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STUDY OF CHROMIUM (III), IRON (III) AND COBALT (III) COMPLEXES WITH SOME NEW SCHIFF BASES

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ABSTRACT

Some complexes of chromium (III), iron (III) and cobalt (III) with some new Schiff bases derived from 2–hydroxy–3–methoxy–5–bromo/iodo benzaldehyde and p–chloroaniline, p–bromoaniline and p–iodoaniline have been synthesized and characterized on the basis of elemental analysis, infrared spectra, electronic spectra, X–ray powder diffraction, molar conductance, biological activity and magnetic measurement with Cr^{3+}, Fe^{3+} and Co^{3+} metal ions. The magnetic moment of complexes Cr^{3+}, Fe^{3+} and Co^{3+} are paramagnetic in nature. The β values show considerable orbital overlaps between M–L bonds.

Key words: Schiff base, Chromium, Cobalt, Iron

INTRODUCTION

The Schiff bases complexes with metals exhibit variety in configuration[1] and structural liability, which are sensitive to molecular environment. Metal complexes are known to play a vital role in metabolic and toxicological functions in biological system[2,3]. The Schiff bases derived from sulfa drugs and salicyldehyde have been reported to possess bacterial and fungicide activity[4]. These Schiff bases have been used as chelating agents[5,6]. In the view of the above fact, we are reporting here the preparation and characterisation of the Schiff bases derived from 2–hydroxy–3–methoxy–5–bromo/iodo benzylidene and p–chloroaniline, p–bromoaniline, p–iodoaniline[7] and their metal ions complexes with Cr^{3+}, Fe^{3+} and Co^{3+}. The structures of the complexes have been established using analytical and spectral data. The results obtained are in good agreement with the ligand field splitting energy.

EXPERIMENTAL

All the chemicals were used of AR grade. The solvents were distilled before use[8]. The elemental analysis is carried out at Department of Chemistry, University of Mumbai. Infra–red spectra were recorded Perkin–Elmer paragon–500 Spectrophotometer using KBr Pallets. ^1H NMR spectra recorded on Perkin–Elmer R–32 spectrometer using TMS as an internal standard.

Electronic spectra were recorded on Cintra–5 GBC UV–Visible Spectrophotometer at University Department of Chemical Technology, Mumbai. The conductivity measurements were carried out on Equi–tonic digital conductivity bridge. Magnetic Susceptibility measurement were carried out using $[HgCO(CNS)_4]$ as a calibrate at Dr. Babasaheb Ambedkar Marathwada University, Aurangabad. X–ray powder diffraction was recorded on Joel–8030 double Goinometry X–ray powder diffract meter at Tata Institute of Fundamental Reserach, Mumbai using Cu–K_α = 1.5418 Å at chart speed $2^o(2\theta)$/min in the range 10–40^o. The densities of the complexes were calculated using specific density bottle in toluene as a solvent. The Schiff bases were synthesized by refluxing aromatic amines like p–chloro, p–bromo and p–iooaniline with bromo and iodovaniline in ethanol in 1:2 molar ratios for ~3 hrs on water bath. After ~3 hrs, the resulting reaction mixture was poured in ice cold water and crystallized from ethanol.

Preparation of metal complexes with 2–hydroxy–3–methoxy–5–bromo/iodo benzylidene–4–chloroaniline: For the synthesis of the complexes, hot ethanolic solution of an appropriate metal salt (0.02M solution of Cr^{3+}, Fe^{3+} and Co^{3+} metal ions) was mixed slowly with ligand (0.02 M) in 1 : 2 molar ratio with constant stirring. After complete addition, the resulting mixtures were heated on a water bath for ~1 hr and then kept for ~24 hrs at room temperature. The colored solid complexes obtained, were filtered, washed with ethanol and dried at 60^oC in oven.

RESULTS AND DISCUSSION

The analytical data and physical data of complexes are given in Table 1. The molar conductance of 10^{-3} M solution of complexes was measured in DMSO. The molar conductivity of complexes indicate that these complexes are non–electrolytic in nature[9]. The complexes decomposed in the temperature range 140–198^oC. The melting point (or decomposition point) reported in open capillary and are uncorrected. The metal contents were estimated by ethylenediamine tetaacetate using xylenol orange as an indicator[10]. The metal ligand ratio of the complexes is found to be 1: 2. These complexes are insoluble in organic solvents like benzene, acetone, ether, chloroform and acetonitrile, but soluble in dimethyl formamide and dimethyl sulfoxide.

