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Coordination Modes of Polydentate Ligands. 2. Template Synthesis of Four-, Five-, and Six-Coordinate Fluorinated Schiff-Base Complexes of Ni^{2+}: Structure of an Octahedral Ni^{2+} Complex Containing Two Tridentate Ligands

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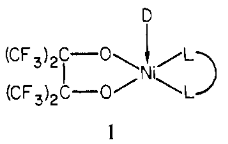
A number of new Schiff-base complexes of nickel(II) have been prepared by template condensation reactions of the fluorinated keto alcohol $CH_3C(O)CH_2C(CF_3)_2OH$ with primary amines, RCH_2NH_2, in the presence of Ni^{2+}. Where R is alkyl or phenyl such that the ligand is difunctional only, the products are, as expected, four-coordinate complexes of square-planar geometry. The incorporation of an extra potential donor into the group R gives a five-coordinate complex for R = $-CH_2N(CH_3)_2$, a six-coordinate complex for R = $-CH_2\text{-}2\text{-}C_5H_4N$, complexes of undetermined structure for R = $2\text{-}C_4H_3O$ and R = $2\text{-}C_5H_4N$, and no additional interactions when R = $-CH_2OCH_3$. These differences are explained in terms of variations in steric requirements and donor strength of the ligands. A complete structural determination has been carried out for the six-coordinate complex (R = $-CH_2\text{-}2\text{-}C_5H_4N$) derived from 2-(2-aminoethyl)pyridine. Crystals are triclinic, space group $P\bar{1}$, with a = 10.180 (5) Å, b = 10.444 (4) Å, c = 8.246 (4) Å, V = 745.5 (6) Å^3, α = 110.13 (3)°, β = 105.00 (4)°, and γ = 106.69 (4)°. The molecule is centrosymmetric with two equivalent, tridentate, ligands in a facial configuration around octahedral Ni^{2+}. Differences between the mode of coordination of this ligand and others in this study are explained in terms of electronic and steric effects.

Introduction

Considerable interest has been shown in the synthesis and structure of Schiff-base complexes of divalent transition-metal ions.[3] In the specific case of nickel(II), a square-planar, diamagnetic, structure is usually found with bidentate, uninegative, ligands derived from salicylaldehyde and related compounds. An increase in the coordination number of the metal ion may be produced in one of three ways: by association, by coordination of one or two additional donor molecules, or by the incorporation of an additional potential donor site into the Schiff-base molecule. The usual coordination number produced by these means is 6, with Ni^{2+} in a roughly octahedral environment. Both steric and electronic factors appear to be important in determining whether or not a particular square-planar metal ion will increase its coordination number. As the ligand field produced by the Schiff base becomes stronger, the d^8 Ni^{2+} ion becomes increasingly stabilized in a square-planar environment, and there is a corresponding decrease in its tendency to go to a six-coordinate system.[4]

In previous studies on highly fluorinated alkoxy complexes of nickel(II), we have shown in many cases that four- and five-coordination at the metal ion is preferred to six-coordination, an effect associated with the steric bulk of the fluorinated groups. Thus, for perfluoropinacol derivatives of type **1**, an increase in the bulk of either the coligand, L-L, or the incoming donor ligand, D, will prevent any interaction, while in no case studied by us is five-coordination exceeded.[5]



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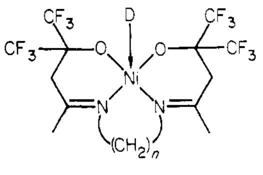

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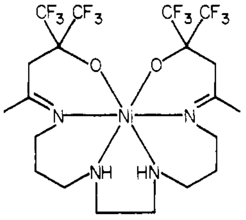
Similarly, for the fluorinated alkoxy Schiff-base complexes **2**, five-coordinate adducts may be prepared by addition of a suitable donor (D = pyridine, primary amines) but a second donor does not coordinate.[6] A six-coordinate Ni^{2+} complex may, however, be prepared by the incorporation of two additional strong donor atoms into the $-(CH_2)_n-$ chain connecting the two N atoms in a type **2** complex, giving **3**.[7]



