Facile Dehydrogenation of α-Amino Acids Chelated to a Ruthenium(II) Ion: (α-Imino acidato)ruthenium(II) Complexes†

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(α-Imino acidato)ruthenium(II) complexes, $[Ru^{II}\{N(R^1)=C(R^2)CO_2\}L_2]^+$ ($R^1 = R^2 =$ Me or $R^1 = R^2 = -(CH_2)_3-$; L = 2,2′-bipyridine (=bpy) or 1,10-phenanthroline (=phen)), were obtained by anodic oxidation at a constant potential of the corresponding (α-amino acidato)ruthenium(II) complexes, *N*-methylalaninato or prolinato complexes, in good to excellent yields. (α-Imino acidato)ruthenium(II) complexes are stable in neutral or acidic aqueous solution. The half-wave potentials of α-imino acidato complexes are 0.73−0.78 V (vs SCE), which are more positive than those of the corresponding α-amino acidato complexes, 0.55−0.59 V. The crystal structure of $[Ru(pro\text{-}H_2)(bpy)_2]ClO_4\cdot 3H_2O$ (pro-H_2 = 1,2-didehydroprolinato) has been determined by single-crystal X-ray analysis. Crystallographic data: space group *C*2/*c*, $a = 21.73(1)$ Å, $b = 19.33(1)$ Å, $c = 14.58(1)$ Å, $\beta = 114.91(5)°$, $Z = 8$, $R = 0.0352$. The length of the C=N double bond of the α-imino acidate moiety is 1.294(5) Å, and Ru−N(imino nitrogen) = 2.042(3) Å. The chelate ring of the α-imino acidato ligand is planar.

Introduction

In biological systems, α-amino acids are oxidatively deaminated to α-keto acids by enzymes such as glutamate dehydrogenase.[1] Extensive studies have been made to mimic the oxidative deamination of α-amino acids to α-keto acids *in vitro*, and it has been found that α-amino acids are oxidatively deaminated in the presence of pyridoxal derivatives and metal ions.[2] On the other hand, most of attempts in the absence of pyridoxal derivatives have failed to give α-keto acids,[3] although oxidative deamination to α-keto acids has been achieved by using the Ce(IV) ion[4] or Fremy's salt.[5] Since the first step of oxidative deamination of α-amino acids is dehydrogenation of the amino group, α-imino acids are postulated as the intermediate; however, it is difficult to isolate α-imino acids because of their instability in an aqueous solution.

A 1,2-diamine or polyamine chelated to a metal ion can be dehydrogenated to the corresponding imine complexes.[6] The dehydrogenation of 1,2-diamine complexes of M(II) ions (M = Fe,[7] Ru,[8] Os[9]) by chemical and/or anodic oxidation to 1,2-diimine complexes has been the focus of a number of studies. As for the dehydrogenation of the ruthenium(II) complexes of 1,2-diamine, Keene and co-workers have proposed that the reaction starts by one-electron oxidation of the metal center, Ru(II) to Ru(III), and involves a Ru(IV) intermediate from which is further abstracted a proton, resulting in an imino group with the Ru(II) ion.[8d] The syntheses of (α-imino acidato)cobalt(III) complexes have been reported.[10−14] Chelation to a metal ion stabilizes the imino acidate moiety against hydrolysis even in neutral or acidic aqueous solutions. (α-Imino acidato)cobalt(III) complexes have been prepared by several methods as follows: (a) intramolecular condensation of α-keto acidate and ammine ligands on the complex;[10] (b) dehydrogenation of the α-amino acidato complex by using potassium permanganate[11] or thionyl chloride;[12] (c) *β*-elimination of a *β*-substituted α-amino acidato complex with an appropriate *β*-substituent as

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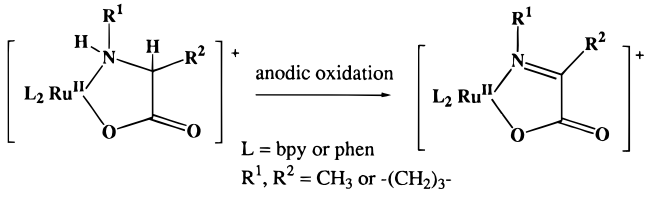
Scheme 1



a leaving group;[13] (d) oxidative decarboxylation−dehydrogenation of α-alkyl-α-aminomalonato complexes.[14] Attempted anodic oxidation of amino acidato Co(III) complexes has failed to afford imino acidato complexes.[11b] Numerous studies have been done to utilize (α-imino acidato)cobalt(III) complexes, since they react with various reagents such as a nucleophile or an electrophile.[10,13,15] Dehydrogenation of α-amino acidato complexes is a promising way to prepare the corresponding α-imino acidato complexes.

We report herein the dehydrogenation of (α-amino acidato)bis(diimine)ruthenium(II) complexes (diimine = bpy, phen) by anodic oxidation at a constant potential to yield the corresponding (α-imino acidato)ruthenium(II) complexes, $[Ru^{II}\{N(R^1)=C(R^2)CO_2\}L_2]^+$ ($R^1 = R^2 = Me$, $-(CH_2)_3-$; L = bpy, phen).

Experimental Section

All chemicals were of reagent grade and were used as received. *cis*-Dichlorobis(2,2′-bipyridine)ruthenium(II) was prepared by using literature procedures.[16] *cis*-Dichlorobis(1,10-phenanthroline)ruthenium(II) was prepared by a method similar to that for the bis(2,2′-bipyridine) complexes.

