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Crystal and Molecular Structure of [11,13-Dimethyl-12-(*p*-methylbenzoyl)-1,4,7,10-tetraaza-10,12-cyclotridecadienato]nickel(II) Hexafluorophosphate

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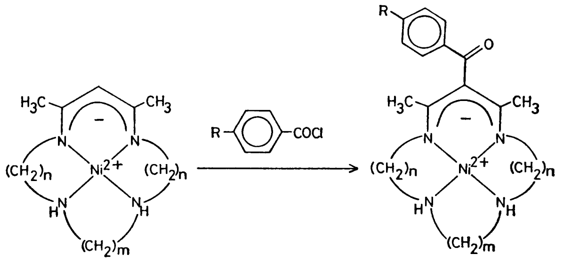
The title complex prepared through an electrophilic substitution of (11,13-diemthyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato)nickel(II) bromide with *p*-methylbenzoyl chloride was subjected to single-crystal X-ray diffraction analysis. The analysis has revealed completion of the substitution reaction, pseudo C_2 symmetry of the macrocyclic complex minus the substituent, and an essentially square planar coordination environment with slight tetrahedral distortion. The substituted *p*-methylbenzoyl group is tilted with respect to the least-squares plane of the conjugated six-membered chelate ring, where the dihedral angle between them is 69.2°.

In our previous paper[1)] we reported synthesis and properties of substituted derivatives $[Ni(Me_2E[Z]dienatoN_4)]PF_6$ (E=benzoyl, *p*-methylbenzoyl, and *p*-nitrobenzoyl; Z=13 and 14) (**2**), which are prepared by electrophilic substitution of $[Ni(Me_2[Z]dienatoN_4)]^+$ (**1**) with *p*-substituted benzoyl chlorides, as shown in Fig. 1. Based on electronic spectral tendencies observed for the series of substituted derivatives (**2**) and considerations on the steric hindrance between the benzoyl and two methyl groups in the acetylacetone residue, we predicted that the conjugated six-membered chelate ring would be perpendicular to the benzoyl group.



1 **2**

Fig. 1. Electrophilic substitution reaction from the parent complex $[Ni(Me_2[Z]dienatoN_4)]^+$ (**1**) to the substituted complex $[Ni(Me_2E[Z]dienatoN_4)]^+$ (**2**), where E denotes *p*-substituted benzoyl group, and Z=13 (n=2, m=2) and Z=14 (n=2, m=3).

In this study, the crystal structure of the title complex has been determined by the single-crystal X-ray diffraction method in order to confirm the completion of the substitution reaction and the above prediction.

Experimental

Physical Measurements. Infrared spectra were recorded with KBr disks on a Shimadzu recording spectrophotometer IR-410. Elemental analysis was performed by Mr. S. Miyazaki at the Technical Service Center of Kumamoto University.

Syntheses. *(11,13-Dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecadienato)nickel(II) Bromide Hemihydrate (1) (n=m=2)*: This parent complex, hereafter abbreviated as $[Ni(Me_2[13]dienatoN_4)]Br\cdot 0.5H_2O$, was prepared by the method of Cummings and Sievers.[2)]

