

Synthesis and Structural Characterisation of Some New Ternary Complexes of Co(II and III) and Ni(II)

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Ternary complexes of Co(II and III) and Ni(II) with isonitrosoacetophenone isonicotinic hydrazide (INAPIH)/isonitrosoacetophenone furoic hydrazide (INAPFH) as primary and 1-(*o*-methoxy anilinomethyl) benzimidazole (MAMB) as secondary ligand have been synthesised and characterised on the basis of analytical, conductance, spectral and TG data.

INTRODUCTION

Isonitrosoketones are expected to behave as versatile potential ambidentate ligands. They form stable chelates with transition metal ions showing a variety of structural features¹⁻⁵. The isonitroso moiety ($>C=NOH$), also referred to as hydroxyamino group in the literature, can coordinate either through nitrogen or oxygen atom producing chelate linkage isomers. Coordinating ability of isonitrosoacetophenone with alkali and alkaline earth metal ions has been explored⁶. Isonitrosoacetophenone has long been employed in the separation and spectrophotometric determination of Ni(II), Pd(II), Co(II) and Fe(II) ions⁷⁻⁹. Here we report the synthesis and structural characterisation of the ternary complexes of Co(II, III) and Ni(II) with isonitrosoacetophenone isonicotinic hydrazide (INAPIH) isonitrosoacetophenone furoic hydrazide (INAPFH) (primary ligand) and 1-(*o*-methoxy anilinomethyl) benzimidazole (secondary ligand) with a view that the synthesised complexes with these biologically active ligands may be of medicinal significance.¹⁰⁻¹²

EXPERIMENTAL

Isonicotinic/furoic hydrazide and benzimidazole were procured from Aldrich Chemical Co. Inc., USA. Isonitrosoacetophenone was prepared as reported in the literature.¹³ INAPIH and INAPFH were prepared by condensing isonitrosoacetophenone with isonicotinic and furoic acid hydrazide respectively for 40–45 min in ethanol. 1-(*o*-Methoxy anilinomethyl) benzimidazole was (MAMB) obtained by refluxing an equimolecular mix of benzimidazole and *o*-methoxy aniline with formalin (40%) using ethanol as a solvent.

Conductivity measurements were carried out on Toshniwal conductivity bridge while IR spectra were taken on Perkin- Elmer 621 spectrophotometer.

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Preparation and isolation of the complexes

The mixed ligand complexes were synthesised by mixing in stoichiometric quantities of an aqueous solution of M(II) nitrate/chloride ($M = \text{Co}^{2+}$ or Ni^{2+}) and ethanolic solutions of INAPIH/INAPFH and MAMB dropwise with constant stirring and adjusting the pH of the reaction mixture to *ca.* 6.6 by the addition of a dilute solution of ammonia. Pink or red coloured complexes of Co(II) and grey or green coloured complexes of Ni(II) were separated. It was noted that brown or red coloured Co(III) complexes were precipitated instead of Co(II) complexes in case of Co(II) chloride, which may probably be due to the ease of oxidation of Co(II) to the corresponding Co(III) complexes under the experimental conditions. This, however, does not happen when $\text{Co}(\text{NO}_3)_2$ is used as the metal salt. The complexes were well washed with appropriate solvents like ethanol/chloroform/dry ether and dried at 110°C . The complexes were recrystallised from methanol.

RESULTS AND DISCUSSION

Analytical data of the present complexes are reported in the Table-1 suggest 1 : 1 : 1 stoichiometric composition of the complexes. The complexes are soluble in DMSO and DMF. The molar conductance values in DMSO at the concentration 10^{-3} M show 1 : 1 electrolytic behaviour of Co(II) and Ni(II) complexes and 1 : 2 electrolytic nature of those of Co(III).

TABLE-1
ANALYTICAL AND CONDUCTANCE DATA OF Co(II), Co(III) AND Ni(II) COMPLEXES

Complex	Found (Calcd.) %					AM $\Omega^{-1} \text{cm}^2 \text{mole}^{-1}$
	C	H	N	Cl	M	
[CoLL''(H ₂ O)]NO ₃	52.34 (52.81)	4.21 (4.24)	16.88 (16.99)	–	8.88 (8.94)	43.1
[CoL'L''(H ₂ O)]NO ₃	52.22 (51.85)	4.14 (4.16)	15.01 (15.12)	–	9.03 (9.09)	39.8
[CoLL''(H ₂ O)]Cl ₂	51.78 (52.10)	4.22 (4.19)	14.57 (14.67)	10.68 (10.61)	8.75 (8.82)	78.2
[CoL'L''(H ₂ O)]Cl ₂	50.82 (51.15)	4.09 (4.11)	12.69 (12.78)	10.70 (10.79)	8.91 (8.97)	77.8
[NiLL''(H ₂ O)]NO ₃	52.61 (52.83)	4.21 (4.25)	16.87 (17.00)	–	8.84 (8.91)	41.6
[NiL'L''(H ₂ O)]NO ₃	51.59 (51.87)	4.13 (4.16)	15.24 (15.13)	–	9.15 (9.06)	40.7
[NiLL''(H ₂ O)]Cl	54.72 (55.04)	4.38 (4.42)	15.37 (15.50)	5.56 (5.60)	9.22 (9.28)	42.2
[NiL'L''(H ₂ O)]Cl	54.31 (54.09)	4.31 (4.34)	13.46 (13.52)	5.67 (5.70)	9.40 (9.45)	41.2

where L = C₁₄H₁₁N₄O₂, L' = C₁₃H₁₀N₃O₃ and L'' = C₁₅H₁₅N₃O

The electronic spectra of the solution of Co(II) complexes in DMF exhibit bands at 8,450–8,300 (ν_1), 17,650–17,450 (ν_2) and 20,370–20,250 cm^{-1} (ν_3) which are assigned to the transitions: ${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$, ${}^4A_{2g}(F)$ and ${}^4T_{1g}(P)$ respectively. The appearance of these bands suggested octahedral geometry around Co(II) ion.