The infrared absorption frequencies of complexes indicate bands at 1580–1600 cm^{-1}(azomethine character) due to C=C and 1600–1680 cm^{-1} due to hydroxy stretching respectively[11,12]. New bands in far– ir region for (M–N and M–O) were obtained at 470–458 cm^{-1} and 445–435 cm^{-1}, respectively[13,14]. ^{1}H NMR bands at δ 3.9 (S, 3H, OCH_3), δ 8.5 (S, 1H, CH=) and multiplet in aromatic ring region are present at δ 6.5–7.6. The electronic spectra of these complexes were recorded in DMSO. The spectrum of Cr^{3+} complex gives three bands at 17241, 24090 and 32258 cm^{-1}, which are assigned to $^4T_{1g}(P)^4 \leftarrow A_{2g}(F)$, $^4T_{1g}(F)^4 \leftarrow A_{2g}(F)$ and $^4T_{2g}(P) \leftarrow {}^4A_{2g}$, respectively. In the Fe^{3+} complex, the three bands are observed at 16435, 23895 and 32000 cm^{-1} and these are attributed to $^4T_{1g}(P) \leftarrow {}^4A_{1g}$, $^4E_g(G) \leftarrow {}^6A_{1g}$ and $^4T_{1g}(G) \leftarrow {}^6A_{1g}$, while in the Co^{3+} complex, the bands observed at 13290, 19630 and 42390 cm^{-1} are assigned to

Table 1. Physical and analytical data

No.	Complexes	Color/Yield (%)	M.P. (°C)	C	H	N	M
1	$^{1}CrL_2$	Brown/66	146	42.80(42.71)	2.80(2.75)	3.56(3.45)	13.24(13.16)
2	$^{1}FeL_2$	Reddish/62	175	42.37(42.28)	2.77(2.69)	3.53(3.48)	14.20(14.12)
3	$^{1}CoL_2$	Yellow/58	169	42.50(42.09)	2.75(2.68)	3.50(3.45)	14.76(14.65)
4	$^{2}CrL_2$	Brown/68	155	38.44(38.42)	2.52(2.42)	3.20(3.14)	11.98(11.89)
5	$^{2}FeL_2$	Reddish/56	149	38.09(37.94)	2.49(2.50)	3.17(3.10)	12.69(12.65)
6	$^{2}CoL_2$	Yellow/54	158	37.84(37.76)	2.47(2.49)	3.15(3.18)	13.28(13.15)
7	$^{3}CrL_2$	Brown/61	187	34.71(34.62)	2.27(2.18)	2.89(2.81)	10.74(10 65)
8	$^{3}FeL_2$	Reddish/63	196	34.43(34.46)	2.25(2.16)	2.86(2.85)	11.47(11.39)
9	$^{3}CoL_2$	Yellow/59	176	34.22(34.13)	2.24(2.15)	2.86(2.80)	12.01(11.83)
10	$^{4}CrL_2$	Brown/64	132	38.22(38.10)	2.50(2.44)	3.18(3.10)	11.83(11.73)
11	$^{4}FeL_2$	Reddish/56	144	37.88(37.74)	2.48(2.39)	3.15(3.09)	12.62(12.45)
12	$^{4}CoL_2$	Yellow/59	149	37.62(37.56)	2.46(2.41)	3.13(3.10)	13.21(13.08)
13	$^{5}CrL_2$	Brown/60	197	34.71(34.73)	2.27(2.17)	2.89(2.85)	10.74(10.61)
14	$^{5}FeL_2$	Reddish/67	192	34.42(34.35)	2.25(2.18)	2.86(2.79)	11.90(11.71)
15	$^{5}CoL_2$	Yellow/57	181	34.21(34.12)	2.24(2.19)	2.85(2.81)	12.05(11.92)
16	$^{6}CrL_2$	Brown/63	166	31.63(31.51)	2.07(1.98)	2.63(2.59)	9.79(9.65)
17	$^{6}FeL_2$	Reddish/52	158	31.40(31.35)	2.05(1.95)	2.61(2.51)	10.38(10.22)
18	$^{6}CoL_2$	Yellow/55	161	31.22(31.23)	2.04(1.94)	2.60(2.54)	10.96(10.65)