[11,13-Dimethyl-12-(p-methylbenzoyl)-1,4,7,10-tetraaza-10,12-cyclotridecadienato]nickel(II) Hexafluorophosphate, $[Ni(Me_2p\text{-}MeBzyl[13]dienatoN_4)]PF_6$ (2) (n=m=2): The previously-described method[1)] was slightly modified. *p*-Methylbenzoyl chloride of 0.321 g (1.5 mmol) and triethylamine of 0.152 g (1.5 mmol) were added to a solution of 0.357 g (1 mmol) of $[Ni(Me_2[13]dienatoN_4]Br\cdot 0.5H_2O$ in 100 cm³ of dichloromethane. The solution was refluxed for 6 h and then evaporated to dryness under reduced pressure. The resultant viscous oil was dissolved in 30 cm³ of water and filtered. The pH of the solution was adjusted to 10 with 6 M NaOH (1 M=1 mol dm^{-3}). The solution was added dropwise to 20 cm³ aqueous solution of excess ammonium hexafluorophosphate to give an orange-red precipitate immediately. The product was collected, recrystallized from a mixture of methanol and dichloromethane and dried *in vacuo*. The yield obtained by this procedure was considerably higher than that obtained by the previously-described method.[1)] Found: C, 42.96; H, 5.12; N, 10.54%. Calcd for $NiON_4C_{19}H_{27}PF_6$: C, 42.97; H, 5.29; N, 10.48%. IR: 3250 (ν_{NH}) and 1645 cm^{-1} ($\nu_{C=O}$). The perchlorate and tetrafluoroborate salts (**2**) (n=m=2) were prepared in the same way except that NH_4PF_6 was replaced by $NaClO_4$ and $NaBF_4$, respectively. $[Ni(Me_2p\text{-}MeBzyl[13]dienatoN_4)]ClO_4$. Found: C, 46.83; H, 5.75; N, 11.60%. Calcd for $NiON_4C_{19}H_{27}ClO_4$: C, 47.00; H, 5.61; N, 11.54%. IR: 3180 (ν_{NH}) and 1635 cm^{-1} ($\nu_{C=O}$). $[Ni(Me_2p\text{-}MeBzyl[13]dienatoN_4)]BF_4\cdot 0.5H_2O$. Found: C, 47.68; H, 5.93; N, 11.73%. Calcd for $NiON_4C_{19}H_{27}BF_4\cdot 0.5H_2O$. Found: C, 47.35; H, 5.80; N, 11.61%. IR: 3200, 3130 (ν_{NH}), and 1635 cm^{-1} ($\nu_{C=O}$).

X-Ray Analysis. Red prismatic crystals of $[Ni(Me_2\text{-}p\text{-}MeBzyl[13]dienatoN_4)]PF_6$ were obtained from a mixture of methanol and dichloromethane at room temperature. The unit cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.71069 Å). A crystal with approximate dimensions of 0.3×0.3×0.5 mm³ was used for intensity measurement. The unit cell parameters were deterimined by the least-squares refinement based on 20 reflections in the range of $10° < 2\theta < 36°$. Crystal data: $NiPF_6ON_4C_{19}H_{27}$, F.W.=531.1, triclinic, space group $P\bar{1}$, a=10.629(5), b=13.424(5), c=9.201(4) Å, α=98.95(4), β=108.11(4), γ=109.85(3)°; V=1122.5(11) Å³, D_m=1.56 (by the flotation method in a mixture of 1,2-dichloroethane and 1,2-dibromoethane), D_x=1.571 g cm^{-3} (Z=2), and μ(Mo $K\alpha$)=10.3 cm^{-1}.

Intensity data were collected by the θ-2θ scan technique with a scan rate of 8° min^{-1}. For weak reflections the peak scan was repeated up to three times depending on their intensities. Three standard reflections were monitored every 100 reflections and their intensities showed a good

TABLE 1. THE FINAL ATOMIC PARAMETERS OF [Ni(Me$_2$*p*-MeBzyl[13]dienatoN$_4$)]PF$_6$$^{a)}$
The anisotropic thermal parameters and the atomic parameters of the hydrogen atoms are deposited as supplementary materials.

