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Synthesis and Characterization of a New Family of Binuclear Nickel(II) Complexes with a Terephthaloyl or Isophthaloyl Bridge

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A new family of binuclear nickel(II) complexes with a terephthaloyl or isophthaloyl bridge have been prepared by the electrophilic substitution reaction of (11,13-dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato)-nickel(II) ($Ni(Me_2[13]dienatoN_4)]^+$) or (12,14-dimethyl-1,4,8,11-tetraaza-11,13-cyclotetradecadienato)nickel(II) ($[Ni(Me_2[14]dienatoN_4)]^+$) containing a nucleophilic center at the γ-carbon and terephthaloyl chloride or isophthaloyl chloride. The complexes were characterized by elemental analyses, infrared spectra, ^{1}H NMR spectra, electronic spectra, and conductivity measurements.

Binuclear metal complexes are of much current interest as models for active sites[1—8] in biological systems such as cytchrome oxidase, hemerythrin, hemocyanin, and laccase. In such complexes, two metal ions are positioned in close proximity by the ligand framework to promote substrate binding between them. Recently binuclear complexes with a flexible chain or a bridging moiety such as *p*-xylene or *m*-xylene have been developed to mimic the reactivity to molecular oxygen and carbon monooxide of hemocyanin,[9—11] since it has been reported that hemocyanin consists of a rather flexible binuclear unit.[12] We wish now to report a new family of ligands with a terephthaloyl or isophthaloyl bridge as their nickel(II) complexes, whose possible structure can be described as face-to-face species and has a substrate binding site. In our previous papers,[13,14] we have reported the synthesis, properties, and crystal structure of the substituted mononuclear nickel(II) complexes (**2**), which have been prepared by the electrophilic substitution reaction of $[Ni(Me_2[Z]dienatoN_4)]^+$ (**1**) (Z=13, 14) with the *p*-substituted benzoyl chlorides, as shown in Fig. 1. The binuclear nickel(II) complexes reported here have been prepared by a similar reaction procedure for the substituted mononuclear complexes by using terephthaloyl chloride or isophthaloyl chloride, instead of benzoyl chloride (Fig. 1). The complexes were characterized by elemental analyses, infrared spectra, ^{1}H NMR spectra, electronic spectra, and conductivity measurements. The properties of the binuclear complexes have been compared with those of the mononuclear complexes.

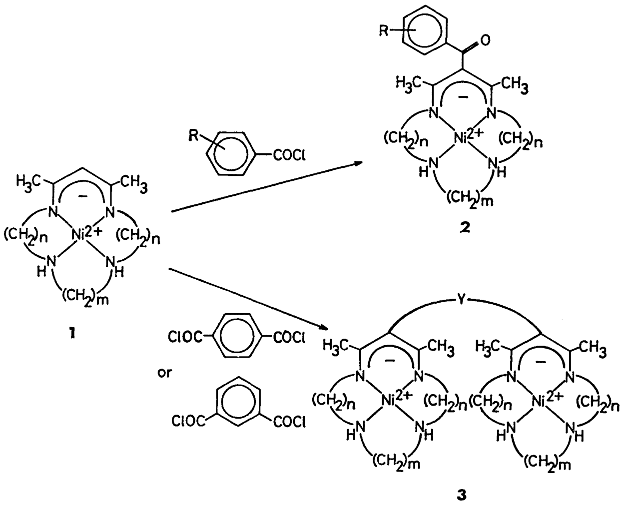

Fig. 1. Reaction scheme from parent complex (**1**) to substituted mononuclear complex (**2**) and binuclear complex (**3**).

1: $[Ni(Me_2[Z]dienatoN_4)]^+$($Z$=13, n=m=2, Z=14, n=2, m=3), **2**: $[Ni(Me_2E[Z]dienatoN_4)]^+$(E=benzoyl, *p*-methylbenzoyl, *m*-methylbenzoyl), **3**: $(Ni_2ter[Z])^{2+}$ or $(Ni_2iso[Z])^{2+}$.

