methyl or methylene groups are added to the macrocycle. Again, increasing the bulk of the ligand will favor the lower charged chloro complexes over the aquo species through solvation effects, thus contributing to the observed increase in chloride affinity for the macrocycle complexes. The decrease with increasing ring size is probably due to steric interactions between the axial positions and the various hydrogen atoms on the macrocyclic ring. The crowding caused by the hydrogen atoms will tend to displace the larger chloride ligand in favor of the smaller aquo ligand.

Summary

The most unusual aspect of the ruthenium macrocycle complexes compared to the simple ammine systems is the appearance of effects due to steric interactions between the macrocycle ligand and the axial positions. These interactions are directly observable in the crystal structure and lead to the splitting of the charge-transfer band in the electronic spectrum. This interaction is also apparent in the decreasing affinity for chloride as the macrocycle ring size increases.

Other trends seen in the properties of the macrocycle complexes are consistent with solvation effects as chelation is increased or as the ring size is increased. The effects of ring size on the electronic spectra and formal potentials are found to be small, as might be expected because there are no e_g electrons.

Acknowledgment. Support of this research by the National Science Foundation under Grant No. CHE79-08633 and the National Institutes of Health (Grant No. GM 13638-14) is gratefully acknowledged as is the help of Proessor K. O. Hodgson and Jeremy Berg in determining the crystal structure.

Registry No. *trans*-[Ru([14]aneN_4)Cl_2]Cl, 56172-98-6; *trans*-[Ru([14]aneN_4)Cl_2]Br, 77827-63-5; *trans*-[Ru([14]aneN_4)Cl_2]-CF_3SO_3, 77827-64-6; *trans*-[Ru(Me_2[14]aneN_4)Cl_2]Cl, 77827-65-7; *trans*-[Ru([14]aneN_4)Br_2]Br, 74202-83-8; $RuCl_2$([14]aneN_4)(PPh_3), 77827-66-8; $RuCl_2$([15]aneN_4)$(PPh_3)_2$, 77846-74-3; $RuCl_2$([15]aneN_4), 77827-67-9; $RuCl_2$([16]aneN_4), 77827-68-0; *trans*-[Ru-[15]aneN_4)Cl_2]Cl, 76705-25-4; *trans*-[Ru([16]aneN_4)Cl_2]Cl, 77827-69-1; *trans*-[Ru([14]aneN_4)Cl(H_2O)]$^+$, 73238-31-0; *trans*-[Ru(Me_2[14]aneN_4)Cl(H_2O)]$^+$, 77827-70-4; *trans*-[Ru([15]aneN_4)Cl(H_2O)]$^+$, 77827-71-5; *trans*-[Ru([16]aneN_4)Cl(H_2O)]$^+$, 77827-72-6; *trans*-[Ru([14]aneN_4)$(H_2O)_2$]$^{2+}$, 77827-73-7; *trans*-[Ru(Me_2[14]aneN_4)$(H_2O)_2$]$^{2+}$, 77827-74-8; *trans*-[Ru([15]aneN_4)$(H_2O)_2$]$^{2+}$, 77827-75-9; *trans*-[Ru([16]aneN_4)$(H_2O)_2$]$^{2+}$, 77846-75-4; $K_2[RuCl_5(OH_2)]$, 14404-33-2; $K_2[RuBr_5(OH_2)]$, 62109-80-2; $RuCl_2(PPh_3)_3$, 15529-49-4; Me_2[14]aneN_4, 39481-23-7.

Contribution from the Evans Chemical Laboratory,
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Simultaneous Synthesis, Separation, and Characterization of Metal Complexes with Monomeric Lacunar Ligands and Dimeric Ligands Capable of Bimetallic Coordination

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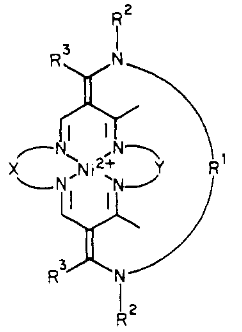
Two important families of ligands are produced simultaneously in a template-moderated ring-closure reaction. Additional examples of lacunar ligands are reported; these form metal complexes in which a protected cavity suitable for sheltering a small molecule is formed in the vicinity of a coordination site. Simultaneously, dimeric ligands are produced that are capable of binding two metal ions, within macrocyclic moieties, in an approximate face-to-face orientation. The isomeric substances were separated by fractional crystallization or by chromatography. Their structures have been established by combination of definitive and correlative means. Generic distinctions between monomers and dimers are made by high-performance liquid and ion-exchange chromatography, by NMR (proton and ^{13}C), and, in some cases, by direct molecular weight determinations on neutral deprotonated derivatives of the nickel(II) complex. Factors favoring monomer and dimer formation are discussed. The monomeric species are the main subject of this paper. ^{13}C NMR show that most of the lacunar complexes have the expected mirror symmetry. Electrochemistry shows that the electron density at the metal ion is insensitive to the nature of the bridge but that substituents can cause alterations in electon density. Thus steric and electronic effects of variations in ligand can be applied separately to the interactions of small molecules such as O_2 or CO with coordinated metal ions. The ligands have been separated from nickel(II) and made available for coordination to other metal ions.

Introduction

Structural variations are being explored for the broad family of bicyclic superstructure complexes shown in structure I. The general structure has been designed for use in various totally synthetic heme protein models. Preliminary reports[1,2] have revealed the synthesis and structure proof for examples of the new complexes. They have also shown that the cobalt(II) complexes of these lacunar ligands are exceptional O_2 carriers:[3] (1) the O_2 affinity of the *lacunar*-cobalt(II) complexes can be made to vary over a range of 5 orders of magnitude by steric means; (2) electronic effects can be used to change the O_2 affinity by at least 1 order of magnitude; (3) the O_2 complexes are formed reversibly in aqueous solution at room temperature; (4) certain of the *lacunar*-cobalt complexes have O_2 affinities as great as those of iron in myoglobin and are the strongest reversible cobalt-based O_2 binders known to react in a one-to-one stoichiometry.[4]



I

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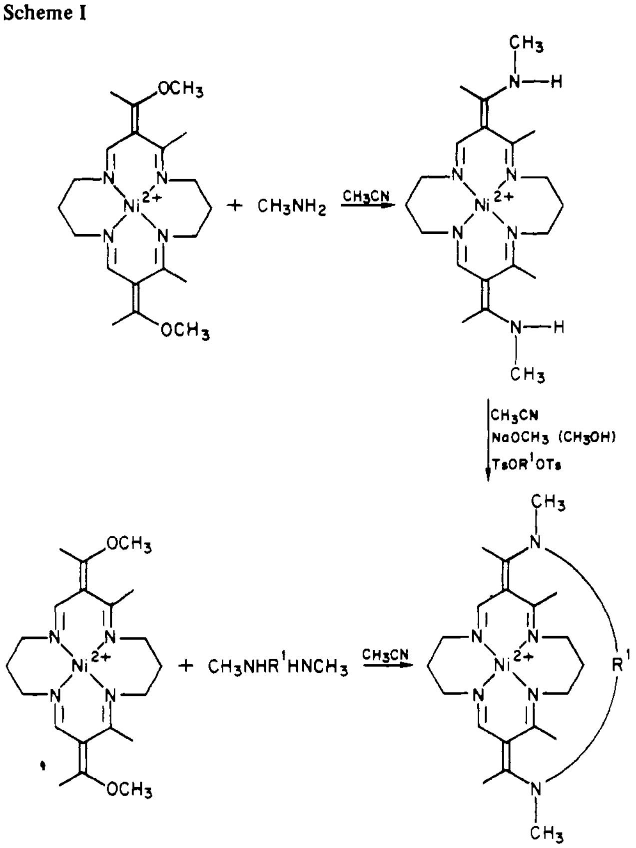
[1] Schammel, W. P.; Mertes, K. S. B.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 1622–1623.

[2] Stevens, J. C.; Jackson, P. J.; Schammel, W. P.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3283–3285.

[3] Stevens, J. C.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3285–3287.

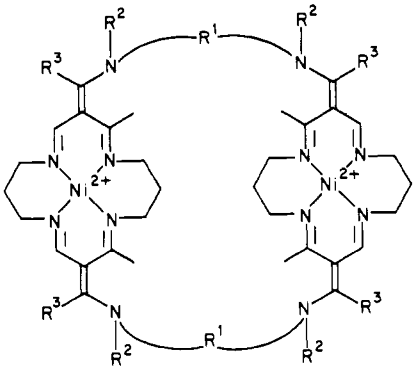
0020-1669/81/1320-2834$01.25/0 © 1981 American Chemical Society

Scheme I



The lacunar ligands having $R^3 = R^2 = CH_3$ and $R^1 = (CH_2)_n$ (n = 4–8) are formed by either of the template processes shown in Scheme I as the sole product of the bicyclization reaction. Consequently the results of studies on these relatively simple synthetic systems have been the subject of an earlier report.[5] Those studies reported a series of five lacunar complexes whose structures differ only in the homologous bridge $CH_3N(CH_2)_nNCH_3$. Electrochemical studies on that series showed that the electron density at the metal ion remains constant through the series. In contrast, this is just the series for which the O_2 affinity of the cobalt(II) complex changes over a range of 5 orders of magnitude.[3] These relationships justify the conclusion that steric factors alone can be used to control O_2 affinity;[3,5] this is a matter of considerable significance to the understanding of the details of the allosteric phenomena of hemoglobin.[6]

The present study explores the effects of variations in R^2, the bridge nitrogen substituent, and of more extensive variations in R^1, the bridging group. Here, the synthesis and characterization of the nickel(II) complexes are reported. In order to understand the behavior of any other structural variants except those just described, it was necessary to resolve a difficult isomer problem. The isomer separation, classification, and structure proof are detailed herein. This report concentrates on the monomeric lacunar complexes (structure I). A separate report details the dimeric, bimetallic isomers which have general structure II.

