

Synthesis and Characterisation of Some New Ruthenium(III) Schiff Base Complexes

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In the present work, the author reports four ruthenium complexes of aromatic Schiff bases.

INTRODUCTION

Although a number of ruthenium(III) coordination complexes have been reported¹, complexes with Schiff base ligands are less known^{2,3}. We report here four ruthenium complexes with aromatic Schiff bases prepared from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as starting material and characterised by physicochemical and spectroscopic data.

EXPERIMENTAL

Carbohydrazide was prepared by the reported method⁴. The 1,5-bis(carbohydrazones) were prepared by reacting carbohydrazide with aromatic aldehydes (viz. salicylaldehyde, cinnamaldehyde, acetophenone or benzaldehyde) in 1 : 2 molar ratio respectively. The purity of the ligands was checked by C, H and N analysis.

The $[\text{RuL}_2\text{Cl}_2]\text{Cl}$ complexes were prepared when 1,5-bis(carbohydrazone) of salicylaldehyde, benzaldehyde, acetophenone or cinnamaldehyde (2 mmol) was dissolved in methanol; to it was added $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (1 mmol). The mixture was then refluxed for 8 hrs. The resulting solid product was filtered and washed with methanol and air-dried.

Magnetic susceptibility was measured by the Faraday method using a Cahn magnetic susceptibility system at room temperature. $\text{Hg}[\text{Co}(\text{CNS})_4]$ was used as a standard for calibration. The electron spin resonance (ESR) spectra were measured on a Bruker 300 ESR instrument with 100 MHz modulation. The spectral g values were calibrated with a DPPH standard.

The X-ray photoelectron spectra were recorded on a VG Scientific ESCA-3MK II electron spectrometer. The MgK_α X-ray line (1253.6 eV) was used for photoexcitation. The $\text{Cu } 2p_{3/2}$ (BE = 932.8 ± 0.2 eV) and $\text{Au } 4f_{7/2}$ (BE = 83.8 ± 0.1 eV) lines were used to calibrate the instrument and $\text{Ag } 3d_{5/2}$ (BE = 368.2 eV) was

used for cross-checking⁵. All the spectra were recorded using the spectrometer parameter of 50 eV pass energy and 4 mm slit width. The reduced full width at half maximum (FWHM) at Au $4f_{7/2}$ (BE = 83.8 eV) level under these conditions was 1.2 eV.

The powder sample was mixed with high purity silver powder to reduce the charging effect. A thin layer of such a sample was pressed on a gold metal gauze which was welded to a nickel sample holder. The Ag $3d_{5/2}$ level (BE = 368.2 eV) obtained from this sample was sharp, and did not show any observable shift. Thus the charging if at all present was negligible.^{6,7} In most of the cases the binding energies were reproducible within ± 0.1 eV. The usual least squares fitting procedure of determining peak position and area was used.

RESULTS AND DISCUSSION

All these complexes $[\text{RuL}_2\text{Cl}_2]\text{Cl}$ are stable with high melting points and insoluble in common organic solvents except DMF and DMSO. Elemental analyses were within $\pm 0.5\%$ for C, H, N and Cl. The molar conductance data (between $65\text{--}90 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) in DMF suggested that complexes are electrolytes of the type 1 : 1 stoichiometry with composition of $[\text{RuL}_2\text{Cl}_2]\text{Cl}$.

The UV spectra of these complexes obtained as Nujol mulls, gave few bands in the region 220 nm, 250 nm and 340 nm mainly attributed to charge transfer and intraligand $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition. The electronic spectra of these complexes show a weak d-d transition band at ca. 699 nm. These peaks have been assigned to a d-d transition of spin paired ($^2t_{2g}$)⁵ ruthenium².

The IR spectra of 1,5-bis(carbohydrazones) give a band in the region $1620\text{--}1600 \text{ cm}^{-1}$ due to $\nu_{\text{C-N}}$ vibrations and a band in the region $3300\text{--}3200 \text{ cm}^{-1}$ due to $\nu_{\text{N-H}}$ vibrations. These bands are observed to split into two components in the spectra of these complexes. The $\nu_{\text{C-N}}$ one component band appears at higher frequency $1640\text{--}1610 \text{ cm}^{-1}$ and other at lower frequency side $1600\text{--}1585 \text{ cm}^{-1}$, while $\nu_{\text{N-H}}$ one component band also appears at higher frequency $3360\text{--}3220 \text{ cm}^{-1}$ and other at lower frequency side $3240\text{--}3160 \text{ cm}^{-1}$. This indicates that in these complexes one of the $\nu_{\text{C-N}}$ groups^{9,10} and one of $\nu_{\text{N-H}}$ groups¹¹ are only coordinated to the ruthenium metal ion and other to be uncoordinated. The bands at 330 cm^{-1} in all these complexes are assigned to $\nu_{\text{Ru-Cl}}$.²

The magnetic moments (μ_{eff}) of these complexes are observed $1.93\text{--}2.18 \text{ BM}$ corresponding to one unpaired electron spin. The ESR spectra of solid complexes have shown axial distortion with g ca. $1.8\text{--}2.2$ at room temperature.

The binding energy data of Ru $3p_{3/2, 1/2}$ photoelectron peak for 1,5-bis (carbohydrazones), $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $[\text{RuL}_2\text{Cl}_2]\text{Cl}$ showed that Ru $3p_{3/2, 1/2}$ binding energy value is more in $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ than $[\text{RuL}_2\text{Cl}_2]\text{Cl}$ complexes (when L is same). From these XPS data one can conclude that 1,5-bis(carbohydrazones) are

coordinated to ruthenium metal ion⁷. Further, O1s photoelectron peaks of 1,5-bis(carbohydrazones) and their metal complexes have shown a single symmetrical photoelectron peak with same binding energy. These observations suggest non-coordination of the oxygen atom of carbonyl group in these ruthenium complexes of 1,5-bis(carbohydrazones).

The N1s photoelectron peak ($-\text{NH}- + -\text{N}=\text{C}-$) in these complexes have shown two unsymmetrical photoelectron peaks, one at 402.8 eV and the other with same value of BE as in carbohydrazone at 401.2 eV. These observations suggest that one side of $-\text{NH}-$ and $-\text{N}=\text{C}-$ nitrogen is coordinated with ruthenium metal ion while the other side is free in these metal complexes.

The $\text{Cl } 2p_{3/2}$ photoelectron spectra of these complexes have shown two $\text{Cl } 2p_{3/2}$ photoelectron peaks, one at 199.2 eV and the other at 198.2 eV with intensity ratio of 2 : 1 respectively. These observations suggest that these complexes have two chlorines in the inner coordination sphere of the metal ion, while one is in the outer sphere since BE of outer sphere chloride should be less than 198.3 eV.^{12,13} Since there was more than one type of carbon in these complexes, the signal due to $\text{C}1s_{1/2}$ overlapped and one broad signal was observed. The data of C1s could not therefore be utilised for the structure analysis.

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(Received: 25 November 1991; Accepted: 10 October 1992.)

AJC-487