Experimental

Physical Measurements. Visible and ultraviolet spectra were obtained with a Hitachi 323 spectrophotometer, while infrared spectra were recorded as KBr disks or Nujol mulls with a Shimadzu IR-410 spectrophotometer. The 100 MHz ^{1}H NMR spectra were recorded on a JEOL MH 100 spectrometer. The solvent used was CD_3CN and in all cases shift measurements were relative to tetramethylsilane. Elemental analysis was performed at the Technical Service Center of Kumamoto University. The thermogravimetric analysis(TGA) was carried out on a Shimadzu TGC 20 type microthermobalance at the heating rate of 5° min^{-1} using *ca.* 10 mg of the sample for each run, according to a method in the literature.[15] Conductivity measurements were carried out on a Denki Kagaku AOC-10 in methanol.

Syntheses. Parent Nickel(II) Complexes (1): (11,13-Dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato)nickel(II) bromide hemihydrate, $[Ni(Me_2[13]dienatoN_4)]Br\cdot 0.5H_2O$; (12,14-Dimethyl-1,4,8,11-tetraaza-11,13-cyclotetradecadienato)nickel(II) bromide monohydrate, $[Ni(Me_2[14]dienatoN_4)]Br\cdot H_2O$; (12,14-dimethyl-1,4,8,11-tetraaza-11,13-cyclotetradecadienato)nickel(II) iodide monohydrate, $[Ni(Me_2[14]dienatoN_4)]I\cdot H_2O$: These parent complexes were prepared by the method of S. C. Cummings *et al.*,[16] and identified by elemental analyses.

Substituted Mononuclear Nickel(II) Complexes (2). [11,13-Dimethyl-12-(*p*-methylbenzoyl)-1,4,7,10-tetraaza-10,12-cyclotridecadienato]nickel(II) hexafluorophosphate, $[Ni(Me_2p\text{-}MeBzyl[13]dienatoN_4)]PF_6$; [12,14-dimethyl-13-(*p*-methylbenzoyl)-1,4,8,11-tetraaza-11,13-cyclotetradecadienato]nickel(II) hexafluorophosphate hemihydrate, $[Ni(Me_2p\text{-}MeBzyl[14]dienatoN_4)]PF_6\cdot 0.5H_2O$: The complexes were prepared by the method described previously,[14] and identified by elemental analyses. [11,13-Dimethyl-12-(*m*-methylbenzoyl)-1,4,7,10-tetraaza-10,12-cyclotridecadienato]nickel(II) iodide, the hexafluorophosphate salt, [12,14-dimethyl-13-(*m*-methylbenzoyl)-1,4,8,11-tetraaza-11,13-cyclotetradecadienato]nickel(II) tetrafluoroborate and the perchlorate salt were first prepared in this work in a similar manner to $[Ni(Me_2p\text{-}MeBzyl[13]dienatoN_4)]PF_6$[14] in order to compare their properties with those of the binuclear complexes with a isophthaloyl bridge, and abbreviated as [Ni(Me$_2$*m*-MeBzyl-

TABLE 1. ELEMENTAL ANALYTICAL DATA AND SELECTED INFRARED FREQUENCIES WITH THEIR ASSIGNMENTS FOR MONONUCLEAR AND BINUCLEAR COMPLEXES

