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# Synthesis and Structural Studies of Cr(III) and Fe(III) Ternary Complexes

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Ternary complexes of Cr(III) and Fe(III) with isonitrosoacetophenone-2-furoic hydrazide/4-chloroisonitrosoacetophenone-2-furoic hydrazide (INAPFH/ClINAPFH) as primary and 1-(*o*-methoxyanilinomethyl) benzimidazole (MAMB) as co-ligand have been synthesised and characterised by chemical analysis, magnetic, spectral and thermogravimetric studies. Analytical data suggested 1 : 1 : 1 (M-L/L′-L″) stoichiometric composition for the isolated complexes [where M = Cr(III)/Fe(III), L = $C_{13}H_{10}N_3O_3$, L′ = $C_{13}H_9N_3O_3Cl$ and L″ = $C_{15}H_{15}N_3O$]. The $\Omega_m$ values of the complexes (178.4–182.6 $ohm^{-1}$ $cm^2$ $mol^{-1}$) in DMF at the concentration $10^{-3}$ M indicate their 1 : 2 electrolytic nature. Comparison of the IR sepctra of ligands and complexes show that tridentate nature of the hydrazide with oximino and azomethine nitrogen and carbonyl oxygen as the donor sites and bidentate behaviour of the co-ligand possessing nitrogen atoms of the C=N (benzimidazole ring) and NH as potential donors. Magnetic moments, reflectance spectral bands and values of ligand field parameters show that the complexes possess octahedral stereochemistry. The complexes are thermally stable up to 150°C and a mass-loss corresponding to one molecule of water in 160–180°C temperature range shows the presence of coordinated water in them. At 570–700°C, organic ligands are completely lost and stable metallic oxides are obtained.

## INTRODUCTION

Acid hydrazides, in addition to their importance in pharmacy, play a prominent role in agriculture and synthesis of many organic compounds. 2-Furoic hydrazide is one of the starting materials in the synthesis of low density foams[1], fungicides[2] and nervous stimulants[3]. Isonitrosoketones form stable chelates with transition metal ions showing a variety of structural features[4–8]. A survey of the literature reveals that the ternary complexes of Cr(III) and Fe(III) with isonitrosoacetophenone-2-furoic hydrazide/4-chlorosonitrosoacetophenone-2-furoic hydrazide as primary and 1-(*o*-methoxy anilinomethyl) benzimidazole as co-ligand have not been studied so far. In the present article, we report the synthesis and structural characterization of these complexes.

## EXPERIMENTAL

Isonitrosoacetophenone and 4-chloroisonitrosoacetophenone were synthesized

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by the reported procedure[9]. 2-Furoic hydrazide was procured from Aldrich Chemical Company Inc., U.S.A. Furoic hydrazide derivatives of the ketones were prepared by condensing isonitrosoacetophenone/4-chloroisonitrosoacetophenone and 2-furoic hydrazide. 1-(*o*-Methoxyanilinomethyl)-benzimidazole was prepared by refluxing a mixture of *o*-methoxyaniline (0.10 mole), formaldehyde (40%) and benzimidazole (0.01 mole) using ethanol as solvent. The ligands were purified by recrystallisation from acetone. All chemicals used were of AnalaR grade. Conductivity measurements were carried on Systronics conductivity bridge. IR spectra were recorded on Perkin-Elmer 783 spectrophotometer. Reflectance spectra were taken on Carl-Zeiss Jena VSU-2P spectrophotometer.

### Perparation and Isolation of the Complexes

The respective hydrazide schiff base (INAPFH/ClINAPFH) dissolved in ethanol (40 mL, 0.01 mol) was mixed with the Mannich base (MAMB) in ethanol (30 mL, 0.01 mol) and 20 mL metal(III) salt solution (0.01 mol) in the same solvent was added dropwise with constant stirring by a magnetic stirrer. The resulting mixture was refluxed for 2–2.5 h. The separated complexes, on cooling, were filtered, washed with ethanol, dry ether and dried *in vacuo* over $P_2O_5$. Yield 60–62%.

