Inorganica Chimica Acta, *120* (1986) 185–189

Noncovalent Interactions in Metal Complexes.
12*. Stereoselectivity of Tetrahedral or Pseudotetrahedral Bis(*N*-*l*-menthylsalicylaldiminato)M(II) and Bis(*N*-*l*-menthyl-3-methylsalicylaldiminato)M(II) (M = Co, Cu, Ni, Zn)

HISASHI ŌKAWA**, MICHIO NAKAMURA and SIGEO KIDA†

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

(Received May 14, 1986)

Abstract

Stereoselectivity of metal(II) complexes of *N*-*l*-menthylsalicylaldimine (H(sal-ment)) and *N*-*l*-menthyl-3-methylsalicylaldimine (H(3-Mesal-ment)) have been studied. Tetrahedral [Zn(sal-ment)$_2$] and pseudotetrahedral [Cu(3-Mesal-ment)$_2$] are revealed to be of the Λ configuration with respect to the metal, based on the circular dichroism induced at the π–π^* transition centered at the azomethine function (26.0 × 10^3 and 27.3 × 10^3 cm^{-1}, respectively). Pseudotetrahedral [Ni(sal-ment)$_2$] and tetrahedral [Co(sal-ment)$_2$] and [Co(3-Mesal-ment)$_2$] also show significant circular dichroism from the visible to the ultraviolet region, indicating the stereoselective formation of a diastereomer. From inspection of the ^{1}H NMR spectra of H(sal-ment) and [Zn(sal-ment)$_2$], it is suggested that the intramolecular interligand interaction between the menthyl residue and the π-system of the ligand gives rise to the stereoselectivity of the complexes.

Introduction

In the preceding papers of this series we have shown that noncovalent interactions occurring between organic residues within a complex molecule give rise to a high stereoselectivity of complexes [1–5]. For example, in 1:3 metal complexes of chiral 1,3-diketones, 1-*l*-menthyloxy-3-benzoylacetone or its homologs [1], the interligand noncovalent interaction between the *l*-methyl and aryl groups leads to a controlled disposition of the diketonate ions about the central metal, producing the *cis*-Δ isomer as the main species. Notably, such noncovalent interactions can cause a stereoselectivity of complexes of labile metal ions such as manganese(III) [1a,c,e] and lanthanoid(III) [1d]. Hence, the lanthanoid(III) complexes possessing chirality with respect to the central metal have been obtained [1d] and applied to stereospecific reactions [6].

In contrast to the large number of studies on stereoselectivity of six-coordinate complexes, very few studies have been reported for tetrahedral complexes. Tetrahedral or pseudotetrahedral complexes of unsymmetrical bidentate chelates are enantiomeric, giving rise to the Δ and Λ absolute configurations with reference to the C_2 axis of the molecule. Following the IUPAC nomenclature [7], two absolute configurations are depicted as Fig. 1. With a very few exception [8], resolution of the enantiomers has hardly been attained because of the high lability of most tetrahedral complexes. When a chiral residue is introduced into a bidentate ligand, however, a noncovalent interaction operating within its metal complex may bring about a free-energy difference between the diastereomers (Δ(1,1) and Λ(1,1), or Δ(d,d) and Λ(d,d)) and thence shift the equilibrium between the diasteromers in one direction. Hoping to find the way to control the configuration of tetrahedral complexes by means of intramolecular noncovalent interactions, in this study we have investigated the stereoselectivity of bis(*N*-*l*-menthylsalicylaldiminato)M(II)[M(sal-ment)$_2$] and bis(*N*-*l*-menthyl-3-methylsalicylaldiminato)M(II) [M(3-Mesal-ment)$_2$] (M = Co, Cu, Ni, Zn). The

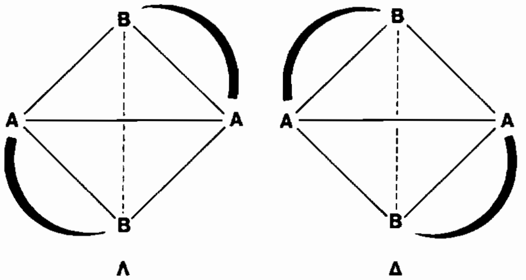

Fig. 1. Absolute configurations.

---

*For Part 11, see ref. 1.