Complex	Found (Calcd) (%)			$\tilde{\nu}$/cm^{-1}		
	C	H	N	NH	C=O	C$\overset{\cdots}{=}$C or C$\overset{\cdots}{=}$N
[Ni(Me$_2$*m*-MeBzyl[13]dienatoN$_4$)]I·0.5H$_2$O	44.01(43.71)	5.42(5.41)	10.55(10.73)	3040	1640	1542
[Ni(Me$_2$*m*-MeBzyl[13]dienatoN$_4$)]PF$_6$	43.15(42.97)	5.41(5.12)	10.50(10.55)	3250	1638	1553
[Ni(Me$_2$*m*-MeBzyl[14]dienatoN$_4$)]BF$_4$·H$_2$O	47.60(47.57)	6.05(6.19)	11.16(11.09)	3150, 3230	1638	1556
[Ni(Me$_2$*m*-MeBzyl[14]dienatoN$_4$)]ClO$_4$·H$_2$O	46.66(46.41)	5.97(6.04)	10.81(10.82)	3150, 3200	1638	1555
(Ni$_2$ter[13])Br$_2$·4H$_2$O	40.50(40.13)	5.75(5.84)	12.50(12.48)	3070, 3140	1622	1542
(Ni$_2$ter[13])(PF$_6$)$_2$	37.78(37.69)	5.12(4.64)	11.72(11.67)	3264	1636	1545
(Ni$_2$iso[13])I$_2$·2H$_2$O	37.71(37.69)	4.92(5.06)	11.67(11.71)	3065	1635	1545
(Ni$_2$ter[14])Br$_2$·3H$_2$O	42.28(42.33)	5.83(5.94)	12.20(12.33)	3050, 3140	1618	1544
(Ni$_2$ter[14])I$_2$·2H$_2$O	39.16(39.06)	4.96(5.28)	11.38(11.38)	3070, 3160	1618	1546
(Ni$_2$ter[14])(ClO$_4$)$_2$·0.5CH$_2$Cl$_2$	42.28(42.33)	5.27(5.22)	12.20(12.30)	3160, 3210	1624	1547
(Ni$_2$ter[14])(BF$_4$)$_2$	43.81(43.39)	5.61(5.68)	12.68(12.65)	3160, 3230	1622	1547
(Ni$_2$ter[14])(PF$_6$)$_2$·2CH$_2$Cl$_2$	35.26(35.29)	4.54(4.54)	9.90(9.71)	3250	1632	1549
(Ni$_2$iso[14])I$_2$·H$_2$O	39.74(39.79)	5.21(5.21)	11.58(11.60)	3030	1623	1538
(Ni$_2$iso[14])(ClO$_4$)$_2$·CH$_2$Cl$_2$	40.81(40.53)	5.23(5.15)	11.91(11.46)	3190	1630	1542
(Ni$_2$iso[14])(BF$_4$)$_2$·2H$_2$O	42.61(42.52)	5.88(5.79)	12.23(12.48)	3220, 3060	1636	1546
(Ni$_2$iso[14])(PF$_6$)$_2$	39.10(39.06)	4.90(4.92)	11.25(11.39)	3240	1640	1548

[13]dienatoN$_4$)]I, [Ni(Me$_2$*m*-MeBzyl[13]dienatoN$_4$)]PF$_6$, [Ni(Me$_2$*m*-MeBzyl[14]dienatoN$_4$)BF$_4$, and [Ni(Me$_2$*m*-MeBzyl[14]dienatoN$_4$)]ClO$_4$, respectively.

Binuclear Nickel(II) Complexes with a Terephthaloyl or Isophthaloyl Bridge (3). μ-[12,12′-Terephthaloyl-bis(11,13-dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato)]dinickel(II) hexafluorophosphate (abbreviated as (Ni$_2$ter[13])(PF$_6$)$_2$). To a solution of [Ni(Me$_2$[13]dienatoN$_4$)]Br·0.5H$_2$O (15 mmol) containing 30 mmol of triethylamine in 200 cm^3 of dichloromethane was added dropwise a solution of 7.5 mmol terephthaloyl chloride in 150 cm^3 dichloromethane during 1 h with vigorous stirring at room temperature. After the completion of the addition, the solution was refluxed for 6 h and then evaporated to dryness under reduced pressure. The resultant orange-red viscous oil was dissolved in 50 cm^3 of water and filtered. The pH of the solution was adjusted to 10 with 6 mol dm^{-3} NaOH. The solution was added dropwise to 30 cm^3 of a saturated aqueous solution of ammonium hexafluorophosphate. After standing for several hours in a refrigerator, a deep-red crystalline material precipitated, it was collected and dried *in vacuo* over P$_2$O$_5$ overnight.

