

UV-VISIBLE AND IR SPECTROSCOPIC STUDIES OF RUTHENIUM(II)-XYLENOL ORANGE COMPLEX

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Abstract

The formation of a Ru^{II}-xylenol orange (XO) complex has been investigated. The respective complex was formed within the pH range of 2.5 to 5.0 during 90 min of heating and has an absorbance maximum at 583 nm. The molar extinction coefficient is 28800 L mol⁻¹ cm⁻¹. The composition of the Ru^{II}-XO complex was determined by the mole ratio and continuous variations methods. The structure of Ru^{II}-XO was proposed according to IR spectroscopic data.

Key words: ruthenium, xylenol orange, complex, UV-VIS, IR spectroscopy, determination

Introduction

Xylenol orange (XO) can successfully be used for the determination of many transition metals, including noble metal ions, such as palladium(II),¹⁻⁴ rhodium(III),^{1,5} and ruthenium(III).^{1,6}

We here report on UV-VIS and IR spectroscopic studies of a novel Ru^{II}-XO complex. Based on these studies, a straightforward method for the determination of ruthenium(II) ions in solution is developed and tested on synthetic and real samples.

Experimental

Reagents and Apparatus.

All ruthenium(II) solutions were prepared by the reduction of an aliquot of a ruthenium(III) chloride solution with hydroxylamine according to Ref. 7 and 8. A ruthenium(III) stock solution was prepared by dissolving RuCl₃·3H₂O in 3 mol L⁻¹ HCl. A standard working solution was prepared by taking an aliquot of the ruthenium(III) stock solution and diluting it with 1 mol L⁻¹ HCl.

Freshly prepared aqueous xylenol orange solutions ($c_{\text{XO}} \approx 10^{-4} \text{ mol L}^{-1}$) from commercially available XO (content 90%, Aldrich Chemicals Inc.) were used. Freshly prepared 0.15 mol L^{-1} solutions of hydroxylamine were utilised. The ion strength of respective solutions was kept constant by using 0.1 mol L^{-1} NaCl solutions.

UV-VIS measurements were performed with an UV-VIS spectrophotometer (Lambda 40, Perkin Elmer) using 1 cm cuvettes against reference solutions. All absorbance measurements were performed at ca. $20 \text{ }^\circ\text{C}$.

The IR spectroscopic measurements were performed with an FT-IR spectrometer (Spectrum 1000, Perkin Elmer). The pH measurements were carried out with a Schott CG model 840 glass electrode pH-meter. For pH-meter calibration purpose standard buffer solutions with $\text{pH} = 4.00$ and $\text{pH} = 10.00$ were applied. The pH value of each solution was adjusted by using diluted HCl and NaOH solutions.

Procedure of ruthenium(II) Determination.

A sample of a solution containing $(0.1\text{-}4.9) \times 10^{-5} \text{ mol L}^{-1}$ of Ru^{II} , Ru^{III} or Ru^{IV} ions (or a mixture of ruthenium ions in different oxidation states) was placed in a 25 mL volumetric flask. To this solution 5 mL of 0.15 mol L^{-1} NH_2OH , 2.5 mL of $2.5 \times 10^{-4} \text{ mol L}^{-1}$ XO and 2.5 mL of 0.1 mol L^{-1} NaCl were added. The pH was adjusted in the acceptable range of 2.7 to 4.0 and distilled water was added. The obtained solutions were boiled for 90 min at $100 \text{ }^\circ\text{C}$. Then the absorbance at $\lambda_{\text{max}} = 583 \text{ nm}$ against the reference solution was measured.

Results and discussion

Ruthenium(II) solutions.

The reduction of Ru^{III} or Ru^{IV} to Ru^{II} could be performed by using a hydroxylamine solution as described in Ref. 7 and 8. The reduction process lasts 7-10 min (Figure 1). The absorption spectra of the appropriate ruthenium(II) solutions correspond to the data of Ref. 9.