General Procedure for the Preparation of (α-Amino acidato)ruthenium(II) Complexes. The (α-amino acidato)bis(2,2′-bipyridine or 1,10-phenanthroline)ruthenium(II) complexes were prepared by a method similar to that described in ref 17 except that (α-amino acidato)bis(1,10-phenanthroline)ruthenium(II) complexes were prepared in ethanol−water (1:1) instead of water and crystallized from ethanol and ethyl acetate. *Caution!* Although these perchlorate salts are moderately stable, they are potential hazards and should therefore be handled with care and in small quantities.

(a) [Ru(*N*-Me-ala)(bpy)$_2$]ClO$_4$·2H$_2$O (1). Yield: 96%. ^{1}H NMR (D$_2$O, 270 MHz),[18] δ: 1.39 (d, C−C*H*$_3$(II), J = 7 Hz), 1.48 (d, C−C*H*$_3$-(I), J = 7 Hz), 1.69 (d, N−C*H*$_3$(I), J = 5 Hz), 2.40 (d, N−C*H*$_3$(II), J = 6 Hz), 3.30 (m, C*H*(I)), 3.80 (m, C*H*(II)), 4.12 (m, N*H*(II)), 4.53 (m, N*H*(I)), 7.0−9.4 (m, 16 H, aromatics). Selected ^{13}C NMR data (D$_2$O, 22.5 MHz), δ: 16.4 (C−*C*H$_3$), 16.7 (C−*C*H$_3$), 37.9 (N−*C*H$_3$), 38.6 (N−*C*H$_3$), 62.7 (*C*H), 185.9 (*C*=O). Anal. Calcd for C$_{24}$-H$_{28}$N$_5$ClO$_8$Ru: C, 44.27; H, 4.34; N, 10.76. Found: C, 44.23; H, 4.36; N, 10.68. UV/visible absorption peaks (H$_2$O) [λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1})]: 487 (6.75 × 10^3), 342 (6.10 × 10^3), 290 (4.30 × 10^4), 250 (sh) (1.33 × 10^4), 241 (1.64 × 10^4), 193 (3.16 × 10^4). FAB-MS, *m*/*z*: 516 (M − ClO$_4$)$^+$.

(b) [Ru((*S*)-pro)(bpy)$_2$]ClO$_4$·2H$_2$O (2). Yield: 90%. ^{1}H NMR (D$_2$O, 270 MHz), δ: 1.6−3.3 (m, 5 H), 3.71 (d (br), 1 H), 3.92 (m, 1 H), 7.0−9.2 (m, 16 H, aromatics). Selected ^{13}C NMR data (D$_2$O, 22.5 MHz), δ: 27.2, 30.8, 31.2, 50.6, 52.4, 64.3, 65.0, 187.5 (*C*=O). Anal. Calcd for C$_{25}$H$_{28}$N$_5$ClO$_8$Ru: C, 45.29; H, 4.26; N, 10.56. Found: C, 44.12; H, 4.15; N, 10.37. UV/visible absorption peaks (H$_2$O) [λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1})]: 467 (9.90 × 10^3), 335 (7.71 × 10^3), 288 (5.16 × 10^4), 252 (sh) (1.43 × 10^4), 241 (1.90 × 10^4), 196 (3.34 × 10^4). FAB-MS, *m*/*z*: 528 (M − ClO$_4$)$^+$.

(c) [Ru(*N*-Me-ala)(phen)$_2$]Cl·4H$_2$O (3). Yield: 77%. ^{1}H NMR (D$_2$O, 270 MHz),[18] δ: 1.47 (d, C−C*H*$_3$(II), J = 6.9 Hz), 1.57 (d, C−C*H*$_3$(I), J = 7.3 Hz), 1.57 (d, N−C*H*$_3$(I), J = 4.3 Hz), 2.47 (d, N−C*H*$_3$(II), J = 5.9 Hz), 3.48 (dq, C*H*(I), J = 7.3, 16 Hz), 4.02 (dq, C*H*(II), J = 6.9, 17 Hz), 4.43 (dq, N*H*(II), J = 5.9, 17 Hz), 4.9 (N*H*(I)), 7.3−9.8 (m, 16 H, aromatics). Selected ^{13}C NMR data (D$_2$O, 22.5 MHz), δ: 16.9 (C−*C*H$_3$), 17.7 (C−*C*H$_3$), 38.3 (N−*C*H$_3$), 38.9 (N−*C*H$_3$), 62.9 (*C*H), 63.0 (*C*H), 186.0 (*C*=O), 186.3 (*C*=O). Anal. Calcd for C$_{28}$H$_{32}$N$_5$ClO$_6$Ru: C, 50.11; H, 4.81; N, 10.44. Found: C, 50.32; H, 4.96; N, 10.74. UV/visible absorption peaks (H$_2$O) [λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1})]: 480 (1.04 × 10^4), 412 (3.23 × 10^3), 263 (8.02 × 10^4), 222 (5.46 × 10^4). FAB-MS, *m*/*z*: 564 (M − Cl)$^+$.

(d) [Ru((*S*)-pro)(phen)$_2$]Cl·3.5H$_2$O (4). Yield: 73%. ^{1}H NMR (D$_2$O, 270 MHz), δ: 1.53 (m), 1.8−2.6 (m), 2.87 (m), 3.49 (m), 4.04 (q, N−C*H*), 4.47 (q, N−C*H*), 5.26 (q, N*H*), 6.28 (q, N*H*), 7.2−9.7 (m, 16 H, aromatics). Selected ^{13}C NMR data (D$_2$O, 67.5 MHz), δ: 22.5, 24.5, 29.6, 47.0, 50.8, 61.6, 61.8, 187.9 (*C*=O). Anal. Calcd for C$_{29}$-H$_{31}$N$_5$ClO$_{5.5}$Ru: C, 51.67; H, 4.63; N, 10.39. Found: C, 51.52; H, 4.85; N, 10.02. UV/visible absorption peaks (H$_2$O) [λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1})]: 463 (1.11 × 10^4), 432 (sh) (1.06 × 10^4), 313 (sh) (5.26 × 10^3), 263 (6.42 × 10^4), 222 (5.14 × 10^4), 202 (4.40 × 10^4). FAB-MS, *m*/*z*: 576 (M − Cl)$^+$.

