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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND BIOLOGICAL ASPECTS OF IRON(lll), COBALT(lll), MANGANESE(lll) AND CHROMIUM(lll) COMPLEXES WITH SCHIFF BASES DERIVED FROM 5-SUBSTITUTED ISATIN

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ABSTRACT

A new series of transition metal chelates of Iron (lll), Cobalt (lll), Manganese (lll) and Chromium (lll) have been isolated from Schiff base derived from 5-bromoisatin/5-methylisatin/5-chloroisatin with 2-aminophenol/2-aminothiophenol. Schiff base ligands and metal complexes can be used in preparation of enzymes along with catalytic nature in biological systems and in preparation of dyes. Structural features of ligands and metal chelates were obtained from their elemental analysis, magnetic moment susceptibilities, molar conductance and spectral (UV-Vis, IR and ^{1}H NMR) studies. The obtained data illustrates that these complexes have composition of $[M(L)_2]Z$ type and octahedral geometry around central metal ion with O/S/N donor atoms. The ligands are of uninegative tridentate nature. The synthesized trivalent metal complexes appear to be 1:1 electrolyte. In addition, biological studies have been carried out *in vitro* for investigated compounds.

KEY WORDS: Schiff bases, isatin, metal chelates, spectral analysis, biological activity

INTRODUCTION

Therapeutic inorganic chemistry has roused a meaningful rising interest in the designing of metal compounds as medicines and diagnostic agents (Cerchiaro *et al*., 2005). The emergence of alternative chemotherapeutic Schiff bases is fascinating the attention of medicinal chemists (Hameed *et al.*, 2017) due to ease of preparation and complexation (Kumar *et al*., 2023). Schiff bases are the condensation products obtained by carbonyl compounds (Sakthivel *et al*., 2020) and amines. They are stable and can tune the ligation aspects by varying denticity and basicity. Schiff bases are used to shape significant group of organic compounds with wide range of biological applications such as anti-cancer (Kar *et al.*, 2022), antibacterial (Shanty *et al*., 2017; Gerdemann *et al*., 2002), antifungal (Hossain *et al*., 2022) and herbicidal properties (Wang *et al*., 2021). Schiff base obtained from different heterocyclic compounds were reported to retain cytotoxic (Tarafder *et al*., 2002), anticonvulsant (Kucukguzel *et al.*, 2004) and antiproliferative activities (Vicini *et al*., 2003). Such type of Schiff bases can act as ligands having functional groups with N and O as donor sites (Kundu *et al*., 2016) for various transition metals.

Isatin is a processed inconstant substrate that can be well-used to prepare a wide range of heterocyclic compounds and as a raw material for drug synthesis (Joaquim *et al*., 2001). Isatin (1H-indole-2,3-dione) and derivatives obtained from it show a large variety of biological activities (Akbar Ali *et al*., 2011; Kakkar, 2019). Isatin, an endogenous molecule, is widely relegated in tissues of mammals and body fluids. It has been detected in blood, urine and tissue using GCMS (Gas Chromatography Mass Spectrometry) and HPLC (High Performance Liquid Chromatography) with an ultraviolet detector (Hamaue *et al*., 1999). In the last few years, Schiff bases of isatin are revealed to evidence broad-spectrum medicinal properties such as antiviral (Elsaman *et al*., 2022), anti-tubercular (Karali *et al*., 2007), antibacterial and antifungal. Analysis of the structure-activity-relationships in isatin derived compounds have affirmed that 5-halogenations (Aanandhi *et al*., 2008) were potent in inducing a noticeable multiplication in activity at variance with different bacteria, virus and fungi. Further interest in the preparation of transition metal chelates of isatin is due to the fact that isatin show keto-enolic equilibrium that can credit its coordination values giving rise to cationic or

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neutral complexes with diverse structure and reactivity.

Owing to these structural and biotic features, shown by 5-substituted isatin derived Schiff base ligands and their transition metal complexes, interest in this field is continuously expanding. The present investigation is oriented towards synthesis of Schiff base ligands derived from 5-substituted isatin with 2-aminophenol/ 2-amino thiophenol and their Fe(lll), Co(lll), Mn(lll) and Cr(lll) complexes and their spectral characterization.

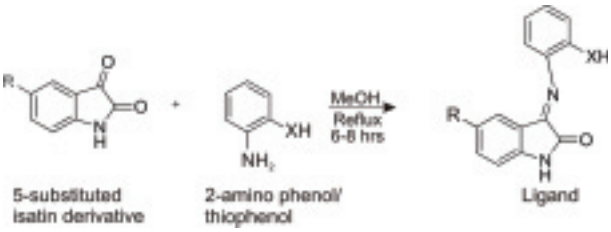
MATERIAL AND METHODS

All chemicals, used in the investigation were purchased from trade sources and used as received without any purification. 2-Aminophenol and 2-amino thiophenol were purchased from Sigma Aldrich. 5-Bromoisatin, 5-methylisatin and 5-chloroisatin were synthesized according to the literature method (Nirma *et al*., 2010). Iron trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$), cobalt dichloride hexahydrate ($CoCl_2 \cdot 6H_2O$) and chromium trichloride hexahydrate ($CrCl_3 \cdot 6H_2O$) were procured from SD Fine Chemicals Ltd. (Mumbai). Manganese triacetate dihydrate was prepared by manganese diacetate tetrahydrate by oxidation method (Lewis *et al*., 1960). All the used organic solvents were of reagent grade.

