

Structural Investigation of Some Cr(III), Fe(III) and Co(III) Biligand Complexes

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The biligand complexes of Cr(III), Fe(III) and Co(III) with 1-(*o*-methoxy anilinomethyl)-benzimidazole (MAB) as primary and 2-thio-pyrogallol (TP) or thiosalicylic acid (TSA) as co-ligand have been isolated and characterised on the basis of analytical, conductance, magnetic moment and spectral data. Their conductance data show that Cr(III) complexes are 1 : 2 electrolytes while Fe(III) and Co(III) complexes are non-electrolytes. IR Spectra reveal that both the ligands possess two donor sites in the complexes under study. On the basis of reflectance spectral and magnetic moment data octahedral configuration is assigned for these complexes.

INTRODUCTION

In view of the biological significance of benzimidazoles¹⁻⁵ and the donor capability⁶ of sulphur compounds, it was considered worthwhile to study the biligand complexes of Cr(III), Fe(III) and Co(III) with 1-(*o*-methoxy anilinomethyl)-benzimidazole (MAB) as primary and 2-thiopyrogallol (TP) or thiosalicylic acid (TSA) as co-ligand.

EXPERIMENTAL

All the reagents used were of AR grade. Solvents were purified before use. 1-(*o*-methoxy anilinomethyl)-benzimidazole was prepared by refluxing an ethanolic solution of benzimidazole (0.01 mol), *o*-methoxy aniline (0.01 mol) and formalin (40%) on water bath for 30–40 min. Yield *ca* 65%, m.p. 112°C. 2-Thiopyrogallol was synthesised by the recommended procedure⁷ and thiosalicylic acid was procured from Aldrich Chemical Company, Inc., USA. The magnetic susceptibility at room temperature was determined on Gouy's electromagnetic balance and corrected for diamagnetism.⁸ IR spectra of the ligands and metal complexes were recorded in the range of 4000–200 cm⁻¹ in KBr/nujol mull on Perkin Elmer 577 and Perkin Elmer 621 spectrophotometers.

Preparation and isolation of complexes

A stream of air was passed through an ethanolic solution of Co(II) chloride hexahydrate for 2 h to get Co(III) chloride.

Ethanolic solution of the Mannich base (10 mmole) was added to the respective

metal salt solution (10 mmole) in the ratio 1 : 1. The mixture was refluxed for 2–3 h at 90°C. The solid complexes separated on cooling were filtered, washed with ethanol, dry ether and dried in *vacuo*.

The biligand complexes were synthesised by refluxing an ethanolic solution of the respective binary complex with 2-thiopyrogallol or thiosalicylic acid dissolved in alcohol for 1 h and cooling at room temperature. The isolated solid products were washed with ethanol, dry ether and dried over fused CaCl₂.

RESULTS AND DISCUSSION

Analytical data Table-1 proposed 1 : 1 : 1 (M–L–L'/L'') stoichiometric composition for the complexes (where L = MAB, L' = deprotonated TP and L'' = deprotonated TSA). Cr(III) complexes are 1 : 2 electrolytes while Co(III) and Fe(III) complexes are non-electrolytes as evidenced by their conductivity data in DMF at the concentration 10⁻³ M (Table-1). Cr(III) complexes start to decompose at 160°C and at 200°C a mass loss corresponding to two water molecules is observed showing them to be coordinated.

TABLE-1
ANALYTICAL AND CONDUCTIVITY DATA OF Cr(III),
Fe(III) AND Co(III) COMPLEXES

S. No.	Compounds	Analysis % (found/calcd.)						Λ_m (ohm ⁻¹ , mole ⁻¹ cm ²)
		Metal	C	H	N	S	Cl	
1.	[CrLL'(H ₂ O) ₂]Cl ₂	9.32 (9.40)	45.74 (45.57)	4.32 (4.34)	7.56 (7.59)	5.74 (5.78)	12.74 (12.82)	132.0
2.	[CrLL''(H ₂ O) ₂]Cl ₂	9.15 (9.20)	46.51 (46.73)	4.26 (4.24)	7.40 (7.43)	5.64 (5.66)	12.47 (12.55)	134.6
3.	[FeLL'Cl ₂]	10.65 (10.72)	48.08 (48.39)	3.82 (3.84)	8.04 (8.06)	6.11 (6.14)	13.55 (13.61)	5.6
4.	[FeLL''Cl ₂]	10.43 (10.48)	49.21 (9.55)	3.74 (3.75)	7.85 (7.88)	5.97 (6.00)	13.37 (13.30)	4.8
5.	[CoLL'Cl ₂]	11.20 (11.25)	48.34 (48.10)	3.79 (3.81)	8.05 (8.01)	6.07 (6.10)	13.60 (13.53)	7.4
6.	[CoLL''Cl ₂]	10.94 (10.99)	49.51 (49.26)	3.71 (3.73)	7.80 (7.83)	5.99 (5.97)	13.30 (13.23)	6.8

