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Synthesis and structural characterization studies of cobalt(III), manganese(III) and iron(III) schiff base complexes

George Lukose^a, K. Mohanan^{b*}, Simi Saju^a and Sherifa Rahim^a

^aDepartment of Chemistry, St. John`s College, Anchal, Kollam, Kerala, India ^bDepartment of Chemistry, University of Kerala, Trivandrum, Kerala, India

ABSTRACT

Coordination behaviour of the ligands towards trivalent metal ions has been investigated by IR, molar conductance, magnetic moments and electronic spectral measurements. The ligands employed are TAA, PAA, ISA and IDA. The ligands and their metal complexes have been investigated with particular reference to the structure and bonding of the ligand moiety in the metal complexes. All the complexes are intensely coloured and are insoluble in water and methanol and soluble in DMSO. They possess 1:2 metal-ligand stoichiometry and formulation of the complexes has been made on the basis of their analytical data and magnetic susceptibility measurements. Molar conductance values were in the range expected for a 1:1 electrolytic species. The bonding nature of the ligands to the metal ion has been determined by careful comparison of the IR spectra of the complexes and the ligands. All the ligands function as neutral tridentate/bidentate, in all the complexes utilizing the carbonyl oxygen atoms and azomethine nitrogen atoms for coordination. IR spectra together with molar conductance values adequately confirmed the ionic nature of acetate group. The cyclic voltammogram of $[Fe(PAA)_2Cl_2]Cl$ showed the quasi-reversible reduction nature. The indexing of the X-ray diffraction pattern obtained for the [Fe(TAA)₂]Cl₃ complex indicated that it has an orthorhombic crystal lattice. The Schiff base ligands and their metal complexes were tested against four pathogenic bacteria (Staphylococcus aureus, Bacillus substilis) as Gram-positive bacteria, and (Escherichia coli, Klebsiella pneumonia) as Gram-negative bacteria. All the metal complexes exhibit higher antibacterial activity than the free ligand. Iron(III) complexes have higher bacterial activity than the other complexes.

Keywords: Schiff base, IR, Cyclic voltammogram, X-ray diffraction, Antibacterial activity.

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and find extensive applications in different fields. Schiff bases and their biologically active complexes have been often used as chelating ligands in the coordination chemistry of transition metals, radiopharmaceuticals for cancer targeting, agrochemicals, model systems for biological macro molecules and catalysts [1-5]. The main target of the present study is to synthesize a series of trivalent metal complexes with some potentially tridentate and bidentate ligands which showed more coordination ability of the highly coloured ligands that incorporate several binding sites. The ligands and their metal complexes have been examined with particular reference to the structure and bonding of the ligand moiety in the metal complexes [6-9]. Coordination behaviour of the ligands towards trivalent metal ions has been investigated by IR, molar conductance, magnetic moments and electronic spectral measurements. The trivalent Schiff base metal complexes are investigated for antibacterial properties.

EXPERIMENTAL SECTION

Reagents

The chemicals used for synthesis in this study were of A.R. grades (Fluka and E-Merck). For physico-chemical

measurements solvents were purified by standard methods given by Weissbarger [10]. The solvents used were of spectroscopic grade.

Physical measurements

Elemental analysis (C, H, N) was obtained using Perkin Elmer elemental analyzer. The melting point of the compounds determined on a melting point apparatus. The purity of ligands and their metal complexes were tested by TLC. Molar conductance measurements were carried out with 10⁻³ M solutions of the complexes in appropriate solvents at room temperature using a Systronics direct reading digital conductivity meter Type 304 with a cell having cell constant of one. Magnetic susceptibility measurements of complexes were measured at room temperature using a Magway MSB Mk1 susceptibility balance. The measurements were made with solid specimens. The standard used was $Hg[Co(NCS)_4]$ and diamagnetic corrections were carried out using Pascal's constants. The infrared spectra of the compounds were recorded using Shimadzu 8201 PC FT infrared spectrophotometer and Perkin Elmer 817 infrared spectrophotometer. Far IR spectra were recorded at room temperature in the solid state on a Polytec FIR 30 Fourier spectrophometer using CsI discs. Electronic spectra of the complexes were recorded in suitable solvents in the range of 250-900 mm, using a Shimadzu 1601 UV-Visible spectrophotometer and a Hitachi 320 UV-Visible spectrometer. Electrochemical behaviour of iron(III) complex was studied with the help of a BAS CV-50 analyser employing glassy carbon as working electrode, Ag/AgCl as reference electrode and platinum wire as auxiliary electrode. The working media consisted of DMSO and Bu_4NPF_6 as supporting electrolyte. The X-ray diffraction pattern iron(III) complex was carried out on a Siemens D 5005 model X-ray Spectrometer. Copper X-ray tubes, for which the wavelength of the strongest radiation ($k\alpha_1$) is approximately (Cu=1.54 Å) is used for the diffraction study. Antibacterial activities of ligands and their complexes have been carried out by agar diffusion method.

