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Note

Synthesis and characterization of mixed-ligand ruthenium(III) complexes with oxalate and acetylacetonate ions

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Abstract

Two mononuclear mixed-ligand ruthenium(III) complexes with oxalate dianion (ox^{2-}) and acetylacetonate ion (2,4-pentanedionate, $acac^-$), $K_2[Ru(ox)_2(acac)]$ (**1**) and $K[Ru(ox)(acac)_2]$ (**2**), were prepared as a candidate for a building block. In fact, reaction of complex **2** with manganese(II) sulfate gave a heterometallic tetranuclear complex, $TBA[Mn^{II}\{(\mu\text{-}ox)Ru^{III}(acac)_2\}_3]$ (**5**) in the presence of tetrabutylammonium (TBA) bromide. The ^1H NMR, UV–Vis, selected IR and FAB mass spectral data of these complexes are presented. Both mixed-ligand ruthenium(III) complexes gave a Nernstian one-electron reduction step in 0.1 mol dm^{-3} Na_2SO_4 aqueous solution on a mercury electrode at 25 °C. Comparison of observed reversible half-wave potentials with calculated values for a series of $[Ru(ox)_n(acac)_{3-n}]^{n-}$ ($n = 0$–3) complexes by using Lever's ligand electrochemical parameters is presented.

Keywords: Ruthenium complexes; Oxalato complexes; Tetranuclear complexes; Mixed-ligand complexes; Electrochemistry; Ligand electrochemical parameters

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1. Introduction

Recently oxalate-bridged ruthenium(III) polymeric compounds with formula $(TBA)[M^{II}Ru^{III}(ox)_3]$ [1a] (TBA^+ = tetra-*n*-butylammonium; M = Mn, Fe and Cu; ox^{2-} = oxalate dianion) and $[Z^{III}Cp_{*2}]$ $[M^{II}Ru^{III}(ox)_3]$ (Z = Co and Fe; M = Mn, Fe, Co, Cu and Zn; Cp* = pentamethylcyclopentadienyl) [1b] were synthesized and their magnetic properties were investigated [1]. To the authors' knowledge, however, only a few papers have been published on discrete bi- or oligonuclear oxalate-bridged ruthenium complexes which have been isolated: $[\{Ru^{II}(py)_4\}_2(\mu\text{-}ox)](BF_4)_2$ (py = pyridine) [2], $[\{(\eta^3:\eta^3\text{-}C_{10}H_{16})Ru^{IV}Cl\}_2(\mu\text{-}ox)]$ [3], $[\{Ru^{II}X(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2(\mu\text{-}ox)]^n$ (X = Cl, $n = 0$; X = PPh_3, $n = {}^{2+}$) [4], and $[Ru^{III}\{(\mu\text{-}ox)M^{II}L_2\}_3]Cl_3$ (M = Cu and Ni; L = ethylenediamine and 2,2′-bipyridine [5]. Preparations of such bi- or oligonuclear complexes require some inert mononuclear mixed-ligand ruthenium(III) complexes with one or two ox^{2-} as a bridging moiety. In fact, in the case of chromium(III) complexes, some inert complexes, $[Cr(salen)(ox)]^-$ [6] (H_2salen = bis(salicylidne) ethylenediamine), $[Cr(bpy)(ox)_2]^-$ [7] (bpy = 2,2′-bipyridine), $[Cr(eddp)(ox)]^-$ [8] (eddp = ethylenediamine-*N*,*N*′-dipropionate), $[Cr(acac)_2(ox)]^-$ [9] ($acac^-$ = acetylacetonate), $[Cr(dpa)(ox)_2]^-$ (dpa = 2,2′-dipyridylamine) [10], and $[Cr(bpym)(ox)_2]^-$ (bpym = 2,2′-bipyrimidine) [11] have been synthesized for preparation of bi- or oligonuclear complexes. On the other hand, the number of studies on mixed-ligand ruthenium complexes with ox^{2-} are limited: $[Ru^{III}(en)_2(ox)][Ru^{III}(en)(ox)_2]$ [12,13] (en = ethylenediamine), $[Ru^{II}(phen)_2(ox)]$ [14] (phen = 1,10-phenanthroline), $[Ru^{II}(bpy)_2(ox)]$ [15–19], $[Ru^{III}(ox)_2(py)_2]^-$ [20] (py = pyridine), $[Ru^{III}(ox)_2(\text{L-aniline})_2]^-$ [20] (L-aniline = a substituted aniline), $[Ru^{II}(tpy)(ox)(H_2O)]$ [21] (tpy = 2,2′,2″-terpyridine), $[Ru^{III}(ox)_2(H_2O)_2]^-$ [22], *cis*-$K[Ru^{II}(ox)_2(en)NO]$ and *cis*-$K[Ru^{II}(Hox)(ox)(en)NO]$

