

Trivalent metal ion directed synthesis and characterization of macrocyclic complexes

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Abstract: A novel series of complexes of the type $[M(\text{TML})\text{X}]_2\text{X}_2$, where TML is a tetradentate macrocyclic ligand, $M = \text{Cr}(\text{III}), \text{Mn}(\text{III})$ or $\text{Fe}(\text{III})$, $\text{X} = \text{Cl}^-, \text{CH}_3\text{COO}^-$ or NO_3^- , were synthesized by template condensation of dibenzoyl and thiocarbohydrazide in the presence of trivalent metal salts in a methanolic medium. The complexes were characterized with the help of elemental analyses, conductance measurements, molecular weight determination, magnetic measurements, electronic, NMR, infrared and far infrared spectral studies. The electronic spectra together with the magnetic moments suggest five coordinate square pyramidal geometry for these complexes. The molar conductance indicates them to be 1:2 electrolytes.

Keywords: macrocyclic complexes, dibenzoyl, trivalent metal salts, thiocarbohydrazide, template synthesis.

INTRODUCTION

The field of coordination chemistry of macrocyclic complexes has undergone spectacular growth during the past few decades. This enormous growth is due to the synthesis of a large number and variety of synthetic macrocycles, which behave as coordinating agents for metal ions.^{1,2} Template reactions have been widely used as the synthetic routes for macrocyclic complexes.^{3–5} Nitrogen containing macrocycles have a strong tendency to form stable complexes with transition metals.⁶ A number of nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications.⁷ Macrocyclic transition metal complexes have been regarded as being better model compounds for metalloporphyrins and metallocorrins.^{8–11} Some macrocyclic complexes have been reported to exhibit antibacterial and antifungal activities.^{12,13} In a previous paper, divalent metal macrocyclic complexes derived from thiocarbohydrazide and dibenzoyl were reported.¹³ In the present paper, the trivalent chromium, manganese and iron complexes derived from thiocarbohydrazide and dibenzoyl are discussed.

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EXPERIMENTAL

All the complexes described in this paper were obtained by template synthesis. To a stirring MeOH solution ($\approx 50 \text{ cm}^3$) of thiocarbohydrazide (10 mmol) was added trivalent chromium, manganese or iron salt (5 mmol) dissolved in the minimum quantity of MeOH (20 cm^3). The resulting solution was refluxed for 0.5 h. Subsequently, dibenzoyl (10 mmol) dissolved in $\approx 20 \text{ cm}^3$ MeOH was added to the refluxing mixture and the refluxing was continued for 6–8 h. The mixture was concentrated to half its volume and kept in a desiccator for two days. The complexes were then filtered, washed with MeOH, Me_2CO and Et_2O and dried *in vacuo*; yield $\approx 45\%$. The complexes are soluble in DMF and DMSO but are insoluble in other common organic solvents and water. They were thermally stable up to $\approx 225\text{--}250^\circ\text{C}$ and then decomposed.

Analytical and physical measurements

The microanalysis of C, H, and N were recorded using an Elementar Vario EL III (Carlo Erba 1108) at CDRI, Lucknow. The metal percentage was determined by the EDTA titration method. The molecular weight was determined cryoscopically. The magnetic susceptibility measurements were performed on a Vibrating Sample Magnetometer (PAR 155) at IIT Roorkee. The electronic spectra were recorded on a Perkin–Elmer spectrophotometer. The IR spectra were recorded on a Beckman infrared spectrophotometer in the range $4000\text{--}667 \text{ cm}^{-1}$ as KBr pellets. The NMR spectra were recorded on a Bruker NMR spectrometer (300 MHz). The conductivity was measured on a digital conductivity meter (HPG System, G-3001).

RESULTS AND DISCUSSION

Several attempts to isolate the free macrocyclic ligand were unsuccessful. The template synthesis of the complexes may be shown by the following scheme:



where M = Cr(III), Mn(III) or Fe(III), X = Cl^- , CH_3COO^- or NO_3^- and TML = tetradentate macrocyclic ligand.

The analytical data of the metal chelates are given in Table I, which shows that the chelates may be represented by the formula: $[\text{M}(\text{C}_{30}\text{H}_{24}\text{N}_8\text{S}_2)\text{X}]_2\text{X}_2$. The measurements of the molar conductance in DMSO show that these chelates are 1:2 electrolytes (conductance $150\text{--}180 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).¹⁴ The test for anions was positive before decomposing and after decomposing, the chelates showed their presence outside and inside of the coordination sphere.