Elemental (carbon, hydrogen and nitrogen) analysis of the ligands and complexes were carried out on Carlo Erba 1108 elemental analyzer at SAIF, CDRI, Lucknow. Fe, Co, Mn and Cr were approximated gravimetrically by precipitating them. Sulphur was assessed gravimetrically in form of $BaSO_4$. The IR spectra of ligands along with complexes were recorded in KBr pellets on Shimadzu 8201 PC spectrophotometer in the range of 4000-200 cm^{-1}. Electronic spectra were noted down on Perkin Elmer Lambda 15UV/VIS spectrophotometer in DM For DMSO. ^1H NMR spectra of prepared ligands and cobalt(III) complexes were recorded in DMSO-d_6 at 90 MHz. Beckman conductivity bridge model RC-18A was used to take electrical conductance measurements in DMF or nitrobenzene at room temperature. Gouy's method was employed to obtain magnetic measurements at room temperature using $Hg[Co(NCS)_4]$ as calibrant. Melting point were taken down with an Ambassador melting point apparatus using capillaries and are uncorrected.

Synthesis of ligands

The ligands were synthesized in three steps. The first and second step includes preparation of 5-substituted isatin according to the literature. In third step, the ligand was prepared by performing reaction of 5-substituted isatin with 2-aminophenol/2-aminothiophenol in 1:1 ratio. 5-Bromoisatin (0.2mol)/5-methylisatin (0.2mol)/5-chloroisatin (0.2mol) were reacted with 2-aminophenol (0.2 mol)/ 2-aminothiophenol (0.2 mol) in methanol (50 ml) and refluxed for 6-8 hours. Coloured solid products were precipitated upon cooling and separated by filtration, washed with methanol and dried *in vacuo* over calcium chloride. The synthesis route of ligands is given in Fig.1.



R	X	Abbreviation
Br	O	BHPIH
Br	S	BMPIH
CH_3	O	MHPIH
CH_3	S	MMPIH
Cl	O	CHPIH
Cl	S	CMPIH

Fig. 1: Synthesis route of ligands

Preparation of Fe(lll), Co(lll), Mn(lll) and Cr(lll) complexes with ligands BHPIH/MHPIH/ CHPIH

To a boiling solution of 0.02 mol of BHPIH/ MHPIH/ CHPIH in methanol (10 ml) was slowly added methanolic solution (10 ml) of $FeCl_3 \cdot 6H_2O$ (0.01 mol), $CoCl_2 \cdot 6H_2O$ (0.01 mol), $Mn(OAc)_3 \cdot 2H_2O$ (0.01 mol) or $CrCl_3 \cdot 6H_2O$ (0.01mol) separately. The reaction with $CoCl_2 \cdot 6H_2O$ was followed by addition of H_2O_2 (0.01mol, 30%) after refluxing for one hour. The reaction mixture was refluxed for next 10-12 hours on water bath. The volume of mixtures was reduced to half by evaporation. The desired coloured complexes were filtered off, washed with methanol and dried *in vacuo* over calcium chloride.

Preparation of Fe(lll), Co(lll), Mn(lll) and Cr(lll) complexes with ligands BMPIH/ MMPIH/ CMPIH

To a boiling solution of 0.02 mol of BMPIH, MMPIH and CMPIH in methanol (10 ml) was added methanolic solution (10 ml) of $FeCl_3 \cdot 6H_2O$ (0.01mol), $CoCl_2 \cdot 6H_2O$ (0.01mol), $Mn(OAc)_3 \cdot 2H_2O$ (0.01mol) or $CrCl_3 \cdot 6H_2O$ (0.01mol). After an hour, the reaction with $CoCl_2 \cdot 6H_2O$ was followed by the addition of H_2O_2 (0.01 mol, 30%). The reaction mixture was further refluxed for 10-12 hours on water bath with constant stirring. The mixture was made alkaline (pH=7-7.5) by adding saturated solution of KOH. The coloured precipitate obtained was filtered, washed many times with distilled water and dried over calcium chloride.