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[23]. Among them, there is no successful example illustrating the preparation of bi- or oligonuclear ruthenium complexes using a mixed-ligand mono- or bis(oxalato)ruthenium complex as a building block.

In this paper preparation and characterization of two new mononuclear mixed-ligand ruthenium(III) complexes with ox^{2-} and $acac^{-}$, $K_2[Ru^{III}(ox)_2(acac)]$ (**1**) and $K[Ru^{III}(ox)(acac)_2]$ (**2**), as a building block for preparation of oligonuclear complexes are presented. Comparison of observed reversible half-wave potentials with calculated values for a series of $[Ru(ox)_n(acac)_{3-n}]$ ($n =$ 0–3) complexes by using Lever's ligand electrochemical parameters is also presented.

2. Experimental

2.1. Physical measurements

Elemental analyses of the complexes were carried out on a Shimadzu Seisakusho Ltd. CHN Analyzer CHN-1A. Electronic spectra in aqueous solutions were recorded on a Hitachi Model 200-20 spectrophotometer. ^1H NMR spectra and mass spectra were recorded with a JEOL JNM GX-270 spectrometer and a JEOL JMS-DX303 instrument, respectively. Voltammetric studies were carried out in aqueous solutions on a Huso Polarograph Model 312 with Huso Potential Scanning Unit Model 321 and a Riken Denshi X-Y Recorder Model F-42CP. A hanging mercury drop electrode (HMDE) of Princeton Applied Research Model 9323 and a glassy carbon electrode (3 mm ϕ) were used as a working electrode, Ag|AgCl was used as a reference electrode, Pt wire was used as an auxiliary electrode and 0.1 mol dm^{-3} sodium sulfate as a supporting electrolyte. All the electrochemical measurements were made at (25.0 ± 0.1) °C.

2.2. Preparation of the complexes

2.2.1. $K_2[Ru(ox)_2(acac)]$ (1)

