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Contribution from the Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210,
and The University of Warwick, Coventry CV4 7AL, U.K.

Synthesis and Characterization of Multiply Substituted Lacunar Macrobicyclic Complexes of Nickel(II), a Representative Crystal Structure, and Preparation of Corresponding Free Ligands

BOHDAN KORYBUT-DASZKIEWICZ, MASSAKI KOJIMA, JAMES H. CAMERON, NORMAN HERRON,
MADHAV Y. CHAVAN, ALAN J. JIRCITANO, BRADLEY K. COLTRAIN, GARY L. NEER,
NATHANIEL W. ALCOCK,* and DARYLE H. BUSCH*

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A general synthetic procedure for the production of a wide variety of substituted versions of previously reported lacunar macrobicyclic nickel(II) complexes is reported. These substitutions lead to complexes with a protected cavity in the vicinity of one axial coordination site and with controlled steric and electronic properties at the metal center and its axial ligands. The X-ray crystal structure of one such multiply substituted complex, (3,11-dibenzyl-14,20-dimethyl-2,12-diphenyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,16-nonaene-κ^4N)nickel(II) hexafluorophosphate, has been completed. The complex crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.126$ (2) Å, $b = 17.629$ (4) Å, $c = 30.666$ (7) Å, and $\beta = 100.87$ (2)°, and the structure was solved by the heavy-atom method to $R = 8.3\%$, $R_w = 10.7\%$ for 3363 reflections. The structure illustrates the demanding steric requirements placed upon the lacuna size and shape by the peripheral substituents of the macrocycle. The ligands reported may be removed from nickel(II) for transferral, intact, to iron(II) or cobalt(II) for investigation of the effect of steric and electronic factors on the strength and durability of their dioxygen adducts. The spectroscopic and electronic properties of a selection of nickel complexes with a range of substitution patterns are presented for comparative purposes.

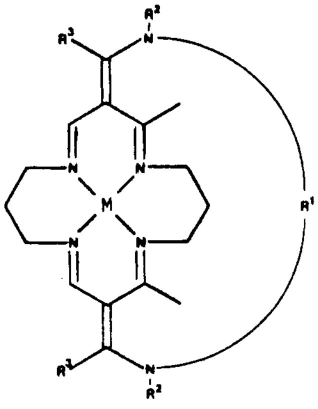
Introduction

Complexes with the general structure I (Figure 1) have been designed for use as various totally synthetic (non-porphyrin) heme protein models. Previous reports have detailed some of their syntheses,[1-3] and three communications have confirmed the utility of this type of ligand system to generate cobalt(II)[4] and iron(II)[5] complexes that display exceptional activity as reversible dioxygen carriers. However, the complexes reported to date represent only a fraction of the many structural possibilities based on substituents at R^1, R^2, and R^3. While the natures of R^1 and R^2 have been fairly comprehensively varied,[2,3] only derivatives having $R^3 = CH_3$ have been described to date.

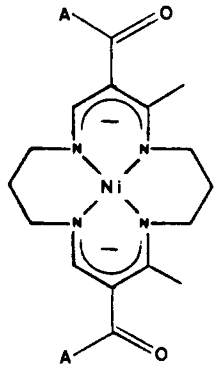
The purpose of the present study is to complete a general synthetic scheme wherein R^1, R^2, and R^3 may be altered at will, producing metal complexes with both steric and electronic control over the nature and strength of axial ligand coordination within the protected cavity. Such a situation is highly desirable since steric and electronic control of O_2 binding, particularly to iron(II), have been utilized to good effect in porphyrin-based systems. The works of Collman[6] and Baldwin[7] have emphasized steric control over small ligand binding to heme type units while Traylor[8] has examined the effects of electronic factors on this type of interaction. Our own work with the previously reported simple iron(II) and cobalt(II) complexes of type I has also indicated the importance of such factors in the production of stable *and* durable dioxygen carriers among purely synthetic metal chelates.[4,5] We have sought, therefore, to devise general synthetic procedures for the systematic variation of the peripheral substituents in structure I so as to directly control the steric and electronic environment of small ligands bound within the lacuna. The present report details the synthesis and characterization of a variety of substituted nickel(II) complexes and corresponding free ligands as examples of this general synthetic route. The crystal structure of one example of such a multiply substituted complex is also presented as an illustration of the spatial distribution of R^1, R^2, and R^3 substituents.

Results and Discussion

Synthesis. The introduction of a substituent in the position R^3 of structure I begins with the basic acylated macrocycle



I



II

II, first prepared by Jager,[9] which is synthesized by published procedures.[10] This material, following further modification, would lead to the previously reported lacunar complexes I where $R^3 = CH_3$. In order to change R^3 in the lacunar complex, the methyl group A of structure II must be replaced by a route such as that illustrated in Scheme I.[11] Deacylation occurs upon refluxing of II in a methanolic solution of *p*-

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* To whom correspondence should be addressed: N.W.A., The University of Warwick; D.H.B., The Ohio State University.

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Table I. Analytical Data for New Complexes

a. Neutral Complexes V

		calcd				found			
R^3	formula	% C	% H	% N	% Ni	% C	% H	% N	% Ni
H	$C_{16}H_{22}O_2N_4Ni$	53.22	6.14	15.52	16.26	53.33	6.34	15.56	16.13
t-C_4H_9	$C_{24}H_{38}O_2N_4Ni$	60.90	8.09	11.84	12.40	60.81	8.23	11.72	12.42
neo-C_5H_{11}	$C_{26}H_{42}O_2N_4Ni$	62.29	8.44	11.18		62.15	8.51	11.05	
n-C_7H_{15}	$C_{30}H_{50}O_2N_4Ni$	64.64	9.04	10.05	10.53	64.71	9.21	10.09	10.37
n-C_9H_{19}	$C_{34}H_{58}O_2N_4Ni$	66.55	9.53	9.13		66.08	9.58	9.20	
C_6H_5	$C_{28}H_{30}O_2N_4Ni$	65.52	5.89	10.91		65.32	5.89	10.89	
$CH_2C_6H_5$	$C_{30}H_{34}O_2N_4Ni \cdot 0.5H_2O$	65.47	6.41	10.18		65.61	6.65	10.17	
CF_3	$C_{18}H_{20}O_2N_4F_6Ni$	43.49	4.06	11.27		43.35	4.45	11.18	
4-OMePh	$C_{30}H_{34}O_4N_4Ni$	62.84	5.98	9.77		62.07	6.34	10.16	
3,5-$(OMe)_2$Ph	$C_{32}H_{38}O_6N_4Ni$	60.68	6.05	8.85		60.59	6.19	8.74	
3,5-$(Me)_2$Ph	$C_{32}H_{38}O_2N_4Ni \cdot H_2O$	65.45	6.32	9.54		65.90	7.28	9.65	
3,5-$(NO_2)_2$Ph	$C_{28}H_{26}O_{10}N_8Ni$	42.84	3.32	13.79		42.55	3.69	13.61	
n-C_5H_{11}	$C_{26}H_{42}O_2N_4Ni$	62.29	8.44	11.18		62.30	8.72	11.23	
n-$C_{17}H_{35}$	$C_{50}H_{90}O_2N_4Ni$	71.66	10.82	6.69		71.21	10.35	6.90	

b. Unbridged Complexes VII

				calcd			found		
R^1	R^2	R^3	formula	% C	% H	% N	% C	% H	% N
H	CH_3	C_6F_5	$C_{30}H_{28}N_6P_2F_{22}Ni \cdot 4CH_3CN$	38.80	3.40	11.91	38.42	3.93	12.01
H	CH_3	p-biphenyl	$C_{42}H_{46}N_6P_2F_{12}Ni$	51.29	4.71	8.55	49.39	4.86	8.41
H	CH_3	p-ClPh	$C_{30}H_{36}N_6Cl_2P_2F_{12}Ni$	40.03	4.03	9.34	37.27	4.14	9.30
H	CH_3	p-FPh	$C_{30}H_{36}N_6P_2F_{14}Ni$	41.54	4.18	9.69	40.88	4.76	9.63

c. Lacunar Complexes I

				calcd				found				synthesis method	% yield
R^1	R^2	R^3	formula	% C	% H	% N	% Ni	% C	% H	% N	% Ni		
m-xylylene	CH_3	H	$C_{26}H_{34}N_6P_2F_{12}Ni$	40.60	4.50	11.40		40.56	4.90	11.40		A	31
	CH_3	3,5-$(OMe)_2$Ph	$C_{42}H_{52}O_4N_6P_2F_{12}Ni$	47.88	4.97	7.98		47.90	5.28	7.81		B	39
	CH_3	n-C_7H_{15}	$C_{40}H_{64}N_6P_2F_{12}Ni$	49.28	6.37	8.62		49.40	6.88	8.59		B	76
	CH_3	C_6H_5	$C_{38}H_{44}N_6P_2F_{12}Ni$	48.90	4.75	9.00		48.68	4.86	9.21		B	62
	H	C_6H_5	$C_{36}H_{40}N_6P_2F_{12}Ni$	47.76	4.45	9.28	6.48	47.65	4.59	9.28	6.29	A	95
	H	n-C_7H_{15}	$C_{38}H_{58}N_6P_2F_{12}Ni$	48.07	6.37	8.85	6.19	48.14	6.56	8.91	6.32	A	75
	$CH_2C_6H_5$	C_6H_5	$C_{50}H_{52}N_6P_2F_{12}Ni$	55.32	4.83	7.74	5.41	55.47	4.89	7.58	5.37	B	47
$(CH_2)_4$	H	C_6H_5	$C_{32}H_{40}N_6P_2F_{12}Ni$	44.83	4.70	9.80	6.85	44.95	4.83	9.93	6.56	A	89
$(CH_2)_4$	CH_3	C_6H_5	$C_{34}H_{44}N_6P_2F_{12}Ni$	46.12	5.01	9.49	6.63	46.07	5.20	9.60	6.47	A	67
$(CH_2)_4$	H	t-C_4H_9	$C_{28}H_{48}N_6P_2F_{12}Ni$	41.15	5.92	10.28		41.14	6.14	10.36		A	7
$(CH_2)_5$	H	C_6H_5	$C_{33}H_{42}N_6P_2F_{12}Ni$	45.49	4.86	9.64		45.79	5.06	9.59		A	60
$(CH_2)_5$	CH_3	C_6H_5	$C_{35}H_{46}N_6P_2F_{12}Ni$	45.14	5.07	9.32		45.14	5.07	9.27		B	32
$(CH_2)_5$	H	t-C_4H_9	$C_{29}H_{50}N_6P_2F_{12}Ni$	41.90	6.06	10.11		42.28	6.21	10.18		A	25
$(CH_2)_6$	H	C_6H_5	$C_{34}H_{44}N_6P_2F_{12}Ni$	46.12	5.01	9.69	6.63	45.97	5.14	9.36	6.37	A	82
$(CH_2)_6$	CH_3	C_6H_5	$C_{36}H_{48}N_6P_2F_{12}Ni$	47.34	5.30	9.20		47.38	5.35	9.11		A	46
$(CH_2)_6$	H	t-C_4H_9	$C_{30}H_{52}N_6P_2F_{12}Ni$	42.62	6.20	9.94	6.94	42.79	6.40	10.00	6.73	A	47
$(CH_2)_6$	H	n-C_7H_{15}	$C_{36}H_{60}N_6P_2F_{12}Ni$	46.52	6.94	9.04	6.25	46.60	7.09	9.15	6.17	A	76
$(CH_2)_6$	CH_3	H	$C_{26}H_{43}N_7P_2F_{12}Ni$	38.92	5.40	12.22		38.73	5.58	12.00		A	68
$(CH_2)_7$	H	C_6H_5	$C_{35}H_{46}N_6P_2F_{12}Ni$	46.74	5.16	9.34	6.53	46.78	5.38	9.41	6.27	A	75
$(CH_2)_7$	CH_3	C_6H_5	$C_{37}H_{50}N_6P_2F_{12}Ni$	47.92	5.43	9.06		47.75	5.58	8.91		B	30
$(CH_2)_7$	H	t-C_4H_9	$C_{31}H_{54}N_6P_2F_{12}Ni \cdot 0.5CH_3CN$	43.68	6.36	10.35		43.73	6.50	10.17		A	23
$(CH_2)_8$	H	C_6H_5	$C_{36}H_{48}N_6P_2F_{12}Ni$	47.34	5.30	9.20		47.12	5.47	9.08		A	50