## RESULTS AND DISCUSSION

Analytical data reported in Table-1 suggest 1 : 1 : 1 stoichiometric composition for the complexes. The ternary complexes are insoluble in common organic solvents and water but dissolve appreciably in DMF and DMSO. The molar conductance data (Table) in DMF at the concentration $10^{-3}$ M indicate their 1 : 2 electrolytic nature.

### Magnetic and Reflectance Spectral Studies

**Cr(III) complexes:** The magnetic moment values of Cr(III) complexes at 300 K ($\mu_{eff}$ = 3.81–3.84 B.M.) correspond to three unpaired electrons and support $O_h$ symmetry of the complexes[10].

Structural information is further supported from the d-d spectral bands in the complexes. The complexes exhibit bands in the range 17,800–17,300, 22,900–23,200 and 37,650–37,540 $cm^{-1}$ assigned to the transitions: $^4A_{2g} \rightarrow {}^4T_{2g}(\nu_1)$, $^4T_{1g}(\nu_2)$ and $^4T_{1g}$ (P)($\nu_3$) respectively. In addition, a band in the range 13,100–12,800 $cm^{-1}$ is also observed which may be due to $^4A_{2g} \rightarrow {}^2T_{2g}, {}^2E_g$ transition.

The decrease in the value of $B_{35}$ is about 30–32% of the free ion value which shows a considerable amount of covalent nature of the bonding of metal with the ligand. The parameter $B_{55}$ has been calculated from the equation: $E(^4A_{2g} \rightarrow {}^2E_g) = 9B_{55} + 3C - 50B_{55}^2/10\,Dq$. The values of $B_{35}$, $B_{55}$, $\beta_{35}$, $\beta_{55}$, covalency parameter ($\beta_{35}/\beta_{55}$) and spin-orbit coupling constant of the Cr(III) complexes are: 706–726 $cm^{-1}$, 600–522 $cm^{-1}$, 0.70–0.68, 0.58–0.5068, 1.38–1.19, 86.5–44.5 $cm^{-1}$ respectively.

**Fe(III) complexes:** The magnetic moments of Fe(III) complexes lie in the range 5.88–5.94 B.M. a characteristic of high spin Fe(III).

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF Cr(III) AND Fe(III) COMPLEXES

| Compound (Colour) | % Analysis, Calcd (Found) | | | | | $\Omega m$ ($ohm^{-1}$ $cm^2$ $mol^{-1}$) | $\mu_{eff}$ (B.M.) |
|---|---|---|---|---|---|---|---|
| | C | H | N | Cl | M | | |
| $[CrLL''(H_2O)]Cl_2$<br>(Blue) | 51.68<br>(51.24) | 4.15<br>(4.19) | 12.92<br>(12.84) | 10.91<br>(10.84) | 8.03<br>(8.10) | 181.40 | 3.83 |
| $[CrL'L''(H_2O)]Cl_2$<br>(Green) | 49.08<br>(49.39) | 3.79<br>(3.77) | 12.27<br>(12.18) | 15.54<br>(15.62) | 7.62<br>(7.56) | 178.84 | 3.81 |
| $[CrLL''(H_2O)](NO_3)_2$<br>(Bluish) | 47.78<br>(47.38) | 3.84<br>(3.81) | 15.92<br>(15.99) | – | 7.42<br>(7.37) | 182.60 | 3.84 |
| $[CrL'L''(H_2O)](NO_3)_2$<br>(Green) | 45.54<br>(45.26) | 3.52<br>(3.50) | 15.18<br>(15.02) | 4.81<br>(4.78) | 7.07<br>(7.02) | 180.80 | 3.83 |
| $[FeLL''(H_2O)]Cl_2$<br>(Blackish) | 51.39<br>(51.06) | 4.13<br>(4.10) | 12.84<br>(12.76) | 10.84<br>(10.91) | 8.54<br>(8.50) | 182.30 | 5.94 |
| $[FeL'L''(H_2O)]Cl_2$<br>(Reddish brown) | 48.82<br>(49.12) | 3.77<br>(3.74) | 12.21<br>(12.29) | 15.46<br>(15.32) | 8.11<br>(8.03) | 179.70 | 5.90 |
| $[FeLL''(H_2O)](NO_3)_2$<br>(Blackish) | 47.53<br>(47.30) | 3.82<br>(3.80) | 15.84<br>(15.71) | – | 7.90<br>(7.84) | 181.20 | 5.88 |
| $[FeL'L''(H_2O)](NO_3)_2$<br>(Blackish) | 45.32<br>(45.02) | 3.51<br>(3.48) | 15.11<br>(15.01) | 4.78<br>(4.74) | 7.53<br>(7.48) | 182.40 | 5.91 |

$L = C_{13}H_{10}N_3O_3$; $L' = C_{13}H_9N_3O_3Cl$ and $L'' = C_{15}H_{15}N_3O$.

