



## Synthesis and Characterization of Novel Chloro-Ru(III) complex with Formamide

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**Abstract:** A new neutral complex has been synthesized in reaction of  $[\text{RuCl}_6]^{3-}$  with formamide in mixed solvent ethanol-water (10:1). Obtained olive green substance was characterized by mass spectrometry, CHN elemental analysis, IR and UV-VIS spectroscopy. Based on experimental data, compound was formulated as  $[\text{RuCl}_3(\text{HCONH}_2)_3] \cdot 0,5\text{C}_2\text{H}_5\text{OH}$ . Relative molecular mass of synthesized compound was determined by MALDI-TOF mass spectrometry as adduct with  $\text{K}^+$  ion to have value of 382.8485. IR spectrum of formamide, indicates coordination through the amide carbonyl oxygen, which is indicated by shift of carbonyl absorption from  $1681\text{ cm}^{-1}$  in free formamide to  $1636\text{ cm}^{-1}$  in synthesized compound. UV-VIS spectrum of synthesized compound in water shows LMCT absorption centered around 300 nm. Hydrolytic profile indicates that compound hydrolyses with fast exchange of first chloride ion with water molecule.

## INTRODUCTION

In recent decades, complexes of Ru(III) are being intensively studied because of their potential use as antitumor (Keppler *et al.*, 2003.) and antibacterial agents (Bolhuisa *et al.* 2011.), their electrontransfer mediating properties (Turkusic *et al.*, 2012), which qualifies them for the design of new electrochemical sensors, and because of their catalytic properties (Kahrović *et al.*, 2003.). Ru(III) complexes with simple amides are poorly explored group of compounds, since the  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  catalytically cleaves amides, and only two crystal structures are reported (Judd *et al.*, 1995; Levason *et al.*, 1997). A number of other metal complexes with simple amides are known and they are neutral adducts obtained from metal salt in direct reaction with formamide (Yilmaz, and Topcu, 1997). Formamide as ligand has potential two donor atoms, but coordination through carbonyl oxygen is preferred. There are some

reports in which the formamide acts as bridging ligand through carbonyl oxygen (Betz and Bino, 1988.).

The study of Ru(III) complexes with amides is of special interest, considering that amides contain peptide link in their structure, and study their interactions with the Ru(III) may give insight into the interaction of Ru(III) with proteins. Due the facts named above, Ru(III) complex with formamide was synthesized from hexachlororuthenate(III), in order to override catalytic effect of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  on cleavage of amides.

## EXPERIMENTAL

### Materials

All chemicals are purchased from commercial sources and used without any purification with exception of formamide which is purified by distillation.

## Preparation of the complex

Complex was prepared in reaction of  $[\text{RuCl}_6]^{3-}$  with formamide in molar ratio of 1:10, in mixed solvent ethanol – water (10:1)

Starting compound  $[(\text{CH}_3)_2\text{NH}_2]_3[\text{RuCl}_6] \times [(\text{CH}_3)_2\text{NH}_2\text{Cl}]$ , which contains  $[\text{RuCl}_6]^{3-}$  ion, was synthesized by literature procedure (Kahrović *et al.*, 2003.) and used for synthesis without any purification.

Reaction was carried out by heating the reaction mixture under reflux at temperature 60 – 70 °C for several hours. Olive green product of synthesis was filtered out after cooling the reaction mixture to the room temperature.

The amount of 0.2 g (0.38 mmol) of  $[(\text{CH}_3)_2\text{NH}_2]_3[\text{RuCl}_6] \times [(\text{CH}_3)_2\text{NH}_2\text{Cl}]$  was suspended in 10 mL of absolute ethanol and mixture was refluxed for 2 hours at 60 – 70 °C. Volume of 0.15 mL (3.8 mmol) of redistilled formamide was added to the suspension and mixture was further refluxed for 3 hours at same temperature, afterwards 1 mL of water was added with additional reflux for 2 hours. System was cooled to the ambient temperature and olive green solid was filtered out. Yield 21,6%.