Synthesis of ligands:

a) Synthesis of 4-N-(2-thienylidene)aminoantipyrine (TAA)

4-Aminoantipyrine (0.01 mol) was dissolved in methanol (30 mL) and to this solution, thiophene-2-carboxaldehyde (0.01 mol) dissolved in methanol (25 mL) was added slowly with constant stirring. The mixture was then refluxed on a water bath for 3 h. It was concentrated to about half of its original volume, cooled and allowed to crystallize. The Schiff base formed was filtered, washed several times with methanol and dried in vacuum. It was further purified by recrystallization from ethanol. Glittering crystals having orange-red colour was obtained.

b) Synthesis of 2,3-dimethyl-1-phenyl-4-[(2-pyrrolyl)methylene]aminantipyrine (PAA)

4-Aminoantipyrine (0.01 mol) was dissolved in methanol (30 mL) and to this solution, pyrrole-2-carboxaldehyde (0.01 mol) dissolved in methanol (25 mL) was added slowly with constant stirring. The mixture was then refluxed on a water bath for 3 h. It was concentrated to about half of its original volume, cooled and allowed to crystallize. The Schiff base formed was filtered, washed several times with methanol and dried in vacuum. It was further purified by recrystallization from ethanol.

c) Synthesis of 2,3-dimethyl-1-phenyl-4-[(3-isatiaylidene)]aminoantipyrine (ISA)

4-Aminoantipyrine (0.01 mol) was dissolved in methanol (30 mL) and to this solution, isatin (0.01 mol) dissolved in methanol (25 mL) was added slowly with constant stirring. The mixture was then refluxed on a water bath for 3 h. It was concentrated to about half of its original volume, cooled and allowed to crystallize. The Schiff base formed was filtered, washed several times with methanol and dried in vacuum. It was further purified by recrystallization from ethanol and yellow colour crystal was obtained.

d) Synthesis of 2,3-dimethyl-1-phenyl-4-[(3-indoyl)methylene]aminoantipyrine (IDA)

4-Aminoantipyrine (0.01 mol) was dissolved in ethanol (30 mL) and to this solution, indole-3-carboxaldehyde (0.01 mol) dissolved in ethanol (25 mL) was added slowly with constant stirring. The mixture was then refluxed on a water bath for 3 h. It was concentrated to about half of its original volume, cooled and allowed to crystallize. The Schiff base formed was filtered, washed several times with methanol and dried in vacuum. It was further purified by recrystallization from ethanol.

Synthesis of metal complexes

Cobalt(III) complex

 $[Co(NH_3)_5(CO_3)]NO_3.^{1/2}H_2O$ was prepared according to a reported procedure. A suspension of pentammine carbonatocobalt(III) nitrate (0.005 mol) in methanol (30 mL) was added in small portions to a refluxing methanolic solutions (50 mL) of the appropriate ligand (0.01 mol) and pH of the solution was adjusted to 5.0-5.5. After continued refluxing for 9 h, mixture was filtered hot and the filtrate was concentrated by evaporation on a waterbath. The brown crystals obtained on subsequent cooling was filtered, washed with methanol and dried in *vacuum*.

Manganese(III) complex

Manganese(III) acetate dihydrate was prepared by a reported method. The ligand (0.01 mol) dissolved in methanol (50 mL) was refluxed on a water-bath and a methanolic solution (30 mL) of manganese(III) acetate (0.005 mol) was added to the above solution in small portions and the refluxing was continued for 5 h. Afterwards, the dark brown solution obtained was evaporated to half of its original volume and allowed to crystallize; dark brown complex that separated was filtered, washed with methanol and dried in *vacuum*.