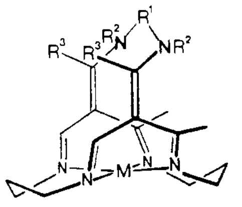

Figure 1. Three-dimensional visualization of lacunar complexes I.

toluenesulfonic acid whereupon the PF_6 salt III may be readily isolated. This material, which has two hydrogen atoms on the α-carbon, may have one of those protons removed (from each α-carbon) by a strong base to generate the highly reactive complex IV. This material is air and moisture sensitive and must be used immediately upon preparation for best results. In dry ether the complex reacts with an acid chloride to reacylate on the α-carbon, provided 2 equiv of triethylamine is present to accept the HCl byproduct. This scheme has been used to produce numerous complexes V with $R^3 = CF_3$, n-C_7H_{15}, C_6F_5, p-C_6H_4OMe, p-C_6H_4Cl, p-C_6H_4F, t-C_4H_9, etc. (Table I). (Clearly, reaction of IV with a diacid chloride, ClOCRCOCl, under high dilution conditions might be expected to yield a bridged material analogous to the lacunar complexes.[12] Such is indeed the case, but these materials will be described in a separate publication.) The complex V where R^3 = H may also be prepared from IV, but with use of techniques slightly modified from those already described and involvement of acylation by a combination of acetic anhydride and formic acid rather than the unavailable acid chloride.

The appropriately substituted complexes V may be treated in a manner identical with that already described[1-3] for the

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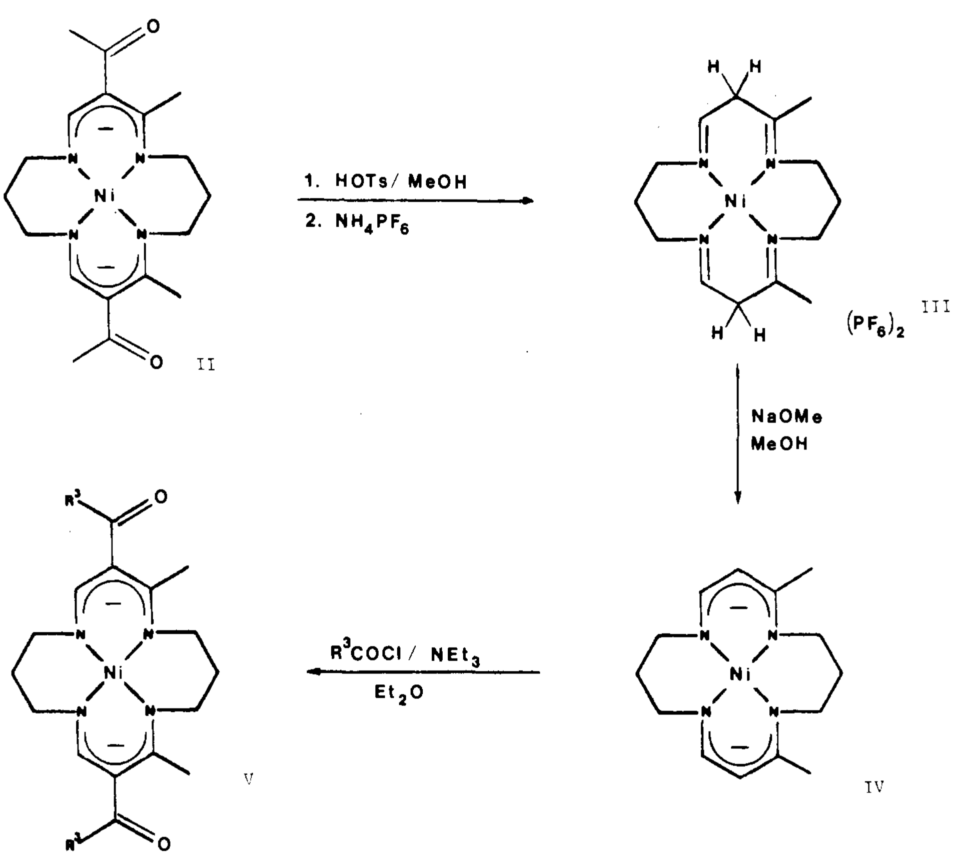
[12] Eilmes, J.; Sledziewska, E. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **1978**, *26*, 441.

Scheme I



reactant having R^3 = CH$_3$ (Scheme II). Methylation with methyl fluorosulfate in dry CH$_2$Cl$_2$ yields the methyl vinyl ether VI,[13] which may then be taken to the desired bridged lacunar macrobicycle by one of two routes,[2] A or B, depending on the availability of diamines of the desired type R^{2}NHR^{1}NHR^2. Experience has shown that the bridging reaction with species VIII is very dependent on the nature and bulk of substituents R^2 and R^3. As these groups are made larger, longer times are required for the bridging reaction and more care must be taken to protect the reaction from moisture since water will slowly reprotonate VIII, rendering it unreactive toward XR^{1}X.

Dimeric structures, where two R^1 groups form bridges between two macrocycles rather than span from side to side across one molecule,[3] constitute a continuing problem in these syntheses, especially when R^2 = H. However, the desired lacunar complex can easily be separated from any of the dimeric contaminants with use of ion-exchange chromatographic techniques as described previously.[3] Schemes I and II may now be combined to generate almost *any* desired combination of R^1, R^2, and R^3 substituents. The properties of a few of these substitution products are described as follows.

Characterization. a. Neutral Complexes V. Elemental analyses for a representative section of the new complexes are presented in Table I. Infrared spectra of the complexes (Table II) are unremarkable and most useful for simple qualitative identification purposes. The electronic spectra in CHCl$_3$ are all very similar with a shoulder at 460–489 nm ($\epsilon \approx (2.4–3.4) \times 10^2$) and typical d–d transitions for Ni^{II}N$_4$ square-planar complexes. Three intense absorptions occur in the UV region at ~293, ~315, and ~333 nm ($\epsilon \approx (2–4) \times 10^4$). ^{13}C NMR spectroscopy is the most effective method of characterizing the neutral complexes V. Table III lists the ^{13}C NMR spectral shifts for these neutral species, and in most cases the spectra correspond to those expected for the mirror symmetric complexes. The complex having R^3 = H is anomalous, however, in that considerable broadening of all resonances is observed as well as three extra signals at 52.7, 48.0, and 28.3 ppm. This behavior is interpreted in terms of a moderately slow (on the NMR time scale) equilibrium between the structures represented in Scheme III. Molecular models indicate that when R^3 = H structure ii gives less steric contact between the methyl group on the macrocycle and R^3 than for any other R^3 groups, all of which appear to be enough to allow the acyl substituent to rotate about its formal single bond to the macrocycle and adopt structure ii as well as i.

Table II. Selected Infrared Bands (cm^{-1}) for Nickel(II) Complexes V

R^3	ν(CO)	ν(CN)	ν(CC)
H	1630	1580	1505
t-C$_4$H$_9$	1615	1575	1500
n-C$_5$H$_{11}$	1618	1580	1495
n-C$_7$H$_{15}$	1620	1585	1500
n-C$_9$H$_{19}$	1622	1585	1505
C$_6$H$_5$	1615	1545	1599, 1581, 1498
CF$_3$	1637	1590	1521
C$_6$F$_5$	1649	1572	1517, 1492
CH$_2$C$_6$H$_5$	1620	1580	1497
neo-C$_5$H$_{11}$		1565	1492

The ^{13}C NMR spectrum of the complex with R^3 = CF$_3$ displays what appears to be an example of through-space ^{19}F–^{13}C coupling. Three resonances appear as quartets, displaying coupling to fluorine (Figure 2); $^1J_{^{19}F-^{13}C}$ = 292.6 Hz and $^2J_{^{19}-^{13}C}$ = 30.9 Hz are the couplings one might expect to observe for the carbons of the CF$_3$ group and carbonyl, respectively. However, for the third resonance to display coupling $^4J_{^{19}F-^{13}C}$ = 4.4 Hz was unexpected and corresponds to the vinyl carbon atom bearing the proton on the macrocyclic ring. This four-bond coupling is unusual since no three-bond

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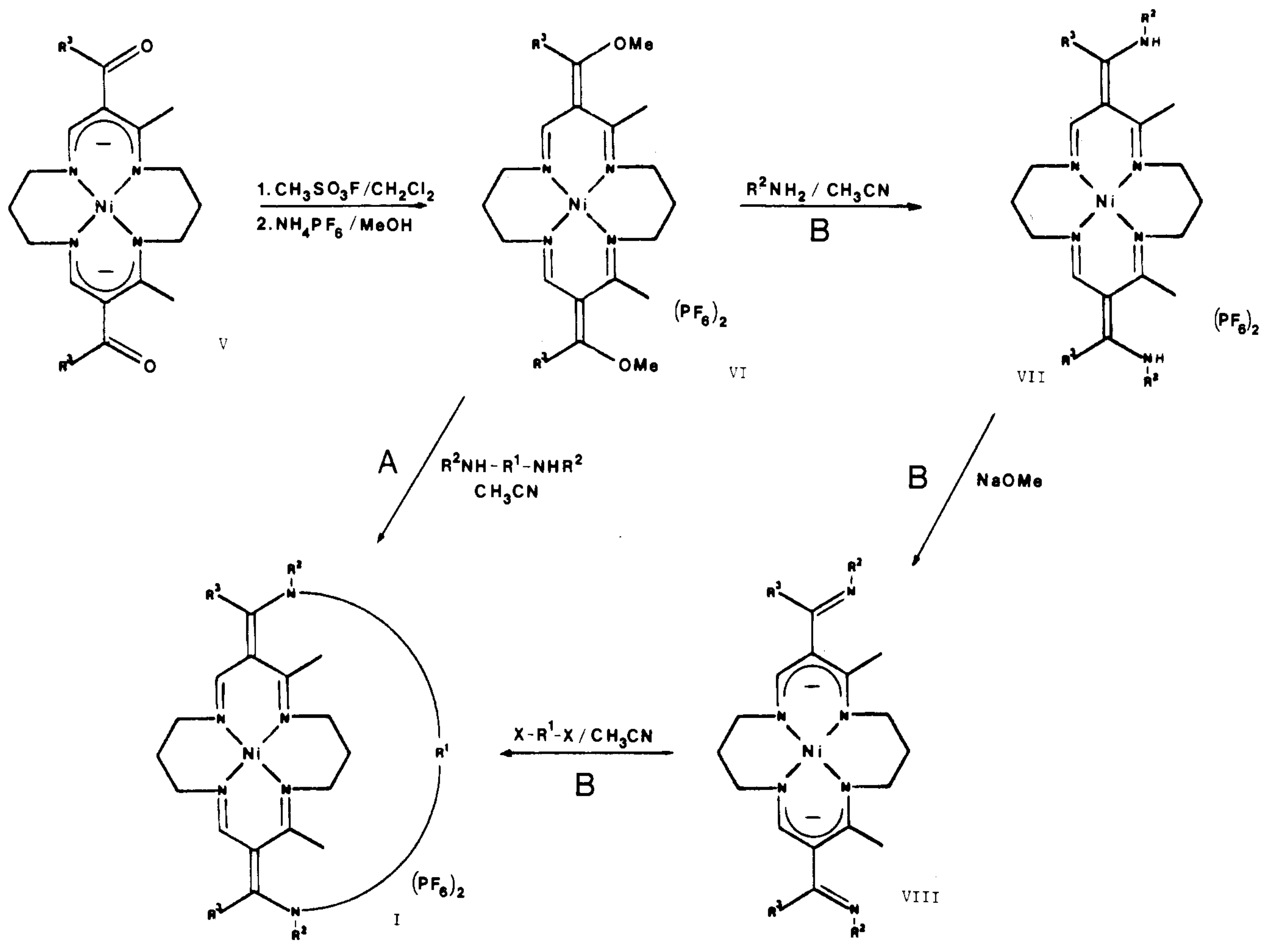
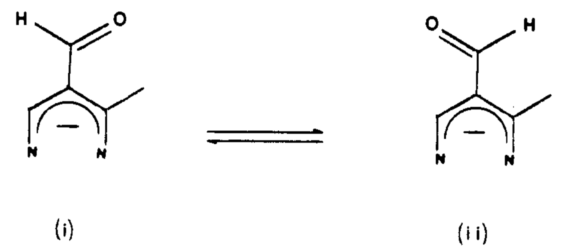
[13] Corfield, P. W. R.; Mokren, J. D.; Hipp, C. J.; Busch, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 4465.

