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Circular Dichroism of Chromium(III) Complexes. VI. Preparation, Optical Resolution, and Circular Dichroism Spectra of (Amino acidato)bis(ethylenediamine)chromium(III) Complexes

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Three (amino acidato)bis(ethylenediamine)chromium(III) complexes were prepared and resolved into their optically active isomers, their absorption and circular dichroism spectra being measured in the spin-forbidden and spin-allowed d-d transition regions. The amino acids used were glycine, L-alanine, and L-phenylalanine, the latter two yielding pairs of diastereomeric, not enantiomeric, isomers in their complexes. The configurational and vicinal CD curves were obtained from the observed CD of each pair of diastereomers. The additivity of configurational and vicinal contributions to the optical activity in the whole region of the d-d transitions was substantiated. The configurational and vicinal CD peaks in the spin-forbidden band region were assigned in connection with those in the first spin-allowed band region.

In contrast to the large number of corresponding Co(III) complexes, only a limited number of Cr(III) complexes containing optically active amino acid chelates are known.$^{1-3)}$ No complex such as $[Cr(am)(N)_4]^{2+}$ (am=amino acid anion) has been prepared, but this type of Cr(III) complex is fundamental for spectroscopic and stereochemical studies on (amino acidato) chromium(III) complexes as for analogous Co(III) complexes on the basis of their chiro-optical spectra.$^{4-7)}$ With use of two ethylenediamines as $(N)_4$ ligands, circular dichroism(CD) spectra of the complexes with optically active amino acids might be separated into the configurational contribution due to the chiral arrangement of three chelate rings around a central Cr(III) ion and the vicinal one due to the chirality around optically active amino acidato ligands as in Co(III) complexes.$^{5-7)}$ For such Cr(III) complexes, the vicinal CD curves in the spin-forbidden transitions might reveal the split components of the excited states as found for the CD in the first band region of Co(III) complexes.$^{5-7)}$ The electronic doublet states would be clarified for the Cr(III) complexes of the present type as has been revealed for the so-called praseo type complexes$^{8)}$ and in more detail than for the tris-chelate complexes.$^{9)}$

This paper deals with the preparation and optical resolution of $[Cr(am)(en)_2]^{2+}$, where am refers to glycine anion(gly), L-alanine anion(L-ala), and L-phenylalanine anion(L-phala), and with their absorption and CD spectra in the d-d transition region. The absolute configuration and additivity of the configurational and vicinal CD curves of these complexes are discussed. The configurational and vicinal CD peaks in the spin-forbidden transition region are elucidated in relation with those in the first spin-allowed transition region by means of the relations$^{8-9)}$ between the rotational strengths for the spin-forbidden transitions and those for the first spin-allowed transitions.

Experimental

Preparation of the Complexes. *1)* $[Cr(gly)(en)_2]Cl_2\cdot 0.5H_2O$: A solution of 1.0 g of *cis*-$[CrCl_2(en)_2]Cl\cdot H_2O$ in 4 cm^3 of water was heated at 80 °C. To the resulting red solution in which the species may be *cis*-$[CrCl(en)_2(H_2O)]^{2+}$ was added 0.3 g of glycine at room temperature. After the pH of the mixture had been adjusted to 8—9 with a 2 mol dm^{-3} potassium hydroxide solution, the solution was warmed at 35 °C for a few hours; when the coloration of the solution turned reddish orange. To this was added a large excess of potassium iodide. On cooling the solution in an ice bath, orange powder was precipitated. This was filtered and washed with methanol and ether. Another crop of the crude complex was obtained from the filtrate by adding methanol. The crude product was purified as follows. An aqueous solution of the obtained powder was poured into an SP-Sephadex C-25 column (ϕ3.5 cm × 30 cm), and the adsorbed complex was eluted with a 0.2 mol dm^{-3} sodium chloride solution at 5 °C in the dark. A yellow orange eluate showing absorption maxima at 478 nm and 359.5 nm was collected. The eluate was reloaded on a short column of SP-Sephadex C-25 after dilution with cold water at 5 °C, and the adsorbed complex on the Sephadex was washed thoroughly with a 0.05 mol dm^{-3} lithium chloride solution. After elution of the adsorbed complex with a 3 mol dm^{-3} lithium chloride solution, the concentrated solution obtained was evaporated to dryness by means of freeze drying. The orange powder contaminated with a large amount of lithium chloride was dissolved completely in a small amount of ethanol. A large excess of ether was added, yellow orange powder being obtained. This was filtered and washed thoroughly with ethanol. Pure chloride was obtained by recrystallization from cold water and ethanol. Found: C, 20.94; H, 6.74; N, 20.60%. Calcd for $[Cr(gly)(en)_2]Cl_2\cdot 0.5H_2O$: C, 20.75; H, 6.67; N, 20.57%.

