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Synthesis, physical characterization and antimicrobial activity of trivalent metal Schiff base complexes

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Abstract: M(III) complexes of Cr, Mn and Fe with a Schiff base derived from 2-amino-4-ethyl-5-hydroxybenzaldehyde and thiocarbohydrazide were synthesized and characterized by several techniques, including elemental analysis (C,H,N), molar conductance measurements, magnetic measurements, and electronic, mass and IR spectral studies. Based on these studies, a five-coordinated square pyramidal geometry for all the complexes was proposed. The Schiff base ligand and the complexes were also tested for their antimicrobial activity (against the bacteria *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Bacillus megaterium*, and the fungi *Kluyveromyces fragilis*, *Rhodotorula rubra*, *Candida albicans* and *Trichoderma reesei*) to assess their inhibiting potential. An attempt was also made to correlate the antimicrobial activity with the geometry of the complexes. All complexes were found to be less active against the pathogens *E. coli*, *S. aureus* and *P. aeruginosa*. The Cr(III) complex showed the best antimicrobial activity, but the ligand alone was found to be active against the fungus *T. reesei*.

Keywords: Co (III), Cr (III) and Fe (III) complexes; Schiff Base; 2-amino-4-ethyl-5-hydroxybenzaldehyde; thiocarbohydrazide; antimicrobial activity.

INTRODUCTION

The field of Schiff base complexes is fast developing because of the wide variety of possible structures for the ligands, depending on the aldehyde and amine used. Many Schiff bases and their complexes have been widely studied because of their industrial and biological applications.^{1,2} Some Schiff bases were tested for fungicidal activity, which is related to their chemical structure.³ Schiff base compounds (–RC=N–) are usually formed by the condensation of a primary amine with an active carbonyl. The cross-linking agents can also be derived from

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metal complexes with O, N or S ligands. For example, an intracoordination salt such as salicylates or anthranilates and aliphatic or aromatic amines can form strong five- or six-membered chelate rings which are able to produce metal containing cross-linking agents with the required properties.⁴⁻⁷ Synthesis of oxovanadium(IV) complexes of Schiff bases derived by the condensation of 2-aminobenzaldehyde with various diamines (1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane) were characterized by elemental analysis, spectral data and electrochemical studies.⁸ The complexes of Co(II), Ni(II), and Cu(II) ions with the Schiff bases derived from the condensation of salicylaldehyde and *o*-aminophenol or 2-aminobenzoic acid were synthesized and characterized by different techniques, in particular, elemental analysis and molar conductance measurements as well as IR and electronic spectroscopy.⁹⁻¹¹

The aim of the present study was to prepare, characterize and determine the antimicrobial activity of Schiff base complexes derived from thiocarbohydrazide and 2-amino-4-ethyl-5-hydroxybenzaldehyde.

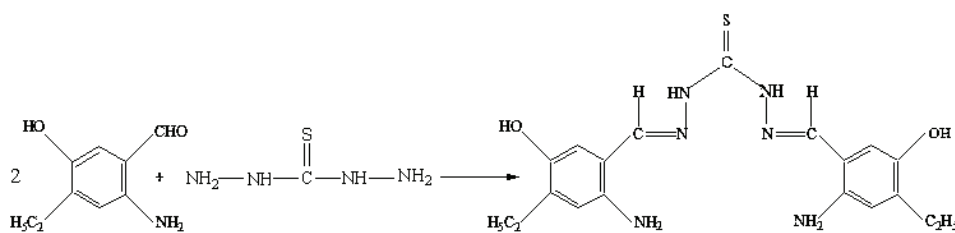
EXPERIMENTAL

Materials

All chemicals used in this work were of analytical reagent grade (anhydrous). CrCl₃, MnCl₃ and FeCl₃ were purchased from Aldrich (New Delhi, India); DMSO, DMF and ethanol were purchased from Sigma (New Delhi, India); 2-amino-4-ethyl-5-hydroxybenzaldehyde and thiocarbohydrazide were purchased from Fluka (Mumbai, India).

Synthesis of the Schiff base

The Schiff base (ligand) was prepared by mixing a warm dilute ethanolic solution of thiocarbohydrazide (5 mmol) with 2-amino-4-ethyl-5-hydroxybenzaldehyde (10 mmol) under reflux for 2 h (Scheme 1). The precipitate was then removed from the reaction mixture by filtration,^{11,12} washed with ethanol and dried in a desiccator over anhydrous CaCl₂. The colour of the solid product was yellow (yield 65 %).

