ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2007, Vol. 52, No. 5, pp. 800–805. © Pleiades Publishing, Inc., 2007.
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PHYSICAL CHEMISTRY
OF SOLUTIONS

Extraction of Chlororuthenium(III) Complexes by Triazole Derivatives from Hydrochloric Acid Solutions

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Received March 21, 2006

Abstract—The extraction of ruthenium(III) by triazole derivatives from hydrochloric acid solutions has been studied. The extraction of ruthenium(III) is implemented by the ion-association mechanism. The composition of the extraction compound has been determined using electronic, ^{1}H NMR, ^{13}C NMR, and IR spectroscopy and elemental analysis.

DOI: 10.1134/S0036023607050269

The extraction techniques of recovery, separation, and preconcentration of precious metals are significant for hydrometallurgy, analytical chemistry, and decontamination of industrial sewages from heavy and rare metals. Recently, the attention of researchers has been drawn by the extraction of precious metals by sulfur- and nitrogen-containing compounds [1–4]. Recent publications concern the synthesis of precious metal complexes with triazole derivatives.

The utility of triazole derivatives substituted in the position 1 for the synthesis of ruthenium(III) complexes was demonstrated in work [6], and the spectrochemical and electrochemical properties of the complex $[Ru(bpy)_2(Phtrz)_2](PF_6)_2$ were studied. The spectrochemical and antitumor properties of complexes $[RuCl_4L \cdot DMSO]$, where L = 1,2,4-triazole, and the isomers of ruthenium(III) complexes with 1,2,4-triazole were studied in works [7, 8].

However, there are no data on the extraction of ruthenium with triazoles substituted in the position 1. This work concerns the extraction of ruthenium(III) with propiconazole (1-2-(2,4-dichlorophenylpropyl-1,3-dioxolan-2-ylmethyl-1H-1,2,4-triazole).

EXPERIMENTAL

The sample contained at least 99.9% of the major substance. Solutions were prepared from accurately weighed portions of the extactant. The compound in the form of a diastereoisomer mixture (55–65% *cis* isomer and 35–45% *trans* isomer) is a pasty substance with T_m = 18–20°C and T_b = 180°C at p = 13.3 Pa and an insignificant water solubility (0.11 g/L at 20°C) [9]. The isomers differ by the opposite positions of the triazole ring above and below the plane relative to the rest of the molecule. Toluene mixed with decanol was used as the diluent to study the extraction properties of this compound. It was found that the maximal ruthenium(III) recovery from hydrochloric solutions occurred when there was at least 10–15 vol % decanol in the mixture with toluene (Fig. 1). In further experiments, 15 vol % decanol in toluene was used. Ruthenium(III) extraction to toluene without decanol was accompanied by the appearance of a third phase, which complicated the investigation; in the presence of decanol, no third phase appeared.

The ruthenium trichloride used contained 46.66% ruthenium(III) (TU 6-09-05-510-76). The salt was dis-

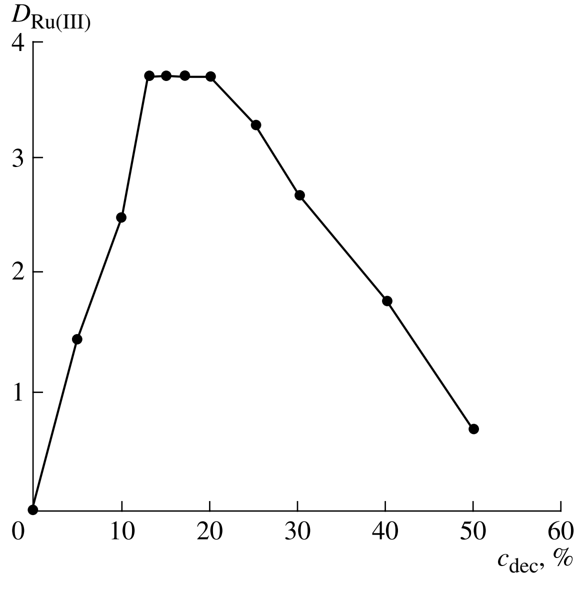


Fig. 1. Effect of the decanol concentration on the ruthenium(III) distribution ratio. c_{HCl} = 3 mol/L. $c_{Ru(III)} = 2 \times 10^{-4}$ mol/L. c_{extr} = 0.1 mol/L. τ_{cont} = 1 h. Diluent: toluene.

