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Alkyl addition and deprotonation of Ni(tmtaa) derivatives and crystal structure of [Ni{(Et)tmtaa}][BF_4]

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Abstract—The reaction of Ni(tmtaa) {(6,8,15,17-tetramethyl-7H,16H-5,9,14,18-tetraaza-dibenzo[b,i]-cyclotetradecenato(2-)-k^4-N,N′,N″,N‴)nickel(II)} with an alkylating agent, R_3OBF_4, yields [Ni{(R)tmtaa}][BF_4] (R = Et (**1**) or Me (**2**)). A monosubstituted product, Ni(R-tmtaa-H) (R = Et (**3**) or Me (**4**)), is then obtained followed by the deprotonation of [Ni{(R)tmtaa}][BF_4]. The crystal structure of [Ni{(Et)tmtaa}][BF_4] reveals a novel structure with one diiminate unit coordinated to nickel on one side and one diimine unit on the other side. In the NiN_4 co-ordination there is a small difference in Ni—N bond lengths according to N type. The absorption bands of **2** and **4** appearing around 600 nm due to metal-to-ligand charge transfer are red shifted from 585 nm ($\varepsilon \sim 7.5\times10^3$) for Ni(tmtaa) to 606 nm ($\varepsilon \sim 8.0\times10^3$) for **3**. © 1997 Elsevier Science Ltd

Keywords: Ni(tmtaa); diiminate; diimine; nickel; alkyl addition; deprotonation.

A large number of dibenzotetraaza[14]annulenes has been synthesized [1]. They are interesting because of their relationship to the naturally occurring porphyrin in biological systems [2]. Nonplanar Ni(tmtaa) {(6,8,15,17-tetramethyl-7H,16H-5,9,14,18-tetraaza-dibenzo[b,i]-cyclotetra-decenato-(2-)-k^4-N,N′,N″, N‴)nickel(II)} have shown atypical substitution reactivity toward acid chlorides [3], alkyl bromide [4] and NBS [5]. Dabrowiak [5] has also demonstrated the addition of bromine to Ni(tmtaa) to give a compound of [Ni(Br_2tmtaa)][Br_2]. Unfortunately, these types of reactions only produce disubstituted products. Monosubstituted Ni(tmtaa) is a very important material in the preparation of face-to-face bimetallic complexes [6]. However, it is very difficult to obtain in good yield according to the methods described previously. Although Ni(Me-taa) [7] and Ni(benzoyl-tmtaa) [8] have been synthesized, two problems remain to be solved. The yields are very low and 2-methoxyacrolein is quite expensive. Recently, we have reported that [Ni(H_2tmtaa)][$AlCl_4$] can be obtained from the reaction of Ni(tmtaa) with dicarbonyl dichloride in the presence of $AlCl_3$ [9]. According to the unusual reactivity of Ni(tmtaa) toward acid, in this paper, we present a method in which the addition of an alkyl group to Ni(tmtaa) yields [Ni{(R) tmtaa}]$^+$ (R = Me or Et) which is then followed by the deprotonation of [Ni{(R)tmtaa}]$^+$ to produce a monosubstituted product [Ni(R-tmtaa)]. The crystal structure of [Ni{(Et)tmtaa}][BF_4] is also presented.

RESULTS AND DISCUSSION

{(7-*ethyl*-6,8,15,17-*tetramethyl*-7*H*,16*H*-5,9,14,18-*tetraaza-dibenzo*[*b,i*]-*cyclo-tetradecenato*(1-))*nickel* (*II*)}*tetrafluoroborate*, [*Ni*{(*Et*)*tmtaa*}][BF_4], *and* {(7-*ethyl*-6,8,15,17-*tetramethyl*-16*H*-5,9,14,18-*tetraaza-dibenzo*[*b,i*]-*cyclotetradecenato*(2-))*nickel*(*II*)}, *Ni*(*Et-tmtaa-H*)

The reaction of Ni(tmtaa) with an alkylating agent, Et_3OBF_4, produces [Ni{(Et)tmtaa}][BF_4] **1** in good yield. [Ni{(Et)tmtaa}][BF_4] can be purified by recrystallization. Followed by the deprotonation of [Ni{(Et)tmtaa}][BF_4], a monosubstituted product, Ni(Et-tmtaa-H) **3**, is obtained according to Scheme 1.