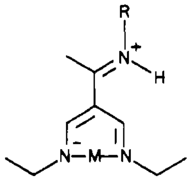


II

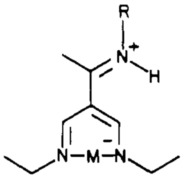
Results and Discussion

Isomerism. Separation and Distinction between Monomers and Dimers. Whereas the complexes having polymethylene bridges and methyl substituents on the bridge nitrogens (as described earlier) form isomerically pure, monomeric lacunar complexes, the corresponding complexes with hydrogens on the bridge nitrogens (the homologous bridge is $HN(CH_2)_nNH$ (n = 4–8)) all form two isomeric species. It is also significant that when the chain gets long enough the N–CH_3 systems also yield isomers, i.e., this occurs with the $CH_3N(CH_2)_{10}NCH_3$ bridge. Further, the xylene diamine derivatives, $(NH)_2$(*p*-xyl) and $(NH)_2$(*m*-xyl), and the derivative of 9,9-bis(3-aminopropyl)fluorene (C_7Fl) also exist in two isomeric forms.

A number of crystal structures[1,2,7,8] have shown that the bridge nitrogens are trigonal planar rather than pyramidal in structure. This is rationalized on the basis of incorporation of the nitrogen lone pair in the conjugated π system of the chelate ring (e.g., resonance structures III and IV). These structures represent edge-on projections of side views of the ligand structures. The NiN_4 coordination plane is perpendicular to the page so that pairs of coordinated nitrogens eclipse each other. Like the precursor of the lacunar ligands,[5,9,10] the new ligands are also saddle shaped.

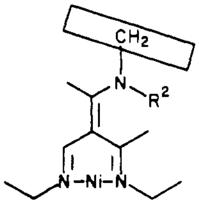


III

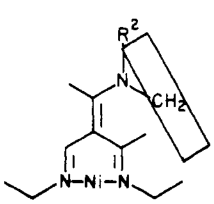


IV

In structures III–VI, the unsaturated rings rise above the NiN_4 plane and the saturated chelate rings project below it. Since the bridge nitrogens are trigonal planar, the remainder of the bridge group may be attached at either of two geometrically distinct bonds as shown in structures V and VI. The bridge may be attached to the nitrogen bond arising essentially perpendicular to the NiN_4 plane; this produces *lid-on* structure V, in which the roof of the cavity is pretty much above the metal ion. Alternatively, the bridging group may be attached to the nitrogen bond that



V



VI

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(4) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem Rev.* **1979**, *79*, 139–179 and references therein.

(5) Busch, D. H.; Olszanski, D. J.; Stevens, J. C.; Schammel, W. P.; Kojima, M.; Herron, N.; Zimmer, L. L.; Holter, K.; Mocak, J. *J. Am. Chem. Soc.* **1981**, *103*, 1472–1478.

(6) Perutz, M. F. *Annu. Rev. Biochem.* **1979**, *48*, 327–86.

(7) Zimmer, L. L. Thesis, The Ohio State University, Columbus, Ohio, 1979.

(8) Matsumoto, N.; Christoph; G. G., Busch, D. H., unpublished results.

(9) Corfield, P. W. R.; Mokren, J. D.; Hipp, C. J.; Busch, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 4465–4466.

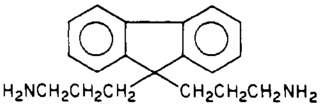
(10) Mokren, J. D. Thesis, The Ohio State University, Columbus, Ohio, 1974.

is approximately parallel to the NiN_4 plane; this places the roof of the cavity to one side of the structure, making it both the back and top of the cavity. This is shown in structure VI and is called the *lid-off* structure. There is no ligand for which both of these isomers have been found. Also, structure V and VI seem not subject to interconversion. The ligand can be removed from nickel and then coordinated to it again with no change in structure. This structural feature is significant for individual species and that subject is addressed later.

The experimentally observed isomerism is associated with the occurrence of both monomeric and dimeric species in which the dimerization occurs in the ligand structure (structures I and II). The isomeric structures have been established unequivocally by a combination of definitive structure proofs for selected examples along with highly correlated techniques for classifying the substances into either of the two isomeric types.

It is not entirely clear what determines whether monomers, dimers, or mixtures will be formed although certain factors and trends are apparent. As expected, elevated temperatures and high-dilution reaction conditions favor the formation of monomeric complexes. Steric factors are important for cases in which the bridge nitrogens are tertiary. For almost all such cases, only one isomer is formed. Certain systems generating only monomers were described in an earlier report.[5] Interestingly, when the bridge contains the aromatic duryl group, dimers are formed. Also trimethylene and dimethylene linkages greatly favor dimer formation. It is concluded that a bulky bridging group favors dimerization. It also seems clear that there is an optimal bridge length for lacunar monomer formation. This is indicated by the fact that very little dimer is formed in the $(NH)_2(CH_2)_6$ system while approximately equal amounts of dimer and monomer are produced in the $(NH)_2(CH_2)_4$ and $(NH)_2(CH_2)_5$ systems. Presumably, the occurrence of dimer alone in the $(CH_2)_2$ system reflects a limit on how short a chain can span the bridging positions in the monomeric lacunar complex.

The separation of the isomers varies in difficulty from system to system. Simple fractional crystallization from mixed solvents (ethanol/acetonitrile) is preferred for the cases where it works efficiently. This includes the $(NH)_2(CH_2)_4$, $(NH)_2(CH_2)_5$, $(NH)_2$(*m*-xyl), and $(NH)_2C_7Fl$ (structure VII) derivatives. With the exception of the $(NH)_2C_7Fl$ derivative, the dimer precipitates from the solution first. The monomer is then isolated from the filtrate by further addition of ethanol followed by evaporation of the solvent. It follows that the monomeric lacunar complex can be difficult to isolate by crystallization, particularly when it is much less abundant than the dimer.



VII

For cases where crystallization failed, chromatographic techniques were used. The isomers of the $(NH)_2$(*p*-xyl) derivative were separated on neutral alumina with use of acetonitrile as the eluant. Ion exchange with CM-Sephadex was necessary to separate the isomers of the $(NH)_2(CH_2)_7$ and $(NH)_2(CH_2)_8$ derivatives. The complexes were converted to water-soluble halide salts and then eluted from the column with Na_2SO_4 solution. The dipositive monomeric species elutes easily while the dimeric tetrapositive species can be eluted only with concentrated Na_2SO_4 solution (0.4–0.6 M).

The successful separation of the isomers can be monitored by a number of techniques. The isomers (PF_6 salts) are separated by high-performance liquid chromatography on C-18 reverse-phase columns at 1000 psi with the use of a solvent mixture of 20% acetonitrile in water. Generally, the monomer elutes first as a sharp band followed by the dimer as a broad band (Figure 1). Proton and ^{13}C NMR spectroscopy are also useful for monitoring the separation (vide infra).

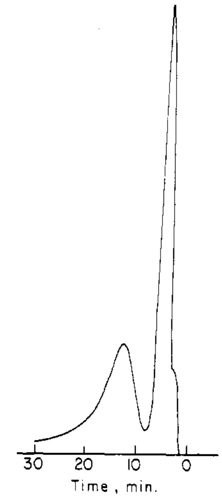
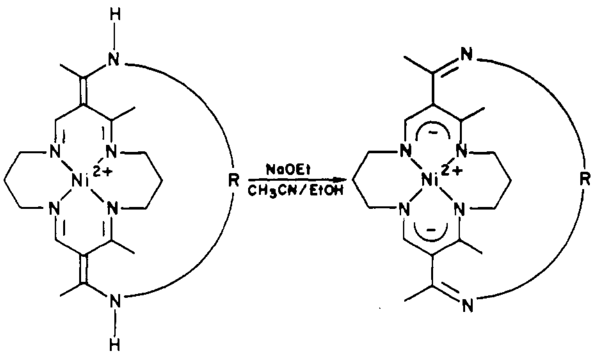


Figure 1. High-pressure LC trace for separation of the monomeric and dimeric forms of the *m*-xylyl-bridged complex: C-18 reverse phase column, 100 psi, 20% acetonitrile in water.

Monomeric Lacunar Complexes from Isomeric Mixtures. Ultimate demonstration of these structures rests on X-ray crystal structure determinations, and seven monomeric lacunar complexes have now been subjected to such determination.[1,2,7,8] Of these, only one has involved a nickel(II) complex.[1]

In addition, for a limited number of cases, definitive structure proof has been provided in other ways. Since the isomerization involves monomers and dimers, colligative properties and molecular weight determinations provide obvious possibilities for drawing the necessary distinction. The complexes are cations so that molecular weight determinations would need to distinguish between species containing three ions and species containing five ions. Such highly charged species as the dimers are likely to give nonideal behavior. This nonideal behavior has frustrated attempts to use molar conductance to resolve the question of ionic weight as well.[7] The great difference in charge type does allow one to use ion-exchange chromatographic behavior as a criterion, however. As stated above, the tetrapositive dimeric ions are held by the column much more tenaciously than are the monomers. This criterion aided in the assignment of structures to the $(NH)_2(CH_2)_n$ isomers.

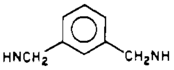
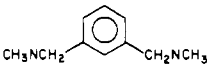
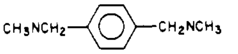
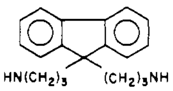
The hydrogen atoms on the bridge nitrogens are acidic and can be removed by strong base. Consequently, the neutral complexes can be produced in solution (eq 1), and in a few cases they have been isolated in pure form. Molecular weights can than be obtained by various means (Table I).



(1)

Satisfactory elemental analyses were obtained for most of the monomeric lacunar complexes and bimetallic dimeric

Table I. Molecular Weights Determined for Monomeric Lacunar Complexes by Vapor-Pressure Osmometry or Mass Spectrometry

bridge	solvent[a]	mol wt	
		found	calcd
$HN(CH_2)_4NH$	C_6H_6	558,[a] 441[b]	440.0
$HN(CH_2)_5NH$		454[b]	454.0
$HN(CH_2)_6NH$	$CHCl_3$	464,[a] 468[b]	469.4
$HN(CH_2)_7NH$	C_6H_6	493[a]	483.4
$HN(CH_2)_8NH$	$CHCl_3$	538[a]	497
	$CHCl_3$	496,[a] 489[b]	489.36
	$CHCl_3$	522[a]	517.4
	$CHCl_3$	526[a]	517.4
	$CHCl_3$	600,[a] 632[b]	633.5

[a] Value from osmometric determination. [b] Value from mass spectrometry.

complexes as shown in Table II. Infrared spectra are rather uninformative but do have a few characteristic features.[7] A sharp N–H stretching absorption is observed in the vicinity of 3400 cm^{-1} for the bridged complexes containing secondary nitrogens. As expected, this band is absent from complexes having a nonhydrogen substituent on the bridge nitrogen. Bands due to C=C and C=N stretches are found in vicinity of 1500–1600 cm^{-1}. In all of the spectra of the xylyl-bridged complexes, there are bands due to the aromatic system in the region from 600 to 800 cm^{-1}.