solved in concentrated hydrochloric acid, followed by filtration, to free it from insolubles. The purified salt corresponded to the composition $RuCl_3 \cdot H_2O$ as determined by elemental analysis. The salt was verified for the absence of ruthenium(IV) by the potassium iodide test and by measuring its electronic absorption spectrum in hydrochloric acid [10]. Solutions were prepared by diluting the stock ruthenium solution in 6 M HCl. The ruthenium(III) concentration was determined spectrophotometrically [11] as the absorption of the blue ruthenium thiourea complex.

When ruthenium(III) solutions are stored for a long period in acid solutions (3–6 mol/L), diffuse absorption bands appear at 29 400–26 300 and 23 255–20 800 cm^{-1} in their electronic absorption spectra in addition to the absorption band at 30 300 cm^{-1}; these new bands are due to partial oxidation of ruthenium(III) by atmospheric oxygen and the appearance of minor ruthenium(IV) in the solution [12]. The extraction was carried out from fresh ruthenium(III) solutions at room temperature (20 ± 0.5)°C and the aqueous-to-organic phase ratio of 1 : 1. Stirring was performed on an R-3 magnetic stirrer. Phase separation was clear and occurred in 1–2 min after the contact was over. Electronic absorption spectra were recorded on a Specord M40 spectrophotometer using glass and silica cells. IR spectra were recorded as thin films on a Specord M80 spectrophotometer. The electrical conductivity of extracts was measured in acetone on a Radelkis OK 102/1 conductometer.

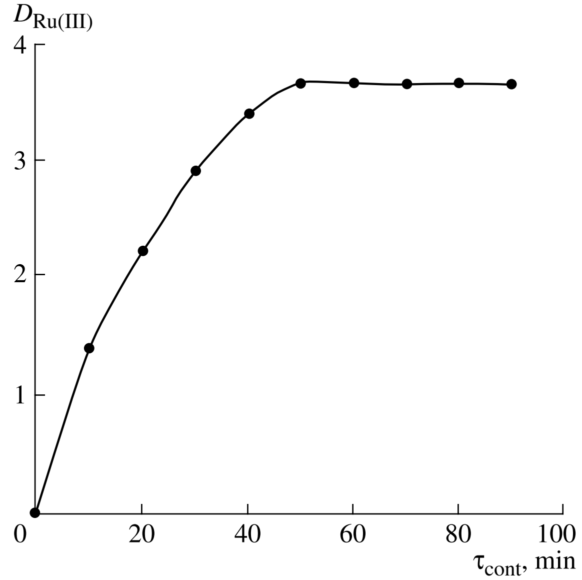


Fig. 2. Effect of the phase contact time on the ruthenium(III) distribution ratio. $c_{Ru(III)} = 2 \times 10^{-4}$ mol/L. c_{extr} = 0.1 mol/L. c_{HCl}= 3.0 mol/L.

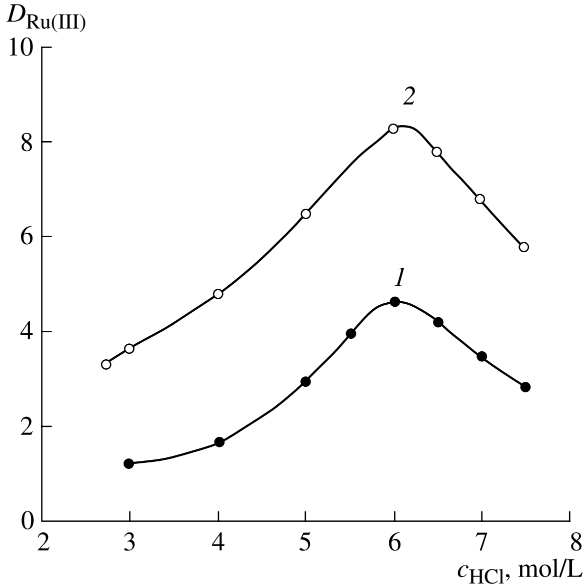


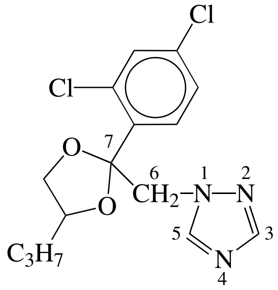
Fig. 3. Effect of the hydrochloric acid concentration on the ruthenium(III) distribution ratio. $c_{Ru(III)} = 1.5 \times 10^{-4}$ mol/L. c_{extr} = (*1*) 0.05 and (*2*) 0.10 mol/L. τ_{cont} = 1 h.

