# Dehydrogenation of α-Amino Acids Chelated to a Co(III) Ion Yielding α-Imino Acidato Complexes[1)]

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The oxidation of the α-amino acidato cobalt(III) complexes with 2,3,2-tet (=3,7-diazanonane-1,9-diamine) or its derivative, where amino acidate ligand was phenylglycinate, alaninate, valinate *N*-methylalaninate, or prolinate, by potassium permanganate was achieved to yield the corresponding α-imino acidato complexes, $[Co^{III}\{N(R^1)=C(R^2)CO_2\}(N_4)]^{2+}$.

It is well known that α-amino acids are oxidatively deaminated to give α-keto acids by enzymes such as glutamate dehydrogenase in biological systems. A number of studies to mimic the oxidation of α-amino acids to the corresponding α-keto acids by nonenzymatic means have been made. Although oxidative deamination of α-amino acids in the presence of pyridoxal derivatives and metal ions has been successfully achieved,[2)] most of attempts in the absence of pyridoxal have produced ammonia, carbon dioxide, and aldehyde due to oxidative decarboxylation[3)] with few successful exceptions.[4)] The first step of the oxidative deamination is the dehydrogenation of amino group, and an α-imino acid is postulated as the intermediate. It is difficult to isolate α-imino acids, however, because they are readily hydrolyzed in aqueous solution to α-keto acids.

Chelated amine complexes such as diamine or macrocyclic tetraamine complexes are dehydrogenated to give imine complexes.[5)] The dehydrogenation of 1,2-diamine complexes of Fe(II),[6)] Ru(II),[7)] Os(II),[8)] and Pt(IV)[9)] ion by chemical and/or anodic oxidation has been reported. The reaction intermediates in higher oxidation state have been proposed for the dehydrogenation of M(II) complexes. On the other hand, analogous polyamine Co(III) complexes have been observed to be resistant to dehydrogenation. Black and Hartshorn have first reported the oxidation of macrocyclic polyamine Co(II) complex to yield the dehydrogenated Co(III) complex.[10)] Martell and his coworkers have reported the oxidative dehydrogenation of the binuclear dioxygen polyamine Co(III) complex to give the diimine complex.[11)]

Recently, it has been reported that α-imino acidato complexes chelated to a cobalt(III) ion were synthesized and found to be stable in neutral or acidic aqueous solution.[12)] α-Imino acidato complexes have been previously prepared by several means: (a) the intramolecular condensation of α-keto acidate and ammine ligands on the complex;[12)] (b) the β-elimination of α-amino acidato complex with an appropriate β-substituent as a leaving group.[12,13)] Extensive studies have been made to utilize α-imino acidato complexes as the intermediate of various α-amino acidato complexes, since they show remarkable reactivity with a nucleophile or an electrophile.[12—14)]

It is of interest to develop the new way for the preparation of the α-imino acidato complexes in the light of its utility. We now report herein that the dehydrogenation of (α-amino acidato)(tetraamine)cobalt(III) complexes using potassium permanganate was accomplished to give the α-imino acidato complexes, $[Co^{III}\{N(R^1)=C(R^2)CO_2\}(N_4)]^{2+}$.[1,15)]

## Experimental

The tetraamine ligands, 3,7-diazanonane-1,9-diamine (=2,3,2-tet)[16)] and 2(*S*),10(*S*)-4,8-diazaundecane-2,10-diamine (=2*S*,10*S*-Me$_2$-2,3,2-tet)[17)] were prepared by the literature methods. The (α-amino acidato)(tetraamine)cobalt(III) complexes were prepared by the method described previously,[18)] except phenylglycinato complexes. Potassium permanganate was analytical grade and used as received. Separations of the diastereomers, *Λ*-β$_2$ and *Δ*-β$_2$ isomers of the (α-amino acidato)(3,7-diazanonane-1,9-diamine)cobalt(III) complexes, were carried out by column chromatography (SP-Sephadex C25 cation exchange resin with 0.38 mol dm$^{-3}$ $NaH_2PO_4$–$Na_2HPO_4$ as eluent).