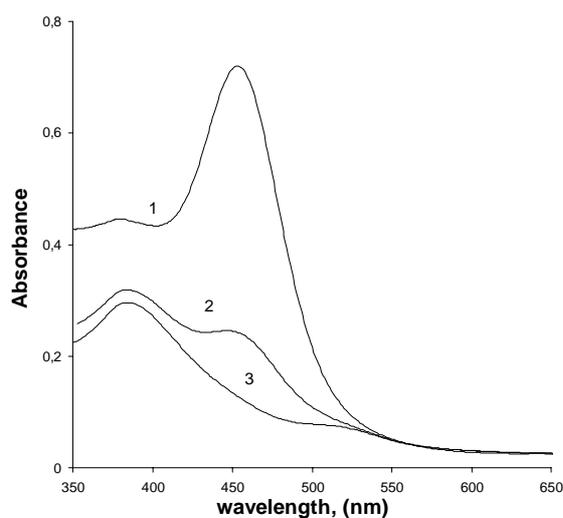


Figure 1. Absorption spectra of the Ru^{III} - Ru^{II} reduction process, $c(\text{Ru}^{\text{II}}) = 1.00 \times 10^{-4} \text{ mol L}^{-1}$, $c(\text{NH}_2\text{OH}) = 1.51 \times 10^{-1} \text{ mol L}^{-1}$, $\text{pH} = 1.0$: 1 - Ru^{III} , $t_{\text{red}} = 0 \text{ min}$; 2 - $\text{Ru}^{\text{II,III}}$, $t_{\text{red}} = 5 \text{ min}$; 3 - Ru^{II} , $t_{\text{red}} = 7.5 \text{ min}$.

Absorption Spectra.

The absorption spectra of xylenol orange and the corresponding violet coloured Ru^{II} -XO complex are shown in Figure 2. While XO has a maximum absorption at 435 nm, at the same conditions the respective Ru^{II} -XO complex absorbs at 583 nm. The shift of the absorption maximum of the Ru^{II} -XO complex is 150 nm in comparison to the maximum of the XO solution. This shifting is typical upon complex formation of XO with transition metal ions¹.

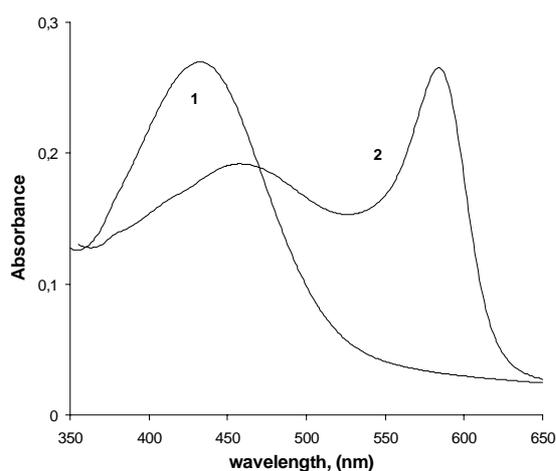


Figure 2. Absorption spectra of xylenol orange and Ru^{II} -XO complex, $\text{pH} = 4.0$, $t_{\text{heat}} = 90 \text{ min}$, $c(\text{NH}_2\text{OH}) = 2.0 \times 10^{-2} \text{ mol L}^{-1}$, $I = 0.05$. (1) absorption spectrum of XO, $c(\text{XO}) = 1.02 \times 10^{-5} \text{ mol L}^{-1}$, (2) absorption spectrum of Ru^{II} -XO, $c(\text{Ru}^{\text{II}}) = 1.60 \times 10^{-5} \text{ mol L}^{-1}$, $c(\text{XO}) = 1.02 \times 10^{-5} \text{ mol L}^{-1}$.

The Effect of pH.

Between pH of 2.5 to 5.0 ruthenium(II) ions form a complex with XO (Figure 3). The best result and hence most stable complex formation is obtained by the optimal pH of 2.7 to 4.0. In this pH range a maximum and constant absorbance is obtained (Figure 3). All consequent investigations were carried out within the pH range of 2.7 to 4.0.