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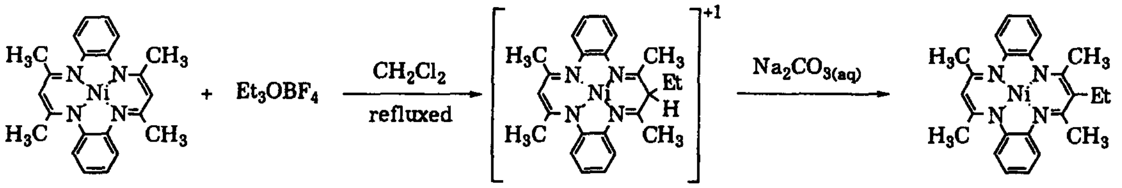


[Ni{(Et)tmtaa}][BF_4]

Ni(Et-tmtaa-H)

Scheme 1.

Unlike the addition of proton [9], [Ni{$(Et)_2$tmtaa}]$^{2+}$ was not observed even in the presence of excess Et_3OBF_4 under vigorous conditions (such as refluxing toluene). The result is probably due to the steric hindrance of the ethyl group.

The ORTEP diagram of [Ni{(Et)tmtaa}]$^+$ cation is illustrated in Fig. 1. The side view of the cation is given in Fig. 2 which reveals the planarity of the NiN_4 plane in the molecule and shows that ethyl group is hanging on above the Ni atom. The result can explain why no [Ni{$(Et)_2$tmtaa}]$^{2+}$ was observed even in the presence of excess Et_3OBF_4. Selected bond distances and bond angles of [Ni{$(Et)_2$tmtaa}][BF_4] are given in Table 1. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2). The coordination geometry around Ni is a square planar. The Ni atom and four nitrogen atoms are coplanar with the mean deviation of 0.012 Å, which is similar to that of Ni(tmtaa) and that of [Ni(H_2tmtaa)]$^{2+}$, but quite different from all of other known M(tmtaa) complexes in which the metal atom is above the N_4 plane with distances ranging from 0.07 Å to 0.76 Å [1,9–11]. The distances between N(1)—C(1) and N(2)—C(3) are 1.296(14) and 1.296(15) Å respectively and indicate some double bond character between N(1)—C(1) and N(2)—C(3). The distances between C(1)—C(2) and C(2)—C(3) are 1.489 (12) and 1.499 (18) Å respectively, which are consistent with a normal carbon–carbon single bond. The average distance (1.874 Å) between Ni—N(1) and Ni—N(2) is somewhat longer than the average distance (1.843 Å) between Ni—N(3) and Ni—N(4). This result shows that the diimine unit is not as good a sigma donor as the diiminate unit. **1** is the first example of a structure in which Ni is coordinated to a diiminate unit in one side and to a diimine unit in the other side.

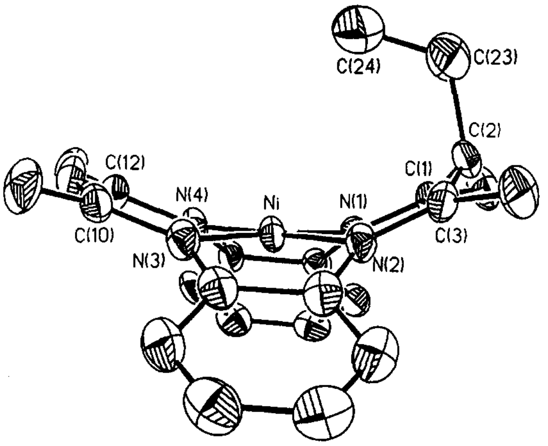


Fig. 2. A side view of one [Ni{(Et)tmtaa}]$^+$ cation illustrating the planarity of NiN(1)N(2)N(3)N(4) of the molecule.