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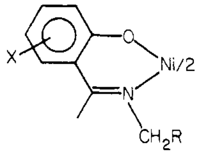
In analogous complexes in which weaker ethereal oxygen donor atoms are present in the chain, the metal remains four-coordinate in the case of Ni^{2+}, but six-coordinate for Co^{2+}; a combination of steric interactions between bulky cis alkoxy groups and the presence of five linked chelate rings produces gross distortions from octahedral geometry in the latter.[7]

It is clear that the "wraparound" nature of the ligand imposes a six-coordinate structure on the metal ion in **3**, and it is therefore of interest to determine the geometry resulting when the fluorinated alkoxy units are incorporated into two potentially tridentate ligands, rather than into one hexadentate unit. Previous workers have reported numerous studies on Schiff-base complexes of the type



where an additional donor site is present in each of the R groups. Whether or not one or both of these coordinate to Ni^{2+} depends upon the nature of R and also upon the type of X substituent present, and the situation is further complicated in many cases by temperature-dependent isomerizations. Thus, Sacconi has reported[8] a five-coordinate complex when R =

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Table I. Analytical and Mass Spectral Data

compd	R	formula	% carbon		% hydrogen		% nitrogen		mass spec, *m/e*	mp, °C
			calcd	found	calcd	found	calcd	found		
6a	$-CH_2CH_2CH_3$	$C_{20}H_{28}F_{12}N_2NiO_2$	39.0	39.0	4.60	4.45	4.55	4.55	614	112-13
6b	$-C_6H_5$	$C_{26}H_{24}F_{12}N_2NiO_2$	45.7	45.7	3.55	3.49	4.10	4.14	682	159-60
6c	$-CH_2OCH_3$	$C_{18}H_{24}F_{12}N_2NiO_4$	34.9	34.9	3.91	3.88	4.53	4.55	618	129-30
6d	$-C_4H_3O$	$C_{22}H_{20}F_{12}N_2NiO_4$	39.9	39.5	3.04	3.30	4.22	4.18	662	210-15 (dec)
6e	$-CH_2N(CH_3)_2$	$C_{20}H_{30}F_{12}N_4NiO_2$	37.2	37.2	4.70	4.65	8.69	8.56	644	149-50
6f	$-C_5H_4N$	$C_{24}H_{22}F_{12}N_4NiO_2$	42.1	42.0	3.24	3.27	8.18	8.36	684	220-25 (dec)
6g	$-CH_2C_5H_4N$	$C_{26}H_{26}F_{12}N_4NiO_2$	43.8	43.7	3.68	3.66	7.86	7.81	712	205-10 (dec)

Table II. Visible-UV Absorption Spectra

compd	R	ν_{max}, cm^{-1} (ϵ)	solvent[a]
6a	$-CH_2CH_2CH_3$	19 350 (81)	d
		15 200 (19), 26 180 (93)	py
6b	$-C_6H_5$	20 000 (77)	d
		15 040 (19), 26 600 (102)	py
6c	$-CH_2OCH_3$	19 270 (54)	d
		15 180 (18), 26 250 (98)	py
6e	$-CH_2N(CH_3)_2$	15 390 (30), 20 580 (27), 25 000 (86)	d
		15 670 (39), 20 620 (48) (sh), 25 510 (150)	py
6g	$-CH_2C_5H_4N$	16 130 (8.2), 21 460 (2.5)	a

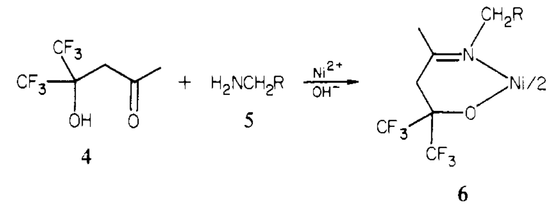
[a] d = dichloromethane; py = pyridine; a = acetone.

