A CD Spectral Study of Square Planar Copper(II) and Nickel(II) Complexes Containing Optically Active N,N,N',N'-tetramethyl(R)-propylenediamine and Various Bidentate Ligands

MASATATSU SUZUKI* and YUZO NISHIDA

Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan, 812

(Received December 10, 1976)

The absorption and circular dichroism (CD) spectra of new square planar copper(II) and nickel(II) complexes with the general formula, [M(tmpn) (A-A)]$^{n+}$ were measured, where tmpn and A-A represent N,N,N',N'-tetramethyl-(R)-propylenediamine and various bidentate ligands such as aminoacids, β-diketones, and dithiocarbamates, respectively. From the CD spectral patterns these complexes were found to be classified into three groups, and the characteristics of CD spectra of three groups were discussed in terms of Liehr's model and the so-called perturbation model.

Introduction

Many studies on the electronic spectra in terms of the circular dichroism (CD) spectra have been published for square planar copper(II) and nickel(II) complexes [2–10], however these studies were limited to some complexes, for example cis-[MN$_2$O$_2$] type complexes with Schiff bases, and [MN$_4$] type complexes with diamines and aminoacid amides, because optically active ligands to form the square planar complexes must be used.

Recently Fukuda and Sone [12] studied copper (II) and nickel(II) mixed chelates, [M(tmen)(A-A)]$^{n+}$, where tmen is N,N,N',N'-tetramethylethylenediamine and A-A is another bidentate ligand, such as ethylenediamine, glycine, or β-diketones, *etc.*, and reported that the square planar mixed chelates are quantitatively formed in some solvents. In this study, a series of optically active mixed chelates, [M(tmpn)(A-A)]$^{n+}$, were prepared by using R-tmpn instead of tmen, where tmpn represents N,N,N',N'-tetramethyl-(R)-propylenediamine. A remarkable feature of these mixed chelates is that they can provide the CD spectra of square planar complexes containing a variety of bidentate ligands with no optical activity with itself, such as β-diketones, diethyldithiocarba-

mate ion, *etc.* The CD spectra of the mixed chelates were measured in order to obtain information about the CD signs in the d–d region and the conformational dissymmetries in the diamine chelate rings, and to compare the CD spectra of copper(II) mixed chelates with those of corresponding nickel(II) mixed chelates.

Analytical data of these new complexes and the abbreviations of the ligands cited in this paper are summarized in Tables I and II, respectively. The assignments of CD peaks in the d–d region of [Cu(tmpn)(acac)]$^+$ and [Ni(tmpn)(acac)]$^+$ were already discussed [11], where Hacac represents acetylacetone.

Experimental

Materials

N,N,N',N'-tetramethyl-(R)-propylenediamine [13] and sodium maleonitrildithiolate [14] were prepared according to the methods described in the literature. Solvents used for spectral measurements were "extra pure" or purified according to the methods described in the literature [15].

Preparation of Complexes

[Cu(tmpn)(gly)] ClO$_4$: To a methanol solution of 2 mmol of Cu(H$_2$O)$_6$(ClO$_4$)$_2$ were added equimolar amounts of tmpn and Hgly, and 2 mmol of NaHCO$_3$ was added to neutralize Hgly. The mixed solution was concentrated to about 5 ml on a water bath and was allowed to stand at room temperature for several days. Bluish violet crystals were separated from the solution.

[Cu(tmpn)(bzac)] ClO$_4$, [Cu(tmpn)(dbm)] ClO$_4$ and [Cu(tmpn)(acac)] ClO$_4$: The preparations of these complexes were similar to those of [Cu(tmen)(β-dik)]-ClO$_4$ [12].

[Cu(tmpn)(mpy)] ClO$_4$: To a methanol solution of 2 mmol of Cu(H$_2$O)$_6$(ClO$_4$)$_2$ were added equimolar amounts of tmpn and Hmpy with stirring, and 2 mmol of NaHCO$_3$ was added to the mixed solution. The mixed solution was evaporated to dryness under

