October, 1982] *Bull. Chem. Soc. Jpn.*, *55*, *3165—3169 (1982)*

Synthesis and Characterization of Substituted Derivatives of (Tetraazacycloalkadienato)nickel(II) Complexes with Uninegative Ligands, and Crystal Structure of Parent Complex $[Ni(Me_2[14]dienatoN_4)]Br\cdot H_2O$

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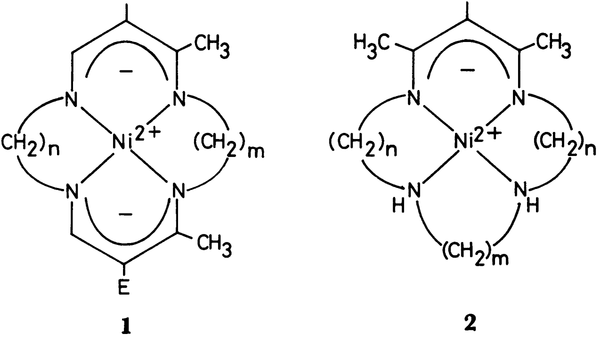
(Recieved February 18, 1982)

The (tetraazacycloalkadienato)nickel(II) complexes $[Ni(Me_2[Z]dienatoN_4)]^+$ (Z = 13, 14), which have an unsaturated chelate ring containing nucleophilic center, react with electrophilic reagents such as benzoyl chloride, *p*-methylbenzoyl chloride, and *p*-nitrobenzoyl chloride to give the substituted derivatives $[Ni(Me_2E[Z]dienatiN_4)]PF_6$. These complexes have been characterized by elemental analyses, ^1H NMR, infrared, and electronic spectra. One of the parent complexes $[Ni(Me_2[14]dienatoN_4)]Br\cdot H_2O$ has been subjected to the single-crystal X-ray diffraction technique and its structural data indicated that the average Ni–N bond distance is longer than that of the corresponding thirteen membered complex.

The γ-position of six-membered diiminato chelate rings[1-6] as well as that of the chelate rings of acetylacetonato complexes[7-9] have been found to be very reactive nucleophilic center. This reactivity has been employed to introduce a large number of substituents into macrocyclic ligands.[1-6] These substituent derivatives have been produced by what have been proposed to be electrophilic attacks on the γ-carbon in a manner similar to substitution in ordinary aromatic rings.

Recently, Busch and coworkers[10,11] reported the synthesis of a broad range of substituted derivatives $[Ni(Me_2E_2[Z]tetraenatoN_4)]$(Z = 14, 15, 16, E = acetyl, carbethoxyethyl, α-naphthylcarbamoyl, ethylcarbamoyl, benzoyl, *p*-methylbenzoyl, *p*-nitrobenzoyl, methylsuccinoyl, nitro) (**1**) by electrophilic substitution reaction at the γ-carbons of the parent complexes $[Ni(Me_2[Z]tetraenatoN_4)]$, where the parent complex has two nucleophilic centers, and elucidated that both the position of the d-d electronic band maxima and the half-wave potential for the Ni^{2+}/Ni^{3+} couple vary linearly with the Hammett substituent constants. This result indicates that the use of substituents affords a powerful technique for controlling the electronic character of the metal ion without altering the stereochemistry of the coordination sphere.



1 **2**

Fig. 1. Structures of $[Ni(Me_2E_2[Z]tetraenatoN_4)]$ (**1**) and $[Ni(Me_2E[Z]dienatoN_4)]^+$ (**2**), where E and Z denote the substituent group and ring size, respectively. The abbreviation used in this report are based on Busch's modified scheme.[15,16]

In this study, the complexes $[Ni(Me_2[Z]dienatoN_4)]^+$ (**2**) firstly synthesized by Cummings and coworkers[12-14] were used as the parent complexes where each parent complex has only one nucleophilic center. The substituted derivatives $[Ni(Me_2E[Z]dienatoN_4)]PF_6$ have been prepared by electrophilic substitution reaction of the parent complex with *p*-substituted benzoyl chlorides and characterized by elemental analyses, infrared, ^1H NMR, and electronic spectra. The effects of the substituents on the properties of the central nickel ion as well as the macrocyclic ring-size effects were examined by the d-d band maxima of the electronic spectra. In addition, the crystal structure of one of the parent complexes $[Ni(Me_2[14]dienatoN_4)]Br\cdot H_2O$ has been determined by the single-crystal X-ray diffraction method in order to investigate the influence of ring-size on the molecular structure.