**Measurements.** Visible and ultraviolet absorption spectra were measured with a Hitachi 340 or Hitachi 220A spectrophotometer. Circular dichroism spectra were recorded on a JASCO J-20 or JASCO J-40A spectropolarimeter. $^1$H NMR and $^{13}$C NMR spectra were recorded on a JEOL FX-90, JEOL EX-270, or JEOL GX-400 spectrometer, chemical shifts being reported in the δ scale in ppm relative to sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) 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.

**Phenylglycinato Complexes:** Phenylglycinato complexes were prepared by the method described previously except that the reaction was carried out under nitrogen atmosphere.[18)] *Λ*-β$_2$-[Co((*R*)-phegly)(2,3,2-tet)](ClO$_4$)$_2$: Anal. Calcd for $CoCl_2O_{10}C_{15}H_{28}N_5$: C, 31.71; H, 4.97; N, 12.32%. Found: C, 31.82; H, 5.11; N, 12.32%. Electronic spectral data, $\lambda_{max}$ 494 nm (ε=134), 349 (145).

*Λ*-β$_2$-[Co((*R*)-phegly)(2*S*,10*S*-Me$_2$-2,3,2-tet)](ClO$_4$)$_2$·3/2H$_2$O: Anal. Calcd for $CoCl_2O_{11.5}C_{17}H_{35}N_5$: C, 32.76; H, 5.66; N, 11.24%. Found: C, 32.57; H, 5.60; N, 11.27%.

Table 1. Electronic and Circular Dichroism Spectral Data of α-Imino Acidato Complexes.

(a) in Neutral aqueous solution

| Complex | Abs. max/nm ($\varepsilon$/$M^{-1}L\,cm^{-1}$) | CD max/nm ($\Delta\varepsilon$/$M^{-1}L\,cm^{-1}$) |
|---|---|---|
| **1a** | 474(174) | 503(1.48), 460(1.60) |
| **3a** | 480(143), 341sh(516) 299sh(1180) | 509(−1.49), 460(−1.35) 359(0.34) |
| **4a** | 489(147), 338sh(336) | — |
| **5a** | 489(153), 345(275) | 526(−1.29), 460sh(−0.36) 372(0.17) |
| **1b** | 474(177), 317sh(5200) | 501(2.04), 461(2.18) |
| **2b** | 483(146), 342sh(386) 298sh(1010) | 513(1.93), 452sh(0.91) 359(−0.23) |
| **3b** | 482(148), 342sh(469) 301sh(1060) | 508(1.93), 467sh(1.67) 360(−0.45) |

(b) in Basic aqueous solution (M/100 NaOH).

| Complex | Abs. max/nm ($\varepsilon$/$M^{-1}L\,cm^{-1}$) | CD max/nm ($\Delta\varepsilon$/$M^{-1}L\,cm^{-1}$) |
|---|---|---|
| **1a** | 515(270), 402sh(673) | 570(0.87), 502(−3.06) 430(0.17) |
| **3a** | 517(242), 403sh(677) | 576(−0.78), 504(3.00) 431(−0.25) |
| **1b** | 513(270), 398sh(734) | 568(1.23), 500(−3.76) 429(0.19) |
| **2b** | 513(235), 398sh(625) | 567(1.21), 499(−2.94) 418(0.46) |
| **3b** | 515(240), 403sh(664) | 573(1.01), 503(−3.25) 425(0.35) |

Electronic spectral data, $\lambda_{max}$ 494 nm ($\varepsilon$=152), 351 (149).