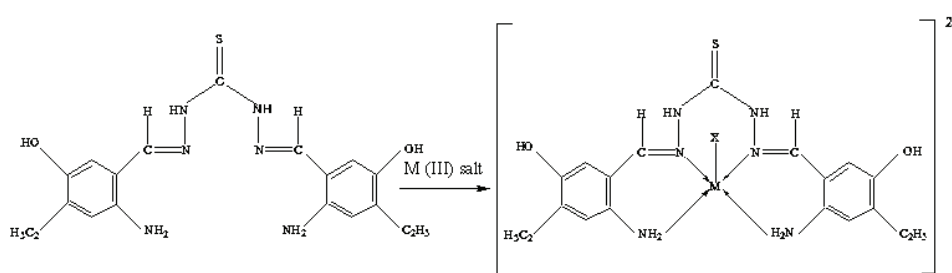


Scheme 1. Synthesis of the Schiff base ligand.

Synthesis of the complexes

The Schiff base was taken in ethanol (50 cm³) and stirred gently for one hour to give a homogeneous solution and then trivalent chromium, manganese or iron chlorides salts (25 cm³) were added (Scheme 2). The resulting solution was refluxed for 6-8 h. The mixture was concentrated to half its initial volume and kept in a desiccator for two days over anhydrous CaCl₂. The complexes were then filtered, washed with ethanol and dried. The complexes were

soluble in DMF and DMSO but insoluble in other common organic solvents and water. They were thermally stable up to 523–553 K and then decomposed.



Scheme 2. Synthesis of the M(III) Schiff base complexes.

Methods and apparatus applied

The microanalyses for C, H, and N were estimated by an elemental analyzer (Perkin Elmer 2400), at SAIF, CDRI, Lucknow, India, and the metal contents of Mn(III), Co(III) and Fe(III) were determined using a Perkin Elmer 5000 atomic absorption spectrophotometer. Table I contains some physical properties of the prepared compounds. The conductivity was measured on a digital conductivity meter (HPG system, G-3001) in DMSO at room temperature. The magnetic susceptibility measurements were performed on a Vibrating Sample Magnetometer (Model PAR 155) at room temperature. The electronic spectra (in DMSO) were recorded on a Hitachi 330 spectrophotometer (5815–32573 cm^{-1}). The IR spectra were obtained using a Perkin Elmer 1650 FT-IR spectrophotometer in the wavenumber range 4000–200 cm^{-1} using Nujol Mull (the molar conductivities, magnetic moments and spectral data are given in Tables I and II). The FAB mass spectra (at room temperature) were recorded on a VG-70-S mass spectrometer. The purity of the Schiff base and its complexes were confirmed by TLC (microcrystalline cellulose (Merck) was used for the preparation of the thin layer, complete separation was achieved with the solvent system acetone/conc. HCl/water (86:8:7); the R_F values increased in the following order of M(II) complexes: Mn, Co, Cu (0.20, 0.34, 0.60)) and HPLC. The HPLC chromatographic instrument consisted of a Waters 600 pump with a Waters 600 controller, a Waters 2996 photodiode array detector with UV detection at 254 nm, a Discovery C_8 column, 15 cm \times 4.6 mm I.D., 5 μm particles. The mobile phase was methanol:25 mmol KH_2PO_4 , pH 3 (20:80) at a flow rate of 1 ml min^{-1} .

Antimicrobial activity

The antibacterial and antifungal activities of the newly synthesized compounds were evaluated by the agar well diffusion method.¹³ All the microbial cultures were adjusted to 0.5 McFarland Standard, which is visually comparable to a microbial suspension containing approximately 1.5×10^8 cfu/ml.¹⁴ 20 ml of agar media was poured into each Petri plate and the plates were swabbed with 100 μl inocula of the test microorganisms and kept 15 min for adsorption. Using an 8 mm-diameter sterile cork borer, wells were bored into the seeded agar plates and these were loaded with 100 μl of a solution of each compound dissolved in the dimethyl sulphoxide (DMSO) at a concentration of 1.0 mg/ml. All the plates were incubated at 300 K for 24 h. The antimicrobial activity of all the synthesized compounds was evaluated by measuring the zone of growth inhibition against the test organisms with zone reader (Hi antibiotic zone scale). The medium with dimethyl sulphoxide (DMSO) as solvent was used as

a negative control whereas media with ciprofloxacin (standard antibiotic) and griseofulvin (standard antifungal drug) were used as the positive controls. The experiments were performed in triplicate.

