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Facile Dehydrogenation of α-Amino Acids Chelated to a Bis(bipyridine)ruthenium(II) Complex: (α-Imino acidato)ruthenium(II) Complexes

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The oxidative deamination of α-amino acids is known to occur *in vivo* such as that of flavoenzyme D-amino acid oxidase and glutamate dehydrogenase. Although an α-imino acid (NH=C(R)CO_2H) is postulated as the intermediate of oxidative deamination of α-amino acids, it is difficult to isolate α-imino acids because of their instability in aqueous solution. We have already reported the novel dehydrogenation of α-amino acids chelated to cobalt(III) by potassium permanganate oxidation to give α-imino acidato Co(III) complexes in moderate to low yields, which are stable in neutral or acidic aqueous solutions.[1] Attempts to achieve the dehydrogenation of α-amino acidato Co(III) complexes by using various oxidizing reagents other than permanganate or by electrochemical oxidation, however, all failed.[2] We report herein that the dehydrogenation of (α-amino acidato)bis(bipyridine)ruthenium(II) complexes was achieved by anodic oxidation to give the α-imino acidato complexes $Ru^{II}(N(R^1){=}C(R^2)CO_2)(bpy)_2$ in good yields. This is the first report of the synthesis of the α-imino acidato Ru(II) complexes.

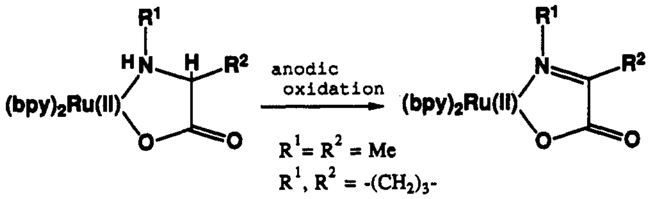
The dehydrogenation of amines or 1,2-diamines coordinated to M(II) ions (M = Fe, Ru, Os) has been the focus of a number of studies.[3] The Ru(II) complexes of 1,2-diamines are easily dehydrogenated by chemical and/or anodic oxidation to the 1,2-diimine complexes. It is presumed that the dehydrogenation involves initial one-electron oxidation of the metal center from Ru(II) to Ru(III), followed by deprotonation of the amino group and then a disproportionation to give a Ru(IV) intermediate which undergoes dehydrogenation to result in the imino group formation.[3b,c]

Table I. Anodic Peak Potentials[a]

complex	E_a, V		complex	E_a, V	
1	0.59	0.73[b]	2	0.56	0.77[c]

[a] Scan rate 50 mV/s, potentials vs. SCE (Pt electrode, in 1 N HCl). [b] $E_{1/2}$, = 0.70 V (E_c = 0.67 V). [c] $E_{1/2}$ = 0.74 V (E_c = 0.72 V).

Scheme I



Cyclic voltammetry (CV) of the (α-amino acidato)ruthenium(II) complexes shows the two anodic peaks and a cathodic peak listed in Table I. An irreversible anodic peak at 0.56–0.59 V is considered to be the one-electron oxidation step of the Ru(II) center of the α-amino acidato complexes to Ru(III). Then, anodic oxidation at constant potential of the α-amino acidato Ru(II) complexes $[Ru(aa)(bpy)_2]X$ (aa = *N*-methylalaninato (*N*-Me-ala) or prolinato (pro); X = Cl or ClO_4)[4,5] was carried out in 1 N HCl with a Pt gauze electrode at the above-mentioned potential under nitrogen. The oxidation products were isolated as the perchlorate salts and were identified as the α-imino acidato complexes $Ru^{II}(N(R^1){=}C(R^2)CO_2)(bpy)_2$: R^1 = Me, R^2 = Me, $[Ru(N\text{-}Me\text{-}ala\text{-}H_2)(bpy)_2]ClO_4{\cdot}2.5H_2O$ (**3**) in 78% yield; R^1 = R^2 = $-(CH_2)_3-$, $[Ru(pro\text{-}H_2)(bpy)_2]ClO_4{\cdot}2H_2O$ (**4**) in 68% yield (Scheme I).[6]

Fast atom bombardment (FAB) mass analysis demonstrates that the *m/z* value of the electrolyzed products is less than that of the α-amino acidato complexes by 2, which proves that

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(1) (a) Yamaguchi, M.; Saburi, M.; Yoshikawa, S. *J. Am. Chem. Soc.* **1984**, *106*, 8293. (b) Yamaguchi, M.; Yamagishi, T.; Hida, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1942.

(2) Recently the dehydrogenation of α-amino acidato Co(III) complexes by reaction with thionyl chloride was reported: (a) Hammershøi, A.; Hartshorn, R. M.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1226. (b) Hammershøi, A.; Hartshorn, R. M.; Sargeson, A. M. *Inorg. Chem.* **1990**, *29*, 4525.

(3) (a) Goto, M.; Takeshita, M.; Sakai, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2491. (b) Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161 and references therein. (c) Keene, F. R.; Ridd, M. J.; Snow, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 7075. (d) Bernhard, P.; Sargeson, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 597.

