Synthesis and Spectroelectrochemical Characterization of a Novel Oxalate-Bridged Binuclear Ruthenium(III) Complex

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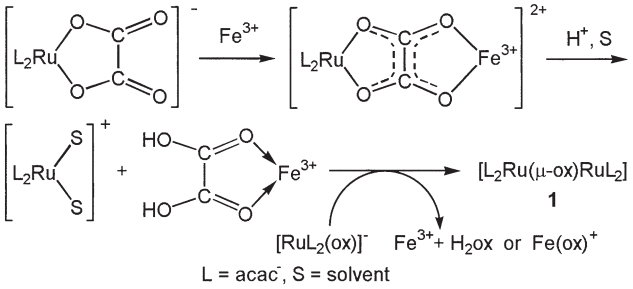
A novel oxalate-bridged binuclear ruthenium(III) complex, $[\{Ru(acac)_2\}_2(\mu\text{-ox})]$ ($acac^-$ = acetylacetonate and ox^{2-} = oxalate), has been prepared via self-dimerization of $K[Ru(acac)_2(ox)]$ in aqueous solutions containing ferric salts as catalyst. The $Ru_2^{III,II}$ mixed-valence species generated electrochemically with $K_c = 10^{5.0}$ for the comproportionation constant exhibits a weak intervalence charge transfer (IVCT) band at 1430 nm. The IR spectra from spectroelectrochemistry indicate a partially localized mixed-valence state (Class II-III behavior).

Bimetallic oxalato complexes $\{[M^{II}M^{III}(ox)_3]^-\}_n$ (ox^{2-} = oxalate dianion, M^{II} = Mn, Fe, Co, Ni, or Cu and M^{III} = Cr, Fe, or Ru) have attracted much attention recently, because these complexes form two- and three-dimensional networks which behave as ferro-, ferri-, or canted antiferromagnets.[1] Homo- and heterometallic oxalate-bridged binuclear complexes of transition metals such as Cr, Mn, Fe, Co, Ni, or Cu, have also been prepared in order to elucidate basic magnetic interactions between metals.[2] Spectroelectrochemistry of binuclear complexes can also provide information on the electronic communication between metals, however, to the authors' knowledge, there has not yet been a report of such a study on oxalate-bridged metal complexes. Furthermore, the number of studies on the synthesis of discrete oxalate-bridged diruthenium complexes is still limited. There have been a few examples: $[\{Ru^{II}(py)_4\}_2(\mu\text{-ox})](BF_4)_2$[3] (py = pyridine), $[\{(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Ru^{IV}Cl\}_2(\mu\text{-ox})]$[4], and $[\{RuX(\eta^6\text{-}p\text{-}Pr^iC_6H_4Me)\}_2(\mu\text{-ox})]^n$ (X = Cl, $n = 0$; X = PPh_3, $n = 2+$)[5]. Herein we report the synthesis of the novel oxalate-bridged binuclear ruthenium(III) complex, $[\{Ru(acac)_2\}_2(\mu\text{-ox})]$ (**1**, $acac^-$ = acetylacetonate) and the spectroelectrochemical characterization of the redox system $\mathbf{1^{0/-/2-}}$.

Complex **1** has been prepared by the self-dimerization reaction of $K[Ru(acac)_2(ox)]$ (**2**) in aqueous solutions containing ferric ions as catalyst. Thus, to an aqueous solution (2 cm^3) of $Fe_2(SO_4)_3{\cdot}nH_2O$ (80 mg, ca. 0.14 mmol) was added $\mathbf{2}{\cdot}H_2O$[6] (500 mg, 1.13 mmol). The solution was stirred in the dark at room temperature for 4 days. The dark purple-red precipitate was collected by filtration with a glass filter, washed with water and ethanol, and dried in vacuo (300 mg, 77% yield).[7]

