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Synthesis and Characterisation of Cr(III), Fe(III) and Co(III) complexes with Biacetyl and Bibenzoyl Monoxime Hydrazone

Rakhi Chaudhary* and Shelly

Department of Applied Sciences & Humanities, Haryana Engineering College, Jagadhri

ABSTRACT

Complexes of Cr(III), Fe(III) and Co(III) with biacetyl mono oxime phenoxy acetyl hydrazone(BAMPxH), bibenzoyl monoxime phenoxy acetyl hydrazone(BBMPxH) have been isolated and characterized by analytical data, molar conductance, magnetic measurement, electronic spectra and thermo–gravimetric analysis. Cr(III), Fe(III) and Co(III) complexes were found to have octahedral structure. This paper describes the preparation and characterization of transition metal complexes of biacetyl monoxime phenoxy acetyl hydrazone (BAMPxH) and bi benzoyl monoxime phenoxy acetyl hydrazone (BBMPxH). The stereo–chemistry of the coordination compounds has been confirmed on the basis of electronic spectral and magnetic moment studies. Racah’s inter–electronic parameter (B), Cubic Ligand field splitting parameter (10Dq) and Nephelauxetic ratio (β), g, λ , h have also been calculated and found that the values are in accordance with the stereo–chemical structure of the coordination compounds. The ligands BAMPxH and BBMPxH are of greater importance since they have ability to chelate metal ion through nitrogen/or oxygen donor centers. Thess ligands can form such type of complexes which are biologically important. Such metal complexes show interesting and important characteristics, especially in areas such as semiconductors, heat resistance materials and gas separators. There has been growing interest for polymeric compounds which are coordinated between ligands and transition metal complexes. on the basis of elemental analysis ,magnetic moment data, conductivity measurements, electronic spectra, IR spectra and thermogravimetric analysis, Cr(III), Fe(III) and Co(III)complexes are suggested to have octahedral geometry.

Key words: BAMPxH, BBMPxH, Cr(III), Fe(III) and Co(III) complexes, 10Dq, B and β

INTRODUCTION

Co-ordination compounds exhibit different characteristics properties which depend on metal ion to which they are bound. Nature of metal ion and ligands effects different properties of metal complexes. Biacetyl monoxime phenoxy acetyl hydrazone and bibenzoyl monoxime phenoxy acetyl hydrazone as ligands can form such type of complexes which are biologically important (1-3). These ligand complexes are of grater importance since it has the ability to chelate metal ion through nitrogen/or oxygen donor centers (4). These metal complexes have found extensive application in various fields of human interest. Parameters $10Dq$, B and β for the complexes have been calculated and are reported (5-7).

EXPERIMENTAL SECTION

All chemicals used were of A.R grade. Melting points of complexes were determined in open capillaries. The conductivity measurements were made on systronic conductometer model. In visible region, the electronic spectra of the complexes in non-aqueous solution were recorded on Bausch and Lomb spectronic-20 spectrophotometer. Solvent blank was run alongwith the solution of the complexes. For reflectance spectra, VSU-2p spectrophotometer was used. Magnesium oxide was used as a reference compound. All the magnetic susceptibility measurements on the powder form of chelates were carried at room temperature using Gouy's magnetic balance and mercury (II) tetrathiocyanato cobaltate $Hg[Co(CNS)_4]$ as calibrant ($\chi_g = 10.44 \times 10^{-6}$ c.g.s. units at $20^\circ C$). All the pH measurements were carried out at room temperature on ELICO digital pH meter in conjunction with glass electrode and standard calomel electrode. The IR spectra of the ligands and complexes were recorded in KBr in the range $4,000-700\text{ cm}^{-1}$ and $4,000-200\text{ cm}^{-1}$ on Beckmann IR 5A spectrophotometer in the Chemistry Department of Central Drug Research Institute, Lucknow. The analytical data, colour Conductivity measurement. And magnetic measurement and magnetic moment have been recorded (8-10).

Materials and methods

Biacetyl monoxime phenoxy acetyl hydrazone was prepared by refluxing biacetyl monoxime (0.1 mol) and phenoxy acetyl hydrazine (0.1 mol) in 100 ml ethanol for 2-hour. The white crystals obtained were filtered, washed and recrystallised from ethanol and dried over anhydrous $CaCl_2$ ($C_{12}H_{15}N_3O_3$) similarly by adopting the same procedure bibenzoyl monoxime phenoxy acetyl hydrazone was prepared (11-14) ($C_{22}H_{19}N_3O_3$).

