Synthesis, Characterization, Coordination Behaviour and Biological Activity of Metal Complexes with Schiff Bases Derived from Isatin/Substituted Isatin

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Abstract

A series of new coordination complexes involving iron(III) and cob... complexes have been prepared with tridentate Schiff bases deriv... condensing isatin / N-methyl isatin / N-methylol isatin with 2-amino phen... amino benzenethiol in methanol in absence / presence of NaOH and prod... type $[M(L)_2]Cl$, $Na[M(L)_2]$ (M = Fe(III) or Co(III); LH = Schiff bases derive... isatin/N-methyl isatin/N-methylol isatin with 2-aminophenol/... aminobenzenethiol) have been isolated. The overall geometry... stereochemistry of these complexes were elucidated by elemental an... magnetic susceptibilities, electronic spectra, infrared spectra, ^{1}H NMR and... conductance measurements. All the trivalent metal ion complexes appea... 1:1 electrolytes. The ligands and their metal complexes have been scree... vitro for antifungal and antibacterial activities. The results indicate that... complexes antifungal and antibacterial activities of ligands increas... complexation due to chelation.

Keywords : Isatin, Schiff Bases, Metal Complexes, Spectral Analysis, Biological Activity

Introduction

Isatin is an endogenous indole with a variety of pharmacological actions including anticonvulsant, antimicrobial and antiviral activities[1-5], inhibition of monoamine oxidase and behavioral effects[6]. The chemical versatility of isatin derivatives has led to their extensive use as synthons for the preparation of many biologically active compounds[7-9]. Literature survey reveals that a lot of work has been done on isatin derived Schiff bases[10-13] and they were reported to exhibit a wide range of CNS activities as potentiation of pentabarbitone induced narcosis[14], analgesic[15-16], anticonvulsant[17-19], antidepressant[20], anti-inflammatory[21], anti HIV[22-23] and antimicrobial activity[24-28]. These Schiff bases can act as ligands having functional groups with nitrogen and oxygen as donor atoms for many transition metals[29-30]. These complexes have been used as catalysts for the oxidative self-coupling of alkyl phenols. Additional interest in the synthesis of transition metal complexes of isatin results from the fact that isatin exhibit an interesting keto-enolic equilibrium that can influence its coordination properties giving rise to cationic or neutral complexes with varied structure and reactivity. On account of these interesting structural and biological features shown by isatin derived Schiff bases and its transition metal complexes, interest in them continues to increase. The present section describes the synthesis and structural features of iron(III) and cobalt(III) derivatives of Schiff base derived from isatin / N-methyl isatin / N-methylol isatin and 2-aminophenol / 2-amino benzenethiol. The structure of ligands derived from the isatin / N-methyl isatin / N-methylol isatin and 2-aminophenol or 2-aminobenzenethiol is given below.
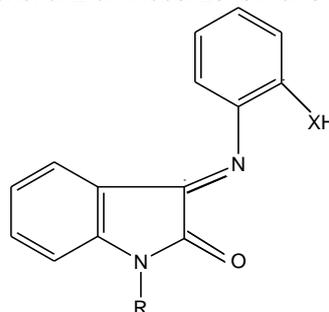
R	X	Abbreviation
H	O	L^1H
H	S	L^2H_2
CH_3	O	L^3H
CH_3	S	L^4H
CH_2OH	O	L^5H
CH_2OH	S	L^6H

Result and Discussion

The physical and analytical data of Schiff bases derived from isatin / N-methylisatin / N-methylolisatin and 2-aminophenol / 2-aminobenzenethiol and their complexes are given in Table 1. All the iron(III) and cobalt(III) complexes are light brown to dark brown in colour. Cobalt(III) complexes are stable but iron(III) complexes are sensitive towards air and moisture. They are soluble in ethanol, methanol, tetrahydrofuran, dimethylsulphoxide while insoluble in water. Molar conductance values of the soluble complexes in DMF (1mM solution at 25°C), indicated high values (94.6-98.2 $\Omega^{-1}mol^{-1}cm^2$) suggesting that they all are electrolyte in nature.