Iron(III) complex

To a hot methanolic solution (30 mL) of the ligand (0.01 mol) added methanolic solution (20 mL) of the ferric chloride (0.005 mol) in small portions with constant stirring. The solution was then refluxed on a water-bath for 5 h. It was then evaporated half of its initial volume and allowed to crystallize. The dark brown complex separated was filtered, washed with methanol and dried in *vacuum*.

Biological activities

The synthesized ligands and their complexes were screened for their biological activities by the reported method [11]. The bacteria were subcultured in agar medium. The petridishes were incubated for 24 h at 37°C. The standard antibacterial drug was also screened under similar conditions for comparison. The wells were dug in the agar media using sterile metallic borer. Growth inhibition (mm) was compared with standard drugs.

RESULTS AND DISCUSSION

Analytical data of the ligands and their trivalent metal complexes are given in Table 1. All the complexes are intensely coloured and are insoluble in water, methanol and soluble in DMSO. Formation of the metal complexes can be represented by the following general equations,

	Elemental analysis				Molar	Magnetic		
Ligand/complex	С	H	N	м	Ohm ⁻¹ cm ² mol ⁻¹	R M		
	64.62	5.08	14.13	-	-	D .111		
TAA	(64.09)	(5.32)	(14.02)			-		
	55.20	4.75	10.16	6.64				
$[Mn(TAA)_2](OAc)_3$	(55.32)	(4.43)	(10.56)	(6.67)	146.78	4.92		
	50.78	3.99	11.10	7.38				
$[Fe(TAA)_2]Cl_3$	(50.61)	(3.73)	(11.08)	(7.42)	149.67	5.90		
	45.77	3.60	15.01	7.02		D		
$[Co(TAA)_2](NO_3)_3$	(45.39)	(4.08)	(15.61)	(7.20)	151.02	D		
DAA	68.55	5.75	19.99	-				
PAA	(68.57)	(5.63)	(19.78)		-	-		
	56.45	3.12	13.86	6.79	50.12	1.00		
$[Mn(PAA)_2(OAc)_2]OAc$	(56.56)	(4.99)	(13.49)	(7.32)	52.13	4.96		
$(\mathbf{E}_{\mathbf{a}}(\mathbf{D}\mathbf{A},\mathbf{A}),\mathbf{C}^{\dagger})$	53.17	4.46	15.50	7.73	51.09	5.07		
[Fe(PAA) ₂ Cl ₂]Cl	(53.10)	(4.35)	(15.61)	(7.45)	51.08	5.97		
$[C_{\alpha}(\mathbf{P}, \mathbf{A}, \mathbf{A}), (\mathbf{N}_{\mathbf{O}}, \mathbf{A})]$ NO	47.71	4.00	19.13	7.32	50.07	D		
$[CO(FAA)_2(INO_3)_2]INO_3$	(47.23)	(4.67)	(18.51)	(7.59)	50.97	D		
IS A	68.66	4.85	16.86	-				
ISA	(68.49)	(4.65)	(16.65)		-	_		
$[M_{P}(ISA), (OAc), IOAc$	65.34	5.11	16.93	6.79	156.08	1 93		
	(65.87)	(4.51)	(16.37)	(6.34)	150.00	4.75		
[Fe(ISA) ₂ Cl ₂]Cl	55.19	3.90	13.55	6.75	159.07	5.91		
	(55.09)	(3.87)	(13.34)	(6.34)	159.07	5.91		
$[C_0(ISA)_2(NO_2)_2]NO_2$	50.17	3.55	16.94	6.48	151.02	D		
[C0(13/4)2(1403)2]1403	(50.12)	(3.34)	(16.32)	(6.34)	151.02	D		
IDA	68.66	4.85	16.87	-	-	-		
112/1	(68.56)	(4.34)	(16.87)					
[Mn(IDA) ₂] (OAc) ₃	58.93	4.16	12.50	6.13				
	(58.18)	(4.23)	(12.34)	(6.34)	50.19	4.98		
[Fe(IDA) ₂] Cl ₃	55.19	3.90	13.55	6.75	10.00			
	(55.35)	(3.53)	(13.45)	(6.81)	49.08	5.98		
$[Co(IDA)_2](NO_3)_3$	52.00	3.67	17.56	6.71	50.05			
L · · · · · · · · · · · · · · · · · · ·	(52.51)	(3.45)	(17.36)	(7.49)	53.37	D		
(Calculated values are given in square brackets); D-Diamagnetic								