Spectra of Co(III) complexes, under study, exhibit three bands in the range 19,350–19,200, 26,050–25,700 and 34,200–34,000 cm^{-1} . The first two bands are assigned to the transitions: ${}^1A_{1g} \longrightarrow {}^1T_{1g}$ and ${}^1A_{1g} \longrightarrow {}^1T_{2g}$ respectively. The third band may be due to charge-transfer transition. The observed spectral bands are in well agreement with the octahedral geometry of the complexes.

The spectra of the present Ni(II) mixed ligand complexes exhibit bands at 10,100–9,800, 16,200–15,880 and 27,300–27,150 cm^{-1} which may be assigned to the transitions: ${}^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)(\nu_1)$, ${}^3T_{1g}(F)(\nu_2)$, ${}^3T_{1g}(P)(\nu_3)$ respectively. A shoulder at about 12,850–12,700 cm^{-1} is also observed which may be due to the transition ${}^3A_{2g} \longrightarrow {}^1E_g$. The positions of the bands suggest the octahedral stereochemistry for the complexes.

A comparison of the infrared spectra of the metal complexes and ligands do not reveal any band in the complexes attributable to the —OH stretching frequency of the NOH group present in INAPIH/INAPFH, the absence of which is also confirmed by the insolubility of the complexes in dilute alkali solution. This observation suggests that the proton of the —NOH group is replaced by the metal ion. The bond formation of the metal with N of oximino group of INAPIH/INAPFH is indicated by the shift of $\nu(\text{N—O})$ (*ca.* 1,010 cm^{-1}) band to higher frequency band¹⁴ (1,050–1,040 cm^{-1}). A positive shift to 20–30 cm^{-1} in $\nu(\text{C=N})$ vibrations (*ca.* 1,610 cm^{-1} in INAPIH/INAPFH) in case of the complexes implies the participation of N of C=N group in coordination. In the spectrum of MAMB, a weak band is observed at 3,330 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 $\text{CH}_2\text{—NH}$ in coordination and it seems to be justified by the negative shift (25–20 cm^{-1}) of $\nu(\text{CH}_2\text{—N})$ vibrations observed at 2,800 cm^{-1} in MAMB. $\nu(\text{C=N})$ of benzimidazole ring (present in MAMB) existing at 1,575 cm^{-1} gets shifted to lower frequency band (1,545–1,535 cm^{-1}) in the complexes suggesting the involvement of nitrogen of C=N group. The band due to C—O—C present in the spectra of MAMB (due to —OCH₃) and INAPFH (due to furan ring oxygen) remains unaltered in the complexes suggesting non-involvement of oxygen of C—O—C in bond formation with the metal. Similarly, the bands due to pyridine ring in INAPIH remain unaltered showing that pyridinic nitrogen does not participate in complexation.

A sharp band is seen in the range 1,665–1,660 cm^{-1} in the spectra of both the hydrazides (primary ligands) which is indicative of the presence of amide-I band [$\nu(\text{C=O})$]. Further, two additional bands observed at 1,515–1,505 cm^{-1} and

1330–1320 cm^{-1} in the above hydrazides may be assigned as amide-II and amide-III bands respectively. In the complexes, these bands appear at 1650, 1525 and 1310 cm^{-1} suggesting the coordination of carbonyl oxygen.

Two non-ligand medium intensity bands appearing at 515–505 and 420–400 cm^{-1} in the spectra of all the complexes may tentatively be assigned as $\nu(\text{M—O})$ and $\nu(\text{M—N})$ vibrations respectively. The existence of broad band around 3430 cm^{-1} and somewhat weaker bands around 850 and 700 cm^{-1} in the complexes, assigned to OH stretching, rocking and wagging vibration¹⁵ respectively confirms the presence of coordinated water in them.

Thermal behaviour

The complexes showed endothermic mass loss in 150–180°C temperature range. The mass loss agrees well with the loss of one molecule of coordinated water. Further decomposition occurred in 340–480°C temperature range with the elimination of the hydrazide ligand. Thereafter, a continuous mass loss is observed in 520–630°C temperature range and the organic part of the complex is completely eliminated leading to the formation of metal oxide (CoO/NiO). Sharp exothermic peaks are observed in 490–650°C temperature range in DTA curves. In case of cobalt complexes, above this temperature, increase in the mass of the residue is observed up to 750°C. At this temperature, the weight of the residue corresponds to the formation of Co_3O_4 . The increase in the mass is probably due to the air oxidation of CoO into Co_3O_4 as observed by Sceney *et al.*¹⁶

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