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Metal Complexes of Amino Acids. XIII.[1] The Relationships between the ^{13}C Chemical Shifts and Ligand Field in the *trans*(*O*)-[Co(O)$_2$(N)$_4$] Type Complexes

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The relationship between the ligand field of the carboxyl groups and the chemical shift of carboxyl carbon or α-carbon has been investigated on the basis of the absorption and ^{13}C-NMR spectral data of the *trans*(*O*)-[Co(OCO–R)$_2$(en)$_2$]X$_n$ type complexes (OCO–R denotes amino acid or fatty acid coordinating unidentately with the carboxyl group to cobalt(III)). The linear correlations were observed between the $\tilde{\nu}_{\max}$ (^{1}E$_g$ component of the first absorption band) and the chemical shifts of carboxyl- and α-carbons.

A number of reports containing an application of ^{13}C-NMR to metal complexes have been published, and the technique has proved to be a very powerful tool for the structural investigation of the complexes. For the metal complexes, the ^{13}C-NMR studies have been concentrated on the cobalt(III) complexes, because most of the cobalt(III) complexes are inert and diamagnetic.[2–24]

Only few papers have been reported on the relation between the d-d absorption spectra and ^{13}C chemical shifts of the metal complexes.[23–25] However, it can be expected that some interesting informations concerning the ligand field will be obtained from the ^{13}C chemical shift data, because both the ligand field and ^{13}C chemical shift are related to the electron density on the ligand.[26–29]

Previously, we reported the ^{13}C-NMR of the *trans*(*O*)-[Co(OCO–R)$_2$(en)$_2$]$^{n+}$ type complexes,[30] where OCO–R denotes amino acid or fatty acid which coordinates to cobalt(III) as a unidentate ligand through its carboxyl group. It has been clarified by the report that such unidentate coordinations of the carboxylic acids to cobalt(III) (R–C$_\alpha$–C$_{\text{oxy}}$–OOH→R–C$_\alpha$–C$_{\text{oxy}}$–COOCo) show the different chemical shift changes, $\Delta_{\text{uni}}(\text{C}_{\text{oxy}})$ $(\delta_{\text{uni}}(\text{C}_{\text{oxy}}) - \delta(\text{C}_{\text{oxy}}))$ and $\Delta_{\text{uni}}(\text{C}_\alpha)$ $(\delta_{\text{uni}}(\text{C}_\alpha) - \delta(\text{C}_\alpha))$, and these shift changes can be also correlated to the chemical shifts of the free acids, $\delta(\text{C}_{\text{oxy}})$ and $\delta(\text{C}_\alpha)$, where $\delta_{\text{uni}}(\text{C}_{\text{oxy}})$ and $\delta_{\text{uni}}(\text{C}_\alpha)$ represent the chemical shifts of C$_{\text{oxy}}$ and C$_\alpha$ of the unidentate ligands in the *trans*(*O*)-[Co(OCO–R)$_2$(en)$_2$]$^{n+}$ type complexes, and $\delta(\text{C}_{\text{oxy}})$ and $\delta(\text{C}_\alpha)$ represent those of the free acids in acidic D$_2$O solutions. The *trans*(*O*)-[Co(OCO–R)$_2$(en)$_2$]$^{n+}$ type complexes are very suitable for the study of the ligand field of the coordinated carboxylic acids, because the ^{1}E$_g$ component in the first absorption band of the complex is well apart from another component.[31] In the present paper we will describe the relation between the chemical shifts and the first absorption bands of the *trans*(*O*)-[Co(OCO–R)$_2$(en)$_2$]$^{n+}$ type complexes.

