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Synthesis and Characterization of Ruthenium (III) Complexes with N-substituted Salicylideneimine

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ABSTRACT

The reaction of Ru (III) chloride with bidentate Schiff bases (HSB) gave anionic complexes of types K[Ru(SB)$_2$Cl$_2$]. The ruthenium(III) complexes have been prepared in the reaction mixture of ruthenium (III) chloride, ethanolamine and 5-X-salicylaldehyde (X= Br or Cl). Potassium dichloro-bis[4-bromo-2-((2-hydroxy ethylimino) methyl) phenolato] ruthenat(III) and Potassium dichloro-bis[4-chloro-2-((2-hydroxy ethylimino) methyl) phenolato] ruthenat(III) were characterized by elemental analysis, IR spectroscopy and ESI mass spectrometry. Elemental analysis and mass spectrometry data of the complexes suggests the stoichiometry is 1:2 (metal-ligand). The results are in accordance with an octahedral environment around the Ru (III) ion.

Keywords: Ruthenium (III) complexes, Schiff bases, IR spectroscopy, mass spectrometry.

INTRODUCTION

Schiff bases are types of ligands which have many applications like a free ligand[1-5] and also in the complexes form with transit metals. The studies of transit metals complexes with the Schiff bases are shown in the previous works[6-12]. Ruthenium forms complexes like Ru(II) and Ru(III) ion. Both of the complexes show antitumorial properties and antibacterial activity[13,14]. Ruthenium complexes derived from salicylaldehide also show biological properties[15].

In general the azomethine group (C=N) which is the functional group of Schiff bases is aided in forming a stable complex by either a second group. In some cases Schiff base synthesized by salicylaldehide and ethanolamine can be used as bidentat or tridentat ligands, in dependence of center metal ion[16,17].

MATERIAL AND METHODS

Materials and Instruments

All reagents and chemicals were used as obtained from Aldrich. The infrared spectra were determined on a Perkin-Elmer System 2000 FT-IR spectrometer with KBr pellets. The mass spectra were measured on an FT-ICR-MS Bruker-Daltonics ESI spectrometer (APEX II, 7 Tesla). Elemental analyses were performed on a VARIO EL microanalyzer (Heraeus).

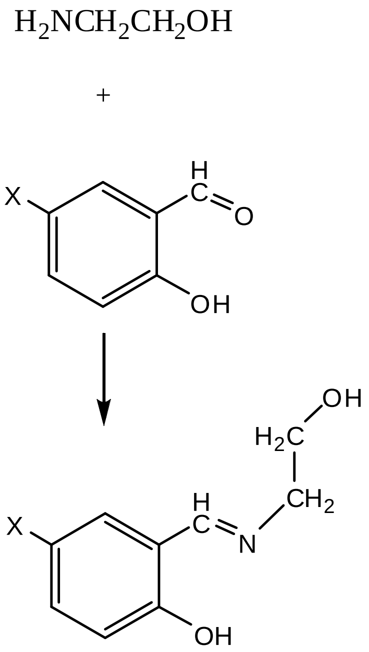
Preparation of complex (1)

Measured 0.5mmol $RuCl_3 \cdot 3H_2O$ and solved in mixture of 10 ml ethanol + 5mL H_2O at 60°C. Also, measured 1mmol of 2-aminoethanol and 1mmol of 5-bromosalicyladehide and solved in 15 mL absolute ethanol at 60°C. Then the second mixture added drop-wise in the ruthenium (III) chloride solution and refluxed for 1 hour. After refluxation, the reaction mixture was cooled at room temperature and added 1mmol of potassium chloride solved in 10 mL water. Precipitated dark green complexe were filtered and washed with diethyl ether. IR(KBr, cm^{-1}): 3432, 1621, 1579, 1457, 1303, 1171, 835, 695, 559; ESI-MS *m/z* 659.9; Elemental analysis: Anal. Calc. for $C_{18}H_{18}Br_2Cl_2KN_2O_4Ru$: C, 31.01%, H, 2.60%, N, 4.02%. Found: C, 31.34%, H, 2.48% N, 4.12%.

