July, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***60***, *2573—2580 (1987)* 2573

# Preparation, Structure, and Circular Dichroism Spectra of [Co(L$_1$)(L$_2$)]$^+$-Type Complexes (L$_1$=Iminodiacetato or *N*-Methyliminodiacetato and L$_2$=3-Azapentane-1,5-diamine or 3-Methyl-3-azapentane-1,5-diamine)

Takaji Yasui,* Ken-ichi Okamoto,† Jinsai Hidaka,† Tomoharu Ama,
and Hiroshi Kawaguchi
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780
†Department of Chemistry, University of Tsukuba, Sakura, Ibaraki 305

(Received January 29, 1987)

Three geometrical isomers (mer, u-fac, and s-fac) possible in each of [Co(ida)(mdien)]$^+$ and [Co(mida)(mdien)]$^+$ and u-fac isomer of [Co(mida)(dien)]$^+$ (ida=iminodiacetate, mida=*N*-methyliminodiacetate, mdien=3-methyl-3-azapentane-1,5-diamine, and dien=3-azapentane-1,5-diamine) were newly prepared, and the u-fac isomers were optically resolved. The geometrical structures of these isomers were assigned on the basis of their absorption and $^{13}$C NMR spectral data. The crystal structure of $(+)^{\rm CD}_{550}$-*u-fac*-[Co(ida)(mdien)]$\cdot$$(+)^{\rm CD}_{575}$-[Co(ox)$_2$(en)]$\cdot$6H$_2$O was determined by X-ray diffraction method. The crystal is monoclinic, space group $P2_1$, $a$=15.793(6), $b$=12.855(3), $c$=7.070(2) Å, $\beta$=96.80(5)°, and $Z$=2. Both of the absolute configurations of the two complex ions take Λ configuration. The relationship between the absolute configurations and the CD spectral behaviors of the u-fac isomers is also discussed.

The mixed-ligand complexes of cobalt(III) with imino-diacetate (ida) or *N*-methyliminodiacetate (mida) and 3-azapentane-1,5-diamine (dien) or 3-methyl-3-azapentane-1,5-diamine (mdien) as the terdentate ligands can exist in three geometrical isomeric forms (mer, u-fac, and s-fac), as shown in Fig. 1. All of the three isomers have been first isolated for [Co(ida)(dien)]$^+$, while the mer and s-fac isomers except for u-fac have been isolated for [Co(mida)(dien)]$^+$.[1] The structures of these isomers were assigned based on their visible absorption and $^1$H NMR spectra.[1] The u-fac isomer of [Co(ida)(dien)]$^+$, which has a chiral structure, was optically resolved by Yoshikawa et al., and the absolute configuration was assigned as ΛΔΛ for the $(-)_{589}$ isomer on the basis of the CD spectrum.[2] Koine et al. reported optical resolution of the mer isomer for [Co(mida)(dien)]$^+$.[3] Gailey et al.[4] and Kawamoto et al.[5] studied, respectively, the $^{13}$C NMR spectra and the Raman spectra of the [Co(ida)$_n$(dien)$_{2-n}$]-type complexes.

Previously, we reported the methods to prepare all the geometrical isomers possible in [Co(ida)$_2$]$^-$,[6] [Co(mida)$_2$]$^-$,[7] [Co(ida)(mida)]$^-$,[6,8] [Co(edma)$_2$]$^+$,[9] [Co(ida)(edma)],[10] and [Co(mida)(edma)].[11] All the preparative reactions were performed under weakly acidic conditions.[6–11]

In the present paper, the preparations of the mixed-ligand type complexes, [Co(ida)(mdien)]$^+$ and [Co(mida)(mdien)]$^+$, will be described, and all the isomers isolated will be characterized on the basis of their absorption and $^{13}$C NMR spectral data. In addition, we report the crystal structure of $(+)^{\rm CD}_{550}$-*u-fac*-[Co(ida)(mdien)]$\cdot$$(+)^{\rm CD}_{575}$-[Co(ox)$_2$(en)]$\cdot$6H$_2$O and will discuss on the relationship between the CD spectral behaviors of the u-fac isomers and the absolute configurations.

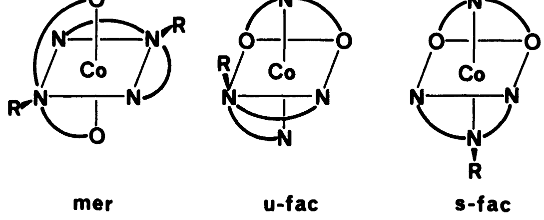

Fig. 1. Three geometrical isomers possible in [Co(Rida)(Rdien)]$^+$ (R=H or CH$_3$).

## Experimental

**Ligands.** Iminodiacetic acid (H$_2$ida) and 3-azapentane-1,5-diamine (dien) were obtained commercially from Wako Pure Chemical Industries, Ltd. and used without further purification. *N*-Methyliminodiacetic acid[12] (H$_2$mida) and 3-methyl-3-azapentane-1,5-diamine trihydrochloride[13] (mdien$\cdot$3HCl) were synthesized by the methods described in the literatures.

**Preparation of Complexes. Three Isomers (mer, u-fac, and s-fac) of [Co(mida)(mdien)]$^+$:** An aqueous solution containing 4.5 g (0.02 mol) of mdien$\cdot$3HCl in 100 cm$^3$ of water was passed through a short Dowex 1X8 (OH$^-$ form) column. The column was washed with ca. 100 cm$^3$ of water. Three grams (0.02 mol) of H$_2$mida and 4.8 g (0.02 mol) of CoCl$_2$$\cdot$6H$_2$O were added to the combined solution of eluate and washings, and the resulting solution was adjusted to pH 6 with 1 mol dm$^{-3}$ NaOH solution. Lead dioxide (15 g, excess) was added into the solution with stirring. After stirring for 30 min at 50 °C, the solution was filtered to remove insoluble materials. The filtrate was poured onto an SP-Sephadex C-25 column ($\phi$4.7 cm×50 cm, K$^+$ form). The adsorbed band, which was not eluted with water, was separated into two bands of purplish-red and orange colors by elution with 0.2 mol dm$^{-3}$ KCl solution. The purplish-red band containing desired complexes was transferred into another SP-Sephadex C-25 column ($\phi$4.7 cm×90 cm, K$^+$

form) and developed with the same eluent. The band separated into two bands of reddish-purple (first-eluted isomer: mer) and pinkish-red (a mixture of u-fac and s-fac isomers) colors. The reddish-purple band was eluted out. The pinkish-red band was transferred into another SP-Sephadex column ($\phi$4.7 cm×90 cm, $NH_4^+$ form) and developed with 0.1 mol dm$^{-3}$ $(NH_4)_2SO_4$ solution. The band easily separated into two bands of red (second-eluted isomer: s-fac) and purple (third-eluted isomer: u-fac) colors.