**Author to whom correspondence should be addressed.

†Present address: Coordination Chemistry Laboratory, Institute for Molecular Science, Okazaki National Institutes, Okazaki 444, Japan.

0020-1693/86/$3.50

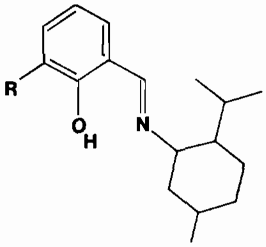

Fig. 2. Chemical structures of ligands: R = H, H(sal-ment); R = CH_3, H(3-Mesal-ment).

chemical structure of the ligands is shown in Fig. 2. Ernst *et al.* [9] have studied stereoselectivities of pseudotetrahedral nickel(II) complexes with *N*-substituted-salicylaldimines. However, they did not investigate the stereoselectivity of the complexes with other metal ions.

Experimental

Syntheses

l-Menthylamine was prepared by the literature methods [10, 11]. 3-Methylsalicylaldehyde was prepared by Duff's reaction [12].

$[M(sal\text{-}ment)_2]$ and $[M(3\text{-}Mesal\text{-}ment)_2]$ were obtained in almost the same way. The synthetic method is exemplified by that for $[Cu(sal\text{-}ment)_2]$. An ethanolic solution (20 cm^3) of *l*-menthylamine (0.2 g) and salicylaldehyde (0.16 g) was refluxed for 2 h. To this was added copper(II) acetate monohydrate (0.13 g) and $NaHCO_3$ (0.11 g). The mixture was refluxed for 2 h and allowed to stand overnight. Brown crystals, which separated from the reaction mixture, were collected and recrystallized from ethanol.

Elemental analyses for the complexes obtained in this study are given in Table I.

TABLE I. Elemental Analyses of Complexes

	Found (%)			Calculated (%)		
	C	H	N	C	H	N
$[Zn(sal\text{-}ment)_2]$	70.15	8.07	4.80	70.13	8.31	4.81
$[Cu(sal\text{-}ment)_2]$	70.23	8.41	4.79	70.39	8.34	4.83
$[Cu(3\text{-}Mesal\text{-}ment)_2]$	70.71	8.41	4.43	71.08	8.62	4.60
$[Ni(sal\text{-}ment)_2]$	71.47	8.46	4.89	70.97	8.41	4.87
$[Co(sal\text{-}ment)_2]$	71.00	8.36	4.82	70.93	8.40	4.87
$[Co(3\text{-}Mesal\text{-}ment)_2]$	71.21	8.49	4.49	71.62	8.68	4.64

Measurements

Elemental analyses were obtained at the Service Center of Elemental Analysis, Kyushu University. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000. Circular dichroism spectra were recorded on a JASCO J-500C Spectropolarimeter. ^1H NMR spectra were obtained with a JEOL Fourier Transform NMR Spectrometer FX-90Q in $CDCl_3$, using tetramethylsilane as an internal standard. Magnetic susceptibilities were measured by the Faraday method at room temperature. The apparatus was calibrated with $HgCo(NCS)_4$ [13]. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828 \times (\chi_A \times T)^{1/2}$, where χ_A is magnetic susceptibility corrected for diamagnetism for all the constituent atoms by the use of Pascal's constants [14].

Results and Discussion

The electronic and circular dichroism spectra of $[Zn(sal\text{-}ment)_2]$ in benzene are given in Fig. 3 This complex is assumed to have a tetrahedral configuration as other $[Zn(sal\text{-}R)_2]$ type complexes [5]. The intense absorption band at 26.0×10^3 cm^{-1} is attributed to the π–π^* transition involving the π-orbital function of the azomethine group [16]. The band is unsymmetrical and probably constituted of two absorption bands. This is confirmed by the associated circular dichroism which shows positive and negative CD bands in this region. Similar split π–π^* transition bands and positive and negative CD bands are observed for *N,N'*-disalicylidene-1,2-(R)-propanediaminatozinc(II), $[Zn(sal\text{-}(R)\text{-}pn)]$ [16], and explained in terms of excitation interaction [17]. The circular dichroism spectrum of this complex is also included in Fig. 3. Metal complexes of H_2-(sal-(R)-pn) are known to show a slight distortion towards tetrahedron and present a sinistral chirole (Λ) owing to a conformational requirement of the