Table 1. Analytical data and other details of trivalent metal complexes

 $MX_3 + 2L \rightarrow [ML_2]X_2$

 $MX_3 + 2L \rightarrow [ML_2X_2]$

where M = Mn(III) or Fe(III), X = OAc or Cl; L=TAA, PAA, ISA or IDA

They possess 1:2 metal-ligand stoichiometry and formulation of the complexes has been made on the basis of their analytical data and magnetic susceptibility measurements. The elemental analysis data (Table 1) of the ligands and their metal complexes are consistent with the calculated results from the empirical formula of each compound. Molar conductance values (Table 1) were in the range expected for a 1:1 electrolytic species [12].

Infrared spectra

The bonding nature of the ligands to the metal ion has been determined by careful comparison of the IR spectra of the complexes and the ligand, TAA. Only those IR bands diagnostic of coordination are considered and they are presented in Table 2. The ring v(C=N) observed at 1590 cm⁻¹ in the spectrum of the ligand is shifted to lower frequency 20-25 cm⁻¹ in the spectra of the metal complexes suggesting the coordination of azomethine nitrogen to the metal ion. Lowering of v(C=N) stretching frequency may be attributed to lowering of v(C=N) bond order as a result of (M-N) bond formation. The v(C=O) band is depressed about 35-40 cm⁻¹ indicating coordination by the C=O group and formation of (M-O) bonds. The additional band observed in the region 330-340 cm⁻¹ can be attributed to (M-S) bond formation. Thus the ligands acted as neutral tridentate coordinating to the metal ion by a bidentate manner through the azomethine nitrogen and carbonyl oxygen. The bonding mode of the ligand, ISA towards the trivalent metal ions has been established through IR spectral data (Table 2). The ligand acted as a neutral bidentate coordinating to the metal ions through ON donor sequence. The ligand, IDA acted as neutral tridentate coordinating the metal ion ONO donor manner. The M-Cl bands are observed in the range 360-370 cm⁻¹ [13,14].

Table 2.	Infrared	spectral	data of	ligands	and their	trivalent	metal c	omplexes

	IR bands (cm ⁻¹)						
Ligand/complexes	N (C=N)	N (C=O)	N (C=O) pyrazoline	N (M-N)	N (M-O)		
TAA	1590	1657	-	-	-		
$[Mn(TAA)_2](OAc)_3$	1570	1615	-	466	534		
[Fe(TAA) ₂]Cl ₃	1568	1618	-	464	538		
$[Co(TAA)_2]NO_3$	1567	1620	-	468	540		
PAA	1635	1713	-	-	-		
[Mn(PAA) ₂ (OAc) ₂]OAc	1615	1674	-	466	540		
[Fe(PAA) ₂ Cl ₂]Cl	1618	1678	-	465	542		
$[Co(PAA)_2(NO_3)_2]NO_3$	1613	1675	-	468	545		
ISA	1590	1646	1658	-	-		
[Mn(ISA)2(OAc)2] OAc	1570	1610	1630	469	538		
[Fe(ISA) ₂ Cl ₂] Cl	1566	1598	1627	473	544		
[Co(ISA) ₂ (NO ₃) ₂] NO ₃	1565	1605	1629	465	540		
IDA	1596	1650	-	-	-		
$[Mn(IDA)_2] (OAc)_3$	1575	1618	-	465	537		
[Fe(IDA) ₂]Cl ₃	1573	1614	-	470	541		
[Co(IDA) ₂] (NO ₃) ₃	1571	1615	-	463	545		

For the manganese(III) complexes, in addition to the ionic acetate, characteristic bands for $v_S(COO^-)$ and $v_{as}(COO^-)$ are observed for coordinated acetate group at ~1380 cm⁻¹ and ~1600 cm⁻¹ respectively. These bands with a separation of Δv 220 cm⁻¹ adequately support monodentate coordination by acetate group. In the case of cobalt(III) complexes, the infrared spectra exhibit band assignable to the ionic nitrate [14]. The strong bands occurring at 1390, 825 and 710 cm⁻¹ corresponds to v_3 , v_1 and v_5 respectively. This is supported by molar conductance measurement. In all the cases the conductance and analytical data are in good agreement with the spectral data.