The reddish-purple eluate containing mer isomer was concentrated under reduced pressure and a large amount of methanol was added to the concentrated solution to eliminate potassium chloride. After methanolic solution was again concentrated, a crude complex was obtained by addition of methanol to the concentrated solution. The crude complex was recrystallized from a small amount of water by addition of a mixture (1:3) of methanol and ethanol. The crude crystals of the u-fac and s-fac isomers were also obtained as sulfate salts from the eluates of the red and purple bands, respectively, by the procedure similar to that described for the mer isomer above. By the use of a short QAE-Sephadex A-25 ($Cl^-$ form) column, the sulfate salts of the u-fac and s-fac isomers were changed to the chloride salts, which were recrystallized from a small amount of water by addition of methanol. The formation molar ratio of the three isomers was mer:u-fac:s-fac=3:7:90. Found for the mer isomer: C, 30.44; H, 6.80; N, 14.31%. Calcd for [Co(mida)(mdien)]Cl·$2H_2O$=$C_{10}H_{26}N_4O_6ClCo$: C, 30.58; H, 6.67; N, 14.27%. Found for the u-fac isomer: C, 29.26; H, 6.84; N, 13.56%. Calcd for [Co(mida)(mdien)]Cl·$3H_2O$=$C_{10}H_{28}N_4O_7ClCo$: C, 29.24; H, 6.87; N, 13.64%. Found for the s-fac isomer: C, 31.30; H, 6.61; N, 14.75%. Calcd for [Co(mida)(mdien)]Cl·$1.5H_2O$=$C_{10}H_{25}N_4O_{5.5}ClCo$: C, 31.30; H, 6.57; N, 14.60%.

**Three Isomers of [Co(ida)(mdien)]$^+$:** The mer, u-fac, and s-fac isomers of this complex were obtained by the same method as that used for [Co(mida)(mdien)]Cl, except that the crystals of the u-fac isomer were obtained by converting the chloride salt to the bromide salt. The formation molar ratio was mer:u-fac:s-fac=4:42:54. Found for the mer isomer: C, 28.71; H, 6.33; N, 15.02%. Calcd for [Co(ida)(mdien)]Cl·$2H_2O$=$C_9H_{24}N_4O_6ClCo$: C, 28.54; H, 6.39; N, 14.79%. Found for the u-fac isomer: C, 26.52; H, 5.57; N, 13.78%. Calcd for [Co(ida)(mdien)]Br·$H_2O$=$C_9H_{22}N_4O_5BrCo$: C, 26.68; H, 5.47; N, 13.83%. Found for the s-fac isomer: C, 29.28; H, 6.28; N, 15.02%. Calcd for [Co(ida)(mdien)]Cl·$1.5H_2O$=$C_9H_{23}N_4O_{5.5}ClCo$: C, 29.24; H, 6.27; N, 15.16%.

**Three Isomers of [Co(mida)(dien)]$^+$ and [Co(ida)(dien)]$^+$:** Two isomers (mer and s-fac) of [Co(mida)(dien)]$^+$ and three isomers of [Co(ida)(dien)]$^+$ were already reported, but there is no report for the u-fac isomer of [Co(mida)(dien)]$^+$. In the present work all the three isomers of these complexes were obtained by the same method as that described above. The formation molar ratios were mer:u-fac:s-fac=23:18:59 for [Co(mida)(dien)]$^+$ and 24:46:30 for [Co(ida)(dien)]$^+$. Found for the newly prepared u-fac isomer: C, 29.34; H, 6.04; N, 15.03%. Calcd for [Co(mida)(dien)]Cl·$1.5H_2O$=$C_9H_{23}N_4O_{5.5}ClCo$: C, 29.24; H, 6.27; N, 15.16%. The chemical formulas of the other isomers were as follows: *mer*-[Co(mida)(dien)]Cl·$1.5H_2O$, *s-fac*-[Co(mida)(dien)]Cl, *mer*-[Co(ida)(dien)]Cl·$H_2O$, and *u-fac*- and *s-fac*-[Co(ida)(dien)]Cl·$0.5H_2O$.

**Optical Resolution.** The racemic u-fac isomers of the four complexes were optically resolved on an SP-Sephadex column using $K_2Sb_2$(*d*-tart)$_2$ aqueous solution as an eluent.

**(+)$^{CD}_{564}$-*u-fac*-[Co(mida)(mdien)]Cl·$3H_2O$:** A solution containing ca. 1.0 g of racemic *u-fac*-[Co(mida)(mdien)]Cl·$3H_2O$ in a small amount of water was poured onto an SP-Sephadex C-25 column ($\phi$4.7 cm×90 cm, $K^+$ form). The adsorbed band was developed with a 0.05 mol dm$^{-3}$ $K_2Sb_2$(*d*-tart)$_2$ solution. After the band had been separated completely into two, each band was eluted out with a 0.1 mol dm$^{-3}$ KCl solution. Each eluate was concentrated under reduced pressure and then ethanol was added to the concentrated solution. Potassium chloride which deposited out was removed by filtration and the filtrate was concentrated to a small volume. Ethanol was added to the concentrated solution and the ethanolic solution was kept in a refrigerator overnight. Violet crystals which deposited were collected by filtration and recrystallized from water by addition of ethanol. The (+)$^{CD}_{564}$ and (−)$^{CD}_{564}$ isomers were obtained from the front and rear eluates, respectively. Found for the (+)$^{CD}_{564}$ isomer: C, 29.37; H, 6.69; N, 13.64%. Calcd for [Co(mida)(mdien)]Cl·$3H_2O$=$C_{10}H_{28}N_4O_7ClCo$: C, 29.24; H, 6.87; N, 13.64%.