Experimental

Preparation of Complexes. trans*(*O*)-Bis(*N*-propylglycine)bis(ethylenediamine)cobalt(III) Perchlorate(*trans*(*O*)-[Co(Hpgly)$_2$(en)$_2$](ClO$_4$)$_3$):* To an aqueous solution containing 5 g of [Co(OH$_2$)$_2$(en)$_2$](ClO$_4$)$_3$ in 50 cm^3 of water, 2.5 g of *N*-propylglycine (Hpgly) was added. The mixture was then evaporated almost to dryness on a water bath at about 80 °C. After cooling, the crude product obtained was dissolved in a small amount of hot water. A few drops of 60% perchloric acid were added to the solution and then cooled in an ice bath. The violet-red crystals obtained were washed with cold water and dried in air. Found: C, 23.55; H, 5.44; N, 11.90%. Calcd for [Co(Hpgly)$_2$(en)$_2$](ClO$_4$)$_3$·H$_2$O: C, 23.49; H, 5.35; N, 11.74%.

trans*(*O*)-Bis(*N*-ethylglycine)bis(ethylenediamine)cobalt(III) Perchlorate (*trans*(*O*)-[Co(Hegly)$_2$(en)$_2$](ClO$_4$)$_3$):* *N*-Ethylglycine hydrochloride (Hegly·HCl, 3 g) was dissolved in 10 cm^3 of water and the pH of the solution was adjusted to *ca.* 7 by adding 1 M NaOH aqueous solution. The neutralized solution was evaporated to dryness using a vacuum evaporator, and the Hegly in the residue was extracted with 30 cm^3 of methanol. The methanolic solution of Hegly was evaporated to dryness. The resulted residue was dissolved in 10 cm^3 of water, and then the solution was added to a solution containing 5 g of [Co(OH$_2$)$_2$(en)$_2$](ClO$_4$)$_3$ in 10 cm^3 of water. The mixed solution was evaporated to a few milliliters on a water bath at about 80 °C. After cooling, the complex deposited was filtered. The crude product was recrystallized from hot water. Found: C, 20.34; H, 5.19; N, 11.96%. Calcd for [Co(Hegly)$_2$(en)$_2$](ClO$_4$)$_3$: C, 20.54; H, 5.17; N, 11.98%.

trans*(*O*)-(Acetato)(glycine)bis(ethylenediamine)cobalt(III) Perchlorate (*trans*(*O*)-[Co(ac)(Hgly)(en)$_2$](ClO$_4$)$_2$):* To an aqueous solution containing 3 g of *trans*(*O*)-[Co(ac)$_2$(en)$_2$](ClO$_4$) (ac=acetate anion) in 30 cm^3 of water was added 1 g of glycine (Hgly). The mixture was then evaporated to a few milliliters on a steam bath. The residual solution was diluted to about 500 cm^3 and then poured into a SP-Sephadex column (C-25, Na$^+$ form, 4.5 cm×50 cm). The adsorbed band was separated into three bands by developing with 0.2 M aqueous solution of sodium perchlorate. The solution of the second eluted band was concentrared to a few milliliters in a vacuum evaporator at 30—40 °C. Ethanol was added to the concentrated solution in order to deposit crude complex. The complex was recrystallized from aqueous solution by adding ethanol. Found: C, 18.32; H, 4.99; N, 13.12%. Calcd for [Co(ac)(Hgly)(en)$_2$](ClO$_4$)$_2$·H$_2$O: C, 18.12; H, 4.94; N, 13.21%.

trans*(*O*)-(Acetato)(β-alanine)bis(ethylenediamine)cobalt(III) Perchlorate (*trans*(*O*)-[Co(ac)(β-Hala)(en)$_2$](ClO$_4$)$_2$):* The mixed ligand complex with acetate and β-alanine (β-Hala) was prepared by a procedure similar to that described for the *trans*(*O*)-[Co(ac)(Hgly)(en)$_2$](ClO$_4$)$_2$. Found: C, 20.51; H, 5.07; N, 13.22%. Calcd for [Co(ac)(β-Hala)(en)$_2$](ClO$_4$)$_2$: C, 20.54; H, 4.98; N, 13.31%.