Table 1: Physical properties and analytical data of ligands and metal complexes

Compound/ Empirical formula	Formula Weight ($gmol^{-1}$)	Yield (%)	Colour	Decom. Temp.(^{0}C)	Analysis found (Calculated) %							
					C	H	N	O	S	Br	Cl	M
BHPIH/ $C_{14}H_9N_2O_2Br$	317.16	72.0	Dark brown	110	53.01 (52.99)	2.86 (2.84)	8.83 (8.82)	10.09 (10.07)	-	25.19 (25.16)	-	-
BMPIH/ $C_{14}H_9N_2OSBr$	333.22	75.0	Light brown	100	50.46 (50.44)	2.72 (2.70)	8.41 (8.40)	4.80 (4.79)	9.62 (9.60)	23.98 (23.97)	-	-
MHPIH/ $C_{14}H_9N_2O_2$	252.27	68.3	Brown	>150	66.66 (66.61)	3.60 (3.59)	11.10 (11.09)	12.68 (12.66)	-	-	-	-
MMPIH/ $C_{15}H_{12}N_2OS$	268.35	81.5	Brown	110	67.14 (67.12)	4.51 (4.49)	10.44 (10.43)	5.96 (5.94)	11.93 (11.92)	-	-	-
CHPIH/ $C_{14}H_9N_2O_2Cl$	272.71	52.0	Dark brown	170	61.62 (61.60)	3.31 (3.30)	10.28 (10.27)	11.74 (11.73)	-	-	13.00 (13.02)	-
CMPIH/ $C_{14}H_9N_2OSCl$	288.77	67.6	Brown	80	58.19 (58.18)	3.14 (3.12)	9.71 (9.70)	5.55 (5.54)	11.10 (11.08)	-	12.28 (12.29)	-
$[Fe(BHPI)_2]Cl$/ $C_{28}H_{16}N_4O_4Br_2ClFe$	723.56	17.6	Blackish brown	<280	46.48 (46.45)	2.23 (2.21)	7.74 (7.72)	8.84 (8.83)	-	22.09 (22.05)	4.90 (4.88)	7.72 (7.71)
$[Fe(BMPI)_2]Cl$/ $C_{28}H_{16}N_4O_2S_2Br_2ClFe$	755.71	57.3	Greenish brown	<300	44.50 (44.48)	2.13 (2.11)	7.41 (7.40)	4.23 (4.22)	8.49 (8.46)	21.15 (21.14)	4.69 (4.68)	7.39 (7.37)
$[Fe(MHPI)_2]Cl$/ $C_{30}H_{22}N_4O_4ClFe$	593.82	24.4	Brown	<290	60.68 (60.67)	3.73 (3.71)	9.43 (9.40)	10.78 (10.77)	-	-	5.97 (5.96)	9.40 (9.39)
$[Fe(MMPI)_2]Cl$/ $C_{30}H_{22}N_4O_2S_2ClFe$	625.96	26	Blackish brown	<280	57.56 (57.54)	3.54 (3.52)	8.95 (8.93)	5.11 (5.10)	10.25 (10.24)	-	5.66 (5.65)	8.92 (8.90)
$[Fe(CHPI)_2]Cl$/ $C_{28}H_{16}N_4O_4Cl_3Fe$	634.66	26.3	Blackish brown	<285	52.99 (52.98)	2.54 (2.53)	8.83 (8.81)	10.08 (10.06)	-	-	16.76 (16.73)	8.80 (8.77)
$[Fe(CMPI)_2]Cl$/ $C_{28}H_{16}N_4O_2S_2Cl_3Fe$	666.80	78.3	Light brown	<295	50.44 (50.43)	2.42 (2.40)	8.40 (8.38)	4.80 (4.77)	9.62 (9.61)	-	15.95 (15.93)	8.38 (8.37)
$[Co(BHPI)_2]Cl$/ $C_{28}H_{16}N_4O_4Br_2ClCo$	726.65	57.8	Black	<305	46.28 (46.26)	2.22 (2.21)	7.71 (7.69)	8.81 (8.80)	-	21.99 (21.96)	4.88 (4.85)	8.11 (8.10)
$[Co(BMPI)_2]Cl$/ $C_{28}H_{16}N_4O_2S_2Br_2ClCo$	758.78	72.7	Light brown	<310	44.32 (44.30)	2.13 (2.12)	7.38 (7.36)	4.22 (4.21)	8.45 (8.44)	21.06 (21.04)	4.67 (4.65)	7.77 (7.73)
$[Co(MHPI)_2]Cl$/ $C_{30}H_{22}N_4O_4ClCo$	596.92	41.4	Blackish brown	<290	60.36 (60.34)	3.71 (3.70)	9.39 (9.38)	10.72 (10.70)	-	-	5.94 (5.92)	9.87 (9.86)
$[Co(MMPI)_2]Cl$/ $C_{30}H_{22}N_4O_2S_2ClCo$	629.04	52.6	Light brown	<300	57.28 (57.26)	3.52 (3.51)	8.91 (8.90)	5.09 (5.06)	10.19 (10.17)	-	5.64 (5.63)	9.37 (9.36)
$[Co(CHPI)_2]Cl$/ $C_{28}H_{16}N_4O_4Cl_3Co$	637.75	23.5	Brown	<285	52.73 (52.72)	2.53 (2.52)	8.79 (8.76)	10.03 (10.02)	-	-	16.68 (16.67)	9.24 (9.22)
$[Co(CMPI)_2]Cl$/ $C_{28}H_{16}N_4O_2S_2Cl_3Co$	669.88	42.1	Greyish brown	<300	50.20 (50.19)	2.41 (2.40)	8.36 (8.34)	4.78 (4.76)	9.57 (9.56)	-	15.88 (15.87)	8.80 (8.79)
$[Mn(BHPI)_2]OAc$/ $C_{30}H_{19}N_4O_6Br_2Mn$	746.25	32.2	Brown	<280	48.29 (48.26)	2.57 (2.56)	7.51 (7.50)	12.86 (12.84)	-	21.41 (21.40)	-	7.36 (7.35)
$[Mn(BMPI)_2]OAc$/ $C_{30}H_{19}N_4O_4S_2Br_2Mn$	778.38	24.0	Brown	<290	46.29 (46.27)	2.46 (2.45)	7.20 (7.18)	8.22 (8.21)	8.24 (8.22)	20.53 (20.52)	-	7.06 (7.04)