**(+)$^{CD}_{550}$-*u-fac*-[Co(ida)(mdien)]Cl·$1.5H_2O$, (+)$^{CD}_{544}$-*u-fac*-[Co(mida)(dien)]Cl·$0.5H_2O$, and (+)$^{CD}_{538}$-*u-fac*-[Co(ida)(dien)]Cl·$2H_2O$:** The racemates were also optically resolved in the same manner as that described for [Co(mida)(mdien)]$^+$. Found for the early eluted (+)$^{CD}_{550}$ isomer: C, 29.34; H, 6.25; N, 15.13%. Calcd for [Co(ida)(mdien)]Cl·$1.5H_2O$=$C_9H_{23}N_4O_{5.5}ClCo$: C, 29.24; H, 6.27; N, 15.16%. Found for the late eluted (+)$^{CD}_{544}$ isomer: C, 31.08; H, 6.05; N, 16.05%. Calcd for [Co(mida)(dien)]Cl·$0.5H_2O$=$C_9H_{21}N_4O_{4.5}ClCo$: C, 30.74; H, 6.02; N, 15.93%. Found for the late eluted (+)$^{CD}_{538}$ isomer: C, 26.59; H, 6.05; N, 15.49%. Calcd for [Co(ida)(dien)]Cl·$2H_2O$=$C_8H_{22}N_4O_6ClCo$: C, 26.35; H, 6.08; N, 15.36%. Previously, Okamoto et al. isolated this isomer as a monohydrate.[14]

**X-Ray Analysis of (+)$^{CD}_{550}$-*u-fac*-[Co(ida)(mdien)]·(+)$^{CD}_{575}$-[Co(ox)$_2$(en)]·$6H_2O$.** This diastereomer was prepared by adding methanol to the solution obtained by passing an aqueous solution of (+)$^{CD}_{550}$-*u-fac*-[Co(ida)(mdien)]Cl through a short QAE-Sephadex column of (+)$^{CD}_{575}$-[Co(ox)$_2$(en)]$^-$ form.

Unit cell parameters and intensity data for the single crystal (ca. 0.09×0.22×0.40 mm$^3$) were measured on a Rigakudenki four-circle diffractometer (AFC-5) with graphite-monochromatized Mo $K\alpha$ radiation. The unit cell parameters were determined by a least-squares refinement based on 25 reflections ($20<2\theta<30°$). Systematic absences led to the space group $P2_1$. Crystal Data: $Co_2C_{15}H_{40}N_6O_{18}$, M.W.=710.4, monoclinic, space group $P2_1$, $a$=15.793(6), $b$=12.855(3), $c$=7.070(2) Å, $\beta$=96.80(5)°, $V$=1425.3(8) Å$^3$, $D_x$=1.655 g cm$^{-3}$, $D_m$=1.66(1) g cm$^{-3}$, $Z$=2, and $\mu$(Mo $K\alpha$)= 1.303 mm$^{-1}$.

The intensity data were collected by the $\omega$—$2\theta$ scan technique up to $2\theta$=60° with scan rate of 3° min$^{-1}$. The intensity data were converted to the Fo data in the usual manner. Absorption corrections were not applied. A total of 3864 independent reflections with $|F_o|>3\sigma(|F_o|)$ of the measured 4664 reflections were considered as 'observed' and used for the structure analysis.

The position of one cobalt atom was determined from a three-dimensional Patterson function. The difference-Fourier maps based on the cobalt position revealed the other cobalt position and then all non-hydrogen atoms. The structure was refined by a full-matrix least-squares refinement using the positional parameters, the anisotropic thermal parameters of the non-hydrogen atoms of the complex ions, and the isotropic thermal parameters of the non-hydrogen atoms of the water molecules (program RFINE by L. W. Finger[15] was used). The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literatures.[16,17] The final residual values were $R$=0.061 and $R_w$=0.066, respectively. We attempted to determine the absolute configurations of the complex ions by an anomalous-scattering technique. When the refinements were carried out by use of a set of the atomic parameters containing the Λ configuration of the complex ions (*Λ*- or *ΛΔΛ-u-fac*-$[Co(ida)(mdien)]^+$ and *Λ*-$[Co(ox)_2(en)]^-$), the residual values converged to $R$=0.058 and $R$w=0.059, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (*Δ*- or *ΔΛΔ-u-fac*-$[Co(ida)(mdien)]^+$ and *Δ*-$[Co(ox)_2(en)]^-$) resulted in the residual values of $R$=0.060 and $R_w$=0.062, respectively. These facts suggest that the former is probably the correct choice. This absolute configuration coincides with the result that $(+)^{CD}_{575}$-$[Co(ox)_2(en)]^-$, which was used as an internal reference, has been assigned to the Λ configuration based on the CD spectral behavior.[18]

The final positional parameters are listed in Table 1. A list of structure factors (Table A) and anisotropic thermal parameters of non-hydrogen atoms of the complex ions (Table B) are kept at the Chemical Society of Japan as Document No. 8745.

**Measurements.** The X-ray analysis calculations were carried out on a FACOM M-382 computer at the University of Tsukuba. The absorption and CD spectra were measured by a Hitachi 557-type spectrometer and a JASCO J-22 spectropolarimeter, respectively. The $^{13}C$ NMR spectra at 25 MHz were recorded on a JEOL JNM-FX 100 spectrometer. The peak positions were measured relative to internal dioxane ($\delta$=67.40).

## Results and Discussion

**Formation Ratio of the Geometrical Isomers.** In the previous studies concerning the reactivity of the $[Co(ida)_2]^-$ (and $[Co(ida)(mida)]^-$)[8] and $[Co(mida)_2]^-$[7] complexes, it was revealed that the mer isomer of the first complex easily isomerizes to u-fac and s-fac isomers in a basic aqueous solution and that the u-fac isomer of the third complex decomposes accompanying reduction of Co(III) to Co(II).

In the bis(terdentate) complexes, the formation ratio of the possible geometrical isomers varied largely with the stereochemistry of the chelate rings and reaction conditions (pH, temperature, etc.). The preparative reaction under basic conditions or using a catalyst such as activated carbon restricted the formation of less stable isomers.[1] As described in the Experimental section, however, the preparation of the present complexes under weakly acidic conditions provided all of the possible isomers. The formation ratios of the three isomers were mer:u-fac:s-fac=24:46:30 for $[Co(ida)(dien)]^+$, 23:18:59 for $[Co(mida)(dien)]^+$, 4:42:54 for $[Co(ida)(mdien)]^+$, 3:7:90 for [Co(mida)-

Table 1. Position and Thermal Parameters (with e.s.d.'s)