## Instrumental methods

Synthesized compound was characterized by MALDI-TOF mass spectrometry, CHN analysis, IR and UV-VIS spectrometry. Mass spectrum was recorded on MALDI-TOF/TOF mass spectrometer (4800 Plus MALDI TOF/TOF analyzer, Applied Biosystems Inc.) equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the negative ion reflector mode. CHN analysis was performed on Perkin Elmer 2400 Series II CHNS analyzer. The infrared spectra were recorded as KBr pellets on a Perkin Elmer spectrum BX FTIR System in the region 4000-400  $\text{cm}^{-1}$ . UV/Vis spectra and hydrolysis were recorded on Perkin Elmer lambda 35 spectrophotometer.

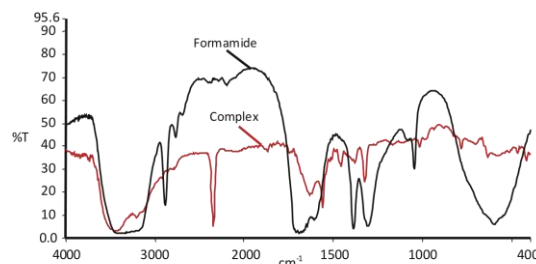
## RESULTS AND DISCUSSION

Novel neutral olive green complex was formulated as  $[\text{RuCl}_3(\text{HCONH}_2)_3] \times 0,5\text{C}_2\text{H}_5\text{OH}$  based on CNH analysis and mass spectrometry results.

The synthesis was carried out in order to examine the possibility of obtaining a defined product in reaction of  $[\text{RuCl}_6]^{3-}$  with formamide. Isolation of synthesized non ionic compound was triggered by addition of water molecules, and even though, the yield was pretty poor. Further investigation of the reaction between hexachlororuthenate(III) and formamide also has to improve yield of the product.

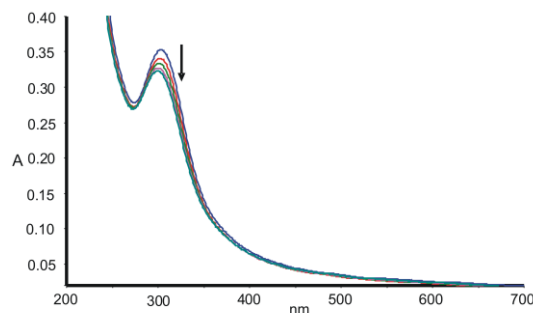
IR spectra of complex compared to IR spectra of formamide (Figure 1) shows shift of the stretching frequency  $\nu(\text{C}=\text{O})$  from 1681  $\text{cm}^{-1}$  in free formamide to 1634  $\text{cm}^{-1}$  in complex which indicates coordination of formamide to Ru(III) through carbonyl oxygen atom.

This assumption is also confirmed by shift of C–N bond stretching frequency  $\nu(\text{C}-\text{N})$  towards higher values of wave numbers, from 1311  $\text{cm}^{-1}$  in free formamide to 1327  $\text{cm}^{-1}$  in complex and  $\delta(\text{NH}_2)$  shift from 1606  $\text{cm}^{-1}$  in formamide to 1564  $\text{cm}^{-1}$  in complex. Weak isolated absorption at 3737  $\text{cm}^{-1}$  in spectrum of complex is assigned to isolated hydroxyl group which confirms that complex is isolated as ethanol solvate.



**Figure 1:** Comparative IR spectra of  $[\text{RuCl}_3(\text{HCONH}_2)_3] \times 0,5\text{C}_2\text{H}_5\text{OH}$  and formamide.

UV-VIS spectrum of synthesized complex in water shows  $\text{Cl} \rightarrow \text{Ru}$  charge transfer absorption at 301 nm, which is in accordance with literature data for chloro-Ru(III) complexes. Hydrolytic profile (Figure 2) shows that synthesized complex rapidly hydrolyses with fast loss of first chloride.



**Figure 2:** Hydrolytic profile of  $[\text{RuCl}_3(\text{HCONH}_2)_3] \times 0,5\text{C}_2\text{H}_5\text{OH}$  in 20 minutes.