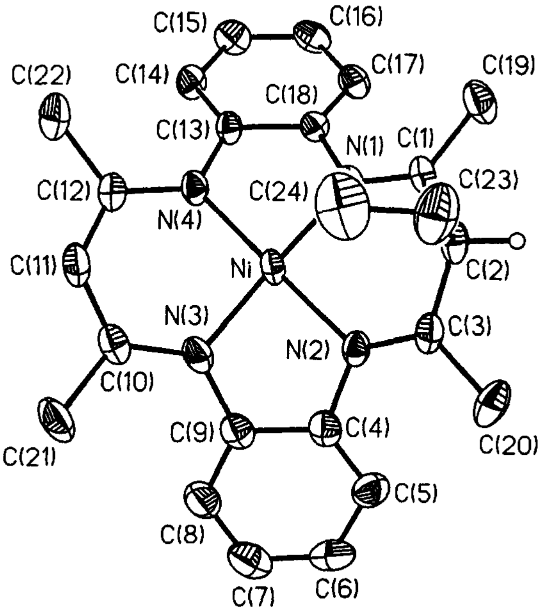


Fig. 1. Structure of [Ni{(Et)tmtaa}]$^+$ cation with atomic numbering scheme. Bond distances (Å) are as follows: Ni—N(1) 1.870(9), Ni—N(2) 1.878(6), N(1)—C(1) 1.294(14), N(2)—C(3) 1.298(15), C(1)—C(2) 1.489(12), C(2)—C(3) 1.505(19). Hydrogen atoms except H(2) are omitted for clarity.

{(7-methyl-6,8,15,17-tetramethyl-7H,16H-5,9,14,18-tetraaza-dibenzo[b,i]-cyclo-tetradecenato(1-))nickel (II)} tetrafluoroborate, [Ni{(Me)tmtaa}][BF_4] and {(7-methyl-6,8,15,17-tetramethyl-16H-5,9,14,18-tetra-aza-dibenzo[b,i]-cyclotetradecenato(2-))nickel(II)}, Ni(Me-tmtaa-H)

Ni(Me-tmtaa-H) can be obtained according to the method used for the preparation of Ni(Et-tmtaa-H) and it can also be obtained in good yield without

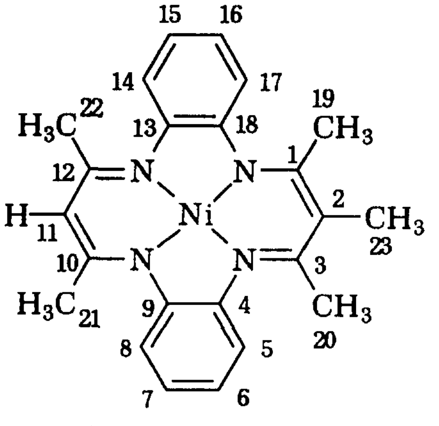
Table 1. Selected bond distances (Å) and bond angles (°) with estimated standard deviations in parentheses for **1**

Ni—N(1)	1.870(9)	Ni—N(2)	1.878(6)
Ni—N(3)	1.853(10)	Ni—N(4)	1.840(6)
N(1)—C(1)	1.296(14)	N(2)—C(3)	1.296(15)
N(3)—C(10)	1.348(12)	N(4)—C(12)	1.358(12)
C(1)—C(2)	1.489(12)	C(2)—C(3)	1.499(18)
C(10)—C(11)	1.377(14)	C(11)—C(12)	1.374(17)
N(1)—Ni—N(2)	93.9(4)	N(1)—Ni—N(3)	177.9(3)
N(2)—Ni—N(3)	85.0(4)	N(1)—Ni—N(4)	85.0(4)
N(2)—Ni—N(4)	178.9(4)	N(3)—Ni—N(4)	96.2(4)
Ni—N(1)—C(1)	124.2(6)	Ni—N(1)—C(18)	109.6(7)
C(1)—N(1)—C(18)	125.9(9)	Ni—N(3)—C(9)	111.0(7)
Ni—N(3)—C(10)	122.6(8)	C(9)—N(3)—C(10)	126.3(10)
C(1)—C(2)—C(3)	118.4(9)	C(1)—C(2)—C(23)	109.5(8)
C(3)—C(2)—C(23)	112.0(9)		

Table 2. Proton NMR data for compounds **1**–**4**, Ni(tmtaa), and $Ni(H_2tmtaa)^{2+}$ [9]