Magnetic Moment

The magnetic moments of the iron(III) and cobalt(III) complexes are summarized in Table 2. The iron(III) complexes (d^5, $t_{2g}^3e_g^2$) for $^6A_{1g}$ ground state (^6S ground term) showed magnetic moment between 5.63-5.92 B.M., there is no T.I.P. effect and no reduction of the moment below the spin only value by spin-orbit coupling with the higher ligand field terms. The magnetic moments are found to be independent of temperature[31]. The cobalt(III) complexes (d^6, $t_{2g}^6e_g^0$) are spin paired complexes possessing the $^1A_{1g}$ ground state (^1S ground term). There is no first order Zeeman effect (J=S=0). It indicates an octahedral surrounding of the donor atoms around the central metal ion producing a strong field[32].

Electronics Spectra

The electronic spectral data of iron(III) and cobalt(III) complexes is given in Table 2.The electronic spectra of all the iron(III) and cobalt(III) complexes were recorded in DMSO and band positions with tentative assignments were obtained. The electronic spectra of iron(III) complexes showed three bands at 13,050-13,710, 16,010-17,650 and 26,615-27,650 cm^{-1}, which are tentatively assigned to $^6A_{1g}\rightarrow^4T_{1g}$ (G), $^6A_{1g}\rightarrow^4T_{2g}$ (G) and $^6A_{1g}\rightarrow^4E_g$ (G) transitions[33]. The brownish colour of the complexes are ascribed to the presence of one or more low lying charge transfer absorption bands in the near infrared region which may be assigned to ligand field charge transfer. The electronic absorption spectra of cobalt(III) complexes low spin d^6 system characteristically exhibit two spin allowed transitions. In all the cobalt(III) complexes the $^1A_{1g}\rightarrow^1T_{1g}$ transition is clearly observed at 20,890-21,160 cm^{-1} while the higher energy $^1A_{1g}\rightarrow^1T_{2g}$ d-d transition was observed as a clearly defined shoulder (26,940-27,610 cm^{-1}) on a much intense charge transfer band. The spin forbidden transitions were not observed in the room temperature solution spectra[34].

Infrared Spectra

The selected IR bands and their tentative assignments are summarized in Table 3. The spectrum of the ligands L^1H and L^2H_2 in their uncoordinated form show a broad band at 3180 and 3200 cm^{-1} respectively attributable to N-H stretching frequency of isatin moiety[35]. A band ranging from 3000 to 3250 cm^{-1} and centered around 3075 cm^{-1} present in the spectra of the ligands derived from 2-aminophenol can be assigned to the hydrogen bonded OH group[36] which disappeared in the metal complexes indicating the formation of metal oxygen bond. A strong band observed at 1618-1635 cm^{-1} in the spectra of all the ligands is attributable to v(C=N) vibrational mode. The bonding of azomethine nitrogen to the metal ion is indicated by shifts in the v(C=N) bond to lower frequencies by 20-30 cm^{-1} in the spectra of complexes[37]. The band due to v(C=O) of isatin moiety[38] was found at 1700-1725 cm^{-1} which shifted to lower frequencies by 30-40cm^{-1}in spectra of complexes except the complexes of ligand L^2H_2.Vibrations characteristic of the phenolic v(C-O) are observed[39] at 1240-1256 cm^{-1} in the spectra of the ligands L^1H, L^3H and L^5H which decreased by 30-40 cm^{-1} in spectra of metal complexes[40]. In case of the ligands L^2H_2, L^4H and L^5H derived from 2-aminobenzenethiol, the SH stretching vibration v(S-H) is not useful, since it displayed very weak bands in both the free ligands and complexes spectra. However, the participation of the SH group in chelation is ascertained from the shift of $v_{asym}(CS)$ and $v_{sym}(CS)$ from 700-706 and 750-756 cm^{-1} to lower or higher wave numbers in the spectra of the complexes. In the spectra of the complexes derived from the ligand L^2H_2 a new band appeared at 1220-1230 cm^{-1}. This new band assigned to v_{c-o} vibrational mode, suggest the enolisation of NH hydrogen of isatin and the coordination through the oxygen of the C-O group. The enolisation of NH hydrogen was further confirmed by disappearance of v(N-H) of the ligand L^2H_2 in the spectra of complexes. However, in the spectra of complexes of the ligand L^1H the vibrations characteristic of the v(N-H) vibrational mode in isatin remains almost unaffected, indicating the noninvolvement of this group in coordination and non-enolisation of the N-H proton. The non-ligand bands appearing in the spectra of complexes in the regions 450-470, 360-385 and 420-450 cm^{-1} can be assigned to v(M-N), v(M-S) and v(M-O) vibrations[41], respectively. Thus from the infrared spectra it is clear that the ligands L^1H, L^3H, L^4H, L^5H and L^6H are bonded to the metal ion in a monobasic tridentate fashion through the deprotonated phenolic oxygen or thiolic sulphur, azomethine nitrogen and carbonyl oxygen of the isatin moiety while the ligand L^2H_2 behave as dibasic tridentate ligand coordinating through thiolic sulphur, azomethine nitrogen and enolic oxygen atoms.