$[Mn(MHPI)_2]OAc$/ $C_{32}H_{25}N_4O_6Mn$	616.51	85.8	Brown	<310	62.34 (62.33)	4.09 (4.08)	9.09 (9.07)	15.57 (15.55)	-	-	-	8.91 (8.89)
$[Mn(MMPI)_2]OAc$/ $C_{32}H_{25}N_4O_4S_2Mn$	648.61	37.1	Brown	<300	59.26 (59.24)	3.88 (3.86)	8.64 (8.63)	9.87 (9.86)	9.89 (9.88)	-	-	8.47 (8.45)
$[Mn(CHPI)_2]OAc$/ $C_{30}H_{19}N_4O_6Cl_2Mn$	657.34	68.6	Blackish brown	<285	54.82 (54.81)	2.91 (2.89)	8.52 (8.50)	14.60 (14.58)	-	-	10.79 (10.78)	8.36 (8.33)
$[Mn(CMPI)_2]OAc$/ $C_{30}H_{19}N_4O_4S_2Cl_2Mn$	689.48	45.1	Brown	<310	52.26 (52.25)	2.78 (2.76)	8.13 (8.11)	9.28 (9.27)	9.30 (9.29)	-	10.28 (10.25)	7.97 (7.95)
$[Cr(BHPI)_2]Cl$/ $C_{28}H_{16}N_4O_4Br_2ClCr$	719.71	33.0	Brown	<295	46.73 (46.71)	2.24 (2.23)	7.78 (7.77)	8.89 (8.88)	-	22.20 (22.18)	4.93 (4.92)	7.22 (7.21)
$[Cr(BMPI)_2]Cl$/ $C_{28}H_{16}N_4O_2S_2Br_2ClCr$	751.84	48.0	Light brown	<280	44.73 (44.72)	2.14 (2.12)	7.45 (7.43)	4.26 (4.25)	8.53 (8.52)	21.26 (21.25)	4.71 (4.70)	6.91 (6.88)
$[Cr(MHPI)_2]Cl$/ $C_{30}H_{22}N_4O_4ClCr$	590.00	57.8	Blackish brown	<305	61.07 (61.05)	3.76 (3.75)	9.50 (9.49)	10.85 (10.84)	-	-	6.01 (6.00)	8.81 (8.80)
$[Cr(MMPI)_2]Cl$/ $C_{30}H_{22}N_4O_2S_2ClCr$	622.11	48.3	Greenish brown	<310	57.92 (57.91)	3.56 (3.55)	9.01 (8.99)	5.14 (5.13)	10.31 (10.30)	-	-	8.36 (8.35)
$[Cr(CHPI)_2]Cl$/ $C_{28}H_{16}N_4O_4Cl_3Cr$	630.81	73.9	Brown	<290	53.31 (53.30)	2.56 (2.55)	8.88 (8.87)	10.14 (10.12)	-	-	15.25 (15.23)	8.24 (8.23)
$[Cr(CMPI)_2]Cl$/ $C_{28}H_{16}N_4O_2S_2Cl_3Cr$	662.94	43.6	Blackish brown	<300	50.73 (50.71)	2.43 (2.41)	8.45 (8.44)	4.83 (4.81)	9.67 (9.64)	-	16.04 (16.03)	7.84 (7.83)