Electronic spectra and magnetic susceptibility

In an octahedral field, ⁵D term of manganese(III) ion with d⁴ configuration splits into ⁵E_{2g} and ⁵T_{2g}. These are the only quintet state present hence only one d-d transition (${}^{5}E_{2g} \rightarrow {}^{5}T_{2g}$) is expected for manganese(III) complexes. However, high-spin octahedral manganese(III) complexes are susceptible to Jahn-Teller distortion. Hence more than one transition involving the split component of ${}^{5}E_{2g}$ and ${}^{5}T_{2g}$ in low symmetry occur. The spectra of some six coordinate manganese(III) complexes are difficult to interpret in all their details, because both static and dynamic Jahn-Teller effects perturb the picture based on octahedral symmetry. Usually, the spin free manganese(III)

complexes with octahedral geometry give one charge transfer band around 25,000 cm⁻¹ and a spin allowed d-d transition band (${}^{5}E_{2g} \rightarrow {}^{5}T_{2g}$) around 20,000 cm⁻¹. In the present complexes, the band around 18,500 cm⁻¹ with a weak shoulder around 23,000 cm⁻¹ is assignable to d-d transition. This broad band occurring at lower frequency with increased intensity indicates the lowering of symmetry from octahedral configuration [15]. The d⁴ configuration of manganese(III) can have either four unpaired electrons or two unpaired electrons in octahedral complexes. Most of the manganese(III) complexes are high-spin and the spin only value expected is 4.90 B.M. In the present complexes the magnetic moments are in the range of 4.92-4.98 B.M corresponding to four unpaired electrons. These values also suggest the absence of any kind of exchange interaction.

Iron(III) with d⁵ configuration has ground state ${}^{6}A_{1g}$ in an octahedral weak field arising out of the free ion term ${}^{6}S$. This is the only sextet state present and it has no angular momentum. Therefore the magnetic moment values are very close to spin-only value of 5.9 B.M. Low-spin complexes with a ground state configuration of ${}^{5}t_{2g}$, usually have considerable orbital contribution to their magnetic moments. At room temperature the magnetic moments of low-spin iron(III) complexes are 2.3 B.M and this is found to be temperature dependent.

Though iron(III) isoelectronic with manganese(II), it is difficult to have any spectra-structure correlation in the case of iron(III) complexes. There is greater tendency for iron(III) to have charge transfer bands in the ultraviolet region, which have sufficiently strong low-energy wings in the visible region to obscure almost completely the weak spin forbidden d-d bands. However spectral feature of iron(III) ion in octahedral surround are well in accordance with the theoretical predictions. All the electronic transitions are thus spin-forbidden, as well as Laporte forbidden, so that the ligand field bands in the spectrum of the iron(III) complex are very weak. In the present iron(III) complexes the weak ligand field bands are masked by the intense charge transfer band at 19600 cm⁻¹ hence it is difficult to have any structure correlation from the spectral data. Iron(III) complexes exhibit an effective magnetic moment between 5.90-5.98 B.M which is close to the value expected for an octahedral geometry and shows absence of super exchange phenomena in the complexes. The cobalt(III) complex exhibited a strong band at 16,220 cm⁻¹ with a shoulder at 22,100 cm⁻¹, arising from ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ transitions respectively. These observations along with diamagnetic nature are indicative of an octahedral geometry around the cobalt(III) ion.





(*M* = *Co*(*III*), *Fe*(*III*) or *Mn*(*III*); (*X* = *Cl/OAc/NO*₃) **Fig. 2. Structure of trivalent metal complexes**

Cyclic voltammetry

During the course of potential cycle (Fig. 1) of $[Fe(PAA)_2Cl_2]Cl$, two reduction peaks are detected at $Ep_c = -0.651$ V and $Ep_a = -0.867$ V. In order to explain the reduction and oxidation processes, the following mechanism has been proposed. The voltammogram of $[Fe(PAA)_2Cl_2]Cl$ showed the quasi-reversible reduction nature.