Scheme II



Scheme III



coupling could be detected and no four-bond coupling to the macrocyclic carbon bearing the methyl group was observed. If one makes a molecular model of this complex, a striking feature of the structure is the proximity of the CF_3 group to the vinyl carbon showing the four-bond coupling, these two groups being locked in close proximity to one another by the rigidity of the total structure. We feel that this enforced proximity is the cause of the coupling, which is therefore occurring through space rather than the normal through-bond effect. Such through-space $^{19}F-^{13}C$ couplings have been observed previously and appear to be relatively commonplace for this pair of nuclei.[14]

b. Unbridged Complexes VI and VII. Standard methylation procedures[12] for each of the neutral derivatives V described above yield the corresponding methyl vinyl ether derivative VI as its PF_6 salt. The complexes where $R^3 = CF_3$ and C_6F_5 have, however, failed, as yet, to undergo the bridging reactions outlined in Scheme II. The material VI with $R^3 = C_6F_5$ does, however, react with methylamine to give a derivative VII with $R^2 = CH_3$. This particular complex is of some interest as it again appears to display "through-space" fluorine–carbon coupling. In this case the coupling is to the R^2 methyl group, which is split into a triplet (Figure 3), $^5J_{^{19}F-^{13}C} = 4.6$ Hz, by

Table III. ^{13}C NMR Spectral Shifts for Complexes V in C^2HCl_3 Solution (Relative to Me_4Si)

R^3	shifts, ppm
H	185.9, 166.9, 161.3, 116.0, 54.4, 49.5, 29.8, 28.8, 17.1
t-C_4H_9	201.7, 167.5, 157.2, 113.8, 55.0, 50.1, 42.8, 30.8, 29.9, 29.6, 20.1
n-C_5H_{11}	194.7, 167.2, 157.7, 115.2, 54.5, 49.8, 38.5, 31.5, 30.3, 29.3, 25.6, 22.2, 19.1, 13.7
n-C_7H_{15}	195.0, 167.5, 158.0, 115.5, 54.8, 50.2, 38.8, 31.7, 30.6, 29.6, 29.2, 26.2, 22.5, 19.4, 14.0
n-C_9H_{19}	194.9, 167.3, 157.8, 115.3, 54.5, 49.9, 38.7, 31.6, 30.3, 29.4, 29.3, 29.0, 25.9, 22.4, 19.2, 13.8
C_6H_5	192.9, 167.8, 160.9, 143.1, 129.7, 128.4, 128.1, 115.2, 54.7, 50.3, 30.5, 29.2, 19.9
CF_3[a]	174.1 (q), 169.6, 159.1 (q), 118.6 (CF_3 q), 110.3, 55.3, 50.3, 30.1, 29.5, 19.7
C_6F_5[b]	177.4, 169.4, 160.4, 116.8, 54.5, 50.2, 30.0, 29.2, 19.6
$CH_2C_6H_5$	192.1, 168.2, 158.9, 137.7, 129.0, 128.4, 126.1, 115.0, 54.8, 50.0, 46.4, 30.5, 29.5, 19.5
neo-C_5H_{11}	193.2, 167.6, 158.3, 116.7, 54.6, 50.4, 49.6, 31.3, 30.8, 30.1, 29.4, 19.1

[a] Items in parentheses refer to multiplicity of peak due to $^{19}F-^{13}C$ coupling. [b] Aromatic carbon resonances occur in the 120–150 ppm range as complex multiplets due to $^{19}F-^{13}C$ coupling.

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[14] Buckingham, A. D.; Cordle, J. E. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 994.

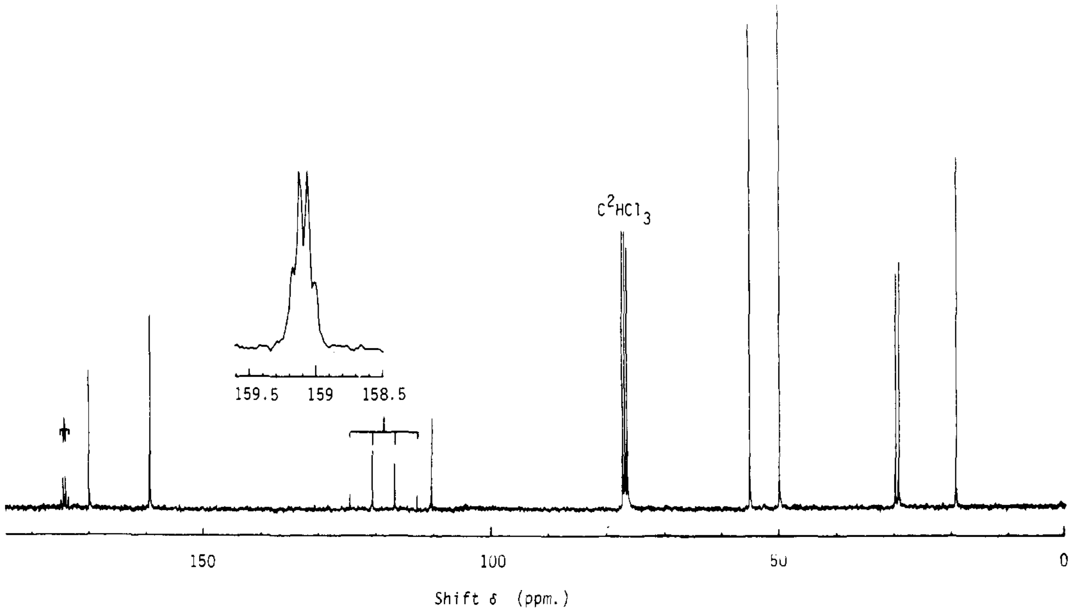

Figure 2. ^{13}C NMR spectrum of the complex V, $R^3 = CF_3$, proton decoupled in C^2HCl_3 at 75.4 MHz.

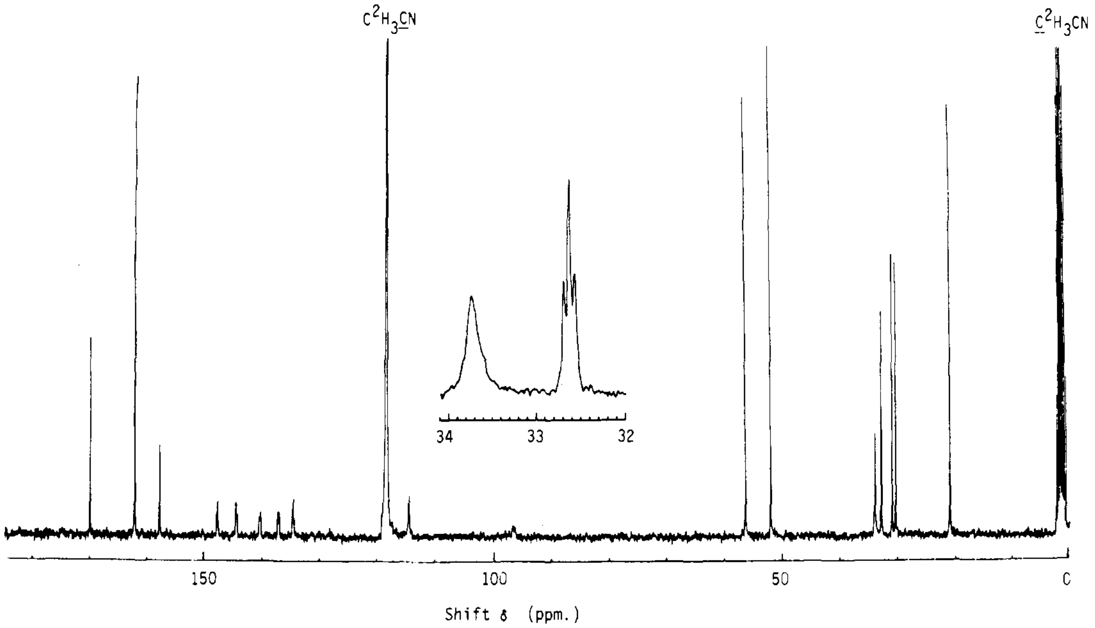

Figure 3. ^{13}C NMR spectrum of complex VII, $R^2 = CH_3$, $R^3 = C_6F_5$, proton decoupled in C^2H_3CN at 75.4 MHz.

coupling to the two ortho fluorines of the aromatic group. As in the case of the neutral complex V having $R^3 = CF_3$, the stereochemical relationship between these fluorine and carbon nuclei, as judged from molecular models, is again such as to rigidly constrain them in very close proximity and is probably the reason for the through-space effect.[14]

c. Bridged Lacunar Complexes I. Table I lists analyses for all new multiply substituted lacunar complexes synthesized during this work. Because of their large number, discussion of their syntheses (Experimental Section) and their properties will be limited to specific examples that typify the series, while, where available, their individual properties are listed in the appropriate tables.

While infrared, electronic, and ^1H NMR spectra of these diamagnetic complexes have utility as tools for the simple qualitative identification of the compounds, by far the most useful characterization technique is ^{13}C NMR spectroscopy. ^{13}C NMR data for the new lacunar complexes are listed in Table IV, and an example of the spectra obtained is given in Figure 4. In all cases, the number and position of the observed resonances are consistent with the assigned mirror symmetric structures I. Changing the substituents R^1, R^2, and R^3 had small, but not strongly systematic, effects on the shifts of the macrocycle carbons a–i (Figure 4). For example, carbon b is markedly affected by the nature of R^3, as might be expected. One spectrum of particular interest is that of R^1 = *m*-xylylene, $R^3 = 3,5\text{-}(OMe)_2Ph$, which gives seven distinct resonances for the eight carbons of the $3,5\text{-}(OMe)_2Ph$ substituent. This is most readily interpreted as indicating that this substituent is not capable of freely rotating about its bond to carbon a of the macrocycle itself. This stands in contrast to all instances where R^3 is a simple unsubstituted phenyl group, when only four resonances are observed, consistent with rapid rotation about the aforementioned bond. These data indicate that the methoxy substituents hinder this rotation probably by their direct interaction either with the macrocycle carbons f and h or else across the entire macrocycle between the substituents on R^3 themselves.