TABLE I. Analytical Data of the New Complexes

Complex	C (%)		H (%)		N (%)	
	found.	calcd.	found	calcd.	found	calcd.
[Cu(tmpn)(bzac)]ClO$_4$	44.59	44.93	5.87	5.98	6.03	6.16
[Cu(tmpn)(bdm)]ClO$_4$	50.83	51.10	5.59	5.61	5.35	5.41
[Cu(tmpn)(mpy)]ClO$_4$	34.29	34.46	5.32	5.32	10.07	10.02
[Cu(tmpn)(dtc)]ClO$_4$	32.47	32.61	6.31	6.34	9.47	9.51
[Cu(tmpn)(mnt)]	39.18	39.56	5.36	5.43	16.62	16.78
[Cu(tmpn)(gly)]ClO$_4$	29.14	29.34	5.96	5.98	11.27	11.43
[Ni(tmpn)(bzac)]B(ph)$_4$	73.68	73.58	7.14	7.23	4.46	4.18
[Ni(tmpn)(mpy)]B(ph)$_4$	67.89	68.21	6.43	6.68	6.37	6.62
[Ni(tmpn)(dtc)]B(ph)$_4$	65.72	65.91	7.32	7.18	6.00	6.40
[Ni(tmpn)(mnt)]	39.83	40.15	5.48	5.47	17.01	17.03

TABLE II. Abbreviations of the ligands

Ligand	Abbr.
N,N,N',N'-tetramethylethylenediamine	tmen
N,N,N',N'-tetramethyl-(R)-propylenediamine	tmpn
ethylenediamine	en
trimethylenediamine	tn
glycine	Hgly
β-alanine	Hβ-ala
acetylacetone	Hacac
benzoylacetone	Hbzac
dibenzoylmethane	Hdbm
2-mercaptopyridine-N-oxide	Hmpy
maleonitrildithiol	H$_2$mnt
diethyldithiocarbamic acid	Hdtc
oxalic acid	H$_2$ox
malonic acid	H$_2$mal

reduced pressure and 5 ml of chloroform was added. Insoluble material was filtered and the filtrate was allowed to stand overnight. Violet–brown crystals were separated from the solution.

[Cu(tmpn)(dtc)](ClO$_4$: To an aqueous methanol (1:1) solution of 2 mmol of Cu(H$_2$O)$_6$(ClO$_4$)$_2$ were added equimolar amounts of tmpn and Nadtc, and the mixed solution was evaporated to dryness under reduced pressure. The residue was dissolved into 20 ml of acetone and insoluble material was filtered off. A few ml of ether was added to the filtrate. Green crystals were separated from the solution.

[Cu(tmpn)(mnt)]: To an aqueous methanol (1:1) solution of 2 mmol of Cu(H$_2$O)$_6$(ClO$_4$)$_2$ were added equimolar amounts of tmpn and Na$_2$mnt and then the mixed solution was heated on a water bath for two hours. A reddish–brown powder was obtained.

[Ni(tmpn)(acac)]B(ph)$_4$ and [Ni(tmpn)(bzac)]B-(ph)$_4$: To a methanol solution of 2 mmol of Ni-

(H$_2$O)$_6$(ClO$_4$)$_2$ were added equimolar amounts of tmpn and the corresponding β-diketones, and 2 mmol of NaHCO$_3$ was added to this mixed solution. The resultant mixture was heated on a water bath for two hours, and then was evaporated to dryness under reduced pressure. Then the solid was dissolved into 20 ml of acetone and filtered in order to separate the insoluble material. A large excess of NaB(ph)$_4$ was added to the acetone solution and the resultant mixture was evaporated to dryness under reduced pressure. Then the solid was dissolved into 20 ml of chloroform. The solution was concentrated to 5 ml by blowing air stream on it and filtered to separate the white precipitate. 10 ml of chloroform was added to the filtrate, concentrated to 5 ml by blowing air stream and filtered to separate the white precipitate. This procedure was repeated until no more white precipitate formed. A few ml of ether were added to the resultant solution, then a red powder was obtained from the solution.

[Ni(tmpn)(mpy)]B(ph)$_4$ and [Ni(tmpn)(dtc)]B-(ph)$_4$: The methods of preparation were similar to those of β-diketonato complexes.

[Ni(tmpn)(mnt)]: The method of preparation was similar to that of the corresponding copper(II) complex.

