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Magnetic Circular Dichroism Spectra of Cobalt(III) Complexes in the Second d-d Absorption Band Region

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The MCD spectra of seventeen cobalt(III) complexes were measured in the visible and near-ultraviolet regions. Their behavior in the second d-d absorption band region were compared with those of the [Co-$(ox)_x(gly)_y(en)_z$] series comprising sixteen complexes (x, y, z=0, 1, 2, 3; and $x+y+z=3$), in which a positive band had been observed on the lower-energy side of the main negative band in this region. For the present work, the positive band was found in $[Co(tn)_3]^{3+}$, *cis*-$[Co(ox)_2(NH_3)_2]^-$, *cis*-$[Co(OH_2)_2(en)_2]^+$, *trans*-[Co(β-ala)$_2$(en)]$^+$, *mer*- and *fac*-[Co(picol)$_3$] (picol=picolinate(1−)), and [Co(acac)$_3$]. It is pointed out that all the complexes exhibiting a positive band were the tris(chelate) or *cis*-bis(chelate) types. Therefore the origin of this band is discussed in terms of the arrangement of two or three chelate rings. A positive band was not observed for complexes containing a CO_3^{2-} ligand, even if they were a tris(chelate) or *cis*-bis(chelate) type. This is explained from a structural basis. The two complexes which had a split second d-d absorption band, *mer-trans*(NH$_3$)-[CoCO$_3$(gly)(NH$_3$)$_2$] and [CoCO$_3$(picol)(NH$_3$)$_2$], showed two negative bands in the corresponding regions to both component absorption bands, in each complex.

In a previous paper,[1] the MCD (magnetic circular dichroism) spectra of $[Co(ox)_x(gly)_y(en)_z]$ series comprising sixteen complexes were reported. All complexes, except $[Co(en)_3]^{3+}$, showed the same MCD-spectra pattern in the spin-allowed second d-d electronic-absorption band region ($^1A_{1g}\rightarrow{}^1T_{2g}(O_h)$), despite the fact that they had various types of ligand atom constitutions and geometrical structures. Some curves are shown in Fig. 1. The spectra were composed of two bands whose signs were positive and negative, from the lower-energy side to the higher. Because other cobalt(III) complexes reported earlier[2–5] did not show a positive band in the corresponding region, the MCD behavior of the series of complexes in the previous study were quite interesting. Only a vague explanation, however, was offered for the origin of the positive band at that time. Then, the MCD spectra of many more cobalt(III) complexes containing nitrogen and oxygen atoms, like in the $[Co(ox)_x(gly)_y(en)_z]$ series complexes, have been measured in order to clarify the origin of this band.

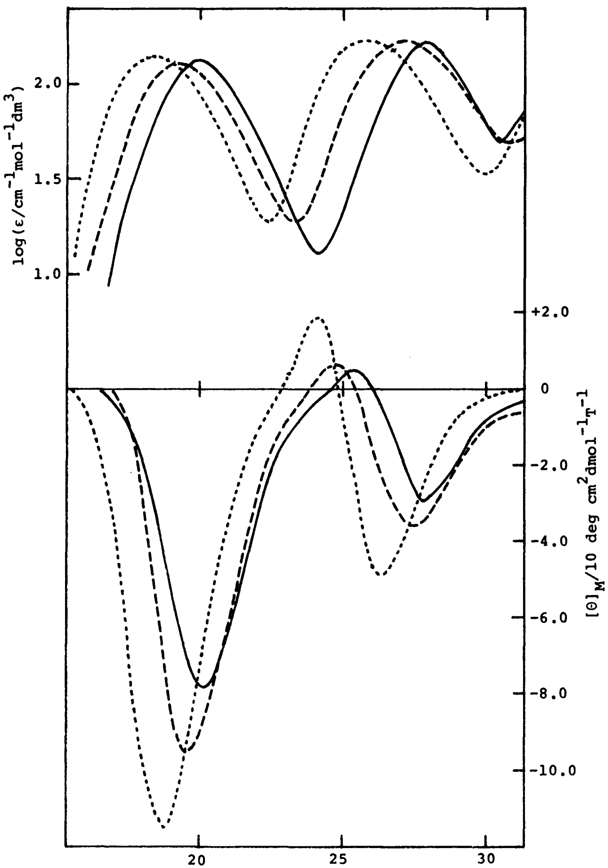

Fig. 1. Absorption and MCD spectra of C$_1$-*cis(O)*-$[Co(gly)_2(en)]^+$ (——), *fac*-[Co(ox)(gly)(en)] (— —), and C$_1$-*cis(N)*-$[Co(ox)(gly)_2]^-$ (----).