RESULTS AND DISCUSSION

We showed that extraction equilibrium during the extraction of ruthenium(III) with propiconazole from 3 M HCl is acquired after 1 h (Fig. 2). All further extraction experiments were carried out during this equilibrium time. Preliminary experiments studied the extraction of hydrochloric acid by the extractant in toluene + 15% decanol solutions. Table 1 lists the chemical shifts for the signals from carbon atoms of the two stereomers of the extractant and its extracts with hydrochloric acid. The signals from the carbon atoms in the positions 3 and 3' in the extracts, isolated from 3 and 4 M HCl, experience the greatest additional chemical shifts. It follows that the triazole nitrogen atom in the position 4 is protonated.

To choose the optimal parameters of ruthenium(III) extraction by the extractant, we studied the metal recovery as a function of hydrochloric acid concentration in the aqueous phase (Fig. 3; curves *1*, *2*). The recovery increased with increasing HCl concentration regardless of the extractant concentration. The effect of the HCl concentration on the ruthenium(III) recovery was studied until the HCl concentration reached 7.5 mol/L. The peak ruthenium recovery was from 6 M HCl. It is known [13] that in the range of the acidities studied (2–6 M HCl), ruthenium exists as $[RuCl_4(H_2O)_2]^-$ and $[RuCl_5 \cdot (H_2O)]^{2-}$. The increase in the ruthenium(III) recovery with increasing acid concentration can be interpreted as an increase in the concentration of the ruthenium(III) extraction species. When the HCl concentration was higher than 6 mol/L, the ruthenium(III) recovery decreased, which can be explained as arising from an increase in the $[RuCl_6]^{3-}$ concentration and the

Table 1. Chemical shifts for the signals from carbon atoms in the ^{13}C NMR spectra of reagent L and its complexes with HCl (in $CDCl_3$)



C in position	L	$(HL)^+$(3 M HCl)	$(HL)^+$(4 M HCl)
3	150.31	149.11	145.87
3'	150.42	149.40	146.40
Δ		–1.20	–4.64
Δ'		–1.02	–4.02
5	143.68	144.27 br	143.71 br
5'	143.98		
Δ		0.59	0.03
6	53.15	54.06	54.49
6'	53.61	54.55	55.00
Δ		0.91	1.34
Δ'		0.94	1.39
7	106.03	106.37 br	105.89 br
7'	106.11		
Δ		0.34	–0.14

coextraction of hydrochloric acid. The main investigations on the extraction of ruthenium(III) were carried out using 3 M HCl with $\tau_{\text{cont}} = 1$ h at room temperature. Under the chosen extraction parameters, $D_{\text{Ru(III)}}$ had significant values and the major species was a single-charge chlororuthenium(III) complex $[RuCl_4(H_2O)_2]^-$. The effect of the chloride ion concentration on the ruthenium(III) recovery from 3 and 4 M HCl is illustrated by Fig. 4. The ruthenium(III) distribution ratio increased with increasing sodium chloride concentration. This was likely on account of an increase in the proportion of the extracted metal species in the aqueous phase. Therefore, chloride ions have a salting-out effect and favor extraction in the range of the sodium chloride concentrations studied.

In order to elucidate the ruthenium(III) extraction mechanism, we studied the distribution ratio $D_{\text{Ru(III)}}$ versus hydrogen ion concentration (solution ionic strength, $I = 4$; NaCl + HCl; c_{HCl} from 4.0 to 3.0 mol/L; $\tau_{\text{cont}} = 1$ h). The $\log D = f(\text{pH})$ plot (Fig. 5) shows that the hydrogen ion concentration affects the ruthenium(III) distribution ratio: $D_{\text{Ru(III)}}$ increases with increasing H^+ concentration. The slope of the plot is –1. This allows us to suggest that the extraction species is the negatively charged species $[RuCl_4(H_2O)_2]^-$.