 $[Fe(III)(PAA)_2Cl_2]^+ + 1e \rightarrow [Fe(II)(PAA)_2Cl_2]^+$

In addition to this, ΔEp value is less than 0.057 V and the ratio of the anodic to cathodic peak current close to unity supports the above single electron transfer mechanism [16]. On the basis of the above spectral data results, the structure (Fig. 2) has been proposed for the tridentate complexes.

Powder X-ray diffraction

The XRD data obtained are presented in Table 3 and its diffraction pattern is shown in Fig. 3. The Bragg angles and the set of inter planar spacing obtained by measuring the X-ray diffraction pattern of the complex were related to the unit cell parameters and Miller indices assigned to the individual reflections with the help of expressions involving $\sin^2\theta$. The relation between $\sin^2\theta$, the Miller indices and the unit cell dimensions is less cumbersome than the relationship between inter planar spacing and the Miller indices [17,18]. The pattern was indexed by trial and error method. The indexing of the X-ray diffraction pattern obtained for the [Fe(TAA)₂]Cl₃ complex indicated that it has an orthorhombic crystal lattice. The diffractogram recorded 19 reflections with 2θ values ranging from 3 to 80° . The maximum recorded was at 7.6488°, which corresponded to 11.7485 Å d-spacing. A careful comparison of the calculated and observed $\sin^2\theta$ values of the complex reveal that they are in good agreement. The unit cell dimensions for the orthorhombic system were calculated using the relation, $\sin^2\theta_{hkl} = Ah^2 + Bk^2 + Cl^2$, where $A = \lambda^2/4a^2$, $B = \lambda^2/4b^2$ and $C = \lambda^2/4c^2$ are the lattice constants. The lattice parameters for the complex [Fe(TAA)₂]Cl₃ are a = 11.6141, b = 9.1283 and c = 5.7990 and the unit cell volume is calculated to be 132.06 Å. The XRD data reveals that the ligand is more symmetric than the metal complex. On coordination the symmetry of the ligand gets lowered.



Fig. 3. Powder X-ray diffraction pattern of [Fe(TAA)₂]Cl₃

Peak No.	d(Å)	Observed sin ² θ	hkl	Observed 20	Calculated 20
1	6.1461	0.0157	200	14.3993	13.7260
2	4.8617	0.0251	210	18.2324	18.7365
3	4.4945	0.0293	011	19.7360	19.7110
4	2.2263	0.0332	111	21.0025	20.8035
5	4.0097	0.0369	110	22.1510	22.1495
6	3.5859	0.0461	310	24.8084	24.2997
7	3.5299	0.0476	301	25.2078	25.6037
8	3.3261	0.0536	120	26.7808	26.9746
9	3.1777	0.0587	400	28.0561	27.6987
10	3.0316	0.0645	220	29.4380	29.4014
11	2.9528	0.0680	021	30.2418	30.0024
12	2.7894	0.0762	401	32.0599	31.5690
13	2.5752	0.0894	500	34.8087	34.8087
14	2.4457	0.0991	212	36.7146	35.7076
15	2.3800	0.1047	420	37.7658	38.2596
16	2.1483	0.1285	230	42.0214	41.8579
17	2.0692	0.1385	031	43.7098	42.2679
18	1.9558	0.1551	103	46.3873	46.5269
19	1.7846	0.1862	303	51.1410	50.7067

Table 3. Powder X-ray diffraction data of [Fe(TAA)₂]Cl₃

Table 4. Antimicrobial activity of the ligands and their complexes

Ligand/aammlayaa	Zone of inhibition (mm)						
Liganu/complexes	S. aureus	B. subtilis	E. coli	K. pneumonia			
TAA	2	1	2	3			
$[Mn(TAA)_2](OAc)_3$	15	13	13	12			
[Fe(TAA) ₂]Cl ₃	18	14	16	14			
[Co(TAA) ₂]NO ₃	13	16	15	10			
PAA	11	17	13	13			
[Mn(PAA) ₂ (OAc) ₂]OAc	15	13	13	12			
[Fe(PAA) ₂ Cl ₂]Cl	18	14	16	14			
[Co(PAA) ₂ (NO ₃) ₂]NO ₃	10	16	11	10			
ISA	12	11	12	13			
[Mn(ISA) ₂ (OAc) ₃]OAc	15	13	13	12			
[Fe(ISA)2Cl2]Cl	18	14	16	14			
$[Co(ISA)_2(NO_3)_2]NO_3$	13	16	15	10			
IDA	10	11	12	13			
[Mn(IDA) ₂](OAc) ₃	17	15	14	19			
[Fe(IDA) ₂] Cl ₃	19	20	21	24			
[Co(IDA) ₂] (NO ₃) ₃	13	13	15	11			