In addition, several cobalt(III) complexes, whose second d-d absorption bands were split, were reported by Shibata and his co-workers in the 1970's.[6–12] It is also interesting to know the MCD behavior of those complexes.

In the present paper, newly obtained MCD data regarding seventeen cobalt(III) complexes, including whose second d-d absorption bands are split, are described and discussed in terms of the origin of the positive MCD band.

Experimental

Materials. *mer-trans(NH$_3$)*-[CoCO$_3$(gly)(NH$_3$)$_2$], and *mer-trans(NH$_3$)*-, *mer-cis(NH$_3$)*- and *fac*-[CoCO$_3$(picol)(NH$_3$)$_2$] were prepared according to the method of Shibata et al.[6,11] All the other complexes described in this paper were synthesized by ordinary methods. The absorption and MCD data of *trans*- and *cis*-$[Co(OH_2)_2(en)_2]^+$ were obtained from a 10% HClO$_4$ solution of *trans*-[Co(OH)(OH$_2$)(en)$_2$](ClO$_4$)$_2$ which was provided by T. Komorita. When this solution was kept standing at room temperature for several hours, the absorption spectrum gradually changed with four isosbestic points(Fig. 2). After a week, the maximum data in the first and second d-d absorption bands of the solution approached the known data of *cis*-[Co(OH$_2$)$_2$-

$(en)_2]^{3+}$.[13,14] Then, the spectra found immediately after dissolving and measured after a week were regarded as the spectra of *trans*-$[Co(OH_2)_2(en)_2]^{3+}$ and *cis*-$[Co(OH_2)_2(en)_2]^{3+}$, respectively.

Measuremens. The electronic absorption spectra were measured by a Shimadzu UV-200 and a Hitachi 330 spectrophotometer. The MCD spectra were recorded in a magnetic field of 1.5 *T* with a JASCO MOE-1 spectropolarimeter. The MCD intensity is expressed in terms of molar ellipticity, $[\theta]_M$, which has the units of deg cm^2 dmol^{-1} T^{-1}. The data of $[Co(acac)_3]$ was obtained in an acetone solution, and *mer*- and *fac*-$[Co(picol)_3]$ were in a 30% $HClO_4$ solution, because they were insoluble or slightly soluble in water. The MCD and electronic absorption spectra of *trans*- and *cis*-$[Co(OH_2)_2(en)_2]^{3+}$ were recorded in a 10% $HClO_4$ solution, as mentioned above. All the other measurements were made in aqueous solutions at room temperature.

Results

The newly obtained MCD data of the seventeen cobalt(III) complexes are listed in Table 1, along with electronic absorption data. Some typical curves in the visible and near-ultraviolet regions are shown in Figs. 2—4.

As can be seen in these Figures, the shapes of the MCD spectra in the first absorption band region ($^1A_{1g}\rightarrow{}^1T_{1g}(O_h)$) are similar to those of the electronic absorption spectra, which indicates that the contribution of the B term is dominant in this region. Such a behavior has also been seen in other cobalt(III) complexes studied earlier.[1]

In the second d–d absorption-band region, however, the pattern of the MCD spectra for several complexes are different from those of the absorption spectra. The MCD behavior observed in the present work can be grouped roughly into the following three types.

In the first type, only a negative band is observed. This is, of course, the most simple pattern, and about half of the complexes listed in Table 1 belong to this type. They are $[Co(NH_3)_6]^{3+}$, $[Co(ox)(NH_3)_4]^+$, $[CoCO_3(en)_2]^+$, $[CoCO_3(NH_3)_4]^+$, *trans*-$[Co(OH_2)_2(en)_2]^{3+}$, *cis*-$[Co(OH_2)_2(NH_3)_4]^{3+}$, and *mer-cis(NH*$_3$*)*- and *fac*-$[CoCO_3(picol)(NH_3)_2]$.