Complex **1** was readily prepared by the self-dimerization reaction of **2** using $FeCl_3$ or $Fe(NO_3)_3$ instead of $Fe_2(SO_4)_3$ in similar yields. However, we could not obtain **1** by other, more conventional methods: i) reaction of $[Ru(acac)_3]$ with H_2ox in water-acetonitrile mixture gave only the starting complex, ii) reaction of *cis*-$[Ru(acac)_2(CH_3CN)_2]CF_3SO_3$[8] (**3**) with K_2ox in water–acetonitrile gave no precipitate, iii) reaction of **3** with **2** in aqueous solution for two weeks and iv) a self-dimerization reaction of **2** in acidic aqueous solution (pH ca.2) *without* ferric ion gave **1** in poor yields, respectively (7% at most). The following speculative reaction scheme can be written with the formation of a heterobinuclear complex as an intermediate, which would then dissociate to a solvent-coordinated ruthenium(III) species and oxalato iron(III). The solvent-coordinated species would react with the starting complex **2** to form binuclear **1**. In some cases the yield of **1** was more than six times of the molar ratio of ferric ion to **2**, indicating that the main catalytic species would be the aqua iron(III) ion rather than an oxalato iron(III) species.



The IR spectrum (KBr) of **1** shows the characteristic bands of the bis-bidentate D_{2h} oxalato bridge: 1633 cm^{-1} for ν_{as}(CO) and 810 cm^{-1} for δ(OCO). The EI-MS spectrum exhibits the parent peak of **1** at $m/z = 687$ and a major peak at 300 corresponding to the $[Ru(acac)_2]^+$ fragment. The ^1H NMR spectrum of **1** in $CDCl_3$ at room temperature shows paramagnetic shifts and three couples of broad singlet peaks, at −54.4 and −53.0 ppm for CH, at −22.66 and −22.28 ppm for methyl, and −16.39 and −15.75 ppm for methyl groups, caused by the mixture of two diastereomers: meso (C_{2h}) and racemic (D_2) forms. Component **1** is EPR silent down to 4 K in the solid state and in frozen CH_2Cl_2 solution, suggesting antiferromagnetic coupling as favored by the assumed coplanar conformation and short metal–metal distance of about 5.5 Å.[2,4] The cyclic voltammogram of **1** in 0.1 M (n-$C_4H_9)_4NBF_4$–CH_2Cl_2 (M = mol dm^{-3}) on a Pt disk electrode at 20°C shows two consecutive Nernstian one-electron reduction waves at −1.00 V and at −1.30 V (vs Fc^+/Fc).[9] These steps correspond to the Ru^{III}/Ru^{II} couple, that is, the first reduction step leads to the $Ru_2^{III,II}$ mixed-valence species and the second one to the $Ru_2^{II,II}$ isovalent form. The comproportionation constant $K_c = 10^{5.0}$ was calculated from the difference of the formal potentials between the first and the second reduction step

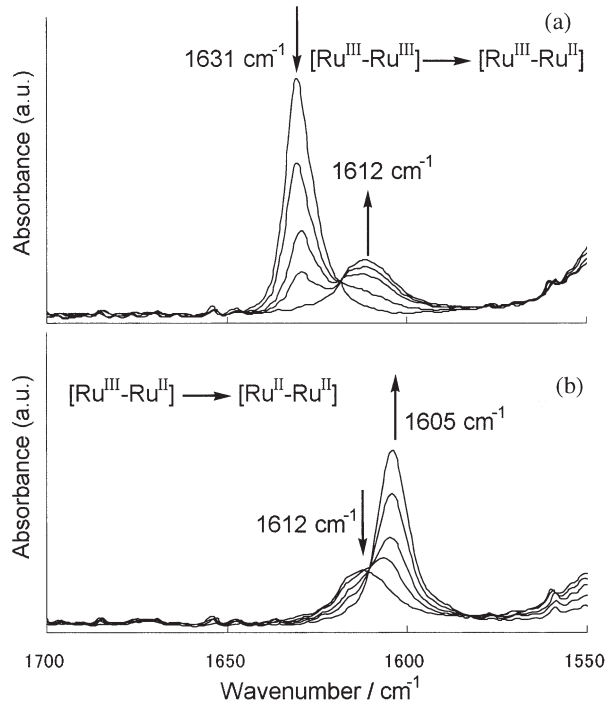


Figure 1. IR spectroscopic changes from spectroelectrochemistry of $\mathbf{1}^{n}$ in 0.1 M (n-$C_4H_9)_4NPF_6$–CH_2Cl_2 at 20 °C: $n = 0$ to -1 (a); $n = -1$ to -2 (b).