The electrochemical properties of the lacunar complexes are listed in Table V. It has been shown previously[2] that the electronic nature of R^1 has essentially no effect on $E_{1/2}$, and so the effects of R^2 and R^3 substituents are of primary concern

Table IV. ^{13}C NMR Resonances for Lacunar Nickel(II) Complexes I, in C^2H_3CN vs. Me_4Si

			resonance shifts, ppm[a]									
R^1	R^2	R^3	a	b	c	d	e, f	g, h	i	j	k	l
m-xylylene	CH_3	H	172.3	161.6	154.3	112.8	55.2 50.8	31.3 29.8	19.9	137.7, 130.4, 129.8, 124.0, 64.9	40.0	
m-xylylene	CH_3	3,5-$(OMe)_2Ph$	173.3	168.1	162.0	114.9	56.6 52.2	30.4 29.6	21.3	137.7, 131.0, 128.4, 126.4, 60.6	47.1	162.8, 162.6, 136.2, 110.0, 108.7, 104.8, 56.0
m-xylylene	CH_3	*n*-C_7H_{15}	177.3	167.2	158.9	112.7	56.7 52.0	30.7 30.1	21.0	137.6, 130.4, 127.3, 126.0, 60.4	45.4	32.4, 30.0, 29.5, 28.8, 23.3, 14.5
m-xylylene	CH_3	C_6H_5	173.6	167.8	161.6	114.9	56.2 52.0	30.2 29.3	20.9	137.5, 130.8, 128.2, 126.0, 60.4	47.0	134.0, 133.3, 131.9, 131.9, 131.1, 130.2
m-xylylene	CH_3	CH_3	174.5	166.9	159.2	113.6	56.4 52.0	30.5 29.8	20.9	137.7, 130.6, 126.9, 125.3, 62.2	45.8	20.6
m-xylylene	H	C_6H_5	171.5	168.7	162.4	111.1	56.0 51.9	30.2 29.4	20.8	138.5, 134.0, 131.2, 127.5, 50.3		134.8, 134.0, 131.7, 130.3
m-xylylene	H	CH_3	170.7	164.3	161.8	114.5	55.2 50.7	30.5 30.1	20.7	140.5, 130.0, 127.3, 124.0, 55.2		14.4
m-xylylene	$CH_2C_6H_5$	CH_3	173.5	167.1	159.7	114.4	56.7 52.1	30.3 29.7	20.8	137.1, 130.4, 129.9, 125.2, 58.9	135.2, 130.3, 130.2, 126.7, 60.0	21.1
m-xylylene	$CH_2C_6H_5$	C_6H_5	172.7	168.3	162.4	115.5	57.8 56.5	30.1 29.4	21.2	137.8, 135.4, 134.0, 133.4, 132.4, 131.2, 130.9, 130.5, 130.2, 130.0, 128.4, 126.4		
$(CH_2)_4$	H	C_6H_5	170.0	169.6	163.2	111.0	54.9 50.4	30.8 29.9	20.6	47.9, 27.3		134.8, 133.7, 131.7, 130.2
$(CH_2)_4$	CH_3	C_6H_5	172.6	169.9	163.0	114.3	57.0 54.7	30.6 29.9	20.7	50.4, 24.4	41.5	133.9, 132.8, 131.5, 130.1
$(CH_2)_5$	CH_3	C_6H_5	173.7	168.7	162.2	114.1	57.5 56.0	30.2 27.5	20.6	51.5, 27.5, 23.5	43.1	134.0, 133.1, 131.5, 130.2
$(CH_2)_6$	H	C_6H_5	171.2	168.8	162.8	109.6	55.9 51.3	30.3 29.4	20.8	48.3, 27.5, 24.0		135.3, 133.5, 131.2, 130.2
$(CH_2)_6$	CH_3	C_6H_5	174.6	168.6	162.9	116.8	57.4 55.9	30.2 27.8	21.1	51.5, 25.0, 24.3	42.0	134.7, 130.6, 130.2
$(CH_2)_6$	H	*t*-C_4H_9	182.1	168.4	159.4	106.9	56.7 51.4	30.8 30.3	20.8	48.7, 27.1, 23.8		40.6, 30.8
$(CH_2)_6$	H	*n*-C_7H_{15}	173.4	169.3	160.6	108.9	57.0 51.5	31.2 30.6	21.3	48.6, 27.7, 23.7		32.5–23.4
$(CH_2)_6$	CH_3	H	167.3	161.9	161.8	110.9	55.4 50.7	30.7 29.9	20.5	54.1, 25.0, 23.4	42.2	
$(CH_2)_7$	H	C_6H_5	172.3	168.7	162.5	109.8	56.5 51.7	30.4 29.8	20.8	48.6, 29.2, 26.9, 25.2		135.2, 133.7, 131.6, 130.1
$(CH_2)_7$	CH_3	C_6H_5	175.7	168.4	162.7	112.8	57.0 52.1	30.7 29.9	20.9	56.7, 27.6, 27.0, 25.5	41.8	134.6, 133.1, 131.4, 130.3

[a] For assignments see Figure 4.

Table V. Electrochemical Data[a] for the First Oxidation of Lacunar Nickel(II) Complexes I

R^1	R^2	R^3	$E_{1/2}$, V	E_p(ox), V	E_p(red), V	$E_{3/4-1/4}$, mV	ref[b]
m-xylylene	CH_3	H	0.94	1.00	0.87	80	
m-xylylene	CH_3	3,5-$(OMe)_2Ph$	0.92	0.98	0.89	70	
m-xylylene	CH_3	*n*-C_7H_{15}	0.81	0.85	0.74	75	
m-xylylene	CH_3	C_6H_5	0.94	0.99	0.89	70	
m-xylylene	CH_3	CH_3	0.78	0.83	0.74	70	3
m-xylylene	H	C_6H_5	~0.92	broad			
m-xylylene	H	CH_3	0.93	0.97	0.89	67	3
m-xylylene	$CH_2C_6H_5$	CH_3	0.82	0.85	0.77	70	3
m-xylylene	*n*-C_4H_9	CH_3	0.79	0.82	0.75	60	3
m-xylylene	$CH_2C_6H_5$	C_6H_5	0.99	1.05	0.94	80	
$(CH_2)_4$	CH_3	C_6H_5	0.91	0.94	0.87	60	
$(CH_2)_4$	H	C_6H_5	0.90	0.93	0.85	80	
$(CH_2)_4$	H	*t*-C_4H_9	irrev				
$(CH_2)_5$	CH_3	C_6H_5	0.91	0.94	0.86	70	
$(CH_2)_5$	H	C_6H_5	0.92	0.95	0.87	60	
$(CH_2)_5$	H	*t*-C_4H_9	0.75	0.78	0.71	60	
$(CH_2)_6$	CH_3	H	0.97	1.00	0.93	60	
$(CH_2)_6$	CH_3	C_6H_5	0.92	0.95	0.88	70	
$(CH_2)_6$	H	*n*-C_7H_{15}	0.92	0.96	0.87	85	
$(CH_2)_6$	H	C_6H_5	0.94	0.98	0.91	75	
$(CH_2)_6$	H	*t*-C_4H_9	0.78	0.81	0.74	60	
$(CH_2)_7$	CH_3	C_6H_5	0.90	0.94	0.87	70	
$(CH_2)_7$	H	C_6H_5	0.92	0.95	0.88	65	
$(CH_2)_8$	CH_3	C_6H_5	~0.90	broad			
$(CH_2)_8$	H	C_6H_5	0.95	1.00	0.90	60	

[a] Conditions: in CH_3CN solution, 0.1 M $(n\text{-}Bu)_4NBF_4$ supporting electrolyte, $Ag^0/AgNO_3$ (0.1 M) reference electrode. [b] All values are from this work unless otherwise noted.

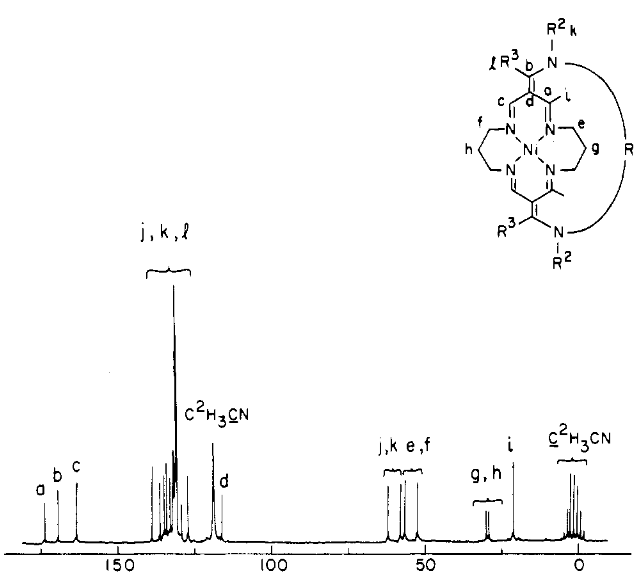

Figure 4. ^{13}C NMR spectrum of complex I, R^1 = *m*-xylylene, R^2 = $CH_2C_6H_5$, R^3 = C_6H_5, proton decoupled in C^2H_3CN at 20.1 MHz. Assignments are as shown.

here. These properties are best discussed in two distinct series for comparative purposes. First, if both R^1 and R^2 are held constant as *m*-xylylene and methyl, respectively, the electronic effect of the vinyl substituent R^3 on the redox properties of the metal center can be examined. The substituent is directly conjugated to the central metal ion and would be expected to influence its redox potential. The redox potentials may be placed in the order $R^3 = CH_3 < n\text{-}C_7H_{15} < 3,5\text{-}(OMe)_2Ph \approx C_6H_5 \approx H$, and this sequence is as one might anticipate based on the electron-donating or -withdrawing properties of these substituents. Since oxidation is the removal of an electron, the more electron density that is removed from the metal ion as a result of the electronic properties of the substituent R^3, the harder it should be to perform the oxidation; i.e., $E_{1/2}$ is more positive. While the trend is as expected, the range of potentials is rather small,[11] indicating that the electronic effect of R^3 is rather small.

Second, if R^1 and R^3 are held constant as *m*-xylylene and methyl, respectively, the electronic effect of the nitrogen substituent R^2 may be examined. R^2, as drawn in Figure 1, might not be expected to markedly influence the redox chemistry of the metal ion. However, it should be realized that these nitrogen atoms are very amide-like in that their lone pairs may well be involved in the conjugation system. This idea is borne out by X-ray data on such compounds (vide infra), which indicate that the coordination geometries of the nitrogen atoms are essentially planar.[1,15] The redox potentials of the complexes lie in the order $R^2 = CH_3 \approx n\text{-}C_4H_9 < CH_2C_6H_5 < H$; again this sequence is as expected on the basis of the electron-donating or -withdrawing properties of R^2, and again the effect is small. However, replacement of $R^3 = CH_3$ by C_6H_5 alters this series dramatically such that now the effect of R^2 on $E_{1/2}$ is almost insignificant. It appears therefore that the electron-donating power of the $R^3 = C_6H_5$ substituent overrides any contribution from R^2.

Both series indicate that a suitable combination of R^2 and R^3 substituents for a given R^1 bridge will allow one to fine tune the electronic environment of the central metal ion, at least over a range of some 210 mV. This is important in view of the utility of this class of iron(II) or cobalt(II) complexes of the lacunar ligands for the reversible binding of dioxygen.[4,5] O_2 affinities and related chemical properties may be carefully controlled by the choice of R^2 and R^3 substituents. Since these electronic effects appear to be transmitted via the π-electron system, the effect may be much greater on iron(II) than on nickel(II).[16] This further suggests that the interaction between Fe(II) and small molecules may be strongly regulated both sterically (R^1) and electronically ($R^2 + R^3$) by use of these ligands.

In order to get a better feel for the three-dimensional nature

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(15) Busch, D. H.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Christoph, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5919.

(16) Dabrowiak, J. C.; Merrell, P. H.; Stone, J. A.; Busch, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 6613. Nakamoto, K. "Advances in the Chemistry of the Coordination Compounds"; Macmillan: New York, 1961; pp 437–446.