The MCD spectra of the second type comprise two bands, a small positive band on the lower-energy side

Table 1. Absorption Maximum and MCD Extremum Data in d-d Absorption Band Region

Complex	First d-d band region		Second d-d band region	
	Absorption	MCD	Absorption	MCD
	σ[a] (log ε)[b]	σ[a] ($[\theta]_M$)[c]	σ[a] (log ε)[b]	σ[a] ($[\theta]_M$)[c]
$[Co(NH_3)_6]Cl_3$	21.0(1.78)	21.0(−2.1)	29.2(1.68)	28.6(−0.5)
$[Co(tn)_3]Cl_3$	20.5(1.88)	20.5(−2.4)	28.5(1.87)	26.5(−0.1) 29.2(+0.5)
$[Co(ox)(NH_3)_4]Cl$	19.7(1.93)	20.0(−6.6)	28.0(2.15)	27.8(−1.5)
cis-$NH_4[Co(ox)_2(NH_3)_2]$	18.1(2.04)	18.5(−10.6)	26.2(2.31)	23.7(+0.3) 26.0(−5.0)
$[CoCO_3(en)_2]Br$	19.6(2.08)	20.0(−9.8)	27.9(2.04)	27.4(−3.9)
$[CoCO_3(NH_3)_4](SO_4)_{1/2}$	19.1(2.05)	19.6(−8.0)	27.5(2.14)	27.0(−2.7)
trans-$[Co(OH_2)_2(en)_2](ClO_4)_3$	18.2(1.50) 22.9(1.54)	18.7(−1.2) 22.4(−1.0)	28.7(1.72)	28.2(−0.8)
cis-$[Co(OH_2)_2(en)_2](ClO_4)_3$	20.3(1.86)	20.1(−4.6)	27.9(1.77)	26.2(+0.5) 29.2(−0.7)
cis-$[Co(OH_2)_2(NH_3)_4](SO_4)_{3/2}$	19.7(1.75)	19.0(−3.2)	28.2(1.65)	28.2(−1.2)
trans-$[Co(\beta\text{-ala})_2(en)]ClO_4$	18.5(2.02) 21.8(1.67)[d]	18.5(−1.9) 21.8(−2.7)	27.5(1.95)	25.6(+0.2) 28.0(−0.8)
mer-$[Co(picol)_3]$	19.0(2.00)	20.0(−10.5)	26.4(2.33)	24.6(+0.8) 27.0(−6.7)
fac-$[Co(picol)_3]$	19.3(2.17)	19.6(−11.1)	26.4(2.55)	24.4(+0.5) 27.0(−6.2)
mer-trans(NH$_3$*)*-$[CoCO_3(gly)(NH_3)_2]$	18.7(1.91)	18.7(−4.1)	24.7(1.71)[d] 27.3(1.96)[d]	24.7(−2.2) 27.3(−1.6)
mer-trans(NH$_3$*)*-$[CoCO_3(picol)(NH_3)_2]$	19.3(1.96)	19.0(−3.0)	24.7(1.65)[d] 27.3(1.86)[d]	24.4(−2.7) 26.7(−1.5)[d]
mer-cis(NH$_3$*)*-$[CoCO_3(picol)(NH_3)_2]$	18.4(2.04)	19.0(−11.6)	26.8(2.29)	26.2(−7.3)
fac-$[CoCO_3(picol)(NH_3)_2]$	19.0(2.11)	19.4(−13.0)	27.0(2.27)	27.0(−7.8)
$[Co(acac)_3]$	16.8(2.12)	16.7(−11.7)	22.0(2.25)[d]	22.0(+1.0) 23.8(−1.3)

a) Wave numbers are given in 10^3 cm^{-1}. b) Logarithms of the molar absorption coefficients are given in log(ε/ cm^{-1} mol^{-1} dm^3). c) Molar ellipticities are given in 10 deg cm^2 dmol^{-1} T^{-1}. d) Shoulders.