Molar conductances were measured in acetonitrile and are consistent with the assignment as 2:1 electrolytes.[11] For the complexes having $(NH)_2$(*m*-xyl), $(NH)_2$(*p*-xyl), and $(NMe)_2$(*m*-xyl) bridges, the conductance was measured as a function of concentration. Onsager plots[12] for examples of the lacunar complexes show a slope ranging from about 450 to 500 Ω^{-1} mol$^{-1.5}$ cm$^{3.5}$ and a value of Λ_0 of 150–170 Ω^{-1} mol^{-1} cm^2 which are in the expected range for 2:1 electrolytes (Table III).

Proton NMR spectral data are summarized in Table IV. All of the complexes have the expected symmetry as described earlier for the $(NCH_3)_2(CH_2)_n$-bridged complexes.[5] The spectra of the complexes having aromatic bridges differ primarily because of the resonances attributable to the aromatic group or to varying N substituents. The NH-containing compounds show a broad resonance around 6.7–7.0 ppm.

^{13}C NMR spectra were also measured for the complexes and assigned through the use of the off-resonance technique. Again the major differences are due to the presence of aromatic resonances and/or the presence or absence of nitrogen subsituents. The ^{13}C resonances are listed in Table IV, and the spectra of the $(NH)_2$(*p*-xyl)- and $(NMe)_2$(*m*-xyl)-bridged complexes are shown in Figure 2.

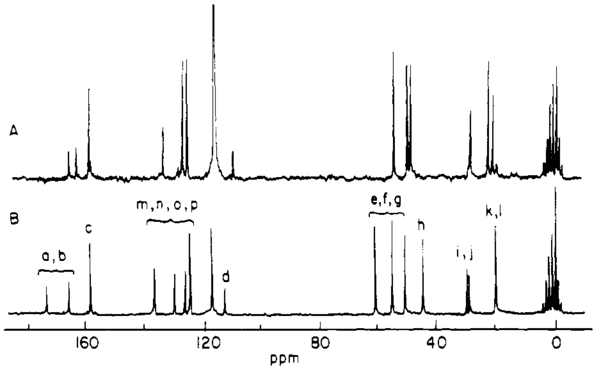


Figure 2. Carbon-13 NMR spectra for the complexes: A, $[Ni((p\text{-}xylyl)(NHEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$; B, $[Ni((m\text{-}xylyl)(MeNEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$. For meaning of labels, see structure VIII.

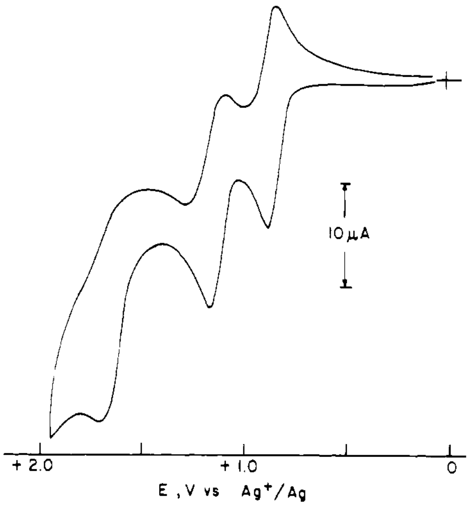
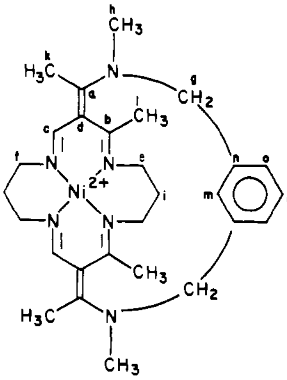


Figure 3. Oxidation processes for $[Ni((CH_2)_6(NHEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$ by cyclic voltammetry: CH_3CN solution, *n*-Bu_4NBF_4 supporting electrolyte, $Ag/AgNO_3$ (0.1 N) reference electrode, Pt-disk electrode, 0.05 V s^{-1} scan rate.

It is significant that in all cases except the $(NH)_2$(*m*-xyl) and C_7Fl derivatives the resonances due to the two kinds of methyl groups directly bonded to the macrocycle are less than one ppm apart, whereas in the spectrum for the exceptional cases, they are much further apart (~6 and ~7 ppm, respectively). From X-ray structure determinations, only the $(NH)_2$(*m*-xyl) complex has the *lid-on* structure, all others are *lid-off*.[1,2,7,8] It seems appropriate to conclude that methyl resonances which are close together (<1-ppm separation) indicate a *lid-off* structure, and methyl resonances which are widely separated (~5–7 ppm) indicate a *lid-on* structure.

Assignments are given by structure VIII and the labels in Figure 2b for $[Ni((m\text{-}xyl)(MeNEthi)_2[16]tetraeneN_4)](PF_6)_2$.



VIII

Electrochemistry. Complete electrochemical data for the monomeric complexes are contained in Table V. The nickel(II) complexes exhibit as many as three consecutive oxidations in the regions around 0.8–0.9 V, 1–1.2 V, and 1.4–2 V and two reductions at ~–1.8 V and –2.5–2.9 V. These processes are illustrated in Figure 3. The low-energy oxidation process is assigned to the Ni^{2+}/Ni^{3+} couple.[13] The behavior

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(11) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122.
(12) Feltham, R. D.; Hayter, R. G. *J. Chem. Soc. A* **1964**, *4587*–4591.

Table II. Elemental Analyses for Monomeric Lacunar and Dimeric Bimetallic Complexes (PF_6 Salts)

		monomer						dimer					
		calcd			found			calcd			found		
bridge	R^2	C	H	N	C	H	N	C	H	N	C	H	N
$(CH_2)_4$	H	36.04	4.95	11.46	36.09	5.18	11.41	36.53[a]	5.20	11.11	36.20	5.10	11.26
$(CH_2)_5$	H	36.97	5.13	11.25	37.35	5.34	11.46	37.55[b]	5.19	11.86	37.31	5.23	11.84
$(CH_2)_6$	H	38.68	5.74	10.41	38.64	5.72	10.53	*c*					
$(CH_2)_7$	H	39.24[b]	5.51	11.44	38.97	5.62	11.50	38.73	5.46	10.84	38.51	5.56	10.72
$(CH_2)_8$	H	40.04[b]	5.66	11.24	40.31	5.97	11.05	39.56	5.62	10.65	39.67	5.41	10.67
C_7Fl	H	48.02	5.23	9.08	48.36	5.36	9.14	48.02	5.23	9.08	47.90	5.34	8.99
m-xyl	CH_3	41.55	4.98	10.38	41.48	5.02	10.40	*d*					
m-xyl	n-C_4H_9	45.05	5.97	9.22	45.71	5.87	9.41	*d*					
m-xyl	$C_6H_5CH_2$	49.97	5.03	8.74	49.63	5.24	8.71	*d*					
m-xyl	H	39.97	4.64	10.76	40.29	4.84	10.84	39.97	4.64	10.76	39.85	5.00	10.83
p-xyl	H	39.97	4.64	10.76	40.15	4.50	10.96	39.97	4.64	10.76	39.87	4.58	10.74
p-xyl	CH_3	41.56	4.98	10.38	41.90	5.37	10.18						

[a] Contains 0.5 mol of ethanol. [b] Contains 0.5 mol of CH_3CN. [c] Only very small amounts of dimer were isolated. [d] Only the monomeric species was found.

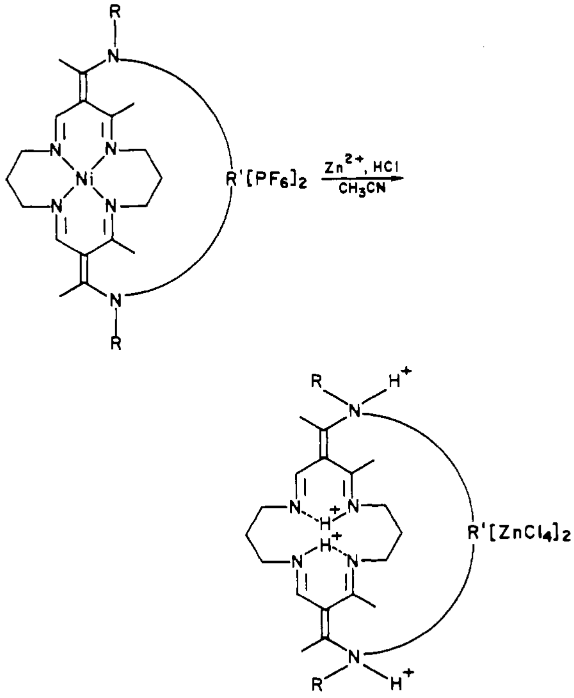
Table III. Onsager Parameters for Monomeric *lacunar*-Nickel(II) Complexes

compd	Λ_0, Ω^{-1} mol^{-1} cm^2	slope, Ω^{-1} mol$^{-1.5}$ cm$^{3.5}$
$[Ni((m\text{-xyl})(NHEthi)_2)Me_2[16]tetraeneN_4)](PF_6)_2$	153	449 ± 53
$[Ni((m\text{-xyl})(MeNEthi)_2)Me_2[16]tetraeneN_4)](PF_6)_2$	171	497 ± 45
$[Ni((p\text{-xyl})(NHEthi)_2)Me_2[16]tetraeneN_4)](PF_6)_2$	171	466 ± 35

of this process for the lacunar complexes is most informative. The homologous $CH_3N(CH_2)_nNCH_3$-bridged family of nickel(II) complexes all undergo oxidation at nearly the same potential,[5] $E_{1/2} = 0.771 \pm 0.013$ V, and the electrode processes are generally well-behaved. The other complexes listed in Table IV which have alkyl substituents, the $(NCH_3)_2(m\text{-xyl})$- and $(N\text{-}n\text{-Bu})_2(m\text{-xyl})$-bridged derivatives, show reversible oxidations at 0.780 and 0.790 V, respectively. Thus we take 0.78 V as the half-wave potential of N-alkyl lacunar complexes. Data are available on eight lacunar complexes in which the bridge nitrogen is otherwise unsubstituted (secondary nitrogen). These include the homologously bridged series $HN(CH_2)_nNH$ (n = 4–8), $(NH)_2C_7Fl$, $(NH)_2(m\text{-xyl})$, and $(NH)_2(p\text{-xyl})$. The values of $E_{1/2}$ for the Ni^{2+}/Ni^{3+} couple for the compounds having the $HN(CH_2)_nNH$ homologous bridge fall in the range 0.820–0.895 V, and the average is 0.849 ± 0.019 V. Two conclusions can be drawn from these comparisons. First, the saturated polymethylene bridge itself generally does not affect the electron density at the metal ion; second, the nature of the substituent on the bridge nitrogens is conveyed to the metal ion by electronic interactions. The electronic effect is probably associated with the π-electron system of the ligand and the planarity of the bridge nitrogens. Both conclusions are of significance to the uses of these ligands. The first requires that the effects of changing the bridge on the binding of small molecules by the cobalt or iron complexes are of steric origin and not electronic. The second conclusion suggests that the O_2 affinities and related chemical properties may be altered by changes in substituents. Since the electronic effect appears to be transmitted via the π-electron system, the effect may be much greater on iron(II) than nickel(II).[14,15] This suggests that the interaction between iron(II) and small molecules may be regulated both sterically and electronically by use of these ligands.