The $K_3[Ru(ox)_3]$ complex [13] (**3**, 2.5 g, ca. 5.2 mmol) was dissolved in water (30 cm^3) and Hacac (0.55 g, 5.5 mmol) was added to the solution. Then the mixture was refluxed for 30 min; the color of the solution turned brown. The brown solution was washed with benzene (ca. 30 cm^3) twice to remove the excess of Hacac and an insoluble substance was filtered off. The filtrate, after being concentrated to ca. 5 cm^3 at 65 °C, was subjected to column chromatography (Sephadex LH-20, 2 cm diameter, 30 cm long). Development with water gave rise to four bands (the first greenish yellow band corresponds to $[Ru(ox)_3]^{3-}$, the second vermilion band to $[Ru(ox)_2(acac)]^{2-}$, the third red band to $[Ru(ox)(acac)_2]^{-}$, and the fourth red–purple band to $[Ru(acac)_3]$); the vermilion eluate of the second band was concentrated to ca. 3 cm^3 at 65 °C. The solution was applied to another Sephadex column of a similar size. The eluate was collected in fractions of a few cubic centimeters. Each fraction was tested for chloride ions which were included in the crude complex **3** (silver nitrate). The fractions that gave negative results were combined and evaporated to dryness at 65 °C. The residue, after being washed with acetone, was collected by filtration, and dried in vacuo; yield 23.3%. *Anal.* Calc. for $C_9H_7K_2O_{10}Ru$ ($M_r = 454.4$): C, 23.79; H, 1.55. Found: C, 23.55; H, 1.41%. FAB-MS(*m*-nitrobenzyl alcohol (*m*-NBA)): *m/z* 328 $[M - ox - K]$, 456 $[M + H]$, 494 $[M + K]$. UV–Vis (H_2O) λ_{max}/nm ($\log(\varepsilon$ /mol^{-1} dm^3 cm^{-1})): 281(3.96); 329(3.64); 496(2.62). IR (KBr pellet) ν/cm^{-1} 1668 ν_a (non-coordinated C=O in ox), 1525 ν (C=O in acac) + ν (C=C in acac).

2.2.2. $K[Ru(ox)(acac)_2]$ (2)

Method (A): a procedure similar to that for complex **1** was used. The ratio amount of Hacac to **3** was 1.5. The red eluate of the third band of the first column chromatography was evaporated to dryness at 65 °C and dried in vacuo for 1 h. The crude crystals were dissolved in acetone–water (50:1 by volume), and insoluble material (probably KCl) was filtered off. The filtrate was evaporated to dryness again. This decantation procedure was repeated until chloride ion was no longer detected; yield 5.6%.

Method (B): the $[Ru(acac)_3]$ [24] (**4**, 2.0 g, 5.0 mmol) was added to a boiling solution of $H_2C_2O_4 \cdot 2H_2O$ (0.32 g, 2.5 mmol) in water (400 cm^3) and the mixture was refluxed for 2 h. After cooling, $K_2C_2O_4 \cdot H_2O$ (0.48 g, 2.6 mmol) was added to the solution. The solution was refluxed for 3 days and then evaporated to ca. 20 cm^3 at 65 °C. After filtration to remove **4**, the filtrate was neutralized with 0.01 mol dm^{-3} KOH aqueous solution. The mixture was evaporated to ca. 20 cm^3 again. A fraction (ca. 3 cm^3) of the evaporated solution was subjected to column chromatography (Sephadex LH-20, 2 cm diameter, 30 cm long). The red eluate of the third band was collected. This chromatographic procedure was repeated seven times. The collected solution was evaporated to dryness. The residue, after being washed with acetone, was collected by filtration, and dried in vacuo; yield 47.2%.

Anal. Calc. for $C_{12}H_{14}KO_8Ru \cdot H_2O$ (M_r (not containing $H_2O) = 426.4$): C, 32.43; H, 3.63. Found: C, 32.19; H, 3.25%. FAB-MS(*m*-NBA): *m/z* 300 $[M - ox - K]$, 328 $[M - acac]$, 428 $[M + H]$, 466 $[M + K]$, 893 $[2M + K]$. UV–Vis (H_2O) λ_{max}/nm ($\log(\varepsilon$/mol^{-1} dm^3 cm^{-1})): 279(4.09); 341(3.84); 495(3.01). IR (KBr pellet) ν/cm^{-1} 1676 ν_a (non-coordinated C=O in ox), 1521 ν (C=O in acac) + ν (C=C in acac).

2.2.3. TBA $[Mn^{II}\{(\mu\text{-}ox)Ru^{III}(acac)_2\}_3]$ (5)

$K[Ru^{III}(ox)(acac)_2]$ (**2**, 80 mg, 0.188 mmol) was dissolved in an aqueous solution (1 cm^3), after stirring for few minutes, aqueous solutions of $MnSO_4 \cdot 4{\sim}5H_2O$ (23 mg, ca. 0.063 mmol: 0.5 cm^3) and TBABr (22 mg, 0.069 mmol: 0.5 cm^3) were added to it. The mixed solution was stirred in the dark at room temperature for several days. The vermeil precipitate was collected by filtration with a glass filter, washed with small amount of water, and dried in vacuo for 1 day; yield 32%.

