

Synthesis and Characterisation of Ruthenium(III) Complexes with Benzimidazole Derivatives

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Complexes of ruthenium trichloride with biologically important benzimidazole derivatives, viz., 2-(hydroxy methyl) benzimidazole, 2-(1-hydroxy ethyl) benzimidazole, 2-(mercapto methyl) benzimidazole, 2-(1-mercapto ethyl) benzimidazole, and 2,2'-bis-benzimidazole have been synthesized by reacting the above metal chloride and ligands respectively in 1:3 molar ratio. These complexes are characterised on the basis of elemental analysis, molar conductance data, room temperature, magnetic moment values, electronic spectral and IR spectral studies.

INTRODUCTION

In recent years the chemistry of ruthenium complexes with biologically important pyridyl and poly pyridyl ligands have been investigated by several researchers¹⁻⁶ because of their key role in photoluminescence, photochemistry and photophysical processes^{7,8}. In view of these studies, the coordination compounds of imidazoles and benzimidazoles with iron and ruthenium metal ions have been investigated⁹⁻¹³.

The present communication describes the synthesis and characterisation of the complexes of ruthenium trichloride with 2-substituted benzimidazoles and 2,2'-bis-benzimidazole derivatives.

EXPERIMENTAL

Ortho-phenylene diamine and carboxylic acids required for the synthesis of the ligands were of reagent grade and used after recrystallisation. Ruthenium trichloride supplied by Aldrich chemicals was repeatedly (3-4 times) evaporated to dryness with concentrated HCl before use.

Preparation of the Ligands

2-(hydroxy methyl) benzimidazole (HMBZH)

2-(1-hydroxy ethyl) benzimidazole (HEBZH)

2-(mercaptomethyl) benzimidazole (MMBZH)

2-(1-mercapto ethyl) benzimidazole (MEBZH)

and 2,2'-bis-benzimidazole (bis-BZH)

were prepared as described in the literature by Phillips¹⁴ and Heins¹⁵ *et al.*

Preparation of Complexes

Tris-(2-(oxymethyl) benzimidazolato) Ruthenium(III): A suspension of RuCl_3 (0.002 mole; 0.415 g) in ethanol was refluxed until dissolution was completed in approximately 1.5 h. To the resulting solution, HMBZH (0.006 mole; 0.835 g) in ethanol was added.

Further the mixture was refluxed for 4 h, during which colour was changed from light brown to yellowish brown. The brown solution was filtered, evaporated under reduced pressure (1 mm) and dried over fused CaCl_2 . Yield: 78%.

The complexes of ruthenium with the ligands, viz., HEBZH, MMBZH, MEBZH and bis-BZH were prepared in a similar manner as described above to give 74%, 79%, 82% and 68% yield respectively.

Ruthenium in the complexes was analysed by thermal decomposition (500–600°C) of the complexes to the oxide (RuO_2). Sulphur was determined gravimetrically as BaSO_4 ; nitrogen was determined by Kjeldahl's method.

Magnetic susceptibilities of the complexes at room temperature were measured on a Guoy's balance using $[\text{HgCo}(\text{SCN})_4]$ as calibrant. Electronic spectra in chloroform were recorded on a visible Sp-8–100 model Pye-Unicam spectrophotometer in the range 350–600 nm. Infrared spectra of the ligands and complexes were recorded on a Perkin-Elmer spectrophotometer model 577 in the range 3000–300 cm^{-1} .

RESULTS AND DISCUSSION

The results of elemental analysis and room temperature magnetic moment values along with the spectral data are recorded in Tables 1 and 2 respectively. The molar conductance in methanol for the complexes (i–v) are under 50 mhos indicating that these complexes are non-electrolytic in nature.

TABLE-I
COLOUR AND ELEMENTAL ANALYSIS FOR RUTHENIUM COMPLEXES (i)–(v)

Compound	Colour	Elemental analysis, % Found (Calcd.)				
		C	H	N	S	Ru
(i) $\text{Ru}(\text{OMBZH})_3$	Brownish	52.64 (53.13)	4.26 (4.45)	15.36 (15.49)	—	17.81 (18.62)
(ii) $\text{Ru}(\text{OEBZH})_3$	Brownish	54.96 (55.47)	4.57 (4.65)	14.25 (14.37)	—	17.16 (17.28)
(iii) $\text{Ru}(\text{SMBZH})_3$	Dark Brown	47.94 (48.79)	3.89 (4.05)	14.10 (14.22)	16.07 (16.28)	16.98 (17.10)
(iv) $\text{Ru}(\text{SEBZH})_3$	Dark Brown	50.72 (51.24)	4.08 (4.30)	13.17 (13.28)	14.99 (15.19)	15.86 (15.97)
(v) $\text{Ru}(\text{SEBZH})_3$	Bluish	62.15 (62.75)	4.97 (5.26)	20.73 (20.90)	—	12.49 (12.57)

The magnetic moment values (Table-2) for the complex derivatives (i–v)

ranges between 1.93–2.16 B.M., corresponding to the presence of one unpaired electron, indicative of their paramagnetic nature.