**General Procedure for the Dehydrogenation of the α-Amino Acidato Cobalt(III) Complexes to Yield the α-Imino Acidato Complexes.** To a solution of the α-amino acidato cobalt(III) complex, *Λ*-β$_2$-[Co(α-amino acidato)(tetraamine)](ClO$_4$)$_2$ (ca. 0.02 M solution, 1 M=1 mol dm$^{-3}$),[19] was added an equimolar amount of 0.1 M $KMnO_4$ aqueous solution all at once, and the mixture was stirred at room temperature until it turned brown. It usually takes 1—3 min. (In the case with the *N*-substituted amino acidato complexes, the reaction mixture turned brown immediately after the addition.) Ethanol was adddd to decompose excess potassium permanganate, and the reaction mixture was stirred at 40—50 °C for 30 min. The brown precipitates were filtered through Celite. The filtrate was poured on a column of SP-Sephadex C25 cation exchange resin (2×40 cm) in the sodium form, then eluted with 0.1—0.2 M NaCl. The orange 2+ band was assigned to the α-imino acidato complex. The orange-red crystals were collected, washed with ethanol, then with ether, and air-dried.

***Λ*-β$_2$-[Co(phegly-H$_2$)(2,3,2-tet)](ClO$_4$)$_2$ (1a).**[20] Yield: 55%. $^1$H NMR ($D_2O$) $\delta$=1.6—3.2 (m, 14H), 7.4—8.1 (m, 5H, Ph). $^1$H NMR (DMSO-$d_6$ with a drop of DCl) $\delta$=12.6 (s, 1H, NH=C). Selected data of $^{13}$C NMR ($D_2O$) $\delta$=172.6, 180.9 (C=O and C=N). Anal. Calcd for $C_{15}H_{26}N_5Cl_2CoO_{10}$: C, 31.82; H, 4.63; N, 12.37%. Found: C, 31.82; H, 4.75; N, 12.47%.

***Δ*-β$_2$-[Co(val-H$_2$)(2,3,2-tet)](ClO$_4$)$_2$ (3a).**[19] Yield: 28%. $^1$H NMR ($D_2O$) $\delta$=1.25, 1.35 (d, 6H, $CH_3$, $J$=6 Hz), 1.6—3.3 (m, 15H). $^1$H NMR (DMSO-$d_6$ with a drop of DCl) $\delta$=11.9 (s, 1H, NH=C). Selected data of $^{13}$C NMR ($D_2O$) $\delta$=172.6 (C=O), 194.5 (C=N). Anal. Calcd for $C_{12}H_{28}N_5Cl_2CoO_{10}$: C, 27.08; H, 5.30; N, 13.16%. Found: C, 27.17; H, 5.38; N, 13.03%.

***Δ*,*Λ*-β$_2$-[Co(*N*-Meala-H$_2$)(2,3,2-tet)]Cl·ClO$_4$ (4a).**[19] Yield: 41%. $^1$H NMR ($D_2O$) $\delta$=2.30 (s, 3H, C–$CH_3$), 3.25 (s, 3H, N–$CH_3$), 1.6—3.1 (m, 14H). Selected data of $^{13}$C NMR ($D_2O$) $\delta$=175.1 (C=O), 184.8 (C=N). Anal. Calcd for $C_{11}H_{26}N_5Cl_2CoO_6$: C, 29.09; H, 5.77; N, 15.42%. Found: C, 28.86; H, 5.75; N, 15.44%.