(4) The (α-amino acidato)bis(2,2′-bipyridine)ruthenium(II) complexes are prepared by a method similar to that described in ref 5. *Caution*! Although these perchlorate salts are moderately stable, they are potential hazards and should therefore be handled with care and in small quantities. Anal. Calcd for $[Ru(N\text{-}Me\text{-}ala)(bpy)_2]ClO_4{\cdot}2H_2O$ (**1**), $C_{24}H_{28}N_5ClO_8Ru$: C, 44.27; H, 4.34; N, 10.76. Found: C, 44.23; H, 4.36; N, 10.68. FAB-MS (*m*-nitrobenzyl alcohol), *m/z*: 516 (M − ClO_4)$^+$. Anal. Calcd for $[Ru(pro)(bpy)_2]ClO_4{\cdot}2H_2O$ (**2**), $C_{25}H_{28}N_5ClO_8Ru$: C, 45.28; H, 4.26; N, 10.56. Found: C, 45.12; H, 4.15; N, 10.37. FAB-MS (*m*-nitrobenzyl alcohol), *m/z*: 528 (M − ClO_4)$^+$.

(5) Vagg, R.; Williams, P. A. *Inorg. Chim. Acta* **1982**, *58*, 101.

0020-1669/93/1332-2981$04.00/0

dehydrogenation took place.[4,6] CV of the α-amino acidato complexes shows that the oxidation is irreversible at any scan rate (from 20 to 500 mV/s); however, a quasi-reversible couple is observed at a potential more anodic than that of the α-amino acidato complexes. On the other hand, the α-imino acidato complexes show a redox potential more anodic ($E_{1/2}$ = 0.70 V (**3**), 0.79 V (**4**)) compared to the anodic potential of the α-amino acidato complexes. Since the redox potential of the above-mentioned quasi-reversible couple is almost identical to that of the α-imino acidato Ru(II) complexes, this quasi-reversible couple is due to the α-imino acidato complex dehydrogenated *in situ* on the surface of the electrode. The absorption maximum of the electronic spectra of the α-imino acidato complexes in the visible region shows a blue shift from 484 nm (α-amino acidato complexes) to 431 nm (α-imino acidato complexes), which reflects the back-bonding character of the α-imino acidato ligand. The ^{1}H and ^{13}C NMR spectral data are also consistent with the structures proposed. Furthermore, the structure of **4** was verified by an X-ray analysis as shown in Figure 1.[7] The five-membered chelate ring of the α-imino acidato ligand is almost planar,[8] and the bond angle N1–Ru–O1 is 78.3(4)°, which is similar to those of the bipyridine ligands.[1b] The bond distance of Ru–N(imino), 2.04(1) Å, is shorter than that of Ru–N(amino) of the (α-amino acidato)bis(bipyridine)ruthenium(II) complexes.[9]

Facile dehydrogenation of (α-amino acidato)bis(bipyridine)-ruthenium(II) complexes was achieved by electrochemical oxidation to give the α-imino acidato complexes in good yields.[13] α-Imino acidate moieties chelated to metal ions react with nucleophiles at the α-carbon and with electrophiles at the β-carbon, providing new synthetic pathways to α-amino acidato complexes and α-imino acidato complexes.[1,14] It is noteworthy that we could not obtain α-amino acidato Ru(III) complexes by oxidation of the Ru(II) complexes but obtained instead α-imino acidato Ru(II) complexes, which is in contrast with the case of α-amino acidato tetraammine Ru(III) complexes.[15] This is probably due to the difference in reactivity between bis(bipyridine)ruthenium(III) complexes and tetraammineruthenium(III) complexes. Mechanistic studies and further investigations of α-imino acidato complexes are now in progress in our laboratory.

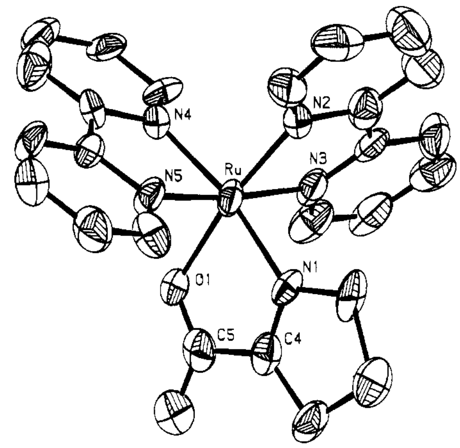

Figure 1. ORTEP drawing of [Ru(pro-H_2)(bpy)$_2$]$ClO_4\cdot 3H_2O$ (**4**). Selected intramolecular distances (Å): Ru–N1, 2.04(1); Ru–N2, 2.02(1); Ru–N3, 2.06(1); Ru–N4, 2.07(1); Ru–N5, 2.06(1); Ru–O1, 2.11(1); N1–C4, 1.32(2). Selected bond angles (deg): N1–Ru–O1, 78.3(4); N2–Ru–N3, 79.8(5); N4–Ru–N5, 79.4(5); Ru–N1–C4, 116(1); N1–C4–C5, 113(2); C4–C5–O1, 118(1); C5–O1–Ru, 113.8(9).