We recorded ruthenium(III) extraction isotherms from 3 M HCl to extractant solutions in toluene + 15% decanol. The slope method was used to estimate the amount of the extractant that enters the composition of the extraction compound. This amount is unity; that is, there is one extractant molecule per ruthenium(III) ion (Fig. 6).

From the combined experimental data, we derived the equation below to describe extraction equilibrium; this equation accounts for the fact that weakly basic attractants can be protonated in contact with hydrochloric acid to yield ion associates [14].

$$[RuCl_4(H_2O)_2]^- + H^+ + L \rightleftharpoons \{(HL)^+ \cdot [RuCl_4(H_2O)_2]^-\}.$$

The unknown activity coefficients did not allow us to calculate the thermodynamic constants of extraction. Therefore, we used the concentration constants of ruthenium extraction, which was calculated from

$$K_{\text{conc}} = [Y_{\text{Ru}^{3+}}]_{\text{org}}/[X_{\text{Ru}^{3+}}]_{\text{aq}} \cdot [S_0 - (Y_{\text{Ru}^{3+}})_{\text{org}}][\text{H}^+ - Y_{\text{Ru(III)org}}]_{\text{aq}},$$

Here, $[Y_{\text{Ru}^{3+}}]_{\text{org}}$ was the equilibrium ruthenium(III) concentration in the organic phase, $[X_{\text{Ru}^{3+}}]_{\text{aq}}$ was the equilibrium ruthenium concentration in the aqueous phase, S_0 was the starting extractant concentration $[\text{H}^+ - Y_{\text{Ru(III)o}}]_{\text{aq}}$. The concentration $[H^+]$ was set constant, because $[Y_{\text{Ru(III)org}}]$ was insignificant (~ 10^{-4}) and $c_{\text{H+}}$ was fixed at 3 mol/L. The values calculated for the concentration constants of ruthenium(III) extraction are listed in Table 2 (K_{conc} ~ 7.9 ± 0.1).

Comparing the electronic spectra of the aqueous phase with the absorption spectrum of the extract obtained upon the extraction of ruthenium(III) with toluene from 3 M HCl, we observed broadening of the absorption band at 25 680 cm^{-1} with an attendant small decrease in its intensity in the extract spectrum; this spectral evolution was induced by the change in the nature of the cation in the extraction complex. This provides evidence in favor of the extraction equation we suggest (Fig. 7).

The conductometric measurements in the organic phases along the extraction isotherms in acetone showed that these phases were electrolytes: λ ~ 90–100 Ω^{-1} cm^2 mol^{-1}; this means that the extracted species was a 1 : 1 electrolyte.

Having studied the temperature effect on ruthenium(III) extraction by the triazole derivative, we found that the extraction capacity of the extractant increased

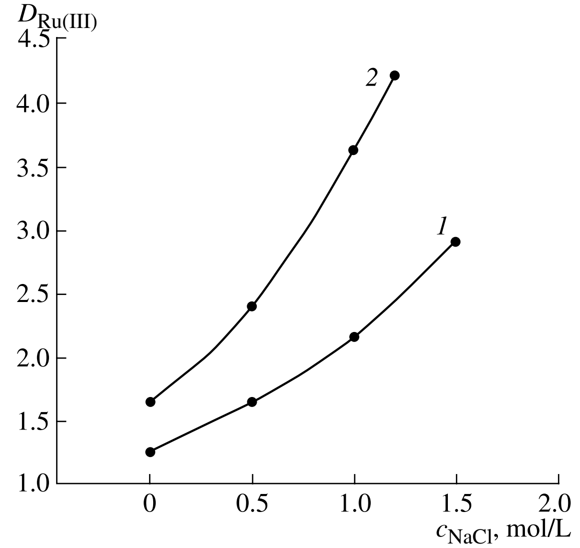


Fig. 4. Effect of the chloride ion concentration on the ruthenium(III) distribution ratio. $c_{Ru(III)} = 2 \times 10^{-4}$ mol/L. c_{extr} = 0.05 mol/L. c_{HCl} = (*1*) 3 and (*2*) 4 mol/L.