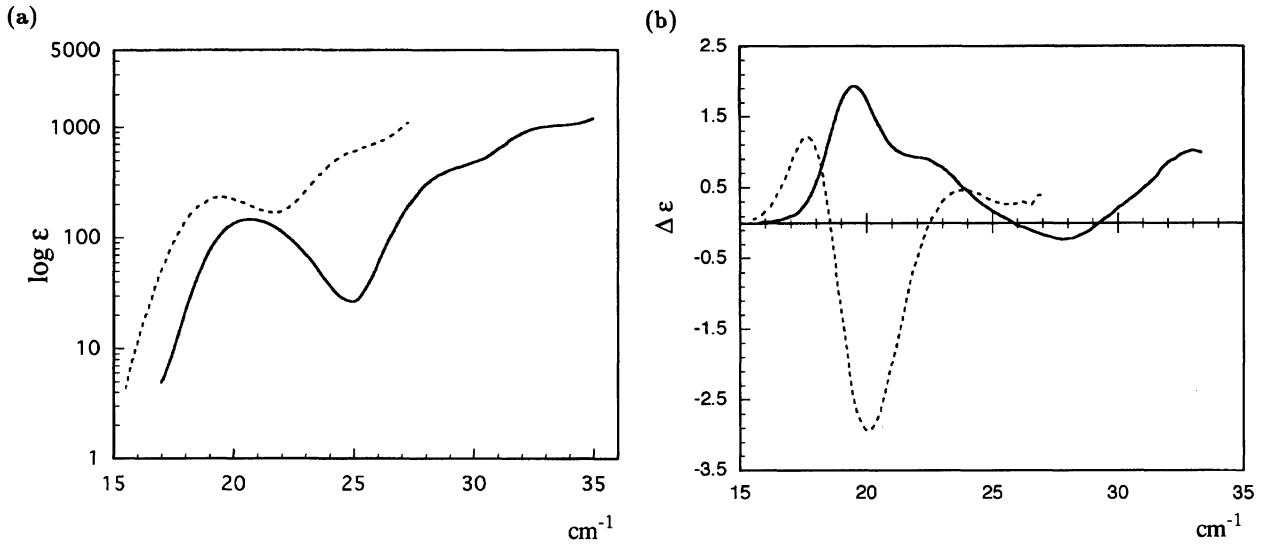



Fig. 1. (a) Electronic absorption and (b) circular dichroism spectra of [Co(ala-$H_2$) (2*S*,10*S*-$Me_2$-3,2-tet)]$^{2+}$ (**2b**) in $H_2O$ (solid line) and M/100 NaOH (dashed line).

***Δ*-*β*$_2$-[Co(pro-$H_2$)(2,3,2-tet)]Cl·$ClO_4$·1/2$H_2O$ (5a).**[19] Yield: 17%. $^1$H NMR ($D_2O$) $\delta$=1.6—3.2 (m, 20H). Selected data of $^{13}$C NMR ($D_2O$) $\delta$=170.8 (C=O), 187.5 (C=N). Anal. Calcd for $C_{12}H_{27}N_5Cl_2CoO_{6.5}$: C, 30.33; H, 5.73; N, 14.73%. Found: C, 30.17; H, 5.35; N, 15.06%.

***Λ*-*β*$_2$-[Co(phegly-$H_2$)(2*S*, 10*S*-$Me_2$-2, 3, 2-tet)]-($ClO_4$)$_2$·2$H_2O$ (1b).**[20] Yield: 55%. $^1$H NMR ($D_2O$) $\delta$=1.37, 1.41 (d, 6H, $CH_3$, $J$=6 Hz), 1.6—3.4 (m, 12H), 7.4—8.1 (m, 5H, Ph). $^1$H NMR (DMSO-$d_6$ with a drop of DCl) $\delta$=12.2 (s, 1H, NH=C). Selected data of $^{13}$C NMR ($D_2O$) $\delta$=172.9, 181.1 (C=O and C=N). Anal. Calcd for $C_{17}H_{34}N_5Cl_2CoO_{12}$: C, 32.39; H, 5.44; N, 11.11%. Found: C, 32.57; H, 5.61; N, 10.97%.