| Atom | $X$ | $Y$ | $Z$ | $B_{eq}/Å^2$ a) | Atom | $X$ | $Y$ | $Z$ | $B_{eq}/Å^2$ a) |
|---|---|---|---|---|---|---|---|---|---|
| CoA | 0.08995(5) | 0.25000 | 0.1395(1) | 1.70 | OB1 | 0.2804(3) | 0.4286(4) | 0.7990(7) | 2.97 |
| NA1 | −0.0205(3) | 0.1759(4) | 0.1314(7) | 1.82 | OB2 | 0.3308(4) | 0.2654(5) | 0.8152(9) | 4.88 |
| NA2 | 0.1984(3) | 0.3144(5) | 0.1031(8) | 2.45 | OB3 | 0.4292(3) | 0.5057(5) | 0.7596(7) | 3.19 |
| NA3 | 0.1507(3) | 0.1910(5) | 0.3798(7) | 2.39 | OB4 | 0.4868(4) | 0.3467(5) | 0.7375(10) | 5.17 |
| NA4 | 0.0578(4) | 0.3648(5) | 0.2939(8) | 2.50 | OB5 | 0.3008(3) | 0.5415(4) | 0.4823(6) | 2.69 |
| OA1 | 0.1261(3) | 0.1373(4) | −0.0049(6) | 2.42 | OB6 | 0.1912(3) | 0.5350(4) | 0.2538(7) | 3.05 |
| OA2 | 0.0853(3) | −0.0109(4) | −0.1448(7) | 3.05 | OB7 | 0.2082(3) | 0.6160(4) | 0.7294(6) | 2.94 |
| OA3 | 0.0384(3) | 0.3166(4) | −0.0841(6) | 2.26 | OB8 | 0.0913(3) | 0.6147(5) | 0.5211(7) | 3.71 |
| OA4 | −0.0882(3) | 0.3532(5) | −0.2472(7) | 3.53 | CB1 | 0.3405(5) | 0.3608(6) | 0.7946(11) | 3.38 |
| CA1 | 0.0718(4) | 0.0672(5) | −0.0475(8) | 2.12 | CB2 | 0.4262(5) | 0.4036(6) | 0.7599(11) | 3.17 |
| CA2 | −0.0126(4) | 0.0738(6) | 0.0335(10) | 2.74 | CB3 | 0.2243(4) | 0.5562(6) | 0·4179(9) | 2.38 |
| CA3 | −0.0866(4) | 0.2427(6) | 0.0241(9) | 2.43 | CB4 | 0.1665(4) | 0.5982(5) | 0.5642(9) | 2.20 |
| CA4 | −0.0432(4) | 0.3085(5) | −0.1167(9) | 2.15 | CB5 | 0.3512(7) | 0.7071(9) | 1.0516(15) | 5.79 |
| CA5 | 0.2674(4) | 0.2872(7) | 0.2597(11) | 3.44 | CB6 | 0.4075(6) | 0.7413(9) | 0.8985(14) | 5.20 |
| CA6 | 0.2438(4) | 0.1838(7) | 0.3511(11) | 3.18 | OW1 | 0.4674(6) | 0.4672(9) | 0.2364(14) | 10.19 b) |
| CA7 | 0.1221(5) | 0.0859(7) | 0.4286(12) | 4.02 | OW2 | 0.2518(5) | 0.8461(7) | 0.4442(11) | 6.92 b) |
| CA8 | 0.1380(5) | 0.2683(7) | 0.5377(10) | 3.89 | OW3 | 0.2480(5) | 0.9294(7) | 0.8046(11) | 7.02 b) |
| CA9 | 0.0580(5) | 0.3280(7) | 0.4912(10) | 3.60 | OW4 | 0.3810(6) | 0.0632(10) | 0.9303(15) | 10.60 b) |
| CoB | 0.32075(6) | 0.5644(1) | 0.7523(1) | 2.37 | OW5 | 0.4765(6) | 0.1783(10) | 0.4669(16) | 10.39 b) |
| NB1 | 0.3351(4) | 0.5930(5) | 1.0221(8) | 3.31 | OW6 | 0.3804(7) | 0.9808(10) | 0.3219(16) | 12.04 b) |
| NB2 | 0.3691(4) | 0.6995(5) | 0.7142(10) | 3.52 | | | | | |

a) $B_{eq}=8\pi^2(U_{12}+U_{22}+U_{33})/3$. b) Isotropic temperature factor.

(mdien)]$^+$. When activated carbon was used as a catalyst,[1] the ratios for the first and second complexes (12:29:59 for [Co(ida)(dien)]$^+$ and 20:0:80 for [Co(mida)(dien)]$^+$) differ from the above ratios. These differences suggest that the formation ratios of the isomers depend not only on a thermodynamic factor but also largely on a kinetic factor. The small ratio of the u-fac isomer in [Co(mida)(mdien)]$^+$ is surely attributed to a strong intramolecular repulsion between the coordinating mida and mdien ligands. However, the small ratios of the mer isomers in [Co(ida)(mdien)]$^+$ and [Co(mida)(mdien)]$^+$ can not be explained only by such the repulsion.

**Geometrical Structure.** Previously, the structures of three geometrical isomers of [Co(ida)(dien)]$^+$ have been assigned on the basis of the visible absorption and $^1$H NMR spectral data.[1] Figure 2 shows the absorption spectra of the mer, u-fac, and s-fac isomers of [Co(ida)(dien)]$^+$ and the newly isolated isomers of [Co(mida)(mdien)]$^+$, and their spectral data are summarized in Table 2, together with those of [Co(mida)(dien)]$^+$ and [Co(ida)(mdien)]$^+$.

For the four complexes, the geometrical isomers which were obtained in the same elution order on a column-chromatographic separation showed quite similar spectral behaviors to one another in the visible absorption region. Such spectral behaviors suggest that the isomers correspond to one another in geometry. All the first-eluted isomers exhibited the first bands with a shoulder (or broad band) in the shorter wavelength side (Fig. 2), which is generally observed for the *trans(O)*-[Co(N)$_4$(O)$_2$]-type complex.[19] This indicates that the structure of these isomers may be assigned to mer.

The structural assignments for the second- and third-eluted isomers of the new complexes can be made on the basis of their $^{13}$C NMR data. Figure 3 shows a stick diagram of the $^{13}$C resonance position for all the isomers. The most simple resonance patterns of the third-eluted isomers are due to two equivalent chelate rings in each of terdentate ligands and indicate that the third-eluted isomers take the s-fac structure having a mirror plane.

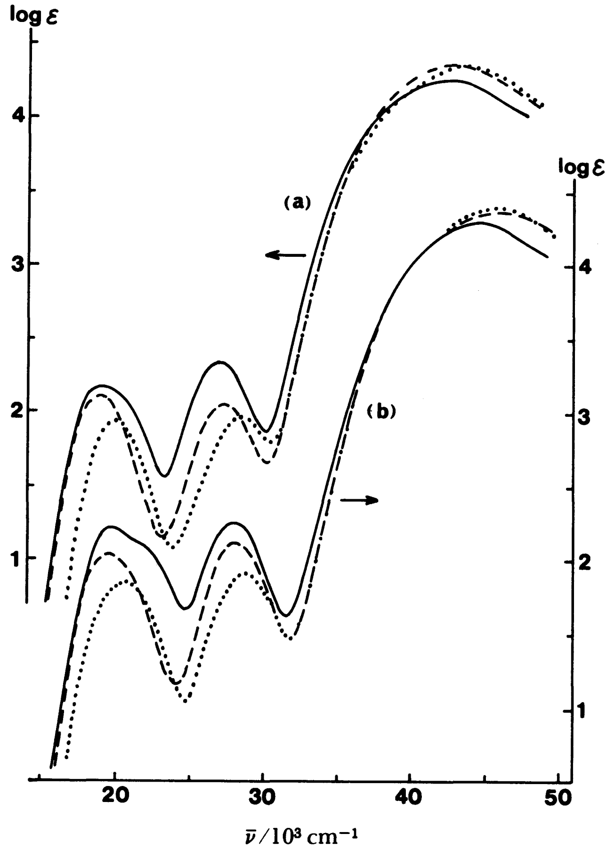

Fig. 2. Absorption spectra of the first-eluted (mer) ——, second-eluted (u-fac) ------, and third-eluted (s-fac) ······ isomers of (a) [Co(mida)(mdien)]$^+$ and (b) [Co(ida)(dien)]$^+$.