The ligand HL and its Cr(III), Mn(III) and Fe(III) complexes were tested for their antibacterial and antifungal activity against the bacteria: *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Bacillus megaterium*, and the fungi: *Kluyveromyces fragilis*, *Rhodotorula rubra*, *Candida albicans* and *Trichoderma reesei* procured from Microbial Type Collection and Gene Bank, Institute of Microbial Technology (IMTECH), Chandigarh, India.

RESULTS AND DISCUSSION

The elemental analyses (C, H, N and M) data of the metal chelates, Table I, showed that they may be represented by the formula $[M(C_{19}H_{24}N_6O_2S)X]X_2$ (M(III) = Cr, Mn and Fe; X = Cl). The purity of the Schiff base and its complexes was confirmed by the TLC and HPLC techniques.

TABLE I. Elemental analysis, molar conductance and magnetic moment of the Schiff base ligand and its metal complexes

Compd.	Molecular formula	FW	Colour	Calcd. (Found)/ %				μ_{eff} μ_{B}	Λ_{M} S cm ² mol ⁻¹
				C	H	N	M		
Ligand (HL)	C ₁₉ H ₂₄ N ₆ O ₂ S	506.62	Yellow	45.0 (45.4)	4.7 (4.8)	16.6 (15.9)	—	—	
Cr complex	[Cr(HL)X]X ₂	558.61	Greenish	40.8 (40.5)	4.3 (4.2)	15.0 (15.0)	9.3 (9.4)	4.35	
Mn complex	[Mn(HL)X]X ₂	562.46	Dark brown	40.5 (40.6)	4.3 (4.2)	14.9 (15.1)	9.9 (9.8)	4.85	
Fe complex	[Fe(HL)X]X ₂	561.56	Orange red	40.6 (40.5)	4.3 (3.3)	15.0 (14.9)	9.8 (9.6)	5.78	

The measurements of the molar conductance in DMSO, Table I, showed that these chelates were 1:2 type of electrolytes (the conductance values were 30–60 S cm² mol⁻¹, whereas the literature range is 30–180 S cm² mol⁻¹).¹⁵ The tests for anions were positive before and after decomposition of the chelates with concentrated HNO₃, showing their presence outside as well as inside the coordination sphere. Several attempts to obtain a single crystal suitable for X-ray crystallography failed. However, the analytical, spectroscopic and magnetic data enabled the prediction of the possible structure of the synthesized complexes. The low molar conductance of the complexes might arise due to the large size of the cation coordination sphere, which might have a low ionic mobility; the values of molar conductance suggest that the complexes were electrolytes and that chloride was present as the counter ion.

The IR and electronic spectral data of the ligand and of the complexes are given in Table II.

The IR spectra provided 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 stretching vibrations.^{16,17} It was noted that a pair of bands corresponding to $\nu(\text{NH}_2)$ at 3245 and 3309 cm^{-1} were present in the spectra of the thiocarbohydrazide. The value of the $\nu(\text{C}=\text{N})$ stretching vibration was found at a lower frequency (1520–1560 cm^{-1}) than the expected value (1580–1650 cm^{-1}). This may be explained based on a drift of the lone pair density of the azomethine nitrogen towards the metal atom,^{18,19} indicating that coordination occurred through the nitrogen of the (C=N) groups. The bands present in the range 3020–3040 cm^{-1} may be assigned to (C–H) stretching vibrations of the benzil and naphthalene rings.²⁰ The C–N stretching was in the range 1000–1300 cm^{-1} . The band near 780 cm^{-1} in thiocarbohydrazide may be assigned to free $\nu(\text{C}=\text{S})$. This band is also present in the spectra of all the complexes, which indicates that sulphur is not coordinating to the metal atom.^{21,22} The band at 3292–3438 cm^{-1} is due to the presence of –OH groups in the complexes. The far IR spectra of the complexes show bands in the region 420–450 cm^{-1} , corresponding to $\nu(\text{M}–\text{N})$ vibrations,^{23–24} which identifies coordination of the azomethine nitrogen.²⁵ The bands present at 290–310 cm^{-1} may be assigned to $\nu(\text{M}–\text{Cl})$ vibrations.^{26,27}

TABLE II. IR spectral bands position (cm^{-1}) and electronic spectral data in DMSO (cm^{-1}) of the Schiff base ligand and its metal complexes