Preparation of complex (2)

Measured 0.5mmol $RuCl_3 \cdot 3H_2O$ and solved in mixture of 10 mL ethanol + 5ml H_2O at 60°C. Also, measured 1mmol of 2-aminoethanol and 1mmol of 5-chlorosalicyladehide and solved in 15 mL absolute ethanol at 60°C. Then the second mixture added drop-wise in the ruthenium (III) chloride solution and refluxed for 1 hour. After refluxation, the reaction mixture was cooled at room temperature and added 1mmol of potassium chloride solved in 10 mL water. Precipitated dark green complex were filtered and washed with diethyl ether. IR(KBr, cm^{-1}): 3430, 1630, 1532, 1458, 1305, 1174, 831, 702, 555; ESI-MS *m/z* 573.0 (M^+); Elemental analysis: Anal. Calc. for $C_{18}H_{18}Cl_4KN_2O_4Ru$: C, 35.54%; H, 2.98%; N, 4.60%. Found: C, 35.95%; H, 2.79%; N, 4.54%.

Scheme 1.



HSB; X=Br or Cl

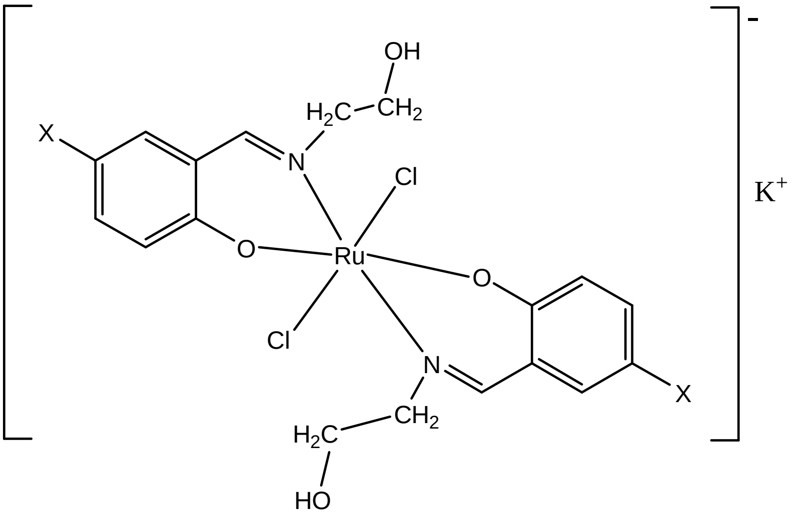


Figure 1. Suggested structure of Ruthenium complexes

X=Br (1); X=Cl (2)

(1) *Potassium dichloro-bis[4-bromo-2-((2-hydroxyethylimino)methyl)phenolato]ruthenat(III)*
(2) *Potassium dichloro-bis[4-chloro-2-((2-hydroxyethylimino)methyl)phenolato]ruthenat(III)*

RESULTS AND DISCUSSION

In this paper we have shown the forming of two Ruthenium(III) complexes in the "in situ" reaction of ruthenium(III) chloride, ethanolamine and 5-bromosalicyladehide or 5-clorosalicyladehide. Elemental analysis and mass spectra suggests that the complexes have1:2 (Ru-ligand) stoichiometry. Based on the elemental analysis and mass spectra the formula $K[Ru(SB)_2Cl_2]$, was suggested for the both complexes.

The general equation for synthesis of Ruthenium complexes(III) is shown in scheme 1.

Elemental analysis

The elemental analysis data match very well with those calculated and they show that ruthenium is coordinated with Schiff bases in 1:2 ratio (Ru-ligand).

Table 1. Elemental analysis data of Ru(III) complexes

Compound		Calc. %			Found %		
		C	H	N	C	H	N
(1)	$C_{18}H_{18}Br_2Cl_2KN_2O_4Ru$	31.01	2.60	4.02	31.34	2.48	4.12
(2)	$C_{18}H_{18}Cl_4KN_2O_4Ru$	35.54	2.98	4.60	35.95	2.79	4.54

IR spectra

The complexes show a broad band of hydroxyl groups at 3550-3300 cm^{-1}[18,19] with maximum absorption in the 3432cm^{-1} **(1)** and 3438 cm^{-1} **(2)**. This band show the H-bonded of free hydroxyl groups in the complexes. The azomethine groups (C=N) at the both of complexes appear with a strong stretching absorption band at 1621 cm^{-1} **(1)** respectively 1630cm^{-1} **(2)**[18,19]. The (C-O) stretching vibrations appear at 1303 cm^{-1} and 1305 cm^{-1}[18,19]. The (C-N) bands appear with a weak band at 1171 cm^{-1} and 1174 cm^{-1}[18,19] (table 2).