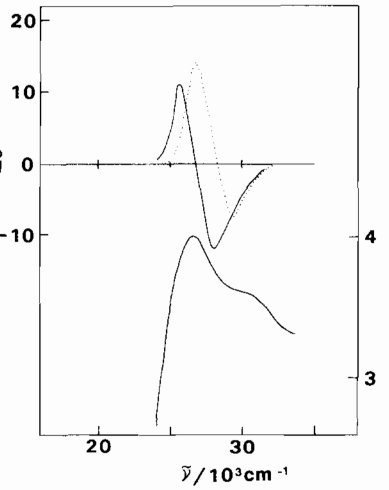

Fig. 3. Electronic and circular dichroism spectra of: (——) $[Zn(sal\text{-}ment)_2]$, and (·····) $[Zn(sal\text{-}(R)\text{-}pn)]$.

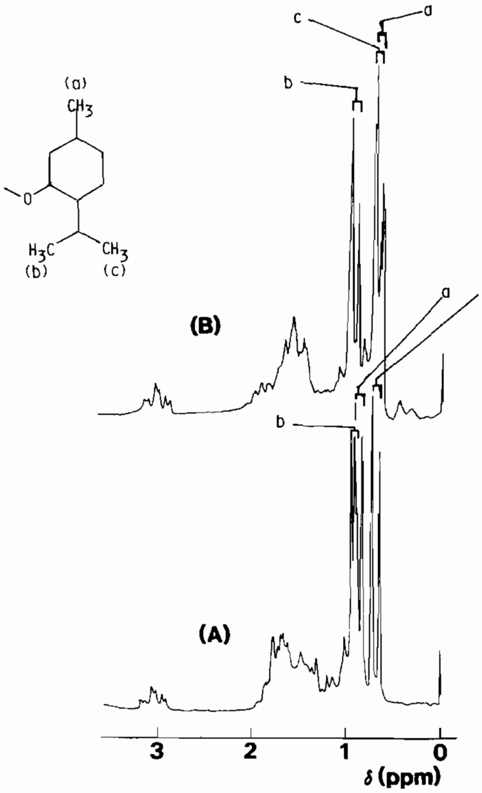

Fig. 4. ^1H NMR spectra of: (a) H(sal-ment), and (b) [Zn(sal-ment)$_2$].

1,2-propane bridge (*gauche* conformation with axial methyl) [16, 18, 19].

As seen in Fig. 3, [Zn(sal-ment)$_2$] and [Zn(sal-(R)-pn)] show a very similar circular dichroism (positive and negative from lower frequency) at the π–π^* transition, indicating that the preferred configuration of the former is also Λ. We assume that the stereoselectivity found for [Zn(sal-ment)$_2$] originates from an intramolecular non-covalent interaction involving the *l*-menthyl group as an interacting counterpart. In a hope to gain an evidence for this, we have examined ^1H NMR spectra of H(sal-ment) and [Zn-(sal-ment)$_2$]. The spectra in the 0–4 ppm region are shown in Fig. 4. The trace A is the 90 MHz NMR spectrum of the ligand which shows three doublets at 0.930, 0.883, and 0.704 ppm, attributable to the methyl groups of the *l*-menthyl residue. Unequivalence of the iso-propyl methyl groups is probably due to the chirality of the menthyl residue. In the light of the ^1H NMR spectral data for *l*-menthol [20], we tentatively assign the 0.883 ppm signal to the methyl (a) and the 0.930 and 0.704 ppm signals to the methyls (b) and (c) (or vice versa) of the iso-propyl (see Fig. 4). Trace B is the spectrum of [Zn-(sal-ment)$_2$] which also shows three methyl signals at 0.937, 0.708, and 0.675 ppm. Inspection of both spectra reveals that the 0.883 ppm signal of the ligand shifts significantly upfield in [Zn(sal-ment)$_2$] (0.675 ppm), while the 0.930 and 0.704 ppm signals shift only slightly downfield on complexation (0.937 and 0.708 ppm, respectively). The result suggests that the methyl (a) of the *l*-menthyl residue interacts with the π-system of the ligand (chelate-π or aromatic-π, or both) and this interaction leads to the stereoselective formation of the Λ configuration of the complex.