The behavior of the complexes containing aromatic groups appear to be exceptional. The first oxidation occurs at significantly higher potentials in the three cases $(NH)_2C_7Fl$, $(NH)_2(m\text{-xyl})$, and $(NH)_2(p\text{-xyl})$. The *p*-xylene case is extreme. Its first oxidation occurs at greater than 1.04 V, at least 0.16 V greater than the average for all the secondary amine-bridged species, and the process is highly irreversible. This emphasizes the unusual nature of this particular complex. It is also remarkably difficult to remove this ligand from the nickel(II) ion (see below). The source of these unusual properties is not apparent from the crystal structure.[1]

Removal of Ligands from Nickel(II). The complexes were synthesized with nickel(II) as the central metal ion for a number of reasons: (1) the synthesis of the parent macrocycle requires the use of nickel(II) as a template for the two macrocyclic ring closures; (2) the nickel(II) complexes are, for the most part, air stable and relatively easy to handle; (3) the nickel(II) complexes are readily characterized, particularly through the use of NMR techniques; (4) the ligands can be removed intact from nickel(II) and coordinated to other metal ions.[2,3] The ligand salts of the complexes were synthesized according to eq 2. The tetrachlorozincate salts of the ligands



(2)

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(13) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109–3118.

(14) Dabrowiak, J. C.; Merrell, P. H.; Stone, J. A.; Busch, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 6613–6622.

(15) Nakamoto, K. "Advances in the Chemistry of the Coordination Compounds"; MacMillan: New York, 1961; pp 437–446.

Table IV. Proton NMR and Carbon-13 NMR Data for Monomeric *lacunar*-Nickel(II) Complexes[a]

substituents[b]			proton NMR data				
R^1	R^2	R^3	methyl	methylene	aromatic	NH	^{13}C NMR Data
$(CH_2)_4$	H	CH_3	2.08, 2.40	1.8,[b] 3.27[b]	7.57	6.68[b]	[g]170.1, 168.4, 161.1, 111.3, 55.7, 50.5, 48.2, 32.0, 30.3, 27.3, 21.1, 20.9
$(CH_2)_5$	H	CH_3	2.14, 2.39	1.7,[b] 3.3[b]	7.53	7.00[b]	170.6, 169.2, 160.4, 111.5, 56.8, 51.3, 49.2, 31.5, 30.3, 22.7, 21.5, 20.6
$(CH_2)_6$	H	CH_3	2.10, 2.45	1.53,[b] 3.3[c]	7.60	6.75[b]	169.5, 169.0, 161, 109.7, 56.8, 51.4, 48.9, 31.0, 30.7, 27.9, 23.8, 21.9, 21.3
$(CH_2)_7$	H	CH_3	2.10, 2.41	1.53,[b] 1.64,[b] 3.26[b]	7.56	6.8[b]	170.5, 167.9, 160.2, 109.1, 56.3, 51.0, 48.4, 30.4, 30.1, 29.5, 25.3, 20.9, 20.3
$(CH_2)_8$	H	CH_3	2.19, 2.33	1.75,[b] 2.36, 3.3[c]	7.6	6.6[b]	
C_7Fl	H	CH_3	1.72, 2.32	1.1,[b,d] 2.2,[b] 3.4[b]	7.5,[b] 7.67, 7.9[b]	6.7[b]	168.6, 168.0, 160.8, 150.3, 149.6, 143.2, 142.0, 128.9, 128.7, 128.6, 128.3, 123.9, 121.1, 113.3, 56.1, 55.8, 51.5, 43.8, 35.2, 30.6, 30.2, 23.7, 21.2, 14.4
m-xyl	CH_3	CH_3	2.08, 2.45, 3.63	3.15,[c] 4.68	7.00, 7.08, 7.22		174.5, 166.9, 159.2, 137.7, 130.6, 126.9, 125.3, 113.6, 62.2, 56.4, 52.0, 45.8, 30.5, 29.8, 20.9, 20.6
m-xyl	*n*-C_4H_9	CH_3	0.97, 2.05, 2.47	3.12,[b] 3.83,[b] 4.68	7.10,[c] 7.17		174.0, 166.3, 158.9, 137.4, 130.4, 126.4, 125.2, 113.9, 59.8, 57.2, 56.6, 52.0, 30.4, 29.9, 20.9, 20.6, 13.9
m-xyl	$C_6H_5CH_2$	CH_3	1.95, 2.67	3.0,[b] 4.58,[e] 5.07[e]	6.90, 7.00, 7.30		173.5, 167.1, 159.7, 137.1, 135.2, 130.4, 130.3, 130.2, 129.9, 126.7, 125.2, 114.4, 60.2, 58.9, 56.7, 52.1, 30.3, 29.7, 21.1, 20.8
m-xyl	H	CH_3	2.20, 2.38	3.3,[b] 4.74[d]	7.32, 7.43, 7.69	6.5[b]	[g]170.7, 164.3, 161.8, 140.5, 130.0, 127.3, 124.0, 114.5, 55.2, 50.7, 47.7, 30.5, 30.1, 20.7, 14.4
p-xyl	H	CH_3	2.02, 2.43	3.23,[d] 4.51	7.03, 7.18, 7.43	*f*	168.2, 165.6, 161.4, 135.7, 128.9, 127.4, 111.9, 56.4, 51.7, 50.6, 30.1, 29.8, 23.6, 22.2
p-xylene	H	CH_3	2.07, 2.50, 3.52	3.05,[c] 4.72	6.98, 7.15, 7.57		[b]167.9, 167.4, 161.0, 135.0, 127.8, 127.5, 113.8, 62.0, 56.0, 51.7, 45.4, 30.2, 29.3, 23.0, 19.3

[a] CD_3CN solution, relative to Me_4Si. [b] Broad. [c] Multiplet. [d] May contain solvent (C_2H_5OH). [e] Quartet. [f] NH not observed. [g] CD_3NO_2 solution.

which result from this treatment were impure in many cases and very difficult to characterize. However, the characterization of several salts is reported here. It should be emphasized that even poorly characterized ligand salts give pure metal complexes in many cases. There are several disadvantages inherent in the use of a tetrachlorozincate as a counterion. The compounds in general are water sensitive, difficult to recrystallize, and pose synthetic difficulties in further reactions as the zinc ion can compete with other metal ions for coordination by the macrocycle. Because of these problems, several of the ligand salts were metathesized with the use of ammonium hexafluorophosphate. The resulting compounds were white to off-white granular materials generally yielding good analytical and spectroscopic data. In particular, the ligands derived from the monomeric $(NH)_2$(*m*-xyl), $(NH)_2$(*p*-xyl), and $(NMe)_2(CH_2)_6$ bridges were studied in detail.

The ligands were removed from Ni^{2+} in acetonitrile with hydrogen chloride gas, the solution showing the deep blue color of the concomitantly formed tetrachloronickelate anion within 30 min. The $(NH)_2$(*p*-xyl) monomer had to be left in a solution saturated with hydrogen chloride for 2 days before ligand removal was essentially complete. Another exception involves the monomeric and dimeric $(NH)_2$(*m*-xyl) species. The monomeric ligand salt remained in solution upon addition of the tetrachlorozincate solution whereas the dimeric product precipitated immediately. The monomeric ligand salt was isolated by rotary evaporation of the HCl/acetonitrile solution. The other free ligand salts precipitated immediately upon addition of the tetrachlorozincate solution.

Acceptable elemental analyses were obtained for the ligands derived from the monomeric $(NH)_2$(*m*-xyl)- and $(NMe)_2$(*m*-xyl)-bridged complexes as tetrachlorozincate salts and for the ligands derived from the monomeric $(NH)_2$(*m*-xyl)- and $(NH)_2$(*p*-xyl)-bridged complexes as hexafluorophosphate salts. Infrared spectra show the presence of broad N–H stretches which are undoubtedly due to hydrogen bonding either to solvent molecules or to other ligands. The rest of the IR spectrum shows few features except in the vicinity of 1600 cm^{-1} and the typical bands due to hexafluorophosphate.

Proton NMR spectra were measured for the hexafluorophosphate ligand salts of the monomeric $(NH)_2$(*m*-xyl)-, $(NH)_2$(*p*-xyl)-, and $(NMe)_2(CH_2)_6$-bridged species, and the data are summarized in Table VI. The most interesting feature of these spectra is the N–H resonance in the vicinity of 10–11 ppm. The remainder of the spectra are shifted relative to the respective nickel(II) complexes, but their assignments are in support of the structures.

Carbon-13 NMR spectra were also recorded for several of the ligands and are included in Table VI. The general patterns of the spectra are very similar to those of the corresponding nickel(II) complexes with each exhibiting mirror symmetry. The range of resonances observed for a given carbon atom with different bridges is much larger than that observed for the nickel(II) complexes, indicating that in the absence of structural constraints imposed by the metal ion the ligand distortions become more pronounced with changes in the bridging group.