Table 2. Absorption Spectral Data of the [Co(L$_1$)(L$_2$)]$^+$-Type Complexes

| Complex | Structure | First band[a] | Second band[a] | CT band[a] |
|---|---|---|---|---|
| [Co(ida)(dien)]$^+$ | mer | 19.65(2.22) | 27.93(2.25) | 44.25(4.29) |
| | | sh. 21.8 (2.08) | | |
| | u-fac | 19.57(2.03) | 28.17(2.11) | 46.08(4.35) |
| | s-fac | 20.70(1.84) | 28.82(1.90) | 45.66(4.38) |
| [Co(mida)(dien)]$^+$ | mer | 19.53(2.20) | 27.25(2.33) | 43.67(4.30) |
| | u-fac | 19.46(2.03) | 28.09(2.02) | 44.25(4.36) |
| | s-fac | 20.41(1.81) | 28.57(1.87) | 44.64(4.35) |
| [Co(ida)(mdien)]$^+$ | mer | 19.16(2.26) | 27.55(2.32) | 43.48(4.30) |
| | u-fac | 19.23(2.03) | 27.70(2.11) | 44.44(4.32) |
| | s-fac | 20.24(1.97) | 28.17(2.00) | 44.64(4.37) |
| [Co(mida)(mdien)]$^+$ | mer | 18.87(2.19) | 26.88(2.34) | 42.55(4.24) |
| | u-fac | 18.90(2.11) | 27.32(2.06) | 42.55(4.35) |
| | s-fac | 19.96(1.95) | 28.33(1.98) | 43.48(4.34) |

a) Wave numbers and log ε values (in parentheses) are given in 10$^3$ cm$^{-1}$ and mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively. sh) Shoulder band.

The single peaks observed for the third-eluted isomers (s-fac), however, appear as doublet peaks in the second-eluted isomers except for the resonance peaks of methyl carbons. These doublet peaks for the second-eluted isomers indicate that the two chelate rings of each terdentate ligand are nonequivalent, as expected for the unsymmetrical (u-fac) structure. This structure was confirmed by X-ray crystal analysis (vide post).

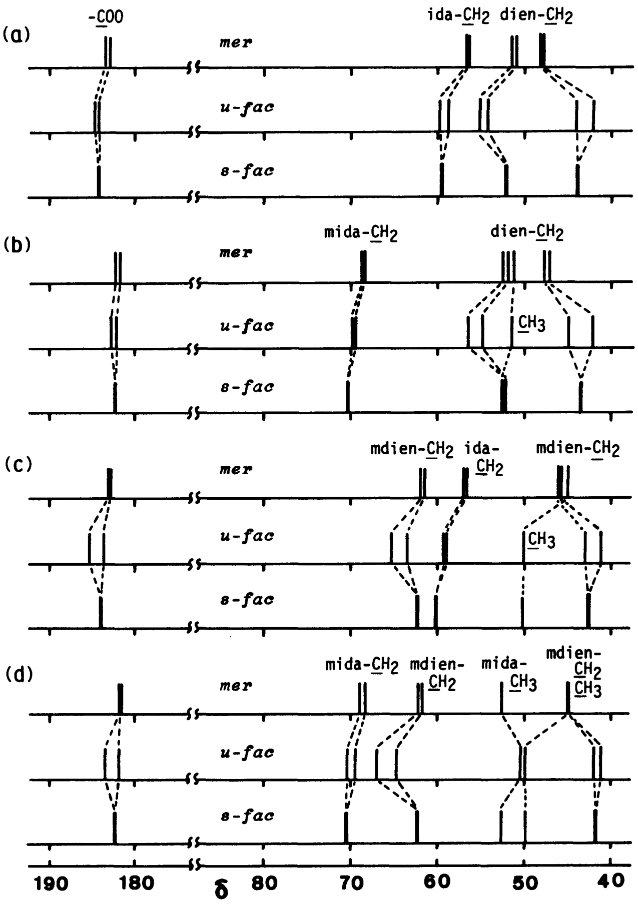

Fig. 3. $^{13}$C NMR spectral patterns of the first-eluted (mer), second-eluted (u-fac), and third-eluted (s-fac) isomers of $[\mathrm{Co(L_1)(L_2)}]^+$-type complexes: (a) [Co(ida)(dien)]$^+$, (b) [Co(mida)(dien)]$^+$, (c) [Co(ida)(mdien)]$^+$, and (d) [Co(mida)(mdien)]$^+$.

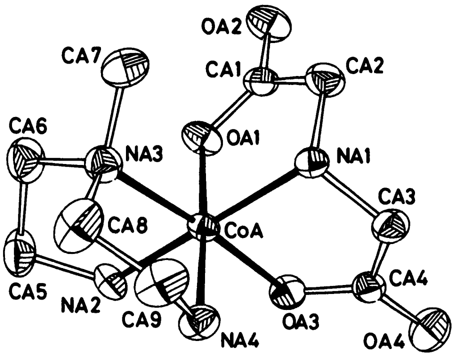

Fig. 4. Perspective view of $(+)^{\mathrm{CD}}_{550}$-*u-fac*-[Co(ida)(mdien)]$^+$ ion.