2) $(+)_{589}$- *and* $(-)_{589}$-$[Cr(gly)(en)_2]^{2+}$: An aqueous solution of $[Cr(gly)(en)_2]Cl_2\cdot 0.5H_2O$ was adsorbed on an SP-Sephadex C-25 column, and the charged complex was eluted with a 0.1 mol dm^{-3} aqueous solution of sodium $(+)_{589}$-tartratoantimonate(III) at a rate of 0.3 cm^3/min at 5 °C in the dark. Equal amounts of two bands, $(+)_{589}$- and $(-)_{589}$-isomers, were eluted separately. Each eluate was reloaded on a short column of SP-Sephadex C-25 after dilution with cold water. Each adsorbed complex was eluted with a 3 mol dm^{-3} lithium chloride solution, the eluates being stored for CD measurements. Isolation of these complexes was unsuccessful. Based on the quantitative analysis of the Cr^{3+} content in these solutions, the absorption spectra of the concentrated solutions coincided in position and intensity with those of the unresolved $[Cr(gly)(en)_2]Cl_2\cdot 0.5H_2O$ in water.

3) $(\Delta\Lambda)$-$[Cr(L\text{-}ala)(en)_2]^{2+}$: This complex ion was prepared by the same method as for the glycinato complex in *1)*. However, it was not isolated owing to decomposition during the course of isolation.

4) $(+)_{589}$- and $(-)_{589}$-[Cr(L-ala)(en)$_2$]$^{2+}$: After the reaction of *cis*-[CrCl$_2$(en)$_2$]Cl·H$_2$O with L-alanine in water as described in *1)*, the mixture was poured into an SP-Sephadex C-25 column (ϕ4 cm × 50 cm). The adsorbed band was eluted with a 0.2 mol dm^{-3} sodium chloride solution at 5 °C in the dark. Of six separate bands, the fourth eluted yellow orange band showed a similar absorption spectrum to that of [Cr(gly)(en)$_2$]$^{2+}$. The dilute aqueous solution of this eluate was resorbed on a column of SP-Sephadex C-25 and the adsorbed complex was resolved into diastereomers by elution with a 0.1 mol dm^{-3} aqueous solution of sodium $(+)_{589}$-tartratoantimonato(III) at a rate of 0.3 cm^3/min at 5 °C in the dark. Two bands were separated: the first and the second bands being $(+)_{589}$- and $(-)_{589}$-diastereomers, respectively. $(+)_{589}$- and $(-)_{589}$-isomers are found to be formed in the ratio 48:52. Each eluate was concentrated by the same procedure as given in *2)*.

5) $(\Delta\Lambda)$-[Cr(L-phala)(en)$_2$]I$_2$: The iodide of this complex was obtained as needle-like crystals by the same method as for the glycinato complex. Recrystallization was carried out from a small amount of water and methanol. Found: C, 26.28; H, 4.52; N, 11.73%. Calcd for [Cr(L-phala)(en)$_2$]I$_2$: C, 26.46; H, 4.44; N, 11.87%.

6) $(+)_{589}$- and $(-)_{589}$-[Cr(L-phala)(en)$_2$]$^{2+}$: Two diastereomers of the L-phenylalaninato complex were obtained by SP-Sephadex column chromatography of the mixture after the reaction as in the case of the L-alaninato complexes in *4)*. The faster and slower eluates of two separate bands were $(+)_{589}$- and $(-)_{589}$-isomers, respectively, their formation ratio being *ca.* 3 : 2.