It is an interesting fact that the monomeric $(NH)_2$(*m*-xyl) ligand spectrum shows simple mirror symmetry, and yet the spectrum of the nickel(II) compound regenerated from it is rather complex. The cause of this must be isomerization in the nickel(II) complex which has a rate of interchange that is slow on the NMR time scale. Such an isomerization could be between the *lid-on* and *lid-off* conformers, but this has not been verified. It is also possible for the xylyl ring to assume two distinctly different orientations, one centered over the metal, the other centered over the side chains of the macrocycle.

Table V. Electrochemical Data for the *lacunar*-Nickel(II) Complexes (CH_3CN Solution, 0.1 N $(n\text{-Bu})_4N\,BF_4$ Supporting Electrolyte, $Ag/AgNO_3$ (0.1 N) Reference Electrode)

ligand (structure I)		oxidation				reduction			
R^1	R^2	$E_{1/2}$, V	Δ_1,[a] mV	E_p, V	Δ_2,[a] mV	$E_{1/2}$, V	Δ_1,[a] mV	E_p, V	Δ_2,[a] mV
$(CH_2)_4$	CH_3	0.77	60	0.79	60	−1.98	70	−2.0	70
		1.07	60	1.12	120			−2.3[h]	
								−2.7	
$(CH_2)_5$	CH_3	0.76	60	0.785	60	−1.92	60	−1.93	90
		1.12	70	1.135	60	−2.41	80	−2.26[n]	80
								~−2.75	
$(CH_2)_6$	CH_3	0.775	67	0.805	65	−1.915	68	−1.94	66
		1.115	69	1.15	74	−2.81	*e*	−2.85[d]	
$(CH_2)_7$	CH_3	0.74	70	0.78	70	−1.90	70	−1.93	80
		1.11	60	1.135	60	−2.45	80	−2.3[n]	100
				~1.6	90			−2.46	
$(CH_2)_8$	CH_3	0.78	80	0.80	70	−1.90	80	−1.95[h]	
		1.20	80	1.23	100	−2.65[d]	90	−2.86	110
				1.60	110				
$(CH_2)_4$	H	0.84	71	0.88	71	−1.945[e]	77	−1.99[b]	157
		1.185	82	1.20[b]	63	−2.56[e]	75	*e*	
		d		1.92	75				
$(CH_2)_5$	H	0.85	70	0.885	78	*d*		−1.93	*e*
		1.16	88	1.17	65	*d*		−2.87	100
$(CH_2)_6$	H	0.895	76	0.925	78	−1.88	92	−1.92	87
		1.18	83	1.225	95	−2.78	*e*	−2.74[d]	
		1.97	175	2.01	205				
$(CH_2)_7$	H	0.82	60	0.90	60	−1.92	155	1.99[b]	260
		1.15	85	1.2[b,d]	90				
$(CH_2)_8$	H	0.84	86	0.87	70	−1.93	50	−1.97	150
		1.14	60	1.17	80	−2.52	90	−2.80[n]	120
C_7Fl	H	0.94	65	0.97	77	−1.885	70	−1.91	75
		c		1.22	78	−2.66	50	−2.54	70
		c		1.38[b]	50	*d*		−2.81	*d*
m-xyl	CH_3	0.78	70	0.83	82	−1.82	68	−1.86	80[b]
		h		1.025	65[b]	−2.37	95	−2.18	50
				1.18					
m-xyl	$n\text{-}C_4H_9$	0.79	60	0.82	70	−1.84	75	−1.85	70
		h		0.98[b,i]	50	*c*		−2.08[b]	55
		h		1.15	*j*				
m-xyl	$C_6H_5CH_2$-	0.82	70	0.85	70	−1.75	85	−1.25[b]	*d*
		h		1.02[b,k]	70	−2.27	*g*	−2.08[b]	50
		h		1.15	*l*				
m-xyl	H	0.925	67	0.97	87	−1.85	90	−1.87[b]	*d*
		1.14	130	1.3[b,g]		−2.47	80	−2.46[b]	*d*
						−2.97	*d*	−2.78[b]	*d*
p-xyl	H	*c, m*		1.05[b]	55	−1.47	60	−1.46[b]	70
						−1.94	80	−1.90[b]	50
						−2.58	*d*	−2.35	70
p-xyl	CH_3	0.81	60	0.84	70	−1.92	50	−1.95	60
		1.13	60	1.14	70	−2.29	100	−2.23	70
		d						−2.77	>150

[a] RPE scan rate 5 mV s^{-1}; CV scan rate 50 mV s^{-1}; $\Delta_1 = |E_{3/4} - E_{1/4}|$ from RPE; $\Delta_2 = |E_p - E_{p/2}|$ from CV. [b] No counterpeak observed in CV. [c] Continued scan produced electrode inhibition (RPE). [d] Irregular or ill-defined wave. [e] Peak is a shoulder. [f] Further reduction is scan-rate dependent. [g] Adsorption is observed. [h] Waves overlap. [i] Follow-up reaction peak at −0.09 V. [j] Peak too small to determine $E_{p/2}$, but peak separation is 70 mV. [k] Follow-up reaction peak at −0.06 V. [l] Peak is too small to determine $E_{p/2}$, but peak separation is 50 mV. [m] Potential is >1.04 V. [n] Peak does not correspond to process seen in RPE.

Table VI. Proton NMR and ^{13}C NMR Data for Monomeric Lacunar Ligand PF_6 Salts

		proton NMR chemical shifts[a]				
bridge	R^2	methyl	methylene	aromatic	NH	^{13}C chemical shifts[a]
m-xyl	H	2.05, 2.37	3.75,[c] 4.15,[c] 4.75	6.37, 7.30[c]	7.82[b]	176.2, 172.4, 156.9, 138.3, 130.6, 127.2, 120.5, 106.2, 54.1, 52.4, 48.2, 27.9, 24.2, 20.7, 15.1
p-xyl	H	2.28, 2.60	3.6,[b] 4.40, 4.70[c]	6.95, 7.20, 7.78	9.05,[b] 10.55	174.9, 160.2, 134.6, 127.8, 126.2, 104.0, 52.3, 50.9, 49.5, 27.6, 24.3, 23.4, 22.3
$(CH_2)_6$	CH_3	2.20, 2.58, 3.62	1.30,[b] 3.75[b]	9.70, 9.95	8.3,[b] 11.1[b]	183.0, 174.2, 156.3, 100.0, 60.0, 52.1, 47.8, 43.4, 28.4, 26.5, 26.1, 24.8, 23.8, 20.3

[a] CD_3CN solution; ppm relative to Me_4Si. [b] Broad. [c] Multiplet.

It is reassuring to note that in the case of the $(NH)_2$(*m*-xyl) bridge, the monomeric and dimeric species retain their integrity and do not interconvert during ligand removal. This has been confirmed by experiments in which the ligand was removed from and put back onto nickel(II) with no change in properties or spectra.

Experimental Section

Measurements. Proton NMR spectra were measured at 60 MHz on either a Varian A-60-A or EM-360L spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP-80 or HX90 spectrometer operating in the Fourier transform mode using either broad-band or off-resonance proton decoupling.

Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and Chemalytics, Inc., Tucson, Az. Many nitrogen analyses were performed in these laboratories with use of a Coleman Model 29 nitrogen analyzer.

Conductance measurements were obtained with an Industrial Instruments, Inc., Model RC 16B conductivity bridge on solutions of about 10^{-3} molarity. Electronic spectra were measured on a Cary Model 17D recording spectrophotometer using matched 1-cm quartz cells. Infrared spectra were obtained with either a Perkin-Elmer 337 or 457 infrared spectrophotometer. Nujol mulls were prepared on a 1:1 sample, and the region from 4000 to 400 cm^{-1} was scanned. Mass spectra were obtained with an MS-9 mass spectrometer at 70 eV.

Electrochemical measurements were performed with either an Indiana Instrument and Chemical Corp. controlled-potential and derivative voltmeter, Model ORN-1988A, with a Hewlett-Packard/Moseley Division X-Y recorder or a Princeton Applied Research Model 173 potentiostat/galvanostat and Model 175 Universal Programmer with a Houston Instrument Omnigraphic^R 2000 recorder. All measurements were made on DMF solutions containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte. An H-type polarographic cell was employed. The working electrode was a platinum-disk electrode formed from the sealing of an 18–20-gauge platinum wire into soft glass. The reference electrode was a silver wire immersed in a 0.1 M DMF solution of silver nitrate. All measurements were made in a Vacuum Atmospheres controlled-atmosphere chamber containing nitrogen.

Molecular weights were determined with a Mechrolab, Inc., vapor pressure osmometer, Model 301A.

(3,11-Diacetyl-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato-N^1,N^5,N^9,N^{13})nickel(II) ([Ni(Ac$_2$Me$_2$[16]tetraenatoN$_4$)]). The complex was synthesized according to the published procedure.[16]

(2,12-Dimethyl-3,11-bis(1-methoxyethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-N^1,N^5,N^9,N^{13})nickel(II) Hexafluorophosphate ([Ni((MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$), (2,12-Dimethyl-3,11-bis(1-(methylamino)ethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-N^1,N^5,N^9,N^{13})nickel(II) Hexafluorophosphate ([Ni((MeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$), (2,12-Dimethyl-3,11-bis(1-(*n*-butylamino)ethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-N^1,N^5,N^9,N^{13})nickel(II) Hexafluorophosphate ([Ni((*n*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$), and (2,12-Dimethyl-3,11-bis(1-(benzylamino)ethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-N^1,N^5,N^9,N^{13})nickel(II) Hexafluorophosphate ([Ni((BZNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$): These four compounds were prepared by the procedures reported previously.