**Crystal Structure of $(+)^{\mathrm{CD}}_{550}$-*u-fac*-[Co(ida)(mdien)]·$(+)^{\mathrm{CD}}_{575}$-[Co(ox)$_2$(en)]·6H$_2$O.** Perspective drawings of the complex cation and anion obtained are given in Figs. 4 and 5 respectively, together with numbering scheme. The bond lengths and angles with their standard deviations are summarized in Table 3. In the complex cation (Fig. 4), the cobalt atom is surrounded octahedrally by two cis oxygen atoms and four nitrogen ones. Both of the ida and mdien ligands, which act as terdentate, take a facial form, and the tertiary amine, NA3, in the mdien ligand is located on the cis position of the nitrogen atom, NA1, in the ida one. As a result, the complex cation, [Co(ida)(mdien)]$^+$, takes an unsymmetric facial configuration, u-fac. The absolute configuration of the complex anion, $(+)^{\mathrm{CD}}_{575}$-[Co(ox)$_2$(en)]$^-$ (Fig. 5), was determined as Λ (see Experimental section) and this result confirms the suggestion made on the basis of the CD spectra.18) Therefore, the absolute configuration of $(+)^{\mathrm{CD}}_{550}$-*u-fac*-[Co(ida)(mdien)]$^+$ can be assigned to ΛΔΛ (net Λ) configuration based on that of $(+)^{\mathrm{CD}}_{575}$-*Λ*-[Co(ox)$_2$(en)]$^-$. This assignment for the $(+)^{\mathrm{CD}}_{550}$ isomer coincides with that made by the $^1$H NMR method using stereospecific deuteration.20)

In the complex cation, the fused five-membered chelate rings in the ida and mdien ligands are not symmetrically equivalent. The ethylenediamine chelate ring in the mdien ligand, NA2–CA5–CA6–NA3, takes similar asymmetric gauche form with $\lambda$ conformation (displacement from the NA2–CoA–NA3 plane: CA5=0.027 and CA6=0.640 Å) to those of *s-fac*- and *u-fac*-[Co(dien)$_2$]$^{3+}$.21,22) The other chelate ring, NA3–CA8–CA9–NA4, takes the unusual form with $\lambda$ conformation (displacement from the NA3–CoA–NA4

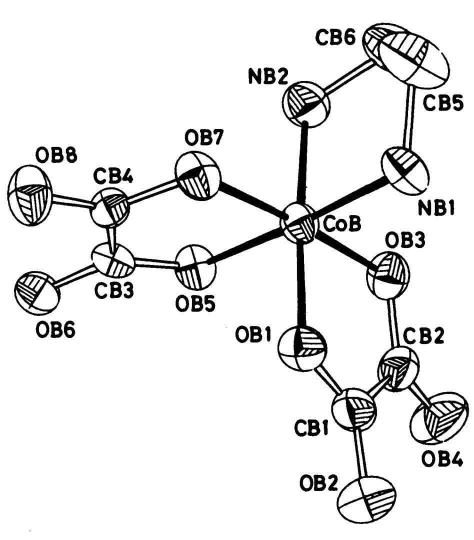

Fig. 5. Perspective view of $(+)^{\mathrm{CD}}_{575}$-[Co(ox)$_2$(en)]$^-$ ion.

Table 3. Interatomic Distances and Bond Angles (with e.s.d.'s)

|  |  |  |  |
|---|---|---|---|
| (a) Bond distance ($l$/Å) |  |  |  |
| $[Co(ida)(mdien)]^+$: |  |  |  |
| CoA-NA1 | 1.983(5) | CoA-NA2 | 1.947(6) |
| CoA-NA3 | 1.999(5) | CoA-NA4 | 1.939(6) |
| CoA-OA1 | 1.899(5) | CoA-OA3 | 1.895(4) |
| NA1-CA2 | 1.495(9) | NA2-CA5 | 1.500(9) |
| NA3-CA6 | 1.511(9) | NA3-CA7 | 1.479(11) |
| NA3-CA8 | 1.525(10) | NA4-CA9 | 1.473(9) |
| OA1-CA1 | 1.257(8) | OA2-CA1 | 1.250(8) |
| OA3-CA4 | 1.286(8) | OA4-CA4 | 1.237(8) |
| CA1-CA2 | 1.514(9) | CA3-CA4 | 1.528(10) |
| CA5-CA6 | 1.543(12) | CA8-CA9 | 1.481(12) |
| $[Co(ox)_2(en)]^-$: |  |  |  |
| CoB-NB1 | 1.930(6) | CoB-NB2 | 1.929(7) |
| CoB-OB1 | 1.901(5) | CoB-OB3 | 1.867(5) |
| CoB-OB5 | 1.920(4) | CoB-OB7 | 1.887(5) |
| NB1-CB5 | 1.499(13) | NB2-CB6 | 1.472(12) |
| OB1-CB1 | 1.292(10) | OB2-CB1 | 1.246(10) |
| OB3-CB2 | 1.314(10) | OB4-CB2 | 1.229(10) |
| OB5-CB3 | 1.253(8) | OB6-CB3 | 1.245(8) |
| OB7-CB4 | 1.291(8) | OB8-CB4 | 1.210(8) |
| CB1-CB2 | 1.508(12) | CB3-CB4 | 1.555(10) |
| CB5-CB6 | 1.544(15) |  |  |
| (b) Bond angle ($\phi$/°) |  |  |  |
| $[Co(ida)(mdien)]^+$: |  |  |  |
| NA1-CoA-NA2 | 170.2(2) | NA1-CoA-NA3 | 100.1(2) |
| NA1-CoA-NA4 | 95.4(2) | NA1-CoA-OA1 | 86.4(2) |
| NA1-CoA-OA3 | 84.4(2) | NA2-CoA-NA3 | 86.1(2) |
| NA2-CoA-NA4 | 92.5(3) | NA2-CoA-OA1 | 85.9(2) |
| NA2-CoA-OA3 | 89.7(2) | NA3-CoA-NA4 | 86.7(2) |
| NA3-CoA-OA1 | 91.3(2) | NA3-CoA-OA3 | 174.9(2) |
| NA4-CoA-OA1 | 177.5(2) | NA4-CoA-OA3 | 90.6(2) |
| OA1-CoA-OA3 | 91.3(2) | CoA-NA1-CA2 | 108.3(4) |
| CoA-NA1-CA3 | 107.4(4) | CA2-NA1-CA3 | 111.2(5) |
| CoA-NA2-CA5 | 112.1(5) | CoA-NA3-CA6 | 106.6(4) |
| CoA-NA3-CA7 | 114.6(4) | CoA-NA3-CA8 | 106.5(4) |
| CA6-NA3-CA7 | 107.7(6) | CA6-NA3-CA8 | 110.7(5) |
| CA7-NA3-CA8 | 110.7(6) | CoA-NA4-CA9 | 108.5(5) |
| CoA-OA1-CA1 | 115.8(4) | CoA-OA3-CA4 | 115.8(4) |
| OA1-CA1-OA2 | 123.5(6) | OA1-CA1-CA2 | 118.4(6) |
| OA2-CA1-CA2 | 118.0(6) | NA1-CA2-CA1 | 110.5(6) |
| NA1-CA3-CA4 | 108.1(5) | OA3-CA4-OA4 | 124.8(6) |
| OA3-CA4-CA3 | 116.4(5) | OA4-CA4-CA3 | 118.7(6) |
| NA2-CA5-CA6 | 108.7(6) | NA3-CA6-CA5 | 106.8(6) |
| NA3-CA8-CA9 | 111.0(6) | NA4-CA9-CA8 | 106.4(6) |
| $[Co(ox)_2(en)]^-$: |  |  |  |
| NB1-CoB-NB2 | 87.9(3) | NB1-CoB-OB1 | 90.3(3) |
| NB1-CoB-OB3 | 92.8(3) | NB1-CoB-OB5 | 176.6(2) |
| NB1-CoB-OB7 | 91.0(2) | NB2-CoB-OB1 | 176.1(2) |
| NB2-CoB-OB3 | 89.5(3) | NB2-CoB-OB5 | 91.2(3) |
| NB2-CoB-OB7 | 93.2(3) | OB1-CoB-OB3 | 87.1(2) |
| OB1-CoB-OB5 | 90.7(2) | OB1-CoB-OB7 | 90.3(2) |
| OB3-CoB-OB5 | 90.5(2) | OB3-CoB-OB7 | 175.4(2) |
| OB5-CoB-OB7 | 85.8(2) | CoB-NB1-CB5 | 108.8(5) |
| CoB-NB2-CB6 | 109.5(6) | CoB-OB1-CB1 | 110.7(5) |
| CoB-OB3-CB2 | 111.8(5) | CoB-OB5-CB3 | 112.1(4) |
| CoB-OB7-CB4 | 112.9(4) | OB1-CB1-OB2 | 124.1(8) |
| OB1-CB1-CB2 | 115.7(7) | OB2-CB1-CB2 | 120.2(8) |
| OB3-CB2-OB4 | 124.4(7) | OB3-CB2-CB1 | 113.5(7) |
| OB4-CB2-CB1 | 122.1(8) | OB5-CB3-OB6 | 125.9(6) |
| OB5-CB3-CB4 | 115.3(5) | OB6-CB3-CB4 | 118.7(6) |
| OB7-CB4-OB8 | 125.2(6) | OB7-CB4-CB3 | 112.8(5) |
| OB8-CB4-CB3 | 122.0(6) | NB1-CB5-CB6 | 106.5(8) |
| NB2-CB6-CB5 | 107.8(8) |  |  |

