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

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The organic Schiff base ligand, salicylidene anthranilic acid have been synthesized from salicylaldehyde and anthranilic acid. Ten complexes of Mn(II), Co(II) and Zn(II) have been prepared by taking metal salt, the ligand salicylidine anthranilic acid and some neutral ligands (pyridine, isoquinoline, quinoline, γ-picoline). Complexes and ligand are characterized on the basis of their elemental analysis, molecular weight measurements, conductance measurements, magnetic susceptibility measurements, UV and IR spectral data.

INTRODUCTION

It is reported that the Schiff base metal complexes have a very special role in the development of inorganic chemistry[1-3]. They are important because they are synthesized not only for research work but also for various applications in different fields[4]. They are also found to have a number of pharmacological utility[5]. Keeping in view the above facts we have synthesized the ligand salicylidene anthranilic acid and its metal complexes with Mn(II), Co(II) and Zn(II) along with some neutral ligands.

EXPERIMENTAL

All chemicals used are of AR grade. The ligand and complexes are prepared by standard procedure as given below.

Preparation of ligand: Schiff base ligand salicylidene anthranilic acid (SAA) was synthesized by addition of the ethanolic solution of salicylaldehyde and anthranilic acid in 1 : 1 molar ratio and refluxing it for 1 h. On cooling an orange-yellow crystalline solid was isolated which was washed with alcohol, ether and dried in vacuum.

Preparation of complexes: A solution of metal salts in ethanol and a solution of ligand (SAA) and neutral ligands in ethanol (pyridine, isoquinoline, quinoline and γ-picoline) in 1 : 1 : 3 molar ratio were mixed and was refluxed for 2 h. When the refluxed solution was cooled, coloured solids separated out. The resulting complexes were filtered, washed with alcohol, ether and dried in vacuum. However the complexes of Co(II) and Zn(II) were synthesized by mixing in 1:1:1 molar ratio (metal salt : SAA : neutral ligand (pyridine, quinoline, isoquinoline and γ-picoline).

The complexes were analysed for metal contents by standard procedure[6]. The carbon, hydrogen and nitrogen were determined by CE-440 elemental analyser. The UV spectra were recorded using a unicom SP 500 spectrophotometer. The IR spectra were recorded in nujol by a unicom SP-200 double beam spectro-

photometer. The magnetic susceptibility was determined at room temperature by Gouy's method. The conductance measurements were carried out in a systronic direct reading conductivity meter 303 using 10^{-3} M DMF solutions. The analytical and physical data were recorded in Table-1.

TABLE-1

Complex/ Compounds	Colour	% Analysis, Found (cal)				μ_{eff} B.M.	λm ohm^{-1} cm^2 $mole^{-1}$
		M	C	H	N		
Ligand (SAA)	Orange-yellow	—	69.62	4.50	5.75	—	—
		—	(69.70)	(4.56)	(5.80)	—	—
[Mn(SAA)(Py)$_3$]	Dirty white	9.80	65.01	4.00	9.89	5.72	15.6
		(10.34)	(65.50)	(4.51)	(10.54)		
[Mn(SAA)(IQn)$_3$]	Yellowish white	7.94	71.92	3.80	7.71	5.86	16.8
		(8.04)	(72.06)	(4.39)	(8.20)		
[Mn(SAA)(Qn)$_3$]	Gray	7.94	71.92	3.80	7.71	5.88	17.0
		(8.04)	(72.06)	(4.39)	(8.20)		
[Mn(SAA)(γ-Pic)$_3$]	White	9.01	66.40	4.82	9.20	5.89	16.6
		(9.58)	(66.97)	(5.23)	(9.76)		
[Co(SAA)(γ-pic)]	Greenish gray	14.94	60.87	3.61	6.65	4.33	18.00
		(15.06)	(61.37)	(4.09)	(7.16)		
[Co(SAA)(Qn)]	Green	13.16	64.10	3.21	6.00	4.37	18.50
		(13.79)	(64.62)	(3.74)	(6.55)		
[Zn(SAA)(Py)]	Whitish yellow	16.91	59.00	3.30	6.80	diamag	25.00
		(17.04)	(59.45)	(3.65)	(7.30)		
[Zn(SAA)(IQn)]	Deep yellow	14.98	63.10	3.13	6.00	diamag	28.50
		(15.07)	(63.66)	(3.69)	6.40		
[Zn(SAA)(γ-pic)]	Golden yellow	16.01	59.81	3.70	6.60	diamag	30.00
		(16.44)	(60.37)	(4.02)	(7.04)		
[Zn(SAA)(Qn)]	Light yellow	14.98	63.10	3.13	6.00	diamag	29.00
		(15.07)	(63.66)	(3.69)	6.40		