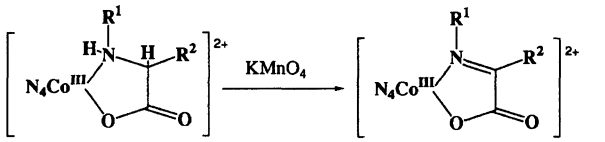
***Λ*-*β*$_2$-[Co(ala-$H_2$)(2*S*,10*S*-$Me_2$-2,3,2-tet)]($ClO_4$)$_2$ (2b).**[21] Yield: 12%. $^1$H NMR ($D_2O$) $\delta$=1.34, 1.36 (d, 6H, $CH_3$, $J$=6 Hz), 2.53 (s, 3H, N=C–$CH_3$), 1.6—3.3 (m, 12H). $^1$H NMR (DMSO-$d_6$ with a drop of DCl) $\delta$=12.4 (s, 1H, NH=C). Selected data of $^{13}$C NMR ($D_2O$) $\delta$=173.6 (C=O), 187.0 (C=N). Anal. Calcd for $C_{12}H_{28}N_5Cl_2CoO_{10}$: C, 27.08; H, 5.30; N, 13.16%. Found: C, 27.17; H, 5.35; N, 13.09%.

***Λ*-*β*$_2$-[Co(val-$H_2$)(2*S*,10*S*-$Me_2$-2,3,2-tet)]($ClO_4$)$_2$ (3b).** Yield: 33%. $^1$H NMR ($D_2O$) $\delta$=1.27, 1.34, 1.36 (d, 12H), 1.6—3.2 (m, 13H). $^1$H NMR (DMSO-$d_6$ with a drop of DCl) $\delta$=11.9 (s, 1H, NH=C). Selected data of $^{13}$C NMR ($D_2O$) $\delta$=170.2 (C=O), 192.0 (C=N). Anal. Calcd for $C_{14}H_{32}N_5Cl_2CoO_{10}$: C, 30.01; H, 5.76; N, 12.50%. Found: C, 30.03; H, 5.78; N, 12.23%.

## Results and Discussion

During the study of various α-amino acidato cobalt(III) complexes, the reaction of the *trans*-dichlorotetraamine cobalt(III) complex with phenylglycine under aerobic conditions was found to yield the unexpected product, light-orange complex, instead of the phenylglycinato complex (=phegly complex). The aqueous solution of this complex shows reversible color change between light-orange color in a neutral or acidic solution and intense dark-red color in a basic solution. The behavior of this complex is similar to that reported for the α-imino acidato complexes (=2-iminocarboxylato complex),[12] and the complex was readily hydrogenated by $NaBH_4$ to give the phenylglycinato complex.[1] The same reaction of tetraamine cobalt(III) complex with phenylglycine except that the reaction was done under nitrogen gave the phenylglycinato complex but no α-imino acidato complex was formed. These facts indicated that the oxidation of phenylglycine took place during the synthesis, and the α-imino acidato complex (=phegly-$H_2$ complex), [Co{NH=C(Ph)$CO_2$}($N_4$)]$^{2+}$,[1] was formed in stead of the corresponding α-amino acidato complex. It is noteworthy that the reactions with other amino acids, such as alanine or valine, under the same conditions did not give the corresponding α-imino acidato complexes but gave the amino acidato complexes.

Obviously, the α-imino acid was considered to be the oxidized product of α-amino acid, and it occurred to us that it was possible to oxidize amino acidato complexes to give the corresponding imino acidato complexes. The oxidation of the phenylglycinato complex, *Λ*-*β*$_2$-[Co(phegly)($N_4$)]$^{2+}$, by potassium permanganate was carried out and yielded the orange complex in a moderate yield, which was identical with the abovementioned α-imino acidato complex, [Co(phegly-$H_2$)-




$R^1$ = H, $R^2$ = Ph
$R^1$ = H, $R^2$ = $CH_3$
$R^1$ = H, $R^2$ = $CH(CH_3)_2$
$R^1$ = $CH_3$, $R^2$ = $CH_3$
$R^1$,$R^2$ = -$(CH_2)_3$-

$N_4$ = 2,3,2-tet
$N_4$ = 2*S*,10*S*-$Me_2$-2,3,2-tet

Scheme 1.