The other binuclear nickel(II) complexes were prepared according to the procedure described above, by using the corresponding parent complex, terephthaloyl chloride or isophthaloyl chloride and the sodium salt of the counter anion. The binuclear complexes prepared in this study are as follows: (Ni$_2$ter[13])Br$_2$, (Ni$_2$ter[13])(PF$_6$)$_2$, (Ni$_2$iso[13])I$_2$, (Ni$_2$ter[14])Br$_2$, [Ni$_2$ter[14])I$_2$, (Ni$_2$ter[14])(ClO$_4$)$_2$, (Ni$_2$ter[14])I$_2$, (Ni$_2$iso[14])(ClO$_4$)$_2$, (Ni$_2$iso[14])(BF$_4$)$_2$, and (Ni$_2$ter[14])(PF$_6$)$_2$, where (Ni$_2$ter[13])$^{2+}$, (Ni$_2$iso[13])$^{2+}$, (Ni$_2$ter[14])$^{2+}$, and (Ni$_2$iso[14])$^{2+}$ denote μ-[12,12′-terephthaloyl-bis(11,13-dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato)]dinickel(II), μ-[12,12′-isophthaloyl-bis(11,13-dimethyl-1,4,7,10-tetra aza-10,12-cyclotridecadienato)] dinickel(II), μ [13,13′-tere phthaloyl-bis(12,14-dimethyl-1,4,8,11-tetraaza-11,13-cyclotetradecadienato)]dinickel(II), and μ-[13,13′-isophthaloyl-bis(12,14-dimethyl-1,4,8,11-tetraaza-11,13-cyclotetradecadienato)]dinickel(II), respectively.

Results and Discussion

Synthesis. As shown in Fig. 1, the binuclear nickel(II) complexes have been prepared by the electrophilic substitution reaction of the parent complex [Ni(Me$_2$[*Z*]dienatoN$_4$)]$^+$ (Z=13, 14) **1** with terephthaloyl chloride or isophthaloyl chloride by the similar reaction procedure for the substituted mononuclear complexes (**2**). The advantages of the present synthetic route for the preparation of bimetallic complex with a bridging group are as follows: (1) Since the complex is derived from the reaction of the parent complex [Ni(Me$_2$[*Z*]dienatoN$_4$)]$^+$ (**1**) containing a coordinated metal center and terephthaloyl chloride or isophthaloyl chloride as a bridging moiety, structural parameters associated with the macrocyclic metal complex and the bridging moiety such as macrocyclic ring size and the orientation of two MN$_4$ planes can be varied independently. (2) Since the parent complex and terephthaloyl chloride or isophthaloyl chloride contain a nucleophilic center and two electrophilic centers, respectively, binuclear species can be obtained easily and selectively without the formation of monomeric and polymeric species.

Elemental analytical data are given in Table 1. As indicated by the elemental analyses, the binuclear nickel(II) complexes tend to crystallize as solvate. The water and dichloromethane as a crystal solvent were detected by thermo-gravimetric analyses (TGA), where the thermal process has a weight change corresponding to the loss of the approximately quantitative molecules of water or dichloromethane estimated by the elemental analyses. The weight loss was observed at 70—100 °C and 40—70 °C for the water and the dichloromethane, respectively.