plane: CA8=−0.019 and CA9=0.599 Å) (Fig. 4). This conformation displacement seems to arise from the result that the NA3-NA4 chelate ring and the amine group, NA1, in the ida ligand repel each other. Similarly, the chelate ring, NA1-CA3-CA4-OA3, in the ida ligand takes an envelope form with $\lambda$ conformation (displacement from the NA1-CoA-OA3 plane: CA3=−0.591 and CA4=−0.318 Å) similar to those of *u-fac*-$[Co(ida)_2]^-$.[23] While, the other chelate ring, OA1-CA1-CA2-NA1, takes nearly planar (displacement from the OA1-CoA-NA1 plane: CA1=−0.014 and CA2=0.097 Å). This planarity seems to depend on the steric repulsion between the OA1-NA1 chelate ring and the methyl group in the mdien ligand. In the complex anion, the ox ligands take similar conformation to those of $[Co(ox)_3]^{3-}$[24] and $[Co(ox)(en)_2]^+$.[25,26] The ethylenediamine takes a reasonable gauche form with $\delta$(lel) conformation.[25-27]

The bond lengths and angles of the complex cation and anion are similar to those of the cobalt(III) complexes with the ida, dien, ox, and en ligands.[22-27] In the complex cation, the Co-N (tertiary) bond of 1.999(5) Å in the mdien ligand is considerably longer than the Co-N (terminal) bond of 1.943(6) Å, and this difference is more remarkable than those in the *u-fac*-$[Co(dien)_2]^{3+}$ [Co-N (secondary) 1.971 and Co-N (terminal) 1.961 Å].[22] The Co-N bond, 1.983(5) Å, in the ida ligand is longer than those of *u-fac*-$[Co(ida)_2]^-$ [1.946(4) and 1.936(4) Å].[23] These results seem to depend mainly on the arrangement of the terdentate ligands around the cobalt atom.

**Absolute Configuration and CD Spectra of the u-fac Isomers.** The CD spectral curves of the u-fac isomers in this work are shown in Fig. 6 and their CD data are summarized in Table 4. All the optically active u-fac isomers isolated from the later eluates on the column chromatographic resolution show similar CD patterns to one another in the first absorption band region. Since the absolute configuration of $(+)^{\mathrm{CD}}_{550}$-*u-fac*-$[Co(ida)(mdien)]^+$ is ΛΔΛ (net Λ), we assign the remaining three u-fac isomers, which show the same

Table 4. CD Spectral Data of the $[\mathrm{Co}(\mathrm{L}_1)(\mathrm{L}_2)]^+$-Type Complexes

| Complex | First band region[a)] | Second band region[a)] | CT band region[a)] |
|---|---|---|---|
| $(+)^{\mathrm{CD}}_{538}$-*u-fac*-[Co(ida)(dien)]$^+$ | 18.59(+2.014) | sh 26.5 (+0.282) | 43.86(−6.405) |
| | 21.05(−1.472) | 28.49(+0.398) | |
| $(+)^{\mathrm{CD}}_{544}$-*u-fac*-[Co(mida)(dien)]$^+$ | 18.38(+2.441) | sh 26.0 (+0.322) | 38.46(+0.560) |
| | 20.62(−1.757) | 28.17(+0.425) | 43.67(−10.27) |
| $(+)^{\mathrm{CD}}_{550}$-*u-fac*-[Co(ida)(mdien)]$^+$ | 18.18(+1.804) | 25.91(+0.417) | 37.59(+0.145) |
| | 20.45(−0.946) | 28.25(+0.419) | 43.29(−2.138) |
| | | | 46.95(+3.592) |
| $(+)^{\mathrm{CD}}_{564}$-*u-fac*-[Co(mida)(mdien)]$^+$ | 17.70(+1.658) | 27.70(+0.507) | 41.67(−7.334) |
| | 19.88(−1.280) | | 45.87(+9.825) |

a) Wave number and $\Delta\varepsilon$ values (in parentheses) are given in $10^3\,\mathrm{cm}^{-1}$ and $\mathrm{mol}^{-1}\,\mathrm{dm}^3\,\mathrm{cm}^{-1}$, respectively. sh) Shoulder band.