Experimental

Physical Measurements. Visible and ultraviolet spectra were obtained with a Hitachi recording spectrophotometer 323, while infrared spectra were recorded as KBr disks with a Shimadzu recording spectrophotometer IR-410. The 100 MHz ^1H NMR spectra were recorded on a JEOL MH 100 spectrometer. The solvent used was acetone-d_6 and in all cases shift measurements were made relative to tetramethylsilane. Elemental analysis was performed by Mr. S. Miyazaki at the Technical Service Center of Kumamoto University.

Syntheses. *3,7-Diazanonane-1,9-diamine* ($H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$) was prepared according to the method of Barefield *et al.*[17] The parent complexes $[Ni(Me_2[Z]dienatoN_4)]X$ (Z = 13, 14 and X = Br, I, PF_6) were prepared by the method of Cummings[12] and identified by elemental analyses and infrared spectra.

(12-Benzoyl-11,13-dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato)nickel(II) Hexafluorophosphate, $[Ni(Me_2Byzl[13]dienatoN_4)]PF_6$, *2*($E = C_6H_5CO-$. n = m = *2*): 0.224 g (1.6 mmol) of benzoyl chloride and 0.126 g (1.6 mmol) of pyridine were added to a solution of 0.357 g (1 mmol) of $[Ni(Me_2[13]dienatoN_4)]Br\cdot 1/2H_2O$ in 100 ml of chloroform. 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 ml of ethanol and addition of excess ammonium hexafluorophosphate in ethanol gave red-orange precipitates. This material was collected, recrystallized from ethanol and

dried *in vacuo.*

*[12-(*p*-Methylbenzoyl)-11,13-dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato]nickel(II) Hexafluorophosphate,* $[Ni(Me_2MeBzyl[13]dienatoN_4)]PF_6$, **2**$(E=\text{p-}CH_3C_6H_4CO\text{–}, \text{n}=\text{m}=2)$: *[12-(*p*-Nitrobenzoyl)-11,13-dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato]nickel(II) Hexafluorophosphate,* $[Ni(Me_2NitroBzyl[13]dienatoN_4)]PF_6$, **2**$(E=\text{p-}NO_2C_6H_4CO\text{–}, \text{n}=\text{m}=2)$: These complexes were synthesized by a method similar to that for $[\mathrm{Ni(Me_2Bzyl[13]dienatoN_4)]PF_6}$ except for using *p*-methylbenzoyl chloride and *p*-nitrobenzoyl chloride instead of benzoyl chloride, respectively.

(13-Benzoyl-12,14-dimethyl-1,4,8,11-tetraaza-11,13-cyclotetradienato)nickel(II) Hexafluorophosphate, $[Ni(Me_2Bzyl[14]dienatoN_4)]PF_6$, **2**$(E=C_6H_5CO\text{–}, \text{n}=2, \text{m}=3)$: 0.210 g (1.5 mmol) of benzoyl chloride and 0.151 g (1.5 mmol) of triethylamine were added to a solution of 0.380 g (1 mmol) of $[\mathrm{Ni(Me_2[14]dienatoN_4)]Br\cdot H_2O}$ in 100 ml dichloromethane. 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 ml of ethanol and small ammount of dichloromethane. The saturated ammonium hexafluorophosphate solution in ethanol was slowly added to the solution to precipitate red-orange material. This material was collected, recrystallized from ethanol and small ammount of chloroform, and dried *in vacuo.*