General Procedure for the Preparation of (α-Imino acidato)ruthenium(II) Complexes. The α-amino acidato complex (100 mg) was dissolved in 1 N HCl (30 mL). Anodic oxidation at constant potential of the α-amino acidato complex was carried out under nitrogen with a Pt gauze working electrode at the potential for oxidation of the Ru(II) center to Ru(III) (see below) in a three-compartment electrochemical cell in which the working electrode and counter electrode were separated by a salt bridge. Electrolysis was continued until the current had fallen below 1% of the initial current. After the solution was neutralized with a saturated aqueous solution of NaHCO$_3$, the product was precipitated by the addition of saturated LiClO$_4$.

(a) [Ru(*N*-Me-ala-H$_2$)(bpy)$_2$]ClO$_4$·2.5H$_2$O (5). Yield: 78%. ^{1}H NMR (D$_2$O, 270 MHz), δ: 2.33 (s, 3 H, C−C*H*$_3$), 3.11 (s, 3 H, N−C*H*$_3$), 7.05−8.6 (m, 16 H, aromatics). Selected ^{13}C NMR data ((CD$_3$)$_2$SO, 22.5 MHz), δ: 17.0 (C−*C*H$_3$), 42.5 (N−*C*H$_3$), 171.6 (*C*=O), 173.0 (*C*=N). Anal. Calcd for C$_{24}$H$_{27}$N$_5$ClO$_{8.5}$Ru: C, 43.81; H, 4.14; N, 10.64. Found: C, 43.76; H, 4.30; N, 10.61. UV/visible absorption peaks (H$_2$O) [λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1})]: 469 (1.18 × 10^4), 442 (sh) (1.02 × 10^4), 395 (6.77 × 10^3), 340 (7.95 × 10^3), 288 (6.00 × 10^4), 252 (sh) (1.57 × 10^4), 241 (2.06 × 10^4), 195 (4.08 × 10^4). FAB-MS, *m*/*z*: 514 (M − ClO$_4$)$^+$.

(b) [Ru(pro-H$_2$)(bpy)$_2$]ClO$_4$·2H$_2$O (6). Yield: 68%. ^{1}H NMR (CD$_3$OD, 270 MHz), δ: 2.05 (m, 1 H), 2.33 (m, 1 H), 2.91 (m, 1 H), 3.12 (m, 2 H), 3.90 (m, 1 H), 7.1−8.8 (m, 16 H, aromatics). Selected ^{13}C NMR data (CD$_3$OD, 100 MHz), δ: 23.8 (*C*H$_2$), 36.1 (*C*H$_2$), 62.3 (*C*H$_2$), 173.5 (*C*=O), 179.7 (*C*=N). Anal. Calcd for C$_{25}$H$_{26}$N$_5$ClO$_8$-Ru: C, 45.43; H, 3.96; N, 10.59. Found: C, 45.51; H, 3.91; N, 10.57. UV/visible absorption peaks (H$_2$O) [λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1})]: 465 (1.06 × 10^4), 440 (sh) (9.43 × 10^3), 388 (6.08 × 10^4), 336 (7.24 × 10^3), 287 (5.33 × 10^4), 251 (sh) (1.43 × 10^4), 240 (1.82 × 10^4), 195 (3.63 × 10^4). FAB-MS, *m*/*z*: 526 (M − ClO$_4$)$^+$.

(c) [Ru(*N*-Me-ala-H$_2$)(phen)$_2$]ClO$_4$ (7). Yield: 81%. ^{1}H NMR (D$_2$O, 270 MHz), δ: 2.39 (s, 3 H, C−C*H*$_3$), 3.08 (s, 3 H, N−C*H*$_3$), 7.3−9.1 (m, 16 H, aromatics). Selected ^{13}C NMR data ((CD$_3$)$_2$SO, 22.5 MHz), δ: 17.0 (C−*C*H$_3$), 42.9 (N−*C*H$_3$), 171.8 (*C*=O), 173.1 (*C*=N). Anal. Calcd for C$_{28}$H$_{22}$N$_5$ClO$_6$Ru: C, 50.88; H, 3.35; N, 10.59. Found: C, 50.58; H, 3.54; N, 10.76. UV/visible absorption peaks (H$_2$O) [λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1})]: 460 (sh) (1.34 × 10^4), 435 (1.37 × 10^4), 316 (sh) (3.81 × 10^3), 264 (7.58 × 10^4), 222 (5.44 × 10^4). FAB-MS, *m*/*z*: 562 (M − ClO$_4$)$^+$.

(d) [Ru(pro-H$_2$)(phen)$_2$]ClO$_4$·0.5H$_2$O (8). Yield: 60%. ^{1}H NMR (D$_2$O, 270 MHz), δ: 1.95 (m, 1 H), 2.25 (m, 1 H), 2.92 (m, 2 H), 3.10 (m, 1 H), 3.95 (m, 1 H), 7.2−9.1 (m, 16 H, aromatics). Selected ^{13}C NMR data (D$_2$O, 67.5 MHz), δ: 24.5 (*C*H$_2$), 36.8 (*C*H$_2$), 63.7 (*C*H$_2$), 176.0 (*C*=O), 179.1 (*C*=N). Anal. Calcd for C$_{29}$H$_{23}$N$_5$ClO$_{6.5}$Ru: C, 51.07; H, 3.40; N, 10.27. Found: C, 50.91; H, 3.49; N, 10.28. UV/visible absorption peaks (H$_2$O) [λ_{max}, nm (ϵ, mol^{-1} dm^3 cm^{-1})]: 455 (sh) (1.43 × 10^4), 434 (1.47 × 10^4), 315 (sh) (4.25 × 10^3), 263 (8.36 × 10^4), 222 (6.22 × 10^4). FAB-MS, *m*/*z*: 574 (M − ClO$_4$)$^+$.