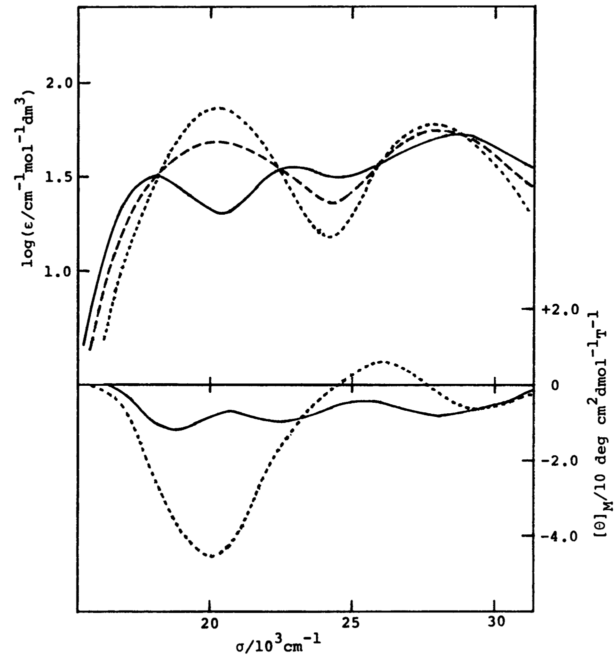

Fig. 2. Spectral change of *trans*-$[Co(OH)(OH_2)(en)_2]^{2+}$ in 10% $HClO_4$ with time: Within 1 h —— (*trans*-$[Co(OH_2)_2(en)_2]^{3+}$), after 2 d — —, and after one week ---- (*cis*-$[Co(OH_2)_2(en)_2]^{3+}$).

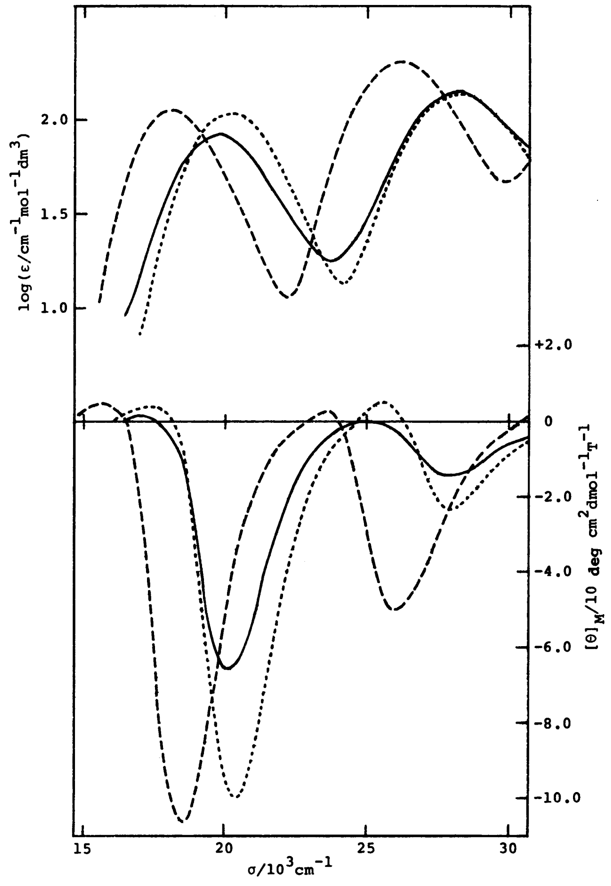

Fig. 3. Absorption and MCD spectra of $[Co(ox)(NH_3)_4]^+$ (——), $[Co(ox)_2(NH_3)_2]^-$ (— —), and $[Co(ox)(en)_2]^+$ (----).

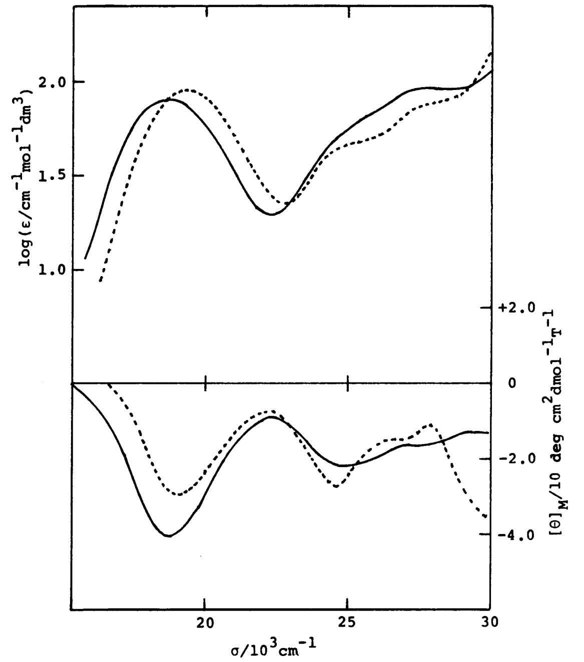

Fig. 4. Absorption and MCD spectra of *mer-trans(NH*$_3$*)*-$[CoCO_3(gly)(NH_3)_2]$ (——), and *mer-trans(NH*$_3$*)*-$[CoCO_3(picol)(NH_3)_2]$ (----).

and a large negative band on higher-energy side. This pattern is what has been seen in the $[Co(ox)_x(gly)_y(en)_z]$ series complexes.[1] In the present work, *cis*-$[Co(OH_2)_2(en)_2]^{3+}$, *trans(O)*-$[Co(\beta\text{-ala})_2(en)]^+$, *mer*- and *fac*-$[Co(picol)_3]$, *cis*-$[Co(ox)_2(NH_3)_2]^-$, and $[Co(acac)_3]$ show this type spectra.