Infrared Spectra. Some selected infrared frequencies and their assignments are given in Table 1. Infrared spectra of the products differ from those of the

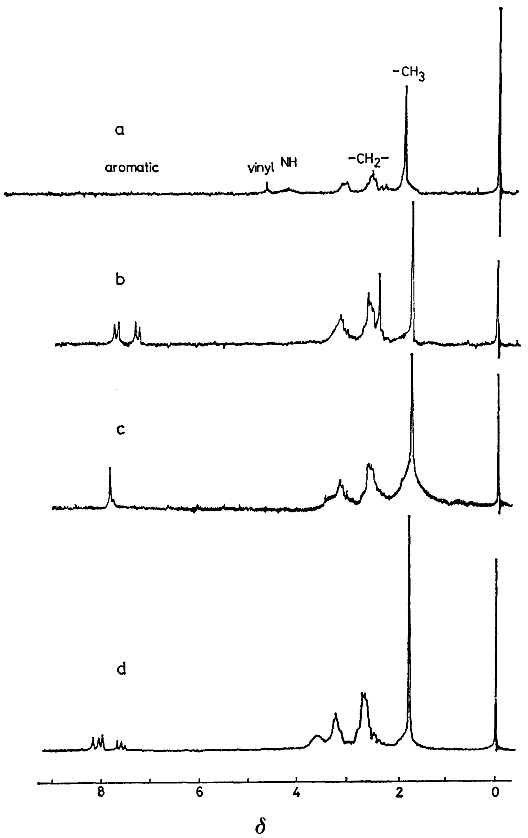

Fig. 2. ^1H NMR spectra in CD_3CN of (a) $[Ni(Me_2[14]dienatoN_4)]I \cdot H_2O$, (b) $[Ni(Me_2p\text{-}MeBzyl[14]dienatoN_4)]PF_6$, (c) $(Ni_2ter[14])(ClO_4)_2 \cdot 0.5CH_2Cl_2$, (d) $(Ni_2iso[14])(ClO_4)_2 \cdot CH_2Cl_2$.

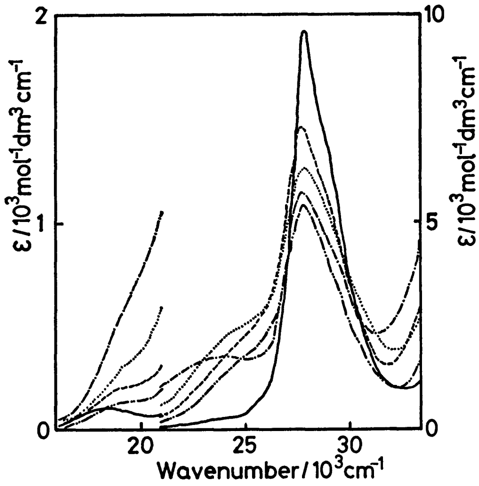

Fig. 3. Absorption spectra in methanol of $[Ni(Me_2[14]dienatoN_4)]PF_6 \cdot 0.5H_2O$(——), $[Ni(Me_2p\text{-}MeBzyl[14]dienatoN_4)]I$(— · · —), $[Ni(Me_2m\text{-}MeBzyl[14]dienatoN_4)]BF_4 \cdot H_2O$(----), $(Ni_2ter[14])Br_2 \cdot 3H_2O$(— · —), $(Ni_2iso[14])(BF_4)_2 \cdot H_2O$(······).

parent complex $[Ni(Me_2[Z]dienatoN_4)]^+$, most notably in the appearance of the intense band at *ca.* 1630 cm^{-1} which can be assigned to C=O stretching mode characteristic for the complexes containing a benzoyl group.[13,17,18)] Two intense bands of the starting material terephthaloyl chloride (1780, 1724 cm^{-1}) or isophthaloyl chloride (1760, 1730 cm^{-1}) which are assigned to C=O stretching mode are absent in the products. The same feature was also observed for the reactants and the products in the mononuclear system,[13,14)] indicating the completion of the substitution reaction and consistent with the formation of the binuclear species.