Measurements. Visible and ultraviolet absorption spectra were measured with a Hitachi 340 or Hitachi 220A spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL FX-90, JEOL

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(18) ^{1}H NMR spectra showed that **1** and **3** were a mixture of two isomers, I and II, shown in parentheses. See text.

Table 1. Crystallographic Data for $[Ru(pro\text{-}H_2)(bpy)_2]ClO_4\cdot 3H_2O$ (**6**)

empirical formula	$C_{25}H_{28}N_5O_9ClRu$
fw	679.05
crystal size	$0.30 \times 0.35 \times 0.10$ mm^3
unit-cell dimens	$a = 21.73(1)$ Å
	$b = 19.33(1)$ Å
	$c = 14.58(1)$ Å
	$\beta = 114.91(5)°$
vol of unit cell	$V = 5556(6)$ Å^3
crystal system	monoclinic
space group	$C2/c$ (No. 15)
Z value	$Z = 8$
densities	$D_{obs} = 1.60$ g/cm^3
	$D_{calc} = 1.62$ g/cm^3
$F(000)$	2768
linear abs coeff	$\mu = 6.22$ cm^{-1} (Mo Kα)
radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
max (sin θ)/λ	0.648
no. of tot. reflns measd	6725
no. of unique reflns	5992
internal consistency	$R_{int} = 0.02$
function minimized[a]	$\sum[w(\|F_o\|^2 - \|F_c\|^2)^2]$
no. of reflns used ($F_o > 3\sigma(F_o)$)	4548
no. of variables	458
residuals[b]	$R = 0.0352$
	$R_w = 0.0355$
goodness of fit	$S = 2.89$
max negative peak in final diff map	-0.51 e/Å^3
max positive peak in final diff map	0.57 e/Å^3

[a] $w = 1.0$. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

EX-270, and JEOL EX-400 spectrometers, chemical shifts being reported on the δ scale in ppm relative to tetramethylsilane (TMS) or sodium 4,4-dimethyl-4-silapentanoate-d_4 (TSP) for ^{1}H NMR and to 1,4-dioxane (67.4 ppm) for ^{13}C NMR. Fast atom bombardment mass spectra (FAB-MS) were obtained on a JEOL JMS-DX300 mass spectrometer by using *m*-nitrobenzyl alcohol as matrix. The calculation of the isotope distribution for the complexes were done by the program MASS written by M.Y.

All electrochemical measurements were made versus the saturated calomel electrode (SCE) at 22 ± 2 °C and are uncorrected for junction potentials. Potential control for electrochemical experiments was obtained with a Hokuto Denko Model HA-101 or HA-501 potentiostat/galvanostat. The waveform generator was a Hokuto Denko Model HB-104 function generator. Cyclic voltammetric experiments were conducted in a two-compartment electrochemical cell equipped with a platinum working electrode, a platinum counter electrode, and a saturated calomel reference electrode, which was separated by a salt bridge. All solutions were deoxygenated by bubbling nitrogen gas through them and were maintained under nitrogen during the experiments.

X-ray Structure Analysis of $[Ru(pro\text{-}H_2)(bpy)_2]ClO_4\cdot 3H_2O$. Deep red crystals of $[Ru(pro\text{-}H_2)(bpy)_2]ClO_4\cdot 3H_2O$ (**6**) were obtained by crystallization from an aqueous solution. The crystal used in the data collection was a deep red plate with the dimensions $0.30 \times 0.35 \times 0.10$ mm^3. The diffraction data were measured on a Mac Science MXC18 four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Within the range $2\theta < 55°$, 5992 independent reflections were obtained, and 4548 reflections with $|F_o| \geq 3\sigma(F_o)$ were used in the further calculations. The intensities were corrected for Lorentz and polarization effects, and no absorption correction was applied.

Crystallographic data are listed in Table 1. Atom scattering factors were taken from the standard source.[19] The structure was solved by direct methods using SIR92,[20] refined by a block-diagonal matrix least-squares method with anisotropic temperature factors for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms, and further refined by a full-matrix least-squares method for the final two cycles. The final discrepancy factors were $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0352$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0355$ with a unit weight, $w = 1.0$. Final positional and thermal parameters for non-hydrogen atoms are listed in Table 2, and selected bond distances and angles are listed in Table 3. All calculations were carried out on a Mac Science MXC18 SYSTEM, and ORTEP was employed for drawing the molecular structure.[21]

