Synthesis and Spectral Characterization of Schiff Base Cr(III), Mn(III), and Fe(III) Novel Macrocyclic Complexes Derived from Thiocarbohydrazide and Dicarbonyl Compound

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Abstract: M(III) Schiff base macrocyclic complexes of the type [HLMX₂] where M = Cr(III), Mn(III), Fe(III) and X = Cl, OAc have been synthesized by condensation of acetylacetone and Thio-carbohydrazide (2:2) in the presence of divalent metal salt in methanolic medium. The complexes have been characterized with the help of elemental analysis, conductance measurements, magnetic measurements and their structural configuration have been determined by various spectroscopic (electronic, IR, ¹H NMR, ¹³C NMR, GCMS) techniques. Electronic and magnetic moments of the complexes indicate that the geometries of the metal centers are octahedral.

Keywords: Metal complexes, Spectroscopic study. Thio-carbohydrazide and acetylacetone.

Introduction

Macrocyclic and compounds have attracted increasing interest owing to their role in the understanding of molecular processes occurring in biochemistry, material science, catalysis¹. It is well known that N and S atoms play a key role in the coordination of metal at the active sites of numerous metallobiomolecules². Metall-organic chemistry is becoming an emerging area of research due to the demand of new metalbased antibacterial and antifungal compounds^{3,4}. The aliphatic or aromatic amines can form strong five of six membered chelates rings which are able to produce the metal containing crosslinking agents with required properties⁵. There are a number of important molecules shows biological activities including antibacterial, antifungal⁶⁻⁹, antidiabetic¹⁰, antitumor¹¹, antiproliferative^{12,13}, anticancer^{14,15}, herbicidal¹⁶, anticorrosion and anti-inflammatory activities⁶ Schiff bases represent an important class of compounds because they are utilized as starting materials in the synthesis of industrial products. Moreover, Schiff bases are regarded as privileged ligands¹⁷. Due to their capability to form complexes with different transition metals can act as catalysts for many different reactions^{18,19}. The discovery and development of effective antibacterial and antifungal drugs with novel mechanism of action have because an urgent

task for infectious diseases research program²⁰. Many investigations have proved that binding of a drug to a metalloelements enhances its activity and in some cases, the complex possesses even more healing properties than the parent drug²¹. In the present article, we report the synthesis and characterization of Schiff base derived from acetylacetone and thio-carbohydrazide, and its metal complexes to gain more information about related structural and spectral properties as well as their antimicrobial activities.

Experimental

Reagents

The entire chemicals used were of the analytical reagent grade, acetylacetone and thio-carbohydrazide procured from Acros and s.d.-fine, respectively. Metal salts were purchased from Merck.

Synthesis of Schiff Base Macrocylic Ligand

The macrocyclic Schiff base ligand have been synthesized by refluxing the reaction mixture of acetyl acetone (2 mmol) in ethanol (30 mL) and Thio-carbohydrazide (2 mmol) in ethanol (20 mL) for 6-8h with addition of 4-5 drops of concentrate HCl. The reaction mixture was filtered, dried under reduced pressure until a solid product was formed that was washed with cold ethanol and recrystallized from hot ethanol (yield 55-60%, scheme 1).

Scheme 1. Synthesis of Schiff base macrocylic ligand.

Synthesis of Cr(III), Mn(III), and Fe(III) Macrocylic Complexes

A solution of trivalent metal salt (1 mmol) in methanol (20 mL) was added to a hot solution (75 °C) of macrocyclic ligand in ethanol (40 mL) and the reaction mixture was refluxed for 10-12h. The complex was precipitated by adding distilled water. The precipitate of the complex was filtered, washed with water, then with hot methanol and finally dried in vacuum desiccator over anhydrous CaCl_2 (yield 40-45%, scheme 2).

Scheme 2. Synthesis of novel macrocyclic Schiff base complexes.