*[13-(*p*-Methylbenzoyl)-12,14-dimethyl-1,4,8,11-tetraaza-11,13-cyclotetradecadienato]nickel(II) Hexafluorophosphate,* $[Ni(Me_2MeBzyl[14]dienatoN_4)]PF_6$, **2**$(E=\text{p-}CH_3C_6H_4CO\text{–}, \text{n}=2, \text{m}=3)$: *[13-(*p*-Nitrobenzoyl)-12,14-dimethyl-1,4,8,11-tetraaza-11,-13-cyclotetradecadienato]nickel(II) Hexafluorophosphate,* $[Ni(Me_2NitroBzyl[14]dienatoN_4)]PF_6$, **2**$(E=\text{p-}NO_2C_6H_4CO\text{–}, \text{n}=2, \text{m}=3)$: The above two complexes were synthesized by a method similar to that for $[\mathrm{Ni(Me_2Bzyl[14]dienatoN_4)]PF_6}$ except for using *p*-methylbenzoyl chloride and *p*-nitrobenzoyl chloride, respectively, instead of benzoyl chloride.

X-Ray Diffraction. Red rhombic crystals of the complex $[\mathrm{Ni(Me_2[14]dienatoN_4)]Br\cdot H_2O}$, suitable for X-ray diffraction study, were prepared by slow evaporation from aqueous solution at room temperature. A crystal with dimensions of 0.4×0.3×0.4 mm was examined with a Rigaku AFC-5 four-circle automated diffractometer. The unit cell dimensions and their estimated standard deviations were obtained from a least-squares fit to 15 high angle reflections ($14° < 2\theta < 38°$) using Mo *Ka* graphite monochromatized radiation ($\lambda = 0.71069$ Å) at 24 ± 1 °C. Systematic absences $h0l$, $l=2n+1$ and $0k0$, $k=2n+1$, indicate the space group $P2_1/c$. The crystal data obtained were as follows: $\mathrm{NiC_{12}H_{25}N_4OBr}$, F. W.= 379.9, monoclinic system, space group=$P2_1/c$, $a=12.637(3)$, $b=11.090(3)$, $c=10.556(1)$ Å, $\beta=91.22(1)°$, $V=1596.1(6)$ Å^3, Z=4, $D_x=1.581$ g cm^{-3}.

The intensity data were collected by the 2θ-θ scan technique with a scan rate of 12°min^{-1}. For weak reflections the peak scan was repeated up to four times depending on their intensities. Three standard reflections were monitored every 100 reflections and their intensities showed a good stability. A total of 3130 reflections with $2\theta \leq 52°$ were collected. The ntensity data were corrected for the Lorentz and polarization effects, but not for the absorption, because of the crystal size and low absorption coefficient. Independent 2181 reflections with $|F_o| > 3\sigma(|F_o|)$ were considered as "observed" and used for the structure determination.

Solution and Refinement of the Structure. The structure was solved by the conventional heavy-atom method and refined by the block-diagonal least-squares method. In the least-squares calculation, the function minimized was $\sum w(|F_o|-k|F_c|)^2$, where $w=1/\sigma(|F_o|)^2$ was adopted. The neutral atomic scattering factors for H, C_{COV}, N, O, Ni, and Br were taken from International Tables for X-ray Crystallography Vol. IV.[18] Anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ for all the component atoms were also taken from the literature.[18] All the calculations were carried out on a FACOM M-200 computer in the Computer Center of Kyushu University by the use of a local version[19] of the UNICS II Crystallographic Computing System.[20,21]

The coordinates of the bromine and nickel atoms were obtained from a three-dimensional Patterson synthesis. Successive Fourier and difference Fourier syntheses revealed all the nonhydrogen atoms except for the water molecule of crystallization. Refinement with isotropic thermal parameters was carried out and the discrepancy indices $R_1=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 13.6 and 13.4%, respectively. After introducing anisotropic thermal parameters, a difference Fourier synthesis was calculated and revealed the missing water molecule. An occupancy factor of 1.0 was applied for the water, considering the peak height and the adjustment of the elemental analysis. Hydrogen atoms were inserted in their calculated positions and included in the refinement. Further refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic ones (4.0 Å^2) for hydrogen atoms gave the final values of 5.2 and 5.1% for R_1 and R_w, respectively. The final difference Fourier synthesis showed no significant feature, peaks being less than 0.5 eÅ^{-3}.