Table 2. Fractional Positional Parameters and Equivalent Isotropic Thermal Parameters for Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso), Å^2
Ru(1)	0.15290(1)	0.22521(2)	0.71227(2)	0.040
Cl(2)	0.12642(6)	0.52433(6)	0.72157(9)	0.070
N(3)	0.20386(15)	0.18274(16)	0.63611(20)	0.045
N(4)	0.12148(14)	0.27562(17)	0.80994(20)	0.046
N(5)	0.19421(15)	0.16295(17)	0.83809(20)	0.047
N(6)	0.10175(15)	0.28615(17)	0.58732(20)	0.048
N(7)	0.06723(15)	0.16800(18)	0.63886(22)	0.050
O(8)	0.24332(13)	0.28394(14)	0.76685(17)	0.050
O(9)	0.34160(15)	0.29503(18)	0.75422(23)	0.073
C(10)	0.1875(3)	0.1277(3)	0.5594(3)	0.065
C(11)	0.2456(3)	0.1289(3)	0.5261(4)	0.080
C(12)	0.2966(2)	0.1812(3)	0.5934(3)	0.061
C(13)	0.26219(19)	0.21004(20)	0.65405(26)	0.049
C(14)	0.28557(19)	0.26702(21)	0.73044(26)	0.050
C(15)	0.0886(2)	0.3368(2)	0.7917(3)	0.055
C(16)	0.0761(2)	0.3716(3)	0.8649(3)	0.064
C(17)	0.0979(2)	0.3428(3)	0.9598(3)	0.069
C(18)	0.1321(2)	0.2808(3)	0.9792(3)	0.063
C(19)	0.14413(18)	0.24767(21)	0.90438(25)	0.049
C(20)	0.18300(18)	0.18323(21)	0.91934(25)	0.048
C(21)	0.2082(2)	0.1444(3)	1.0077(3)	0.064
C(22)	0.2440(3)	0.0847(3)	1.0143(3)	0.069
C(23)	0.2553(2)	0.0644(3)	0.9325(3)	0.068
C(24)	0.2297(2)	0.1046(2)	0.8462(3)	0.058
C(25)	0.1208(2)	0.3493(2)	0.5707(3)	0.061
C(26)	0.0850(3)	0.3857(3)	0.4827(4)	0.075
C(27)	0.0280(3)	0.3561(3)	0.4089(4)	0.080
C(28)	0.0074(2)	0.2924(3)	0.4252(3)	0.070
C(29)	0.04441(19)	0.25753(23)	0.51556(26)	0.054
C(30)	0.02608(19)	0.19046(23)	0.54318(28)	0.055
C(31)	−0.0293(2)	0.1500(3)	0.4811(4)	0.073
C(32)	−0.0431(3)	0.0889(3)	0.5146(4)	0.084
C(33)	−0.0023(3)	0.0673(3)	0.6116(4)	0.082
C(34)	0.0519(2)	0.1080(3)	0.6706(4)	0.067
O(35)	0.1331(2)	0.5933(2)	0.6936(3)	0.098
O(36)	0.1191(3)	0.5266(3)	0.8127(4)	0.191
O(37)	0.1849(2)	0.4853(3)	0.7387(4)	0.144
O(38)	0.0696(3)	0.4906(3)	0.6508(4)	0.159
O(39)	0.3214(2)	0.4404(2)	0.7819(3)	0.123
O(40)	0.0907(5)	−0.0460(5)	0.8145(7)	0.313
O(41)	0.0656(3)	0.1706(6)	0.3177(5)	0.254

Table 3. Selected Intramolecular Bond Distances (Å) and Bond Angles (deg) with Their Estimated Standard Deviations in Parentheses

Ru(1)−N(3)	2.042(3)	N(3)−Ru(1)−O(8)	77.9(2)
Ru(1)−N(4)	2.065(3)	N(4)−Ru(1)−N(5)	78.9(2)
Ru(1)−N(5)	2.057(3)	N(6)−Ru(1)−N(7)	79.2(2)
Ru(1)−N(6)	2.058(3)	N(3)−Ru(1)−N(4)	167.8(2)
Ru(1)−N(7)	2.039(4)	N(5)−Ru(1)−N(6)	173.8(2)
Ru(1)−O(8)	2.113(3)	N(7)−Ru(1)−O(8)	171.0(2)
N(3)−C(10)	1.475(6)	Ru(1)−N(3)−C(13)	115.8(3)
N(3)−C(13)	1.294(5)	Ru(1)−O(8)−C(14)	114.9(3)
C(10)−C(11)	1.532(8)	N(3)−C(13)−C(14)	116.6(4)
C(11)−C(12)	1.515(8)	O(8)−C(14)−C(13)	114.7(4)
C(12)−C(13)	1.487(6)		
C(13)−C(14)	1.495(6)	N(3)−C(10)−C(11)	105.1(4)
O(8)−C(14)	1.282(5)	C(10)−C(11)−C(12)	106.4(5)
O(9)−C(14)	1.241(5)	C(11)−C(12)−C(13)	102.7(4)
		N(3)−C(13)−C(12)	115.0(4)
		C(10)−N(3)−C(13)	110.6(4)

(19) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(20) SIR92: Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

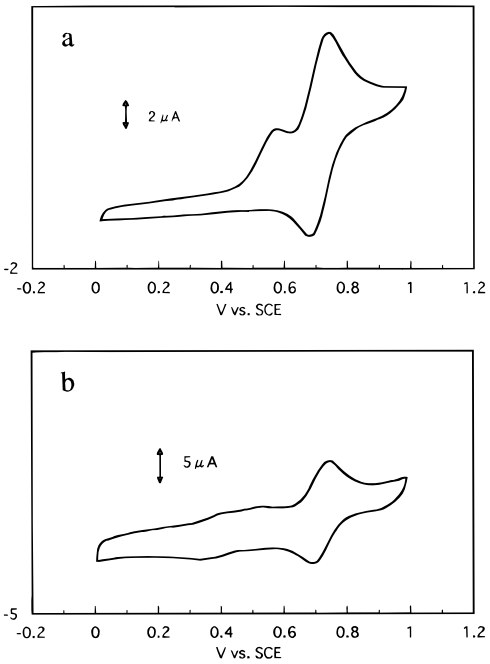


Figure 1. Cyclic voltammograms of (a) $[Ru(N\text{-Me-ala})(bpy)_2]^+$ (**1**) and (b) $[Ru(N\text{-Me-ala-H}_2)(bpy)_2]^+$ (**5**) in 1 N HCl (Pt working electrode; scan rate 20 mV/s).