Analytical and Physical Measurements

The microanalysis of C, H, and N were estimated by elemental analyzer (Perkin Elmer 2400), at SAIF, CDRI, Lucknow, India and the metal contents of Mn (III), Co (III) and Cu (III) was determined using atomic absorption spectrophotometer Perkin Elmer 5000. (See Table I containing also some physical properties of the prepared compounds). The conductivity was measured on digital conductivity meter (HPG system, G-3001) in DMSO at room temperature. The magnetic susceptibility measurements were carried out on Vibrating Sample Magnetometer (Model PAR 155) at room temperature. Electronic spectra (in DMSO) were recorded on a Hitachi 330 spectrophotometer (5815-32573 cm⁻¹). The IR spectra were performed using a FT-IR spectrophotometer Perkin Elmer 1650 in the range 4000–200 cm⁻¹ using Nujol Mull. ¹H NMR and ¹³C NMR spectra (at room temperature) (in DMSO-d₆) were recorded on a Bruker AVANCE II 300 DRX or average 400 DRX spectrometer with reference to Me₄Si (0.0 ppm). The FAB mass spectra (at room temperature) were recorded on VG-70-S mass spectrometer. The purity of the Schiff base and its complexes were confirmed also by TLC [microcrystalline cellulose (E. Merck) was used for the preparation of thin layer, complete separation was achieved with the solvent system acetone/conc. HCl/water (86:8:7). R_F values increase in the following order of M(III) complexes: Cr, Mn, Fe (0.28, 0.42, 0.61)] and HPLC. The HPLC chromatographic apparatus consisted of a model waters 600 pump with waters 600 controller, waters 2996 photodiode array detector with UV detection 254 nm, flow rate 1ml/min a discovery C₈, 15cm X 4.6mm I.D, 5μm particles and mobile phase methanol:25 mm KH₂PO₄ (20:80) PH=3 techniques.

Results and Discussion

Mass Spectra

The FAB mass Spectra of Cr(III), Mn(III) and Fe(III) Schiff base complexes have been recorded. The molecular ion (M⁺) peaks obtained from various complexes are as follows: (1) m/e = 340.48 (Ligand), (2) m/e = 474.93 (complex 1), (3) m/e = 522.12 (complex 2), (4) m/e = 470.08 (complex 3), (5) m/e = 517.27 (complex 4), (6) m/e = 470.32 (complex 5), (7) m/e = 517.51 (complex 6). This data is in good agreement with the proposed molecular formula for these complexes. In addition to the peaks due to the molecular ion, the spectra exhibit

peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peak intensity gives an idea of the stability of the fragments.

Infrared Spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The presence of a single medium band in the region 3250–3330 cm^{-1} in the complexes may be assigned to N-H stretch²². It was noted that a pair of bands corresponding to $\nu(\text{NH}_2)$ at 3245 cm^{-1} and 3309 cm^{-1} are present in the spectra of the thiocarbohydrazide. The value of $\nu(\text{C}=\text{N})$ stretching vibration is found lower (1520–1560 cm^{-1}) than the expected value (1580–1650 cm^{-1}). This lower value of $\nu(\text{C}=\text{N})$ stretching may be explained on the basis of a drift of lone pair density of azomethine nitrogen towards the metal atom²³ indicating that coordination takes place through nitrogen of (C=N) groups. The bands present in the range 3020–3040 cm^{-1} may be assigned due to (C–H) stretching vibrations of benzil and naphthalene ring²⁴. The C–N stretch in the range 1000–1300 cm^{-1} . The band near 780 cm^{-1} in thiocarbohydrazide may be assigned as being due to free $\nu(\text{C}=\text{S})$. The band at 3292–3438 cm^{-1} is due to the presence of OH group in the complexes. This band is also present in the spectra of all the complexes, which indicate that sulphur is not coordinating to the metal atom²⁵. The far infrared spectra show bands in the region 420–450 cm^{-1} corresponding to $\nu(\text{M}–\text{N})$ vibrations²⁶. The presence of bands in all complexes in the region 420–450 cm^{-1} originates from the (M–N) azomethine vibrational modes and identifies coordination of azomethine nitrogen²⁷. The bands present at 290–310 cm^{-1} may be assigned due to $\nu(\text{M}–\text{Cl})$ vibrations²⁸.

The appearance of two characteristic bands in the ranges 1561–1559 cm^{-1} and 1370–1367 cm^{-1} in the case of complexes was attributed to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, respectively, indicating the participation of the carboxylate oxygen in the complexes formation. The mode of coordination of carboxylate group has often been deduced from the magnitude of the observed separation between the $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$. The separation value, $\Delta\nu(\text{COO}^-)$, between $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, in these complexes were more than 190 cm^{-1} (191–193 cm^{-1})²⁹.

¹H NMR

A survey of literature reveals that the NMR spectroscopy has been proved useful in establishing the structure and nature of many Schiff base ligand and their complexes. The ¹H NMR spectra of Schiff base ligand (HL) was recorded in d_6 -dimethylsulfoxide (DMFO- d_6) solution using Me_4Si (TMS) as internal standard. The ¹H NMR spectra of the ligand shows broad signal at 9.4–12.1 ppm due to the –NH [30]. The multiplets in the region 1.12–1.56 ppm may be assigned to aliphatic proton³⁰.