Atom	*x*	*y*	*z*	B/Å^2	Atom	*x*	*y*	*z*	B_{eq}/Å^2	b)
Ni	1328(1)	3427(1)	3868(1)	3.1	C(17)	3132(8)	9409(5)	2968(9)	4.7	
O	45(5)	6992(4)	3844(6)	5.6	C(18)	2108(7)	8647(5)	3348(8)	4.0	
N(1)	2498(5)	4823(4)	5158(6)	3.1	C(19)	5316(8)	10042(6)	2269(10)	5.9	
N(2)	2449(5)	2920(4)	5373(6)	3.5	P	2606(2)	2083(2)	−294(2)	4.5	
N(3)	370(6)	1952(4)	2492(6)	3.9						
N(4)	−17(5)	3759(4)	2475(6)	3.6	F(1)	313(1)	272(0)	154(1)	6.1(0.1)	0.75
C(1)	3683(7)	4864(5)	6586(8)	4.1	F(2)	206(1)	147(1)	−212(1)	7.1(0.2)	0.65
C(2)	3914(7)	3823(5)	6185(8)	4.1	F(3)	426(1)	252(1)	−8(1)	7.8(0.2)	0.60
C(3)	2276(7)	1823(5)	4576(8)	4.1	F(4)	102(1)	137(1)	−42(1)	7.9(0.3)	0.50
C(4)	720(8)	1222(5)	3456(9)	4.8	F(5)	298(1)	317(1)	−83(2)	8.0(0.3)	0.40
C(5)	−1149(7)	1763(5)	1679(8)	4.8	F(6)	287(1)	105(1)	−2(2)	9.2(0.4)	0.40
C(6)	−1125(7)	2774(6)	1124(8)	4.5	F(7)	134(1)	254(1)	−42(2)	9.5(0.4)	0.40
C(7)	18(6)	4758(5)	2516(7)	3.3	F(8)	160(1)	96(1)	−1(2)	4.9(0.3)	0.28
C(8)	1101(7)	5702(5)	3745(8)	3.3	F(9)	394(1)	174(1)	10(2)	5.2(0.3)	0.28
C(9)	2276(6)	5728(5)	5048(7)	3.2	F(10)	220(2)	306(2)	−82(2)	7.7(0.5)	0.25
C(10)	3247(7)	6774(5)	6341(8)	4.4	F(11)	389(2)	306(1)	−40(2)	6.0(0.4)	0.25
C(11)	−1136(8)	4856(6)	1159(9)	4.9	F(12)	95(2)	190(1)	−65(2)	3.8(0.3)	0.24
C(12)	1025(7)	6790(5)	3693(8)	3.6	F(13)	248(2)	105(2)	−171(3)	6.1(0.5)	0.20
C(13)	2165(6)	7622(5)	3335(7)	3.1	F(14)	281(3)	313(2)	104(3)	7.7(0.6)	0.20
C(14)	3200(6)	7406(6)	2983(7)	3.2	F(15)	328(3)	203(2)	153(3)	7.6(0.6)	0.20
C(15)	4208(7)	8173(5)	2613(8)	3.7	F(16)	186(3)	204(2)	−205(3)	7.7(0.6)	0.20
C(16)	4188(7)	9210(5)	2643(7)	3.8	F(17)	253(2)	113(2)	61(3)	6.4(0.5)	0.20

a) The final atomic coordinates for the nondisordered atoms and the disordered atoms are multiplied by 10^4 and 10^3, respectively. b) Occupancy factors.

stability. A total of 3125 reflections with $2.5° < 2\theta < 45°$ was collected, of which independent 2768 reflections with $|F_o| > 3\sigma(|F_o|)$ were considered as "observed" and used for the structure analysis. The intensity data were corrected for the Lorentz and polarization effects, but not for the absorption.

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 $\Sigma w(|F_o| - k|F_c|)^2$ where $w = 1/\sigma(|F_o|)^2$ was adopted. The neutral atomic scattering factors for H, C_{cov}, N, O, F, P, and Ni were taken from International Tables for X-Ray Crystallography, Vol. IV.[3] Anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for all the component atoms were also taken from Ref. 3. All the calculations were carried out on a FACOM M-200 computer at the Computer Center of Kyushu University by use of the UNICS II Crystallographic Computing System.[4–6]

The coordinates of the nickel atom were obtained from a three-dimensional Patterson synthesis. A Fourier synthesis based on the nickel position revealed all the nonhydrogen atoms except for the fluorine atoms of anion PF_6^-. In the course of structure analysis, it became apparent that the fluorine atoms were subjected to disorder. The occupancy factors were assigned to the possible fluorine positions located in the difference Fourier map according to the peak heights. Hydrogen atom positions were located in the difference Fourier map and included in the final least-squares calculation, where isotropic thermal parameters were used for the disordered fluorine atoms and the hydrogen atoms. The final values for $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were 6.65 and 6.59%, respectively. The final difference Fourier synthesis showed no significant features except for two peaks (*ca.* 0.8 e Å^{-3}) appearing in the PF_6^- region.

Final positional parameters with their estimated standard deviations are given in Table 1. Lists of structure factors, anisotropic thermal parameters of nonhydrogen atoms, and atomic parameters of hydrogen atoms have been deposited at the Chemical Society of Japan as Document No. 8306.

Results and Discussion

The perspective drawing of [Ni(Me$_2$*p*-MeBzyl[13]-dienatoN$_4$)]$^+$ cation with the atom numbering scheme is shown in Fig. 2. Interatomic bond distances, angles, and torsion angles are given in Table 2.