Table III. Summary of Crystal Data, Intensity Collection, and Structure Refinement of $Ni[OC(CF_3)_2CH_2C(CH_3)NCH_2CH_2(C_5H_4N)]_2$

formula (mol wt)	$NiF_{12}O_2N_4C_{26}H_{26}$ (713.25)
a, Å	10.180 (5)
b, Å	10.444 (4)
c, Å	8.246 (4)
α, deg	110.13 (3)
β, deg	105.00 (4)
γ, deg	106.69 (4)
cryst syst	triclinic
space group	$P\bar{1}$
V, Å^3	745.5 (6)
d_{calcd}, g/cm^3	1.589
cryst dimens, mm	0.56 × 0.41 × 0.23
cryst faces	$(100), (\bar{1}00), (01\bar{1}), (0\bar{1}1), (\bar{1}11), (1\bar{1}\bar{1}), (\bar{1}\bar{1}\bar{1}), (111)$
abs coeff (μ), cm^{-1}	7.19
radiation	Mo K$\bar{\alpha}$ (λ = 0.710 69 Å)
2θ scan speed, deg/min	2.0–5.0 (θ/2θ scan)
scan range, deg	1.05 below Kα_1 to 1.10 above Kα_2
bkgd/scan time ratio	0.5
data collcd	2θ of 4.5 to 50° $+h,\pm k,\pm l$
no. of data scanned	2690
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	2323
no. of variables	205
R, %	6.16
R_w, %	6.84

$-CH_2N(C_2H_5)_2$ and X = 5-Cl, in which only one of the two diethylamino groups is coordinated to Ni^{2+}, whereas various complexes of other geometries are present with different X substituents. Holm and co-workers[9] have studied a large range of complexes where R contains a potential oxygen donor site ($-CH_2OCH_3$ or $-CH_2OH$) and find octahedral, tetrahedral, or square-planar geometry at nickel, depending on the nature of X and R. A pyridyl residue may be incorporated into the R group by carrying out the Schiff-base condensation with either 2-(aminomethyl)pyridine[10] or 2-(2-aminoethyl)pyridine;[11] in both cases, the nickel(II) complexes are generally six-coordinate with distorted octahedral geometry.

In this paper, we report the template synthesis[12] of a series of nickel complexes of Schiff-base type ligands containing fluorinated alkoxy groups:



As reference compounds, and in order to demonstrate that an additional donor site is not essential for the template condensation reaction to occur, we have made two compounds in which R contains no potential donor, namely **6a** (R = $-CH_2CH_2CH_3$) and **6b** (R = $-C_6H_5$). In the remaining compounds, additional coordination to the metal is possible, either through oxygen in **6c** (R = $-CH_2OCH_3$) and **6d** (R = 2-C_4H_3O (furanyl)) or through nitrogen in **6e** (R = $-CH_2N(CH_3)_2$), **6f** (R = 2-C_5H_4N), and **6g** (R = $-CH_2$-2-C_5H_4N). A complete structural determination on the last compound has shown octahedral coordination to Ni^{2+} from two equivalent tridentate ligands.

Experimental Section

General Information. Infrared spectra were recorded on a Beckman 4250 instrument, visible–UV spectra on Cary 14 and 118 spectrometers, and mass spectra on a Varian MAT 311A. Microanalyses were performed by Guelph Chemical Laboratories; all analytical and mass spectral data are in Table I.

Synthesis. The keto alcohol 5,5,5-trifluoro-4-(trifluoromethyl)-4-hydroxy-2-pentanone (**4**) was prepared by the condensation of hexafluoroacetone with acetone as described previously.[6] Amines were commercial samples (Aldrich) used without further purification.

In a typical template condensation reaction, $NiCl_2 \cdot 6H_2O$ (1.2 g, 5.0 mmol) in warm ethanol was added to *n*-butylamine (0.73 g, 10 mmol) in ethanol, followed by **4** (2.24 g, 10 mmol) and KOH (0.65 g, 11 mmol) in ethanol. The solution was heated under reflux for 6 h, then stirred at 20 °C for 12 h, filtered to remove precipitated KCl, and evaporated to dryness on a rotary evaporator. The residual solid was recrystallized from ethanol to yield **6a**, red crystals. Remaining type **6** complexes were prepared in a similar way. **6b**: using benzylamine; red needles from CH_2Cl_2/ethanol. **6c**: using (2-methoxyethyl)amine; red microcrystals from CH_2Cl_2/ethanol. **6d**: using 2-furfurylamine; yellow-tan powder from ethanol. **6e**: using *N,N*-dimethylethylenediamine; green powder from ethanol. **6f**: using 2-(aminomethyl)pyridine; yellow-orange powder from CH_2Cl_2/ethanol. **6b**: using 2-(2-aminoethyl)pyridine; tan powder giving blue crystals on slow recrystallization from CH_2Cl_2/ethanol.