Proton Magnetic Resonance Spectra

The proton magnetic resonance spectra of the ligands and their cobalt(III) complexes (Table 4) have been recorded in deuterated dimethylformamide. The spectrum of the free ligands L^1H, L^3H and L^5H show a peak at δ 12.10-12.18 ppm characteristic of intramolecular hydrogen bonded O-H group. This signal was found to be disappeared in the spectra of corresponding metal complexes and this is a clear indication that the phenolate group is coordinated to the metal ion through the phenolic

oxygen after deprotonation. The signals at δ 9.56 and 9.80 ppm in the spectra of the free ligands L^1H and L^2H_2 respectively are assignable to the –NH proton of the isatin moiety. No major shift was observed for this proton in the spectra of the complexes of the ligand L^1H, indicating the non involvement of this group in coordination. While in the spectra of complexes of the ligand L^2H_2 this signal was found to be disappeared, suggesting the enolisation of the carbonyl group of isatin moiety which has already proved by infrared spectra. The signal due to –SH proton appear at δ 9.34-9.60 ppm in the spectra of free ligand L^2H_2, L^4H and L^6H and they disappear in the spectra of the corresponding metal complexes, suggesting coordination of sulphur to metal ion after deprotonation. The signal due to CH=N proton appear at ca. δ 8.56-8.90 ppm in the spectra of all the Schiff bases's. These signals showed downfield shift in complexes and is probably due to lone pair donation by the azomethine nitrogen to cobalt. The protons of the benzene and indole ring give signals in the region δ 7.66-7.90 ppm as a multiplet and were found slightly downfield in the complexes due to coordination of the various groups present in the ring.

Thermal analysis:

The thermal studies TGA reveals that the complexes of iron(III) and cobalt(III) showed a two step weight loss in air. The first stage starts above 100°C implying that there is neither water nor solvent molecule attached to the complexes. In the complexes of the ligand L^1H and L^2H_2 the first degradation step starts at 100°C and continues up to 280°C involving loss of HCl and 1/2 O_2 molecule while in the complexes of the ligands L^3H, L^4H, L^5H and L^6H the first degradation starts at 145°C corresponding to removal of methyl group as methane present in the ligand moiety. The second decomposition step starts at 300°C and continues upto 600°C in all metal complexes involving decomposition of the remaining organic moiety which constitute approximately 86% of the mass of the complexes, leaving behind the respective metal oxide. Finally, the thermo gram shows a straight line which did not change even on heating up to 700°C indicating that there is no further change. Hence, respective metal oxide is the end product of all the complexes.