Anal. Calc. for $C_{52}H_{78}NO_{24}MnRu_3$ ($M_r = 1459.32$): C, 42.80; H, 5.39; N, 0.96%. Found: C, 42.45; H, 5.58; N, 0.90%. FAB-MS(*m*-NBA): *m/z* 1702 [*M* + TBA], UV–Vis (CH_3CN) λ_{max}/nm (log(ε/mol^{-1} dm^3 cm^{-1})): 343 (4.41); 493 (3.65). IR (KBr pellet) ν/cm^{-1} 1633 ν_a(C=O in ox), 810 δ(OCO). ^{1}H NMR ($CDCl_3$) δ: −51 (s, br, 6H, CH in acac); −22.83, −22.46, −21.40 (m, br, 18H, CH_3 in acac); −16.54, −15.89 (m, br, 18H, CH_3 in acac); −0.46, −1.26, 3.37 (m, br, C_4H_9).

3. Results and discussion

Complex **1** was prepared from **3** as a starting material in fairly good yield (23.3%); other 2,4-pentanedionato complexes, **2** and **4**, were formed in a few percent, while **2** was prepared from the same starting material in very poor yield (5.6%) by method (A). When complex **4** was employed as a starting material [method (B)], **2** was obtained in good yield (47.2%), and other oxalato complexes were formed on a small scale; complex **1** was formed in about 10% and **3** in a few percent. Furthermore complex **4** was able to be recovered from the reactant mixture in ca. 20%.

Both mixed-ligand complexes were readily obtained by means of the ligand exchange reactions of the tris–chelate complexes in aqueous solution:

$$K_3[Ru(ox)_3] + Hacac \rightleftarrows K_2[Ru(ox)_2(acac)] + KHox \quad (1)$$

and

$$[Ru(acac)_3] + 1/2H_2ox + 1/2K_2ox \rightleftarrows K[Ru(ox)(acac)_2] + Hacac \quad (2)$$

Complex **3** has been known as a starting material for syntheses of several oxalatoruthenium complexes in aqueous solution [13]. Complex **4** has also been known as a good starting material for preparation of bis(acetonitrile)bis(acetylacetonato)ruthenium(II) [25] and -ruthenium(III) [26], of organometallic alkene [27], alkyne [28], bis(cyclooctene) [29], diene [30] complexes with bis(acetylacetonato)ruthenium(II), and of some homoleptic tris(*N*,*S*-bidentate)ruthenium(III) complexes [31] in organic solvents. However, no reports have been published on the ligand substitution reaction of **4** in aqueous solution. Some reports on the ligand substitution reaction of **4** in an organic solvent including a small amount of water have been published, but the water has been used to enrich the reduction power of zinc or zinc amalgam for ruthenium(III) to ruthenium(II) [25,27–29].

The ^{1}H NMR spectrum of **2** in D_2O at ambient temperature is shown in Fig. 1(a). The NMR data of the oxalato ruthenium(III) complexes in D_2O are listed in Table 1 together with the data of **4** in the same solvent. The NMR spectra of **2** exhibit paramagnetic shifts. The assignment of the methyne (=CH–) and methyl signals in the mixed-ligand complexes with C_2 symmetry was based on the integral ratios and on the comparison with the spectrum of **4**. During the assignment, we noticed that the integral ratio of the methyne protons to the methyl protons of acac ligand in Fig. 1(a) was smaller than the expected. This spectrum was recorded immediately after the complex was dissolved in D_2O (probably within 1 h including accumulation time). When the solution was allowed to stand for a week at 5 °C, the methyne proton signal disappeared completely as shown in Fig. 1(b). This fact indicates that the rate of exchange reaction between the methyne hydrogen and the deuterium of the solvent is relatively fast. In the case of **4**, no indication of deuterium exchange was observed.