As shown in Fig. 2, the present X-ray analysis confirmed the completion of the substitution reaction. The macrocyclic cation, minus the substituent *p*-methylbenzoyl group, exhibits nearly exactly a C_2 symmetry, where the twofold axis passes through C(8) and Ni. The nickel ion is coordinated with two iminate and two secondary amine nitrogen atoms in an essentially square planar fashion. However, there is a slight tetrahedral distortion, because the deviations of the constituent atoms from the least-squares plane NiN_4 are in the range from −0.13 to 0.13 Å and because the dihedral angle between the planes Ni–N(1)–N(2) and Ni–N(3)–N(4) is 11.5°. The four Ni–N bond distances fall into two groups, depending on the difference between iminate and secondary amine nitrogen atoms. The average Ni–N (iminate) bond distance of 1.821(6) Å agree with 1.83(1) Å of the parent complex [Ni(Me$_2$[13]dienatoN$_4$)]ClO$_4$[7] within experimental error but is considerably shorter than 1.862-

Table 2. Bond distances, angles, and torsion angles of [Ni(Me$_2$$p$-MeBzyl[13]dienatoN$_4$)]PF$_6$

Bond distance	l/Å		l/Å
	[Ni(Me$_2$$p$-MeBzyl[13]dienatoN$_4$)]$^+$ cation		
Ni-N (1)	1.810(5)	C (7)-C (8)	1.402(10)
Ni-N (2)	1.902(6)	C (8)-C (9)	1.423(10)
Ni-N (3)	1.900(6)	C (7)-C (11)	1.513(10)
Ni-N (4)	1.832(6)	C (9)-C (10)	1.479(10)
N (1)-C (1)	1.489(9)	C (8)-C (12)	1.497(10)
N (1)-C (9)	1.326(9)	C (12)-O	1.203(9)
N (2)-C (2)	1.472(9)	C (12)-C (13)	1.507(10)
N (2)-C (3)	1.462(10)	C (13)-C (14)	1.344(9)
N (3)-C (4)	1.482(10)	C (13)-C (18)	1.396(10)
N (3)-C (5)	1.464(10)	C (14)-C (15)	1.383(10)
N (4)-C (6)	1.484(10)	C (15)-C (16)	1.395(10)
N (4)-C (7)	1.323(9)	C (16)-C (17)	1.344(11)
C (1)-C (2)	1.509(10)	C (16)-C (19)	1.507(12)
C (3)-C (4)	1.491(11)	C (17)-C (18)	1.395(11)
C (5)-C (6)	1.517(11)		
	PF$_6^-$ anion		
P-F (1)	1.588(7)	P-F (10)	1.604(22)
P-F (2)	1.573(8)	P-F (11)	1.577(19)
P-F (3)	1.586(10)	P-F (12)	1.605(16)
P-F (4)	1.582(11)	P-F (13)	1.688(24)
P-F (5)	1.576(14)	P-F (14)	1.612(27)
P-F (6)	1.548(16)	P-F (15)	1.631(28)
P-F (7)	1.631(16)	P-F (16)	1.543(27)
P-F (8)	1.639(15)	P-F (17)	1.621(25)
P-F (9)	1.588(16)		
Bond angle	ϕ/°		ϕ/°
N (1)-Ni-N (2)	87.9(2)	C (5)-C (6)-N (4)	106.9(6)
N (1)-Ni-N (3)	170.2(2)	N (4)-C (7)-C (8)	121.6(6)
N (1)-Ni-N (4)	97.4(2)	N (4)-C (7)-C (11)	117.6(6)
N (2)-Ni-N (3)	87.6(2)	C (8)-C (7)-C (11)	120.6(6)
N (2)-Ni-N (4)	170.2(2)	C (7)-C (8)-C (9)	126.1(6)
N (3)-Ni-N (4)	88.1(2)	C (7)-C (8)-C (12)	117.3(6)
Ni-N (1)-C (1)	112.6(4)	C (9)-C (8)-C (12)	116.5(6)
Ni-N (1)-C (9)	126.6(4)	C (8)-C (9)-N (1)	121.4(6)
C (1)-N (1)-C (9)	120.0(5)	C (8)-C (9)-C (10)	119.6(6)
Ni-N (2)-C (2)	106.7(4)	N (1)-C (9)-C (10)	118.8(6)
Ni-N (2)-C (3)	109.1(4)	O-C (12)-C (8)	122.1(6)
C (2)-N (2)-C (3)	119.4(5)	O-C (12)-C (13)	119.3(6)
Ni-N (3)-C (4)	107.7(4)	C (8)-C (12)-C (13)	118.3(5)
Ni-N (3)-C (5)	105.9(4)	C (12)-C (13)-C (14)	122.6(6)
C (4)-N (3)-C (5)	119.5(6)	C (12)-C (13)-C (18)	117.5(6)
Ni-N (4)-C (6)	112.1(4)	C (14)-C (13)-C (18)	119.7(6)
Ni-N (4)-C (7)	126.4(4)	C (13)-C (14)-C (15)	121.5(6)
C (6)-N (4)-C (7)	121.1(5)	C (14)-C (15)-C (16)	119.7(6)
N (1)-C (1)-C (2)	107.4(5)	C (15)-C (16)-C (17)	118.0(7)
C (1)-C (2)-N (2)	105.5(5)	C (15)-C (16)-C (19)	118.9(6)
N (2)-C (3)-C (4)	106.1(6)	C (17)-C (16)-C (19)	122.9(7)
C (3)-C (4)-N (3)	107.3(6)	C (16)-C (17)-C (18)	122.9(7)
N (3)-C (5)-C (6)	106.5(6)	C (13)-C (18)-C (17)	117.8(6)
Torsion angle	ϕ/°		
C (9)-C (8)-C (12)-C (13)	69.4		
C (9)-C (8)-C (12)-O	65.4		
C (7)-C (8)-C (12)-C (13)	69.5		
C (7)-C (8)-C (12)-O	65.4		

