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Synthesis and Characterization of (μ-Alkoxo)bis(μ-carboxylato)diruthenium Complexes, Na[$\mathrm{Ru_2}$(dhpta)(μ-$\mathrm{O_2CR)_2}$] (dhpta$\mathrm{H_5}$ = 1,3-diamino-2-hydroxypropane tetraacetic acid). A Ruthenium Analogue of Model Systems for Iron-oxo Proteins

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The first ruthenium analogue of hemerythrin models with μ-alkoxo bridging, Na[Ru(dhpta)(μ-$\mathrm{O_2CR)_2}$] (**1**: R = $\mathrm{CH_3}$, **2**: R = $\mathrm{C_6H_5}$, **3**: R = $\mathrm{C_6H_4}$-*p*-OH, **4**: R = $\mathrm{C_6H_4}$-*p*-$\mathrm{NH_2}$) have been prepared and characterized, and the crystal structure of **1** has been determined; these compounds undergo two one-electron reductions to the $\mathrm{Ru^{II}Ru^{III}}$ and $\mathrm{Ru^{II}Ru^{II}}$ states with large separations (~0.6 V) between the successive redox potentials, allowing the formation of stable mixed-valence species.

There is increasing interest in non-heme diiron proteins, including hemerythrin,1) ribonucleotide reductase,2) methane monooxygenase,3) and several purple acid phosphatases.4) In this regard, the low molecular weight models of μ-oxo, μ-hydroxo, and μ-alkoxo diiron complexes have been the subject of considerable investigation,5) since the independent contributions by Lippard6) and Wieghardt.7) In contrast with a wide variety of diiron model complexes, the ruthenium analogue involving (μ-oxo)bis(μ-carboxylato)diruthenium and (μ-hydroxo)bis(μ-carboxylato)diruthenium cores have been limited to $\mathrm{[Ru^{III}_2(Me_3tacn)_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2]^{2+}}$ (**5**), $\mathrm{[Ru^{III}_2(Me_3tacn)_2(\mu\text{-}OH)(\mu\text{-}O_2CR)_2]^{3+}}$ (**6**), $\mathrm{[Ru^{III}Ru^{IV}(Me_3tacn)_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2]^{3+}}$ (**7**) ($\mathrm{Me_3tacn}$ = 1,4,7-trimethyl-1,4,7-triazacyclononane),8) $\mathrm{[Ru^{III}_2(tmp)_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{2+}}$ (**8**) (tmp = tris(1-pyrazolyl)methane),9) $\mathrm{[Ru^{III}_2(py)_6(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{2+}}$ (**9**) (py = pyridine),10) $\mathrm{[\{(1\text{-}MeIm)_3Ru^{III}\}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2]^{2+}}$ (**10**) and the one-electron oxidation product of (**10**), $\mathrm{[\{(1\text{-}MeIm)_3Ru\}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2]^{3+}}$ (**11**) (1-MeIm = 1-methylimidazole).11)

Here, we wish to report the synthesis and characterization of (μ-alkoxo)bis(μ-carboxylato)diruthenium complex by using a binucleating ligand, 1,3-diamino-2-hydroxypropane tetraacetic acid (dhpta$\mathrm{H_5}$), which is the first example of structurally characterized ruthenium analogue of hemerythrin models with μ-alkoxo bridging.

$\mathrm{RuCl_2(DMSO)_4}$ (5.0 mmol),12) where DMSO is dimethyl sulfoxide, was treated with dhpta$\mathrm{H_5}$ (2.5 mmol) in water at 85 °C for 1 h. The solution was kept to pH 5 by 1.0 M sodium hydroxide. Then, a water solution or suspension of carboxylic acid (adjusted pH 5 by NaOH) was added to the reaction solution. The mixture was incubated at 85-90 °C for 5-36 h (monitored by electronic absorption spectra), and was chromatographed on a gel permeation column (Sephadex G-15) eluted with water. The reddish violet fraction was collected, and concentrated to ca. 20 mL, and addition of ethanol gave crystals formulated as $Na[Ru_2(dhpta)(O_2CR)_2]$ (**1**: R = CH_3, yield 40%; **2**: R = C_6H_5, yield 25%; **3**: R = C_6H_4-*p*-OH, yield 26%; **4**: R = C_6H_4-*p*-NH_2, yield 9%).[13] Complexes **1-4** could also be prepared by an one-pot reaction of $RuCl_2(DMSO)_4$ with dhptaH5 and RCO_2H in a slightly acidic solution. In the electronic absorption spectra, a weak absorption band, similar to that of (μ-hydroxo)bis(μ-carboxylato)diruthenium complex **6**, was observed around 490 nm (ε=1900-2400 $M^{-1}cm^{-1}$).