The NH frequency in a series of the binuclear complexes $(Ni_2ter[14])X_2$ (X=Br, I, ClO_4, BF_4, PF_6) as well as that of the substituted mononuclear complexes shifts to lower energy in the order of the basicity of the counter anion, $Br<I<ClO_4<BF_4<PF_6$. As the same phenomenon observed for the parent complexes $[Ni(Me_2[Z]dienatoN_4)]X$ (X=Br, I, SCN, NO_3, BF_4, PF_6, Z=13, 14) was explained due to the hydrogen bond between the secondary amine nitrogen atom and the counter anion[16)] and the existence of the hydrogen bond was confirmed by the X-ray analysis of $[Ni(Me_2[14]dienatoN_4)]Br \cdot H_2O$,[13)] the shift observed for the binuclear complexes can be also considered due to the hydrogen bond.

^1H NMR Spectra. Proton magnetic resonance spectra of the binuclear nickel(II) complexes, along with the substituted mononuclear complexes and the parent complex are shown in Fig. 2. The spectrum consists of four distinct regions with resonances attributable to methyl (singlet), methylene (multiplet), aromatic, and NH (broad) protons. As anticipated, the vinyl proton resonance at the γ-carbon of the parent complex has disappeared in the binuclear and substituted mononuclear complexes, since the electrophilic substitution reaction takes place at the γ-carbon. The methyl proton signal of the binuclear and substituted mononuclear complexes is shifted to a higher magnetic field than that of the parent complex. This can be attributed to the ring current effect of the benzene ring and the shielding effect of the carbonyl group of the substituent, because it has been confirmed for $[Ni(Me_2p\text{-}MeBzyl[13]dienatoN_4)]PF_6$ by single-crystal X-ray analysis[14)] that the substituent is nearly perpendicular to the unsaturated six-membered chelate ring to which the methyl groups are attached.

Electronic Spectra. Visible and ultraviolet spectra of the complexes were obtained on 10^{-3}—10^{-4} mol dm^{-3} solutions in methanol or acetonitrile. The spectra of the parent complex, the substituted mononuclear complex, and the binuclear complexes are shown in Fig. 3. Electronic spectra of some of the binuclear complexes, especially those of the 13-membered complexes, were not measured due to the sparing solubility. The spectra of the substituted mononuclear complex and the binuclear complex consist of a broad band in the visible region assignable to the d-d transition with an extinction coefficient on the order of *ca.* (100—500) $\times 10^3 mol^{-1} dm^3 cm^{-1}$ which resembles the d-d transition of other square planar nickel(II) complexes.[19)] There are also several peaks in the ultraviolet region assignable to the charge-transfer bands. As shown in Fig. 3, when the substituent of the electron withdrawing group, such as benzoyl group, is replaced at the γ-carbon, the d-d transition band shifts to higher energy and a new band with an extinction coefficient *ca.* (2000—3000) $\times 10^3 mol^{-1} dm^3 cm^{-1}$ appears at (23—

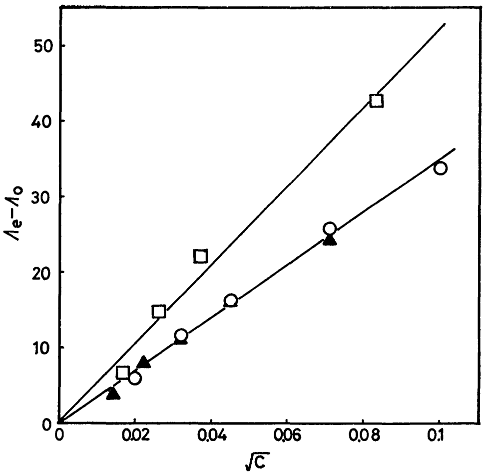

Fig. 4. Onsager plots for parent, substituted mononuclear, and binuclear nickel(II) complexes in methanol.
(a): [Ni(Me$_2$[14]dienatoN$_4$)]I·H$_2$O(○), (b): [Ni(Me$_2$*p*-MeBzyl[13]dienatoN$_4$)]PF$_6$(▲), (c): (Ni$_2$iso[14])I$_2$·H$_2$O(□).

25)×10^3 cm^{-1}.

