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A DIRUTHENIUM(III)-μ-OXO COMPLEX WITH AMINO ACID BRIDGES AND ITS OXIDATIVE DEAMINATION IN THE PRESENCE OF OXYGEN

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Abstract—A stable diamagnetic complex of the type $[(Ru^{III}edta)_2\text{-}\mu\text{-}(amino\text{-}acidato)_2\text{-}\mu\text{-}oxo]^{6-}$ is reported. The amino acid bridge in the presence of oxygen undergoes oxidative deamination, as shown by the formation of an α-keto acid and the liberation of NH_3. The reaction is catalytic.

μ-Oxo-μ-diacetato diiron(II) cores in non-haeme proteins are known to be active centres.[1,2] Depending on the nature of the bridging groups these proteins act as oxygen carriers,[1,2] oxygen activating systems[3,4] and in the hydrolysis of phosphoric acid esters.[5,6] This led to extensive research in the chemistry of μ-oxo-μ-diacetato diiron(III) complexes with reference to their optical and magnetic properties and structures.[7] There has been a growing interest in developing the parallel chemistry of μ-oxo-ruthenium(III) complexes.[8,9] The iron and ruthenium complexes studied so far incorporate simple carboxylates as bridges[10] rather than amino acids, as in the natural systems.[1–6] In this paper we report diruthenium(III)-μ-oxo complexes with bridged amino acids, viz. alanine, phenylalanine and valine complexes, which have been characterized in solution as well as in the solid state. The complexes are stable under inert atmosphere and undergo oxidative deaminations under oxygen. The reactions were found to be catalytic.

EXPERIMENTAL

Materials

$RuCl_3$ was purchased from Johnson Matthey. All other chemicals used were of A.R. grade. All organic solvents were purified using known procedures.[11,12]

$K[Ru(edtaH)Cl]\cdot 2H_2O$ (**1**) was prepared by a known procedure.[13]

Syntheses of $Na_6[(edtaRu)_2\text{-}\mu_2\text{-amino acid-}\mu\text{-oxo}]$

Compound **1** *(0.2 mmol) and the appropriate* amino acid were dissolved in H_2O (10 cm^3) and the solution degassed with nitrogen. The pH was raised to 10.5 and the solution left overnight when it turned maroon. The solution was transferred to a flask containing degassed acetone (100 cm^3) and left under nitrogen for a week at 0°C. A dark purple solid separated, which was washed with ethanol, acetone and dried *in vacuo*. All operations were performed using the Schlenk technique. The yields ranged from 22 to 25%. Physicochemical data for the complexes are presented in Table 1.

Physical measurements

Absorption spectra were recorded on a Shimadzu UV–vis 160 spectrophotometer equippd with a TCC-240A temperature controller. Electrochemical studies were performed on PAR (model 174A) electrochemical equipment. The cyclic voltammogram (CV) at pH 10.5 was recorded using a mercury electrode as the working electrode and S.C.E. as the reference electrode. Raman spectra were recorded on a Spex Ramalog spectrometer

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Table 1. Physicochemical data for $Na_6[(EDTARu)_2$-μ^2-amino acid-μ-O] complexes

Amino acid	Elemental analysis[a] C	H	N	λ_{max} (ε)[b]
Phenylalanine (**2**)	35.8(36.2)	3.2(3.5)	6.4(6.7)	548(14,500)
α-Alanine (**3**)	27.9(28.1)	2.4(2.3)	7.2(7.6)	552(12,600)
Valine (**4**)	31.0(30.9)	3.7(3.8)	7.1(7.2)	554(10,800)

[a] Values in parentheses are calculated.
[b] In degassed H_2O.

using 514.5 nm line of an Ar ion laser (Spectra-physics) for excitation.

Kinetics

The complex was dissolved in degassed NaOH (0.001 M) and the pH was adjusted to 10.5 with HCl and oxygen was then bubbled through. The kinetics of the deamination of amino acid bridged complexes were followed spectrophotometrically by monitoring the disappearance of the characteristic peak λ_{max} of the bridged dimer complexes. The concentration of dissolved oxygen was varied by passing through an oxygen and nitrogen mixture of varying composition. The rate constant data are reproducible to within $\pm 4\%$.