The X-ray structure of **1** is shown in Fig. 1.[14] The complex anion consists of two ruthenium atoms bridged by the alkoxide of dhpta and the two acetate ligands to give a confacial bioctahedral structure, which is similar to that found in $(Me_4N)[Fe_2L(O_2CCH_3)_2]$ (L = N,N'-(2-hydroxy-5-methyl-1,3-xylylene)bis(N-carboxymethylglycine)).[15] The Ru-Ru distance of 3.433(3) Å is out of the range for Ru-Ru single bond which was observed in μ-oxo diruthenium(III) complexes.[8,9,10,11] The two bridging acetates are almost planar with torsion angles of O(11)-Ru(1)-Ru(2)-O(12) = 8.3(7)° and O(21)-Ru(1)-Ru(2)-O(22) = 7.0(8)°.

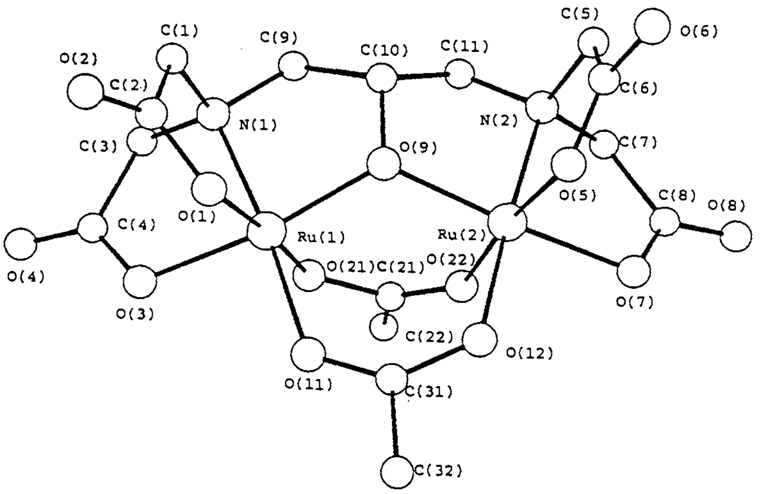

Fig. 1 A perspective drawing of the complex anion, $[Ru_2(dhpta)(\mu\text{-}O_2CCH_3)_2]^-$ **1**. Selected bond distance (Å) and angle (°): Ru(1)-Ru(2) 3.433(3)Å; Ru(1)-O(9)-Ru(2) 124.1(7)°.

The Ru-Ru distances of **1-4** determined by EXAFS analyses fall within the range of 3.42-3.44 Å , the binuclear core being hardly affected by the carboxylato ligands.[16] The EXAFS study for **1** in both solid and solution states indicated no structural change around the dinuclear core on dissolution in water.

The ^1H NMR spectra of **1-4** in D_2O showed isotropically shifted features in the range of -6-54 ppm, and that of **1** was in agreement with the crystal structure.

The electrochemistry of **1-4** was studied by cyclic voltammetry. In all cases, two one-electron reduction processes were observed at ca. -0.34 V ($E^1_{1/2}$) and ca. -0.94 V ($E^2_{1/2}$) vs Ag/AgCl in pH6.88 phosphate Buffer. The reduction potentials, $E^1_{1/2}$ and $E^2_{1/2}$, were independent of the carboxylate ligands. The former couple was reversible or *quasi*-reversible with i^1_{pa}/i^1_{pc} ~1 for scan rates (v) between 50 and 500 mVs^{-1} and the ratio $i^1_p/v^{1/2}$

was constant in accord with a diffusion-controlled process. The potential separations, $\Delta E^1 = |E^1_{pa} - E^1_{pc}|$, were in the range of 62-89 mV indicating an one-electron transfer per dimer. The latter wave was irreversible with $i^2_{pa} < i^2_{pc}$ preventing further detailed discussion, however, i^2_{pc} was nearly equal to i^1_{pc}, suggesting that the observed redox couples were corresponding to two stepwise one-electron reduction processes designated in eq 1.

$$[\mathrm{Ru^{III}_2(dhpta)L_2}]^- \overset{E^1_{1/2}}{\underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}} [\mathrm{Ru^{II}Ru^{III}(dhpta)L_2}]^{2-} \overset{E^2_{1/2}}{\overset{+e^-}{\longrightarrow}} [\mathrm{Ru^{II}_2(dhpta)L_2}]^{3-} \quad (1)$$

$$\mathrm{L = RCO_2^-}$$

The most remarkable feature is the large separation between the two redox potentials $E^1_{1/2}$ and $E^2_{1/2}$ ($|E^1_{1/2} - E^2_{1/2}| = 0.60$ V). The comproportionation constant K_c as defined eq 2 is calculated to 2×10^{10} which is larger than that of $[\mathrm{Ru_2(tacn)_2(\mu\text{-}OH)_2(O_2CCH_3)}]^{3+}$ (2×10^8) (**11**).[17] From these, the mixed-valence diruthenium species $[\mathrm{Ru^{II}Ru^{III}(dhpta)(\mu\text{-}O_2CR)_2}]^{2-}$ (**12**) is expected to be more stable than the corresponding dimer from **11**.