¹³C NMR of the Schiff base ligand, the signal appeared in the region 113–158 are assigned to aromatic carbon. The signal at 198.3–185.6, 182.8–171.2, 165.4–150.7 and 148.1–15.8 ppm are due to C=S, C=N, C=O and CH_3 respectively.

Magnetic Measurements and Electronic Spectral Studies

The electronic spectra of Cr (III) complexes 1 and 2 showed absorption band in the region 8950–9310, 13150–13520, 17550–18450 and 27380–27780 cm^{-1} attributed to ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_{1g}$, ${}^4\text{B}_{1g} \rightarrow {}^4\text{B}_{2g}$, ${}^4\text{B}_{1g} \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{B}_{1g} \rightarrow {}^4\text{E}_g$ transition indication of octahedral geometry³¹. The magnetic moment value for this complex was found to be 4.38–4.68 B.M.

The absorption spectral bands of manganese (III) complexes 3,4 showed three spin allowed transitions: ${}^5\text{B}_{1g} \rightarrow {}^5\text{A}_{1g}$, ${}^5\text{B}_{1g} \rightarrow {}^5\text{B}_{2g}$, ${}^5\text{B}_{1g} \rightarrow {}^5\text{E}_g$ appearing in the ranges 12250–12550, 16150–18860, and 35450–35720 cm^{-1} , respectively consistent with a typical Mn(III) in an octahedral environment³². The magnetic moment values for these complexes were found in the range 4.92–5.14 B.M expected for octahedral nickel complexes.

The electronic spectra of the iron (III) complexes (5) and (6) gave two bands at 9850–9980, and 27650–27760 cm^{-1} , which could be assigned to the transitions ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$, respectively, suggesting an octahedral geometry around Fe (III) ion³³. The complexes 5 and 6 show magnetic moment values in the range 5.38–5.45 B.M., which is smaller than the calculated value for two Fe (III) ions in octahedral geometries and this may be due to antiferromagnetism between the two ion-centers.

The spectral characterization show the formula for macrocyclic complexes as $[\text{M}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{X}_2]\text{X}$ where $\text{M} = \text{Cr(III)}, \text{Mn(III)}, \text{Fe(III)}$, and $\text{X} = \text{Cl}^-, \text{CH}_3\text{COO}^-$. The measurements of molar conductance in DMSO are 21–66 $\text{Scm}^2\text{mol}^{-1}$. All complexes give satisfactory elemental analyses data as shown in table 1. On the bases of various studies like elemental analysis, conductance measurements, magnetic susceptibilities, IR, NMR, electronic and mass spectral studies the geometry of the complexes are octahedral.

Table 1. Elemental analysis in % and molar conductance (Λ_M in DMSO) in $\text{Scm}^2\text{mol}^{-1}$ and magnetic moment (μ_{eff}) in μ_B of the Schiff base ligand and its metal complexes.

Complex	FW	Colour	C	H	N	M	Λ_M	μ_{eff}
			Calc. (Found)	Calc. (Found)	Calc. (Found)	Calc. (Found)		
$\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2$	340.48	yellow	42.33 (42.28)	5.92 (5.91)	32.91 (32.85)			
$[\text{Cr}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{Cl}_2]\text{Cl}$	498.83	Orange	28.89 (28.81)	4.04 (4.12)	22.47 (22.48)	10.42 10.40	59	4.38
$[\text{Cr}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{OAc}_2]\text{OAc}$	569.61	Greenish Yellow	37.96 (37.95)	5.13 (5.14)	19.67 (19.72)	9.13 (9.15)	66	4.68
$[\text{Mn}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{Cl}_2]\text{Cl}$	501.78	Brown	28.72 (28.70)	4.02 (4.00)	22.33 (22.35)	10.95 (10.91)	21	4.92
$[\text{Fe}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{OAc}_2]\text{OAc}$	572.56	Gray	37.76 (37.75)	5.11 (5.05)	19.57 (19.55)	9.60 (9.55)	28	5.14
$[\text{Fe}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{Cl}_2]\text{Cl}$	502.68	Light Yellow	28.67 (28.65)	4.01 (3.98)	22.29 (22.32)	11.11 (11.12)	29	5.38
$[\text{Fe}(\text{C}_{12}\text{H}_{20}\text{N}_8\text{S}_2)\text{OAc}_2]\text{OAc}$	573.46	Reddish	37.84 (37.85)	5.10 5.05	19.54 (19.51)	9.74 (9.70)	38	5.45

Conclusion

The analytical data show the presence of one metal ion per ligand molecule and suggest a mononuclear structure for the complexes. The electronic spectral data is in the favor of octahedral geometry of the complexes.

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