Detection of NH_3 *and α-keto acids*

The complex was dissolved in degassed NaOH, the pH adjusted to 10.5 and then oxygen was slowly bubbled through. The outlet of the reaction vessel was connected to another vessel containing HCl (0.1 M). Bubbling was continued for 24 h, after which time the HCl was back-titrated with standard NaOH. Meanwhile, bubbling of oxygen was continued and NH_3 collected as described above. This procedure was continued for 72 h until there was no appreciable change in the titre value of NaOH. From the difference in titre values before and after back-titration the amount of NH_3 was determined. From another experiment the presence of NH_3 was confirmed using Nesslers reagent.

After completion of the reaction with oxygen (72 h) the solution was acidified and the complex precipitated with ethanol and filtered. The filtrate was reduced to 4 cm^3, again acidified and the volume reduced *in vacuo*. A white solid separated, which gave a positive test for the keto group with 2,4-dinitrophenylhydrazine, and the presence of the —COOH group was confirmed by the effervescence of CO_2 on addition of $NaHCO_3$.

RESULTS AND DISCUSSION

Characterization of complexes **2–4**

Complexes **2–4** are formulated as $Na_6[Ru_2(edta)_2$-μ-(amino acid)$_2$-μ-O] on the basis of elemental analysis, UV–vis and proton NMR spectra. The absorption spectra of the complexes exhibit a strong band around 550 nm, which is assigned to M ← O charge-transfer in the Ru^{III}—O—Ru^{III} group. The assignment is based on comparison of the absorption spectra of the μ-oxo-diacetato diruthenium(III) complexes reported so far.[8–11] A similar complex of ethylenediamine exhibits a band at 565 nm. The shift in the reported complexes may be due to stronger binding of edta. These complexes, as also reported, are essentially diamagnetic (Evan's method). For the sake of clarity the details for complex **2** will be given. Similar results were obtained with complexes **3** and **4**. λ_{max} and $E_{1/2}$ were of course different.

The proton NMR spectrum exhibits peaks at 2.328 (CH_2 of ethylenediamine), 2.775 (CH_2 of —CH_2COO in edta), 3.050 (CH of amino acid), 3.375 (CH_2 of amino acid) and 7.550 ppm (phenyl protons of amino acid).

The laser Raman spectrum exhibits bands due to symmetric and asymmetric stretching of Ru^{III}—O—Ru^{III} at 636 and 729 cm^{-1} (Fig. 4), respectively. These values are *ca* 80 cm^{-1} towards a higher frequency compared with Fe^{III} complexes[14] and may be due to more diffused 4*d* orbitals in ruthenium(III).

The DPP and CV of the complex exhibit peaks at −0.28 and −0.44 V, due to stepwise reduction of Ru^{3+} to Ru^{2+}.

Complex **2** was dissolved in degassed NaOH (0.001 M) solution and the pH was adjusted to 10.5 by adding HCl (0.1 M). The absorption spectrum of complex **2** at pH 10.5 exhibited a band at 539 nm [Fig. 1(b)], whose intensity was low compared with those of μ-oxo-μ-carboxylato complexes pre-

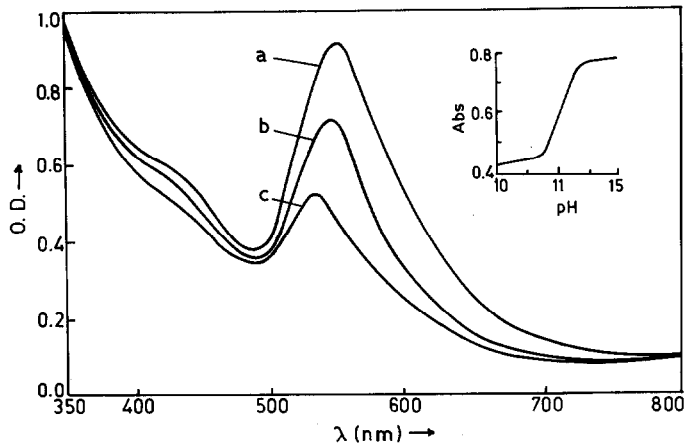


Fig. 1. Absorption spectra of complex **2**: (a) under nitrogen at pH 11.2, (b) under nitrogen at pH 10.5 and (c) after passing oxygen through (15 min) at pH 10.5. (Inset shows plot of absorbance at 548 nm as a function of pH under nitrogen.)

viously reported.[8-11] One of the reasons could be the dissociation of the complex to a monomeric species.