$$[\mathrm{Ru^{III}_2(dhpta)L_2}]^- + [\mathrm{Ru^{II}_2(dhpta)L_2}]^{3-} \overset{K_c}{\rightleftharpoons} 2\,[\mathrm{Ru^{II}Ru^{III}(dhpta)L_2}]^{2-} \quad (2)$$

$$\mathrm{L = RCO_2^-}$$

A potentiostatic electrolysis of **2** at -1.4 V vs Ag/AgPF$_6$ in DMF was carried out until the color of the solution fully changed from reddish violet to dark orange (Fig. 2). The broad characteristic absorption centered at ~1830 nm is probably corresponding to an intervalence charge-transfer transition of the mixed-valence species **12**, as compared with that (1800 nm) of $[\mathrm{Ru^{II}Ru^{III}(\mu\text{-}OMe)_2(bipy)_2}]^{3+}$ (bipy = 2,2'-bipyridine).[18]

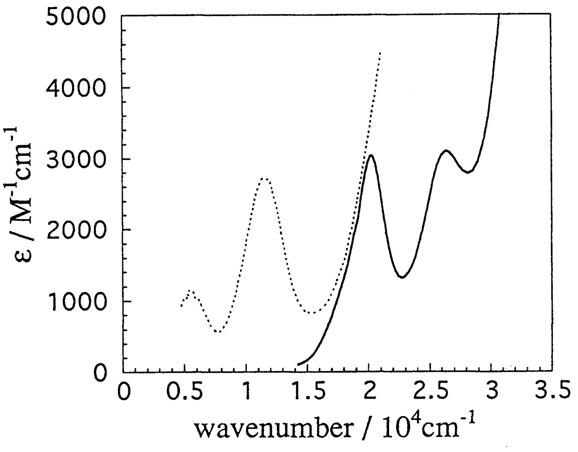

Fig. 2. Electronic absorption spectra of **2**; (a) — before and (b) ···· after potentiostatic electrolysis.

The present complexes **1**-**4** should provide a new route to mixed-valence diruthenium(II,III) the sites which might involve important magnetic, electronic, and catalytic properties in comparison with diiron centers in biology. We are now trying to trap the mixed-valence diruthenium(II, III) complexes, and detailed electrochemical and magnetic studies are also in progress.

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13) Analytical for **1**: Anal. Found: C, 27.03; H, 2.96; N, 4.19%. Calcd for $C_{15}H_{19}N_2O_{13}Ru_2Na$: C, 27.28; H, 2.90; N. 4.24%. For **2**: Anal. Found: C, 34.78; H, 3.51; N, 3.23%. Calcd for $C_{25}H_{23}N_2O_{13}Ru_2Na{\cdot}4H_2O$: C, 35.05; H, 3.65; N, 3.27%. For **3**: Anal. Found: C, 34.69; H, 3.87; N, 3.18%. Calcd for $C_{25}H_{23}N_2O_{15}Ru_2Na{\cdot}3H_2O$: C, 34.49; H, 3.35; N, 3.22%. For **4**: Anal. Found: C, 33.57; H, 4.37; N, 6.11%. Calcd for $C_{25}H_{25}N_4O_{13}Ru_2Na{\cdot}5H_2O$: C, 33.19; H, 3.90; N, 6.19%.

14) Compound **1** crystallized in the orthorhombic system, space group $Pca2_1$ with a = 21.359(4) Å, b = 7.484(2) Å, c = 12.930(2) Å, V = 2067 Å^3, and Z = 4. From 1116 independent reflections ($I > 3\sigma(I)$) collected with Mo Kα radiation (λ = 0.7107 Å) within the sphere of $2\theta < 50°$ on a Rigaku AFC5S diffractometer, the structure was solved by direct methods with MITHRIL (C. J. Gilmore, *J. Appl. Cryst.,* **17**, 42, (1984)) and refined by full-matrix least-squares with anisotropic temperature factors for the Ru and Na atoms and isotropic ones for the other non-hydrogen atoms to R = 0.065 and Rw = 0.044 ($w = 1/\sigma^2(Fo)$). All calculations were performed on a Digital Vax station 3100 M38 with TEXSAN-TEXRAY Structure Analysis Package (Molecular Structure Corporation). It should be noted that the crystal was obtained as twin and was cut into two pieces along the ***bc*** plane, one of which was used in the data collection.

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