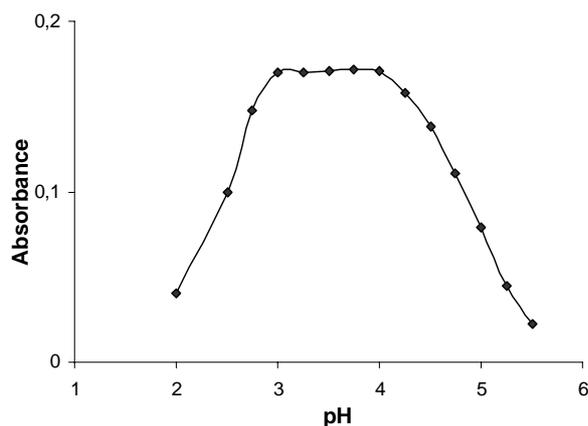


Figure 3. Influence of pH on absorbance of ruthenium(II)-xylenol orange complex, $c(\text{Ru}^{\text{II}}) = 1.60 \times 10^{-5} \text{ mol L}^{-1}$, $c(\text{XO}) = 1.02 \times 10^{-5} \text{ mol L}^{-1}$, $c(\text{NH}_2\text{OH}) = 2.0 \times 10^{-2} \text{ mol L}^{-1}$, $t_{\text{heat}} = 90 \text{ min}$, $I = 0.05$, $\lambda = 583 \text{ nm}$.

Influence of Hydroxylamine Concentration.

The influence of the hydroxylamine concentration on the complex formation of ruthenium(II)-XO was studied (Figure 4).

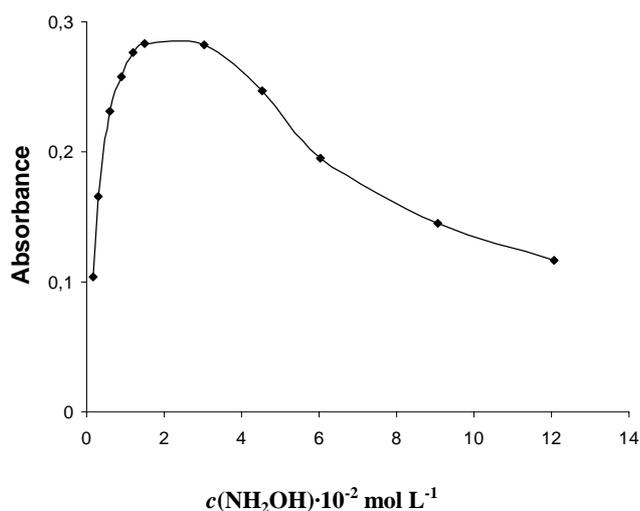


Figure 4. Influence of hydroxylamine concentration on absorbance of ruthenium(II)-xylenol orange complex, $c(\text{Ru}^{\text{II}}) = 1.60 \times 10^{-5} \text{ mol L}^{-1}$, $c(\text{XO}) = 1.02 \times 10^{-5} \text{ mol L}^{-1}$, $\text{pH} = 3-4$, $t_{\text{heat}} = 90 \text{ min}$, $\lambda = 583 \text{ nm}$.

The maximal absorbance of the ruthenium(II)-XO complex is obtained at the concentration of NH_2OH 1.5×10^{-2} – 3.5×10^{-2} mol L^{-1} ; that values correspond to 1000–2000 surplus of $c(\text{NH}_2\text{OH})$ to $c(\text{Ru}^{\text{II}})$. Lower concentrations of hydroxylamine (Figure 4) are not sufficient to reduce all Ru^{III} to Ru^{II} . However, at higher then optimal hydroxylamine concentrations, the maximal absorbance of the Ru^{II} -XO complex is not obtained because of increasing of ion strength. The optimal ion strength for Ru^{II} -XO complex formation is $I = 0.04$ – 0.08 .

Influence of Temperature.