Measurements. Absorption spectra were obtained on a Shimadzu UV-200S spectrophotometer, and CD spectra on a JASCO MOE-1 spectropolarimeter. The quantitative absorption spectra of the unresolved glycinato and L-phenylalaninato complexes were measured on the basis of their elemental analytical results. The molar absorption coefficients of the L-alaninato complex were determined on the basis of quantitative analysis of the Cr^{3+} content in sample solutions, since this complex could not be isolated. The values of the molar absorption coefficients (ε=86.06 mol^{-1} dm^3 cm^{-1} at 478 nm and ε=71.68 mol^{-1} dm^3 cm^{-1} at 359.5 nm) obtained by this method seem reasonable in comparison with those of the other amino acidato complexes: ε=87.05 at 478 nm and 76.65 mol^{-1} dm^3 cm^{-1} at 359.5 nm for the glycinato complex, and ε=86.72 at 478 nm and 72.42 mol^{-1} dm^3 cm^{-1} at 359.5 nm for the L-phenylalaninato complex. The CD measurements of the present optically active complexes were performed by using the sample solutions in *ca.* 2 mol dm^{-3} lithium chloride solutions in which the Cr^{3+} content was determined by quantitative analysis and/or the molar absorption coefficients of the first absorption band. In the latter case, it is assumed that each diastereomer of the L-alaninato and L-phenylalaninato complexes has equal molar absorption coefficients, since those of diastereomers of [Co(ox)$_2$(L-ala)]$^{2-}$,[7] [Co(mal)$_2$(L-phala)]$^{2-}$,[7] and [Cr(L-ala)(en)$_2$]$^{2+}$[5] have been found to be equal.

Chemical Analysis. Chromium content was determined by spectrophotometric analysis of CrO$_4$$^{2-}$ at 372 nm after oxidation of the complexes with hot alkaline hydrogen peroxide.

Results and Discussion

Absorption and Circular Dichroism Spectra. The first and second absorption band maxima of the three amino acidato complexes coincide with each other (Fig. 1). The positions agree with those predicted from the rule of average environment[10] or Yamatera's rule[11] by using the first and second band positions for [Cr(en)$_3$]$^{3+}$ and [Cr(ox)$_3$]$^{3-}$.

The CD spectra of the complexes give only one component in the first band region and two components with opposite signs in the second band region (Figs. 1 and 2). The CD intensities of these complexes are comparable to those of tris-chelate

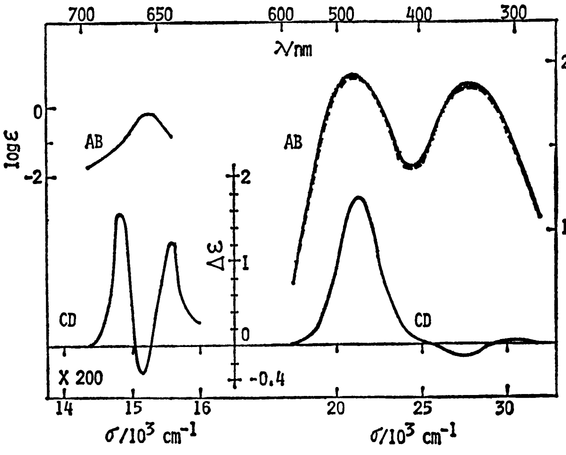

Fig. 1. Absorption curves (upper) of [Cr(gly)(en)$_2$]$^{2+}$ (——), [Cr(L-ala)(en)$_2$]$^{2+}$ (----), and [Cr(L-phala)(en)$_2$]$^{2+}$ (······); observed CD curves (lower) of $(+)_{589}$-[Cr(gly)(en)$_2$]$^{2+}$.

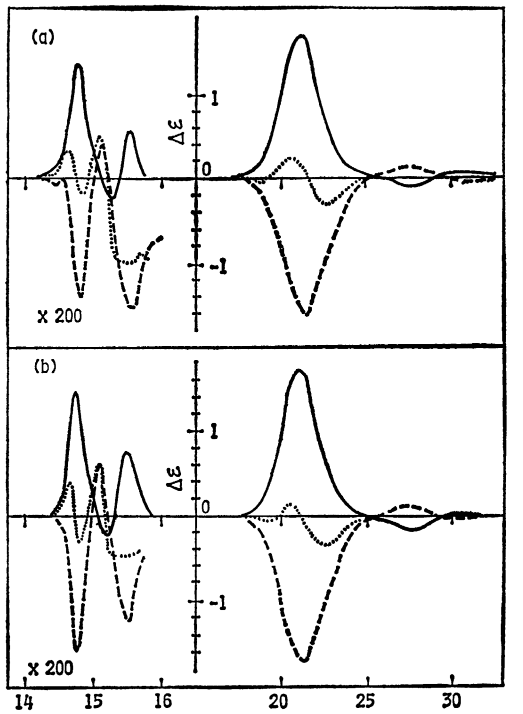

Fig. 2. (a) CD curves of $(+)_{589}$-[Cr(L-ala)(en)$_2$]$^{2+}$ (——) and $(-)_{589}$-[Cr(L-ala)(en)$_2$]$^{2+}$ (----), and calculated vicinal CD curve (2$\Delta\varepsilon$(L)) of [Cr(L-ala)(en)$_2$]$^{2+}$ (······). (b) CD curves of $(+)_{589}$-[Cr(L-phala)(en)$_2$]$^{2+}$ (——) and $(-)_{589}$-[Cr(L-phala)(en)$_2$]$^{2+}$ (----), and calculated vicinal CD curve (2$\Delta\varepsilon$(L)) of [Cr(L-phala)(en)$_2$]$^{2+}$ (······).