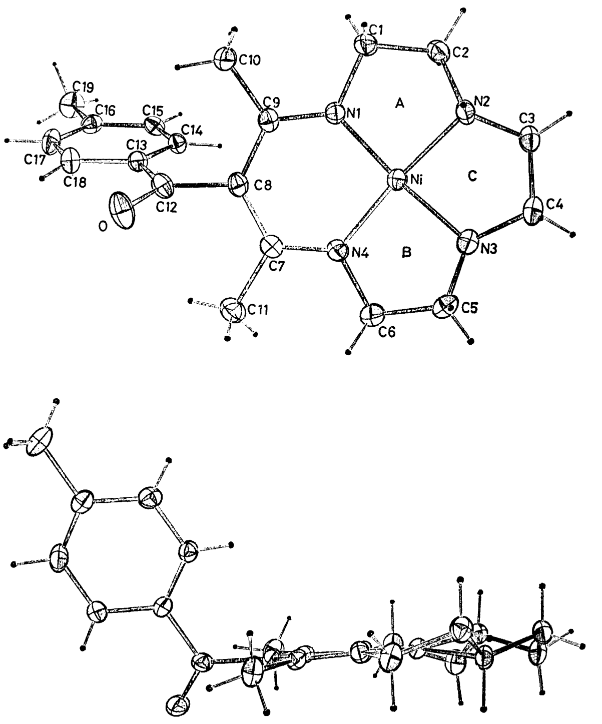


Fig. 2. ORTEP plots of [Ni(Me$_2$$p$-MeBzyl[13]dienato-N$_4$)]$^+$ with the atom numbering scheme.

(6) Å of the 14-membered complex [Ni(Me$_2$[14]dienatoN$_4$)]Br·H$_2$O.[1] The average Ni–N (amine) distance of 1.901(6) Å is also compatible with that of the parent complex **1** ($n=m=2$)[7] and shorter than that of the 14-membered complex **2** ($n=2$, $m=3$).[1]

For the unsaturated six-memberd chelate ring, the planarity is preserved, where the deviations of the constituent atoms from the least-squares plane defined by the Ni, N(1), N(4), C(7), C(8), and C(9) are within ±0.03 Å. The C–C and C–N bonds of the unsaturated chelate ring are intermediate between the corresponding single and double bond distances.[8] This result indicates that the chelate ring is a π-electron conjugated system.