RESULTS AND DISCUSSION

In methanolic solution, ligands and metal solutions undergo following reactions:

$$MZ_3{\cdot}nH_2O + 2L'H \xrightarrow{MeOH} [ML'_2]Z + 2ZH$$

$$CoCl_2{\cdot}6H_2O + 2L'H \xrightarrow{MeOH/H_2O_2} [ML'_2]Z + 2ZH$$

$$MZ_3{\cdot}nH_2O + 2L''H \xrightarrow{MeOH,\ KOH} [ML''_2]Z + 2ZH$$

$$CoCl_2{\cdot}6H_2O + 2L''H \xrightarrow{MeOH/H_2O_2,KOH} [ML''_2]Z + 2ZH$$

M=Fe,Mn,Cr; Z= Cl or OAc; n=$6H_2O$ or $2H_2O$

L'= BHPIH, MHPIH and CHPIH; L''=BMPIH, MMPIH and CMPIH

Scheme for synthesis of complexes

Spectroscopic results and analytical data hold up the proposed structure of the ligand and metal complexes. Ligands are dissolvable in EtOH, MeOH, DMSO and DMF while the complexes are solvable in DMSO and DMF. All the precipitated complexes are coloured crystalline powder. Conductivity measurements in DMF showed that the complexes are electrolytic in nature. The physical and analytical data of ligands and complexes are given in Table 1.

Magnetic moment and electronic spectra

The data of magnetic moment and electronic absorption bands of Cr(III), Mn(III), Fe(III) and Co(III) were recorded in DMSO and band positions are summarized in Table 2. The observed magnetic moment values (Lewis *et al*., 1960) at room temperature for Cr(III) complexes were found in the range 3.81-3.92 BM consistent with the theoretical spin only value (μ_{eff}=3.87 BM) for Cr^{3+} (d^3) system suggesting the octahedral geometry around Cr(III) metal ion. Mn(III) complexes showed magnetic moment in range of 4.86-5.02 BM which is in magnificent agreement with spin only moment (4.90 BM) for a high spin d^4 (S=2) configuration generally observed for mononuclear Mn(III) complex (Sengupta *et al*., 1980). High magnetic moment values for Fe(III) complexes (5.41-5.83 BM) are consistent with a high spin configuration (Bhattacharjee *et al*., 2010). The Co(III) complexes are diamagnetic as anticipated for a low spin d^6 system (S=0) corresponding to t_{2g}^6 configuration in octahedral environment (Sharma *et al*., 2018).

The electronic spectra of Fe(III) complexes showed three band at range of 13,010-13,650;16050-17, 660 and 26,605-27,670 cm^{-1}, normally set for $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4E_g(G)$ transitions (Figgis *et al*., 1999). The brown colour of complex is due to appearance of one or more low lying charge transfer absorption bands.

Table 2: Magnetic moments (B.M.) and electronic spectral data (cm^{-1}) of the complexes

Complexes	μ_{eff} (B.M.)	Band observed (cm^{-1})	Assignments
$[Fe(BHPI)_2]Cl$	5.65	13320 16050 26605	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4E_g(G)$
$[Fe(BMPI)_2]Cl$	5.79	13512 17660 26890	as above
$[Fe(MHPI)_2]Cl/$	5.51	13211 16695 27470	as above
$[Fe(MMPI)_2]Cl/$	5.71	13345 16880 26526	as above
$[Fe(CHPI)_2]Cl$	5.41	13010 17335 27670	as above
$[Fe(CMPI)_2]Cl$	5.83	13650 16720 27110	as above
$[Co(BHPI)_2]Cl$	Dia.	20930 26920	$^1A_{1g} \rightarrow {}^1T_{1g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$
$[Co(BMPI)_2]Cl$	Dia.	20870 27600	as above
$[Co(MHPI)_2]Cl$	Dia.	20310 27430	as above
$[Co(MMPI)_2]Cl$	Dia.	20360 27010	as above
$[Co(CHPI)_2]Cl$	Dia.	21180 27210	as above
$[Co(CMPI)_2]Cl$	Dia.	21050 27455	as above
$[Mn(BHPI)_2]OAc$	5.02	19500 18050	CT $^5E_g \rightarrow {}^5T_{2g}$
$[Mn(BMPI)_2]OAc$	4.85	20300 18335	as above
$[Mn(MHPI)_2]OAc$	4.89	19885 18645	as above
$[Mn(MMPI)_2]OAc$	4.96	19770 18090	as above
$[Mn(CHPI)_2]OAc$	4.92	19950 18580	as above
$[Mn(CMPI)_2]OAc$	4.86	20115 18620	as above
$[Cr(BHPI)_2]Cl$	3.87	16200 21000 25150	$^4A_{2g} \rightarrow {}^4T_{2g}$ (F) $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) $^4A_{2g} \rightarrow {}^4T_{1g}$ (P)
$[Cr(BMPI)_2]Cl$	3.92	17700 22303 31210	as above
$[Cr(MHPI)_2]Cl$	3.95	17665 23540 28650	as above
$[Cr(MMPI)_2]Cl$	3.89	16665 22890 26478	as above
$[Cr(CHPI)_2]Cl$	3.81	16930 24400 31540	as above
$[Cr(CMPI)_2]Cl$	3.90	18600 23625 32550	as above