$$\mathrm{LMOML} \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} 2\mathrm{LMOH} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} 2\mathrm{ML(H_2O)}$$

If this is so then an increase in pH would favour the formation of the dimer and the spectrum at higher pH would have shown an increase in absorbance. However, the spectrum of **2** at pH 11 showed a shift in λ_{max} to 548 nm with ε_{max} comparable to those of reported complexes.[8-11] Such behaviour is reminiscent of the protonation/deprotonation of the μ-oxo group.[11]

$$\mathrm{LMOML} \overset{+H^+}{\rightleftharpoons} \mathrm{L\overset{H}{M}OML} \qquad (1)$$

Decreasing the pH of the solution from 11.0 to 10.5 resulted in the reappearance of the peak at 539 nm. When the pH of the complex solution was again adjusted to 11.0 (addition of NaOH) the peak at 548 nm reappeared. Thus, increases and decreases of pH back and forth reproduced the spectrum at the corresponding pH value, demonstrating the existence of an equilibrium [eq. (1)]. From the plot of absorbance vs pH (Fig. 1 inset) the dissociation constant (pK_a) for reaction (1) was found to be 10.9 ± 0.1 ($T = 35°C$, $\mu = 0.1$). Thus, the species at pH 10.5 under nitrogen is a μ-hydroxo rather than a μ-oxo species.

On passing oxygen through the above solution the peak shifts further to 533 nm [Fig. 1(c)]. This may be due to the coordination and concomitant reduction of oxygen by transfer of electrons from Ru^{3+}. DPP (Fig. 2) and CV of this solution exhibit a peak at +0.04 V, assigned to an Ru^{4+}/Ru^{3+} couple. Due to oxidation of Ru^{3+} to Ru^{4+} the acidity of μ-OH increases and, therefore, it becomes deprotonated to form a μ-oxo species. Thus, the

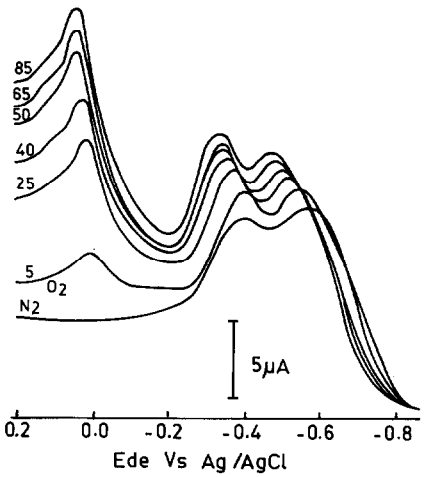


Fig. 2. DPP of **2** under nitrogen and under oxygen at different time intervals (indicated on DPP in minutes); $T = 35°C$, $\mu = 0.10$ M (KCl).

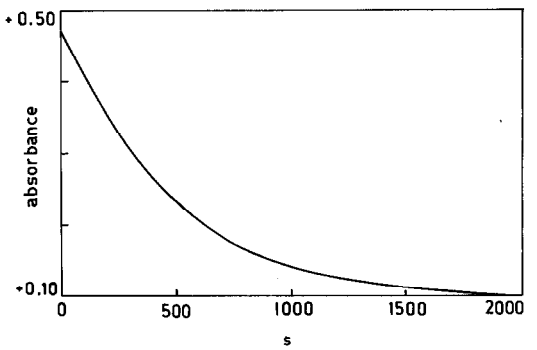


Fig. 3. Trace showing the decrease in intensity of the peak at 533 nm after passing oxygen through a solution of complex **2**; $T = 35°C$, $\mu = 0.10$ M (KCl).

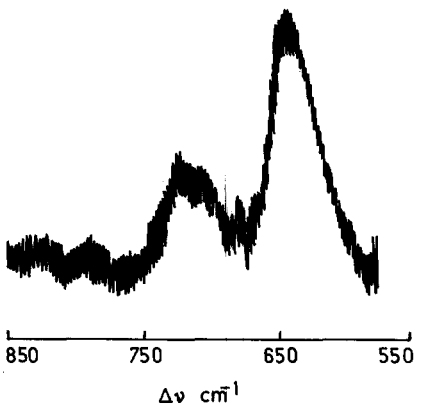


Fig. 4. Raman spectrum of complex **2**, excitation line: 514.5 nm, Ar ion 50 mW. Average of two scans.

species at pH 10.5 under oxygen is a μ-oxo peroxo diruthenium(IV) complex (**2a**).