Spectral Measurements

The absorption spectra were measured by a Hitachi EPS-2 spectrophotometer at room temperature. The circular dichroism spectra were obtained with a Jasco ORD-UV/5 optical rotatory dispersion recorder with a CD attachment at room temperature. Absorption and CD spectra of [Cu(tmpn)(ox)], [Cu(tmpn)(mal)] and [Cu(tmpn)(β-ala)]$^+$ which were not obtained in crystals were measured in the following manner. The appropriate amount of Cu(H$_2$O)$_6$-(ClO$_4$)$_2$ was dissolved in water and the concentration of copper(II) ion of the solution was determined by

TABLE III. Absorption and CD spectral data of the mixed chelates

Complex	Absorption $\nu_{max} \times 10^3$ cm^{-1} (log ϵ)		CD $\nu_{max} \times 10^3$ cm^{-1} ($\Delta\epsilon$)		Solvent**
[Cu(tmpn)(ox)]	16.4 (2.03)		14.8 (+0.09)	16.9 (−0.39)	a
[Cu(tmpn)(gly)]$^+$	17.2 (2.01)		15.5 (+0.15)	18.8 (−0.36)	c
[Cu(tmpn)(acac)]$^+$	18.5 (2.04)		17.6 (−0.27)	19.4 (+0.09)	b
			21* (−0.18)		
[Ni(tmpn)(acac)]$^+$	20.5 (1.83)		17.8 (−0.21)	19.8 (+0.54)	b
			22.1 (−0.51)		
[Cu(tmpn)(mpy)]$^+$	18.5 (2.15)		14* (−0.15)	17.7 (+0.84)	b
			20* (−0.21)		
[Ni(tmpn)(mpy)]$^+$	20.7 (2.04)		15.8 (−0.06)	18.7 (+0.27)	b
			21.0 (+0.06)		
[Cu(tmpn)(dtc)]$^+$	15.6 (2.06)*	19.6 (2.40)	16.3 (−0.12)	20.0 (+0.18)	b
[Ni(tmpn)(dtc)]$^+$	17.4 (1.81)*	20.8 (2.10)	19.3 (+0.66)		b
[Cu(tmpn)(mnt)]	10.4*	20.8 (2.69)	16.3 (+0.12)	20.8 (−1.62)	b
[Ni(tmpn)(mnt)]	11.6 (1.20)	18.2 (1.70)	18.1 (+0.18)	21.7 (+0.33)	b
	21.3 (2.23)				

* = shoulder **a, water; b, tetrachloroethane; c, acetone.

EDTA titration, PAN being used as an indicator. The solution was separated into three portions and to each portion were added equimolar amounts of tmpn, Na$_2$ox, Na$_2$mal or β-ala. The resultant solutions were diluted to the appropriate concentration (9.96 × 10^{-3} M). These solutions were used to measure CD and absorption spectra.

Results and Discussion

The CD and absorption spectral data of the new complexes are summarized in Table III. It is very clear that the mixed chelates obtained in this study are classified into three groups according to the CD spectral patterns in the d–d region: (i) Aminoacidato and dicarboxylato copper(II) mixed chelates in which a (+, −) sign pattern was observed from lower energy in the d–d region; (ii) β-diketonato and pyridine-N-oxide-2-mercaptato mixed chelates in which a (−, +, −) sign pattern was observed in the d–d region, and (iii) Diethyldithiocarbamato mixed chelates.

The CD and absorption spectra of the mixed chelates of the group (i), [Cu(tmpn)(ox)] and [Cu(tmpn)(mal)], are given in Fig. 1. From the CD spectra it is possible to elucidate the effect of the size of optically inactive bidentate chelate rings on the CD spectrum (i.e., the variation of A–M–A angle). It is well known that the oxalate ion forms a five-membered chelate ring (A–M–A angle is smaller than 90° [16]) and the malonate ion forms a six-membered chelate ring (A–M–A angle is larger than 90° [17]). Thus it is concluded that the CD spectra of
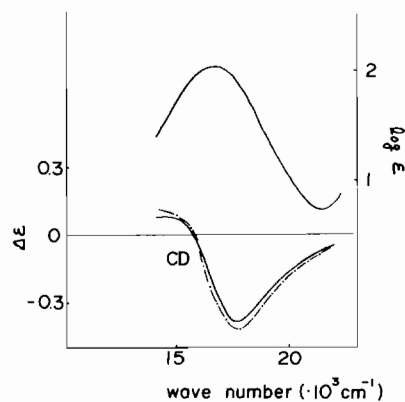

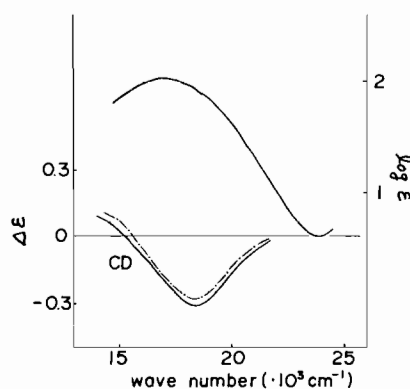Figure 1. CD and absorption spectra of [Cu(tmpn)(ox)] (——) and [Cu(tmpn)(mal)] (−·−·) in H$_2$O.