Preparation of Complexes

The $[Cr(HBMPxH)_2Cl.H_2O]$ complex was prepared by refluxing a hot solution of H_2BMPxH (0.002 mol) and chromium chloride hexa hydrate (0.001 mol) in 50 ml ethanol for 1 hour. The solid complex was isolated after the addition of diethyl ether with scratching. The $[Co(HBMPxH)_2Cl.H_2O]$ was produced by the same procedure using equimolar ratio of $CoCl_2.6H_2O$ and H_2BMPxH . The complex $[Fe(HBMPxH)_2Cl.H_2O]$ was isolated by refluxing H_2BMPxH (0.001 mol) and $FeCl_3.6H_2O$ (0.001 mol) in 50 ml ethanol for 1 hr. On concentration and cooling complex was separated out. The same method was applied for the isolation of the complexes of benzil monoxime phenoxy acetyl hydrazone. The complexes obtained were filtered, washed with ethanol ether and dried over anhydrous $CaCl_2$. The metal and chloride contents were analysed using standard methods(15-16).

RESULT AND DISCUSSION

The analytical data of the complexes are in agreement with their molecular formulae as shown in Table-1. All the complexes are stable at room temperature, non hygroscopic insoluble in water and readily soluble in DMF and DMSO. The molar conductivity data show that the complexes are non electrolytes in nature. The magnetic moments of the complexes, under study indicates that Cr(III) complexes are having three unpaired electrons and fall in the range required for octahedral configuration. The magnetic moment values of the complexes under study agreed with the value suggested for high spin octahedral Fe(III) complexes. The weak paramagnetic character of Co(III) complexes is ascribed to second order Zeeman effect with high ligand field. The electrolytic nature of Cr (III), Fe(III) and Co (III) complexes is further confirmed by formation of white curdy precipitates by addition of alcoholic solution of AgNO₃ to the solution of complexes in DMSO. The molecular weight of complexes determined by Rast Camphor method correspond with the weight of the formula(17).

Analytical data of Cr(III), Fe(III) and Co(III) complexes with ligands

S.No.	Complex	% Calcd. (Found)					colour
		C	H	N	Cl	Metal	
1.	[Cr(C ₁₂ H ₁₄ N ₃ O ₃) ₂ Cl(H ₂ O)]	47.70 (47.88)	4.83 (4.98)	13.82 (13.96)	5.80 (5.90)	8.50 (8.64)	(Greenish)
2.	[Cr(C ₂₂ H ₁₈ N ₃ O ₃) ₂ Cl(H ₂ O)]	61.98 (62.15)	4.35 (4.47)	9.80 (9.88)	4.0 (4.17)	6.0 (6.12)	(Grey)
3.	[Fe(C ₁₂ H ₁₄ N ₃ O ₃) ₂ Cl(H ₂ O)]	47.45 (47.57)	4.80 (4.95)	13.70 (13.87)	5.72 (5.86)	9.10 (9.22)	(Blackish)
4.	[Fe(C ₂₂ H ₁₈ N ₃ O ₃) ₂ Cl(H ₂ O)]	61.75 (61.87)	4.32 (4.45)	9.73 (9.84)	4.0 (4.16)	6.42 (6.54)	(Dark Black)
5.	[Co(C ₁₂ H ₁₄ N ₃ O ₃) ₂ Cl(H ₂ O)]	47.22 (47.33)	4.80 (4.93)	13.70 (13.80)	5.70 (5.83)	9.54 (9.68)	(Reddish Brown)
6.	[Co(C ₂₂ H ₁₈ N ₃ O ₃) ₂ Cl(H ₂ O)]	61.70 (61.87)	4.32 (4.45)	9.72 (9.84)	4.02 (4.16)	6.78 (6.90)	(Reddish Brown)

Magnetic measurements:

[Cr(C₁₂H₁₄N₃O₃)₂Cl(H₂O)] and [Cr(C₂₂H₁₈N₃O₃)₂Cl(H₂O)]

The magnetic moments of the complexes, under study, are 3.85 and 3.84 B.M. respectively. These values indicate that these complexes have three unpaired electrons and fall in the range required for octahedral configuration (18-19).