The reflectance spectra of Fe(III) complexes exhibit bands in the range 16,400–16,550, 21,400–21,600 and 24,500–24,620 $cm^{-1}$ corresponding to the transitions: ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^4T_{2g}$ and ${}^4E_g$ respectively. The values of parameters 10Dq, B, $\beta$, Dqz, Dt, $\delta\sigma$ and $\delta\pi$ for the complexes are: 7,516–7,582 $cm^{-1}$, 683.3–689.5 $cm^{-1}$, 0.530–0.625, –1025 to –1015 $cm^{-1}$, 2,527.6–2,551.9 $cm^{-1}$, –284.3 to –281.8 $cm^{-1}$ and –379.1 to –375.8 respectively. The values arc corresponding to the high spin octahedral Fe(III) complexes.

## IR Spectra

The band, characteristic to —OH stretching frequency of the >NOH group present in INAPFH/C1INAPFH, is not identified in the spectra of ternary complexes showing the deprotonation and subsequent replacement of proton of >NOH group by the metal ion. The bond formation of the metal with oximino nitrogen is indicated by the positive shift of 15–20 $cm^{-1}$, in 1,015–1,010 $cm^{-1}$ band[11]. A positive shift of 20–30 $cm^{-1}$ in $\nu C{=}N$ vibrations (*ca.* 1,610 $cm^{-1}$ in INAPFH/C1INAPFH) in case of the complexes shows the participation of azomethine nitrogen in complexation. A sharp band is seen in the range 1,665–1,660 $cm^{-1}$ in the spectra of both the hydrazides indicating the presence of amide–I band [$\nu(C{=}O)$]. Further, two additional bands observed at 1,515–1,505 (w) and 1,330–1,320 (sh) $cm^{-1}$ in the hydrazides may be assigned as amide-II and amide-III bands[12] respectively. In the complexes, these bands appear at 1,650, 1,525 and 1,310 $cm^{-1}$ suggesting the coordination of carbonyl oxygen.

In the spectrum of MAMB, a weak band is observed at 3330 $cm^{-1}$ which may be due to N—H stretching vibrations. This band is not located in the spectra of ternary complexes and instead of it, a new band appears at *ca.* 3,300 $cm^{-1}$ which indicates the involvement of nitrogen of $CH_2$—NH in coordination of it seems to be justified by the negative shift (20–15 $cm^{-1}$) of ν($CH_2$—N) vibrations in the complexes (2,800 $cm^{-1}$ in MAMB). ν(C═N) of benzimidazole ring (present in MAMB) existing at 1,575 $cm^{-1}$ gets shifted to lower frequency band (1,540–1,535 $cm^{-1}$) in the ternary complexes suggesting the involvement of nitrogen of C═N. The bands due to C—O—C present in the spectra of MAMB and INAPFH/ClINAPFH remain unaltered in the complexes.

Two non-ligand medium intensity bands occurring at 510–505 and 425–415 $cm^{-1}$ in the spectra of complexes may tentatively be assigned as ν(M—O) and ν(M—N) vibrations respectively. The existence of broad band around 3,425 $cm^{-1}$ and somewhat weaker bands around 850 and 700 $cm^{-1}$ in the complexes, assigned to —OH stretching, rocking and wagging vibrations[13] respectively confirms the presence of coordinated water in them.

## Thermal behaviour

The thermo-oxidative degradation of the complexes was studied by thermogravimetry. The initial endothermic weight loss in 160–180°C temperature range corresponds to a water molecule essentially present in the coordination sphere. Further decomposition occurred in 370–490°C temperature range with the elimination of the hydrazide moiety. Thereafter, a continuous mass loss was observed in 670–700°C range and organic ligands were completely lost forming the corresponding metal oxides.

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