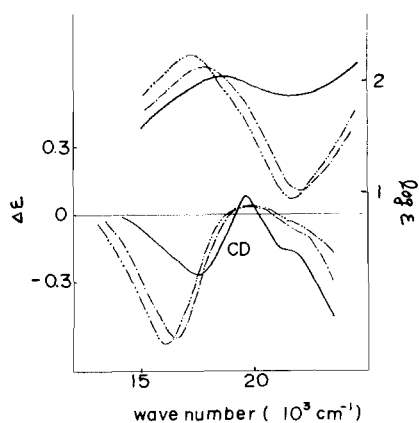Fig. 2. CD and absorption spectra of [Cu(tmpn)(gly)]$^+$ (——) and [Cu(tmpn)(β-ala)]$^+$ (−·−) in H$_2$O.

Figure 3. CD and absorption spectra of [Cu(tmpn)(acac)]⁺ in
tetrachloroethane (——), methanol (—·—) and DMSO (—··—).

Figure 4. CD and absorption spectra of [Cu(tmpn)(mpy)]⁺
in tetrachloroethane (——), methanol (—·—) and DMSO
(—··—).

Figure 5. CD and absorption spectra of [Cu(tmpn)(dtc)]⁺ in
tetrachloroethane (——), methanol (—·—) and DMSO
(—··—).

these mixed chelates are independent of the A–M–A angle formed by optically inactive bidentate ligands. The CD spectra of [Cu(tmpn)(gly)]⁺ and [Cu(tmpn)-(β-ala)]⁺ are similar to each other (*cf.* Fig. 2). However, as mentioned in our previous paper [18], CD spectra of [Pd(tmpn)(en)] and [Pd(tmpn)(tn)]²⁺ are different from each other, in which a significant interligand steric hindrance is present. Fukuda [12] pointed out that in [Cu(tmen)(gly)]⁺, the interligand steric hindrance between amino hydrogens of glycinate ion and N-methyl hydrogens of tmen is smaller than that in [Cu(tmen)(en)]²⁺. The similarity of the CD spectra of [Cu(tmpn)(gly)]⁺ and [Cu(tmpn)(β-ala)]⁺ supports this assumption.

For the complexes of the group (ii), three Cotton effects were observed in the d–d region and hereafter they will be termed as α, β and γ bands from lower energy, respectively. As shown in Fig. 3, three Cotton effects were observed for [Cu(tmpn)(acac)]⁺ in tetrachloroethane and nitromethane, whereas the γ band was not observed in the other solvents uded (acetonitrile, acetone, methanol, DMF and DMSO). The same (−, +, −) sign pattern was observed for [Ni(tmpn)-acac)]⁺ in tetrachloroethane, but the relation of CD intensities of α, β and γ bands is much different from that of [Cu(tmpn)(acac)]⁺ as shown in Table III. Nishida *et al.* [9] found that there is a resemblance between electronic and CD spectra of square planar copper(II) and nickel(II) complexes containing the same ligands in the d–d region. According to Liehr's theory [19], it is expected that for copper(II) and nickel(II) complexes with the same ligands, the CD signs of d–d bands arising from the same electronic transitions are identical and the CD intensities of nickel(II) complexes are twice as those of copper-(II) complexes. Actually for many copper(II) and nickel(II) complexes containing the same ligands, it was found that the CD intensities of nickel(II) complexes are larger than those of copper(II) complexes, and the sign of the main component of Cotton
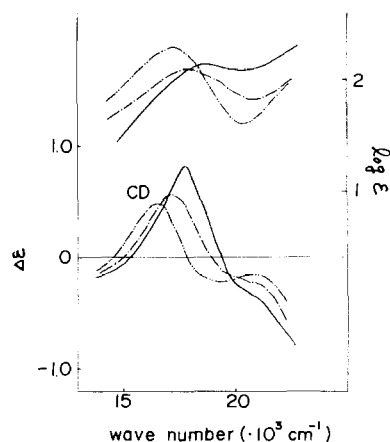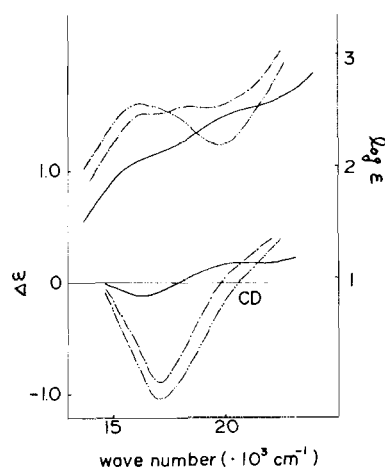
effect is identical [2–9], where the main component means the largest Cotton effect in the d–d region. In this study, it was found that β-diketonato copper(II) and nickel(II) mixed chelates show the same CD sign pattern but show different CD intensity.