Final positional parameters of nonhydrogen atoms with their estimated standard deviations are given in Table 1. List of structure factors, anisotropic thermal parameters and atomic parameters of hydrogen atoms have been deposited at the Chemical Society of Japan as Document No. 8252.

Results and Discussion

Crystal Structure of Parent Complex $[Ni(Me_2[14]dienatoN_4)]Br\cdot H_2O$. The crystal structure viewed along the b axis is shown in Fig. 2, where possible hydrogen bonds are drawn by dotted lines. A perspective drawing of the cation $[\mathrm{Ni(Me_2[14]dienatoN_4)]^+}$ with the atom numbering scheme is shown in Fig. 3. The

TABLE 1. ATOMIC PARAMETERS FOR $[\mathrm{Ni(Me_2[14]DIENATON_4)]Br\cdot H_2O}$

Atom	x	y	z	B_{eq}/Å^2
Br	6576(1)	1700(1)	555(1)	5.0
Ni	2375(1)	3027(1)	2349(1)	2.8
N1	1309(5)	3134(6)	3427(6)	3.3
N2	2393(5)	4784(5)	2393(6)	3.4
N3	3536(4)	2933(5)	1340(5)	2.9
N4	2379(4)	1354(5)	2338(5)	3.2
C1	1086(7)	4391(8)	3814(8)	4.5
C2	1405(6)	5178(8)	2761(8)	4.7
C3	2709(6)	5467(8)	1262(7)	4.5
C4	3704(7)	5111(8)	872(8)	4.7
C5	3738(7)	3841(8)	345(8)	4.3
C6	3575(7)	1711(7)	756(7)	4.0
C7	3266(6)	805(8)	1734(7)	4.2
C8	1748(6)	622(7)	2880(7)	3.5
C9	989(6)	1024(7)	3616(8)	3.8
C10	818(6)	2239(8)	3914(8)	4.0
C11	17(7)	2497(9)	4882(9)	5.4
C12	1855(7)	−742(7)	2725(8)	4.7
Ow	5324(5)	3030(7)	2813(6)	6.7

TABLE 2. BOND LENGTHS AND ANGLES OF $[Ni(Me_2[14]\text{-}dienatoN_4)]Br \cdot H_2O$ WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Bond length	l/Å		l/Å
Ni-N(1)	1.869(6)	N(4)-C(7)	1.508(10)
Ni-N(2)	1.944(7)	N(4)-C(8)	1.322(10)
Ni-N(3)	1.930(6)	C(1)-C(2)	1.486(12)
Ni-N(4)	1.855(6)	C(3)-C(4)	1.480(13)
N(1)-C(1)	1.486(11)	C(4)-C(5)	1.516(13)
N(1)-C(10)	1.308(11)	C(6)-C(7)	1.508(12)
N(2)-C(2)	1.476(11)	C(8)-C(9)	1.381(12)
N(2)-C(3)	1.486(11)	C(8)-C(12)	1.529(12)
N(3)-C(5)	1.485(11)	C(9)-C(10)	1.405(12)
N(3)-C(6)	1.490(11)	C(10)-C(11)	1.538(13)
(b) Bond angle	θ/°		θ/°
N(1)-Ni-N(4)	94.0(2)	N(2)-C(3)-C(4)	117.7(7)
N(1)-Ni-N(2)	86.2(2)	C(3)-C(4)-C(5)	112.5(7)
N(2)-Ni-N(3)	93.2(2)	C(4)-C(5)-N(3)	111.2(7)
N(3)-Ni-N(4)	86.5(2)	C(5)-N(3)-C(6)	108.3(6)
Ni-N(1)-C(1)	113.1(5)	N(3)-C(6)-C(7)	108.0(6)
Ni-N(1)-C(10)	126.9(5)	C(6)-C(7)-N(4)	105.0(6)
Ni-N(2)-C(2)	106.9(5)	C(7)-N(4)-C(8)	118.0(6)
Ni-N(2)-C(3)	119.6(5)	N(4)-C(8)-C(9)	123.1(7)
Ni-N(3)-C(5)	121.3(4)	C(8)-C(9)-C(10)	124.4(7)
Ni-N(3)-N(6)	108.3(4)	C(10)-N(1)-C(1)	119.6(6)
Ni-N(4)-C(7)	114.1(4)	C(9)-C(10)-N(1)	123.4(7)
Ni-N(4)-N(8)	127.5(5)	N(4)-C(8)-C(12)	119.8(7)
N(1)-C(1)-C(2)	106.2(6)	C(12)-C(8)-C(9)	117.0(7)
C(1)-C(2)-N(2)	107.8(6)	N(1)-C(10)-C(11)	119.7(7)
C(2)-N(2)-C(3)	110.0(6)	C(11)-C(10)-C(9)	116.7(7)
(c) Intermolecular length		l/Å	
Br···Ow*	3.307(6)	*(x,y,z)	
Br···Ow*	3.341(8)	*$(x,1/2-y,-1/2+z)$	
Ow···N(3)*	2.866(8)	*(x,y,z)	
Ow···HN3*	1.92(6)	*(x,y,z)	
Br···N(2)*	3.325(6)	*$(1-x,-1/2+y,1/2-z)$	
Br···NH2*	2.46(6)	*$(1-x,-1/2+y,1/2-z)$	