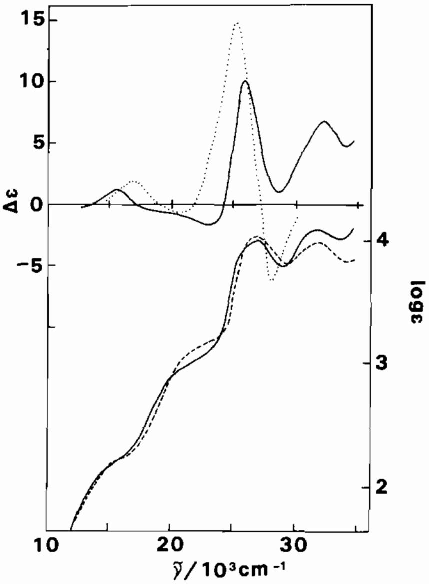

Fig. 5. Electronic and circular dichroism spectra of: (——) [Cu(sal-ment)$_2$], (-----) [Cu(3-Mesal-ment)$_2$], and (.....) [Cu(sal-(R)-pn)].

Electronic spectra of [Cu(sal-ment)$_2$] and [Cu(3-Mesal-ment)$_2$] are given in Fig. 5. Both show three absorption bands below 30×10^3 cm^{-1}. The absorption at 15–16×10^3 cm^{-1} is assigned to a d–d transition. The 20–22×10^3 cm^{-1} absorption is assigned to a CT transition [18] and the absorption at 27×10^3 cm^{-1} to the π–π^* transition involving the azomethine π-function [16, 18]. The electronic spectra are similar to each other on a whole, but a substantial difference between the two complexes can be observed from careful examination of the spectra. In the spectrum of [Cu(sal-ment)$_2$], the d–d band is seen at 16×10^3 cm^{-1} and the CT band at 22×10^3 cm^{-1}. This is the spectrum typical of planar copper(II) with *N-R*-salicylaldiminate ligands [21–24]. On the other hand, the spectrum of [Cu(3-Mesal-ment)$_2$] exhibits the d–d band at 15×10^3 cm^{-1} and the CT band at 20.5×10^3 cm^{-1}. This spectrum is similar to those of [Cu(sal-R)$_2$] with iso-propyl or tert-butyl as the N-substituent, whose configurations have been shown to be pseudotetrahedral [22]. Hence, we may conclude that [Cu(sal-ment)$_2$] adopts an essentially planar configuration while [Cu(3-Mesal-ment)$_2$] a pseudotetrahedral configuration. The distorted configuration of [Cu(3-Mesal-ment)$_2$] is also supported by its considerably large magnetic moment (1.97 BM at room temperature) as predicted from ligand field theory [25, 26]. The moment of [Cu(sal-ment)$_2$] (1.83 BM) is quite common for planar copper(II) complexes.

The circular dichroism spectrum of [Cu(3-Mesal-ment)$_2$] is shown in Fig. 5, together with the spectrum of [Cu(sal-(R)-pn)] to which the Λ configuration has been assigned [18]. For the latter complex positive and negative CD bands are seen at 25×10^3 and 28×10^3 cm^{-1}, respectively, associated with its π–π^* transition band (27.3×10^3 cm^{-1}). Splitting of the π–π^* transition may be explained in terms of exciton inteaction [18], similarly to the case for the zinc(II) complex. Notably, the CD spectral feature of [Cu(3-Mesal-ment)$_2$] and [Cu(sal-(R)-pn)] at the π–π^* transition is very similar, though the negative CD band of the former complex is not resolved. The result suggests that the preferred configuration of [Cu(3-Mesal-ment)$_2$] is also Λ. The stereoselectivity found for this complex may also be explained by the same concept as that for [Zn(sal-ment)$_2$]. In the region below 25×10^3 cm^{-1}, the circular dichroism spectrum of [Cu(3-Mesal-ment)$_2$] somewhat differs from that of [Cu(sal-(R)-pn)]. This may reflect the difference in their degree of distortion towards a tetrahedron, i.e., the distortion is larger for the former than for the latter. [Cu(sal-ment)$_2$] shows no marked circular dichroism in the region up to 35×10^3 cm^{-1}, as expected from its planar configuration.