The CD and absorption spectra of [Cu(tmpn)-(mpy)]⁺ are shown in Fig. 4. In all solvents used, this mixed chelate also exhibits the (−, +, −) sign pattern as well as that of [Cu(tmpn)(acac)]⁺ in tetrachloroethane. However the CD intensity patterns are different between [Cu(tmpn)(acac)]⁺ and [Cu(tmpn)-(mpy)]⁺ as shown in Fig. 3 and Fig. 4. In [Ni(tmpn)-(mpy)]⁺, the signs of α and β bands are the same as those of α and β bands in [Cu(tmpn)(mpy)]⁺, whereas the sign of γ band is reversed (*cf.* Table III). From the above results, it was found that there is a resemblance of CD sign between copper(II) and nickel(II) mixed chelates of the group (ii); however, there is a considerable difference for the relative
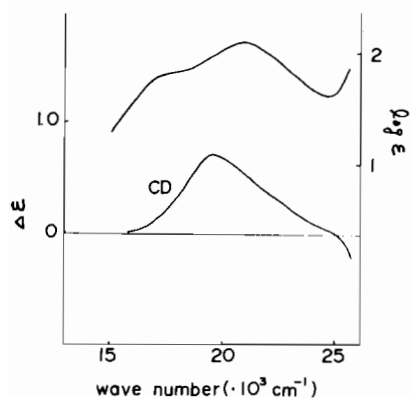
Figure 6. CD and absorption spectra of [Ni(tmpn)(dtc)]$^+$ in tetrachloroethane.

Figure 7. Absorption spectra of [Cu(tmpn)(acac)]$^+$ (——) and [Ni(tmpn)(acac)]$^+$ (— · —) in tetrachloroethane.

Figure 8. Absorption spectra of [Cu(tmpn)(dtc)]$^+$ (——) and [Ni(tmpn)(acac)]$^+$ (— · —) in tetrachloroethane.

CD intensities between them, the reasons for this being discussed in the last section.

[Cu(tmpn)(dtc)]$^+$ and [Ni(tmpn)(dtc)]$^+$ mixed chelates show very different CD spectra from those of the mixed chelates of the group (i) and group (ii) as shown in Fig. 5 and Fig. 6. Two small (–, +) Cotton effects were observed for [Cu(tmpn)(dtc)]$^+$, corresponding to the two absorption bands in tetrachloroethane, but in all other solvents the small positive Cotton effect disappears and only a large negative Cotton effect was observed. As seen in Fig. 6, only one large positive Cotton effect was observed for [Ni(tmpn)(dtc)]$^+$. Thus no similarity was found for CD spectra of [Cu(tmpn)(dtc)]$^+$ and [Ni(tmpn)(dtc)]$^+$.

From the above experimental results it was found that the nickel(II) and copper(II) complexes with the same ligands do not always show similar CD spectra. For [Cu(tmpn)(dtc)]$^+$ and [Ni(tmpn)(dtc)]$^+$, even the signs of main components in CD spectra are different. This fact cannot be explained in terms of the d–p and d–f mixing terms only [20], because the dissymetric potentials of copper(II) and nickel(II) mixed chelates arising from the conformational dissymmetries are identical. In order to understand the above facts, it should be noted that remarkable differences are found in the absorption spectra, especially in the ultraviolet region (25–35 × 10^3 cm^{-1}), as shown in Figs. 7 and 8. Since d–d transitions, metal–ligand charge transfer transitions and interligand transitions lie energetically close to each other, it seems necessary for the investigation on the rotatory powers of d–d transitions to take into consideration the contributions arising from the effect of mixing between d–d and charge transfer transitions, as pointed out in the so-called perturbation model [20, 21]. The above contributions may be the main origin for the characteristics of the CD spectra of group (ii) and group (iii) complexes.