The identities of the seven new complexes **6a–6g** were established by elemental and mass spectroscopic analyses (Table I), which in each case showed peaks corresponding to the parent ion. Infrared spectra were consistent with the proposed structures, showing absorptions at 1660–1670 cm^{-1} associated with the C=N bond, together with other absorptions associated with the various substituent groups. Visible–UV spectra for each complex were recorded in nondonor and donor solvents; all data are in Table II, with the exception of compounds **6d** and **6f**, which gave only strong general absorption starting near 25 000 cm^{-1}.

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(12) We use the phrase "template synthesis" to refer to condensation reactions that will only occur in the presence of a metal ion.

Table IV. Positional Parameters ($\times 10^4$)

atom	*x*	*y*	*z*
Ni	0	0	0
F_1	−3770 (5)	−1200 (5)	542 (7)
F_2	−3461 (6)	−2701 (7)	1618 (8)
F_3	−5229 (5)	−3475 (6)	−1042 (9)
F_4	−4174 (6)	−5444 (5)	−2647 (7)
F_5	−2306 (6)	−4581 (4)	−54 (6)
F_6	−1962 (7)	−4583 (5)	−2498 (8)
O_1	−1308 (4)	−1742 (4)	250 (5)
N_1	−1934 (5)	47 (5)	−1579 (6)
N_2	359 (5)	−1452 (5)	−2362 (6)
C_1	−2718 (6)	−2728 (6)	−944 (8)
C_2	−3804 (7)	−2530 (9)	54 (12)
C_3	−3794 (8)	−4320 (7)	−1528 (10)
C_4	−3309 (7)	−2605 (7)	−2814 (8)
C_5	−3208 (6)	−1079 (8)	−2515 (9)
C_6	−4675 (8)	−961 (9)	−3304 (12)
C_7	−1768 (7)	1529 (7)	−1227 (8)
C_8	2035 (8)	−2264 (7)	−569 (9)
C_9	1150 (6)	−2254 (6)	−2336 (8)
C_{10}	1274 (8)	−3107 (7)	−4010 (10)
C_{11}	653 (8)	−3031 (7)	−5618 (9)
C_{12}	−120 (8)	−2161 (8)	−5641 (9)
C_{13}	−224 (7)	−1390 (6)	−3985 (7)

Structure Determination

(i) X-ray Data Collection and Reduction. Crystallization performed by slow evaporation of the solvent from a CH_2Cl_2 solution yielded pale blue blocks of $Ni[OC(CF_3)_2CH_2C(CH_3)NC_2H_4(C_5H_4N)]_2$ (**6g**). Diffraction experiments were performed on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo K$\bar{\alpha}$ radiation. On the basis of the observed extinctions, the compound crystallized in a triclinic space group, either *P*1 or $P\bar{1}$. $P\bar{1}$ was confirmed by structure solution and refinement. The final lattice parameters were obtained from 15 machine-centered reflections. The data ($+h,\pm k,\pm l$) were collected in three shells ($4.5 \leq 2\theta \leq 30$, $30 \leq 2\theta \leq 45$, $45 \leq 2\theta \leq 50°$). Machine parameters, crystal data, and data collected parameters are summarized in Table III.

Three standard reflections were recorded every 200 reflections; their intensities showed no statistically significant change over the duration of data collection. However, a stepwise correction based on the standards was applied to account for any minor fluctuations in the power of the X-ray beam. Correction factors ranged between 0.9926 and 1.0023. The data were processed by using the SHELX-76 package.[13] Out of a total of 2690 observed reflections, 2323 with $F_o^2 > 3\sigma(F_o^2)$ were used in refinement.