Biological screening

The iron(III) and cobalt(III) complexes together with their parent L^1H, L^2H_2, L^3H, L^4H and L^5H and L^6H were tested for in vitro growth inhibitory activity against various pathogenic fungi and bacteria. Proper temperature, necessary nutrients and growth medium free from other microorganisms were employed for the preparation of the cultures of fungi and bacteria by using aseptic technique. The biological activities of compounds were evaluated in three replicates.

Antifungal Screening

The antifungal activities were evaluated against *Aspergillus niger* and *Fusarium udum* by the agar plate diffusion technique. Cultures of the test fungi were prepared in a potato dextrose agar (PDA) medium and were purified by single spore isolation technique.[42,43] The Schiff bases derived from isatin / N-methylisatin / N-methylol isatin with 2-aminophenol / 2-aminobenzenethiol and its metal complexes were dissolved in 50, 100 and 200 ppm concentrations in MeOH and then mixed with the PDA medium (glucose, starch, agar-agar and H_2O). Untreated aseptic PDA medium served as control. The media were poured into sterilized Petri dishes. After solidification, 5 mm discs of five-day-old fungi were transferred to the center of the plate. The plates were incubated at 27±1°C. The radial growth of fungi was measured at 12 h intervals from 36 h after inoculation. The percentage inhibition was calculated as 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.

Antibacterial Screening

The antibacterial activities were evaluated against *Escherichia coli*(-) and *Staphylococcus aureus*(+) by the paper disc plate method.[44] The nutrient agar media (peptone, beef extract, NaCl, agar-agar and H_2O) and 5 mm 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 soaked in different solutions of the compounds, dried and then placed in the Petri dishes previously seeded with the test organism. The plates were incubated for 24-30 h at 28±2°C. The zone of inhibition thus formed around each disc containing the test compound was measured accurately in mm.

The results of biological screening have been compared with the conventional fungicide ridomil and the conventional bactericide streptomycin, taken as standard in each case. It is evident that although the Schiff bases derived from isatin / N-methyl isatin / N-methylol isatin with 2-aminophenol / 2-amino benzenethiol alone are quite toxic, their activity increased upon complexation (Table 5). The concentration plays a vital role in increasing the degree of inhibition. It is clear from the data that Schiff bases derived from isatin show less inhibitory effect for fungal and bacterial strain than the metal complexes. The Co(III) complexes show very good activity than Fe(III) complexes. In general metal complexes are more potent than their ligands, hence may serve as vehicles for activation as principal cytotoxic species. These complexes exhibit stronger fungicidal activity than bactericidal activity.

Thus, on the basis of elemental analysis, electrical conductance measurements and spectral (electronic, infrared and ^1H NMR) data, the following structures can be proposed for the complexes.
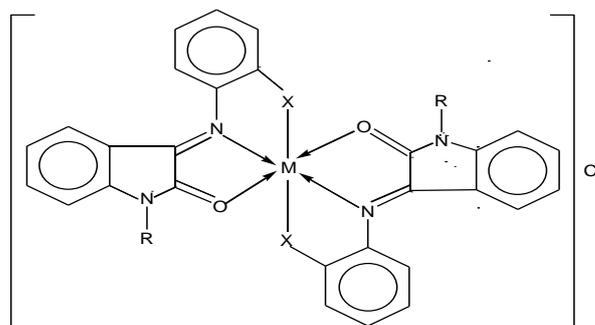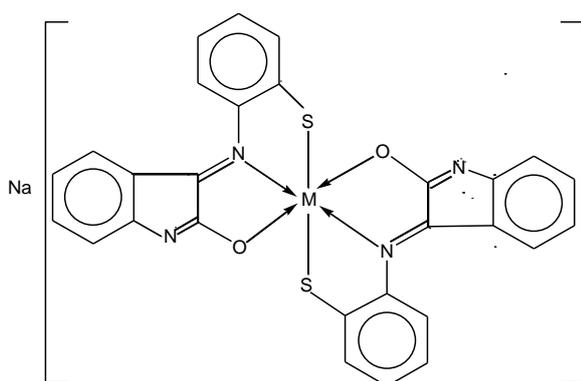
M = Fe(III), Co(III)