Other complexes, *trans*(*O*)-[Co(Haa)$_2$(en)$_2$]$^{3+}$ (Haa=L-alanine, β-alanine, γ-aminobutyric acid, hydroxyl-L-proline, glycine, L-leucine, L-proline, and L-serine)[32] and *trans*(*O*)-

[Co(a)$_2$(en)$_2$]$^+$ (a=acetate, propionate, and butyrate anions),[30] examined in this study, were prepared by the methods described in the references.

Measurements. The electronic absorption spectra of the complexes were measured with Hitachi 557 spectrophotometer in aqueous solution. The ^{13}C-NMR spectra were measured on a JEOL Model MFT-100 spectrometer in pulsed Fourier transform/proton noise decoupled mode at 25.15 MHz in deuterium oxide solution. The ^{13}C chemical shifts were measured relative to benzene (capillary) and converted into chemical shifts from TMS by the relation

$\delta_{TMS}=\delta_{benzene}-128.5$ (ppm).[26]

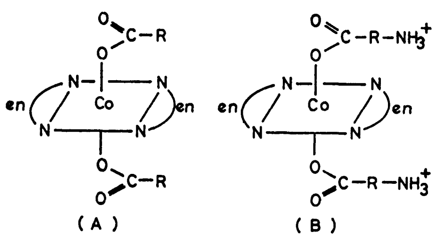


Fig. 1. Structures of the *trans*(*O*)-[Co(O)$_2$(N)$_4$] type complexes.
(A): *trans*(*O*)-[Co(OCO–R)$_2$(en)$_2$]$^+$ (OCO–R= fatty acid), (B): *trans*(*O*)-[Co(OCO–R–NH$_3^+$)$_2$(en)$_2$]$^{3+}$ (OCO–R–NH$_3^+$=amino acid).

Results and Discussion

At least three factors are important in determining carbon chemical shifts. These are the diamagnetic term (σ_d), the paramagnetic term (σ_p), and the anisotropy of neiboring atoms (σ_{others}).[29] Of these terms, σ_p makes major contribution to carbon chemical shifts.[26] The σ_p was related to the charge density, bond order of the carbon, and other factors (the averaged excitation energy (ΔE), the mean inverse cube radius for the carbon 2p orbitals ($<r^{-3}>_{2p}$), and so on) by Karplus *et al.*[26] The ^{13}C chemical shifts are mainly influenced by the electron density of the carbons in a series of related compounds, if the differences in the σ_d, σ_{others}, and ΔE among the carbons under consideration are small. This was experimentally demonstrated by Horsley *et al.*[27] and Miyajima *et al.*[28] who plotted the ^{13}C chemical shifts against the charge density changes of the carbons in the substituted compounds relative to the parent compound.

The change of the substituent at α-carbon of carboxylic acid is attended with the change in the electron density at the carboxyl group, which is one of the reasons of the chemical shift change of the carboxyl carbon in the acid. It is expected that the change in the electron density at the carboxyl group also brings about the band shift in the first absorption band region of the cobalt(III) complex. The complex of the type *trans*(*O*)-[Co(OCO–R)$_2$(en)$_2$]$^{n+}$ is suitable to study this effect, because the ^1E_g component in the first absorption band is sufficiently apart from another component[30,31] ($^1A_{2g}$) in the same band (Fig. 2).

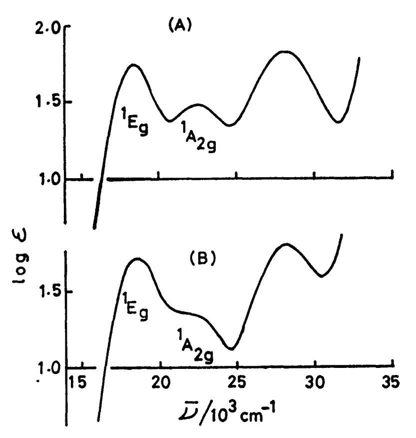


Fig. 2. Absorption spectra of the *trans*(*O*)-[Co(O)$_2$(N)$_4$] type complexes.
(A): *trans*(*O*)-[Co(Hgly)$_2$(en)$_2$]$^{3+}$, (B): *trans*(*O*)-[Co(bu)$_2$(en)$_2$]$^+$ (bu=butyrate anion).