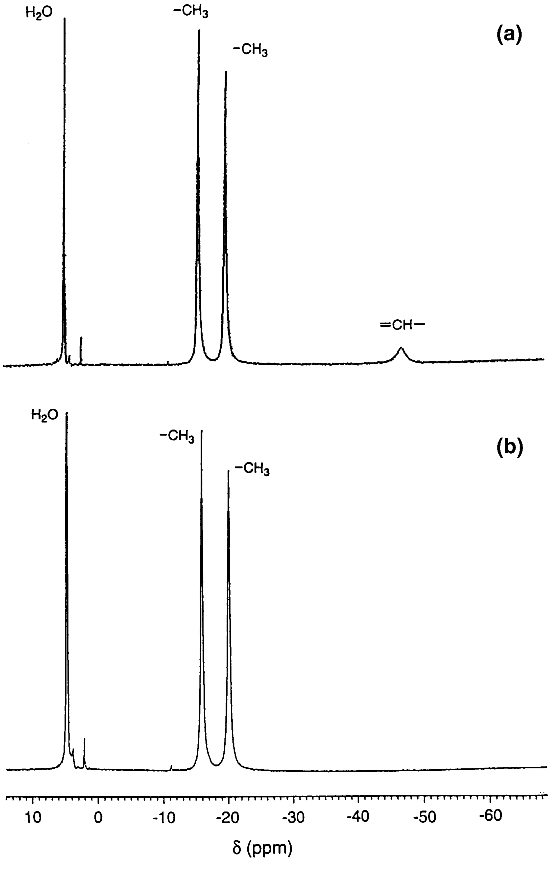

Fig. 1. ^{1}H NMR spectra of K[Ru(ox)(acac)$_2$] in D_2O at ambient temperature. (a) The spectrum was recorded immediately after the complex was dissolved in D_2O. (b) The spectrum was recorded after the solution was allowed to stand for a week at 5 °C.

Table 1
^{1}H NMR data (in D_2O) and electrochemical data for oxalato ruthenium(III) complexes together with $[Ru(acac)_3]$

Complex	δ^a(ppm)		Ru^{III}/Ru^{II}	
	–CH_3	=CH–	$E_{1/2}{}^b$ (V)	$\Delta E_p{}^c$ (mV)
$K_3[Ru(ox)_3]$ (**3**)			-0.653^d	61^d
$K_2[Ru(ox)_2(acac)]$ (**1**)	-11.16^e	-38.4^f	−0.503	63
$K[Ru(ox)(acac)_2]$ (**2**)	-15.86^e -19.97^e	-47.1^f	−0.507	59
$[Ru(acac)_3]$ (**4**)	-5.90^e	-29.9^f	-0.471^g	

[a] H_2O ($\delta = 4.70$ ppm) is used as internal reference.

[b] Reversible half-wave potential against Ag|AgCl (sat'd KCl) determined from the polarograms by means of the conventional logarithmic plot method.

[c] Cyclic voltammetric peak separation at sweep rate of 0.1 V s^{-1}.

[d] Data taken from [32]. The electrochemical measurements were made in a medium of 0.1 mol dm^{-3} KCl aqueous solution at 20.0 °C. Reversible half-wave potential against Ag|AgCl (sat'd KCl).

[e] Singlet signal.

[f] Broad signal.

[g] Data taken from [33]. The electrochemical measurements were made in a medium of 0.2 mol dm^{-3} KCl aqueous solution at 25.0 °C. The original $E_{1/2}$ was −0.516 V vs. SCE, so the listed value (−0.471 V) was converted on the basis of the potential difference, −0.045 V between SCE and Ag|AgCl (sat'd KCl).