(ii) Structure Solution and Refinement. Atomic scattering factors were taken from the tabulation of Cromer and Waber.[14] The unit cell is consistent with $Z = 1$, which for $P\bar{1}$ requires that the nickel atom sits at the origin of the unit cell. All other non-hydrogen atoms were located from a difference map. Full-matrix least-squares refinement with all non-hydrogen atoms described isotropically yielded $R = 12.05\%$. The pyridine and methylene hydrogen atom positions were calculated. Methyl hydrogen atom positions were located from a difference map. A C–H bond length of 1.08 Å was assumed, and hydrogen atom temperature factors were fixed at 1.2 times the isotropic temperature of the bonded C atom. In the final cycle, in which the hydrogen atom contributions were included, all non-hydrogen atoms were described anisotropically. The maximum shift/σ on a parameter was 0.004. A final difference Fourier showed no peaks of chemical significance, the largest being a 1.0-electron peak associated with the Ni atom. Final values of R and R_w were 6.16 and 6.84%, respectively. The following data for $Ni[OC(CF_3)_2CH_2C(CH_3)NC_2H_4(C_5H_4N)]_2$ (**6g**) are tabulated: position parameters (Table IV), selected interatomic distances and angles (Table V), temperature factors (Table S-I, supplementary material), and hydrogen atom coordinates and temperature factors (Table S-II). Interatomic distances and bond angles associated with the CF_3 groups (Table S-III) and values of $10|F_o|$ and $10|F_c|$ (Table S-IV).

Table V. Selected Interatomic Distances (Å) and Angles (deg)

	Distances		
Ni-O	2.033 (3)	C_7-N_1	1.422 (7)
Ni-N_1	2.086 (4)	C_7-C_8	1.550 (8)
Ni-N_2	2.209 (4)	C_8-C_9	1.507 (8)
O-C_1	1.346 (6)	C_9-C_{10}	1.423 (8)
C_1-C_2	1.558 (9)	C_{10}-C_{11}	1.353 (9)
C_1-C_3	1.536 (8)	C_{11}-C_{12}	1.363 (11)
C_1-C_4	1.567 (8)	C_{12}-C_{13}	1.375 (9)
C_4-C_5	1.495 (9)	C_9-N_2	1.319 (7)
C_5-C_6	1.525 (8)	C_{13}-N_2	1.349 (7)
C_5-N_1	1.281 (8)		
	Angles		
$ONiN_1$	88.8 (2)	$C_4C_5C_6$	116.6 (5)
$ONiN_2$	85.9 (2)	$C_4C_5N_1$	119.5 (5)
$ONiN_1'$[a]	91.2 (1)	$C_6C_5N_1$	123.8 (6)
$ONiN_2'$[a]	94.1 (1)	$C_2C_1C_4$	107.7 (5)
N_1NiN_2	82.0 (2)	$C_2C_1C_3$	109.4 (5)
N_1NiN_2'[a]	98.0 (2)	$C_3C_1C_4$	106.3 (5)
$NiOC_1$	126.6 (3)	$N_1C_7C_8$	109.8 (5)
NiN_1C_5	124.4 (4)	$C_7C_8C_9$	117.6 (5)
NiN_2C_7	112.4 (3)	$C_8C_9N_2$	116.0 (5)
NiN_2C_{13}	113.7 (3)	$C_8C_9C_{10}$	116.0 (5)
$C_5N_1C_7$	122.2 (5)	$N_2C_9C_{10}$	120.4 (5)
$C_{13}N_2C_9$	117.5 (5)	$C_9C_{10}C_{11}$	120.0 (6)
NiN_2C_9	128.5 (4)	$C_{10}C_{11}C_{12}$	119.9 (5)
OC_1C_3	108.5 (5)	$C_{11}C_{12}C_{13}$	117.1 (6)
OC_1C_4	115.1 (4)	$C_{12}C_{13}N_2$	124.9 (6)
OC_1C_2	109.9 (5)	$C_1C_4C_5$	113.9 (5)

[a] Atoms marked with prime indicated the symmetry-related atom.