Results and Discussion

Synthesis of (α-Amino acidato)ruthenium(II) Complexes. Treatment of *cis*-$[RuCl_2(bpy \text{ or } phen)_2]$ with sodium α-amino acidate in hot water or ethanol−water affords the (α-amino acidato)bis(bipyridine or phenanthroline)ruthenium(II) complex $[Ru(aa)(bpy \text{ or } phen)_2]X$ (aa = *N*-methylalaninato or (*S*)-prolinato; X = Cl or ClO_4).[18] The NMR spectra of these complexes reveal that they consist of approximately equal amounts of two diastereomers: Δ-*S* and Λ-*S* for (*S*)-prolinato complexes and Δ-*S*/Λ-*R* and Λ-*S*/Δ-*R* for *N*-methylalaninato complexes. For *N*-methylalaninato complexes, two isomers, I and II, are assigned by H−H COSY spectra, as shown in the Experimental Section.[18] We assume that isomer I is Δ-*S*/Λ-*R*, because the *N*-methyl groups of isomer I resonate in a higher magnetic field compared to those of isomer II due to the ring current effect of bipyridine or phenanthroline.

Cyclic voltammetry (CV) of the (α-amino acidato)ruthenium(II) complexes in 1 N HCl shows two anodic peaks and a cathodic peak as shown in Figure 1 for **1**; the data are listed in Table 4.[22] An irreversible anodic peak at 0.55−0.59 V (vs SCE), which is irreversible at any scan rate (20−500 mV/s), is considered to be the one-electron oxidation of the Ru(II) center of the α-amino acidato complexes to Ru(III). On the other hand, a quasi-reversible couple is observed at 0.70−0.75 V, which is attributed to the product oxidized by an EC reaction as discussed later.

Dehydrogenation of (α-Amino acidato)ruthenium(II) Complexes. Anodic oxidation of the (α-amino acidato)ruthenium(II) complexes was carried out at constant potential, 0.55−0.59 V (vs SCE), which is attributed to the potential for oxidation of the Ru(II) center to Ru(III), in 1 N HCl with a Pt gauze working electrode under nitrogen. The oxidation products, which were identified as the α-imino acidato complexes $[Ru^{II}(N(R^1)=C(R^2)CO_2)(bpy \text{ or } phen)_2]X$ ($R^1 = R^2 = Me$, $-(CH_2)_3-$; X = ClO_4, Cl), were isolated as the perchlorate or chloride salts in 60−81% yield.[23] The cyclic voltammogram of an α-imino acidato complex displays a reversible couple as shown in Figure 1b, which is identical with that observed with α-amino acidato complexes. The half-wave potentials of the α-imino acidato complexes listed in Table 4 are more positive than the anodic potentials of the corresponding α-amino acidato complexes.

As shown in Figure 2, the ruthenium complex ion was observed by fast atom bombardment mass analysis, and the isotope distribution of the ions was in good agreement with the calculated one. The *m*/*z* value of the electrolyzed product is less than that of the starting α-amino acidato complex by 2, which clearly proves that dehydrogenation took place in anodic oxidation of the α-amino acidato complex.[24]

Table 4. Anodic Peak and Half-Wave Potentials[a]

	E_a, V		$E_{1/2}$, V	
complex	1 N HCl	0.1 N TEAP/AN	1 N HCl	0.1 N TEAP/AN
1	0.59	0.72	0.70 (0.06)	0.80 (0.10)
2	0.56	0.71	0.74 (0.06)	n.o.[b]
3	0.59	0.68	0.72 (0.05)	0.82 (0.07)
4	0.55[c]	0.68	0.75 (0.06)[c]	0.85 (0.09)
5			0.70 (0.05)	n.m.[d]
6			0.74 (0.06)	n.m.[d]
7			0.72 (0.06)	n.m.[d]
8			0.75 (0.06)	n.m.[d]

[a] Scan rate 50 mV/s unless stated otherwise; potentials vs SCE; Pt electrode; in 1 N HCl or in 0.1 N tetraethylammonium perchlorate (TEAP)/acetonitrile (AN). Peak separations in parentheses. [b] Cathodic peak was not observed. Anodic peak is 0.92 V. [c] Scan rate 20 mV/s. [d] Not measured.

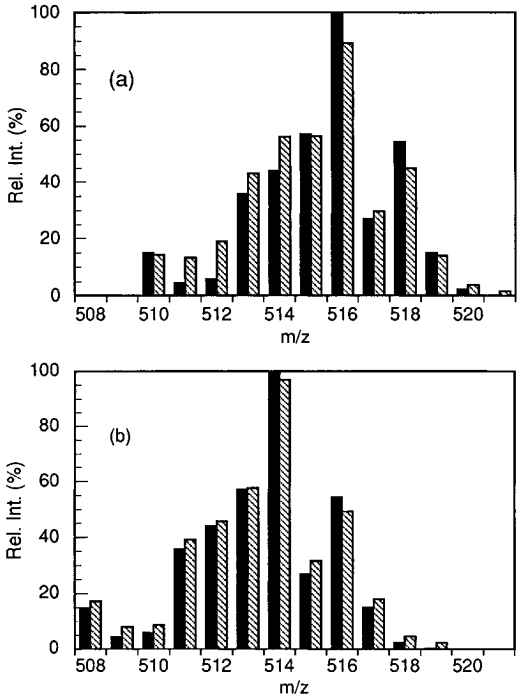


Figure 2. Partial fast atom bombardment mass spectra of (a) $[Ru(N\text{-Me-ala})(bpy)_2]^+$ (**1**) and (b) $[Ru(N\text{-Me-ala-H}_2)(bpy)_2]^+$ (**5**). Observed data are shown by hatched bars, and calculated data by solid bars.