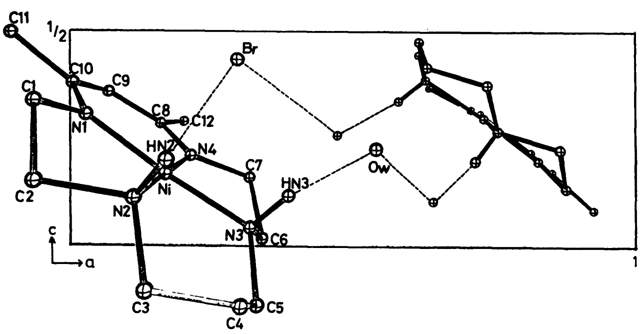


Fig. 2. Projection of the crystal structure $[Ni(Me_2[14]\text{-}dienatoN_4)]Br \cdot H_2O$ along the b axis.

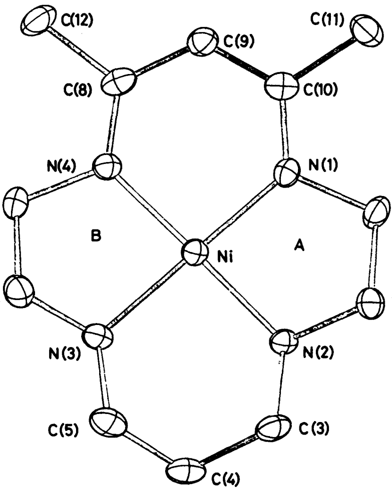


Fig. 3. ORTEP plot of $[Ni(Me_2[14]dienatoN_4)]^+$ Hydrogen atoms have been omitted for clarity.

interatomic bond distances, angles and the intermolecular bond distances with their estimated standard deviations are given in Table 2.

As shown in Fig. 2 and Table 2, the atoms Br and Ow are hydrogen bonded to the secondary amine nitrogen atoms N(2) $(1-x, -1/2+y, 1/2-z)$ and N(3), respectively, and the evidence of the hydrogen bonds from this X-ray analysis confirmed the prediction of Cummings[12] based on the infrared and ^1H NMR spectra. The hydrogen bonds between the NH-proton and the electronegative anions have been studied for the complexes $[Ni(Me_2[Z]dienatoN_4)]X$ (X=Br, I, SCN, BF_4, NO_3, PF_6; Z=13, 14) by the infrared and ^1H NMR spectra, in which the NH band shifts to higher energy with the change of the anion $Br^- > I^- > SCN^- > NO_3^- > BF_4^- > PF_6^-$.[12]

As shown in Fig. 3, the macrocyclic cation exhibits nearly exactly Cs-m symmetry, although not required crystallographically. The pseudomirror plane containing Ni, C(4), and C(9) atoms is perpendicular to the coordination plane NiN_4. This molecular symmetry is also observed in the dicationic analogous compound with the same ring size $[Co^{II}(Me_2[14]dieneN_4)\cdot H_2O](PF_6)_2$,[22] while the analogous compound with thirteen ring size $[Ni(Me_2[13]dienatoN_4)]ClO_4$[23] exhibits C_2 symmetry.