The presence of a single medium band in the region $\approx 3250\text{--}3300 \text{ cm}^{-1}$ in the complexes may be assigned to N–H stretch.^{15,16} 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 spectrum of the thiocarbohydrazide but are absent in the infrared spectra of all the complexes. Furthermore, the disappearance of the absorption band near 1700 cm^{-1} due to $\nu(\text{C}=\text{O})$ and the appearance of an absorption band near $1595\text{--}1615 \text{ cm}^{-1}$ indicates the formation of a macrocyclic Schiff's base.¹⁷ The lower values of $\nu(\text{C}=\text{N})$ may be explained on the basis of a drift of the lone pair density of the azomethine nitrogen towards the metal atom,^{18,19} indicating that coordination occurs through the nitrogen of the C=N groups. Another set of medium intensity bands in the region $\approx 1490\text{--}1580 \text{ cm}^{-1}$ are attributed to $\nu(\text{C}=\text{C})$ of phenyl groups

and the bands at $\approx 840\text{--}880\text{ cm}^{-1}$ to C–H out of plane bending of phenyl groups. The band near 780 cm^{-1} in thiocarbohydrazide may be assigned as being due 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.^{20,21} The absence of bands near 2550 cm^{-1} (characteristic of a thiol group) rules out the possibility of thione–thiol tautomerism.²¹ The C–N stretch occurs in the range $1300\text{--}1000\text{ cm}^{-1}$.

TABLE I. Analytical data of the trivalent chromium, manganese and iron complexes derived from thiocarbohydrazide and dibenzoyl

Complexes	M	C	H	N	Colour	M_r g mol ⁻¹
[Cr(C ₃₀ H ₂₄ N ₈ S ₂)Cl]Cl ₂	7.16 (7.23)	49.87 (50.06)	3.27 (3.33)	15.34 (15.57)	Greenish brown	719
[Cr(C ₃₀ H ₂₄ N ₈ S ₂)(NO ₃)](NO ₃) ₂	6.43 (6.51)	45.08 (45.11)	2.97 (3.00)	19.20 (19.29)	Light brown	798
[Cr(C ₃₀ H ₂₄ N ₈ S ₂)(OAc)](OAc) ₂	6.47 (6.59)	54.56 (54.75)	4.09 (4.18)	14.15 (14.19)	Yellowish brown	789
[Mn(C ₃₀ H ₂₄ N ₈ S ₂)Cl]Cl ₂	7.68 (7.61)	49.67 (49.86)	3.19 (3.32)	15.37 (15.51)	Dark brown	722
[Mn(C ₃₀ H ₂₄ N ₈ S ₂)(OAc)](OAc) ₂	6.89 (6.94)	54.23 (54.54)	4.06 (4.16)	14.12 (14.14)	Blackish brown	792
[Fe(C ₃₀ H ₂₄ N ₈ S ₂)Cl]Cl ₂	7.68 (7.74)	49.67 (49.79)	3.19 (3.31)	15.37 (15.49)	Orange red	723
[Fe(C ₃₀ H ₂₄ N ₈ S ₂)(NO ₃)](NO ₃) ₂	6.89 (6.98)	44.79 (44.88)	2.78 (2.99)	19.11 (19.20)	Reddish brown	802
[Fe(C ₃₀ H ₂₄ N ₈ S ₂)(OAc)](OAc) ₂	6.92 (7.06)	54.43 (54.47)	4.11 (4.16)	14.05 (14.12)	Dark brown	793

The far IR spectra show bands in the region $\approx 420\text{--}470\text{ cm}^{-1}$ corresponding to $\nu(\text{M}\text{--}\text{N})$ vibrations.^{22–24} The presence of bands in the spectra of all the complexes in the $420\text{--}470\text{ cm}^{-1}$ region originate from (M–N) azomethine vibrational modes and gives some indication about the coordination of azomethine nitrogens.²⁵ The bands present at $290\text{--}310\text{ cm}^{-1}$ may be assigned to $\nu(\text{M}\text{--}\text{Cl})$ vibrations.²² The characteristic bands due to $\nu(\text{M}\text{--}\text{S})$ are not present in the far IR spectra, which again rules out the possibility of coordination through sulphur atom.