Table 2. IR spectral data of Ru(III) complexes

Compound	υ(O-H)	υ(C=N)	υ(C–O)	υ(C–N)
(1)	3432	1621	1303	1171
(2)	3438	1630	1305	1174

Mass spectra

The *m/z* values of complexes prove that complexes were formed in the above mentioned ratio. The experimental values of ESI-MS are almost the same with theoretically calculated (table 3).

Table 3. Mass spectra of Ru(III) complexes

	(1)	**(2)**
	$C_{18}H_{18}Br_2Cl_2N_2O_4Ru$	$C_{18}H_{18}Cl_4N_2O_4Ru$
m/z Found ($M - K^+$)	659.9	573.0

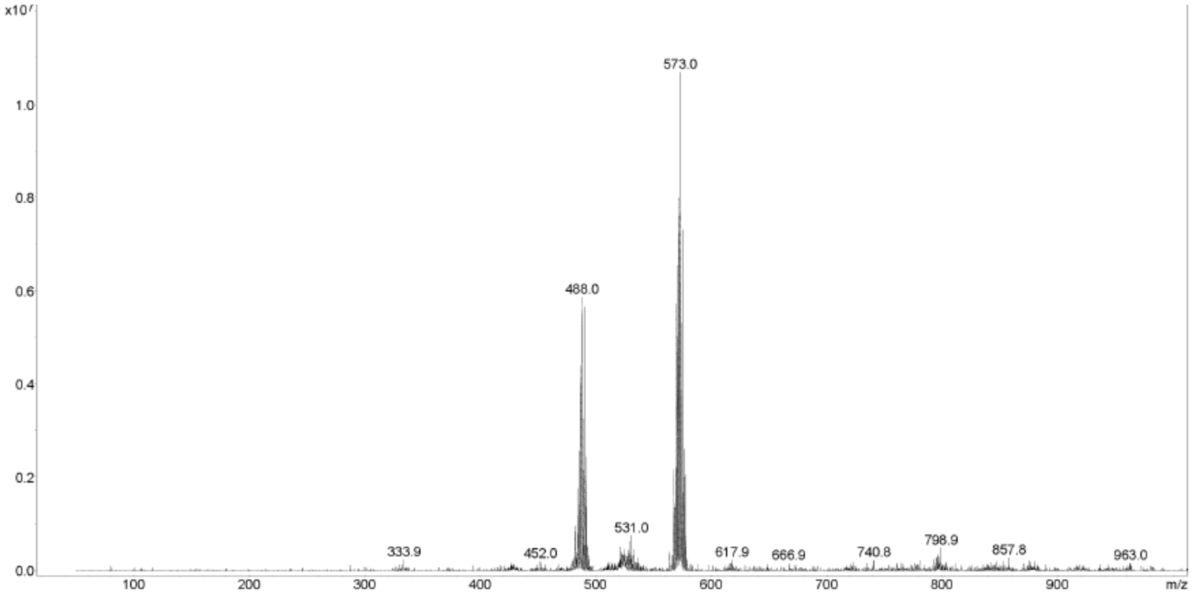


Figure 2. Mass spectra of ruthenium complex (2)

CONCLUSION

The data of elemental analysis, IR spectra and mass spectra show that Schiff bases 4-bromo-2-((2-hydroxyethylimino)methyl)phenol, synthesized "in situ" reaction are coordinated with ruthenium(III) ion and form Potassium dichloro-bis[4-halogenato-2-((2-hydroxyethylimino) methyl)phenolato]ruthenat(III) complexes. The ruthenium(III) ion are coordinated with Schiff bases through phenolic oxygen and azomethine nitrogen. Ruthenium(III) has completed the six-coordinated octahedral structure with two chloride ions and formed anion complexes.

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