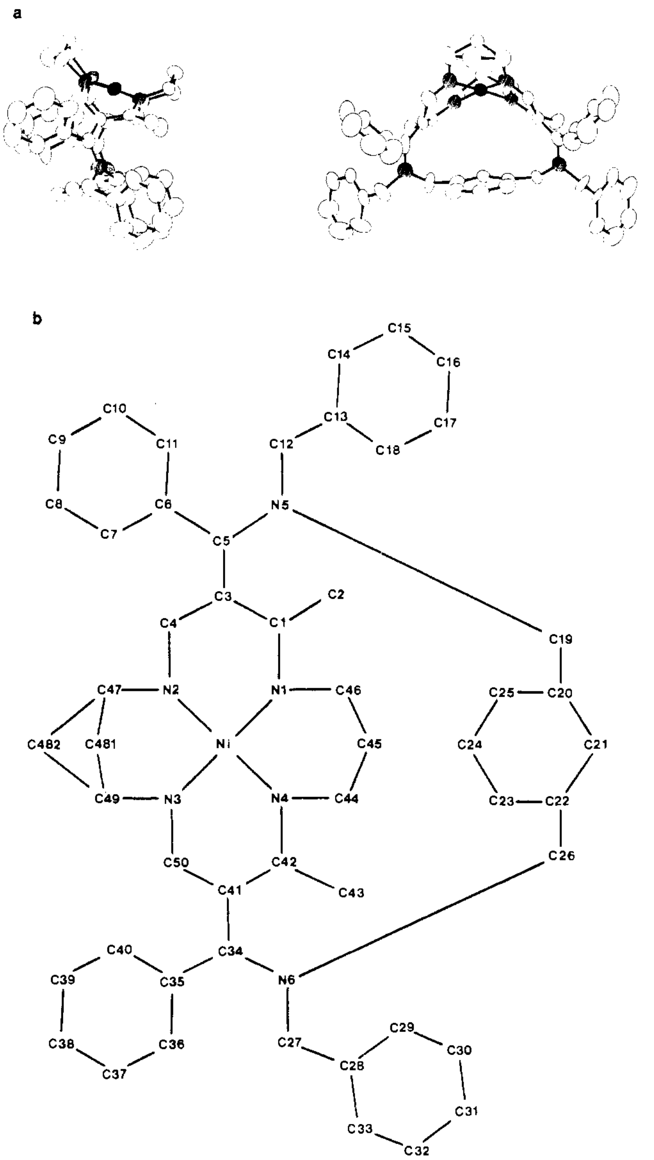

Figure 5. (a) ORTEP plots of I, R^1 = *m*-xylylene, $R^2 = CH_2C_6H_5$, $R^3 = C_6H_5$. Thermal ellipsoids are drawn at the 50% probability level. The nickel and nitrogen atoms are shaded for clarity. (b) Atom-labeling scheme for the structure shown in part a.

of multiply substituted complexes I, an X-ray crystallographic analysis was performed on one of the most heavily substituted complexes, the iron(II) complex of which has already shown considerable promise as a reversible dioxygen carrier.[5]

Structure of I, R^1 = *m*-Xylylene, $R^2 = CH_2C_6H_5$, R^3 = Phenyl. The atom-numbering scheme and structure of the cation are shown in Figure 5, while a space-filling version of the structure is shown in Figure 6. Clearly, the cation has the expected distribution of substituents, and the space-filling view of the structure indicates the highly protected, sterically restricted nature of the lacuna. Features of special interest in this structure are the canted nature of the R^3 phenyl substituents (at 52 and 57° to the NiN_4 plane) in such an orientation as to preclude these groups being extensively conjugated into the unsaturated π system of the basic macrocycle. The bridging, R^1 = *m*-xylylene, roof of the lacuna is likewise canted at 36° to the NiN_4 plane and is in an orientation similar to that observed previously for a related *m*-xylylene-bridged structure (30°).[15] While disorder in the conformation of one of the two saturated chelate rings is evident (Figure 5; $\sim$50% occupancy of each position) it is also apparent that, in this structure, both of these rings adopt the boat-type conformation (at least part of the time). This structure is the first of its kind to show this phenomenon, and its origin probably arises from the interaction of the central carbon atoms C(45), C(48) of the rings with substituents R^1 and R^3, respectively. A chair conformation in either ring would be expected to lead to close contact with these substituents.

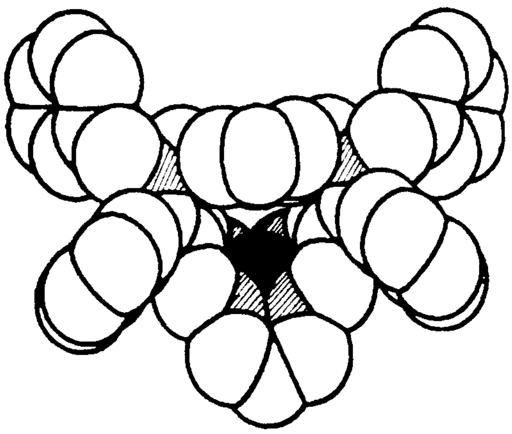

Figure 6. Space-filling representation of structure I, R^1 = *m*-xylylene, $R^2 = CH_2C_6H_5$, $R^3 = C_6H_5$, viewed in the same direction as for Figure 5a. The nickel atom and nitrogen atoms are shaded for clarity.

The NiN_4 coordination sphere is planar, the nickel atom residing essentially in the plane of the four nitrogen atoms. Likewise, all five aromatic rings are planar as expected. As has been observed in previous structures of this type,[1,15] the bridge-nitrogen atoms N(5), N(6) are both essentially trigonal planar (N(5) and N(6) each 0.06 Å out of the plane defined by the three bonded carbon atoms), indicating again that the nitrogen lone pair is indeed conjugated into the π system of the parent macrocycle. The structure has, as expected, the *lid-off* bridge geometry.[1,15] Bond lengths and angles (Table VI) are closely similar to those reported for simpler complexes of type I[1,15] and as such lie within the expected ranges.

Perhaps the most important reason for determining this crystal structure was to assess the effects of the bulky substituents at R^2 and R^3 on the size, shape, and accessibility of the protected cavity. The dimensions of the cavity itself are width (N(5) to N(6)) 7.27 (2) Å, height corresponding to the cavity entrance from the N(1)N(2) plane to C(24) 5.37 (2) Å, and height at the rear of the cavity (N(1)N(4) plane to C(21)) 3.74 (2) Å. For comparison, the lid-off iron(II) complex of I where R^1 = *m*-xylylene, $R^2 = CH_3$ and $R^3 = CH_3$ has the corresponding cavity dimensions[15] 7.34, 4.96, and 3.57 Å, indicating that the lacuna's size and shape have changed remarkably little as a result of increasing the steric bulk of R^2 and R^3 and so are largely determined by the nature of R^1. The large effects of R^2 and R^3 come in their alteration of the accessibility of the lacuna from the outside of the molecule, and this is best illustrated in the space-filling representation of the structure in Figure 6. The lacuna entrance is rendered more hydrophobic and is lengthened by the substituent R^3 in particular, and it may well be that this protection of the lacuna entrance from solvent is responsible for this ligand generating iron(II) complexes of remarkable stability with respect to autoxidation.[5]

In the unit cell the individual cations are flanked by noncoordinated, disordered hexafluorophosphate anions, the major contacts between ions being electrostatic. In addition a disordered molecule of solvent ethanol does not appear to interact with any of the major ions via hydrogen bonding.

Ligand Salts. For investigation of the ability of ligands of type I to generate dioxygen carrier complexes it is necessary to remove the ligand, intact, from nickel(II) and transfer it to iron(II) or cobalt(II). The removal of the ligands from nickel(II) is easily achieved with use of gaseous HBr in

Table VI. Bond Lengths (Å) and Angles (deg) with Their Estimated Standard Deviations for Structure I, R^1 = *m*-Xylylene, R^2 = Benzyl, R^3 = Phenyl

A. Bond Distances

(a) Coordination Sphere

Ni-N(1)	1.88 (2)	Ni-N(3)	1.89 (2)
Ni-N(2)	1.88 (2)	Ni-N(4)	1.89 (1)

(b) Ligand

N(1)-C(1)	1.30 (2)	C(26)-N(6)	1.49 (2)
N(1)-C(46)	1.49 (2)	N(6)-C(27)	1.50 (2)
C(1)-C(2)	1.54 (2)	N(6)-C(34)	1.31 (2)
C(1)-C(3)	1.45 (2)	C(27)-C(28)	1.51 (2)
C(3)-C(4)	1.46 (2)	C(28)-C(29)	1.40 (2)
C(3)-C(5)	1.39 (2)	C(28)-C(33)	1.42 (2)
C(4)-N(2)	1.29 (2)	C(29)-C(30)	1.41 (2)
C(5)-C(6)	1.53 (2)	C(30)-C(31)	1.43 (2)
C(5)-N(5)	1.35 (2)	C(31)-C(32)	1.39 (3)
C(6)-C(7)	1.41 (2)	C(32)-C(33)	1.41 (3)
C(6)-C(11)	1.38 (2)	C(34)-C(35)	1.49 (2)
C(7)-C(8)	1.39 (3)	C(34)-C(41)	1.42 (2)
C(8)-C(9)	1.36 (3)	C(35)-C(36)	1.39 (2)
C(9)-C(10)	1.37 (3)	C(35)-C(40)	1.40 (2)
C(10)-C(11)	1.42 (3)	C(36)-C(37)	1.43 (2)
N(5)-C(12)	1.49 (2)	C(37)-C(38)	1.38 (3)
N(5)-C(19)	1.49 (2)	C(38)-C(39)	1.43 (3)
C(12)-C(13)	1.54 (2)	C(39)-C(40)	1.43 (3)
C(13)-C(14)	1.39 (2)	C(41)-C(42)	1.47 (2)
C(18)-C(18)	1.38 (2)	C(41)-C(50)	1.44 (2)
C(14)-C(15)	1.43 (3)	C(42)-C(43)	1.53 (2)
C(15)-C(16)	1.38 (3)	C(42)-N(4)	1.30 (2)
C(16)-C(17)	1.39 (2)	N(4)-C(44)	1.48 (2)
C(17)-C(18)	1.39 (2)	C(44)-C(45)	1.53 (2)
C(19)-C(20)	1.55 (2)	C(45)-C(46)	1.52 (2)
C(20)-C(21)	1.41 (2)	N(2)-C(47)	1.49 (2)
C(20)-C(25)	1.40 (2)	C(47)-C(481)	1.51 (3)
C(21)-C(22)	1.38 (2)	C(47)-C(482)	1.46 (4)
C(22)-C(23)	1.38 (2)	C(481)-C(49)	1.49 (3)
C(22)-C(26)	1.51 (2)	C(482)-C(49)	1.56 (4)
C(23)-C(24)	1.40 (2)	C(49)-N(3)	1.48 (2)
C(24)-C(25)	1.44 (2)	N(3)-C(50)	1.31 (2)

(c) PF_6^- Anions

P(1)-F(11)	1.56 (2)	P(2)-F(21)	1.50 (2)
P(1)-F(12)	1.55 (2)	P(2)-F(22)	1.46 (2)
P(1)-F(13)	1.46 (3)	P(2)-F(23)	1.43 (2)
P(1)-F(14)	1.55 (2)	P(2)-F(24)	1.57 (2)
P(1)-F(15)	1.49 (2)	P(2)-F(25)	1.52 (2)
P(1)-F(16)	1.47 (2)	P(2)-F(26)	1.43 (2)

(d) Solvent Ethanol

C(OH)1-C(OH)2	1.36 (10)	C(OH)2-O(OH)	1.65 (10)

B. Bond Angles

(a) Metal Coordination Sphere

N(1)-Ni-N(2)	90.2 (4)	N(3)-Ni-N(4)	88.8 (4)
N(2)-Ni-N(3)	90.8 (4)	N(4)-Ni-N(1)	91.1 (4)