Heating of the solutions is necessary for Ru^{II} -XO complex formation, which can clearly be seen by the colour change from yellow to violet. Colour of the Ru^{II} -XO complex develops during 90 min of heating on a water bath at 100 °C. After the heating period (0 min to 150 min), the solutions were allowed to cool (to the temperature 18–22 °C), diluted to the mark with distilled water in a volumetric flask and mixed. The influence of heating time on Ru^{II} -XO complex formation is shown in the Figure 5. The obtained Ru^{II} -XO complex is stable at least for 72 h.

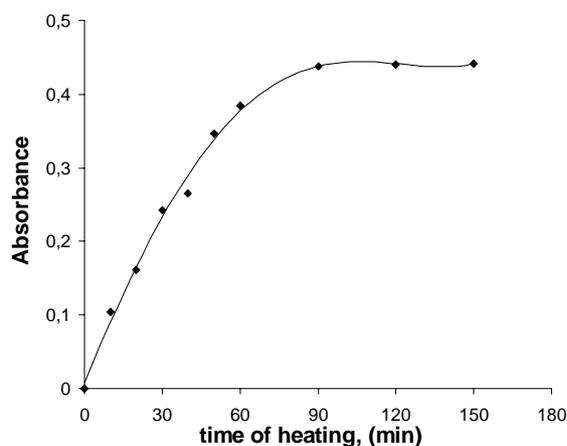


Figure 5. Influence of heating time on Ru^{II} -XO complex formation, $c(\text{Ru}^{\text{II}}) = 3.20 \times 10^{-5}$ mol L^{-1} , $c(\text{XO}) = 2.04 \times 10^{-5}$ mol L^{-1} , $c(\text{NH}_2\text{OH}) = 2.0 \times 10^{-2}$ mol L^{-1} , pH = 3–4, $I = 0.05$, $\lambda = 583$ nm, $T = 100$ °C.

Effect of the Reagent Concentration.

In order to study the effect of the xylenol orange concentration on the Ru^{II} -XO complex formation, a series of absorbances were measured at various concentrations of XO against reagent blanks of the same concentration (Figure 6). The absorbance of the

ruthenium(II)-XO complex increases with increasing XO concentration (Figure 6). Higher XO concentrations then ratio $c(\text{XO}) / c(\text{Ru}^{\text{II}}) = 0.6-0.65$ decrease the absorbance.

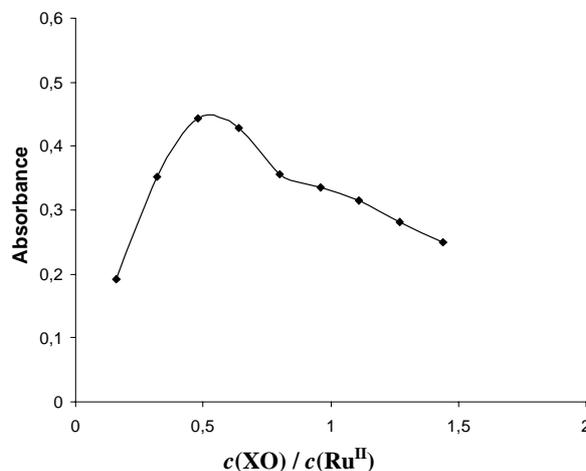


Figure 6. Variation of the absorbance of Ru^{II} -XO complex versus XO concentration, $c(\text{Ru}^{\text{II}}) = 3.20 \times 10^{-5} \text{ mol L}^{-1}$ = constant, $c(\text{NH}_2\text{OH}) = 3.0 \times 10^{-2} \text{ mol L}^{-1}$, $\text{pH} = 2.7-4.0$, $t_{\text{heat}} = 90 \text{ min}$, $I = 0.07$, $\lambda = 583 \text{ nm}$.

Composition of Complex.

The composition of the respective Ru^{II} -XO complex was determined by the mole ratio and Job's method of continuous variations (Figures 6 and 7).¹¹

From Figures 6 and 7 it is evident that only one distinctive Ru^{II} -XO complex is formed. The molar ratio of xylenol orange to ruthenium(II) in this complex is 1 : 2. The formation of a homobinuclear ruthenium(II) complex with xylenol orange explains why only 0.6-0.65 ratio of XO to Ru^{II} is necessary.