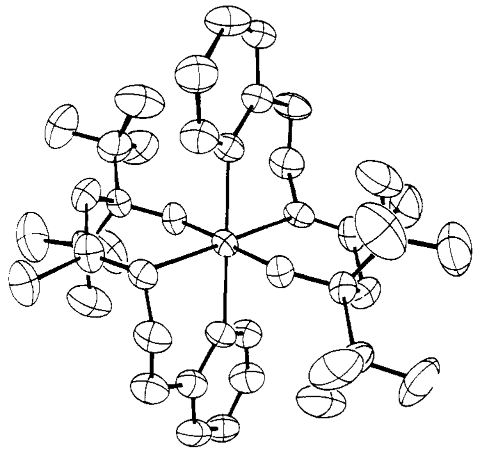
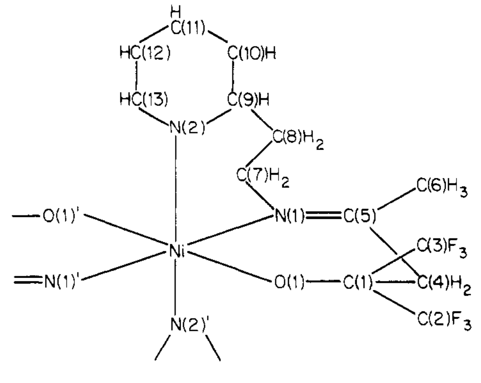


Figure 1.

Structure Description

An ORTEP view of the molecule of **6g** is shown as Figure 1. Since the Ni atom is located at a crystallographic inversion center, the molecule is required to be centrosymmetric, and the two identical ligands are each coordinated in a facial configuration to Ni^{2+}. The atom-numbering scheme is shown, with the primes denoting atoms related by the center of symmetry.



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The nickel ion is in essentially octahedral coordination. Bite angles within the chelate rings are marginally less than 90° [$\angle O_1NiN_1 = 88.8$ (2)°, $\angle N_1NiN_2 = 82.0$ (2)°, $\angle O_1NiN_2 = 85.9$ (2)°], while angles between the two ligands are greater than 90° [$\angle O_1NiN_1' = 91.2$ (1)°, $\angle O_1NiN_2' = 94.1$ (1)°, $\angle N_2NiN_2' = 98.0$ (2)°].

The six-membered iminoalkoxy ring is in the "halfboat" conformation that we have found previously,[7,15,16] but bond lengths to the metal are significantly longer than in four-coordinate complexes. Thus, the Ni–alkoxy oxygen bond length in **6g** is 2.033 (3) Å, whereas we have previously found 1.843 (2) Å in a type **2** complex[15] and other workers have reported Ni–O distances of 1.852 (3) Å in the bis(perfluoropinacolato)nickelate(II) ion[17] and 1.843 (5) Å in bis(salicylaldoximato)nickel.[18]

Similarly, the Ni–imino nitrogen bond length in **6g** is 2.086 (4) Å, compared with 1.896 (3) Å in a type **2** complex,[15] 1.855 (5) Å in bis(salicyladoximato)nickel(II)[18] and 1.85 Å in nickel bis(dimethylglyoxime).[19] The Ni–pyridine nitrogen bond length in **6g** is 2.209 (4) Å, similar to that in other pyridine complexes of six-coordinate nickel(II), e.g. 2.133 (4) Å in *trans*-$NiCl_2(py)_4$.[20] In a five-coordinate Schiff-base complex,[8] the Ni–imino nitrogen bond lengths are reported as 1.93 Å for the bidentate ligand and 2.04 Å for the tridentate ligand; the Ni–pyridine distance is 2.25 Å.

An increase in bond lengths to Ni^{2+} would, of course, be expected on going from low-spin, square-planar geometry to high-spin, octahedral geometry in the d^8 ion, and the dimensions of the coordination sphere around the metal in complex **6g** do not suggest any steric hindrance between the ligating groups.