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Supplementary Material Available: Tables of crystal data, atom coordinates, thermal parameters, bond lengths and angles, and least-squares planes and a figure showing the atom-numbering scheme for **4** (7 pages). Ordering information is given on any current masthead page.

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(6) Anal. Calcd for [Ru(N-Me-ala-H_2)(bpy)$_2$]$ClO_4\cdot 2.5H_2O$ (**3**), $C_{24}H_{27}N_5ClO_{8.5}Ru$: C, 43.81; H, 4.14; N, 10.64. Found: C, 43.76; H, 4.30; N, 10.61. ^{1}H NMR (D_2O, 270 MHz), δ: 2.33 (s, 3 H, C–CH_3), 3.11 (s, 3 H, N–CH_3), 7.05–8.6 (m, 16 H, aromatics). ^{13}C NMR (CD_3OD, 22.5 MHz, except for bpy moieties), δ: 17.0 (q, C–CH$_3$), 42.5 (q, N–CH$_3$), 171.6 (s, C=O), 173.0 (s, C=N). FAB-MS (m-nitrobenzyl alcohol), m/z: 514 (M – ClO_4)$^+$. Anal. Calcd for [Ru(pro-H_2)(bpy)$_2$]$ClO_4\cdot 2H_2O$ (**4**), $C_{25}H_{26}N_5ClO_8Ru$: C, 45.43; H, 3.96; N, 10.59. Found: C, 45.51; H, 3.91; N, 10.57. ^{1}H NMR (CD_3OD, 270 MHz), δ: 2.0 (m, 1 H), 2.3 (m, 1 H), 2.9 (m, 1 H), 3.1 (m, 2 H), 3.9 (m, 1 H). ^{13}C NMR (CD_3OD, 67.5 MHz, except for bpy moieties), δ: 23.8 (t, C–CH$_2$–C), 36.1 (t, CH$_2$–C=), 62.3 (t, CH$_2$–N), 173.5 (s, C=O), 179.7 (s, C=N). FAB-MS (m-nitrobenzyl alcohol), m/z: 526 (M – ClO_4)$^+$.

(7) X-ray analysis of **4**: monoclinic, $C2/c$, with a = 21.82(1) Å, b = 19.35(1) Å, c = 14.595(5) Å, β = 115.16(5)°, V = 5577(3) Å^3, D_{calcd} = 1.618 g cm^{-3}, D_{obsd} = 1.60 g cm^{-3}, Z = 8, μ(Mo Kα) = 6.22 cm^{-1}. The structure was solved by heavy-atom methods; R = 0.051 and R_w = 0.075 ($w = 1/(\sigma(F_o)^2 + (0.045F_o)^2)^{1/2}$ for 1544 reflections. No absorption correction was applied.

(8) Distances (Å) from the least-squares plane through the five atoms of the α-imino acidato chelate ring: Ru, –0.003; N1, 0.014; C4, –0.020; C5, 0.017; O1, –0.007.

(9) Ru–N(amino) bond distances determined by X-ray analysis of the (α-amino acidato)bis(bipyridine)ruthenium(II) complexes: [Ru((S)-ala)(bpy)$_2$]$ClO_4\cdot 0.5H_2O$,[10] 2.071(11), 2.130(11) Å; [Ru((S)-thr)(bpy)$_2$]$ClO_4\cdot 5H_2O$,[11] 2.118(9), 2.142(10) Å; [Ru((S)-allothr)(bpy)$_2$]$ClO_4\cdot 5H_2O$,[11] 2.121(7), 2.130(7) Å; [Ru(gly)(bpy)$_2$]$ClO_4\cdot 2H_2O$,[12] 2.135(4) Å.

(10) Stephens, F. S.; Vagg, R. S.; Williams, P. A. *Inorg. Chim. Acta* **1983**, *72*, 253.

(11) Goodwin, T. J.; Williams, P. A.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1984**, *88*, 165.

(12) Anderson, M. A.; Richards, P. G.; Stark, A. G.; Stephens, F. S.; Vagg, R. S.; Williams, P. A. *Inorg. Chem.* **1986**, *25*, 4847.

(13) Chemical oxidation of (α-amino acidato)bis(bipyridine)ruthenium(II) complexes using Ce(IV) ion readily affords α-imino acidato complexes: Mori, T.; Yamamoto, T.; Yamaguchi, M.; Yamagishi, T. Unpublished results.

(14) Harrowfield, J. MacB.; Sargeson, A. M.; Whimp, P. O. *Inorg. Chem.* **1991**, *30*, 1792 and references therein.

(15) The preparation and X-ray analysis of the (glycinato)tetraammineruthenium(III) complex has been reported.[16]

(16) (a) Ilan, Y.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1655. (b) Ilan, Y.; Kapon, M. *Inorg. Chem.* **1986**, *25*, 2350.