ respectively. The magnetic moment values (5.78 to 5.89 BM) and electronic spectra¹¹ are in accordance with the octahedral geometry around the metal ion. The Co(II) complex shows two bands at 9500 and 16800 cm^{-1} which may be assigned to the transitions ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ and ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{P})$ respectively suggesting octahedral geometry. The μ_{eff} values (3.3 and 3.9 BM) suggest high spin octahedral geometry.

As expected Zn(II) complexes are diamagnetic. The complexes are suggested to be six coordinated, probably having octahedral stereochemistry based on the analytical, IR and conductance data.

REFERENCES

1. A.Z. Sami and C.R. Jejurkar, *Indian J. Chem.*, **34A**, 241 (1993).
2. F. Kurzer and M. Wilkinson, *J. Chem., Soc.*, 1218 (1969).
3. E. Hoggarth, *J. Chem. Soc.*, 4811 (1952).
4. N.R. Sengupta, *Indian J. App. Chem.*, **29**, 33 (1966).
5. A. Mahindra, J.M. Fischer and M. Rabinovitz, *Nature (London)*, **303**, 64 (1983).
6. L.J. Bellamy, *Infrared Spectra of Complex Molecule*, Methuen, London, p. 82 (1968).
7. Dawes, J.M. Waters, T.M. Waters, *Inorg. Chem. Acta*, **66**, 29 (1987).
8. M. Mohan, A. Kumar, M. Kumar, N.K. Jha, *Inorg. Chim. Acta*, **132**, 2 (1987).
9. V.S. Shrivastava, C.P. Bhasin, G.C. Saxena, *J. Md. Chem. Soc.*, **136**, 2 (1987).
10. A.K. Das, D.V. Raman Rao, *Chem. Ind. (London)*, 186 (1973).
11. V. Banarjee and A.K. Dey, *J. Indian Chem. Soc.*, **41**, 59, 99 (1962).
12. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam (1968).
13. B.N. Figgis, *Introduction to Ligand Field*, Wiley Eastern, New Delhi, p. 279 (1976).

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