The reflectance spectrum of [Ni(sal-ment)$_2$] shows d–d bands at 6.8×10^3, 13.6×10^3, and 17.5×10^3 cm^{-1}, indicating the geometry around the metal to be tetrahedral [27–30]. This structure is supported by its magnetic moment (3.21 BM) determined on a solid sample (moments for tetrahedral nickel(II) complexes with salicylaldimines fall in the range 3.2–3.3 BM [30]). In benzene solution, however, the complex exhibits absorptions at 16.8×10^3, 24.0×10^3, and 30.5×10^3 cm^{-1} (Fig. 6), characteristic of pseudotetrahedral nickel(II) [9]. As is seen in Fig. 6, the complex exhibits intense circular dichroism from the visible to near ultraviolet region, indicating a stereoselective formation of a diastereomer in solution.

The electronic spectra of [Co(sal-ment)$_2$] and [Co(3-Mesal-ment)$_2$] are shown in Fig. 7. They present d–d bands at 7.5×10^3, 11×10^3, and 18×10^3 cm^{-1}, characteristic of tetrahedral cobalt(II) [15, 31–33]. Furthermore, powder samples of both complexes show magnetic moments common for tetrahedral cobalt(II) (4.37 BM for [Co(sal-ment)$_2$] and 4.22 BM for [Co(3-Mesal-ment)$_2$]), hence, it is obvious that the configuration of the complexes is tetrahedral both in solution and in the solid state. The circular dichroism spectra of the complexes are included in Fig. 7. Significant positive circular dichroism is induced at the 18×10^3 cm^{-1} band and negative circular dichroism at the 21×10^3 cm^{-1} band. This suggests the stereoselective formation of a diastereomer.

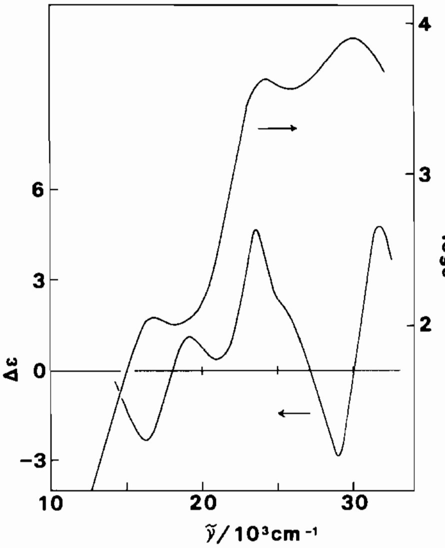

Fig. 6. Electronic and circular dichroism spectra of [Ni(sal-ment)$_2$].

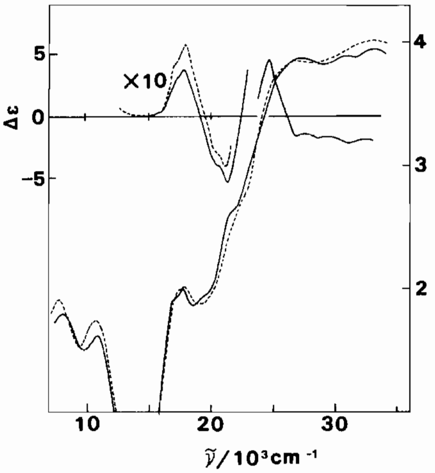

Fig. 7. Electronic and circular dichroism spectra of: (———) [Co(sal-ment)$_2$] and (.....) [Co(3-Mesal-ment)$_2$].

From the present study it is evident that [M(sal-ment)$_2$] (M = Co, Ni, Zn) and [M(3-Mesal-ment)$_2$] (M = Cu, Co) adopt a tetrahedral or pseudotetrahedral structure and show a stereoselectivity to form predominantly a diastereomer, effected by an intramolecular noncovalent interaction. The preferred configuration for the cobalt(II) and zinc(II) complexes is determined to be Λ. The absolute configuration for the cobalt(II) and nickel(II) complexes can not be determined explicitly, because CD spectral data for the enantiomers of tetrahedral cobalt(II) and nickel(II) complexes are lacking. However, we presume that the stereoselectivity of these complexes comes from the same origin as suggested for [Zn(sal-ment)$_2$] (i.e., intramolecular noncovalent interaction between the *l*-menthyl residue and the π-system), giving rise to the Λ form predominantly.