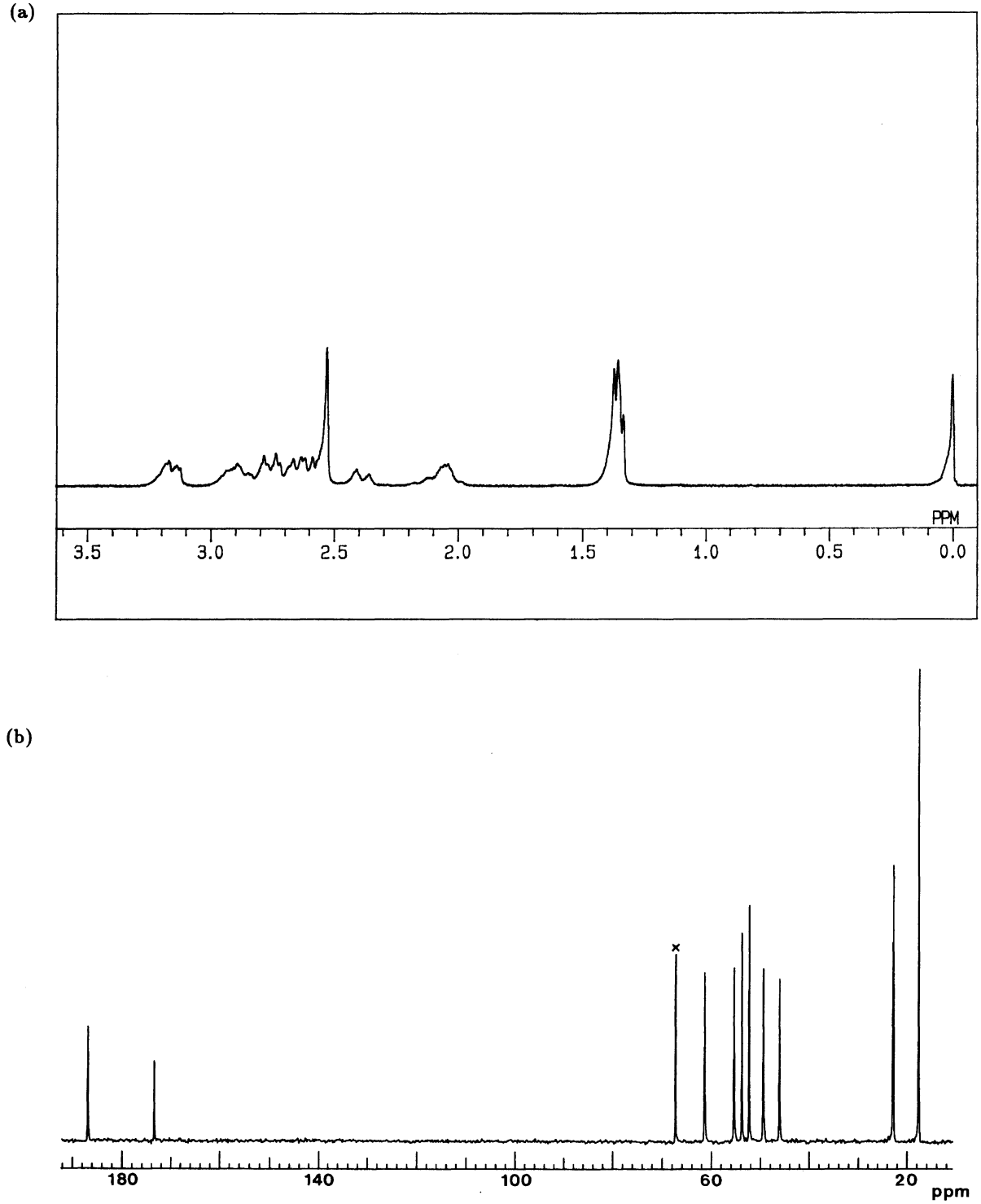



Fig. 2. (a) $^{1}$H NMR and (b) $^{13}$C NMR spectra of [Co(ala-$H_2$) (2*S*,10*S*-$Me_2$-2,3,2-tet)]$^{2+}$ (**2b**).