Experimental

Materials and Methods

$FeCl_3.6H_2O$ and $CoCl_2.6H_2O$ were purchased from Merck and 2-Amino phenol and 2-Amino benzenethiol were purchased from Sigma Aldrich. All the organic solvents used were of AnaR grade. Iron and cobalt were estimated gravimetrically by precipitating them as hydroxides and reducing to respective metals. C, H and N analysis were carried out on Carlo Erba 1108 elemental analyzer at SAIF, Central Drug Research Institute, Lucknow. Chlorine was estimated as silver chloride and sulphur was estimated gravimetrically as $BaSO_4$[45]. The IR spectra were recorded in KBr pellets on Shimadzu 8201 PC in the range 4000-200 cm^{-1}. Electronic spectra were recorded on Perkin Elmer Lambda 15 UV/VIS spectrophotometer in DMF and DMSO. ^1H NMR spectra of ligands and the cobalt complexes were recorded in CDCl$_3$ or deuterated DMF using a Bruker DRX-300 at a sweep width of 900 hertz. Electrical conductance measurements were made on a Beckman conductivity bridge model RC-18A in DMF at 25^{0}C. Thermogravimetric analysis (TGA) was carried out on a Du Pont TGA 2950 analyzer in the synthetic air atmosphere with a heating rate of 10^{0}C per minute. Magnetic measurements were determined by Gouy's method using Hg[Co(NCS)$_4$] as calibrant. Melting point were recorded with an Ambassador melting point apparatus by using thin capillaries and are uncorrected.

Synthesis of Schiff base ligands:

To a methanolic solution (50 cm^3) of isatin / N-Methyl isatin / N-Methylol isatin (0.2 mol) was added methanolic solution (20 cm^3) of 2-amino phenol / 2-amino benzenethiol (0.2 mol). The resulting mixture was refluxed for 4-5 hours and then cooled in ice. The ligands were precipitated as brown solid which was filtered off, washed with methanol and dried in vacuo over calcium chloride.

Synthesis of metal Schiff base complexes:

(A) Reaction of iron(III) chloride and cobalt(III) chloride with Schiff bases derived from   isatin / N-Methylisatin / N-Methylolisatin and 2-aminophenol :

To a boiling solution of L^{1}H (0.02 mol), L^{3}H (0.02 mol) and L^{5}H (0.02 mol) in methanol (20 cm^3)

was slowly added a methanolic solution (10 cm^3) of $FeCl_3$·6H$_2$O (0.01 mol) and CoCl$_2$.6H$_2$O (0.01 mol) separately. The reaction mixture was refluxed for 6-8 hours on water bath with constant stirring for iron(III) complexes while the resulting mixture was refluxed for one hour and H$_2$O$_2$ (0.01 mol, 30%) was added gradually and again the mixture was refluxed for next 5-6 hours for cobalt(III) complexes. The volumes of both mixtures were reduced to one half by evaporation. The desired complexes precipitated which were filtered off, washed with methanol and dried in vacuo over calcium chloride.

$$FeCl_3 \cdot 6H_2O + 2L^nH \xrightarrow[pH = 7]{MeOH} [Fe(L^n)_2]Cl + 2HCl$$

$$CoCl_2 \cdot 6H_2O + 2L^nH \xrightarrow[pH = 7]{MeOH/H_2O_2} [Co(L^n)_2]Cl + HCl$$
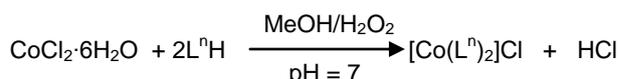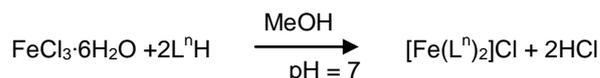
L^{n}H = L^{1}H, L^{3}H, L^{5}H