(21) Johnson, C. K. ORTEP Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

(22) The cyclic voltammograms in a neutral solution (1 N NaCl) were almost identical with those in an acidic solution. For example: E_a = 0.54 V (vs SCE) and $E_{1/2}$ = 0.75 V (0.08) for **2** (scan rate 50 mV/s; Pt electrode; peak separation in parentheses).

(23) Chemical oxidations of (α-amino acidato)bis(bipyridine or phenanthroline)ruthenium(II) complexes using an oxidizing reagent such as the Ce(IV) ion have been readily carried out to afford α-imino acidato complexes: Mori, T.; Yamamoto, T.; Yamaguchi, M.; Yamagishi, T. Manuscript in preparation.

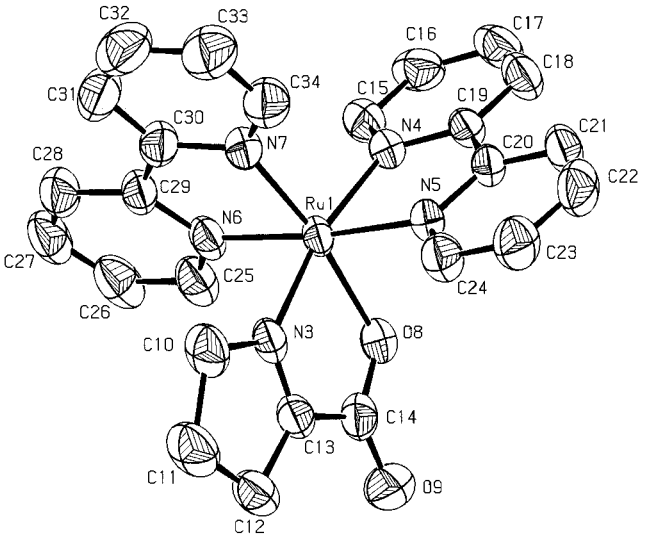
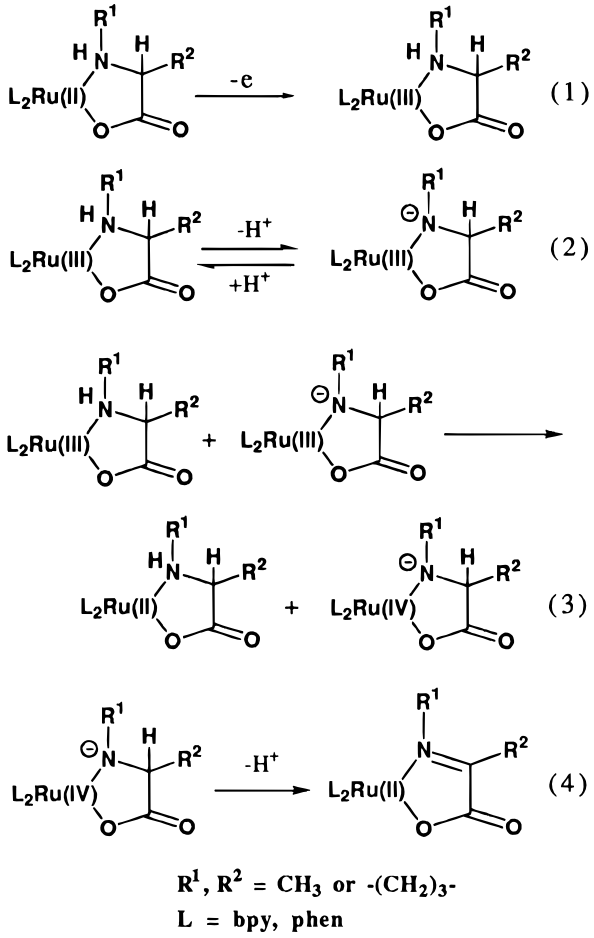


Figure 3. ORTEP drawing of $[Ru(pro\text{-}H_2)(bpy)_2]ClO_4 \cdot 3H_2O$ (**6**).

The ^1H and ^{13}C NMR spectra of the α-imino acidato complexes are consistent with the structures proposed. The ^1H NMR spectra of α-imino acidato complexes derived from the *N*-methylalaninato complexes **5** and **7** exhibit downfield shifts of the *C*-methyl group (0.82−0.94 ppm) and the *N*-methyl group (0.61−1.51 ppm) compared to those of the *N*-methylalaninato complexes **1** and **3**. These downfield shifts are similar to those observed with the (α-imino acidato)cobalt(III) complexes.[16b] The ^{13}C NMR spectra of (α-imino acidato)ruthenium(II) complexes display two peaks at 171−180 ppm, and a peak resonating at lower magnetic field is assigned to the C═N carbon by measurements using selective long-range decoupling with NOE.[14b]

An X-ray structure analysis of $[Ru(pro\text{-}H_2)(bpy)_2]ClO_4 \cdot 3H_2O$ (**6**) was performed, and the ORTEP drawing is shown in Figure 3 along with the numbering in the molecule. The bond distance of N(3)−C(13) is 1.294(5) Å, which is normal for a C═N double bond. The chelate ring of the α-imino acidato ligand is almost planar: distances (Å) from the least-squares plane through the five atoms of the chelate ring are 0.0000 (Ru(1)), 0.0065 (N(3)), −0.0139 (C(13)), 0.0099 (C(14)), and −0.0014 (O(8)), respectively (see Supporting Information). The bite angle of the imino acidato chelate N(3)−Ru(1)−O(8) is 77.9-(2)°, which is similar to those of the bipyridines. The bond distance of Ru(1)−N(3)(imino nitrogen), 2.042(3) Å, is similar to those of Ru−N(imino) in the bipyridines, 2.039−2.065 Å, and is shorter than those of Ru−N(amino), 2.07−2.14 Å, in the analogous (α-amino acidato)bis(bipyridine)ruthenium(II) complexes, which reflects the difference in *σ*-bond radii between sp^2 and sp^3 nitrogen atoms.[26]

Scheme 2



This is the first time, as far as we know, that an (imino acidato)ruthenium(II) complex has been obtained; however, the molecular structures of several (imino acidato)cobalt(III) complexes have been reported.[12d,27] The Co−N(imino) bond distances and the bite angles of the imino acidate chelate rings of the Co(III) complexes are 1.89−93 Å and 82.7−84.0°, respectively. Longer Ru−N(imino) bond lengths and smaller bite angles for the (imino acidato)ruthenium(II) complexes may reflect the larger radius of the ruthenium(II) ion compared to the cobalt(III) ion.