$(N_4)]^{2+}$ (Scheme 1). Furthermore, the dehydrogenation of other $\alpha$-amino acidato complexes, such as alaninato, valinato, prolinato, and *N*-methylalaninato complexes by potassium permanganate was successfully achieved to yield the corresponding $\alpha$-imino acidato complexes, $[Co\{N(R^1)=C(R^2)CO_2\}(N_4)]^{2+}$, where $N_4$ were 2,3,2-tet or 2*S*,10*S*-$Me_2$-2,3,2-tet (yield: 12—55 %).[21]

Table 1 summarizes the electronic absorption and circular dichroism spectral data of the $\alpha$-imino acidato cobalt(III) complexes. In neutral or acidic solution the absorption maxima of the electronic spectra of the $\alpha$-imino acidato complexes in the visible region are 474—489 nm, which show blue shifts (12—20 nm) from those of the corresponding $\alpha$-amino acidato complexes: 20 nm for the phegly-$H_2$ complexes and 12—14 nm for other $\alpha$-imino acidato complexes. It is possibly due

to the back-bonding character of the α-imino acidate ligands. It is consistent with the fact that the Co–N(imino) bond length, 1.90(1) Å, is significantly shorter than the Co–N(amino) ones, 1.97 Å (average), in the crystal structure of **3b**,[23] which reflects the difference of σ-bond radii between $sp^2$ and $sp^3$ nitrogen atoms.[24] As shown in Fig. 1, a neutral or acidic aqueous solution of the imino acidato complex is orange, and a solution of the α-imino acidato complex having no *N*-alkyl group shows an instant and reversible color change to intense dark red by basification. The absorption maxima of the complexes without *N*-alkyl group in basic solution are 513—515 nm. This is attributed to the deprotonation of the imino group coordinated to the Co(III) ion (Eq. 1).[12] The $pK_a$ values determined by spectrophotometrical titration are 9.2 (**1a**), 10.1 (**3a**), 9.3 (**1b**), 9.7 (**2b**), and 10.6 (**3b**), respectively. This spectral behavior and the $pK_a$ values are similar to those reported for $[Co\{NH{=}C(R)CO_2\}(NH_3)_4]^{2+}$: 10.36 for R=$CH_3$ and 9.50 for R=Ph.[12b] Although the imino acidato complexes are not considerably stable in basic solution, the UV/visible spectra of the complexes prepared in this study show no change over at least 15 min.

$$[Co\{NH{=}C(R)CO_2\}(N_4)]^{2+} \overset{OH^-}{\rightleftharpoons} [Co\{N{=}C(R)CO_2\}(N_4)]^{+}. \quad (1)$$

The circular dichroism (CD) spectra of the α-imino acidato complexes also show a distinctive change by pH change, as shown in Fig. 1. The CD spectrum of the ala-$H_2$ complex, **2b**, derived from Λ-$\beta_2$-[Co(ala)(2*S*,10*S*-$Me_2$-2,3,2-tet)]$^{2+}$ in a neutral solution shows a positive Cotton effect corresponding to the first absorption band, which indicates that the α-imino acidato complex have the same configuration, Λ, as the α-amino acidato complex around the metal ion. The assignment of the absolute configuration of the α-imino acidato complex has been confirmed by X-ray structure determination.[23] On the other hand, in a basic solution the CD spectrum shows the negative Cotton effect. Other α-imino acidato complexes listed in Table 1 show similar behaviors in their CD spectra. Furthermore, the fact that the CD spectra of the α-imino acidato complex derived from (*S*)-amino acidato complex is identical with that derived from (*R*)-amino acidato complex indicates the loss of the asymmetric carbon.[25]