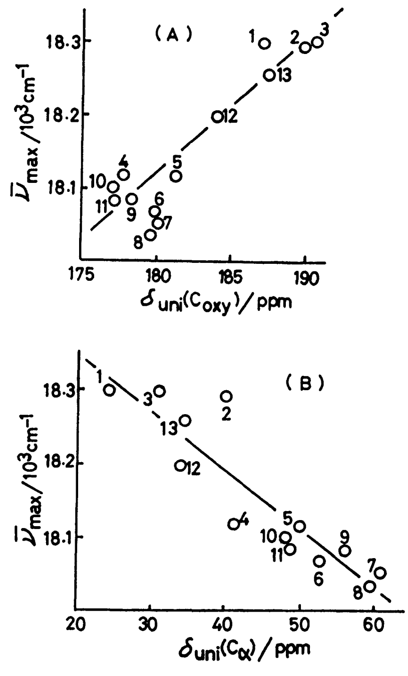
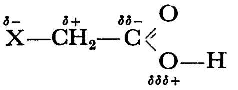


Fig. 3. Plots of first absorption maxima (^1E_g) of *trans*(*O*)-[Co(O)$_2$(N)$_4$] type complexes *vs.* ^{13}C chemical shifts. (A): For carboxyl carbon (C_{oxy}), (B): for α-carbon (C_α). 1: Acetic acid, 2: butyric acid, 3: propionic acid, 4: glycine, 5: L-alanine, 6: L-leucine, 7: L-proline, 8: hydroxy-L-proline, 9: L-serine, 10: *N*-ethylglycine, 11: *N*-propylglycine, 12: β-alanine, 13: γ-aminobutyric acid.

The plots of $\tilde{\nu}_{max}$ (^1E_g component of the first absorption band) *vs.* $\delta_{uni}(C_{oxy})$ and $\tilde{\nu}_{max}$ *vs.* $\delta_{uni}(C\alpha)$ are shown in Fig. 3. The data provided here reveal that the linear correlations are present between $\tilde{\nu}_{max}$ and $\delta_{uni}(C_{oxy})$ and between $\tilde{\nu}_{max}$ and $\delta_{uni}(C\alpha)$. That is to say, both the $\delta_{uni}(C_{oxy})$ and $\delta_{uni}(C\alpha)$ values are closely related to the ligand field of the carboxylic acid. The sign of the slope of Fig. 3(A) is opposite to that of the slope of Fig. 3(B). If we assume that the chemical shift of the carbon is related to the electron density as mentioned above, the following consideration is possible. The substituent at α-carbon which causes a decrease of the electron density on the α-carbon will cause an increase of the π-electron density on the carboxyl carbon neighboring to the α-carbon and cause a decrease of the electron density on the oxygen atom of the carboxyl group. These processes are shown in the following scheme. A decrease of the electron density on the



$$\overset{\delta-}{X}—\overset{\delta+}{C}H_2—\overset{\delta\delta-}{C}\langle^{O}_{\underset{\delta\delta\delta+}{O}—H}$$

(as compared with CH_3COOH)

coordinated oxygen atom weakens the ligand field of the carboxylic acid, and increases of the electron densities on the α- and carboxyl carbon cause the shift changes of their ^{13}C-NMR to higher field side. Accordingly, the $\bar{\nu}_{max}$ value becomes larger as the $\delta_{uni}(C_{oxy})$ value becomes larger (to lower field) and the $\delta_{uni}(C\alpha)$ becomes smaller (to higher field).