Systems Involving Four- and Five-Carbon Bridges. Monomeric (2,9,11,17-Tetramethyl-3,8,12,16,19,23-hexaazabicyclo[8.7.7]tetracosa-1,9,11,16,18,23-hexaene-κ^4N)nickel(II) Hexafluorophosphate ([Ni((CH$_2$)$_4$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$) and Dimeric (2,9,11,17,19,26,28,34-Octamethyl-3,8,12,16,20,25,29,33,36,40,43,47-dodecaazatricyclo[15.7.7.7^{10,18}]octatetraconta-1,9,11,16,18,26,28,33,35,40,42,47-dodecaene-κ^8N)dinickel(II) Hexafluorophosphate ([Ni$_2$((CH$_2$)$_4$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$), Monomeric (2,10,19,25-Tetramethyl-3,9,13,17,20,24-hexaazabicyclo[9.7.7]pentacosa-1,10,12,17,19,24-hexaene-κ^4N)nickel(II) Hexafluorophosphate and Dimeric (2,10,12,18,20,28,30,36-Octamethyl-3,9,13,17,21,27,31,35,38,42,45,49-dodecaazatricyclo[27.7.7^{11,19}]pentaconta-1,10,12,17,19,28,30,35,37,42,44,49-dodecaene-κ^8N)dinickel(II) Hexafluorophosphate ([Ni$_2$((CH$_2$)$_5$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$). These pentamethylene- and tetramethylene-bridged complexes and the corresponding dimers were prepared by closely similar procedures. The synthesis is described below for the pentamethylene case; for the tetramethyl case, one need only substitute 1,4-diaminobutane for 1,5-diaminopentane.

A solution of 1.44 g of 1,5-diaminopentane (14 mmol) in 500 mL of acetonitrile was added slowly, dropwise, over a 3-h period with stirring to a solution of [Ni((MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (10 g, 14 mmol) in 500 mL of acetonitrile. During the course of the addition, the color of the solution changed from yellow-green to deep yellowish brown. The volume of the solution was reduced to about 30 mL by rotary evaporation keeping the bath temperature at about 30 °C. The resulting solution was loaded onto an alumina column (2.5 cm × 20 cm) and was eluted with acetonitrile. The yellow band was collected, leaving a dark brown band near the top of the column. After the volume of the eluate was reduced to about 30 mL, the product was precipitated by slow addition of ethanol and reduction of the volume on the rotary evaporator; yield 8.7 g (82%). The product consisted of an approximately 1:1 mixture of two isomers, as determined by high-performance liquid chromatography and ^{13}C NMR. The two isomers were separated by fractional crystallization as follows: 8–10 g of the nickel complex was dissolved in 40 mL of acetonitrile. Absolute ethanol was slowly added to incipient cloudiness (about 150 mL). The solution was put in the refrigerator for about 3 days during which time fraction I crystallized and was collected. To the filtrate was added 50 mL of absolute ethanol, and the solution was returned to the refrigerator for another 3 days. Fraction II precipitated and was collected. Finally the volume of the filtrate was reduced to about 50 mL by rotary evaporation, and fraction III was collected. Fractions I and III contained pure dimer and monomer, respectively, while fraction II was usually a mixture and could be resubjected to the fractional crystallization procedure. The isomeric purity of the complexes could be determined by high-performance liquid chromatography or ^{13}C NMR.

(2,11,20,26-Tetramethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-κ^4N)nickel(II) Hexafluorophosphate ([Ni((CH$_2$)$_6$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$). To a solution of 20 g of [Ni((MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ (28 mmol) in 1 L of acetonitrile was added, dropwise with stirring, a solution of 3.3 g (28 mmol) of 1,6-hexanediamine in 1 L of acetonitrile. The resultant red solution was taken to dryness on a rotary evaporator and the residue redissolved in 25 mL of acetonitrile. This solution was chromatographed on a column of Woelm neutral alumina (2.5 cm × 20 cm), eluting with acetonitrile. The yellow band was collected, and the solvent was removed by rotary evaporation. The residue was slurried with ethanol, and the product was isolated by suction filtration, washed with ether, and dried in vacuo; yield 19 g (90%).

The crude product contains very small amounts of dimer (<5%) which can be separated and identified by ion exchange on CM-Sephadex as described for the heptamethylene- and octamethylene-bridged species.

Systems Involving Seven- and Eight-Carbon Bridges. Monomeric (2,12,14,20-Tetramethyl-3,11,15,19,22,26-hexaazabicyclo[11.7.7]heptacosa-1,12,14,19,21,26-hexaene-κ^4N)nickel(II) Hexafluorophosphate ([Ni((CH$_2$)$_7$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$) and Dimeric (2,12,14,20,22,32,34,40-Octamethyl-3,11,15,19,23,31,35,39,42,46,49,53-dodecaazatricyclo[31.7.7^{13,21}]tetrapentacosa-1,12,14,19,21,32,34,39,41,46,48,53-dodecaene-κ^8N)dinickel(II) Hexafluorophosphate ([Ni$_2$((CH$_2$)$_7$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$), Monomeric (2,13,15,21-Tetramethyl-3,12,16,20,23,27-hexaazabicyclo[12.7.7]octacosa-1,13,15,20,22,27-hexaene-κ^4N)nickel(II) Hexafluorophosphate ([Ni((CH$_2$)$_8$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$) and Dimeric (2,13,15,21,23,34,36,42-Octamethyl-3,12,16,20,24,33,37,41,44,48,51,55-dodecaazatricyclo[33.7.7^{14,22}]hexapentacosa-1,13,15,20,22,34,36,41,43,48,50,55-dodecaene-κ^8N)dinickel(II) Hexafluorophosphate ([Ni$_2$((CH$_2$)$_8$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$). The procedure is essentially the same for the two sets of isomers. It is presented here for the heptamethylene case. Two solutions, one containing 5.0 g (7.05 mmol) of [Ni((MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ in 500 mL of acetonitrile and the other containing 1.0 g (7.76 mmol) of $NH_2(CH_2)_7NH_2$ in 500 mL of acetonitrile, were added very slowly to a vigorously stirred solution that was initially 500 mL of acetonitrile solvent. The product was chromatographed on a column of Woelm neutral alumina (2.5 cm × 20 cm), eluting with acetonitrile. The yellow band was collected, and the solvent was removed by rotary evaporation. The residue was slurried with ethanol, and the product was isolated by suction filtration, washed with ether, and dried in vacuo; yield 2.3 g (41%).

To a solution of 2.0 g of the mixture of isomers (prepared as described above), dissolved in 20 mL of acetone, was added a solution of 2.5 g of tetra-*n*-butylammonium chloride in 15 mL of acetone. The yellow powder was collected by filtration and then dissolved in water and loaded onto CM-Sephadex by passing the solution through a small column (ϕ 1 × 5 cm). The loaded resin was then transferred to the top of a larger CM-Sephadex column (ϕ 3 × 30 cm), and elution was begun with 0.2 M aqueous Na_2SO_4. The column showed two separate yellow bands whose ratio appeared to be about 10:1. The effluent

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[16] Riley, D. P.; Busch, D. H. *Inorg. Synth.* **1978**, *18*, 36–44.

due to the fast moving band was collected, and 1.5 g of NH_4PF_6, dissolved in 50 mL of water, was added. The precipitated hexafluorophosphate salt (monomer) was filtered and recrystallized from acetonitrile/ethanol; yield 1.4 g.

The second band was not easily eluted by dilute Na_2SO_4 solution but remained near the top of the column. The concentration of the eluant was raised to 0.4 M in Na_2SO_4, and four yellow bands developed in the column. The predominant band (second from bottom) was collected. Hexafluorophosphate was used to precipitate the cation, and a yield of 0.04 g of dimer was obtained. The minute amounts of substances in the other bands were not isolated. The yield of dimer could be increased by carrying out the ring closure at higher concentration.

The octamethylene derivatives were prepared and separated by a closely similar procedure; yields 35% (monomer), 3–4% (dimer).

System Containing the 9,9-Bis(3-aminopropyl)fluorene Bridge. Monomeric (2,12,14,20-Tetramethyl-3,11,15,19,22,26-hexaazapentacyclo[11.7.7.$4^{7,7}$.$4^{28,29}$.$4^{30,31}$]nonatriconta-1,12,14,19,21,26,28(29),30(31),32,34,36,38-dodecaene-κ^4N)nickel(II) Hexafluorophosphate ($[Ni((C_7Fl)(NHEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$) and Dimeric (2,12,14,20,22,32,34,40-Octamethyl-3,11,15,19,23,31,35,39,42,46,49,53-dodecaazadecacyclo[31.7.$7^{13,21}$.$4^{7,7}$.$4^{27,27}$.$4^{55,56}$.$4^{57,58}$.$4^{67,68}$.$4^{69,70}$]octaheptaconta-1,12,14,19,21,32,34,39,41,46,48,53,55(56),57(58),59,61,63,65,67(68),69(70),71,73,75,77-tetracosaene-κ^8N)dinickel(II) Hexafluorophosphate ($[Ni_2((C_7Fl)(NHEthi)_2Me_2[16]tetraeneN_4)_2](PF_6)_4$). The bridging diamine, 9,9-bis(3-aminopropyl)fluorene, was first converted to the dihydrochloride salt. Twenty grams of ligand was dissolved in $CHCl_3$ and filtered and the solvent removed by evaporation. The residual oil was redissolved in 200 mL of 6 M HCl, evaporated to dryness, dissolved in 250 mL of EtOH, and filtered. Ether was added to the filtrate until incipient precipitation. The solution was then cooled overnight, and the white-brown precipitate was subsequently collected by filtration, washed with ether, and dried in vacuo; yield 20 g (80%).

The ring closure was accomplished as follows. The diamine hydrochloride (5.051 g) was dissolved in 50 mL of ethanol and neutralized with ethoxide (0.657 g of Na dissolved in 25 mL of ethanol); NaCl separated and was filtered after stirring for 30 min. The solution was diluted with 900 mL of CH_3CN and added dropwise to 10.14 g of $[Ni((MeOEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$ in 1 L of CH_3CN. After the addition was complete, the yellow-orange solution was reduced in volume to a syrupy mass which was redissolved in 70% CH_2Cl_2/30% CH_3CN (50 mL). The solution was passed through a neutral alumina column (14 × 4 cm, packed under CH_2Cl_2), eluting with 70% CH_2Cl_2/30% CH_3CN. The yellow-green band was collected (~200–300 mL). The solution was evaporated to 50–100 mL, and ethanol was added slowly until crystals began to form. After standing overnight, the solution was filtered, yielding the yellow-green crystalline product which was washed with ethanol and ether and dried in vacuo; yield 3.7 g. High-performance LC and ^{13}C NMR show the material to be isomerically pure (monomer).