The tris(trimethylenediamine) complexes, $[Co(tn)_3]^{3+}$, also exhibits two bands whose signs are opposite to each other. In this complex, however, the small band on the lower-energy side is negative and the dominant band on the higher-energy is positive. Since such a unique behavior of the sign of trimethylenediamine complexes has been reported elsewhere,[15] this complex is also included in the second group.

The two complexes which have a split second d–d absorption band, *mer-trans*(NH_3) form of $[CoCO_3(gly)(NH_3)_2]$ and $[CoCO_3(picol)(NH_3)_2]$, show the third type MCD behavior. They exhibit two negative bands in this region; each band is observed in a region corresponding to the component absorption band (Fig. 4).

Discussion

In the previous study on the MCD of $[Co(ox)_x(gly)_y(en)_z]$ series complexes,[1] the positive MCD band in the second d–d electronic absorption band region was suggested to be related to the presence of a coordinated carboxylato group. In the present work this assumption is also applicable for *trans(O)*-[Co(*β*-

ala)$_2$(en)]$^+$, *mer*- and *fac*-[Co(picol)$_3$], and *cis*-[Co(ox)$_2$(NH$_3$)$_2$]$^-$, which have coordinated carboxylato ligands and show a positive band. For [Co(ox)(NH$_3$)$_4$]$^+$, however, only a negative band is observed, in spite of the presence of two carboxylato groups. On the other hand, the two complexes which have no carboxylato ligands, [Co(tn)$_3$]$^{3+}$ and *cis*-[Co(OH$_2$)$_2$(en)$_2$]$^{3+}$, exhibit a positive band. From these facts, the previous suggestion that the origin of the positive band is connected with the presence of a coordinated carboxylato ligand will require reconsideration.

In the oxalato complexes, it is noticeable that the different types of MCD behavior is observed for a tetraammine-type complex of [Co(ox)(NH$_3$)$_4$]$^+$ (group 1), from a diammine-type complex of [Co(ox)$_2$(NH$_3$)$_2$]$^-$ and a bis(ethylenediamine)-type complex of [Co(ox)(en)$_2$]$^+$ (group 2), as can be seen in Fig. 3. The same aspect with the latter was also seen in another study on the MCD of (amino acidato)cobalt(III) complexes.[16] A positive band was observed in bis(ethylenediamine) complexes, [Co(amac)(en)$_2$]$^{2+}$, but not in tetraammine-type complexes, [Co(amac)(NH$_3$)$_4$]$^{2+}$, in which amac denotes glycinato and DL-alaninato ligands. Additionally, a positive band was not observed in the pentaammine-type complexes of [Co(Hamac)(NH$_3$)$_5$]$^{3+}$ either (Hamac=glycine, L-alanine, L-serine, L-phenylalanine and β-alanine).

In the three diaqua complexes, *trans*- and *cis*-[Co(OH$_2$)$_2$(en)$_2$]$^{3+}$ and *cis*-[Co(OH$_2$)$_2$(NH$_3$)$_4$]$^{3+}$, the positive band is observed only in *cis*-[Co(OH$_2$)$_2$(en)$_2$]$^{3+}$. Because other complexes studied to date have shown the same MCD-spectra pattern among their geometrical isomers, e.g., C$_2$-cis, C$_1$-cis and trans isomers of [Co(gly)$_2$(en)]$^+$ and [Co(ox)(gly)$_2$]$^-$ and mer and fac isomers of [Co(gly)$_3$], [Co(picol)$_3$], and [Co(ox)(gly)(en)], this difference in the MCD between the trans and cis isomers of [Co(OH$_2$)$_2$(en)$_2$]$^{3+}$ is interesting.[1]

As a result of these observations, it can be pointed out that the complexes exhibiting a positive band (group-2 complexes in the present work and the [Co(ox)$_x$(gly)$_y$(en)$_z$] series complexes in previous work) are all tris(chelate) or *cis*-bis(chelate) type. This fact leads us to a new assumption that the existence of the positive MCD band in question can be associated with a particular arrangement of two or three chelate rings.