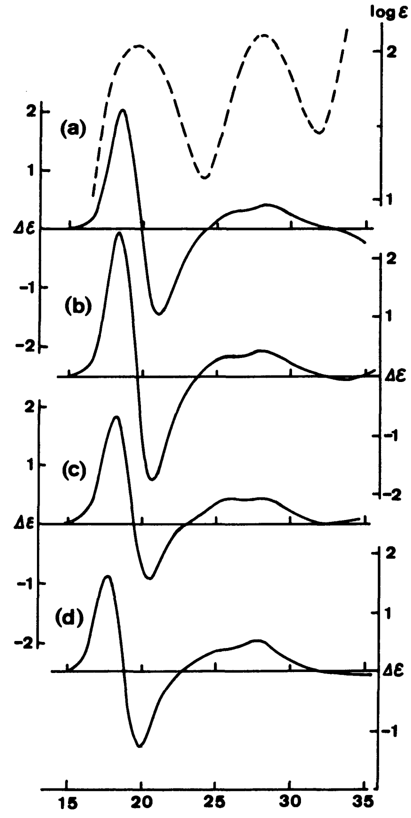

Fig. 6. Absorption and CD spectra of the u-fac isomers: (a) $(+)^{\mathrm{CD}}_{538}$-[Co(ida)(dien)]$^+$, (b) $(+)^{\mathrm{CD}}_{544}$-[Co(mida)(dien)]$^+$, (c) $(+)^{\mathrm{CD}}_{550}$-[Co(ida)(mdien)]$^+$, and (d) $(+)^{\mathrm{CD}}_{564}$-[Co(mida)(mdien)]$^+$.

CD pattern as that of $(+)^{\mathrm{CD}}_{550}$-*u-fac*-[Co(ida)(mdien)]$^+$, to be the ΛΔΛ configuration.

For the cobalt(III) complexes with bidentate ligands such as ethylenediamine, glycinate, oxalate, and so on, their CD spectral patterns in the first absorption band region have successfully been related with their absolute configurations.[28)] However, the CD spectral behaviors of the cobalt(III) complexes with linear terdentate-*N,N,N*, -*N,N,O*, and -*O,N,O* ligands differ significantly from those of the cobalt(III) complexes with the bidentate one. In other words, the cobalt(III) complexes with the terdentate ligands, which take the same absolute configuration (for example, ΛΔΛ in this case), exhibit similar CD pattern in the first absorption band region, in spite of a difference in the type of chromophore. For example, $(+)_{589}$-*u-fac*-[Co(dien)$_2$]$^{3+}$ ([Co(N)$_6$]),[22)] $(+)^{\mathrm{CD}}_{514}$-*fac*($N_\mathrm{t}$)*cis*($N_\mathrm{c}$)- and $(+)^{\mathrm{CD}}_{527}$-*mer*($N_\mathrm{t}$)*cis*($N_\mathrm{c}$)-[Co(edma)(dien)]$^{2+}$ ([Co(N)$_5$(O)]),[29)] $(+)^{\mathrm{CD}}_{543}$-*trans*(*O*)- and $(+)^{\mathrm{CD}}_{534}$-$C_1$-*cis*(*O*)-[Co(edma)$_2$]$^+$ ([Co(N)$_4$(O)$_2$]),[9)] $(+)^{\mathrm{CD}}_{572}$-*mer*(*O*)*cis*($N_\mathrm{c}$)- and $(+)^{\mathrm{CD}}_{565}$-*fac*(*O*)-[Co(ida)(edma)] ([Co(N)$_3$(O)$_3$]),[11)] and $(-)_{546}$-*u-fac*-[Co(ida)$_2$]$^-$ ([Co(N)$_2$(O)$_4$]),[2,30)] which have been determined to be the ΛΔΛ configuration, exhibited in common a positive and a negative CD bands from the lower energy in the first absorption band region, as in the case of the present ΛΔΛ-u-fac isomers. These facts suggest that the empirical treatment[28)] applied favorably for the cobalt(III) complexes with the bidentate ligands can not be directly applied for those with the terdentate ones. In order to discuss these CD spectral behaviors, however, more data will be needed.

## References

1) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

2) Y. Yoshikawa, A. Kondo, and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **12**, 351 (1976).

3) N. Koine, T. Tanigaki, J. Hidaka, and Y. Shimura, *Chem. Lett.*, **1980**, 871.

4) K. Gailey, K. Igi, and B. E. Douglas, *J. Coord. Chem.*, **5**, 171 (1976).

5) T. Kawamoto, T. F. Maruyama, T. Yasui, K. Okamoto, J. Hidaka, and H. Einaga, *Bull. Chem. Soc. Jpn.*, **59**, 2393 (1986).

6) T. Yasui, H. Kawaguchi, N. Koine, and T. Ama, *Bull. Chem. Soc. Jpn.*, **56**, 127 (1983).

7) T. Ama, H. Kawaguchi, and T. Yasui, *Chem. Lett.*, **1981**, 323.

8) H. Kawaguchi, T. Ama, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **57**, 2422 (1984).

9) T. Ama, H. Kawaguchi, T. Yasui, K. Matsumoto, and S. Ooi, *Bull. Chem. Soc. Jpn.*, **58**, 2561 (1985).

10) T. Ama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **59**, 1471 (1986).

11) T. Ama, R. Niiyama, H. Kawaguchi, and T. Yasui, *Bull. Chem. Soc. Jpn.*, **60**, 119 (1987).

12) M. Mori, M. Shibata, E. Kyuno, and F. Maruyama, *Bull. Chem. Soc. Jpn.*, **35**, 75 (1962).

13) M. Kojima, M. Iwagaki, Y. Yoshikawa, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 3216 (1977).

14) K. Okamoto, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **48**, 2456 (1975).

15) L. W. Finger, RFINE-2, Geophysical Lab. Carnegie Institution, Washington, D. C., 1972.

16) International Tables for X-Ray Crystallography, Kynoch Press, Birmingham (1974), Vol. IV.

17) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

18) B. E. Douglas, R. A. Haines, and J. C. Brushimiller, *Inorg. Chem.*, **2**, 1194 (1963).

19) N. Matsuoka, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **40**, 1868 (1967).

20) T. Ama, S. Kaizaki, H. Kawaguchi, and T. Yasui, *Chem. Lett.*, **1987**, 441.

21) M. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 470 (1972).

22) M. Konno, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 739 (1973).

23) A. B. Corradi, C. G. Palmieri, M. Nardelli, M. A. Pellinghelli, and M. E. V. Tani, *J. Chem. Soc., Dalton Trans.*, **1973**, 655.

24) K. R. Butler and M. R. Snow, *J. Chem. Soc. A*, **1971**, 565.

25) T. Aoki, K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **46**, 159 (1973).

26) K. Toriumi, S. Sato, and Y. Saito, *Acta Crystallogr., Sect. B*, **33**, 1378 (1977).

27) C. J. Hawkins, "Absolute Configuration of Metal Complexes," John-Wiley & Sons, Inc., New York (1971).

28) Y. Saito, "Inorganic Molecular Dissymmetry," in series of Inorganic Chemistry Concepts, Springer-Verlag, Berlin Heidelberg (1979), Vol. 4, pp. 132—148.

29) T. Yasui, T. Shikiji, N. Koine, T. Ama, and H. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **60**, 595 (1987).

30) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **8**, 1145 (1969).