For [Cu(tmpn)(mnt)] and [Ni(tmpn)(mnt)], some absorption peaks were observed in the near-infrared region (10–11 × 10^3 cm^{-1}), as shown in Table II. However we could not measure the CD spectra for these bands because of the limitation of the instrument. Similar bands have been reported for [Cu(mnt)$_2$]$^{2-}$ and [Ni(mnt)$_2$]$^{2-}$ complexes, which were assigned to the $d_{x^2-y^2} \rightarrow d_{xy}$ transition [22].
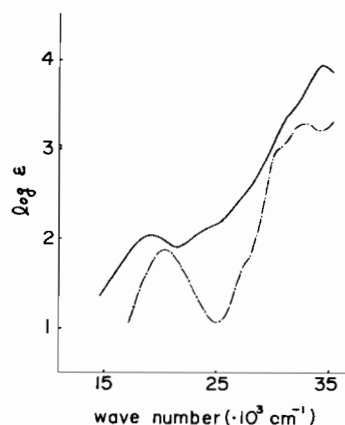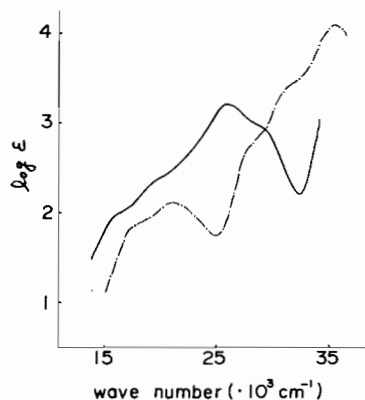
Acknowledgments

References

1 Part III of the series, "A study of the electronic spectra of metal complexes by circular dichroism".
2 B. Bosnich, *J. Am. Chem. Soc., 90,* 627 (1968).

3 R. S. Downing and F. L. Urbach, *J. Am. Chem. Soc.*, *91*, 5977 (1969).

4 R. S. Downing and F. L. Urbach, *J. Am. Chem. Soc.*, *92*, 5861 (1970).

5 R. D. Gillard, *J. Inorg. Nucl. Chem.*, *26*, 1455 (1964).

6 T. Yasui, Bull. *Chem. Soc. Jpn.*, *38*, 1746 (1965).

7 T. Komorita, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, *42*, 168 (1969).

8 J. W. Chang and R. B. Martin, *J. Phys. Chem.*, *73*, 4277 (1969).

9 Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn.*, *43*, 3814 (1970).

10 J. R. Gollogly, C. J. Hawkins and C. L. Wang, *Inorg. Nucl. Chem. Lett.*, *6*, 215 (1970).

11 Y. Nishida and S. Kida, unpublished work.

12 Y. Fukuda and K. Sone, *J. Inorg. Nucl. Chem.*, *34*, 2315 (1972); *Bull. Chem. Soc. Jpn.*, *45*, 465 (1972).

13 R. W. Moshier and L. Splater, *J. Org. Chem.*, *21*, 1050 (1956).

14 D. Vavion and R. H. Holm, *Inorg. Syn.*, *10*, 11 (1967).

15 J. A. Riddick and W. B. Bunger, "Organic Solvents", Wiley, New York (1970).

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

17 K. R. Butler and M. R. Snow, *Chem. Commun.*, 550 (1971).

18 Part II of this series, M. Suzuki and Y. Nishida, *J. Inorg. Nucl. Chem.*, in press.

19 A. D. Liehr, *J. Phys. Chem.*, *68*, 3629 (1964).

20 F. S. Richardson, *J. Chem. Phys.*, *54*, 2453 (1971).

21 S. F. Mason, *J. Chem. Soc. A*, 667 (1971).

22 H. B. Gray, "Transition Metal Chemistry", vol. 1, ed. by R. L. Carlin, Marcell Dekker, New York (1965), pp. 239–287.