Additional increments of ethanol were added to the filtrate, the solution was rotovaped to reduce its volume, and ethanol was again added to give a yellow precipitate which high-performance LC showed to be ~80–90% the second isomer (dimer). The yellow precipitate was dissolved in the minimum volume of CH_3CN, and ethanol was added until the solution appeared cloudy. After the solution cooled overnight, 0.46 g of impure monomer (70–80%) was isolated. The filtrate was reduced in volume and added to a stirred volume of ether (300 mL) to give a yellow powder that was collected, washed with ethanol and ether, and dried in vacuo; yield 3.41 g. High-performance LC showed the product to be isomerically pure (dimer).

High-performance LC is used with difficulty in this case. The isomers are not so well resolved, and the first band is some 5 times more intense than the second.

While the second isomer isolated has been labeled and named as a dimer, this is tenuous at best since these isomers do not behave precisely as do the well-established cases. Further, preliminary observations suggest that the second, more soluble isomer may convert into the more abundant form.

System Involving the *m*-Xylene Bridge. Monomeric (2,12,14,20-Tetramethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.7.$1^{5,9}$]octacosa-1,5,7,9(28),12,14,19,26-nonaene-κ^4N)nickel(II) Hexafluorophosphate ($[(Ni(m\text{-}xyl)(NHEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$) and Dimeric (2,12,14,20,22,32,34,40-Octamethyl-3,11,15,19,23,31,35,39,42,46,50,54-dodecaazapentacyclo[31.7.7.$7^{13,21}$.$1^{5,9}$.$1^{25,29}$]hexapentaconta-1,5,7,9(56),12,14,19,21,25,27,29(48),32,34,39,41,46,49,54-octadecaene-κ^8N)dinickel(II) Hexafluorophosphate ($[Ni_2((m\text{-}xyl)(NHEthi)_2)Me_2[16]tetraeneN_4)_2](PF_6)_4$). Ten grams (14.1 mmol) of $[Ni((MeOEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$ was dissolved in 750 mL of acetonitrile. To this solution was added a solution of 1.92 g (14.1 mmol) of *m*-xylylenediamine dissolved in 750 mL of acetonitrile over a period of 6 h. The yellow solution was rotary evaporated to 25 mL while maintaining a temperature of no greater than 30 °C in the heating bath. The solution was applied to a column (2.5 cm × 18 cm) of neutral Woelm alumina and was eluted with acetonitrile, giving a single yellow band. The solution volume was again reduced at 30 °C, and ethanol was added to yield the yellow product which was isolated and dried in vacuo; yield 6.8 g (62%).

The above product was shown by high-performance LC to be a mixture of two products (monomer and dimer) which were separated as follows. Six grams (7.7 mmol) of the mixture was dissolved in 100 mL of acetonitrile. To this solution was added 500 mL of ethanol, causing a slight cloudiness. The solution was refrigerated for 30 h to yield a yellow precipitate which was collected and dried in vacuo; yield 3.21 g (54%). This fraction was shown by high-performance LC to be primarily the dimeric species.

The volume of the filtrate from above was reduced by approximately one-third to yield a yellow precipitate which was collected after cooling in a refrigerator overnight. The product was washed with ethanol and dried in vacuo; yield 2.5 g (42%). This was shown by high-performance LC to be a very pure sample of the monomeric species.

If the above reaction is carried out in refluxing acetonitrile rather than at room temperture, the product is essentially pure monomer on the basis of high-performance LC analysis.

(2,11,13,19-Tetramethyl-3,10,14,18,21,25-hexaazatricyclo[10.7.7.$2^{5,8}$]octacosa-1,5,7,11,13,18,20,25,27-nonaene-κ^4N)nickel(II) Hexafluorophosphate ($[Ni((p\text{-}xyl)(NHEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$) and (2,11,13,19,21,30,32,38-Octamethyl-3,10,14,18,22,29,33,37,40,44,47,51-dodecaazapentacyclo-[29.7.7.$7^{12,20}$.$2^{5,8}$.$2^{24,27}$]hexapentaconta-1,5,7,11,13,18,20,24,26,30,32,37,39,44,46,51,53,55-octadecaene-κ^8N)dinickel(II) Hexafluorophosphate ($[Ni_2((p\text{-}xyl)(NHEthi)_2Me_2[16]tetraeneN_4)_2](PF_6)_4$). To a suspension of 2.36 g (11.3 mmol) of *p*-xylylenediamine dihydrochloride in 100 mL of ethanol was added 0.55 g (23.9 mmol) of sodium metal. After 2 h of stirring, the sodium chloride was filtered off and the filtrate was diluted to 500 mL with acetonitrile. A second solution was prepared containing 8.0 g (11.3 mmol) of $[Ni((MeOEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$ dissolved in 500 mL of acetonitrile. These two solutions were added simultaneously to 500 mL of refluxing acetonitrile over a period of 7 h. The resulting yellow solution was evaporated to dryness, and the residue was dissolved in 30 mL of acetonitrile. The solution was applied to a column of neutral Woelm alumina (2.5 cm × 25 cm) and was eluted very slowly with acetonitrile. The product was collected as two fractions from the column, the first as a yellow-green band and the second as a broad yellow band. The volumes of both fractions were reduced and ethanol added to yield the solid yellow products. Proton NMR showed fraction I to be primarily the dimeric species and fraction II the monomer; yield of dimer 0.7 g (8%), yield of monomer 3.1 g (35%). When this synthesis was carried out at room temperature rather than at reflux, the yields of monomer and dimer were more nearly equal but the overall yield was about the same.

(2,3,11,12,14,20-Hexamethyl-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 ($[Ni((m\text{-}xyl)(MeNEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$). To a solution of 5.0 g (7.1 mmol) of $[Ni((MeNHEthi)_2Me_2[16]tetraeneN_4)](PF_6)_2$[17] dissolved in 500 mL of acetonitrile was added a solution prepared by the reaction of 0.34 g (14.9 mmol) of sodium metal with 10 mL of methanol. The solution was heated to reflux, and a solution containing 1.87 g (7.1 mmol) of α,α'-dibromo-*m*-xylene dissolved in 250 mL of acetonitrile was added dropwise over a period of 4 h. After the solution was cooled and filtered, the volume was reduced to 20 mL and the product was chromatographed on a column of neutral Woelm alumina (25 cm × 2.5 cm), eluting with acetonitrile. The yellow band was collected, the volume reduced, and ethanol added to yield the yellow crystalline product which was collected and dried in vacuo; yield 4.3 g (75%).

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[17] Schammel, W. P.; Zimmer, L. L.; Busch, D. H. *Inorg. Chem.* **1980**, *19*, 3159–3167.

(3,11-Di-*n*-butyl-2,12,14,20-tetramethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.9.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene-κ^4*N*)nickel(II) Hexafluorophosphate ([Ni((*m*-xyl)(*n*-BuNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$). Three grams (4.0 mmol) of [Ni((*n*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)]I$_2$[17] was dissolved in 500 mL of methanol and heated to reflux. To this solution was added a solution prepared by the reaction of 0.19 g (8.3 mmol) of sodium metal with 10 mL of methanol. A solution of 1.26 g (4.8 mmol) of α,α'-dibromo-*m*-xylene dissolved in 250 mL of methanol was added very slowly to the first solution over a period of 5 h, during which time the color changed from deep red to yellow-orange. When the addition was complete, the volume was reduced to 100 mL, and 3.5 g (21.5 mmol) of ammonium hexafluorophosphate in 25 mL of methanol was added. An orange product formed and was collected. This product was dissolved in 25 mL of acetonitrile and passed through a column of neutral Woelm alumina (2.5 cm × 25 cm), eluting with acetonitrile. The major yellow band was collected, the volume reduced, and ethanol added. Further volume reduction yielded the yellow-orange product which was isolated and dried in vacuo.

(3,11-Dibenzyl-2,12,14,20-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^4*N*)nickel(II) Hexafluorophosphate ([Ni((*m*-xyl)(BZNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$). To a solution of 1.8 g (2.2 mmol) of [Ni((BZNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)]I$_2$[17] in 400 mL of methanol was added a solution prepared by the reaction of 0.11 g (4.8 mmol) of sodium metal with 10 mL of methanol. The solution became deep red in color and was heated to reflux. A solution of 1.1 g (4.2 mmol) of α,α'-dibromo-*m*-xylene dissolved in 250 mL of methanol was added dropwise to the above solution. During the addition, the solution became yellow-orange. When the addition was complete, the solution was cooled and the volume was reduced to 100 mL. Three and one-half grams (21.5 mmol) of ammonium hexafluorophosphate in methanol was added to yield a yellow precipitate. The product was dissolved in 10 mL of acetonitrile and passed through a column of neutral Woelm alumina (2.5 cm × 10 cm), eluting with acetonitrile. The yellow band was collected, the solution volume was reduced, and ethanol was added to yield a yellow crystalline product which was isolated and dried in vacuo; yield 1.0 g (47%).

2,3,11,12,14,20-Hexamethyl-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 Tetrachlorozincate ([(*m*-xyl)(MeNEthi)$_2$Me$_2$[16]tetraene](ZnCl$_4$)$_2$). Hydrogen chloride gas was bubbled through a solution of 1.5 g (1.9 mmol) of [Ni((*m*-xyl)(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ dissolved in 50 mL of acetonitrile until the solution turned blue. Slow addition of a solution of tetrachlorozincate anion (prepared by reaction of 0.75 g (11.5 mmol) of granular zinc metal with hydrogen chloride gas in 50 mL of acetonitrile) resulted in formation of a white precipitate). This ligand salt was filtered, washed with acetonitrile and ether, and dried in vacuo; yield 1.40 g (78%). Anal. Calcd for C$_{28}$H$_{44}$N$_6$Zn$_2$Cl$_8$: C, 38.26; H, 5.04; N, 9.56. Found: C, 39.34; H, 5.63; N, 10.33.

2,12,14,20-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 Tetrachlorozincate ([(*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](ZnCl$_4$)$_2$). The same procedure was used as described in previous synthesis with use of 3.0 g (3.8 mmol) of [Ni((*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ and 1.5 g (23.1 mmol) of zinc metal. No precipitate formed upon addition of the tetrachlorozincate solution. The solution volume was reduced and fresh acetonitrile added several times, resulting in the formation of the white, granular ligand salt which was collected, washed with acetonitrile, and dried in vacuo; yield 2.25 g (69%). Anal. Calcd for C$_{26}$H$_{40}$N$_6$Zn$_2$Cl$_8$: C, 36.70; H, 4.74; N, 9.88. Found: C, 36.55; H, 5.07; N, 9.91.