(B) Reaction of iron(III) chloride and cobalt(III) chloride with Schiff bases derived from N-Methyl isatin / N-Methylol isatin and 2-amino benzenethiol :

To a hot solution of L^{2}H$_2$ (0.02 mol), L^{4}H (0.02 mol)   in methanol (25 cm^3) was slowly added methanolic solution (10 cm^3) of FeCl$_3$·6H$_2$O (0.01 mol) and CoCl$_2$·6H$_2$O (0.01 mol) seperately. The resulting mixture was refluxed for 6-8 hours for iron(III) complexes while the mixture was refluxed for one hour, H$_2$O$_2$ (0.01 mol, 30%) was added gradually and again the mixture was refluxed for next 5-6 hours for cobalt(III) complexes. The mixtures were then made alkaline (pH = 7.4) by adding saturated solution of NaOH (0.01 mol). Reduced the volume of both solutions to one half of the original volume and filtered the brown coloured complexes separated out, washed many times with distilled water and dried in vacuo over calcium chloride.

$$FeCl_3 \cdot 6H_2O + 2L^nH \xrightarrow[pH = 7-8]{MeOH, NaOH} [Fe(L^n)_2]Cl + 2HCl$$

$$CoCl_2 \cdot 6H_2O + 2L^nH \xrightarrow[pH = 7-8]{MeOH / H_2O_2, NaOH} [Co(L^n)_2]Cl + HCl$$
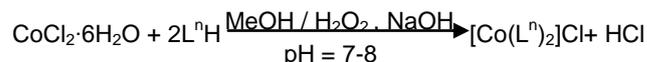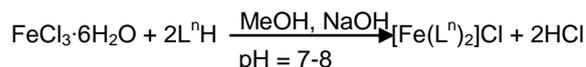
L^{n}H = L^{4}H, L^{6}H

(C) Reaction of iron(III) chloride and cobalt(III) chloride with Schiff bases derived from isatin and 2-aminobenzenethiol :

To a methanolic solution (20 cm^3) of N-Methylolisatin (0.02 mol) was added methanolic solution (10 cm^3) of 2-aminobenzenethiol (0.02 mol) and methanolic solution (10 cm^3) of FeCl$_3$·6H$_2$O (0.01 mol) and CoCl$_2$·6H$_2$O (0.01 mol) separately. Refluxed the reaction mixture for 6-8 hours for iron(III) complexes while for cobalt(III) complexes after half an hour of refluxion H$_2$O$_2$ (0.01 mol, 30%) solution was added to mixture and the mixture was refluxed for next 6-8 hours, After that the reaction mixtures were made alkaline (pH = 7.4) by adding saturated solution of NaOH (0.01 mol). The brown coloured complex precipitated immediately but was digested on water bath for half an hour. Cooled the solution and filtered

the complex, washed many times with distilled water and dried *in vacuo* over calcium chloride.
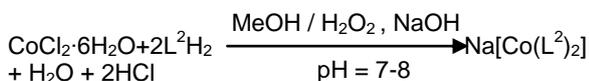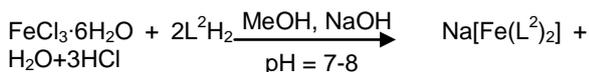
$$FeCl_3 \cdot 6H_2O + 2L^2H_2 \xrightarrow[pH = 7-8]{MeOH, NaOH} Na[Fe(L^2)_2] + H_2O + 3HCl$$

$$CoCl_2 \cdot 6H_2O + 2L^2H_2 \xrightarrow[pH = 7-8]{MeOH / H_2O_2, NaOH} Na[Co(L^2)_2] + H_2O + 2HCl$$

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