complexes such as $(+)_{589}$-$[Cr(en)_3]^{3+}$ and $(+)_{589}$-$[Cr(ox)(en)_2]^+$.[9)] This confirms the chelation of amino acidato ligands in the complexes. Since the faster eluted $(+)_{589}$-isomers of these complexes exhibit a positive CD band in the first band region, they are assigned to a Λ absolute configuration. Thus, the slower eluted $(-)_{589}$-isomers with a negative CD band in this region take a Δ configuration. The elution order is the same as that found for the corresponding Co(III) complex with glycine anion.[12)] A preliminary experiment of the optical resolution for the trimethylenediamine complex, $[Cr(gly)(tn)_2]^{2+}$, indicates that the faster eluted band on SP-Sephadex column chromatography exhibits a negative CD band in the first band region and is assigned to a Δ configuration. The inversion of the elution order for the ethylenediamine and trimethylenediamine complexes is also found for the corresponding Co(III) complexes.[12b)]

It has been revealed for several Co(III) complexes[5–7)] that the configurational and vicinal contributions are separable and almost additive on the CD curves in the spin-allowed d-d absorption band region. However, there is no application of the additivity rule to the CD of chromium(III) complexes in both the spin-forbidden and spin-allowed band regions. The vicinal CD due to one coordinated optically active amino acidato ligand, $\Delta\varepsilon(\text{L})$, and the configurational CD, $\Delta\varepsilon(\Delta)$ or $\Delta\varepsilon(\Lambda)$, have been calculated by applying the following relations to the observed CD curves, $\Delta\varepsilon(\Delta_\text{L})$ and $\Delta\varepsilon(\Lambda_\text{L})$, of Δ- and Λ-$[Cr(am)(en)_2]^{2+}$.

$$\Delta\varepsilon(\text{L}) = 1/2\{\Delta\varepsilon(\Delta_\text{L}) + \Delta\varepsilon(\Lambda_\text{L})\}$$

$$\Delta\varepsilon(\Delta) = 1/2\{\Delta\varepsilon(\Delta_\text{L}) - \Delta\varepsilon(\Lambda_\text{L})\}$$

$$\Delta\varepsilon(\Delta) + \Delta\varepsilon(\Lambda) = 0$$

The calculated configurational curves from the CD data of each diastereomer of the L-alaninato and L-phenylalaninato complexes agree with the observed curve of the glycinato complex, $(+)_{589}$-$[Cr(gly)(en)_2]^{2+}$, in the lower frequency spin-forbidden band region as well as in the first and second spin-allowed band regions (Fig. 3). The configurational CD in the spin-forbidden band region is similar in appearance to that of $(+)_{589}$-$[Cr(en)_3]^{3+}$,[9)] but the half-bandwidths of the complexes are approximately twice as wide as that of $(+)_{589}$-$[Cr(en)_3]^{3+}$.[9)] Assuming pseudo D_3 symmetry for the present complexes as for $[Cr(ox)(en)_2]^+$,[9)] one positive configurational CD component in the first spin-allowed band region is due to the $^4E(^4T_{2g})$ state. Then, three CD peaks of the configurational curves in the spin-forbidden band region are assigned to the $^2E(^2E_g)$, $^2A_2(^2T_{1g})$, and $^2E(^2T_{1g})$ states from the lower frequency side according to the theoretical relation of the rotational strengths for these d-d transitions.[9)]

The calculated vicinal CD curves of the L-alaninato and L-phenylalaninato complexes in the first band region give three components, (−), (+), and (−) from the lower frequency side (Fig. 2). This CD

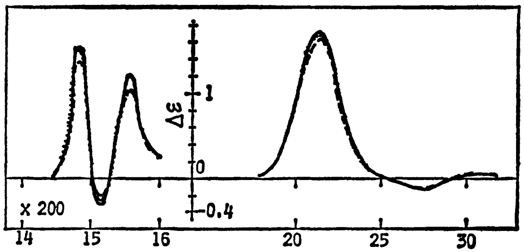

Fig. 3. Calculated configurational CD curves of $[Cr(\text{L-ala})(en)_2]^{2+}$ (----) and $[Cr(\text{L-phala})(en)_2]^{2+}$ (……), and observed CD curve of $(+)_{589}$-$[Cr(gly)(en)_2]^{2+}$ (——).