Antibacterial activities

The *in vitro* antibacterial activity of the Schiff base ligands and their metal complexes were tested at a concentration of 2 mg/ml using the agar well diffusion method. The growth inhibition zones were measured in diameter (mm) and the results are listed in Table 4. All the tested compounds showed good biological activity against microorganism. The obtained results (Fig. 4) indicate that the complexes were more effective against some microbes under identical experimental conditions. Iron(III) complex has higher bacterial activity than the other complexes. The bioactivity of the ligands and their complexes is found to be order Fe(III) > Co(II) >Mn(II) > L. The observed higher antimicrobial activities of the complexes can be explained on the basis of Tweedy's chelation theory [19-22]. Chelation will enhance the lipophilic character of the central metal atom, which subsequently favours its permeation through the lipid layers of the cell membrane and blocking the metal binding sites on enzymes of microorganisms.



Fig. 4. Antimicrobial activity of ligands and their metal complexes

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REFERENCES

[1] G H Hamor; D Watson. J. Pharma. Sci., 2006, 60, 925.

[2] M K Taylor; K D Trotter; J Reglinski; L E A Berlouis; A R Kennedy; C M Spickett; R J Sowden. *Inorg. Chim. Acta*, **2008**, 361, 2851.

[3] S Rayati; N Torabi; A Chaemi; S Mohebbi; A Wojtczak; A Kozakiewicz A. Inorg. Chim. Acta, 2008, 361, 1239.

[4] S Ren; R Wang; K Komatsu; P Bonaz-Krause; Y Zyrianov; CE Mckenna; C Csipke; Z A Tokes; E J Lien. J. Med. Chem., 2002, 45, 410.

[5] N Raman; A Thangaraja; C Kulandaisamy. *Transition Met. Chem.*, 2003, 28, 29.

[6] S R Kelode; P R Mandlik. J. Chem. Pharm. Res., 2012, 4(9), 4181.

[7] M B Fugu; N P Ndahi; B B Paul; A N Mustapha. J. Chem. Pharm. Res., 2013, 5(4), 22.

[8] R Shakru; N J P Subhashini; K S Kumar; Shivaraj. J. Chem. Pharm. Res., 2010, 2(1), 38.

[9] G P Deshapande; M P Wadekar; V M Raut; G H Murhekar. J. Chem. Pharm. Res., 2011, 3(1), 72.

- [10] A Weissberger; P S Proskauer; J A Hiddick; B E Troops. Organic Solvents, Interscience, New York, 1956.
- [11] A K Sadana; Y Miraza; K R Aneja; O Prakash. Eur. J. Med. Chem., 2003, 38, 533.

[12] W J Geary. Coord. Chem. Rev., 1971, 7, 81.

- [13] T D Thangadurai; S K Ihm. Synt. React. Inorg. Met.-Org. Chem., 2005, 35, 499-507.
- [14] K Nakamoto. Infrared and Raman spectra of Inorganic and Coordination compounds, Wiley, Canada, 2009.
- [15] B M Gatehouse; S E Livinstone; R S Nyholm. J. Chem. Soc., 1957, 15, 4222.
- [16] B Murukan; K Mohanan. J. Enzy. Inhib. Med. Chem., 2007, 22, 65.
- [17] A Anthonysamy; S Balasubramanian. Inorg. Chem. Commun., 2005, 8, 908.
- [18] Cullity, B. D. *Elements of X-ray diffraction*, Addision Wisely Pub., 2nd Edn., **1978**.
- [19] R W M D'Eye; E Wait. X-ray Powder Photography in Inorganic Chemistry, London, Butterwoths, 1960.
- [20] B G Tweedy. Phytopathalogy, 1964, 55, 910.
- [21] S C Singh; Gupta N; R V Singh. Indian J. Chem., 1995, 34(A), 733.
- [22] N Raman. Res. J. Chem. Environ., 2005, 9, 79.