Table 2
Comparison of observed reversible half-wave potentials with calculated ones for a series of $[Ru(ox)_n(acac)_{3-n}]^{n-}$ ($n = 0$–3) complexes in aqueous medium^a

Complex	Ru^{III}/Ru^{II}		
	$E_{obs}{}^b$ (V)	$E_{calc}{}^c$ (V)	$\sum E_L$
$K_3[Ru(ox)_3]$ (**3**)	−0.456	−1.51	−1.02
$K_2[Ru(ox)_2\ (acac)]$ (**1**)	−0.306	−1.31	−0.84
$K[Ru(ox)(acac)_2]$ (**2**)	−0.310	−1.10	−0.66
$[Ru(acac)_3]$ (**4**)	−0.275	−0.90	−0.48

[a] Reversible half-wave potential against NHE.

[b] The listed values were converted on the basis of the potential difference, 0.197 V between NHE and Ag|AgCl (sat'd KCl).

[c] The listed values were calculated by Eq. (3) (see text) using tabulated $\sum E_L$ values.

Therefore, the presence of oxalate ligand promotes the reaction.

Both complexes **1** and **2** in 0.1 mol dm^{-3} Na_2SO_4 aqueous solution underwent a one-electron reduction process on a mercury electrode at ca. −0.50 V (versus Ag|AgCl). These were Nernstian one-electron processes with no following reaction as indicated by the analyses of the polarographic and the voltammetric data. The reversible half-wave potential ($E_{1/2}$) of the Ru^{III}/Ru^{II} couple was determined from the polarograms by means of the conventional logarithmic plot method. The electrochemical data are summarized in Table 1 together with the data of **3** [32] and **4** [33].

Oxidative measurements for a Ru^{IV}/Ru^{III} couple were attempted under the same conditions except on a glassy carbon electrode. In the potential range 0 to +1.00 V (versus Ag|AgCl), no oxidation wave was observed.

It should be noted that in spite of the difference in reversible half-wave potentials between the tris–chelate complexes, the half-wave potentials of the mixed-ligand complexes are almost identical. Lever has obtained good linear relationships between observed Ru^{III}/Ru^{II} reversible or quasi-reversible half-wave potentials for many ruthenium complexes measured in organic phase or in water and $\sum E_L$, where E_L is a ligand electrochemical parameter [34]. The $E_L(L)$ values for over 200 ligands, which contain acac and oxalate ions, have been presented in the literature; the $E_L(L)$ value is −0.08 V (versus NHE) for the acac ligand and −0.17 V for the ox ligand. Observed Ru^{III}/Ru^{II} reversible half-wave potentials for a series of $[Ru(ox)_n(acac)_{3-n}]^{n-}$ ($n = 0$–3) complexes have been compared with the calculated values by using the following equation [34] as shown in Table 2:

$$E_{calc}\ (V) = 1.14\left[\sum E_L\right] - 0.35. \tag{3}$$

The differences in potentials between the observed and the calculated values are large: ca 0.7 V for complex **4** to ca 1.0 V for **3**. The differences seem to be caused by the difference in net charge on the complexes, because Eq. (3) has been obtained from the data set of net 2+ charged species [34]. More data of net negative charged species are required to evaluate Eq. (3), which could be valid for the negative charged ruthenium species.

One of the oxalate mixed-ligand ruthenium complexes, **2** is a useful building block for the synthesis of binuclear ruthenium(III) complex [35] and heterometallic tetranuclear complexes with another transition metal ion as a central metal and with three $[Ru(ox)(acac)_2]^-$ as a peripheral unit. In fact, the tetranuclear complex **5** has been prepared by the reaction of complex **2** with $MnSO_4$ in aqueous solution containing TBABr in relatively good yield. The preparation of other heterometallic tetranuclear complexes and their magnetic properties will be presented in subsequent papers.

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