(b) Ligand

Ni-N(1)-C(1)	123 (1)	C(27)-N(6)-C(34)	122 (1)
Ni-N(1)-C(46)	120 (1)	N(6)-C(27)-C(28)	110 (1)
C(1)-N(1)-C(46)	117 (1)	C(27)-C(28)-C(29)	119 (1)
N(1)-C(1)-C(2)	122 (1)	C(27)-C(28)-C(33)	119 (1)
N(1)-C(1)-C(3)	121 (1)	C(29)-C(28)-C(33)	122 (1)
C(2)-C(1)-C(3)	117 (1)	C(28)-C(29)-C(30)	119 (1)
C(1)-C(3)-C(4)	115 (1)	C(29)-C(30)-C(31)	120 (2)
C(1)-C(3)-C(5)	127 (1)	C(30)-C(31)-C(32)	121 (2)
C(4)-C(3)-C(5)	117 (1)	C(31)-C(32)-C(33)	120 (2)
C(3)-C(4)-N(2)	125 (1)	C(32)-C(33)-C(28)	119 (2)
C(3)-C(5)-C(6)	119 (1)	N(6)-C(34)-C(35)	121 (1)
C(3)-C(5)-N(5)	125 (1)	N(6)-C(34)-C(41)	123 (1)
C(6)-C(5)-N(5)	116 (1)	C(35)-C(34)-C(41)	117 (1)
C(5)-C(6)-C(7)	117 (1)	C(34)-C(35)-C(36)	120 (1)
C(5)-C(6)-C(11)	120 (1)	C(34)-C(35)-C(40)	119 (1)
C(7)-C(6)-C(11)	123 (1)	C(36)-C(35)-C(40)	121 (1)
C(6)-C(7)-C(8)	119 (1)	C(35)-C(36)-C(37)	121 (1)
C(7)-C(8)-C(9)	120 (2)	C(36)-C(37)-C(38)	117 (2)
C(8)-C(9)-C(10)	121 (2)	C(37)-C(38)-C(39)	124 (2)
C(9)-C(10)-C(11)	121 (2)	C(38)-C(39)-C(40)	116 (2)
C(10)-C(11)-C(6)	116 (2)	C(39)-C(40)-C(35)	121 (1)
C(5)-N(5)-C(12)	123 (1)	C(34)-C(41)-C(42)	125 (1)
C(5)-N(5)-C(19)	122 (1)	C(34)-C(41)-C(50)	116 (1)
C(12)-N(5)-C(19)	115 (1)	C(42)-C(41)-C(50)	118 (1)
N(5)-C(12)-C(13)	110 (1)	C(41)-C(42)-C(43)	117 (1)
C(12)-C(13)-C(14)	117 (1)	C(41)-C(42)-N(4)	120 (1)
C(12)-C(13)-C(18)	121 (1)	C(43)-C(42)-N(4)	122 (1)
C(14)-C(13)-C(18)	122 (1)	C(42)-N(4)-C(44)	117 (1)
C(13)-C(14)-C(15)	117 (2)	C(42)-N(4)-Ni	119 (1)
C(14)-C(15)-C(16)	120 (2)	C(44)-N(4)-Ni	125 (1)
C(15)-C(16)-C(17)	121 (2)	N(4)-C(44)-C(45)	110 (1)
C(16)-C(17)-C(18)	119 (1)	C(44)-C(45)-C(46)	112 (1)
C(17)-C(18)-C(13)	121 (1)	C(45)-C(46)-N(1)	109 (1)
N(5)-C(19)-C(20)	111 (1)	C(4)-N(2)-Ni	120 (1)
C(19)-C(20)-C(21)	119 (1)	C(4)-N(2)-C(47)	117 (1)
C(19)-C(20)-C(25)	118 (1)	Ni-N(2)-C(47)	123 (1)
C(21)-C(20)-C(25)	122 (1)	N(2)-C(47)-C(481)	113 (2)
C(20)-C(21)-C(22)	119 (1)	N(2)-C(47)-C(482)	109 (2)
C(21)-C(22)-C(23)	122 (1)	C(47)-C(481)-C(49)	116 (2)
C(21)-C(22)-C(26)	118 (1)	C(47)-C(482)-C(49)	115 (2)
C(23)-C(22)-C(26)	120 (1)	C(481)-C(49)-N(3)	113 (1)
C(22)-C(23)-C(24)	119 (1)	C(482)-C(49)-N(3)	114 (2)
C(23)-C(24)-C(25)	121 (1)	C(49)-N(3)-Ni	125 (1)
C(24)-C(25)-C(20)	117 (1)	C(49)-N(3)-C(50)	114 (1)
C(22)-C(26)-N(6)	114 (1)	Ni-N(3)-C(50)	121 (1)
C(26)-N(6)-C(27)	116 (1)	N(3)-C(50)-C(41)	124 (1)
C(26)-N(6)-C(34)	122 (1)		

(c) Solvent Ethanol

C(OH)1-C(OH)2-O(OH)	88 (6)

methanol followed by metathesis to the PF_6^- salt, which may be isolated as a white or yellow powder. These salts are generally ill characterized but can be approximated to the formulation $H_4L(PF_6)_4$. Despite the nonideal properties of these salts, their use in the synthesis of other metal complexes has generally given satisfactory results leading to well-characterized complexes[4,5,15] of the desired ligands.

Conclusions. A general synthetic scheme has been described wherein nickel(II) complexes of structure I may be synthesized bearing almost any combination of substituents R^1, R^2, R^3. These complexes are generally well characterized and are easy to prepare in relatively large quantities. In turn the ligand portion of the complexes may be removed intact from nickel(II) and isolated as stable ligand salts. Preliminary work on the iron(II) complexes of some ligands described herein has indicated that they are remarkably stable dioxygen carriers whose binding constants for O_2 and autoxidation stability can be carefully controlled by the choice of appropriate substituents R^1, R^2, R^3.[5] This work fosters our conviction that ligands of type I will eventually lead to reversible dioxygen carrier complexes of tremendous potential for a variety of applications.[17]

Experimental Section

Materials. Solvents and reagents used in the synthesis of nickel(II) complexes were reagent grade and were used without further purification unless otherwise noted.

Measurements. ^{13}C NMR spectra were recorded on Bruker WP80 (20.115 MHz) or Bruker WM300 (75.43 MHz) spectrometers. Fully proton-decoupled spectra were recorded in C^2H_3CN, and in all cases, shift measurements were made relative to tetramethylsilane, $\delta = 0$. Visible and ultraviolet spectra were obtained with a Cary Model 17D recording spectrophotometer, and infrared spectra were recorded as Nujol mulls between KBr disks with either a Perkin-Elmer 457 or a Perkin-Elmer 283B recording spectrophotometer.

Electrochemical measurements were performed with a Princeton Applied Research Corp. Model 173 potentiostat/galvanostat equipped

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[17] Steward, R. F.; Estep, P. A.; Sebastian, J. J. S. *Inf. Circ.—U.S. Bur. Mines* **1959**, *No. 7906*. Burke, D. P. *Chem. Week* **1980**, *127* (2), 18.

Table VII

time, h	*a*, Å	*b*, Å	*c*, Å	*β*, deg	*V*, Å^3
initial	10.149 (1)	17.665 (3)	30.667 (6)	100.78 (1)	5400 (2)
130	10.129 (2)	17.630 (4)	30.659 (6)	100.85 (1)	5377 (2)
230	10.124 (2)	17.627 (4)	30.672 (8)	100.90 (20)	5375 (2)

with a Model 175 linear programmer and a Model 179 digital coulometer. Current vs. potential curves were measured on a Houston Instruments Model 2000 XY recorder. All measurements were performed in a Vacuum Atmospheres glovebox under an atmosphere of dry nitrogen. The working electrode for voltammetric curves was a platinum disk, with potentials measured vs. an Ag^0/Ag^+ (0.1 M CH_3CN) reference. The working electrode was spun at 600 rpm by a synchronous motor for the rotating platinum electrode (RPE) voltammograms at a 50 mV/s scan rate. Half-wave potentials ($E_{1/2}$) were taken as the potential at half the height of the RPE voltammogram. The value $E_{3/4-1/2}$, also obtained from the RPE voltammogram, was used as a measure of the reversibility of the redox couple ($E_{3/4-1/4}$ for a reversible one-electron couple is 60 mV). Elemental analyses were performed by Galbraith, Inc., Knoxville, TN, and are reported in Table I for new complexes.

Syntheses. a. Neutral Complexes V. (3,11-Diacetyl-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2−)-κ^4N)nickel(II) (structure II), (4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N)nickel(II) hexafluorophosphate (structure III), and (4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2−)-κ^4N)nickel(II) (structure IV) were prepared as previously described by Streeky.[11]

(3,11-Diformyl-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2−)-κ^4N)nickel(II) (Structure V, R^3 = H). A mixture of 1.5 mL (0.022 mol) of formic acid and 3.6 mL (0.022 mol) of acetic anhydride (prepared 12 h previously) was slowly added to a stirred solution of 3.05 g (0.01 mol) of IV and 6.6 mL (0.045 mol) of triethylamine in 300 mL of dry ether. The solution was stirred for 1 h, and 50 mL of $CHCl_3$ was added to dissolve all solid products. The resultant solution was passed through a neutral-alumina chromatography column (2.5 × 20 cm). The absorbed orange band was eluted with $CHCl_3$, and the eluate volume was reduced to about 30 mL. This solution was passed through a second neutral-alumina column (2.5 × 30 cm) packed with ether–chloroform (1:1) and was eluted with 1:1 chloroform–ether. The orange band was collected, and after the volume was reduced, the product was precipitated with ether. Recrystallization from ether–dichloromethane yielded 2.4 g (56%) of the desired complex as light orange crystals.

(3,11-Bis(2,2-dimethylpropanoyl)-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2−)-κ^4N)nickel(II) (Structure V, R^3 = *t*-C_4H_9). A 0.022-mol amount of trimethylacetyl chloride was added to a stirred solution containing 3.05 g (0.01 mol) of IV and 3.35 mL (0.024 mol) of triethylamine in 300 mL of dry ether. Orange product and Et_3NHCl precipitated immediately and after $^1/_2$ h were collected and washed with water. The ether filtrate was evaporated to dryness and the residue combined with solid product by dissolution in $CHCl_3$. The deep red solution was passed through a neutral-Al_2O_3 column with $CHCl_3$ eluent. The red-orange fast-moving band was collected and evaporated to give a red oil, which may be recrystallized from dichloromethane–ether to yield orange crystals, yield 3.8 g (80%).

(3,11-Di-*n*-octanoyl-, (3,11-Bis(3,3-dimethylbutanoyl)-, (3,11-Dibenzoyl, (3,11-Phenylacetyl-, and (3,11-Bis(pentafluorobenzoyl)-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2−)-κ^4N)nickel(II) (Structures V with R^3 = *n*-C_7H_{15}, *neo*-C_5H_{11}, C_6H_5, $CH_2C_6H_5$, and C_6F_5, Respectively). These five complexes were synthesized by using procedures identical with that described for V (R^3 = *t*-C_4H_9) above, substituting 0.022 mol of the appropriate acid chloride. Yields are in the range 80–90%. All other R^3 derivatives in Table I are synthesized by using this procedure with similar yields, except R^3 = CF_3, which is synthesized as follows:

(4,10-Dimethyl-3,11-bis(perfluoroacetyl)-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2−)-κ^4N)nickel(II) (Structure V, R^3 = CF_3). Perfluoroacetyl chloride gas (PCR Inc., Gainesville, FL) was bubbled through a frit into a solution of 3.05 g (0.01 mol) of IV and 3.35 mL (0.024 mol)e of triethylamine in 300 mL of dry dichloromethane. A color change from deep red to red-orange takes place, and after 15 min the reaction mixture was rotavaporated to dryness. The residue was dissolved in $CHCl_3$ eluent, and the fast-moving red band was collected. This solution was evaporated to dryness and recrystallized from hot $CHCl_3$ to yield fibrous yellow crystals, yield 2.5 g (50%).

b. Methylated Complexes VI. Vinyl methyl ether derivatives VI are prepared from the appropriate neutral derivative V by using procedures identical with those already described for the complex V, R^3 = CH_3.[12] The complex V, R^3 = *t*-C_4H_9, is less reactive than the others toward methyl fluorosulfate, and the alkylation reaction takes 5 h. The CH_2Cl_2 solvent used has to be very dry, else small amounts of water lead to half-protonated–half-alkylated products. Yields of VI: R^3 = H, 35%; R^3 = *t*-C_4H_9, 60%; R^3 = *n*-C_7H_{15}, 86%; R^3 = C_6H_5, 73%; R^3 = C_6F_5, 75%; R^3 = CF_3, 65%; R^3 = *neo*-C_5H_{11}, 82%.

c. Unbridged Complexes VII. (3,11-Bis[1-(benzylamino)-benzylidene]-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene)nickel(II) Hexafluorophosphate (Structure VII, R^2 = $CH_2C_6H_5$, R^3 = C_6H_5). A 3.0-g (0.0036-mol) amount of VI, R^3 = C_6H_5, was dissolved in 25 mL of CH_3CN, and 0.8 g (0.0075 mol) of benzylamine was dripped in until a deep orange solution resulted. After evaporation to dryness the complex may be recrystallized from boiling methanol in essentially quantitative yield as deep yellow crystals.