Compound	CH_3 H-19,20	CH_3 H-21,22	CH_3 24(Et)/23(Me)	CH_2 H-23(Et)	H-11	H-2	Aromatic
1	2.58	2.22	1.89	2.74	4.99	4.62	6.84–7.28
2	2.57	2.21	2.31 (d)	—	4.98	4.52	6.82–7.26
3	2.14	2.05	1.10	2.27	4.78	—	6.48–6.75
4	2.11	2.05	1.94	—	4.79	—	6.51–6.72
Ni(tmtaa)	2.08	2.08	—	—	4.99	4.99	6.54–6.72
$Ni(H_2tmtaa)^{2+}$	2.38	2.38	—	—	2.173, 2.175	2.173, 2.175	6.51–7.16

the purification of $[Ni\{(Me)tmtaa\}][BF_4]$. Because the methyl group is smaller than the ethyl group, it offers less steric hindrance. In the presence of excess Me_3OBF_4, the addition of two methyl groups on Ni(tmtaa) was observed according to NMR spectroscopic studies [12]. In order to determine two different methyl groups, [Ni(Me-tmtaa-H)] was studied by the nuclear Overhauser effect difference spectroscopy. It demonstrated a H-21/H-22 (2.05 ppm) hydrogen signal enhancement upon irradiation of H-11 (4.79 ppm). The ^1H NMR data of compounds 1-4, Ni(tmtaa), and $Ni(H_2tmtaa)^{2+}$ are summarized in Table 2.

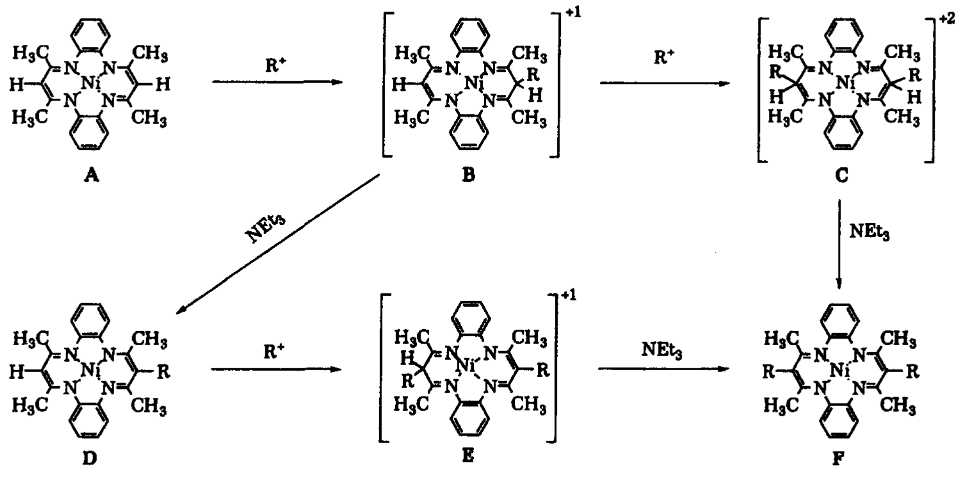


[Ni(Me-tmtaa-H)]

After examining the reactions of Ni(tmtaa) with acids, R_3OBF_4 ($R = CH_3$, C_2H_5), bromine, benzoyl chlorides and benzyl bromides, we propose that the formation of products for these reactions can be outlined as shown in Scheme 2. Among these, **C** can be obtained only when R is a small group such as a proton, bromine or methyl group.

Infrared spectra

IR spectra of **1** and **2** showed three intense bands about 1647, 1527, and 1470 cm^{-1} in the 1400–1700 cm^{-1} range. A strong imine (C=N) absorption due to the macrocyclic framework was observed at 1647 cm^{-1} for **1** and 1645 cm^{-1} for **2**. Two absorptions due to the diiminate were observed at 1527 and 1470 cm^{-1} for **1** and 1540 and 1463 cm^{-1} for **2**. However, compounds **3** and **4** only revealed bands of diiminate units



R$^+$ =H$^+$, Me$^+$, Et$^+$, Br$^+$, PhC(O)$^+$, CH$_3$C(O)$^+$, PhCH$_2$$^+$, and etc.

Scheme 2.

at 1531 and 1459 cm^{-1} for **3** and at 1533 and 1455 for **4**.