The nickel ion has a square planar coordination geometry within the deviations of ±0.03 Å and its four coordination sites are occupied by two iminate and two secondary amine nitrogen atoms. The four Ni–N bond distances fall into two groups, attributing to the difference between iminate and secondary amine nitrogen atoms. The average Ni–N (iminate) bond distance of 1.862(6) Å is shorter than the Ni–N (amine) of 1.937(7) Å. In addition, these two values are longer than the corresponding bond distances of Ni–N (iminate) (1.85(1) Å) and Ni–N (amine) (1.88(1) Å) in the case of $[Ni(Me_2[13]dienatoN_4)]^+$, respectively.[23]

For the unsaturated six-membered chelate ring, the planarity is preserved, in which the deviation from the least-squares plane defined by Ni, N(1), N(4), C(8), C(9), and C(10) is in the range from −0.03 to 0.03 Å. The C–C and C–N bond distances of the unsaturated chelate ring are intermediate between the corresponding single and double bond distances, respectively,[24] consistent with the conjugated chelate ring. The saturated six-membered chelate ring takes a chair conformation in which Ni and C(4) atoms displaced at −0.67 and 0.71 Å from the least-squares plane through N(3), N(2), C(3), and C(5), respectively. The

TABLE 3. ELEMENTAL ANALYSIS OF SUBSTITUTED COMPLEXES, $[\mathrm{Ni(Me_2E[Z]dienatoN_4)]PF_6}$ [a)]

Substituent(E)	Z	C(%)	H(%)	N(%)
C_6H_5CO	13	41.80(41.81)	4.65(4.87)	10.88(10.84)
p-$CH_3C_6H_4CO$	13	43.08(42.97)	5.27(5.12)	10.62(10.55)
p-$NO_2C_6H_4CO$	13	38.22(38.46)	4.29(4.30)	12.20(12.46)
C_6H_5CO	14	42.85(42.97)	5.16(5.12)	10.59(10.55)
p-CH_3CH_4CO	14	43.35(43.51)	5.46(5.20)	10.11(10.12)
p-$NO_2C_6H_4CO$ [b)]	14	39.83(39.61)	4.61(4.55)	12.12(12.16)

a) Calculated values are given in parentheses. b) Calcd for $\mathrm{NiPF_6O_3N_5C_{19}H_{26}\cdot 1/2H_2O}$.

TABLE 4. INFRARED SPECTRA FOR THE 13- AND 14-MEMBERED RING DERIVATIVES OF $[\mathrm{Ni(Me_2E[Z]\ dienatoN_4)]PF_6}$ [a)]

Substituent (E)	Ring size (Z)	$\tilde{\nu}/\mathrm{cm^{-1}}$ Assignment ν_{NH}	$\nu_{C=O}$	Bzyl	$\nu_{C=C,C=N}$
H	13	3240	—	—	1560,1540,1524
C_6H_5CO	13	3240	1640	1590	1558,1550,1540
p-$CH_3C_6H_4CO$	13	3250	1643	1600	1560,1550,1540
p-$NO_2C_6H_4CO$	13	3220	1632	1598	1560,1540,1535
H	14	3220	—	—	1555,1550,1530
C_6H_5CO	14	3230	1635	1590	1560,1555,1540
p-$CH_3C_6H_4CO$	14	3230	1640	1600	1560,1555,1540
p-$NO_2C_6H_4CO$	14	3260	1636	1598	1560,1540,1525

a) Spectra were obtained by KBr method.