($\Delta E^{\circ} = 0.30$ V).[10] The value of K_c for **1** is larger than those ($10^{2.7-3.8}$) for oxalate-bridged dinickel(III,II) complexes with azacyclam,[11] but is smaller than the $K_c = 10^{8.5}$ for the corresponding diiron(III,II) complex, [{Fe(acac)$_2$}$_2$(μ-ox)].[12]

The UV–vis–NIR spectroscopic changes from spectroelectrochemistry[13] of $\mathbf{1}^{\mathbf{0}\rightarrow\mathbf{1}-}$ in 0.1 M (n-$C_4H_9)_4NPF_6$–CH_2Cl_2 at 20 °C show a weak IVCT band at $\lambda_{max} = 1430$ nm ($\varepsilon = 500\,M^{-1}\,cm^{-1}$) for the $Ru_2^{III,II}$ mixed-valent species in addition to an MLCT ($d_{Ru} \rightarrow \pi^*$) band at 485 nm. Further reduction to isovalent $\mathbf{1}^{2-}$ diminishes the IVCT band and shifts the MLCT band to 516 nm. The observed IVCT band width at half height ($\Delta\nu_{1/2} = 4800\,cm^{-1}$) is somewhat larger than the value calculated by the Hush formalism ($\Delta\nu_{1/2}$(calcd) $= 4000\,cm^{-1}$).[14] This indicates that the $\mathbf{1}^{-}$ ion (EPR: $g_{\perp} = 2.33$, $g_{\parallel} = 1.68$) is a mixed-valent compound of Class II in the Robin and Day classification,[15] therefore, the electronic coupling, $H_{AB} = 500\,cm^{-1}$ is given by the corresponding Hush equation.[16]

The IR spectra from spectroelectrochemistry[13] suggest that $\mathbf{1}^{-}$ ion is a partially localized Class II–III mixed-valence species.[17] In the native state, **1** exhibits a single ν_{as}(CO) band at 1631 cm^{-1} (Figure 1a). During one-electron reduction the intensity of this band decreases, and a new, weaker and broader band ($\Delta\nu_{1/2} = 16\,cm^{-1}$) appears at 1612 cm^{-1}. The doubly reduced species, $\mathbf{1}^{2-}$ gives rise to an intense, sharper single ν_{as}(CO) band at 1605 cm^{-1} (Figure 1b). This indicates that the electron transfer rate in mixed-valent $\mathbf{1}^{-}$ is close to the time scale for IR motions, that is, the charge is partially localized.

In conclusion, we have synthesized a novel oxalate-bridged binuclear ruthenium(III) complex via self-dimerization reaction of the corresponding mononuclear complex using ferric salts as catalyst. We have demonstrated for the first time that oxalate-bridged mixed-valent binuclear complexes can exhibit rather strong electronic coupling between the metals.

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7 1: mp 250 °C (decomposition); Anal. Calcd. for $C_{22}H_{28}O_4Ru_2{\cdot}H_2O$ C, 37.50; H, 4.29%. Found: C, 37.43; H, 4.25%. UV–vis (CH_2Cl_2 λ_{max}/ nm (ε/M^{-1} cm^{-1})): 282(23700), 343(15500), 506(3830).

8 Complex **3** was prepared by a modified literature method: using 20% excess CF_3SO_3H instead of $HClO_4$ to [Ru(acac)$_3$]; Y. Kasahara, Y. Hoshino, K. Shimizu, and G. P. Satô, *Chem. Lett.*, **1990**, 381; K. Oomura, D. Ooyama, Y. Satoh, N. Nagao, H. Nagao, F. S. Howell, and M. Mukaida, *Inorg. Chim. Acta*, **269**, 342 (1998).

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10 The K_c value was calculated by the following equation: $K_c = \exp(\Delta E^{\circ}F/RT)$.

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13 The UV–vis–NIR and IR spectra were measured by stepwise controlled-potential electrolyses with an OTTLE cell holding the CaF_2 windows, the Pt minigrid working and counter electrodes, and the Ag wire pseudoreference electrode: M. Krejčik, M. Daněk, and F. Hartl, *J. Electroanal. Chem.*, **317**, 179 (1991). The 1st and 2nd reduction steps are completely reversible. The spectra returned quantitatively to the original shapes when the potentials were reversed.

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