Electronic spectra

The electronic spectra of compound **3**, **4**, and Ni(tmtaa) covering the 250–800 nm range are listed in Table 3. The absorption bands appearing around 400 nm are attributed to π–π^* transitions within ligand molecules [13]. The extremely intense π–π^* transitions are slightly red shifted from 392 nm ($\varepsilon \sim 3.8 \times 10^4$) for Ni(tmtaa) to 396 ($\varepsilon \sim 3.5 \times 10^4$) for **3**. The absorption band appearing around 600 nm is due to CT transitions from metal to ligand which is consistent with that of the square-planar coordination of nickel(II). The molar extinction coefficients of these bands are larger than those assigned for *d*–*d* bands [14]. The band is also red shifted from 585 nm ($\varepsilon \sim 7.5 \times 10^3$) for Ni(tmtaa) to 606 nm ($\varepsilon \sim 8.0 \times 10^3$) for **4** which seems to indicate that the conjugated systems in **3** and **4** are slightly increased. The result is consistent with that (Me-tmtaa)$^{2-}$ and (Et-tmtaa)$^{2-}$ are better σ donors than tmtaa^{2-}. It seems to indicate that there is no extra steric hindrance effect after the replacement of the hydrogen atom by a methyl or ethyl group on the β-position of diiminate units. This result is quite different from that observed for benzoyl groups [15].

Table 3. The electronic spectra of Ni(Et-tmtaa-H), Ni(Me-tmtaa-H) and Ni(tmtaa) covering the 250–800 nm range

Compound	Electronic spectra in nm (ε)
Ni(Et-tmtaa-H)	271 (41000), 396 (27800), 599 (6680)
Ni(Me-tmtaa-H)	271 (48500), 396 (35300), 606 (8040)
Ni(tmtaa)	269 (45000), 392 (38000), 585 (7500)

EXPERIMENTAL

All manipulations were carried out under dry nitrogen. Solvents were dried by refluxing for at least 24 h over sodium/benzophenone (toluene, hexane, ether) and freshly distilled prior to use. Dichloromethane was distilled from P_2O_5. Deuterated solvents (Aldrich) were dried over molecular sieves. Ni(tmtaa-H) [1(c)] was prepared according to the literature methods. Et_3OBF_4 (1 M, CH_2Cl_2), Me_3OBF_4, and other chemicals were purchased from Aldrich and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer with chemical shifts given in ppm from the internal TMS. Mass spectra were recorded on a Jeol Jms-HX 110. Microanalysis were performed using a Heraeus CHN-O-Rapid instrument. Electronic absorption spectra were obtained in methylene chloride solutions (2.5×10^{-5} M) using matched 1 cm quartz cells and were recorded with a Shimadzu UV-160 spectrophotometer. Infrared spectra were obtained from a Bruker Equnox 55 spectrometer.

Preparations

[Ni{(Et)tmtaa}][BF$_4$]. To a solution of Ni(tmtaa) (0.62 g, 1.54 mmol) in CH_2Cl_2 (60 cm^3), Et_3OBF_4 (1 M, 1.69 cm^3, 1.69 mmol) was added, and the mixture then was refluxed for 10 h. After being cooled to 25°C, the mixture was filtered. Hexane (5 cm^3) was added into the filtrate to give a dark green solution. After standing for 6 h, a green powder was observed which was then removed by filtration and the procedure repeated three times [16]. A filtrate was obtained after filtration which was then concentrated to 30 cm^3. Hexane (30 cm^3) was slowly diffused into the filtrate. Dark green needle crystals were collected from the mixture after 2 days. Yield: 0.43 g (78.0%). ^{1}H NMR (CDCl$_3$, ppm): 6.84–7.28 (m, 8H), 4.99 (s, 1H), 4.62 (t, J_{H-H} = 4.0 Hz, 1H), 2.74 (doublet of quartet, 2H), 2.58 (s, 6 H), 2.22 (s, 6H), 1.89 (t, J_{H-H} = 4.8 Hz, 3H). ^{13}C NMR(CDCl$_3$, ppm): 21.85, 22.80 (CH$_3$), 12.41, 28.97 (CH$_2$CH$_3$), 65.38 (NC*C*HCN), 111.11, 121.21, 111.76, 111.85, 128.86, 142.86, 147.76 (aromatic). Found: C, 52.6; H, 5.0; N, 10.0 Calc. for [Ni{(Et) tmtaa}][BF$_4$]·0.5CH$_2$Cl$_2$: C, 51.9; H, 5.0; N, 9.6%. Infrared spectrum (cm^{-1}, from 1700–1400 cm^{-1}, KBr): 1647 (C=N), 1527, 1470 (diiminate).