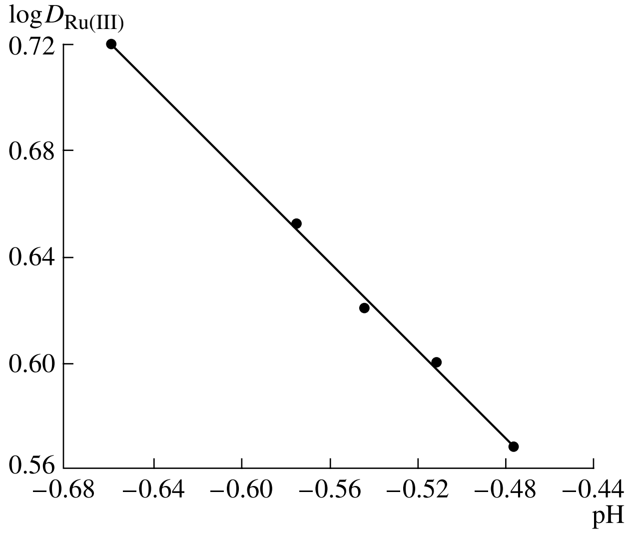


Fig. 5. Effect of the chloride ion concentration on the ruthenium(III) distribution ratio. $c_{Ru(III)} = 2 \times 10^{-4}$ mol/L. c_{extr} = 0.05 mol/L. $I = 4$. $n = -1$.

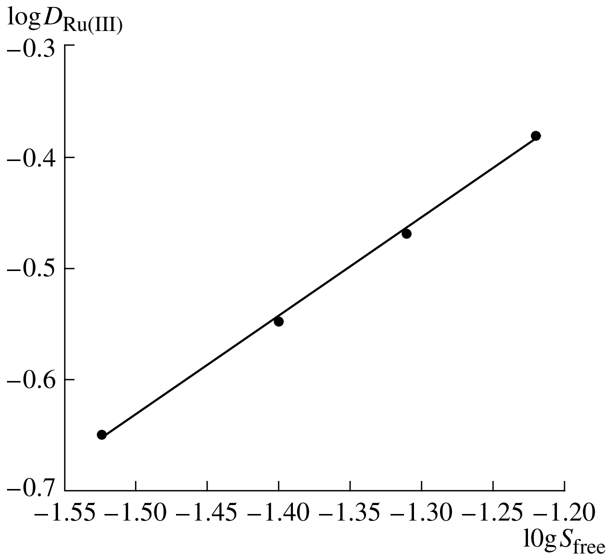


Fig. 6. Effect of the free extractant concentration on the ruthenium(III) distribution ratio. c_{HCl} = 3.0 mol/L. $X_{Ru(III)}$ = 3×10^{-4} mol/L. τ_{cont} = 1 h. $q = 1$.

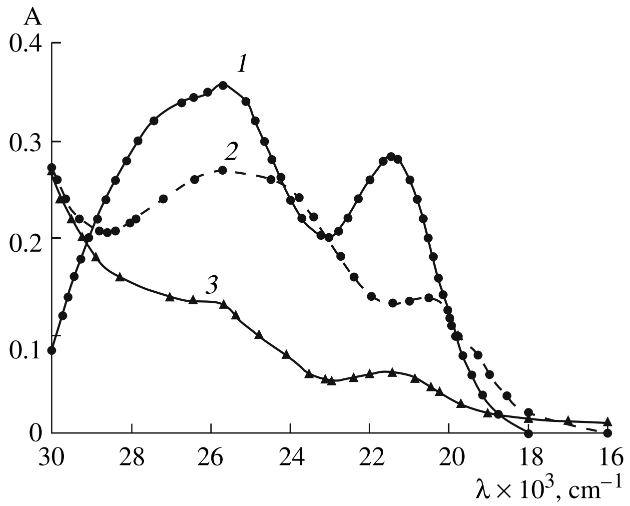


Fig. 7. Electronic absorption spectra for (*1*) the starting ruthenium(III) solution in 3 M HCl, (*2*) the organic phase after the extraction of ruthenium(III), and (*3*) the aqueous phase after the extraction of ruthenium(III).

insignificantly in response to increasing temperature (Fig. 8). From the log $\log D = f(1/T)$ plot, we derived the enthalpy of extraction ΔH equal to 6.13 kcal/(mol K).

$$Q = -\Delta H = 2.3R\tan\alpha$$
$$= -[4.575(-1.34)] = 6.13\ \text{kcal/(mol K)}.$$

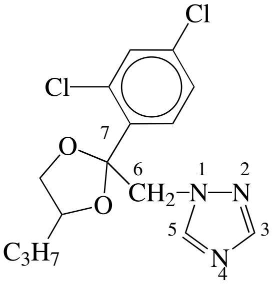
From the investigation of the temperature effect on the ruthenium extraction, it follows that the extraction reaction is endothermic.