^{1}L.= 2– hydroxy –3– methoxy –5–bromo benzylidene–4– chloroaniline
^{2}L.= 2– hydroxy –3– methoxy –5–bromo benzylidene–4– bromoaniline
^{3}L.= 2– hydroxy –3– methoxy –5–bromo benzylidene–4– iodoaniline
^{4}L.= 2– hydroxy –3– methoxy –5–iodobenzylidene–4– chloroaniline
^{5}L.= 2– hydroxy –3– methoxy –5–iodobenzylidene–4– bromoaniline
^{6}L.= 2– hydroxy –3– methoxy –5–iodobenzylidene–4– iodoaniline

Table 2. Electronic spectra and Boh magnetons. (B.M.)

No.	Complexes	β	1 – b	$b^{1/2}$	Δ (%)	B.M. μ_{eff}
1	$^{1}CrL_2$	0.992	0.008	0.0632	0.806	4.81
2	$^{2}FeL_2$	0.989	0.011	0.0741	1.112	5.84
3	$^{3}CoL_2$	0.988	0.012	0.0774	1.214	3.74
4	$^{4}CrL_2$	0.993	0.007	0.0591	0.704	4.84
5	$^{5}FeL_2$	0.991	0.009	0.0670	0.908	5.80
6	$^{6}CoL_2$	0.990	0.010	0.0707	1.010	3.71

$^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}(F)$, $^{4}A_{2g}(F) \leftarrow {}^{4}T_{1g}(F)$ and $^{2}T_{1g}(F) \leftarrow {}^{4}T_{1g}(F)$. The various parameters such as β, 1 – β, $b^{1/2}$ and δ % have been calculated[15-17] and are reported in Table 2. From the electronic spectral data, the complexes may be assigned an octahedral geometry. The biological activities were

Table 3. Cell data and crystall lattice parameters for [CoL_2] Complex

a (Å) = 19.9545 D_{cal} (g/cm^{-3}) = 1.7106

b (Å) = 12.7417 D_{obs} (g/cm^{-3}) = 1.6948

c (Å) = 13.6513 Space group = $P_{2/m}$

β = 120.194 Crystal system = monoclinic

V $(Å)^3$ = 4885.09 Z = 6

D_{obs}	D_{cal}	h	k	I	I/Io	2θ
8.6215	8.6237	2	0	0	64	10.26
7.6945	7.6937	1	0	1	64	11.50
6.8203	6.8257	0	2	0	53	12.98
6.2283	6.2317	–1	0	2	53	14.22
5.9694	5.9783	–3	1	1	54	14.84
5.6443	5.6378	–3	0	2	58	15.70
4.6178	4.6160	1	0	2	49	19.22
4.4749	4.4825	4	–1	2	51	19.84
4.2725	4.2794	1	3	1	65	20.79
3.8634	3.6820	1	1	3	54	23.02
3.6014	3.5958	2	2	3	100	24.72
3.4531	3.4495	5	0	0	71	25.80
3.3289	3.3249	–6	0	2	83	26.78
3.2714	3.2712	1	0	3	65	27.26
3.0893	3.0908	4	2	1	57	28.90
2.6984	2.6967	1	5	0	32	33.20

determined using disc diffusion method[18] by measuring inhibition zone. All the complexes were screened for their antibacterial activity using *E. coli, Azobactreia, B. subtitis, S. typhi* and *S. dysentrae* at 150 ppm concentration using tetracycline as a standard. The complexes 4, 9 and 16 were found to be active (zone inhibition 14–19 mm) in comparison to active tetracycline (18–20 mm) against all the microbes. The X–ray powder pattern of cobalt (III) complex with 2–hydroxy–3–methoxy–5–bromo benzylidene–4–iodoaniline is reported. The nature of spectra indicates low crystallinity of the complexes. The major refluxes were used to calculate crystal lattice parameters using Back–cal program on computer by Ito's method[19] and chekcell. The observed values are reported in Table 3. The systems were found monoclinic with space group $P_{2/m}$[20,21]. The Z = 6 factor values were calculated from density of the complexes using toluene as a solvent[22]. The observed value of density was 1.6948 cm^{-3}, while one is calculated 1.7012 g/cm^{-3}

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