The consideration mentioned above is based on the effect from the substituent at α-carbon. Another effect to be taken into account is that from the cobalt(III) chromophore. Making a rough estimation, the substituent effect at α-carbon nearly equals in both *trans(O)*-$[Co(OCO\text{-}R)_2(en)_2]^{n+}$ and free carboxylic acid. Therefore, the effect from the substituent at α-carbon may be cancelled for the $\Delta_{uni}(C\alpha)$. The $\Delta_{uni}(C\alpha)$ value should be related rather to the residual effect which will originate from the cobalt(III). Accordingly, the relation between $\Delta_{uni}(C\alpha)$ and $\bar{\nu}_{max}$ may be more intimate than that between $\delta_{uni}(C\alpha)$ and $\bar{\nu}_{max}$. Similarly, the relation between $\Delta_{uni}(C_{oxy})$ and $\bar{\nu}_{max}$ may be more intimate than that between $\delta_{uni}(C_{oxy})$ and $\bar{\nu}_{max}$. Figure 4 shows the plots of $\Delta_{uni}(C_{oxy})$ *vs.* $\bar{\nu}_{max}$ and $\Delta_{uni}(C\alpha)$ *vs.* $\bar{\nu}_{max}$. There are linear relations between them. These relations can be represented by the following equations. Where r and N are correlation

$$\Delta_{uni}\,(C_{oxy})/\text{ppm} = 12.37\,\bar{\nu}_{max}/10^3\,\text{cm}^{-1} - 216.62$$
$$(r = 0.96,\ N = 13)$$

$$\Delta_{uni}\,(C_\alpha)/\text{ppm} = 13.79\,\bar{\nu}_{max}/10^3\,\text{cm}^{-1} - 248.22$$
$$(r = 0.95,\ N = 13)$$

coefficient and number of measurements, respectively. The slopes for the two equations are nearly equal to each other with the same sign. Though one might think that the Δ_{uni} value results from the magnetic anisotropy arising from the cobalt(III) chromophore,[33] the calculated chemical shift changes based on the anisotropy are much smaller than the observed ones.

In the present study, we prepared the mixed ligand complexes of the type *trans(O)*-$[Co(OCO\text{-}R)(OCO\text{-}R')(en)_2]^{n+}$. The $\bar{\nu}_{max}$ values of the mixed type complexes are nearly equal to the mean value of the two $\bar{\nu}_{max}$ of *trans(O)*-$[Co(OCO\text{-}R)_2(en)_2]^{n+}$ and -$[Co(OCO\text{-}R')_2(en)_2]^{n+}$. That is, the $\bar{\nu}_{max}$ of *trans(O)*-$[Co(ac)(Hgly)(en)_2]^{2+}$ (18.21×10^3 cm^{-1}) is nearly equal to the mean value (18.21×10^3 cm^{-1}) of the two $\bar{\nu}_{max}$ of *trans(O)*-$[Co(ac)_2(en)_2]^+$ (18.30×10^3 cm^{-1}) and *trans(O)*-$[Co(Hgly)_2(en)_2]^{3+}$ (18.12×10^3 cm^{-1}). Similar relation was observed for *trans(O)*-$[Co(ac)(\beta\text{-Hala})(en)_2]^{2+}$, -$[Co(ac)_2(en)_2]^+$, and -$[Co(\beta\text{-Hala})_2(en)_2]^{3+}$ (Table 1). These results suggest that the ^1E_g component of the mixed type complex can be expressed by the two ligand fields of *trans*-position. On the other hand, the $\Delta_{uni}(C_{oxy})$ and $\Delta_{uni}(C\alpha)$ values of the mixed