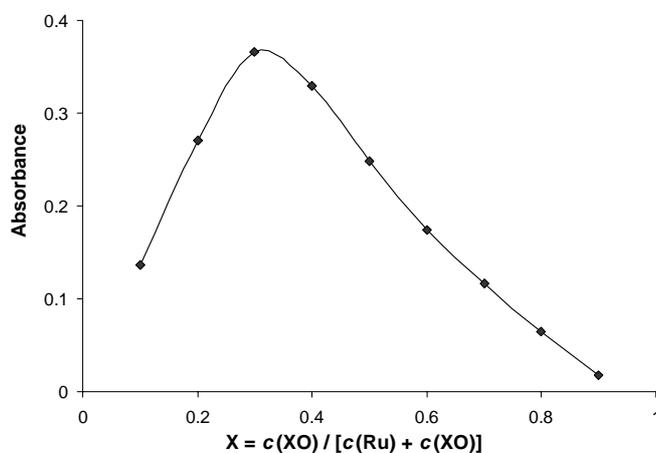


Figure 7. The continuous variations curve for ruthenium(II)-XO complex, $\text{pH} = 2.7-4.0$, $c(\text{NH}_2\text{OH}) = 3.0 \times 10^{-2} \text{ mol L}^{-1}$, $t_{\text{heat}} = 90 \text{ min}$, $I = 0.07$, $\lambda = 583 \text{ nm}$.

Effect of the Order of Reagent Adding.

The varying orders in which the reagents were added are presented in Table 1.

Table 1. Influence of order of reagent adding on the absorption of Ru^{II}-XO complex at 583 nm, $c(\text{Ru}^{\text{II}}) = 3.21 \times 10^{-5} \text{ mol L}^{-1}$, $c(\text{XO}) = 2.05 \times 10^{-5} \text{ mol L}^{-1}$, $c(\text{NH}_2\text{OH}) = 2.0 \times 10^{-2} \text{ mol L}^{-1}$, pH = 3-4, $t_{\text{heat}} = 90 \text{ min}$, $I = 0.05$, $n = 6$, $P = 0.95$.

No	Order of reagent adding	ΔA_{583}	RSD %
1	(Ru _{sol} + XO _{sol} + NH ₂ OH _{sol} + NaCl _{sol}) _{pH<2} adjust pH = 3-4	0.438	0.46
2	(Ru _{sol} + XO _{sol} + NH ₂ OH _{sol} + NaCl _{sol}) _{pH<2} wait 5 min, adjust pH = 3-4	0.439	0.51
3	(Ru _{sol} + NH ₂ OH _{sol}) _{pH<2} wait 5 min + XO _{sol} + NaCl _{sol} adjust pH = 3-4	0.436	0.57
4	(Ru _{sol} + NH ₂ OH _{sol}) _{pH<2} adjust pH = 3-4 + XO _{sol} + NaCl _{sol} , adjust pH = 3-4	0.441	0.63
5	(Ru _{sol} + XO _{sol}) _{pH<2} adjust pH = 3-4 + NH ₂ OH _{sol} + NaCl _{sol} , adjust pH = 3-4	0.366	0.49
6	(Ru _{sol} + NaCl _{sol}) _{pH<2} adjust pH = 3-4 + XO _{sol} + NH ₂ OH _{sol} , adjust pH = 3-4	0.390	0.74
7	(Ru _{sol} adjust pH = 3-4) + XO _{sol} + NH ₂ OH _{sol} + NaCl _{sol} , adjust pH = 3-4	0.376	0.68

where Ru_{sol}, XO_{sol}, NH₂OH_{sol} and NaCl_{sol} - aliquots of Ru, XO, NH₂OH and NaCl solutions; ΔA_{583} – the difference of absorbances of complex and reference solutions.