Molar Conductivity. The molar conductance was measured in methanol as a function of concentration, and the Onsager plots are shown in Fig. 4. For the parent complex [Ni(Me$_2$[14]dienatoN$_4$)]I·H$_2$O and the substituted mononuclear complex [Ni(Me$_2$*p*-MeBzyl[13]dienatoN$_4$)]PF$_6$, Onsager plots show the slopes of 351 and 349 S mol^{-1} cm$^{3.5}$ and the Λ_0 values of 114 and 98 S cm^2, respectively, in which their slopes are somewhat higher than the expected value for 1:1 electrolytes.[20,21] On the other hand, Onsager plots of the binuclear complex (Ni$_2$iso[14])I$_2$·H$_2$O gave a slope of 525 S mol^{-1} cm$^{3.5}$ and the Λ_0 value of 114 S cm^2, which are in the expected range for 2:2 electrolytes.[20,21]

Based on the above described results, it was established that the binuclear complexes are formed, while the detailed structure remains uncertain for the present. The crystal structure determination of (Ni$_2$iso[14])I$_2$·H$_2$O is in progress in our laboratory.

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References

1) D. H. Busch, G. G. Christoph, L. L. Zimmer, S. C. Jackels, J. J. Grzybowski, R. C. Callahan, M. Kojima, K. A. Holter, J. Mocak, N. Herron, M. Chavan, and W. P. Schammel, *J. Am. Chem. Soc.*, **103**, 5107 (1981).
2) M. J. Gunter, L. N. Mander, K. S. Murray, and P. E. Clark, *J. Am. Chem. Soc.*, **103**, 6784 (1981).
3) A. E. Martin and J. E. Bulkowski, *J. Am. Chem. Soc.*, **104**, 1434 (1982).
4) V. Mckee, J. V. Dagdigian, R. Bau, and C. A. Reed, *J. Am. Chem. Soc.*, **103**, 7000 (1981).
5) J. T. Landrum, D. Grimmett, K. J. Haller, W. R. Scheidet, and C. A. Reed, *J. Am. Chem. Soc.*, **103**, 2640 (1981).
6) N. Oishi, Y. Nishida, and S. Kida, *Chem. Lett.*, **1981**, 1031.
7) M. Suzuki, H. Kanatomi, and I. Murase, *Chem. Lett.*, **1981**, 1745.
8) W. Kanda, M. Nakamura, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **55**, 471 (1982).
9) J. E. Bulkowski, P. L. Burk, M. F. Ludmann, and A. Osborn, *J. Chem. Soc., Chem. Commun.*, **1977**, 498.
10) J. Powell and C. J. May, *J. Am. Chem. Soc.*, **104**, 2636 (1982).
11) J. Birker, H. Hendriks, and J. Reedijk, *Inorg. Chim. Acta*, **55**, L17 (1981).
12) J. M. Brown, L. Powers, B. Kimcaid, J. A. Larrabee, and T. G. Spiro, *J. Am. Chem. Soc.*, **102**, 4210 (1980).
13) N. Matsumoto, K. Wakizaka, and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, **55**, 3165 (1982).
14) N. Matsumoto and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, **56**, 134 (1983).
15) A. Ohyoshi, S. Hiraki, T. Odate, S. Kohata, and J. Oda, *Bull. Chem. Soc. Jpn.*, **48**, 230 (1975).
16) S. C. Cummings and R. T. Sievers, *Inorg. Chem.*, **9**, 1131 (1970).
17) N. Matsumoto, M. Imaizumi, and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, **55**, 3170 (1982).
18) J. A. Streeky, D. G. Pillsbury, and D. H. Busch, *Inorg. Chem.*, **19**, 3148 (1980).
19) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam (1968).
20) R. D. Feltham and R. G. Hayter, *J. Chem. Soc., A*, **1964**, 4587.
21) R. G. Hayter, *J. Am. Chem. Soc.*, **84**, 3046 (1962).