We have not yet done an extensive mechanistic study; however, it seems likely that the mechanism of this reaction is analogous to that of the dehydrogenation of (amine)ruthenium complexes to give imine complexes, which was proposed by Keene and co-workers, as shown in Scheme 2.[8d,28] The first step is one-electron oxidation of the metal ion from Ru(II) to Ru(III) (eq 1), and next step is proton dissociation of the amino group (eq 2). Then electron transfer between two Ru(III) species, the associated form and the dissociated form, provides the original Ru(II) complex and the Ru(IV) intermediate (eq 3). Finally, a proton is abstracted from the Ru(IV) intermediate to give the (α-imino acidato)ruthenium(II) complex (eq 4). The overall reaction is two-electron oxidation. Sargeson and co-workers have also proposed a similar mechanism for the dehydrogenation of a (hexaamine cage)ruthenium(III) complex to a (hexaimine)ruthenium(II) complex and have observed a ruthenium(IV) intermediate.[29]

(24) It is noteworthy that in some experiments the α-imino acidato complex was obtained as a byproduct of the synthesis of the N-substituted α-amino acidato complex because these α-amino acidato complexes are readily dehydrogenated. For instance, they are partly dehydrogenated in hot water (90 °C) under air for 1 day.[25] Care must be taken to obtain the pure ruthenium(II) complexes with N-substituted α-amino acids.

(25) Ishidai, H.; Yamaguchi, M.; Yamagishi, T. Unpublished results.

(26) Bond distances of Ru−N(amino) determined by X-ray analysis of the (α-amino acidato)bis(bipyridine)ruthenium(II) complexes: $[Ru((S)\text{-ala})(bpy)_2]ClO_4 \cdot 0.5H_2O$,[26a] 2.071(11), 2.130(11) Å; $[Ru((S)\text{-thr})(bpy)_2]ClO_4 \cdot 5H_2O$,[26b] 2.118(9), 2.142(10) Å; $[Ru((S)\text{-allothr})(bpy)_2]ClO_4 \cdot 5H_2O$,[26b] 2.121(7), 2.130(7) Å; $[Ru((gly)(bpy)_2]ClO_4 \cdot 2H_2O$,[26c] 2.135(4) Å. (a) Stephens, F. S.; Vagg, R. S.; Williams, P. A. *Inorg. Chim. Acta* **1983**, *72*, 253. (b) Goodwin, T. J.; Williams, P. A.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1984**, *88*, 165. (c) Anderson, M. A.; Richards, P. G.; Stark, A. G.; Stephens, F. S.; Vagg, R. S. Williams, P. A. *Inorg. Chem.* **1986**, *25*, 4847.

(27) (a) Yamaguchi, M.; Yamagishi, T.; Hida, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1942. (b) Robertson, G. B.; Whimp, P. O. *Aust. J. Chem.* **1975**, *28*, 2129.

(28) Ridd, M. J.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733.

Taube and Ilan have reported the preparation and X-ray analysis of a (glycinato)tetraammineruthenium(III) complex.[30] In contrast, we could not obtain (α-amino acidato)bis(diimine)-ruthenium(III) complexes, but (α-imino acidato)ruthenium(II) complexes instead. This is probably due to the difference in reactivity between bis(diimine)ruthenium(III) complexes and tetraammineruthenium(III) complexes.[31]

(α-Imino acidato)ruthenium(II) complexes are readily obtained by anodic oxidation at constant potential. Although (α-imino acidato)cobalt(III) complexes have been already prepared, this is the first example of the dehydrogenation of an (α-amino acidato)ruthenium(II) complex giving rise to the corresponding α-imino acidato complex, as far as we know. Since α-imino acidate moieties chelated to a metal ion are so reactive that the α-carbon can be attacked by a nucleophile and the *β*-carbon can be attacked by an electrophile, α-imino acidato complexes are useful compounds for the syntheses of various α-amino acidato complexes.

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Supporting Information Available: Tables of positional and isotropic thermal parameters for hydrogen atoms, anisotropic temperature factors for non-hydrogen atoms, bond distances, bond angles, torsion angles, interatomic distances, and least-squares planes and cell packing diagrams (24 pages). Ordering information is given on any current masthead page.

IC941264N

(29) Bernhard, P.; Sargeson, A. M. *J. Am. Soc. Chem.* **1989**, *111*, 597.
(30) (a) Ilan, Y.; Taube, H. *Inorg. Chem.* **1983**, *22*, 1655. (b) Ilan, Y.; Kapon, M. *Inorg. Chem.* **1986**, *25*, 2350.
(31) The Ru(II/III) half-wave potential for $[Ru(gly)(NH_3)_4]^{+/2+}$ is −0.24 V (vs SCE) at pH 1: Diamond, S. E. Ph.D. Thesis, Stanford University, 1975. Ilan, Y.; Kfir, A. *Inorg. Chem.* **1987**, *26*, 2872.