[Fe(C₁₂H₁₄N₃O₃)₂Cl(H₂O)] and [Fe(C₂₂H₁₈N₃O₃)₂Cl(H₂O)]

The magnetic moment values of the complexes under study are 5.90 and 5.92 B.M. respectively. These values fairly agreed with the value suggested for high spin octahedral complexes of Fe(III).

[Co(C₁₂H₁₄N₃O₃)₂Cl(H₂O)] and [Co(C₂₂H₁₈N₃O₃)₂Cl(H₂O)]

The weak paramagnetic character of Co(III) complexes is ascribed to second order Zeeman effect with high ligand field term(19). Both the complexes are diamagnetic in nature. The

magnetic moment values (0.40 and 0.42 B.M.) show the octahedral nature of the complexes involving d^2sp^3 hybridization (20-22).

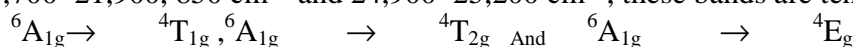
REFLECTANCE SPECTRA:

Cr(III) Complexes

The reflectance spectra of the present Cr(III) complexes show bands in 22,040–21,800 and 15,400–15,520 cm^{-1} range with a shoulder at 20,400 cm^{-1} . The bands at 21,600–21,810 and 15,375–15,480 cm^{-1} have been assigned to ${}^4A_{2g} \rightarrow {}^4T_{1g}$ and ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transitions (23-26).

Fe(III) Complexes:

The reflectance spectra of Fe(III) complexes exhibit bands in the range 16,745–16,900 cm^{-1} , 21,700–21,900, 850 cm^{-1} and 24,900–25,200 cm^{-1} , these bands are tentatively assigned as



Co(III) Complexes:

In the reflectance spectra of complexes, three bands have been observed in the range 19,250 – 19,500 cm^{-1} , 25,980–26,460 cm^{-1} and 34,000–34,250 cm^{-1} , of which the first two bands may be assigned to the following transitions: ${}^1A_{1g} \rightarrow {}^1T_{1g}$, ${}^1A_{1g} \rightarrow {}^1T_{2g}$

IR Spectra

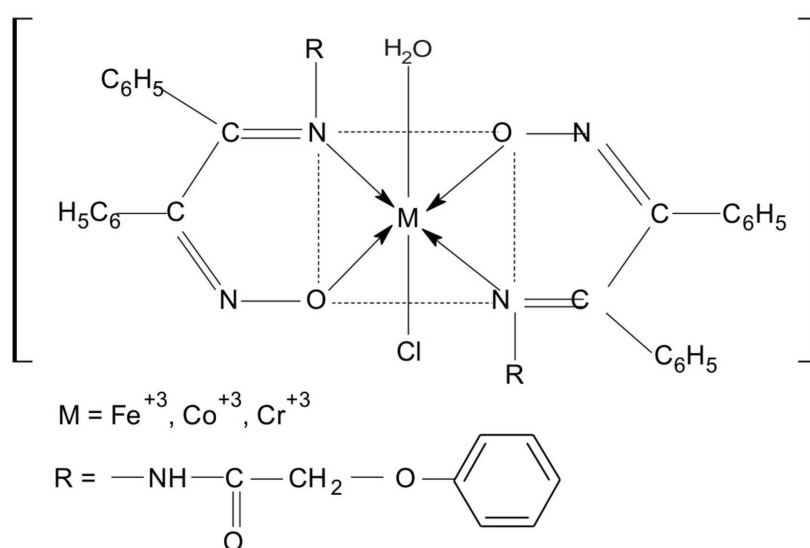
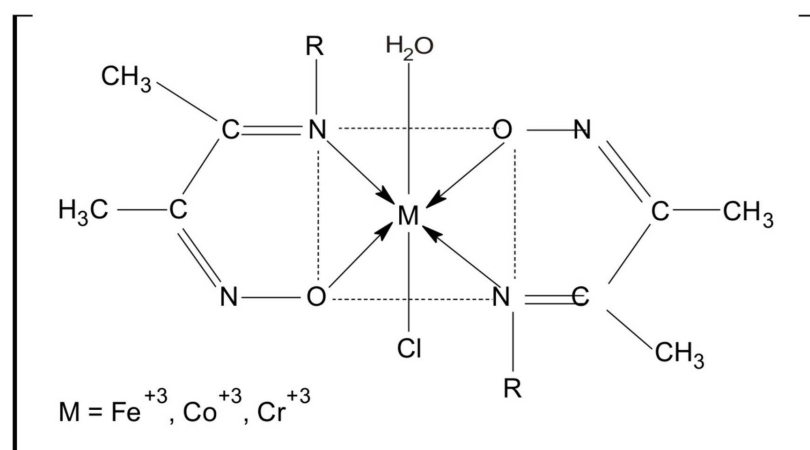
The infrared spectra of the Cr(III), Fe(III) and Co(III) complexes show some band shifts which reveal the coordination modes of the ligands with the metal ion in the present complexes. The main vibrational bands (cm^{-1}) of biacetyl monoxime phenoxy acetyl hydrazone (H_2BMPxH) and benzil monoxime phenoxy acetyl hydrazone ($H_2BBMPxH$) and its complexes are reported (27-30).