The electronic absorption spectra of Co(III) complexes low spin d^6 system show two spin allowed transitions which are at 20,870-21,180 and 26,920-27,600 cm^{-1}. These bands are formed due to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ d-d transition (Radanovic *et al*., 1993). Electronic spectral data for Mn(III) complexes show a band at 19500-20300 cm^{-1} which can be attributed to ligand-metal charge transfer and a shoulder at 18050-18620 cm^{-1} may be assigned to $^5E_g \rightarrow {}^5T_{2g}$ (Sharma, 2011). The Cr(III) metal complexes show spin allowed transitions $^4A_{2g} \rightarrow {}^4T_{2g}$(F), $^4A_{2g} \rightarrow {}^4T_{1g}$(F) and $^4A_{2g} \rightarrow {}^4T_{1g}$(P) in range of 16200-18600, 21000-24400 and 25150-32550 cm^{-1} respectively in order of their increasing energy.

IR spectra

The acquired characteristic IR bands of ligands and complexes are shown in Table 3. The spectrum of ligands derived from 2-aminophenol shows a wide band in range of 3000 to 3250 cm^{-1} and pointed around 3075 cm^{-1} which can be allocated to the hydrogen bonded OH group (Murukan *et al*., 2006). A strong-featured band observed at 1620-1640 cm^{-1} in the spectra of all ligands is attributed to (C=N) vibrational mode. The band due to (C=O) of isatin segment (Naumov *et al*., 2001) was found at 1710-1740 cm^{-1} which transferred to lower frequencies by 30-40 cm^{-1} in the spectral data of complexes. Vibrational characteristic of phenolic (C-O) bands are observed (West *et al*., 1990) at 1250-1260 cm^{-1} in the spectra of ligands BHPIH, MHPIH and CHPIH which decreased by 30-40 cm^{-1} in the spectra of metal ion complexes. The wide band due to hydrogen bonded OH of the 2-aminophenol moiety vanished from the region 3000-3250 cm^{-1} in the spectra of metal complexes indicating the deprotonation of OH group with formation of metal-oxygen bond. The ligands BMPIH,

Table 3: Infrared spectral data (cm^{-1}) of ligands and its complexes

Compounds	ν(O-H)	ν(C=N)	ν(C=O)	ν(N-H)	ν(M-O)	ν(M-S)	ν(M-N)
BHPIH	3100	1627	1719	3030	-	-	-
BMPIH	-	1636	1710	3230	-	-	-
MHPIH	3060	1640	1740	3170	-	-	-
MMPIH	-	1624	1720	3300	-	-	-
CHPIH	3250	1620	1738	3010	-	-	-
CMPIH	-	1631	1724	3260	-	-	-
$[Fe(BHPI)_2]Cl$	-	1605	1679	3288	438	-	470
$[Fe(BMPI)_2]Cl$	-	1617	1675	3209	-	401	488
$[Fe(MHPI)_2]Cl$	-	1612	1700	3160	433	-	472
$[Fe(MMPI)_2]Cl$	-	1607	1687	3296	-	405	481
$[Fe(CHPI)_2]Cl$	-	1609	1707	3003	430	-	480
$[Fe(CMPI)_2]Cl$	-	1611	1690	3250	-	404	479
$[Co(BHPI)_2]Cl$	-	1613	1687	3015	435	-	488
$[Co(BMPI)_2]Cl$	-	1591	1680	3218	-	403	487
$[Co(MHPI)_2]Cl$	-	1604	1706	3154	439	-	476
$[Co(MMPI)_2]Cl$	-	1606	1681	3289	-	400	489
$[Co(CHPI)_2]Cl$	-	1592	1699	2991	436	-	479
$[Co(CMPI)_2]Cl$	-	1597	1686	3248	-	402	476
$[Mn(BHPI)_2]OAc$	-	1600	1689	3024	431	-	482
$[Mn(BMPI)_2]OAc$	-	1608	1679	3220	-	402	489
$[Mn(MHPI)_2]OAc$	-	1598	1705	3154	439	-	475
$[Mn(MMPI)_2]OAc$	-	1603	1684	3278	-	400	481
$[Mn(CHPI)_2]OAc$	-	1605	1707	2988	440	-	477
$[Mn(CMPI)_2]OAc$	-	1596	1690	3244	-	405	471
$[Cr(BHPI)_2]Cl$	-	1601	1683	3019	432	-	479
$[Cr(BMPI)_2]Cl$	-	1595	1676	3226	-	403	485
$[Cr(MHPI)_2]Cl$	-	1625	1709	3143	437	-	473
$[Cr(MMPI)_2]Cl$	-	1590	1682	3291	-	404	483
$[Cr(CHPI)_2]Cl$	-	1588	1698	2998	436	-	490
$[Cr(CMPI)_2]Cl$	-	1618	1689	3240	-	401	478

MMPIH and CMPIH attained from 2-aminothiophenol do not show useful S-H stretching vibration, since it exhibited very weak bands in free ligands and complex spectra. The involvement of the SH group in chelation is established from the shift of ν_{asym}(CS) and ν_{sym}(CS) from710-715 and 750-756 cm^{-1} to lower or higher wave numbers in the spectral data of the complexes (Mishra, 1999). The bonding of azomethine nitrogen to metal ion was confirmed by lowering of frequency by 20-35 cm^{-1} in the spectra of obtained complexes (Sharma *et al*., 1987).