The above synthesis illustrates the procedure adopted for synthesis of all unbridged derivatives VII and is based on previously detailed procedures.[2,3] In all cases (except R^3 = CF_3) simple reaction of a primary amine with the methyl vinyl ether complex VI with the appropriate R^3 group in dry acetonitrile leads to complexes VII where R^2 is the amine substituent. When R^2 = CH_3 is desired, methylamine gas is simply bubbled through an acetonitrile solution of the appropriate complex VI for 10 min until the color change from green to orange-red is complete. Yields in all instances are essentially quantitative.

d. Bridged Lacunar Complexes I. Previous publications[2,3] have detailed the two procedures used to complete the lacunar complexes with the bridge R^1. Starting with methylated complexes VI, reaction with an appropriate dimaine at high dilution leads to a bridged complex I. Alternately starting with the unbridged N-substituted complex VII, and deprotonating the amine with sodium methoxide, structure VIII, allows one to bridge with a dibromo or ditosyl hydrocarbon also at high dilution. An example of each type of reaction is provided below. Analyses of new compounds prepared by these routes are given in Table I.

Method A. (3,11,14,20-Tetramethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene-κ^4N)nickel(II) Hexafluorophosphate (Structure I, R^1 = *m*-Xylyl, R^2 = CH_3, R^3 = H). A 10-g (0.0015-mol) amount of VI, R^3 = H, dissolved in 250 mL of CH_3CN and 0.25 g (0.0015 mol) of α,α'-bis(dimethylamino)-*m*-xylene in 250 mL of CH_3CN were simultaneously and very slowly dripped into 250 mL of stirred refluxing CH_3CN. The addition should take ~2 h, after which time a deep orange solution is present, which is rotavaporated down to 10 mL volume and chromatographed on neutral alumina with CH_3CN as eluent. The fast-moving yellow-green band is collected and evaporated to dryness and the product recrystallized from CH_3CN–EtOH to yield 0.35 g (31%) of deep yellow crystals.

Method B. (3,11-Dibenzyl-14,20-dimethyl-2,12-diphenyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9-(28),12,14,19,21,26-nonaene-κ^4N)nickel(II) Hexafluorophosphate (Structure I, R^1 = *m*-Xylyl, R^2 = $CH_2C_6H_5$, R^3 = C_6H_5). A 5.0-g (0.051-mol) amount of VII, R^2 = $CH_2C_6H_5$, R^3 = C_6H_5, was dissolved in 250 mL of dry CH_3CN, and a solution of 0.24 g (0.01 mol) of sodium in 10 mL of CH_3OH was added. The orange solution immediately turned deep red and was heated to reflux under dry N_2. To the refluxing solution was slowly added dropwise with vigorous stirring a solution containing 1.35 g (0.0051 mol) of α,α'-dibromo-*n*-xylene in 250 mL of CH_3CN. The addition takes ~1 h, and the resultant solution is refluxed for 26 h, after which time the solution is deep orange and a crystalline precipitate of NaBr is evident. After filtration and rotavaporation to dryness the orange gum is redissolved in 5 mL of CH_3CN as eluent. The fast-moving yellow band is collected and rotavaporated to dryness and the resultant yellow product recrystallized from CH_3CN–EtOH to yield 2.6 g (47%) of large deep

Table VIII. Details of Crystal Structure Solution

goodness of fit	$[(\Sigma w(\|F_o\| - \|F_c\|^2)/(\text{NREF} - \text{NV})]^{1/2} = 1.94$
NREF	3363
NV (no. of variables)	667
max shift/error	0.3
R(final)	0.083
R_w(final)	$[\Sigma w\|\Delta F\|^2/\Sigma\|F_o\|^2]^{1/2} = 0.107$
w (weight)	see text
largest peak in final diff map	0.4 e/Å^2

yellow crystals, which were suitable for X-ray crystallography (vide infra).

α,α'-Bis(methylamino)-*m*-xylene. This secondary diamine was not commercially available and so was synthesized by standard organic chemistry techniques.[18] α,α'-Diamino-*m*-xylene (25 g, 0.183 mol) was heated with 98% formic acid (50 mL). After a vigorous reaction the solution was refluxed for 4 h; then the excess HCOOH was taken off under vacuum. The resultant clear liquid solidified and was recrystallized from 100 mL of ethanol; yield 31.7 g, 88%. The IR spectrum shows peaks at 3380, 1650, and 1540 cm^{-1}, consistent with the secondary amide product.

This formamide derivative, 31.7 g, was placed in a Soxhlet thimble over a THF solution (500 mL) containing 12 g of $LiAlH_4$ under reflux. The amide slowly dissolved over 8 h, and the solution was refluxed for 40 h. Aqueous NaOH (50 mL, 1 M) was cautiously added, and large quantities of white solid were filtered off. The THF was rotavaporated off and the resulting oil extracted with ether (3 × 50 mL). The oil was dried over KOH and distilled (157 °C under house vacuum) to yield 9 g, 33%, of the diamine as a colorless liquid. A further 5 g of the dihydrochloride salt was recovered from the residues.

All other bridged complexes I are synthesized by slight variations on one of these two procedures as noted in Table I, and yields of a few examples are quoted in Table I.

Free Ligand Salts. The free ligands of the above synthesized nickel(II) complexes may be prepared as their PF_6 salts by the following general method. A slurry of the nickel(II) complex as its PF_6 salt in dry methanol is exposed to anhydrous HBr by bubbling the gas through the solution for 15 min. All of the solid dissolves in this time, and the color lightens to a pale gold. The solution is rotavaporated to small volume, and water is added whereupon a yellow-white precipitate will form. Addition of an aqueous solution of NH_4PF_6 brings out more flocculent precipitate, which may then be filtered and washed with water, isopropyl alcohol, and ether before air drying. The ligand salts so prepared are generally crude, and no analytical data are available;[2,3] however, using such salts directly in the synthesis of cobalt(II) or iron(II) complexes leads to well-characterized complexes of the expected type.[4,5,15]

Crystal Data. Orange block-shaped crystals of I, R^1 = *m*-xylyl, R^2 = $CH_2C_6H_5$, R^3 = C_6H_5, were grown from CH_3CN-EtOH by slow cooling: $NiC_{50}H_{52}N_6P_2F_{12}\cdot C_2H_5OH$, M_r = 1085.6, monoclinic space group $P2_1/c$, a = 10.126 (2) Å, b = 17.629 (4) Å, c = 30.666 (7) Å, β = 100.87 (2)°, V = 5376 (2) Å^3, T = 291 (2) K, d_{measd} (chloroform–bromoform) = 1.38 g cm^{-3}, d_{exptl} = 1.398 g cm^{-3}, Z = 4, μ(Mo Kα) = 4.97 cm^{-1}, F(000) = 2240. Data were collected with a Syntex $P2_1$ four-circle automated diffractometer. The maximum 2θ was 50°, with scan range ±1.0° (2θ) around the Kα_1–Kα_2 angles, the scan speed was 2–29° min^{-1} (increased to 3.5–29° min^{-1} after 4000 reflections) depending on the intensity of a 2-s prescan, and backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 100 reflections and showed irregular changes during the early part of the data collection (about 5% in F maximum); these variations could not be compensated for by rescaling. Simultaneously, the cell constants changed as shown in Table VII. This probably reflects some small rearrangement of cell contents. As the values appear to have stabilized by the middle of the data collection, the average of the two later values was used in further calculations.

Unit cell dimensions and their esds were obtained by a least-squares fit to 15 high-angle reflections. A total of 3363 observed reflections ($I/\sigma(I) > 3.0$), from 10 196 collected, were used in refinement and corrected for Lorentz, polarization, and absorption effects, the last with ABSCOR.[19] Systematic absences $h0l$, $l = 2n + 1$ and $0k0$, k =

Table IX. Final Atomic Coordinates for Complex I, R^1 = *m*-Xylylene, R^2 = Benzyl, R^3 = Phenyl