TABLE-2
MOLAR CONDUCTANCE, MAGNETIC MOMENT AND ELECTRONIC
SPECTRAL DATA FOR THE COMPLEXES

Compound	Molar conductance in mho cm ² mol ⁻¹	Magnetic moment in B.M.	Absorbance in nm	10 Dq values in cm ⁻¹
(i)	10.8	1.93	363	27540
(ii)	10.2	1.95	360	27770
(iii)	10.4	1.94	375–365	26610
(iv)	20.2	1.95	362	27400
(v)	30.6	2.03	430	23250

The electronic spectra of these complex derivatives (i–v) shows a continuous decrease in absorption from 350–600 nm. The spectra of (i–iv) complex derivatives show a distinct absorption maxima at 363, 360, 365 and 362 nm respectively, whereas the spectrum of derivative (v) show a plateau around 450 nm. The differences in the position of absorption maxima in the spectra of these complexes can be attributed to the dissimilarities in the coordination field of the ligand around the metal ion.

The field generated by the ligands in case of complexes (i) and (ii) is of N₂O₃ type; in (iii) and (iv) it is of N₂S₃ type and in (v) it is of N₃N₃ type. However, the ligand field strength in the complexes (i–iv) are of nearly same magnitude (10 Dq = 27000 cm⁻¹) and are higher as compared to that of complexes of Ru(III) with bis-BZH. In all the complexes (i–v) five-membered chelate rings are formed by the ligands around the metal ion. On the basis of 10 Dq values, the absorption maxima in the electronic spectra of these derivatives may be assigned to ²T_{2g} → ²A_{2g} transition in the Ru(III) ion.

IR spectrum of the ligand in (KBr) shows the following prominent absorption bands in the range 3200–2900 cm⁻¹ and 1410 cm⁻¹, corresponding to ν_{asym}(N—H) stretching and δ(N—H) bending vibrations. The bands around 2560 cm⁻¹ in the spectra of MMBZH and MEBZH were assigned to ν_{asym}(S—H) stretching vibrations.

The absorption bands assigned to ν_{asym}(O—H) stretching and bending vibration in the IR spectra of HMBZH and HEBZH respectively were found to be absent in the spectra of ruthenium complexes. The absence of these bands in the spectra of complex derivatives (i–ii) is indicative of the deprotonation of O—H group of the ligand, which is expected to take place on reaction with ruthenium trichloride. The above conjecture is further supported by the formation of Ru—O bond, observed at 365 and 348 cm⁻¹ in the spectra of the (i) and (ii) complex derivatives. Similarly absorption bands characteristic of the ligands due to ν_{asym}(S—H) stretching vibration also disappeared in the spectra of complex derivatives (iii) and (iv). Deprotonation of the S—H group of the ligand during the reaction with ruthenium trichloride was further supported by the

presence of weak absorption band due to Ru—S bond at 345 and 330 cm^{-1} respectively. It may be mentioned that IR bands for Ru—S vibrations in some of the ruthenium complexes with sulphur ligands¹⁶ have been observed as weak to medium intensity absorption bands in the range 400–300 cm^{-1} .

The position of absorption bands at 3200–1410 cm^{-1} assigned to $\nu_{\text{asym}}(\text{N—H})$ and $\delta(\text{N—H})$ vibrations observed in the spectra of the ligands remains unaffected in the spectra of corresponding complexes of Ru(III) (i–v). On the basis of above observation it can be considered that the N—H group of benzimidazole nucleus is not deprotonated during the complex formation with ruthenium trichloride.

The absorption band due to asymmetric C=N stretching vibrations (pyridyl nitrogen) of benzimidazole nucleus which is observed at 1610 cm^{-1} in the spectra of complex derivative, meaning thereby that no effect on C=N stretching vibration takes place due to coordination of tertiary nitrogen atom of benzimidazole ring with the metal ion. A similar observation was reported by Ghosh and coworkers¹⁷ in case of the large number of complexes of benzimidazolyl ligands with transition metal ions.

The absorption bands of medium intensity in the IR spectra of complex derivative (v) observed at 310 and 305 cm^{-1} have been assigned to $\nu_{\text{asym}}(\text{Ru—N})$ stretching vibrations. Further the absence of absorption band due to Ru—Cl bond in the spectra of above complexes is supportive of the formation of Ru—N bond.

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