Compd.	ν (NH_2)	ν ($\text{C}=\text{N}$)	ν ($\text{C}=\text{S}$)	ν ($\text{M}–\text{Cl}$)	ν ($\text{M}–\text{N}$)	–OH str.	–OH ben.	UV–Vis maxima, cm^{-1} (extinction coefficients, $\text{m}^3 \text{mol}^{-1} \text{cm}^{-1}$)
Ligand (HL)	3250	1560	740	295	410	3327	1350	27027 (35.8)
Cr complex	3280	1530	760	310	400	3292	1352	8950–9300 (24.5, 8.20)
Mn complex	3260	1560	730	290	440	3375	1380	22200–22575 (32.4, 12.6)
Fe complex	3310	1520	780	397	450	3438	1332	9540–9830 (18.3, 8.9)

The FAB mass spectra of the ligand and the Cr (III), Mn (III) and Fe (III) complexes were recorded. All the spectra exhibited parent peaks due to molecular ions (M^+). The proposed molecular formula of these complexes was confirmed by comparing their molecular formula weights with the m/z values. The molecular ion peaks obtained were as follows: m/z 506 (ligand), 558 (Cr(III) complex), 562 (Mn(III) complex) and 561 (Fe(III) complex). These data are in good agreement with the proposed molecular formula for these complexes, *i.e.*, $[\text{M}(\text{C}_{19}\text{H}_{24}\text{N}_6\text{O}_2\text{S})\text{X}]\text{X}_2$, where $\text{M} = \text{Cr(III)}$, Mn(III) and Fe(III) , and $\text{X} = \text{Cl}^-$. In addition to the peaks due to the molecular ions, the spectra exhibited peaks assignable to various fragments arising from the thermal cleavage of the complexes. The peak intensity suggested the stability of the fragments.

The electronic spectra of the Schiff base and its complexes were recorded in DMSO. The absorption spectra of free ligand consisted of an intense band centered at 370 nm (27027 cm^{-1}), attributed to the $n \rightarrow \pi^*$ transition of the thioxo group. Another intense band in the higher energy region of the spectra of the free ligand was related to the $n \rightarrow \pi^*$ transition of the benzene rings.²²

Magnetic moment of the Cr(III) complex was $4.35\ \mu_B$ at room temperature, which is close to the predicted value for three unpaired electrons in the metal ion.²⁸ The electronic spectrum of the Cr(III) complex showed bands in the range $8950\text{--}9310\text{ cm}^{-1}$. The spectral bands are consistent with that of a five-coordinated Cr(III) complex, the structure of which was confirmed by X-ray diffraction measurements.²⁹ Based on the analytical data, spectral studies and electrolytic nature of the complex, a square-pyramidal geometry may be assigned for this complex.³⁰ The electronic spectral bands may be assigned as: ${}^4B_1 \rightarrow {}^4E^a$, ${}^4B_1 \rightarrow {}^4B_2$, ${}^4B_1 \rightarrow {}^4A_1$ and ${}^4B_1 \rightarrow {}^4E^b$.

The magnetic moment of the Mn(III) complex was $4.85\ \mu_B$, which indicates a high spin d^4 system.²⁸ The electronic spectra of the manganese complex show three d–d bands, which lay in the range $12250\text{--}12590\text{ cm}^{-1}$ and may be assigned to charge transfer transitions. The spectrum resembles those reported for five coordinated, square pyramidal Mn(III) complexes.³⁰ This is further supported by the presence of a broad ligand field band at 20400 cm^{-1} . The various bands may be assigned as follows: ${}^5B_1 \rightarrow {}^5A_1$, ${}^5B_1 \rightarrow {}^5B_2$ and ${}^4B_1 \rightarrow {}^5E$. The band assignments in single electron transitions may be made as: $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively, in order of increasing energy. However, the complex did not have idealized C_{4v} symmetry.

The magnetic moment of the Fe (III) complex was $5.78\ \mu_B$, corresponding to five unpaired electrons and is close to the predicted high spin values for this metal ion.²⁸ The electronic spectra of the Fe (III) complex showed various bands in the range $9820\text{--}9970\text{ cm}^{-1}$, which are consistent with the range of spectral bands reported for five coordinate square pyramidal Fe(III) complex.³¹ The various bands can be assigned as: $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{z^2}$. Any attempt to make accurate assignment was difficult due to the interactions of the metal–ligand π -bond systems lifting the degeneracy of the d_{xz} and d_{yz} pair.

Based on the various characterisation results, the structure shown in Scheme 2 may be proposed for all the complexes.