Discussion

With all seven primary amines, Schiff-base condensation reactions occurred readily in the presence of Ni^{2+}, demonstrating that this ion, like Cu^{2+},[16] would catalyze the reaction of the keto alcohol **4** with monofunctional amines. The product in each case was a neutral bis(iminoalkoxy) complex of Ni^{2+}, but four different types of structure were observed:

(i) With R = $-CH_2CH_2CH_3$ (**6a**) or $-C_6H_5$ (**6b**), the products were, as expected, bright red in color with spectra characteristic of four-coordinate, square-planar nickel(II). The same result was found with R = $-CH_2OCH_3$ (**6c**), indicating that the methoxy group was not interacting with the metal ion. Extinction coefficients for the absorption peak at 19000–20000 cm^{-1} were in the range 54–81, which we have previously shown[15] to indicate a trans arrangement of the N_2O_2 donor set. In each case, use of pyridine as a solvent gave green solutions with spectra characteristic of five-coordinate Ni^{2+}; no stable solvates remained on evaporation in air.

The failure of the methoxy group to coordinate is not unexpected, in view of the demonstration by Holm[9] that this group coordinates only weakly in Schiff-base adducts. Clearly, the additional bulk of the fluorinated alkoxy groups has completely disfavored the coordination of this weak donor, although a stronger donor (pyridine) can still be accommodated.

(ii) When R = $-CH_2N(CH_3)_2$, the complex (**6e**) was green and gave a spectrum consistent with five-coordinate Ni^{2+}. No significant change was seen in pyridine solution, indicating that an increase in six-coordination did not occur. Clearly, the bulk of the dimethylamino group is such that only one of the two potential ligands can coordinate.

(iii) When R = $-C_4H_3O$ (**6d**) or $-C_5H_5N$ (**6f**), the nature of the products could not be determined unambiguously. The complexes were orange-brown in color, giving only general absorption above 25000 cm^{-1}; they precipitated from solution as fine powders, and single crystals could not be obtained. An associated structure may be suggested, in which some additional coordination to nickel has occurred, but no definite assignement can be made. It is clear, however, that simple intramolecular coordination from the additional potential donor is not favored, probably because of the unfavorable geometry of the additional five-membered chelate ring that would be required.

(iv) For R = $-CH_2C_5H_5N$ (**6g**), the initial product of condensation was an orange-brown compound similar to those of type iii above. However, in this case, slow crystallization brought about rearrangement to yield well-defined blue crystals of the six-coordinate complex whose structure we have determined. That this occurs with **6g**, rather than with the similar pyridyl complex **6f**, may be attributed to the presence of one extra methylene group in the chain connecting the pyridine ring to the remaining part of the Schiff-base ligand. The two linked, six-membered chelate rings provide the ideal geometry for fitting the two tridentate ligands around octahedral nickel(II). It is the chelate effect that provides the slight extra driving force necessary to overcome steric and electronic effects and produce a six-coordinate complex, whereas the coordination of free pyridine molecules to Ni^{2+} in **6a**–**6c** and similar complexes stops at five-coordination.

This study demonstrates once again that relatively subtle changes in ligand geometry are capable of producing quite different modes of coordination in complexes where two or more configurations are close in energy. In particular, we have shown that, in a sterically crowded Schiff-base complex of nickel(II), the maximum degree of coordination of the metal can only be achieved by a combination of favorable factors, including the bulk and donor strength of the additional potential ligand together with the chelate effect associated with a ring of suitable size.

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Registry No. **4**, 10487-10-2; **5a**, 109-73-9; **5b**, 100-46-9; **5c**, 109-85-3; **5d**, 617-89-0; **5e**, 108-00-9; **5f**, 3731-51-9; **5g**, 2706-56-1; **6a**, 89530-66-5; **6b**, 89530-67-6; **6c**, 89530-68-7; **6d**, 89530-69-8; **6e**, 89530-70-1; **6f**, 89530-71-2; **6g**, 89530-72-3.

Supplementary Material Available: Tables S-I–S-IV giving temperature factors, hydrogen atom parameters, interatomic distances and angles associated with the CF_3 groups, and observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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