References

1 (a) H. Okawa, K. Ueda and S. Kida, *Inorg. Chem., 21,* 1594 (1982); (b) M. Nakamura, H. Okawa and S. Kida, *Chem. Lett.,* 547 (1984); (c) M. Nakamura, H. Okawa and S. Kida, *Inorg. Chim. Acta, 96,* 111 (1984); (d) M. Nakamura, H. Okawa, S. Kida and S. Misumi, *Bull. Chem. Soc. Jpn., 57,* 3134 (1984); (e) M. Nakamura, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn., 58,* 3377 (1985); (f) S. Maeda, M. Nakamura, H. Okawa and S. Kida, *Polyhedron,* in press.

2 M. Nakamura, M. Kato, H. Okawa, T. Ito and S. Kida, *Bull. Chem. Soc. Jpn.,* in press.

3 H. Okawa, Y. Numata, A. Mio and S. Kida, *Bull. Chem. Soc. Jpn., 53,* 2248 (1980).

4 M. Nakamura, H. Okawa, T. Inazu and S. Kida, *Bull. Chem. Soc. Jpn., 55,* 2400 (1982).

5 M. Nakamura, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn., 56,* 1642 (1983).

6 M. Nakamura, *Thesis,* Kyushu University, Hakozaki, Fukuoka, 1986.

7 J. Fujita and Y. Shimura, in K. Nakamoto and P. J. McCarthy (eds.), 'Spectroscopy and Structure of Metal Chelate Compounds', Wiley, New York, 1968, Chap. 3.

8 (a) Fr. Hein and H. Regler, *Naturwissenschaften, 23,* 320 (1935); (b) W. H. Mills and R. A. Gott, *J. Chem. Soc.,* 3121 (1926).

9 (a) R. E. Ernst, M. J. O'Cornor and R. H. Holm, *J. Am. Chem. Soc., 89,* 6164 (1967); (b) *90,* 5735 (1968).

10 E. Beckmann, *Justus Liebigs Ann. Chem., 250,* 322 (1889).

11 N. L. McNiven and J. Reed, *J. Chem. Soc.,* 153 (1952).

12 J. C. Duff, *J. Chem. Soc.,* 547 (1941).

13 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.,* 331 (1959).

14 E. A. Boudreaux and L. N. Mulay, 'Theory and Applications of Molecular Paramagnetism', Wiley-Interscience, New York, 1960, pp. 491–495.

15 S. Yamada, *Coord. Chem. Rev., 1,* 415 (1966).

16 B. Bosnich, *J. Am. Chem. Soc., 90,* 627 (1968).

17 W. Moffit, *J. Chem. Phys., 25,* 467 (1956).

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

19 A. Pasini, M. Gullotti and R. Ugo, *J. Chem. Soc., Dalton Trans.,* 346 (1977).

20 H. A. Szymanski and R. E. Yelin, 'NMR Band Handbook', IFI/Plenum, New York, 1968, p. V281.

21 J. Ferguson, *J. Chem. Phys., 34,* 1612 (1961).

22 L. Socconi and M. Ciampolini, *J. Chem. Soc.,* 276 (1964).

23 M. Von Stackelberg, *Z. Anorg. Chem., 253,* 136 (1947).

24 E. C. Lingafelter, G. L. Simmons and B. Morosin, *Acta Crystallogr.,* 1222 (1961).

25 B. N. Figgis, *Nature (London), 182,* 1568 (1958).

26 J. H. Griffiths, *Trans. Faraday Soc., 54,* 1109 (1958).

27 C. Furlani and G. Morpurgo, *Z. Physik. Chem., 28,* 93 (1961).

28 D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc., 83,* 4161 (1961).

29 M. R. Fox, E. C. Lingafelter, P. L. Orioli and L. Sacconi, *Nature (London), 197,* 1104 (1963).

30 J. R. Miller, *Adv. Inorg. Chem. Radiochem., 4,* 133 (1962).

31 B. O. West, *J. Chem. Soc.,* 4944 (1960); 1374 (1962).

32 H. Nishikawa, S. Yamada and R. Tsuchida, *Z. Naturforsch., 176,* 78 (1962); *Z. Anorg. Allg. Chem., 316,* 278 (1962).

33 H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jpn., 37,* 8, 1154 (1964); *38,* 1506 (1965).