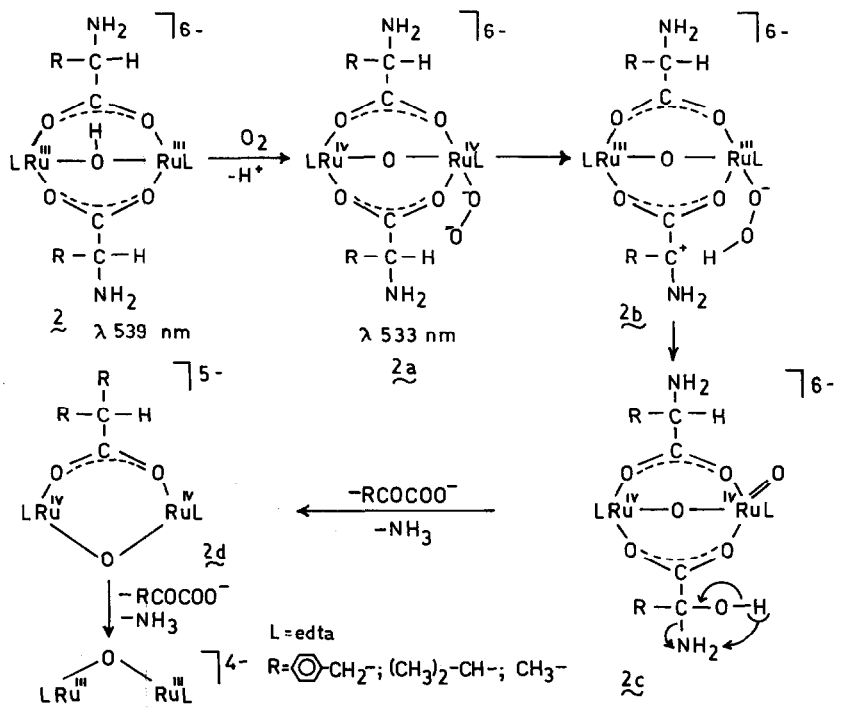
$$\overset{H}{LMOML} \xrightarrow{O_2} LMOML(O_2)+H^+ \qquad (2)$$

Complex **2a** could not be isolated due to its instability under oxygen.

Oxidation of amino acid

On passing oxygen through a solution of the complex the peak at 533 nm starts decreasing (Fig. 3) until the spectrum resembles that of **1** in the absence of the amino acid. The reaction mixture gives a positive test for the α-keto acid and NH_3 as produced. The amount of NH_3 varied between 70–75% of the theoretical value. To account for these observations a possible mechanism is given below in Scheme 1.

In Scheme 1 hydride is abstracted from the α-carbon atom of the coordinated amino acid, which ultimately transfers its $2e^-$ to two ruthenium(IV) centres resulting in an Ru^{III}–Ru^{III} hydroperoxo species (**2d**). The cleavage of the C—H bond is facilitated by the presence of the R groups on C(2) atoms. An OH^- is then transferred to the α-carbonium ion thus produced to give **2c**.[15] The prototropic changes result in the formation of the keto acid and elimination of NH_3 to give complex **2d**. Species **2d** once again undergoes the same sequence of reactions and a second molecule of coordinated amino acid is oxidized (reaction requires **2c** and **2d** in Scheme 1). If at this stage the solution is degassed with argon and fresh amino acid added then the 539 nm peak again builds up. On passing oxygen through once again it disappears, repeating the cycle. Several such cycles could be run, indicating the catalytic nature of the reaction. If hydride abstraction takes place as proposed above then k_{obs} should follow the order valine > α-alanine > phenylalanine, since the R group with better electron donating properties will facilitate the hydride abstraction. The k_{obs} calculated are 1.31×10^{-3}, 0.85×10^{-3} and 0.68×10^{-3}



Scheme 1.

s^{-1} for valine, alanine and phenylalanine, respectively, thus supporting the assumption.

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15. Due to the μ-oxo-μ-carboxylato core an electron can be transferred to the other metal ion via bridges. Thus, Ru^{III}–Ru^{V} species, which may have formed initially, results in Ru^{IV}–Ru^{IV} species ultimately.