[Ni(Et-tmtaa-H)]. To a solution of [Ni{(Et) tmtaa}][BF$_4$] (0.43 g, 0.83 mmol) in CH$_2$Cl$_2$ (30 cm^3), Na$_2$CO$_3$ (0.26 g, 3.4 mmol) in H$_2$O (50 cm^3) was added, and the mixture then was stirred for 2 h. After separation, the organic layer was dried over MgSO$_4$ and then filtered. The filtrate was concentrated to 15 cm^3, and hexane (30 cm^3) was then slowly added into the mixture to give dark green plate-like crystals. Yield: 0.19 g (54%). ^{1}H NMR (CDCl$_3$, ppm): 6.48–6.75 (m, 8H), 4.78 (s, 1H), 2.27 (q, J_{H-H} = 7.4 Hz, 2H), 2.14 (s, 6H), 2.05 (s, 6H), 1.10 (t, J_{H-H} = 7.4 Hz, 3H). ^{13}C NMR(CDCl$_3$, ppm): 19.79, 21.59 (CH$_3$), 14.92, 23.31 (CH$_2$CH$_3$), 111.05, 117.74, 120.67, 121.44, 121.90, 122.16, 147.38, 148.56 (aromatic). Found: C, 67.3; H, 6.1; N, 13.1 Calc.: C, 67.2; H, 6.1; N, 13.1%. Infrared spectrum (cm^{-1}, from 1700–1400 cm^{-1}, KBr): 1531, 1459 (diiminate). *m/z* 428 (M$^+$, 82%), 412 (M$^+$-CH$_3$, 100%). UV/Vis (CH$_2$Cl$_2$), λ/m (ε_{max}/dm^3 mol^{-1} cm^{-1}): 271 (41000), 396 (27800), 599 (6680).

[Ni{(Me)tmtaa}][BF$_4$]. To a solution of Ni(tmtaa) (0.40 g, 1.0 mmol) in CH$_2$Cl$_2$ (60 cm^3), Me$_3$OBF$_4$ (0.16 g, 1.1 mmol) was added, and the mixture then was refluxed for 4 h. After being cooled to 25°C, the mixture was filtered. Hexane (5 cm^3) was added into the filtrate and stood overnight. A filtrate was obtained after filtration and concentrated to 30 cm^3. Hexane (30 cm^3) slowly diffused into the filtrate. Dark green plate crystals were obtained. Yield: 0.31 g (62%). ^{1}H NMR (CDCl$_3$, ppm): 6.82–7.26 (m, 8H), 4.98 (s, 1H), 4.22 (q, J_{H-H} = 7.2 Hz, 1H), 2.57 (s, 6 H), 2.33 (d, J_{H-H} = 7.2 Hz, 3H), 2.21 (s, 6H). ^{13}C NMR(CDCl$_3$, ppm): 21.82, 22.48, 59.68, 65.384, 111.66, 121.33, 122.88, 128.98, 142.766, 147.80, 157.16, 179.03. Found: C, 51.5; H, 4.8; N, 10.3 Calc. for [Ni{(Me)tmtaa)}][BF$_4$]·0.5CH$_2$Cl$_2$: C, 51.8; H, 4.8; N, 10.3%. Infrared spectrum (cm^{-1}, from 1700–1400 cm^{-1}, KBr): 1645 (C=N), 1540, 1463 (diiminate).