The ¹H-NMR spectra of the complexes show peaks at 7.08–7.78 ppm (multiplets), corresponding to aromatic ring protons.²⁶ The singlet at 11.7–12.1 ppm may be assigned to –NH protons.²⁷

The magnetic moment of the chromium complexes was in the range from 4.12 to 4.46 μ_B . The electronic spectra of the chromium complexes show bands at $\approx 9000\text{--}9300\text{ cm}^{-1}$, $13000\text{--}13300\text{ cm}^{-1}$, $17450\text{--}18300\text{ cm}^{-1}$, $27400\text{--}27800\text{ cm}^{-1}$ and 34800 cm^{-1} . However, these spectral bands cannot be interpreted in terms of four or six coordinated environment around the metal atom. In turn, the spectra are consistent with that of five coordinated Cr(III) complexes, the structures of which

have been confirmed from X-ray measurements.²⁸ Thus, bearing in mind the analytical data and electrolytic nature of these complexes, a five coordinated square pyramidal geometry can be assumed for these complexes. Thus, assuming the symmetry C_{4v} for these complexes,²⁹ the various spectral bands can be assigned as: ${}^4B_1 \rightarrow {}^4E^a$, ${}^4B_1 \rightarrow {}^4B_2$, ${}^4B_1 \rightarrow {}^4A_2$ and ${}^4B_1 \rightarrow {}^4E^b$.

The magnetic moment of the manganese complexes lay in the range from 4.85 to 4.92 μ_B . The manganese complexes show bands in their electronic spectra which lay in the range 22200–12570 cm^{-1} , 16000–18900 cm^{-1} and 35400–35700 cm^{-1} . The higher energy band at 35400–35700 cm^{-1} may be assigned to charge transfer transitions. The spectra resemble those reported for five coordinate square pyramidal manganese porphyrins.^{25,29} This idea is further supported by the presence of the broad ligand field band at 20400 cm^{-1} , diagnostic of C_{4v} symmetry, and thus the various bands may be assigned as follows: ${}^5B_1 \rightarrow {}^5A_1$, ${}^5B_1 \rightarrow {}^5B_2$, and ${}^5B_1 \rightarrow {}^5E$, respectively. The band assignment in single electron transition 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 complexes do not have an idealized C_{4v} symmetry.

The magnetic moment of the iron complexes lay in the range from 5.78 to 5.94 μ_B . The iron (III) complexes show bands in their electronic spectra in the range 9830–9980 cm^{-1} , 15500–15580 cm^{-1} and 27500–27700 cm^{-1} and these bands do not suggest an octahedral or tetrahedral geometry around the metal atom. The spectral bands are consistent with the range of spectral bands reported for five coordinate square pyramidal iron(III) complexes.³⁰ Assuming C_{4v} symmetry for these complexes, 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 an accurate assignment is 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 all the above-given results, the proposed structure of the complexes described in this paper is as shown in Fig. 1.

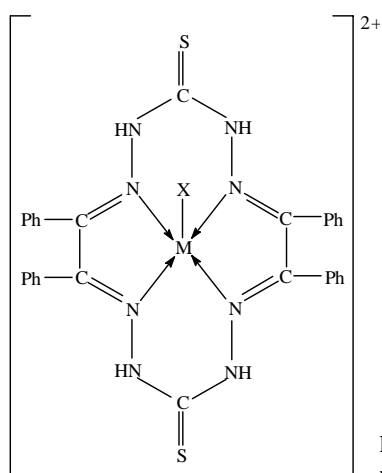


Fig. 1. The proposed structure of the $[M(C_{30}H_{24}N_8S_2)X]^{2+}$, where $M(\text{III}) = \text{Cr, Mn or Fe}$ and $X = \text{Cl}^-, \text{NO}_3^-$ or CH_3COO^- .

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ИЗВОД

УСМЕРЕНА СИНТЕЗА И КАРАКТЕРИЗАЦИЈА МАКРОЦИКЛИЧНИХ
КОМПЛЕКСА ТРОВАЛЕНТНИХ МЕТАЛНИХ ЈОНА

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Нова серија комплекса типа $[M(TML)X]X_2$, где је TML тетраденантни макроциклични лиганд, $M = Cr(III)$, $Mn(III)$ или $Fe(III)$ и $X = Cl^-$, CH_3COO^- или NO_3^- , синтетисана је тем-платном кондензацијом дибензоила и тиокарбохидразида у метанолу, у присуству тровалентних соли метала. Комплекси су окарактерисани елементалном анализом, мерењем проводљивости, одређивањем молекулске масе, магнетним мерењима и електронским, NMR, инфра-црвеним и далеким инфрацрвеним спектралним испитивањима. Електронски спектри и вредности магнетних момената комплекса указују на њихову квадратну пирамидалну структуру са координационим бројем пет. Моларна проводљивост указује на то да су комплекси 1:2 електролити.

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