Hydrolytic profile of  $[\text{RuCl}_3(\text{HCONH}_2)_3] \times 0,5\text{C}_2\text{H}_5\text{OH}$  does not show significant resistance towards hydrolysis compared with hydrolytic profile of  $[\text{RuCl}_6]^{3-}$  which is in agreement with the fact that formamide is not ligand with strong coordination abilities, and stabilization of  $[\text{RuCl}_6]^{3-}$  is moderate.

Analytical and spectral characteristics of the novel compound are given below.

**Trichlorotriformamideruthenium(III):** MALDI-TOF ( $m/z$ ):  $[\text{M}+\text{K}]^+$  calcd for  $\text{C}_3\text{H}_9\text{Cl}_3\text{N}_3\text{O}_3\text{Ru}$ , 382.8367; found, 382.8485.; Anal. calcd for  $[\text{RuCl}_3(\text{HCONH}_2)_3] \times 0,5\text{C}_2\text{H}_5\text{OH}$ : C 12.67, H 3.52, N 11.08. Found: C 13.14, H 3.31, N 11.49.; IR data for formamide (KBr,  $\text{cm}^{-1}$ ) 1681  $\nu(\text{C}=\text{O})$ , 1311  $\nu(\text{C}-\text{N})$ , 1606  $\delta(\text{NH}_2)$ ; IR data for  $[\text{RuCl}_3(\text{HCONH}_2)_3] \times 0,5\text{C}_2\text{H}_5\text{OH}$  (KBr,  $\text{cm}^{-1}$ ) 1634  $\nu(\text{C}=\text{O})$ , 1327  $\nu(\text{C}-\text{N})$ , 1564  $\delta(\text{NH}_2)$ ; UV-VIS ( $\text{H}_2\text{O}$ ) LMCT  $\lambda_{\text{max}}$  301 nm

## CONCLUSIONS

Novel neutral complex of Ru(III) with formamide was synthesized from  $[\text{RuCl}_6]^{3-}$  as starting compound. Based on analytical data complex was formulated as  $[\text{RuCl}_3(\text{HCONH}_2)_3] \times 0,5\text{C}_2\text{H}_5\text{OH}$ . Formamide is coordinated to Ru(III) through carbonyl oxygen. New synthetic pathway in which formamide complex with Ru(III) is synthesized from anionic octahedral complex

$[\text{RuCl}_6]^{3-}$  is significant and shows that  $[\text{RuCl}_6]^{3-}$  can be used as good starting material for synthesis of Ru(III) complexes with amides in order to override catalytic effect of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , as the most used starting compound for synthesis of Ru(III) complexes, on cleavage of amides.

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## Summary/Sažetak

Sintetiziran je novi neutralni kompleks u reakciji  $[\text{RuCl}_6]^{3-}$  sa formamidom u mješovitom rastvaraču etanol-voda (10:1). Dobivena maslinasto zelena supstanca karakterizirana je masenom spektrometrijom, CHN analizom, IR i UV-VIS spektroskopijom. Na osnovu eksperimentalnih podataka spoj je formuliran kao  $[\text{RuCl}_3 \cdot x(\text{HCONH}_2)_3] \cdot x0,5\text{C}_2\text{H}_5\text{OH}$ . Relativna molekulska masa sintetiziranog spoja određena je MALDI-TOF masenom spektrometrijom kao adukt sa  $\text{K}^+$  jonom i ima vrijednost 382.8285. IR spektar sintetiziranog spoja, u poređenju sa IR spektrom formamida, ukazuje na koordinaciju preko karbonilnog kisika iz formamida, što je potvrđeno pomakom karbonilne apsorpcije sa  $1681 \text{ cm}^{-1}$  u formamidu na  $1636 \text{ cm}^{-1}$  u sintetiziranom spoju. UV-VIS spektar sintetiziranog spoja u vodi pokazuje LMCT apsorpciju centriranu oko 300 nm. Hidrolitički profil ukazuje da spoj podliježe hidrolizi uz brzu zamjenu prvog hloridnog jona molekulom vode.