The time necessary to reduce Ru^{III} to Ru^{II} has no influence on the absorption of the ruthenium(II)-XO complex (entries 1 and 2, Table 1) at strong acidic pH in presence of XO_{sol}, NaCl_{sol}. Order of adding aliquot of NaCl or XO at strong acidic pH conditions as described in the experiments 1 to 3 seems to have no influence on the absorption of the Ru^{II}-XO complex, as long as aliquot of NH₂OH is mixed with aliquot of ruthenium(III) solution.

These experiments return that pH condition (pH<2 or pH = 3-4) has no influence on the reduction process of Ru^{III} to Ru^{II} when only aliquot of NH₂OH is mixed with aliquot of ruthenium(III) solution (entries 3 and 4).

At pH of 3 to 4 the state of ruthenium ions in the solutions changes. As a result of this, the process of reduction of Ru^{III} to Ru^{II} becomes complicated in the presence of reagents XO or NaCl (entries 5 or 6), or their mixture (entry 7) and a lower absorption has been measured.

Since by the method 1 (Table 1) a maximum of absorption of the Ru^{II}-XO complex was obtained, this way of adding the reagents was used in the consequent investigations.

Influence of Interfering Ions.

The determination of ruthenium in different samples is generally complicated due to the presence of other noble metals in the sample, which can interfere with the ruthenium determination by other spectrophotometric methods.^{6-10,12-14} The separation of

Pt, Pd, Ir, Rh and Os ions is necessary in this case, which takes additional time for analysis. For this reason, the influence of other noble metals on the Ru^{II}-XO complex formation was studied as well (Table 2).

Complex formation of palladium(II) ions with XO is observed in a strong acidic environment^{2,4} and at pH 5.8-6.2.³ The results of our studies show that Pd^{II} ions do not interfere the Ru^{II} with XO determination until the ratio 1 : 1 at pH = 3-4 (Table 2).

Rhodium(III) ions form a complex with XO within the pH range of 2.7 to 3.3.⁵ As results of our investigation show (Table 2), rhodium(III) ions do not interfere with the ruthenium(II) determination until the ratio 1 : 1 at pH = 3.5-4 which could be explained by lower stability of Rh^{III}-XO complex in comparison with Ru^{II}-XO.

Iridium(IV) ions do not interfere with the ruthenium(II)-xylenol orange complex formation till ratio 1 : 5. Higher ratio of Ir^{IV} decreases the absorbance of Ru^{II}-XO. Osmium(IV) and platinum(IV) ions obstruct the determination of Ru^{II} at the higher ratio then Ru^{II} : Os^{IV} = 1 : 7 and Ru^{II} : Pt^{IV} = 1 : 15.

Table 2. Selectivity of complex formation of ruthenium(II) with XO at pH = 3-4.

Ion	Ru ^{II} : Ion	Ion	Ru ^{II} : Ion
Pd ^{II}	1 : 1	Sr ^{II}	1 : 40
Ir ^{IV}	1 : 5	F ⁻	1 : 40
Pt ^{IV}	1 : 15	Br ⁻	1 : 200
Os ^{IV}	1 : 7	J ⁻	1 : 60
Rh ^{III}	1 : 1	NO ₃ ⁻	1 : 20
Al ^{III} (masking agent)	1 : 2	SO ₄ ²⁻	1 : 50
Ca ^{II}	1 : 40	CO ₃ ²⁻	1 : 35
Mg ^{II}	1 : 30	CH ₃ COO ⁻	1 : 5

Such ions as Ca²⁺, Mg²⁺, and Sr²⁺ form with XO complex at the pH = 10.5.^{1,15} The results of our studies show: these ions have no influence on Ru^{II}-XO complex until ratio 1 : 40, 1 : 30 and 1 : 40, respectively.

The presence of fluoride ions do not interfere ruthenium(II)-XO complex formation till ratio Ru^{II} : F⁻ = 1 : 40 (Table 2), the absorption of the corresponding complex decreases at higher surplus of F⁻ ions. Aluminium ions clearly interfere with the Ru^{II}-XO complex formation, however, F⁻ ions were used as masking agent for Al³⁺ in the ratio Ru²⁺ : Al³⁺ : F⁻ = 1 : 2 : 40. Cations, such as Cd²⁺, Ni²⁺, Be²⁺, Cu²⁺, Zr⁴⁺, Fe²⁺, Zn²⁺, Hg²⁺ prevent the formation of Ru^{II}-XO. Small amounts of Be²⁺ and Zr⁴⁺ could be masked by fluoride ions.