saturated five-membered chelate rings (A and B) are all found to occupy gauche conformation with absolute configuration $\lambda\delta$ or $\delta\lambda$ (C(1), 0.09, C(2) −0.52 Å from the plane of Ni, N(1), and N(2): C(6)−0.47, C(7) 0.14 Å from the plane of Ni, N(3), and N(4)), while the absolute configuration of the five-membered chelate rings of $[\mathrm{Ni(Me_2[13]dienatoN_4)]^+}$ is $\lambda\lambda$ or $\delta\delta$, either.[23)]

As a consequence of the planarity of the conjugated six-membered chelate rings, the combination of the absolute configuration of two five-membered chelate rings ($\lambda\delta$ or $\delta\lambda$) and the chair-conformation of the saturated six-membered chelate ring, the molecular symmetry of the complex should exhibit Cs-m symmetry and the two hydrogen atoms bonded to secondary amine nitrogens are placed on the same side from the coordination plane ($\mathrm{NiN_4}$).

Synthesis and Characterization of the Substituted Derivatives. The parent complex $[\mathrm{Ni(Me_2[Z]dienatoN_4)]^+}$ (Z=13, 14) which has an iminato chelate ring containing a nucleophilic center reacts with electrophilies to produce the derivatives that are substituted at the γ-position. The substituted derivatives $[\mathrm{Ni(Me_2E[Z]dienatoN_4)]PF_6}$ where E denotes benzoyl, p-methylbenzoyl and p-nitrobenzoyl, and Z=13 and 14, were characterized by elemental analyses, infrared and ^{1}H NMR spectra. Elemental analyses for the substituted derivatives are given in Table 3. Some selected infrared and ^{1}H NMR spectral data with their assignments are given in Tables 4 and 5. Infrared spectra of the products differ from the parent complexes, most notably in the appearance of C=O stretch at *ca.* 1640 cm^{-1}. Two vibrations (*ca.* 1740 and 1770 cm^{-1}) due to C=O stretching vibrations of the starting material, benzoyl chlorides, are absent in the products, supporting the introduction of the substituent. These features are also observed in the substituent complexes $[\mathrm{Ni(Me_2E_2[Z]tetraenatoN_4)]}$ (**1**) and their parent complexes, supporting the formation of the complex $[\mathrm{Ni(Me_2E[Z]dienatoN_4)]^+}$ (**2**). As anticipated, the –CH reasonance at the γ-position has disappeared since the substituted group is introduced at the γ-position.

Electronic Spectra: Visible and ultraviolet spectra of the complexes were obtained on the 10^{-3}—10^{-4} M solution in methanol over the range from 14 to 48 × 10^3 cm^{-1} and the band maxima are given in Table 6. This type of complexes showed several band maxima in the ultraviolet region of the spectra with extinction coefficient in the range from 1500 to 10000 M^{-1} cm^{-1} which agree with assignment of the bands as representing charge-transfer transition. The spectra also exhibit a broad band in the visible region with an extinction coefficient in the range 100—200 M^{-1} cm^{-1} which is attributable to the d-d transition band.

As shown in Table 6, the energy of d-d band maxima increase, when the substituent group such as benzoyl group is attached to the γ-carbon of the conjugated six-membered chelate ring. This indicates that the electronic property of the central nickel ion is affected

TABLE 5. ^{1}H NMR SPECTRA OF $[\mathrm{Ni(Me_2E\ [Z]dienatoN_4)]PF_6}$ [a)]

Substituent	Z	CH [b)]	CH [c)]	NH [d)]	CH_2 [e)]	CH_3
H	13	—	4.77(s)	4.78	3.63—2.82	1.91
C_6H_5CO	13	7.69(q)	—	5.11	3.73—2.88	1.73
p-$CH_3C_6H_4CO$	13	7.61(q)	—	—	3.30—2.82	2.42*,1.75
p-$NO_2C_6H_4CO$	13	8.21(q)	—	5.13	3.75—2.87	1.77
H	14	—	4.80(s)	3.92	3.57—2.58	1.92
C_6H_5CO	14	7.73(q)	—	3.33	2.82(s)	1.80
p-$C_6H_3C_6H_4CO$	14	7.52(q)	—	—	2.81(s)	2.43*,1.82
p-$NO_2C_6H_4CO$	14	8.23(q)	—	4.11	3.53—2.81	1.80

a) Chemical shifts in ppm downfield from an internal TMS standard at 100 MHz in acetone-d_6. b) Signals for the benzoyl group. c) Signals for the γ-position proton. d) Center of broad signal. e) Boundaries of multiplet region. (s) Singlet. (q) Quartet. * Signals for the methyl proton of p-methylbenzoyl group.