It is reasonable to consider that the MCD behavior is affected by the arrangement of the chelate rings. For example, a D$_3$ or a pseudo D$_3$ symmetrical field would be produced around the central metal atom in tris(chelate)- and *cis*-bis(chelate)-type complexes. Then, the origin of the positive band might be associated with the electronic transition split in a D_3 (or pseudo D_3) symmetrical field caused in such a way. Namely, this band is assignable to one of the two component bands of E and A$_1$ in the T$_{2g}$ (O$_h$) transition, which have opposite signs to each other. As an alternative explanation, it is also reasonable to consider that this band appears as a positive wing of the A term, which exhibits a dispersion-type curve, in a degenerated component of E in a D_3 (or pseudo D_3) symmetrical field. Although a full explanation can not be offered at the present stage, all experimental facts described above can be explained well from this assumption.

The tris(chelate)-type complex of [Co(en)$_3$]$^{3+}$ has not exhibited a positive band, as mentioned above. The MCD curve of this complex, however, is considerably asymmetrical and its shape suggests that a small positive band on the lower-energy side is hidden by a successive large negative band.[1]

The complexes containing a carbonato chelate ligand do not show a positive band either, even though they are the tris(chelate) or *cis*-bis(chelate) type. This might be explained in terms of distorted structures, which is brought about by a four-membered carbonato chelate ring. For example, it has been reported for [CoCO$_3$(NH$_3$)$_4$]$^+$ that the bite angle of the carbonato chelate ring is 70° and that the distance of the Co–N bond containing the nitrogen atom at a position trans to the carbonato oxygen atom is considerably longer (2.03 Å) than those containing the nitrogen atoms at the cis positions (1.93 and 1.95 Å).[17] Thus, the complexes containing a chelated carbonato ligand are inadequate for determining the MCD behavior in parallel with the other tris(chelate) or *cis*-bis(chelate) type complexes which have nearly octahedral structures.

The two complexes which have a split second d–d absorption band, *mer-trans(NH$_3$)*-[CoCO$_3$(gly)(NH$_3$)$_2$] and [CoCO$_3$(picol)(NH$_3$)$_2$], show two MCD bands in the corresponding regions (Fig. 4). Because their signs are both negative and their positions are almost the same as those of the component electronic absorption bands, each MCD band in both complexes is assignable to have a dominant B term character.

References

1) N. Matsuoka and Y. Shimura, *Bull. Chem. Soc. Jpn,,* **49**, 2118 (1976).

2) A. J. McCaffery, P. J. Stephens, and P. N. Schatz, *Inorg. Chem.*, **6**, 1614 (1967).

3) R. L. Russell and B. E. Douglas, *Inorg. Chim, Acta*, **3**, 426 (1969).

4) R. L. Russell and B. E. Douglas, *Inorg. Nucl. Chem, Lett.*, **9**, 1251 (1973).

5) H. Kato and J. Gohda, *Bull. Chem. Soc. Jpn.*, **46**, 636 (1973).

6) S. Kanazawa and M. Shibata, *Bull. Chem. Soc. Jpn.*, **44**, 2424 (1971).

7) S. Nakashima and M. Shibata, *Bull. Chem. Soc. Jpn.*, **47**, 2069 (1974).

8) S. Nakashima and M. Shibata, *Bull. Chem. Soc, Jpn.*,

48, 3128 (1975).

9) T. Ito and M. Shibata, *Inorg. Chem.,* **16**, 108 (1979).

10) Y. Ida, S. Fujinami, and M. Shibata, *Bull. Chem. Soc. Jpn.,* **50**, 2665 (1977).

11) Y. Ida, M. Sakai, S. Sakai, and M. Shibata, *Bull. Chem. Soc. Jpn.,* **50**, 2807 (1977).

12) K. Okazaki and M. Shibata, *Bull. Chem. Soc, Jpn,,* **52**, 1391 (1979).

13) F. Basolo, *J. Am. Chem. Soc.,* **72**, 4393 (1950).

14) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.,* **6**, 1265 (1952).

15) K. Nakayama, T. Komorita, and Y. Shimura, *Bull. Chem. Soc. Jpn.,* **57**, 2930 (1984).

16) E. Ueda, N. Matsuoka, and Y. Shimura, *Bull. Chem. Soc. Jpn.,* **51**, 1895 (1978).

17) G. A. Barclay and B. F, Hoskins, *J. Chem, Soc.,* **1962**, 586.