The $^1H$ and $^{13}C$ NMR spectral data are consistent with the structures proposed. The $^1H$ NMR spectrum of $[Co\{NH{=}C(CH_3)CO_2\}(2S,10S\text{-}Me_2\text{-}2,3,2\text{-}tet)]^{2+}$ complex (**2b**), shown in Fig. 2, demonstrates that the methyl group resonating at 2.53 ppm as a singlet shows a 1.1-ppm downfield shift compared to that of the alaninato complex resonating at 1.45 ppm as a doublet. Similarly, the spectrum of *N*-Meala-$H_2$ complex (**4a**) exhibits downfield shifts of its *C*-methyl group (0.9 ppm) and *N*-methyl group (1.0 ppm) compared to those of the *N*-Meala complex. In the case of val-$H_2$ complexes (**3a** and **3b**) two methyl groups of the isopropyl group show 0.2—0.3-ppm downfield shifts. The imino protons are observed at 11.9—12.6 ppm in acidic DMSO-$d_6$.[12] The $^{13}C$ NMR spectra of the α-imino acidato complexes demonstrate two characteristics peaks at 170—192 ppm, which are attributed to the $sp^2$ carbons of C=O and C=N groups. A peak resonating at lower magnetic field, 180—192 ppm, was assigned to the C=N carbon.[26]

α-Imino acidato cobalt(III) complexes were obtained by the oxidation of α-amino acidato complexes using potassium permanganate. To the best of our knowledge, this is the first report of the dehydrogenation of α-amino acidato complexes to give the corresponding α-imino acidato complexes.[1,15,23,28] It is noteworthy that attempts to achieve the dehydrogenation of α-amino acidato cobalt(III) complex by using various other oxidizing reagents than potassium permanganate such as hydrogen peroxide, Fenton's reagent, manganese dioxide, bromine, sodium hypochlorite, nitric acid, lead tetraacetate, *t*-butoxy chloride, and *N*-bromosuccinimide, or by anodic oxidation have all failed.[15] On the other hand, we have found that α-amino acidato ruthenium(II) complexes with bis(bipyridine or phenanthroline) can be readily dehydrogenated by chemical and/or anodic oxidation.[29] The contrast of the reactivity on dehydrogenation is probably due to the difference of the mechanism. It is assumed that α-amino acidato Ru(II) complexes are dehydrogenated through the Ru(IV) intermediate by analogy with the mechanism proposed for the dehydrogenation of the Ru(II) complexes with diamine,[7] or polyamine.[30] However, the Co(III) ion is unlikely to become higher oxidation state. It has been reported that potassium permanganate oxidized α-amino acids to ammonia, carbon dioxide and other oxidized organic products,[3a,31] and the addition of Cu(II) ion decreased the oxidizability of α-amino acids by potassium permanganate.[32] Consequently, we assume that the role of Co(III) ion is to protect carboxylate group against the oxidative decarboxylation and to protect imino group against hydrolysis. Since it is known that α-imino acidate chelates react with both a nucleophile and an electrophile, α-imino acidato complexes are useful intermediates for the synthesis of various α-amino acidato complexes.[12—14]

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20) Alternatively, phegly-$H_2$ complexes were obtained by the reaction of ammonium $\alpha$-phenyl-$\alpha$-aminomalonate and *trans*-dichloro Co(III) complex of tetraamine: M. Yamaguchi, M. Saburi, and S. Yoshikawa, unpublished results.

21) Interestingly, some attempts to dehydrogenate the alaninato complex with 2,3,2-tet, $\Lambda$(or $\Delta$)-$\beta_2$-[Co(ala)-(2,3,2-tet)]$(ClO_4)_2$ by potassium permanganate failed, contrary to the alaninato complex with 2*S*, 10*S*-$Me_2$-2,3,2-tet, but the imino acidato complex, $\beta_2$-$[Co(NH{=}C(CH_3)CO_2)$-(2,3,2-tet)$]^{2+}$ was obtained by the other method, $\beta$-elimination reaction of the $\beta$-chloroalaninato complex.[22]

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