The non-ligand bands emerging in the spectra of the complexes in regions 470-490, 400-405 and 430-440 cm^{-1} may be assigned to ν(M-N) (Tripathi *et al*., 2008), ν(M-S) (Chandra *et al*., 2002) and ν(M-O) (El-Sawaf *et al*.,

1998) vibrations. Therefore, from the infrared spectra, it is evident that the Schiff base ligands BHPIH, BMPIH, MHPIH, MMPIH, CHPIH and CMPIH are bonded to the metal ion in a monobasic tridentate pattern through the deprotonated phenolic oxygen or thiolic sulphur, azomethine nitrogen and carbonyl oxygen of the isatin moiety.

^{1}H NMR spectral analysis

The ^{1}H NMR spectral analysis of Schiff base ligands and their Co(III) complexes (Table 4) have been carried out in DMSO-d_6. The following conclusions can be derived on analysing the spectra of the ligands and their complexes:

a) The spectrum of free ligands BHPIH, MHPIH and CHPIH show a characteristic peak due to intra molecular hydrogen bonded -OH group at δ 12.14-12.19 ppm. Disappearance of this signal in corresponding metal complexes indicates that the phenolate group is corelated to the centre metal ion along the phenolic oxygen after deprotonation.

b) The signal at δ 9.60-9.85 ppm in the spectral data of non-coordinated ligands are consignable to the N-H proton of the isatin component. No major alteration was observed for such proton in the spectra of the complexes indicating non-involvement of this group in coordination.

c) The signal due to S-H proton emerge at δ 9.30-9.52 ppm in spectra of the ligands BMPIH, MMPIH and CMPIH and they vanish in spectra of the corresponding metal complexes suggesting coordination of the sulphur to central metal ion after deprotonation.

d) The peaks of the protons of benzene ring are obtained in the region δ 7.60-7.90 ppm as a multiplet and were found moderately downfield in the complexes due to coordination of the numerous groups present in the ring.

Biological Screening

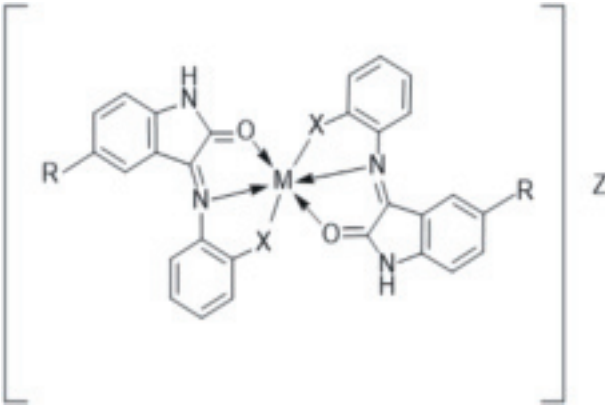
All the ligands and complexes were tested for *in vitro* growth inhibitory activity against pathogenic bacteria. Conventional temperature, vital nutrients and growth medium free from other pathogens were emersed for preparation of cultures. The anti-bacterial activities were estimated against *Escherichia coli* (-) and *Staphylococcus aureus* (+) by the paper disc plate method. The nutrient agar media (beef extract, NaCl, agar-agar and water) and 5mm diameter paper discs (Whatman No.1) were used. The compounds were dissolved in methanol in 100 and 500 ppm concentrations. The filter paper discs were submerged in different solutions, dried and placed in Petri dishes already seeded with the test organisms. The dishes were incubated for 24-30 h at 28±2^{0}C. The formed zone of inhibition around each disc was measured precisely.

The ligands as well as complexes were screened against *Aspergillus niger* and *Aspergillus alternatum* by agar plate diffusion method using potato dextrose agar (PDA). Solutions of each compound with concentration of 50, 100 and 200 ppm in DMSO were prepared for testing and then mixed with the PDA medium (potato, glucose, agar-agar and water). The media were poured on sterilized Petri dishes. 5mm discs of five-day old fungi were transferred to the center of plate after solidification. The plates were incubated at 25±1^{0}C. The radial growth of fungi was measured at 12 hrs gap from 36 hrs after inoculation. The percentage inhibition was determined with following formula:

$$\% \text{ Inhibition} = \frac{100(C-T)}{C}$$

where, C and T are the diameters of the fungi colony in the control (an untreated plate) and test plates respectively.