Table 6. Electronic absorption bands for the 13- and 14-membered ring derivatives [Ni(Me$_2$E[Z]dienatoN$_4$)]PF$_6$[a,b]

Substituent(E)	Z	d-d Transition $\tilde{\nu}/10^3\,\mathrm{cm}^{-1}(\varepsilon)$	Other transitions $\tilde{\nu}/10^3\,\mathrm{cm}^{-1}(\varepsilon)$
H	13	20.2(143)	28.2(8500) 29.4(5900) 36.1(4100) 39.3(6100)
C_6H_5CO	13	21.4(540)	28.3(7400) 35.6(1300) 39.6(5400)
p-$CH_3C_6H_4CO$	13	21.4(548)	28.2(8000) 38.4(25400)
p-$NO_2C_6H_4CO$	13	—	21.1(1400) 24.0(1600) 28.4(7200) 37.5(21200)
H	14	18.6(104)	27.8(4300) 28.9(3700) 35.5(2400) 39.2(4000)
C_6H_5CO	14	19.6(210)	27.8(7200) 35.6(4700) 39.4(21900)
p-$CH_3C_6H_4CO$	14	19.6(196)	27.8(7100) 38 0(22300)
p-$NO_2C_6H_4CO$	14	—	23.3(1800) 27.9(7200) 37.6(21500)

a) For details of structures refer to Fig. 1. b) Spectra were obtained in methanol.

through the conjugated π-system of the iminato chelate ring by the electronic property of the substituent group. The energy difference of the d-d band maxima of [Ni(Me$_2$[Z]dienatoN$_4$)]$^+$ and [Ni(Me$_2$Bzyl[Z]dienatoN$_4$)]$^+$ (1.2 and $1.0\times10^3\,\mathrm{cm}^{-1}$ for Z=13 and 14, respectively) is nearly half of that of [Ni(Me$_2$[Z]tetraenatoN$_4$)] and [Ni(Me$_2$Bzyl$_2$[Z]tetraenatoN$_4$)] (2.3, 2.1, and $2.8\times10^3\,\mathrm{cm}^{-1}$ for Z=14, 15, and 16, respectively[11])). This result is consistent with the fact that the former (**2**) and latter (**1**) complexes have one and two substituent groups, respectively.

As seen in Table 6, the maximum wavenumber of the d-d transition band of [Ni(Me$_2$E[13]dienatoN$_4$)]PF$_6$ is greater than that of [Ni(Me$_2$E[14]dienatoN$_4$)]PF$_6$, indicating that the ligand field strength of the thirteen membered complex is greater than that of the fourteen membered complex. This is consistent with that the average Ni–N bond distance of the former complex is shorter than that of the latter, as being evidenced by the crystal structure determinations of [Ni(Me$_2$[13]dienatoN$_4$)]ClO$_4$[23] and [Ni(Me$_2$[14]dienatoN$_4$)]Br·H$_2$O.

The linear correlation between the d-d band maxima and the Hammett substituent constants of the *p*-substituted benzoyl derivatives has not been clearly observed in the present complexes (**2**), while it was observed in the complexes (**1**).[11] This might be the result of that the overall planarity between the conjugated chelate ring and the substituted π-system of benzoyl group is preserved for the complex (**1**), while the charge-delocalized chelate ring can be perpendicular to the benzoyl group for the complex (**2**), owing to the steric hindrance between the neighbouring two methyl groups and the substituent group at the γ-position.

The authors are grateful to Prof. S. Kida at the Faculty of Science, Kyushu University for allowing them to use the diffractometer.

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