The acetic ions form weak complex with ruthenium ions^{10,16} and may be presented in the solutions of ruthenium(II)-xylenol orange complex until ratio 1 : 5. Oxalic, tartaric, citric acids and EDTA form complex with ruthenium ions.^{10,17,18} According to results of our investigation, oxalic, tartaric, citric ions and EDTA obstruct the formation of Ru^{II}-XO complex.

Calibration Curve and Sensitivity.

A linear dependence was obtained for following concentrations of ruthenium(II): (0.5-12)×10⁻⁶ mol L⁻¹ and (1.6-49.2)×10⁻⁶ mol L⁻¹ at concentrations of XO which correspond to the ratio Ru^{II} : XO = 1 : 0.5-0.65. The existence of two partially overlapping linear ranges is explained by necessity to increase the XO concentration for the second linear range. The molar absorptivity of the Ru^{II}-XO complex at 583 nm was determined to be 2.88(±0.05)×10⁴ L mol⁻¹ cm⁻¹ (RSD = 1.5 %).

The limit of determination of ruthenium(II) with XO had been calculated according to Ref. 19 and determined to be C_{min, k=10} = 6.5(±0.6)×10⁻⁷ mol L⁻¹, RSD = 7% (for the first linear range). The sensitivity of the reaction, as expressed by Sandell's notation,²⁰ is 7.0 ng/cm².

IR-spectroscopic Studies.

The Ru^{II}-XO complex described above could be isolated by evaporation of the solvent. IR-spectra were recorded for the sodium salt of xylenol orange (for comparison) and for the Ru^{II}-XO complex (Table 3).

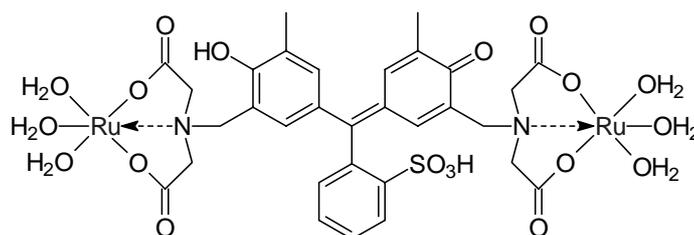
The absorption bands at 1632 and 1400 cm⁻¹ correspond to the asymmetric and symmetric ν(COO⁻) frequencies of the appropriate pentasodium xylenol orange salt. The difference Δν is indicative for a monodentate structure,²¹⁻²³ which corresponds to the structure of xylenol orange in Ref. 1.

Table 3. Characteristic IR absorption bands for Na₅XO and Ru^{II}₂-XO.

Na ₅ XO	Ru ^{II} ₂ -XO	Assignment
ν [cm ⁻¹]	ν [cm ⁻¹]	
-	1874	C=O
1632	1570	(-COO) ⁻ as
1400	1460	(-COO) ⁻ s
-	995	Ru - O
-	554	Ru - N

The absorption band at 1874 cm^{-1} can be assigned to the $\nu(\text{C}=\text{O})$ frequency of the $\text{C}_6\text{H}_2(\text{O})$ moiety, whereas the absorptions at 1570 and 1460 cm^{-1} correspond to the asymmetric and symmetric $\nu(\text{COO}^-)$ frequencies.²¹⁻²⁵ Also a vibration at 554 cm^{-1} is found, which corresponds to the formation of a donor $\text{N} \rightarrow \text{Ru}$ bond.²⁵

Based on these data, following structure for the $\text{Ru}^{\text{II}}_2\text{-XO}$ complex can be proposed:



The coordination number at the ruthenium(II) ions is six with three aqua ligands and a tripodal-bound $\text{N}(\text{CH}_2\text{COO})_2$ moiety. This structural arrangement affords an octahedral surrounding at Ru^{II} .