Table 1. CD data of $[Cr(am)(en)_2]^{2+}$ complexes
(Wave numbers are given in 10^3 cm^{-1}.)

Observed CD extrema of $(+)_{589}$- and $(-)_{589}$-$[Cr(am)(en)_2]^{2+}$				
$(+)_{589}$-(gly) $\sigma(\Delta\varepsilon)$	$(+)_{589}$-(L-ala) $\sigma(\Delta\varepsilon)$	$(-)_{589}$-(L-ala) $\sigma(\Delta\varepsilon)$	$(+)_{589}$-(L-phala) $\sigma(\Delta\varepsilon)$	$(-)_{589}$-(L-phala) $\sigma(\Delta\varepsilon)$
14.81(+7.77[a)])	14.77(+6.64[a)])	14.79(−7.09[a)])	14.75(+7.25[a)])	14.78(−7.96[a)])
15.15(−1.58[a)])	15.28(−1.25[a)])	15.12(+1.96[a)])	15.20(−1.18[a)])	15.09(+3.03[a)])
15.58(+6.04[a)])	15.57(+2.70[a)])	15.56(−7.70[a)])	15.52(+3.85[a)])	15.53(−6.07[a)])
21.46(+1.91)	21.15(+1.65)	21.46(−1.63)	21.10(+1.70)	21.42(−1.71)
27.55(−0.16)	27.70(−0.12)	27.47(+0.11)	27.62(−0.16)	27.47(+0.10)
30.45(+0.04)	30.40(+0.04)	30.40(−0.02)	30.53(+0.03)	30.40(−0.03)

Obtained configurational CD extrema			Obtained vicinal CD extrema		
Λ-(L-ala) $\sigma(\Delta\varepsilon)$	Λ-(L-phala) $\sigma(\Delta\varepsilon)$	Assignment(D_3)	(L-ala) $\sigma(\Delta\varepsilon)$	(L-phala) $\sigma(\Delta\varepsilon)$	Assinment(D_4)
14.79(+6.81[a)])	14.77(+7.58[a)])	$^2E(^2E_g)$	14.60(+0.83[a)])	14.64(+1.00[a)])	$^2A_1(^2E_g)$
15.15(−1.40[a)])	15.13(−1.66[a)])	$^2A_2(^2T_{1g})$	14.84(−0.50[a)])	14.81(−0.74[a)])	$^2B_1(^2E_g)$
15.58(+5.20[a)])	15.53(+4.96[a)])	$^2E(^2T_{1g})$	15.11(+1.19[a)])	15.06(+1.55[a)])	$^2A_2(^2T_{1g})$
21.46(+1.62)	21.28(+1.70)	$^4E(^4T_{2g})$	15.60(−2.53[a)])	15.35(−1.30[a)])	$^2E(^2T_{1g})$
27.62(−0.12)	27.62(−0.13)		18.45(−0.013)	19.01(−0.031)	$^4E(^4T_{2g})$
30.49(+0.03)	30.49(+0.03)		20.58(+0.105)	20.49(+0.080)	
			22.72(−0.168)	22.67(−0.165)	$^4B_2(^4T_{2g})$

a) CD intensities are multiplied by 10^3.