[Ni(Me-tmtaa-H)]. (i) To a solution of [Ni{(Me) tmtaa}][BF$_4$] (0.10 g, 0.19 mmol) in CH$_2$Cl$_2$ (30 cm^3), KOH (1.0 g, 18 mmol) in H$_2$O (50 cm^3) was added, and the mixture then was stirred for 20 min. After separation, the organic layer was washed with H$_2$O (50 cm^3) twice and was dried over MgSO$_4$ and then filtered. The filtrate was dried *in vacuo*. Yield: 0.08 g (99%). ^{1}H NMR (CDCl$_3$, ppm): 6.51–6.72 (m, 8H), 4.79 (s, 1H), 2.11 (s, 6H), 2.05 (s, 6H), 1.94 (s, 3H). ^{13}C NMR(CDCl$_3$, ppm): 17.07, 21.31, 21.67, 111.02, 111.22, 120.66, 121.43, 121.75, 121.82, 147.22, 148.35, 154.97, 156.13. Found: C, 66.6; H, 5.9; N, 13.0 Calc.: C, 66.5; H, 5.8; N, 13.5%. Infrared spectrum (cm^{-1}, from 1700–1400 cm^{-1}, KBr): 1533, 1455 (diiminate). *m/z* 414 (M$^+$, 100%). UV/Vis (CH$_2$Cl$_2$), λ/m (ε_{max}/dm^3 mol^{-1} cm^{-1}): 271 (48500), 396 (35300), 606 (8040).

(ii) A mixture of Ni(tmtaa) (0.40 g, 1 mmol) and Me$_3$OBF$_4$ (0.16 g, 1.1 mmol) in CH$_2$Cl$_2$ (50 cm^3) was refluxed under N$_2$ for 4 h. After cooling to 25°C, the mixture was filtered and the filtrate was then added to ice cold KOH(aq) (5 g KOH in 150 cm^3 H$_2$O). After separation, the organic layer was dried over MgSO$_4$ and then filtered. The filtrate was dried *in vacuo*. Ni(Me-tmtaa-H) was obtained after separation from Ni(tmtaa-H) (0.08 g, 20%) by neutral Al$_2$O$_3$ column using CH$_2$Cl$_2$ as eluent. Yield: 0.30 g (72%). ^{1}H NMR (CDCl$_3$, ppm): 6.51–6.72 (m, 8H), 4.79 (s, 1H), 2.11 (s, 6H), 2.05 (s, 6H), 1.94 (s, 3H).

Crystallography

Crystal data. C$_{24}$H$_{27}$N$_4$NiBF$_4$·1.5CH$_2$Cl$_2$, **1**·1.5CH$_2$Cl$_2$ [17], M = 644.4, triclinic, space group $P\bar{1}$ (No. 2), cell constants a = 11.299 (1), b = 11.372 (2), c = 13.596 (2) Å, α = 72.65 (1)°, β = 73.64 (1)°, γ = 61.34 (1)°, V = 1443.0 (5) Å^3, Z = 2, $d_{calc.}$ = 1.483 g/cm^3, μ(Mo-K_α) = 0.999 mm^{-1}, T = 293 K, λ = 0.71073 Å, F(000) = 662. Dark green, moisture-sensitive needles. Crystal size 0.2 mm × 0.5 mm × 0.5 mm.

Data collection. Single crystals were obtained by letting hexane slowly diffuse into a solution of **1** in CH$_2$Cl$_2$. A suitable crystal of complex **1** was sealed in a thin-walled glass capillary under a nitrogen atmosphere and mounted on a Siemens R3m/V diffractometer. The crystallographic data were collected using an θ-2θ scan mode with Mo-K_α radiation. Cell constants were obtained by least-squares analysis on position of 54 random reflections in the 2θ range of 10 to 30°. 4188 reflections were collected of which 3957 reflections were independent.

Structure analysis and refinement. The structure was solved by direct methods and subsequent Fourier difference techniques using Siemens SHELXTL PLUS (VMS) program [18]. All non-H atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic for H atoms which were refined using a riding model. An ORTEP drawing is shown with 30% probability ellipsoids. The final wR (F^2) was 0.090 and conventional R(F) 0.074 using 2351 observed reflections ($I > 2.0\ \sigma(I)$).

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REFERENCES

1. (a) Cotton, F. A. and Czuchajowska, J., *Poly-*

hedron 1990, **9,** 2553 and references cited therein; (b) Peng, S.-M. and Goedken, V. L., *J. Am. Chem. Soc.*, 1976, **98,** 8500; (c) Place, D. A., Ferrara, G. P., Harland, J. J. and Dabrowiak, J. C., *J. Heterocycl. Chem.* 1980, **17,** 439.