To verify the participation of the triazole nitrogen atom N_4 in the formation of an ion associated with the ruthenium(III) ion $[RuCl_4(H_2O)_2]^-$ during the extraction of ruthenium(III) from 3 M HCl, we recorded ^{1}H and ^{13}C NMR spectra. Table 3 displays the chemical shifts δ and additional chemical shifts $\Delta\delta$ for the signals from methylene and methyne protons (CH_2 and CH) in the ^{1}H spectra of the extractant and its extract with HCl and ruthenium(III).

Table 2. Distribution and constants of ruthenium(III) extraction with triazole derivatives

Equilibrium ruthenium(III) concentration, mol/L		Concentration constant of extraction
$X_{Ru(III)}$	$Y_{Ru(III)}$	
c_{extr} = 0.04 mol/L (K_{av} = 7.1 ± 0.1)		
4.6×10^{-4}	1.3×10^{-4}	7.1
8.6×10^{-4}	2.45×10^{-4}	7.2
1.31×10^{-3}	3.65×10^{-4}	7.0
1.67×10^{-3}	4.7×10^{-4}	7.1
2.18×10^{-3}	6.25×10^{-4}	7.3
c_{extr} = 0.05 mol/L (K_{av} = 9.5 ± 0.1)		
3.35×10^{-4}	1.55×10^{-4}	9.3
7.1×10^{-4}	3.25×10^{-4}	9.2
1.39×10^{-3}	5.0×10^{-4}	7.4
1.1×10^{-3}	6.3×10^{-4}	10.6
1.78×10^{-3}	8.1×10^{-4}	10.9
c_{extr} = 0.06 mol/L (K_{av} = 7.1 ± 0.1)		
2.8×10^{-4}	1.9×10^{-4}	7.1
5.8×10^{-4}	3.85×10^{-4}	7.2
9.25×10^{-4}	6.15×10^{-4}	7.0
1.14×10^{-3}	7.6×10^{-4}	7.1
1.44×10^{-3}	9.5×10^{-4}	7.3

Table 3. Chemical shifts δ (ppm) for the proton signals in the ^{1}H NMR spectra of reagent L and its complexes with HCl and ruthenium(III)(in $CDCl_3$)



C in position	L	$(HL)^+$ (3 M HCl)	$\{(HL)^+ \cdot [RuCl_4(H_2O)_2]^-\}$
3	7.60	7.91 br	7.98 br
3'	7.60		
Δ		0.31	0.38
5	7.88	8.46	
5'	7.98	8.54	8.62 br
Δ		0.58	0.74
Δ'		0.56	
6	4.43	4.67	4.77 br
6'	4.51	4.71	
Δ		0.24	0.34
Δ'		0.20	
H^+		6.56	6.32

From the interpretation of the chemical shifts for the extractant and its extract with HCl and ruthenium(III), it also follows that the greatest additional chemical shifts are experienced by the signals from methyne and methylene protons in the positions 3, 5, and 6: 0.37, 0.38, 0.74, and 0.34 ppm for the ruthenium(III) complex and 0.31, 0.58, and 0.24 ppm for the complex of the extractant with hydrochloric acid. The proton signal in the H^+L complex appears at 6.32 ppm in the ruthenium(III) complex $\{(H^+L) \cdot [RuCl_4(H_2O)_2]^-\}$ and at 6.56 ppm in the hydrochloric acid complex $[H^+L]$. These data also confirm the ruthenium(III) extraction in the form of ion associates. The extractant is protonated at the triazole nitrogen atom N_4.