The antimicrobial results, Table III, showed that HL (ligand) exhibited moderate activity against all the tested bacteria and *C. albicans* fungus. HL showed high antifungal activity against *K. fragilis* and *T. reesei* but no activity against *R. rubra*. The Cr(III) complex showed high antibacterial and antifungal activity against *B. megaterium*, *K. fragilis*, *R. rubra* and *C. albicans*, moderate activity against *E. coli*, *S. aureus* and *P. aeruginosa*, but no activity against *T. reesei*. The Mn(III) complex exhibited moderate activity against *P. aeruginosa* and *B. megaterium*,

was highly effective against *K. fragilis*, *C. albicans* and *T. reesei*, but showed no activity against *E. coli*, *S. aureus* and *R. rubra*. The Fe(III) complex exhibited moderate activity against *S. aureus*, *P. aeruginosa*, *B. megaterium* and *T. reesei*, had a higher effect against *K. fragilis* and *C. albicans*, but no activity against *E. coli* and *R. rubra* microorganisms.

TABLE III. Antibacterial and antifungal activity of the standards, solvent, ligand and its metal complexes

Cmpd.	Inhibition zone, mm							
	<i>E. coli</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>B. megaterium</i>	<i>K. fragilis</i>	<i>R. rubra</i>	<i>C. albicans</i>	<i>T. reesei</i>
Ligand (HL)	7	7	7	8	12	0	9	14
Cr complex	9	8	7	16	18	16	12	0
Mn complex	0	0	9	7	10	0	15	12
Fe complex	0	8	9	7	15	0	12	7
Ciprofloxacin	24	20	22	24	–	–	–	–
Griseofulvin	–	–	–	–	24	24	24	23
DMSO (control)	0	0	0	0	0	0	0	0

Antibacterial and antifungal activities of the ligand and its metal complexes were compared with those of the standard drugs ciprofloxacin and griseofulvin. The variation in the activity of different metal complexes against different microorganisms depends on the impermeability of the cell or differences in the ribosomes in the microbial cells.³² The lipid membrane surrounding the cell favours the passage of any lipid soluble materials and it is known that liposolubility is an important factor controlling antimicrobial activity.^{33,34}

In the present study, the low activity of the metal complexes may be due to their low lipophilicity, because of which penetration of the complex through the lipid membrane was decreased and hence, they could neither block nor inhibit the growth of the microorganisms.

CONCLUSIONS

The analytical data showed the presence of one metal ion per ligand molecule and suggested a mononuclear structure for the complexes $[M(C_{19}H_{24}N_6O_2S)X]X_2$. The electronic spectral data is in favour of a square pyramidal geometry of the complexes. The ligand and its Cr(III), Mn(III) and Fe(III) complexes were tested for antimicrobial activity against some pathogens. All the complexes were found to be less active against the bacteria *E. coli*, *S. aureus* and *P. aeruginosa*, whereas the Cr(III) complex showed the best antimicrobial activity against the bacterium *B. megaterium* and the fungi *K. fragilis* and *R. rubra*. The free ligand ($C_{19}H_{24}N_6O_2S$) was found to be active against the fungus *T. reesei*.

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ИЗВОД

СИНТЕЗА, ФИЗИЧКА КАРАКТЕРИЗАЦИЈА И АНТИМИКРОБНА АКТИВНОСТ ТРОВАЛЕНТНИХ МЕТАЛНИХ КОМПЛЕКСА СА ШИФОВИМ БАЗАМА

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Синтетисани су М(III) комплекси Cr, Mn и Fe са Шифовим базама изведеним из 2-амино-4-етил-5-хидроксibenзалдехида и тиокарбохидразида и окарактерисани помоћу неколико техника коришћењем елементалне анализе (C, H, N), моларне проводљивости, магнетним мерењима, електронским, масеним и IR спектралним проучавањима. На основу тога за ове комплексе је предложена пето-координациона квадратно-пирамидална геометрија и нађено да су потенцијални антимикробни агенси. Лиганд Шифове базе и комплекси су такође тестирани према бактеријама *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* и *Bacillus megaterium*, и гљивицама *Kluyveromyces fragilis*, *Rhodotorula rubra*, *Candida albicans* и *Trichoderma reesei* да би се утврдила њихова инхибиторска моћ. Такође је покушано да се доведе у везу биолошка активност са геометријом комплекса. Нађено је да су сви комплекси били мање активни према патогенима *E. coli*, *S. aureus* и *P. aeruginosa*, док је Cr(III) комплекс био најактивнији, а сам слободни лиганд је показао активност према гљивици *T. reesei*.

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