2. (a) Honeybourne, C. L., *Tetrahedron* 1973, **29,** 1549; (b) Herron, N. and Busch, D. H., *J. Am. Chem. Soc.* 1981, **103,** 1236; (c) Baldwin, J. E. and Huff, J., *J. Am. Chem. Soc.* 1973, **95,** 5757; (d) Truex, T. J. and Holm, R. H., *J. Am. Chem. Soc.* 1972, **94,** 4529.
3. (a) Sakata, K., Koyanagi, K. and Hashimoto, M., *J. Heterocycl. Chem.*, 1995, **32,** 329; (b) Sakata, K. and Itoh, M., *J. Heterocycl. Chem.* 1992, **29,** 921.
4. Sakata, K., Hashimoto, M., Hamada, T. and Matsuno, S., *Polyhedron* 1996, **15,** 967.
5. Ferrara, G. P. and Dabrowiak, J. C., *Inorg. Nucl. Chem. Letters* 1978, **14,** 31.
6. (a) Collman, J. P., Wagenknecht, P. S. and Hutchison, J. E., *Angew. Chem. Int. Ed. Engl.* 1994, **33,** 1537; (b) Collman, J. P., Elliott, C. M., Halbert, T. R. and Tovrog, B. S., *Proc. Natl. Acad. Sci. U.S.A.* 1977, **1,** 18; (c) Durand, R. R. Jr., Bencosme, C. S., Collman, J. P. and Anson, F. C., *J. Am. Chem. Soc.* 1983, **105,** 2710; (d) Kajiwara, T., Yamaguchi, T., Kido, H., Kawabata, S., Kuroda, R. and Ito, T., *Inorg. Chem.* 1993, **32,** 4990.
7. Ansell, C. W. G., Chung, M. F. H. Y. J., Mcpartlin, M. and Tasker, P. A., *J. Chem. Soc., Dalton Trans.* 1982, 2113.
8. (a) Eilmes, J., *Polyhedron* 1985, **4,** 943; (b) Sakata, K., Tagami, H., and Hashimoto, M., *J. Heterocycl. Chem.* 1989, **26,** 805.
9. Tsai, Y.-H. and Lin, C.-C., *Chem. Lett.* 1996, **2,** 101.
10. Wang, Y., Peng, S.-M., Lee, Y.-L., Chuang, M.-C., Tang, C.-P. and Wang, C.-J., *J. Chinese Chem. Soc.* 1982, **29,** 217.
11. (a) Cotton, F. A. and Czuchajowska-Wiesinger, J., *Acta Cryst.* 1992, **C48,** 1434; (b) Dunn, S. C., Batsanov, A. S. and Mountford, P., *J. Chem. Soc., Chem. Commun.* 1994, 2007.
12. {(7,16-Dimethyl-6,8,15,17-tetramethyl-5,9,14,18-tetraaza-dibenzo[b,i]-cycle-tetradecenato(2-)) nickel(II)}, Ni(Me$_2$-tmtaa), was determined by spectroscopic analysis. ^{1}H NMR (CDCl$_3$, ppm): 6.52 (m, 5H), 2.07 (s, 6H), 1.91 (s, 3H); *m/z*: 428 (M$^+$, 41%).
13. (a) Bailey, C. L., Bereman, R. D., Rillema, D. P. and Nowak, R., *Inorg. Chem.* 1984, **23,** 3956; (b) Cutler, A. R., Alleyne, C. S. and Dolphin, D., *Inorg. Chem.* 1985, **24,** 2281; (c) Bailey, C. L., Bereman, R. D. and Rillema, D. P., *Inorg. Chem.* 1986, **25,** 3149; (d) Sakata, K., Hashimoto, M. and Naganawa, T., *Inorg. Chim. Acta* 1985, **98,** L11–L14.
14. Lever, A. B. P., *Inorganic Electronic Spectroscopy*, 2nd Ed. Elsevier, Amsterdam (1984).
15. Sakata, K. and Itoh, M., *J. Heterocycl. Chem.* 1992, **29,** 921.
16. [Ni(H$_2$tmtaa)][BF$_4$]$_2$ is completely removed by this procedure.
17. Tables giving full details of the crystal data, data collection, structure solution parameters, atomic coordinates of all atoms, bond distances, bond angles and anisotropic and isotropic thermal parameters of nonhydrogen atoms are available.
18. *SHELXTL PLUS*. Siemens Crystallographic Research Systems, Siemens, (1990).