It is evident that the activity increased after complexation. The concentration plays an important role in the degree of inhibition. Thus, it can be concluded that the complexes are more potent than the corresponding ligands. Therefore, on the basis of elemental analysis, molar conductance results and spectral data, the following structure of metal complex can be proposed (Fig. 2)



M= Cr(lll), Mn(lll), Fe(lll) and Co(lll); Z = Cl or OAc

Fig. 2: Structure of complexes

CONCLUSION

The present investigation revealed synthesis of Iron(lll), Cobalt(lll), Manganese(lll) and Chromium(lll) complexes in which BHPIH, BMPIH, MHPIH, MMPIH, CHPIH and CMPIH act as monobasic tridentate ligand coordinating through O/S/N donor atoms and forming octahedral chelates. The analytical studies suggest the formula of the complexes as $[M(L)_2]Z$ where L = ligand

Table 4: ^{1}H NMR spectral data (δ, ppm) of the ligands and their Co(III) complexes

Compounds	CH_3	N-H	S-H	O-H	Aromaticring
BHPIH	-	9.62	-	12.15	7.81
BMPIH	-	9.85	9.46	-	7.65
MHPIH	1.4	9.71	-	12.19	7.84
MMPIH	1.5	9.60	9.30	-	7.75
CHPIH	-	9.78	-	12.14	7.68
CMPIH	-	9.80	9.52	-	7.90
$[Co(BHPI)_2]Cl$	-	9.61	-	-	7.74
$[Co(BMPI)_2]Cl$	-	9.85	-	-	7.61
$[Co(MHPI)_2]Cl$	1.3	9.73	-	-	7.80
$[Co(MMPI)_2]Cl$	1.7	9.62	-	-	7.62
$[Co(CHPI)_2]Cl$	-	9.75	-	-	7.60
$[Co(CMPI)_2]^{Cl}$	-	9.81	-	-	7.73

Table 5: Antibacterial and antifungal activities of the ligands and its complexes

Compounds	Antibacterial activity Inhibition zone (μgmL^{-1})				Antifungal activity Inhibition zone (μgmL^{-1})					
	E. Coli		*S. aureus*		*A. niger*			*A. alternatum*		
	100ppm	500ppm	100ppm	500ppm	50ppm	100ppm	200ppm	50ppm	100ppm	200ppm
BHPIH	15	22	11	16	10	21	25	12	22	26
BMPIH	09	16	12	15	07	23	29	09	17	28
MHPIH	12	20	14	22	09	15	31	13	19	31
MMPIH	10	19	12	27	08	19	28	16	27	33
CHPIH	18	23	10	17	21	26	30	11	24	29
CMPIH	14	21	09	14	24	29	33	14	18	25
$[Fe(BHPI)_2]Cl$	22	24	13	18	15	24	34	16	28	36
$[Fe(BMPI)_2]Cl$	14	19	18	21	12	27	41	11	22	32
$[Fe(MHPI)_2]Cl$	15	24	19	27	11	17	39	22	24	34
$[Fe(MMPI)_2]Cl$	14	20	15	32	14	22	39	21	35	47
$[Fe(CHPI)_2]Cl$	20	28	11	21	22	29	38	15	26	33
$[Fe(CMPI)_2]Cl$	16	22	14	16	27	30	27	17	21	27
$[Co(BHPI)_2]Cl$	17	20	19	22	13	23	33	14	21	31
$[Co(BMPI)_2]Cl$	17	22	20	21	09	26	32	16	24	33
$[Co(MHPI)_2]Cl$	14	26	17	24	14	18	36	17	22	47
$[Co(MMPI)_2]Cl$	12	23	14	29	11	21	29	19	33	44
$[Co(CHPI)_2]Cl$	16	29	15	20	22	28	31	18	29	32
$[Co(CMPI)_2]Cl$	19	22	12	18	25	36	37	21	24	29
$[Mn(BHPI)_2]OAc$	21	23	20	24	16	26	36	18	27	34
$[Mn(BMPI)_2]OAc$	19	18	19	24	14	28	35	15	25	36
$[Mn(MHPI)_2]OAc$	16	25	18	26	17	20	38	20	23	40
$[Mn(MMPI)_2]OAc$	15	21	17	31	16	25	30	22	36	46
$[Mn(CHPI)_2]OAc$	23	32	16	19	24	30	33	17	27	30
$[Mn(CMPI)_2]OAc$	18	23	18	21	26	37	35	23	31	32
$[Cr(BHPI)_2]Cl$	19	25	17	25	18	25	38	22	24	34
$[Cr(BMPI)_2]Cl$	15	21	23	28	19	37	33	17	29	38
$[Cr(MHPI)_2]Cl$	17	28	20	27	23	25	42	24	26	44
$[Cr(MMPI)_2]Cl$	14	25	18	30	17	22	32	25	37	47
$[Cr(CHPI)_2]Cl$	22	31	20	22	25	31	34	20	32	33
$[Cr(CMPI)_2]Cl$	23	24	17	20	23	38	41	26	29	36

and Z= Cl or OAc. The values of molar conductance show the electrolytic nature of metal complexes. The results of antimicrobial activity suggest the enhanced activity of complexes against microbes in comparison to ligands.

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