behavior is similar to that of the corresponding Co(III) complexes[5] except their CD intensities. In the spin-forbidden band region, the vicinal CD curves exhibit four components with alternate signs; (+), (−), (+), and (−) from the lower frequency side. The intensity ratios between the configurational and vicinal CD components in the first spin-allowed band region are found to be almost equal to those between the configurational and vicinal CD ones on the lowest frequency side of the spin-forbidden band region (Table 1). This suggests that the intensity borrowing mechanism of the spin-forbidden transitions *via* spin-orbit coupling for the rotational strengths due to the vicinal effect is also operative and valid as in the case of the configurational effect. Of the four vicinal CD components in the spin-forbidden band region, two components on the lower frequency side, (+) and (−), are covered under the band envelope of the configurational CD component on the lowest frequency side in this region; *e.g.*, (+) one for $(+)_{589}$-$[Cr(gly)(en)_2]^{2+}$ (Fig. 2). Thus, the two peaks correspond to the splitting components of the configurational CD peak, which was previously assigned to the $^2E(^2E_g)$ state. The remaining vicinal components, (+) and (−), might correspond to the central $^2A_2(^2T_{1g})$ and the highest frequency $^2E(^2T_{1g})$ configurational CD bands, respectively, in view of the positions of their CD peaks. The large splitting interval of *ca.* 250 cm^{-1} obtained for the $^2E(^2E_g)$ state is comparable to those observed for such tetragonal complexes as $[CrX(NH_3)_5]^{n+}$ type.[13] The splitting interval of the $^2E(^2E_g)$ state for tris(ethylenediamine)chromium(III) complex has been found to be *ca.* 18 cm^{-1}.[14] Assuming that the present complexes belong effectively to holohedrized tetragonal (D_4) symmetry,[15] two vicinal CD peaks on the lower frequency side of the first band, (−) and (+), might be due to the splitting components of the ^4E state, and the remaining negative highest frequency peak to the $^4B_2$ one. The total rotational strength for the $^4E \leftarrow {}^4B_1$ transition in a tetragonal (D_4) field seems to be given by the sum of those for two individual transitions in a lower symmetry field. Thus, the signs of the rotational strengths for the $^4E \leftarrow$ and $^4B_2 \leftarrow {}^4B_1$ transitions are positive and negative, respectively, since the positive component of the ^4E state is much larger than the negative one (Fig. 2 and Table 1). On the basis of the theoretical relation between the rotational strengths for the spin-allowed and magnetic dipole allowed transitions and those for the spin-forbidden transitions of tetragonal Cr(III) complexes (Ref. 8, Table 2 third column), four vicinal CD peaks in the spin-forbidden band region are assigned as follows. Since the rotational strengths for the $^2A_1$, $^2A_2 \leftarrow {}^4B_1$ transitions should have the same signs as those for the $^4E \leftarrow {}^4B_1$ transition, two positive peaks are assigned to the $^2A_1$ and $^2A_2$ states from the lower frequency side. Two remaining negative peaks might be due to the $^2B_1$ and ^2E one from the lower frequency side, the rotational strengths of which are expected to have the same signs as those of the $^4B_2$ state (Table 1). It seems plausible that the orbitally nondegenerate $^2A_2(D_4)$ and the degenerate $^2E(D_4)$ components for the vicinal CD correspond to the nondegenerate $^2A_2(D_3)$ and degenerate $^2E(D_3)$ ones for the configurational CD, respectively.

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References

1) R. D. Gillard, S. H. Laurie, D. C. Price, D. A. Phipps, and C. F. Weick, *J. Chem. Soc., Dalton Trans.*, **1974**, 1385.
2) H. Oki, *Bull. Chem. Soc. Jpn.*, **50**, 680 (1977).
3) S. S. Minor, G. Witte, and G. W. Everett, Jr., *Inorg. Chem.*, **15**, 2052 (1976).
4) Y. Shimura, *Bull. Chem. Soc. Jpn.*, **31**, 315 (1958).
5) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); S. K. Hall and B. E. Douglas, *ibid.*, **8**, 372 (1969).
6) N. Matsuoka, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **9**, 719 (1970); *Bull. Chem. Soc. Jpn.*, **45**, 2491 (1972).
7) K. Yamasaki, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **42**, 119 (1969).
8) S. Kaizaki and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **48**, 3611 (1975).
9) S. Kaizaki, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **12**, 142 (1973).
10) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford (1962).
11) H. Yamatera, *Bull. Chem. Soc. Jpn.*, **31**, 95 (1958).
12) a) M. Kojima, H. Takayanagi, and J. Fujita, *Bull. Chem. Soc. Jpn.*, **50**, 1891 (1977); b) H. Yoneda, S. Yamasaki, and K. Maruyama, *Proc. 26th Symposium on Coodination Chemistry*, Sapporo, Japan, August 1976, p. 234.
13) C. D. Flint and A. P. Matthews, *J. Chem. Soc., Faraday Trans, 2*, **69**, 419 (1973).
14) I. B. Trabjerg and C. J. Ballhausen, *Mol. Phys.*, **20**, 811 (1971).
15) C. E. Schäffer, *Pure Appl. Chem.*, **24**, 361 (1970).