L = C₁₅H₁₅N₃O, L' = C₆H₅SO₂ and L'' = C₇H₅SO₂

Cr(III) complexes have magnetic moments of 3.98 and 4.01 B.M. corresponding to three unpaired electrons. The reflectance spectra of the Cr(III) complexes show bands in 21,750–21,600 cm⁻¹ and 15,480–15,400 cm⁻¹ range with a shoulder at about 20,100 cm⁻¹. The first two bands have been assigned to ⁴A_{2g} → ⁴T_{1g} and ⁴A_{1g} → ⁴T_{2g} transitions, respectively.⁹ The shoulder may be due to tetragonal distortion. The values of 10 Dq, B, β, L.F.S.E., λ and g are 21,600 cm⁻¹, 881.63, 0.85, 74.05 (kcal/mole), 27.91, 1.99 respectively for complex-1 and 21,750 cm⁻¹, 887.74, 0.86, 74.57 (kcal/mole), 42.2, 1.98 respectively for com-

plex-2. The calculated values are in accordance with those found for octahedral complexes of Cr(III).

Fe(III) complexes exhibit bands in the range 16,800–16,700 cm^{-1} , 21,850–21,700 cm^{-1} and 25,100–24,900 cm^{-1} which may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^4T_{2g}(G)$ and ${}^4E_g(G)$ transitions, respectively. Further, the band observed at about 28,000 cm^{-1} is expected to be the charge transfer band (L \rightarrow M). The bands observed at around 17,400 cm^{-1} and 29,400 cm^{-1} may be due to the split of ${}^4T_{1g}$. On the basis of observed bands the complexes are assumed to possess octahedral configuration and D_{4h} symmetry.¹⁰ The calculated values of 10 Dq, B and β are 7,656 cm^{-1} , 969 and 0.535 respectively for complex-3 and 7,700 cm^{-1} , 700 and 0.54 respectively for complex-4.

The magnetic moments of Co(III) complexes are 0.36 and 0.34 B.M. suggesting their diamagnetic nature. Two bands have been observed in the range 19,400–19,250 cm^{-1} and 26,350–25,980 cm^{-1} which may be assigned to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. The observed bands are in well agreement with the octahedral geometry.¹¹ The calculated values of 10 Dq, B, β and L.F.S.E. are 19,400 cm^{-1} , 511, 0.365, 22.17 (kcal/mole) respectively for complex-5 and 19,250 cm^{-1} , 507, 0.362, 22.0 (kcal/mole) respectively for complex-6.

Infrared spectra

The (C=N) stretching frequency band existing at 1630–1625 cm^{-1} in the infrared spectrum of MAB shows a negative shift of 25–30 cm^{-1} in complexes suggesting the involvement of *tert.* nitrogen atom of the heterocyclic ring in coordination. The absorption band characteristic of (C—O—C) stretching seen at 1100–1095 cm^{-1} in the spectrum of the Mannich base was located on the same position showing its non-involvement in complexation. A weak absorption band centred at 3340–3320 cm^{-1} in the spectrum of Mannich base attributable to (N—H) stretching frequency gets shifted to 3315–3290 cm^{-1} band suggesting the participation of nitrogen atom of (N—H) in complexation process.

A moderately weak band existing at 2560 cm^{-1} in the spectrum of co-ligands due to (S—H) stretch gets disappeared in the spectra of complexes which shows the deprotonation of —SH group. The formation of (M—S) bond in the chelates is confirmed by the appearance of a new weak band at *ca.* 310 cm^{-1} in their spectra. A strong band around 3500 cm^{-1} occurring in the spectrum of 2-thiopyrogallol is assigned to νOH (phenolic).¹² In the spectra of biligand complexes, a band, in addition to it is seen at 3470–3460 cm^{-1} which shows that both the —OH groups present in TP do not participate in complexation. It is further verified by the appearance of these bands (at *ca.* 3500 and 3470–3460 cm^{-1}) in the binary complexes with 2-thiopyrogallol. In the spectra of coordination compounds with TSA as co-ligand, the symmetric vibration of carbonyl group present at *ca.* 1310 cm^{-1} is shifted to higher wavenumber (1370–1350 cm^{-1}) while the antisymmetric stretch, $\nu(\text{C}=\text{O})$, gets shifted to lower wavenumber (1630–1615 cm^{-1}) compared to TSA (1685–1680 cm^{-1}). The position of antisymmetric stretch in complexes at Sl. No. 2, 4 and 6 clearly indicates that the metal ion forms a bond with the carbonyl oxygen of TSA.

Some non-ligand bands at 520–500, 430–420 and 235–230 cm^{-1} (except in chromium complexes) may be assigned to $\nu(\text{M—O})$, $\nu(\text{M—N})$ and $\nu(\text{M—Cl})$ stretching vibrations, respectively. The H—O—H stretching vibration band in Cr(III) complexes is probably merged with OH band of 2-thiopyrogallol. The existence of somewhat weaker bands around 850 and 700 cm^{-1} in the Cr(III) complexes is most probably due to OH rocking and wagging vibrations¹³ of coordinated water.

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