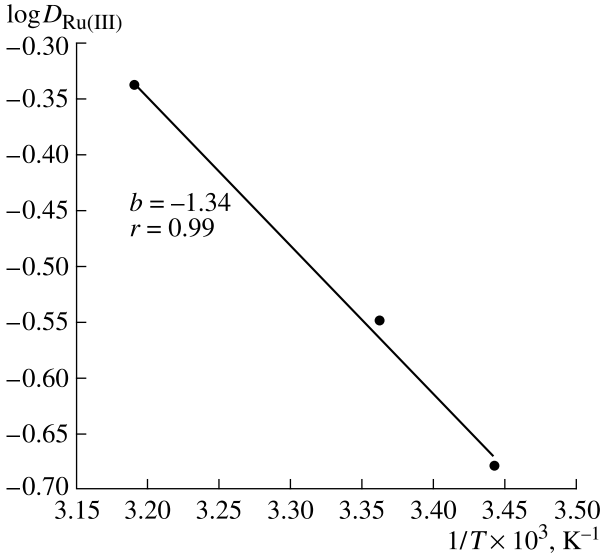
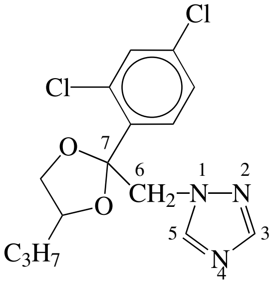


Fig. 8. Effect of temperature on the ruthenium(III) distribution ratio. $c_{Ru(III)} = 2 \times 10^{-4}$ mol/L. $c_{extr} = 0.05$ mol/L. $c_{HCl} =$ 3.0 mol/L.

To confirm the extractant protonation via the triazole nitrogen atom N_4, we recorded ^{13}C NMR spectra for the extractant and its complexes with hydrochloric acid and ruthenium(III) isolated from 3.0 M HCl (Table 4). The signals from the carbon atoms in the positions 3, 5, 6, and 7 experience the greatest additional chemical shifts. In the hydrochloric acid complex, the signals from the carbon atoms in the same positions also experience the greatest additional chemical shift. These distinction of the spectra of the complexes from the extractant spectrum also confirms our suggestion that ruthenium(III) is extracted as the ion associate $[RuCl_4(H_2O)]^- \cdot (H^+L)$ with the extractant being protonated at the triazole nitrogen atom N_4.

The IR spectra of the ruthenium(III) complex with the extractant were also recorded. The ν(Ru–Cl)

Table 4. Chemical shifts δ (ppm) for the carbon signals in the ^{13}C NMR spectra of reagent L and its complexes with HCl and ruthenium(III) in ($CDCl_3$)



C in position	L	$(HL)^+$ (3M HCl)	$\{(HL)^+ \cdot [RuCl_4(H_2O)]^-\}$
3	150.31	149.11	147.52
3'	150.42	149.40	147.95
Δ		–1.20	
Δ'		–1.02	–2.79
			–2.47
5	143.68	144.27 br	145.26 br
5'	143.98	0.29	1.28
Δ			
6	53.15	54.06	54.49
6'	53.61	54.55	55.00
Δ		0.91	1.34
Δ'		0.94	1.39
7	106.03	106.37	105.72 br
7'	106.11		
Δ		0.43	–0.31

absorption region in the IR spectrum of $[RuCl_6]^{3-}$ is 290–332 cm^{-1} [15, 16]. In the IR spectrum of the complex $\{(HL)^+ \cdot [RuCl_4(H_2O)_2]^-\}$, the ν(Ru–Cl) stretches appear as a strong broad band at 320 cm^{-1}. Along with the absorption band at 320 cm^{-1}, there is absorption due to the ν(Ru–O) stretches at 390 cm^{-1}, which appears as a weak absorption band and matches the literature data for the *mer* configuration [17]; this is another piece of evidence in favor of the entrance of $[RuCl_4(H_2O)_2]^-$ ruthenium ions into the extracted species. The bending vibrations δ(OH) appear as a weak absorption band at 1650 cm^{-1}. The librational vibrations of water molecules $\rho(H_2O)$ appear as a weak band at 648 cm^{-1}. The elemental analysis of the extraction complex confirms our suggested composition: Ru : C : N = 1 : 4 : 1.

In summary, the extraction of ruthenium(III) from 3.0 M HCl solution is due to ion association. Ion associates are formed through the protonation of the triazole nitrogen atoms in the position 4.

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