The IR–spectrum of the free ligand shows three intense bands at 1690, 1640 and 1400 cm^{-1} assigned to $\nu(C=O)$, $\nu(C=N)$ imine and $\nu(C=N)$ oxime respectively. The medium intense bands at 1020 and 980 cm^{-1} are attributed to $\nu(NO)$ and $\nu(N-N)$ stretches. The two bands observed at 3300 and 3200 cm^{-1} are probably due to $\nu(N-OH)$ oxime and $\nu(NH)$ and broad nature of the $\nu(OH)$ stretching vibration and its wave number suggests the intramolecular hydrogen bonding. Also the broad weak bands in the regions 1960–1800 and 2400–2300 cm^{-1} may support the presence of intra molecular hydrogen bonding (OH–N). The free ligand shows band for $\nu NH \sim 3280-3310 \text{ cm}^{-1}$ which do not shifted in the complexes suggesting that the ligand acts in keto form. The IR–spectrum of the complexes shows that H_2BMPxH and $H_2BBMPxH$ behaves as a mononegative bidentate ligand coordinating through (C=N) imine and the deprotonated oxime oxygen (NO^-). This mode of chelation is expected due to the disappearance of $\nu(OH)$ stretch, the shift of $\nu(C=N)$ imine to lower wave number with the remaining $\nu(C=O)$ (31-34) stretch nearly in the same position, indicates its non participation in coordination. The characteristic absorption bands of the free ligand are shifted on complexation and new vibration bands characteristic of complexes appeared showing that $H_2BMPxH/H_2BBMPxH$ behaves in a bidentate manner. The infra red spectra of all the complexes are similar indicating the presence of the same ligands throughout the series. The absence of $>C=O$ stretching frequencies and the appearance of a strong band at around 1625 cm^{-1} attributed to the coordinated $>C=N$ stretching mode suggest the condensation of the biacetyl monoxime/benzil monoxime with phenoxy acetyl hydrazone. The infrared spectra of ligands show no characteristic absorption bands assignable to either C=O or

NH₂ groups indicating the formation of ligands. Strong bands appearing in the region 1584–1576 cm⁻¹ are attributed to $\nu(\text{C}=\text{N})$ in both ligands. The strong as well as sharp bands at 1220 cm⁻¹ are due to the (N–O) stretching vibration. The strong bands observed around ~775 cm⁻¹ are assigned to (C=N–O) deformation vibration. Bands characteristic of methyl groups of diacetyl monoxime are observed in the 1454–1458 [$\nu_{\text{asy}}(\text{C}-\text{CH}_3)$] and 1380–1386 cm⁻¹ [$\nu_{\text{asy}}(\text{C}-\text{CH}_3)$] regions in the IR spectra of both the ligands(35-36).

Proposed structures

Thus on the basis of above discussion following structures can be proposed(37-38). Hence on the basis of elemental analysis, magnetic moment data, conductivity measurements, electronic spectra, IR spectra and thermogravimetric analysis, Cr(III), Fe(III) and Co(III) complexes are suggested to have octahedral geometry(39-40).



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