RESULTS AND DISCUSSION

The analytical data (Table-1) show that the composition of the complexes are MLL'_3 [where M = Mn(II) L = Schiff base (SAA), L′ = pyridine, isoquinoline, quinoline and γ-picoline] and MLL′ [where M = Co(II), Zn(II), L = Schiff base (SAA) and L′ = pyridine, quinoline, isoquinoline and γ-picoline]. The low molar conductance values (15–30 ohm^{-1} cm^2 mol^{-1}) of the complexes indicate their non-electrolytic nature. The molecular weight measurement values by Rast's camphor method indicate that all the complexes are monomeric in nature. The melting point of the complexes were found to be above 230°C.

The IR spectra of (SAA) salicylidene anthranilic acid shows a broad band in the region 3400–2600 cm^{-1} due to ν_{OH} mode of carboxylic and phenolic OH group. The band at 1680 cm^{-1} due to $\nu_{C=O}$ of free —COOH group of the ligand is shifted by 40–50 cm^{-1} in all the complexes indicating the absence of the the COOH group[7,8].

The 1630 cm^{-1} band due to stretching vibration of azomethane in the ligand appears at 1600 cm^{-1} in all the complexes indicating that azomethane group is involved in the co-ordination[9]. The band at 1855 and 1635 cm^{-1} is due to ν_{asym} and ν_{sym} vibrations of the COO^- group. $\Delta\nu(\nu_{asym} - \nu_{sym})$ value of 220 cm^{-1} indicates unidentate carboxylate coordination[10, 11]. The band around 1400 cm^{-1} due to plane bending vibrations of phenolic O—H in free ligand is absent in the complexes indicating the deprotonation of phenolic O—H group. The band at 1200 cm^{-1} due to stretching vibrations of $\nu_{(C—O)}$ (phenoxide group) in the ligand is shifted and appears around 1230–1220 cm^{-1} in the complexes. The above IR data suggest that the ligand acts as binegative tridentate ligand[12]. The IR spectra of complexes show additional bands at 1620 cm^{-1} and 1580 cm^{-1}, suggesting coordination of the ligands (pyridine, γ-picoline, quinoline and isoquinoline) through N atom[13].

The electronic spectra of Mn^{2+} show three weak bands around 14340, 16500 and 20000 cm^{-1} which can be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ and $6A_{1g} \rightarrow 4A_{1g}(4G)$ respectively. These transitions suggest an octahedral geometry around the metal ion. The magnetic moment values (5.72–5.89 BM) of the complexes support the octahedral geometry[14]. The Co^{2+} complexes show two bands at *ca.* 8940–8870 cm^{-1} and *ca.* 15390–15250 cm^{-1} assigned to transition $^2A_{2g} \rightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ respectively. These transitions suggest a tetrahedral structure around the metal ion[14, 15]. The magnetic moment values (4.33–4.37 BM) also support the tetrahedral structure. The Zn^{2+} complexes are found to be diamagnetic as expected[16]. The Zn(II) complexes are suggested to be four co-ordinated with a tetrahedral stereochemistry around the metal ion based on analytical data.

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