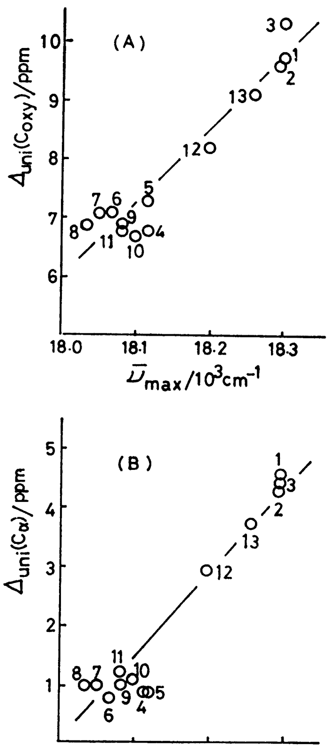


Fig. 4. Plots of ^{13}C chemical shift changes *vs.* first absorption maxima of the *trans(O)*-$[Co(O)_2(N)_4]$ type complexes.
(A): For carboxyl carbon (C_{oxy}), (B): for α-carbon (C_α). Numbers making the data plots correspond to the ordinal numbers of the complexes in Fig. 3.

TABLE 1. ABSORPTION MAXIMA OF THE *trans(O)*-$[Co(OCO\text{-}R)_2(en)_2]^{n+}$ TYPE COMPLEXES

trans(O) type complexes	$\bar{\nu}_{max}/10^3$ cm^{-1}
$[Co(Hgly)_2(en)_2]^{3+}$	18.12
$[Co(\beta\text{-Hala})_2(en)_2]^{3+}$	18.20
$[Co(ac)_2(en)_2]^+$	18.30
$[Co(ac)(Hgly)(en)_2]^{2+}$	18.21
$[Co(ac)(\beta\text{-Hala})(en)_2]^{2+}$	18.26

TABLE 2. CHEMICAL SHIFT CHANGES OF THE *trans(O)*-$[Co(OCO\text{-}R)_2(en)_2]^{n+}$ TYPE COMPLEXES

Carboxylic acid[a]	*trans(O)* type complexes	$\Delta_{uni}(C_{oxy})$ ppm	$\Delta_{uni}(C_\alpha)$ ppm
ac	$[Co(ac)_2(en)_2]^+$	+9.7	+4.5
Hgly	$[Co(Hgly)_2(en)_2]^{3+}$	+6.8	+0.9
β-Hala	$[Co(\beta\text{-Hala})_2(en)_2]^{3+}$	+8.2	+2.9
ac	$[Co(ac)(Hgly)(en)_2]^{2+}$	+9.7	+4.5
Hgly		+6.7	+1.0
ac	$[Co(ac)(\beta\text{-Hala})(en)_2]^{2+}$	+9.9	+3.8
β-Hala		+8.2	+2.4

a) ac = CH_3COO^-, Hgly = $CH_2(NH_3^+)COO^-$, and β-Hala = $CH_2(NH_3^+)CH_2COO^-$.

type complex are nearly equal to those of the corresponding ligands in the *trans*(*O*)-[Co(OCO–R)$_2$(en)$_2$]$^{n+}$ and -[Co(OCO–R')$_2$(en)$_2$]$^{n+}$ complexes but not to the mean value (Table 2).

Ćelap *et al.*[23,24] and Stewrat *et al.*[11] pointed out that the ^{13}C chemical shift of a ligand is affected by another ligand at *trans*-position to it. However, no distinctive difference of the *trans*-effect was observable for the complexes examined in the present study. That is to say, the ^{13}C resonance peaks of a carboxylate ligand in the mixed complex appears independently of another carboxylate ligand at *trans*-position. These results suggest that the *trans*-effect is not necessarily to be connected directly with the linearities in Figs. 4(A) and 4(B). Therefore, one should consider the effects (the through-space and through-bond effects of cobalt(III) ion, *etc.*) other than the *trans*-effect, which is responsible for the difference of the Δ_{uni} values, relating to the electron density. What effect is most responsible to the Δ_{uni} values is very interesting problem. However, there are some uncertain points remaining at present stage, although some of them were clarified by this study.

It has been clarified by this study that the chemical shifts of the coordinated carboxylic acids are closely related to the ligand fields of the acids and demonstrated that the ^{13}C chemical shifts are useful to estimate the ligand fields of the carboxylic acids.

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