	x	y	z
Ni	0.0683 (1)	0.0065 (1)	0.4090 (1)
P(1)	0.0283 (7)	0.2326 (3)	0.1186 (2)
P(2)	0.5321 (5)	0.1590 (4)	0.3599 (2)
F(11)	−0.0238 (22)	0.3045 (9)	0.0910 (6)
F(12)	−0.0990 (19)	0.2286 (9)	0.1400 (7)
F(13)	0.1520 (28)	0.2393 (12)	0.1010 (10)
F(14)	0.0918 (18)	0.1674 (8)	0.1497 (6)
F(15)	0.0794 (26)	0.2880 (10)	0.1544 (6)
F(16)	−0.0379 (35)	0.1796 (13)	0.0870 (7)
F(21)	0.6504 (19)	0.1125 (11)	0.3530 (10)
F(22)	0.5334 (25)	0.2019 (13)	0.3190 (6)
F(23)	0.4258 (18)	0.2030 (15)	0.3722 (6)
F(24)	0.5444 (18)	0.1266 (15)	0.4080 (7)
F(25)	0.6422 (19)	0.2126 (15)	0.3824 (6)
F(26)	0.4376 (23)	0.1052 (12)	0.3370 (8)
N(1)	−0.0891 (9)	−0.0259 (5)	0.3705 (3)
N(2)	0.1707 (11)	−0.0531 (7)	0.3768 (4)
N(3)	0.2263 (9)	0.0466 (6)	0.4440 (3)
N(4)	−0.0336 (9)	0.0672 (5)	0.4413 (3)
N(5)	−0.0642 (10)	0.0441 (6)	0.2387 (3)
N(6)	0.0720 (10)	0.2990 (6)	0.4283 (3)
C(1)	−0.0984 (12)	−0.0298 (7)	0.3276 (4)
C(2)	−0.2308 (13)	−0.0529 (8)	0.2972 (4)
C(3)	0.0188 (12)	−0.0235 (7)	0.3072 (4)
C(4)	0.1427 (14)	−0.0529 (8)	0.3339 (4)
C(5)	0.0207 (12)	−0.0051 (8)	0.2633 (4)
C(6)	0.1315 (13)	−0.0374 (8)	0.2411 (4)
C(7)	0.1321 (16)	−0.1165 (8)	0.2346 (5)
C(8)	0.2376 (18)	−0.1486 (11)	0.2176 (6)
C(9)	0.3339 (21)	−0.1030 (14)	0.2059 (7)
C(10)	0.3329 (22)	−0.0258 (14)	0.2124 (8)
C(11)	0.2294 (16)	0.0098 (11)	0.2303 (6)
C(12)	−0.0784 (15)	0.0508 (9)	0.1895 (4)
C(13)	−0.2144 (14)	0.0176 (8)	0.1662 (4)
C(14)	−0.2978 (20)	0.0644 (10)	0.1366 (5)
C(15)	−0.4174 (21)	0.0314 (12)	0.1114 (7)
C(16)	−0.4554 (18)	−0.0406 (11)	0.1211 (6)
C(17)	−0.3730 (15)	−0.0852 (9)	0.1526 (5)
C(18)	−0.2514 (14)	−0.0553 (8)	0.1746 (4)
C(19)	−0.1380 (13)	0.1033 (8)	0.2594 (5)
C(20)	−0.0392 (12)	0.1581 (7)	0.2888 (4)
C(21)	−0.0718 (11)	0.1853 (7)	0.3286 (4)
C(22)	0.0088 (12)	0.2403 (7)	0.3522 (4)
C(23)	0.1252 (12)	0.2654 (8)	0.3394 (4)
C(24)	0.1587 (14)	0.2378 (8)	0.3000 (4)
C(25)	0.0723 (14)	0.1843 (8)	0.2725 (5)
C(26)	−0.0383 (12)	0.2773 (7)	0.3911 (4)
C(27)	0.0959 (15)	0.3827 (7)	0.4353 (5)
C(28)	−0.0282 (14)	0.4198 (7)	0.4465 (5)
C(29)	−0.0678 (15)	0.4008 (8)	0.4866 (5)
C(30)	−0.1766 (18)	0.4402 (9)	0.4988 (6)
C(31)	−0.2457 (16)	0.4972 (10)	0.4700 (6)
C(32)	−0.2031 (17)	0.5165 (10)	0.4310 (7)
C(33)	−0.0962 (19)	0.4766 (8)	0.4178 (5)
C(34)	0.1544 (11)	0.2486 (7)	0.4496 (4)
C(35)	0.2873 (13)	0.2718 (7)	0.4762 (4)
C(36)	0.3861 (15)	0.3020 (9)	0.4552 (5)
C(37)	0.5181 (19)	0.3171 (12)	0.4795 (8)
C(38)	0.5401 (19)	0.3059 (10)	0.5248 (8)
C(39)	0.4440 (20)	0.2742 (11)	0.5482 (6)
C(40)	0.3145 (16)	0.2578 (8)	0.5218 (5)
C(41)	0.1244 (11)	0.1699 (7)	0.4486 (4)
C(42)	−0.0081 (12)	0.1378 (7)	0.4516 (4)
C(43)	−0.0961 (13)	0.1843 (7)	0.4773 (4)
C(44)	−0.1509 (1)	0.0329 (6)	0.4562 (4)
C(45)	−0.1721 (13)	−0.0485 (7)	0.4392 (4)
C(46)	−0.2077 (13)	−0.0517 (8)	0.3889 (4)
C(47)	0.2915 (16)	−0.0970 (10)	0.3979 (5)
C(481)	0.3384 (23)	−0.0782 (14)	0.4463 (8)
C(482)	0.3936 (34)	−0.0439 (19)	0.4194 (11)
C(49)	0.3534 (12)	0.0038 (9)	0.4575 (5)
C(50)	0.2374 (12)	0.1192 (7)	0.4524 (4)
C(OH)1	0.4771 (61)	0.2970 (38)	0.1722 (25)
C(OH)2	0.5588 (75)	0.2363 (40)	0.1845 (16)
O(OH)	0.4409 (57)	0.2025 (46)	0.2097 (18)

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(18) Sander, M.; Burmeister, D. *Chem. Ber.* **1962**, *95*, 964.

$2n + 1$, indicated the space group $P2_1/c$.

Solution and Refinement of the Crystal Structure. The structure was solved by heavy-atom methods and refined to $R \approx 0.16$, with anisotropic temperature factors, with no problems. At this point a difference map showed further peaks, which were taken to be an EtOH of solution. C(48) also showed evidence of disorder, occupying two positions. These were included at 0.5 occupancy and refined isotropically. Further refinement led to convergence at $R = 0.083$, $R_w = 0.107$. Although the PF_6 anions and the EtOH showed evidence of disorder (large temperature factors), no alternative atomic positions could be discerned on a difference map. Those hydrogen atoms whose positions are completely defined were included at fixed positions and not refined; other hydrogen atoms were omitted.

Final refinement was by least squares in large blocks. An empirical weighting scheme of the form $w = 1/(1.0 + ((F - B)/A)^2)$ was used, where A was taken as 60.0 and B as 25.0. This was shown to be satisfactory by a weight analysis. Computing was with the X-RAY 76 system[20] on Burroughs B6700 and CDC 7600 computers. Scattering factors in the analytical form and anomalous dispersion factors (for Ni and P) were taken from ref 21. Final solution details are in Table VIII, final atomic coordinates are in Table IX, and a listing of anisotropic temperature factors and observed and calculated structure factors are listed as supplementary material.

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Registry No. I (R^1 = *m* = xylylene, R^2 = CH_3, R^3 = H), 88635-25-0; I (R^1 = *m*-xylylene, R^2 = CH_3, R^3 = 3,5-$(OMe)_2Ph$), 88635-27-2; I (R^1 = *m*-xylylene, R^2 = CH_3, R^3 = *n*-C_7H_{15}), 88635-29-4; I (R^1 = *m*-xylylene, R^2 = CH_3, R^3 = C_6H_5), 88635-31-8; I (R^1 = *m*-xylylene, R^2 = H, R^3 = C_6H_5), 88635-33-0; I (R^1 = *m*-xylylene, R^2 = H, R^3 = *n*-C_7H_{15}), 88635-35-2; I (R^1 = *m*-xylylene, R^2 = $CH_2C_6H_5$, R^3 = C_6H_5), 88635-37-4; I (R^1 = $(CH_2)_4$, R^2 = H, R^3 = C_6H_5), 88635-39-6; I (R^1 = $(CH_2)_4$, R^2 = CH_3, R^3 = C_6H_5), 88610-65-5; I (R^1 = $(CH_2)_4$, R^2 = H, R^3 = *t*-C_4H_9), 88610-67-7; I (R^1 = $(CH_2)_5$, R^2 = H, R^3 = C_6H_5), 88610-69-9; I (R^1 = $(CH_2)_5$, R^2 = CH_3, R^3 = C_6H_5), 88610-71-3; I (R^1 = $(CH_2)_5$, R^2 = H, R^3 = *t*-C_4H_9), 88610-73-5; I (R^1 = $(CH_2)_6$, R^2 = H, R^3 = C_6H_5), 88610-75-7; I (R^1 = $(CH_2)_6$, R^2 = CH_3, R^3 = C_6H_5), 88610-77-9; I (R^1 = $(CH_2)_6$, R^2 = H, R^3 = *t*-C_4H_9), 88610-79-1; I (R^1 = $(CH_2)_6$, R^2 = H, R^3 = *n*-C_7H_{15}), 88635-15-8; I (R^1 = $(CH_2)_6$, R^2 = CH_3, R^3 = H), 88610-81-5; I (R^1 = $(CH_2)_7$, R^2 = H, R^3 = C_6H_5), 88610-83-7; I (R^1 = $(CH_2)_7$, R^2 = CH_3, R^3 = C_6H_5), 88610-85-9; I (R^1 = $(CH_2)_7$, R^2 = H, R^3 = *t*-C_4H_9), 88610-87-1; I (R^1 = $(CH_2)_8$, R^2 = H, R^3 = C_6H_5), 88610-89-3; I (R^1 = *m*-xylylene, R^2 = CH_3, R^3 = CH_3), 77827-37-3; I (R^1 = *m*-xylylene, R^2 = H, R^3 = CH_3), 77827-31-7; I (R^1 = *m*-xylylene, R^2 = $CH_2C_6H_5$, R^3 = CH_3), 77827-39-5; IV, 74466-59-4; V (R^3 = H), 88611-06-7; V (R^3 = *t*-C_4H_9), 88611-07-8; V (R^3 = *neo*-C_5H_{11}), 88611-08-9; V (R^3 = *n*-C_7H_{15}), 88610-90-6; V (R^3 = *n*-C_9H_{19}), 88611-09-0; V (R^3 = C_6H_5), 74466-43-6; V (R^3 = $CH_2C_6H_5$), 88611-10-3; V (R^3 = CF_3), 88611-11-4; V (R^3 = 4-OMePh), 88611-12-5; V (R^3 = 3,5-$(OMe)_2Ph$), 88611-13-6; V (R^3 = 3,5-Me_2Ph), 88611-14-7; V (R^3 = 3,5-$(NO_2)_2Ph$), 88611-15-8; V (R^3 = *n*-C_5H_{11}), 88611-16-9; V (R^3 = *n*-$C_{17}H_{35}$), 88611-17-0; V (R^3 = C_6F_5), 88610-91-7; VI (R^3 = H), 88610-93-9; VI (R^3 = *t*-C_4H_9), 88610-95-1; VI (R^3 = *n*-C_7H_{15}), 88610-97-3; VI (R^3 = C_6H_5), 88610-99-5; VI (R^3 = CF_3), 88611-01-2; VI (R^3 = *neo*-C_5H_{11}), 88611-03-4; VII (R^2 = CH_3, R^3 = C_6F_5), 88635-17-0; VII (R^2 = CH_3, R^3 = *p*-biphenyl), 88635-19-2; VII (R^2 = CH_3, R^3 = *p*-ClPh), 88635-21-6; VII (R^2 = CH_3, R^3 = *p*-FPh), 88635-23-8; VII (R^2 = $CH_2C_6H_5$, R^3 = C_6H_5), 88611-05-6; formic acid, 64-18-6; acetic anhydride, 108-24-7; trimethylacetyl chloride, 3282-30-2; perfluoroacetyl chloride, 354-32-5; benzylamine, 100-46-9; α,α'-dibromo-*m*-xylene, 626-15-3; α,α'-bis(methylamino)-*m*-xylene, 23399-62-4; α,α'-bis(methylamino)-*m*-xylene (formamide derivative), 59276-03-8; α,α'-diamino-*m*-xylene, 1477-55-0.

Supplementary Material Available: Listings of anisotropic temperature factors and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Guelph, Ontario N1G 2W1, Canada, and Département de Chimie, Université de Montréal, Montréal, Québec H3C 3V1, Canada

Crystal Structure of Tetrakis(μ-trifluoroacetato)bis[(triphenylphosphine)cadmium(II)]: A Dimer Containing the Tetrakis(carboxylato)dimetal Framework

TIM ALLMAN,[1a] RAM C. GOEL,[1a] N. K. JHA,[1a] and ANDRÉ L. BEAUCHAMP*[1b]

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The title compound belongs to the monoclinic space group $P2_1/c$, with $a = 10.011$ (7) Å, $b = 18.062$ (5) Å, $c = 15.135$ (4) Å, $\beta = 118.34$ (4)°, and $Z = 2$ $[Cd(CF_3COO)_2P(C_6H_5)_3]_2$ molecules per cell. The structure was solved on 1741 observed reflections to an R factor of 0.038. The unit cell contains discrete centrosymmetric dimeric molecules in which the Cd atoms are part of a framework of four bridging carboxylate ligands, similar to those found with Mo(II), Cu(II), Cr(II), and Rh(II). The apical sites are occupied by PPh_3 ligands (Cd–P = 2.524 Å), but the Cd–P bond does not lie along the Cd–Cd axis (Cd–Cd–P = 153.7°). The Cd–Cd separation (3.452 Å) is consistent with the absence of metal–metal bonding. One pair of carboxylate groups is symmetrically coordinated (Cd–O–C = 128.2 and 132.8°) as usually found in tetrakis(μ-carboxylate) frameworks, but the other pair undergoes considerable distortion (Cd–O–C = 109.0 and 154.2°).

Introduction

Our knowledge of tertiary phosphine complexes of cadmium has, until recently, been limited to the complexes of cadmium(II) halides,[2,3] which were first reported[2] in 1940. Complexes of cadmium(II) thiocyanate with tri-*tert*-butyl-,[4] tri-

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