Application to samples

A powerful method of ruthenium(II) determination with xylenol orange was developed. This method was tested on synthetic solutions in presence of different noble metal ions and on real samples (Tables 4 and 5).

Table 4. The results of ruthenium determination in synthetic solutions in the presence of different noble metal ions, $n = 5$, $P = 0.95$.

$\text{Ru}_{\text{added}} 10^{-5}\text{ mol L}^{-1}$	$\text{Ru}_{\text{det}} 10^{-5}\text{ mol L}^{-1} \bar{x} \pm \Delta x$	Ru : Rh	Ru : Pd	Ru : Pt	Ru : Ir	Ru : Os	RSD %
3.21	3.16 ± 0.05	1 : 1	—	1 : 15	1 : 2	—	1.29
3.21	3.20 ± 0.03	—	1 : 1	1 : 10	1 : 2	1 : 5	0.78
4.01	3.94 ± 0.06	1 : 1	—	1 : 15	—	—	1.35
4.01	4.09 ± 0.08	—	1 : 1	—	—	1 : 5	1.64
4.01	4.01 ± 0.05	—	1 : 1	1 : 10	—	—	1.05
4.82	4.88 ± 0.07	1 : 1	—	—	1 : 2	1 : 2	1.23

where $\Delta x = t(P, f) \times S \times n_j^{-0.5}$, $f = n - 1$.

The results for the samples (Table 5) obtained by the determination of ruthenium(II) with xylenol orange are in agreement with the values determined by using method of ruthenium determination with o-phenantroline (o-phen).⁷⁻¹⁰

Table 5. The results of ruthenium determination in samples, $n = 5$, $P = 0.95$.

Sample	W_{theorRu} %	W_{practRu} %	$C_{\text{theorRu}} 10^{-5}$ mol L^{-1}	o-phen	$C_{\text{practRu}} 10^{-5} \text{ mol L}^{-1}$ XO ($x \pm \Delta x$)	RSD %
$(\text{NH}_4)_2[\text{RuNOCl}_5]$	29.3	29.7	2.01	2.03	2.04 ± 0.05	2.16
$\text{K}_4[\text{Ru}_2\text{OCl}_{10}] \times \text{H}_2\text{O}$	27.0	26.9	1.35	1.32	1.33 ± 0.04	2.20
$\text{Yb}_2\text{Pt}_2\text{SnRu}$	10.6	10.7	1.64	1.61	1.59 ± 0.04	2.01

where $\Delta x = t(P, f) \times S \times n_j^{-0.5}$, $f = n - 1$.

Conclusions

Optimal conditions for the formation of $\text{Ru}^{\text{II}}\text{-XO}$ have been investigated. The structure of the complex was additionally confirmed by IR spectroscopic studies. A new method was developed, which allows determination of ruthenium(II) from solutions which contain ruthenium in different oxidation states, such as Ru^{II} , Ru^{III} and Ru^{IV} . The proposed method is more sensitive than other spectrophotometric procedures for ruthenium determination ($C_{\text{min,Ru-XO}} = 6.5 \times 10^{-7} \text{ mol L}^{-1}$, $C_{\text{min,Ru-o-phen}} = 5 \times 10^{-6} \text{ mol L}^{-1}$,^{7,8} $C_{\text{min,Ru-chromeazuroIS}} = 4 \times 10^{-6} \text{ mol L}^{-1}$,¹²) and is recommended for ruthenium determination in different samples.

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Povzetek

Raziskovali smo nastanek "Ru^{II}-xylenol orange" (XO) kompleksa. Ta se je tvoril pri pH 2,5 do 5,0 med 90 minutnim segrevanjem in ima absorpcijski vrh pri 583 nm. Molarni ekstinkcijski koeficient je 28800 L mol⁻¹ cm⁻¹. Sestava Ru^{II}-XO kompleksa je bila določena na osnovi molskega razmerja in drugih metod. Struktura Ru^{II}-XO je bila predpostavljena na osnovi IR spektroskopskih podatkov.