The conformation of the triethylene tetramine moiety (trien) is similar to that of the trien in [Cu(trien)-SCN]NCS[9] and of the parent complex [Ni(Me$_2$[13]-dienatoN$_4$)]ClO$_4$.[7] Two of the three saturated five-membered chelate ring (A and B, Fig. 2) are found to have an asymmetrical gauche conformation and their absolute configurations are $\lambda\lambda$ and/or $\delta\delta$, as indicated by the deviations 0.05 and 0.65 Å for C(1) and C(2), respectively, above the N(1)–Ni–N(2) plane and 0.65 and 0.05 Å for C(5) and C(6), respectively, below the N(3)–Ni–N(4) plane. The remaining five-membered chelate ring (C) has a symmetrical gauche conformation with the deviations 0.33 and −0.34 Å for C(3) and C(4), respectively, from the plane N(2)–Ni–N(3). The two hydrogen atoms bonded to the secondary amine nitrogen atoms are positioned at the different side on the NiN$_4$ plane.

The molecular symmetry and dimensions of the macrocyclic cation, minus the substituent p-methylbenzoyl group, are similar to those of the parent complex.[7] This result indicates that the blue shift of the d-d transition band of the substituted complex from the parent complex can be achieved without altering the stereochemistry of the coordination sphere, in which the band maxima are 20.2 and 21.4×10^3 cm^{-1} for [Ni(Me$_2$[13]dienatoN$_4$)]PF$_6$ and [Ni(Me$_2$$p$-MeBzyl-[13]dienatoN$_4$)]PF$_6$, respectively.[1]

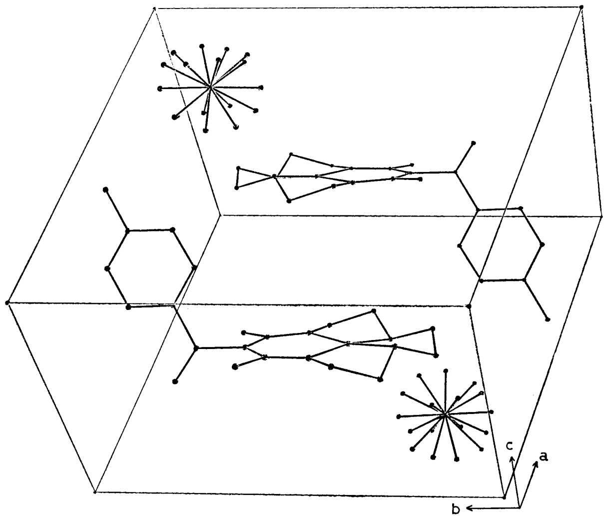


Fig. 3. Perspective view of the contents of the unit cell showing the cation and anion packing. Atoms are represented by points for clarity.

The most striking feature of the present molecular structure is non-coplanarity between the conjugated six-membered chelate ring and the p-methylbenzoyl group, where the dihedral angle between them is 69.2°. The overall molecular symmetry is not C$_2$, although the ^{1}H NMR spectra gave the methyl proton resonance of the acetylacetone residue as a singlet signal.[1] The methyl proton signal of the substituted complex (1.75 ppm) is shifted to a higher magnetic field than that of the parent complex (1.91 ppm). This can be interpreted in terms of the ring current effect of the benzene ring and the shielding effect of the carbonyl group of the p-methylbenzoyl group based on the present X-ray analysis.

Figure 3 shows the packing diagram of complex [Ni(Me$_2$$p$-MeBzyl[13]dienatoN$_4$)]PF$_6$. Anion PF$_6^-$ suffers from disorder. Judging from the occupancy factors of the disordered fluorine atoms and the geometry, anion PF$_6^-$ seems to be rotating randomly about the octahedral axes F(1)–P–F(2) and F(3)–P–F(4). There is no intermolecular bond distance which corresponds to any possible hydrogen bonds between the secondary amine nitrogen atoms and anion PF$_6^-$. The infrared frequency due to the NH vibrational mode in the series of complexes [Ni(Me$_2$$p$-MeBzyl[13]-dienatoN$_4$)]X with X=ClO$_4^-$, BF$_4^-$, and PF$_6^-$ moves to higher energy side in the order of counter anions ClO$_4^-$<BF$_4^-$<PF$_6^-$. This can be interpreted in terms of the hydrogen bond between the secondary amine nitrogen atoms and the anion or water molecule. In complex [Ni(Me$_2$$p$-MeBzyl[13]dienatoN$_4$)]BF$_4$·0.5H$_2$O, the NH band splits into two bands (3200 and 3130 cm^{-1}). Such a split has also been observed in complex [Ni(Me$_2$[14]dienatoN$_4$)]Br·H$_2$O, in which the Br and the water molecule are hydrogen bonded to

the secondary amine nitrogen atoms.[1]

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