2,12,14,20-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 Hexafluorophosphate ([(*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$). One gram (1.2 mmol) of [(*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](ZnCl$_4$)$_2$ was dissolved in 50 mL of water and filtered. A solution of 3.0 g (18.4 mmol) of ammonium hexafluorophosphate dissolved in 20 mL of water was added dropwise to yield the white granular solid which was collected and dried in vacuo; yield 0.74 g (72%). Anal. Calcd for C$_{26}$H$_{39}$N$_6$P$_3$F$_{18}$: C, 35.87; H, 4.52; N, 9.65. Found: C, 35.72; H, 4.75; N, 9.89.

2,11,13,19-Tetramethyl-3,10,14,18,21,25-hexaazatricyclo[10.7.7.2^{5,8}]octacosa-1,5,7,11,13,18,20,25,27-nonaene Hexafluorophosphate ([(*p*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$). Hydrogen chloride gas was bubbled through a solution of 4.0 g (5.1 mmol) of [Ni((*p*-xyl)(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ dissolved in 300 mL of acetonitrile. The flask was stoppered and set aside for 2 days during which time the solution turned green. A solution of tetrachlorozincate anion (prepared by the reaction of 4.0 g (61.5 mmol) of zinc metal with hydrogen chloride gas in 200 mL of acetonitrile) was added to yield the white tetrachlorozincate ligand salt which was collected, washed with acetonitrile, and dried in vacuo; yield 4.1 g (91%). The above product was dissolved in 100 mL of water and filtered. Dropwise addition of 10.0 g (61.3 mmol) of ammonium hexafluorophosphate dissolved in 50 mL of water resulted in formation of an off-white precipitate which was collected and dried in vacuo; yield 3.8 g (91%). Anal. Calcd for C$_{26}$H$_{39}$N$_6$P$_3$F$_{18}$: C, 35.87; H, 4.52; N, 9.65. Found: C, 33.94; H, 4.17; N, 9.21.

(2,3,10,11,13,19-Hexamethyl-3,10,14,18,21,25-hexaazatricyclo[10.7.7.2^{5,8}]octacosa-1,5,7,11,13,18,20,25,27-nonaene-κ^4*N*)nickel(II) Hexafluorophosphate ([Ni((*p*-xyl)(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$). To a solution of 6.7 g (9.5 mmol) of [Ni((MeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$ dissolved in 500 mL of acetonitrile was added a solution prepared by the reaction of 0.46 g (20.0 mmol) of sodium metal with 10 mL of methanol. A second solution of 2.50 g (9.5 mmol) of α,α'-dibromo-*p*-xylene dissolved in 500 mL of acetonitrile was prepared. The two solutions were added simultaneously to 500 mL of refluxing acetonitrile over a period of 7 h. After the solution was cooled and filtered, the volume was reduced to 20 mL and the product was chromatographed on a column of neutral Woelm alumina (25 cm × 2.5 cm), eluting with acetonitrile. The yellow band was collected, the volume reduced, and ethanol added to yield the yellow crystalline product which was collected and dried in vacuo; yield 5.2 g (68%). Anal. Calcd for [NiC$_{28}$H$_{40}$N$_6$P$_2$F$_{12}$]: C, 41.56; H, 4.98; N, 10.38. Found: C, 41.90; H, 5.37; N, 10.18.

2,3,10,11,13,19-Hexamethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene hexafluorophosphate ([(CH$_2$)$_6$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$) was reported earlier.[5]

2,3,8,9,11,17-Hexamethyl-3,8,12,16,19,23-hexaazabicyclo[8.7.7]tetracosa-1,9,11,16,18,23-hexaene Hexafluorophosphate ([(CH$_2$)$_4$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$). The yield was 4.12 g (71%). Anal. Calcd for C$_{24}$H$_{43}$N$_6$P$_3$F$_{18}$: C, 33.89; H, 5.10; N, 9.80. Found: C, 32.42; H, 5.21; N, 9.69.

2,3,9,10,12,18-Hexamethyl-3,9,13,17,20,24-hexaazabicyclo[9.7.7]pentacosa-1,10,12,17,19,24-hexaene Hexafluorophosphate ([(CH$_2$)$_5$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$). The yield was 0.5 g (68%).

2,3,10,11,19,25-Hexamethyl-3,10,14,17,20,24-hexaazabicyclo[10.7.6]hexacosa-1,11,13,17,19,24-hexaene Hexafluorophosphate ([(CH$_2$)$_6$(MeNEthi)$_2$Me$_2$[15]tetraeneN$_4$](PF$_6$)$_3$). The yield was 0.70 g (78%). Anal. Calcd for C$_{25}$H$_{45}$N$_6$P$_3$F$_{18}$: C, 34.77; H, 5.14; N, 9.73. Found: C, 34.10; H, 5.31; N, 10.02.

These ligand salts and most of the others can be prepared by slight modifications of the procedures described above.

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Registry No. [Ni((CH$_2$)$_4$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-09-9; [Ni$_2$((CH$_2$)$_4$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$, 77827-11-3; [Ni((CH$_2$)$_5$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-13-5; [Ni$_2$((CH$_2$)$_5$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$, 77827-15-7; [Ni((CH$_2$)$_6$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-17-9; [Ni$_2$((CH$_2$)$_6$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$, 77846-68-5; [Ni((CH$_2$)$_7$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-19-1; [Ni$_2$((CH$_2$)$_7$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$, 77827-21-5; [Ni((CH$_2$)$_8$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-23-7; [Ni$_2$((CH$_2$)$_8$(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$, 77827-25-9; [Ni((C$_7$Fl)(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-27-1; [Ni$_2$((C$_7$Fl)(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$, 77827-29-3; [Ni((*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-31-7; [Ni$_2$((*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$, 77827-33-9; [Ni((*p*-xyl)(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 70140-55-5; [Ni$_2$((*p*-xyl)(NHEthi)$_2$Me$_2$[16]tetraeneN$_4$)$_2$](PF$_6$)$_4$, 77827-35-1; [Ni((*m*-xyl)(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-37-3; [Ni((*m*-xyl)(*n*-BuNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77846-70-9; [Ni((*m*-xyl)(BZNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-39-5; [(*m*-xyl)(MeNEthi)$_2$Me$_2$[16]tetraene](ZnCl$_4$)$_2$, 77827-41-9; [(*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](ZnCl$_4$)$_2$, 77827-42-0; [(*m*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 77826-03-0; [(*p*-xyl)(NHEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 77826-05-2; [Ni((*p*-xyl)(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 77827-44-2; [(CH$_2$)$_6$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 76863-25-7; [(CH$_2$)$_4$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 77826-07-4; [(CH$_2$)$_5$(MeNEthi)$_2$Me$_2$[16]tetraene](PF$_6$)$_3$, 77846-61-8; [H$_3$(CH$_2$)$_6$(MeNEthi)$_2$Me$_2$[15]tetraeneN$_4$](PF$_6$)$_3$, 77846-63-0; [Ni((CH$_2$)$_4$(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 76800-64-1; [Ni((CH$_2$)$_5$(MeNEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 76791-39-4; [Ni((CH$_2$)$_6$(MeNEthi)$_2$Me[16]tetraeneN$_4$)](PF$_6$)$_2$, 73914-16-6; [Ni((CH$_2$)$_7$(MeNEthi)$_2$Me[16]tetraeneN$_4$)](PF$_6$)$_2$, 76791-37-2; [Ni((CH$_2$)$_8$(MeNEthi)$_2$Me[16]tetraeneN$_4$)](PF$_6$)$_2$, 76791-41-8; [Ni((MeOEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 70021-28-2; [Ni((MeNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)](PF$_6$)$_2$, 74466-02-7; [Ni((*n*-BuNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)]I$_2$, 77880-78-5; [Ni((BZNHEthi)$_2$Me$_2$[16]tetraeneN$_4$)]I$_2$, 77880-79-6; 1,4-diaminobutane, 110-60-1; 1,5-diaminopentane, 462-94-2; 1,6-hexanediamine, 124-09-4; NH$_2$(CH$_2$)$_7$NHz, 646-19-5; NH$_2$(CH$_2$)$_8$NH$_2$, 373-44-4; 9,9-bis(3-aminopropyl)fluorene, 2409-19-0; 9,9-bis(3-aminopropyl)fluorene dihydrochloride, 23328-59-8; *m*-xylylenediamine, 1477-55-0; *p*-xylylenediamine dihydrochloride, 51964-30-8; α,α′-dibromo-*m*-xylene, 626-15-3; α,α′-dibromo-*p*-xylene, 623-24-5.

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Synthesis of New 1-Halo-1-alkyltetrachlorocyclotriphosphazenes, Including the First Cyclophosphazenes with a P–I Bond[1]

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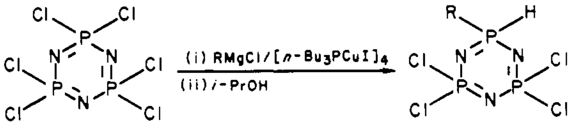
The syntheses of the first series of 1-halo-1-alkyltetrachlorocyclotriphosphazenes [halogen X = Cl (III), X = Br (IV), X = I (V)] are described, together with the structural characterization of these compounds. Compounds of type III are polymer precursors. Species of type V are the first examples of phosphazenes with a phosphorus–iodine bond. Surprisingly, the substitution reactions of these compounds with organic nucleophiles take place at a position geminal to the alkyl group.

Investigations into the chemistry of new cyclic phosphazenes are important for a number of reasons.[2,3] Small ring phosphazenes are of interest as "monomers" for the synthesis of new macromolecules,[4,5] as models for the reactions of high polymeric phosphazenes,[2,5] as polymerization initiators and mechanistic probes, and for studies related to the bonding within the phosphazene skeleton.[6]

In a recent paper[7,8] we described the synthesis of a new series of air- and moisture-sensitive cyclic phosphazenes (II) which contained a phosphorus–hydrogen bond. These compounds were synthesized via the reaction of hexachlorocyclotriphosphazene (I) with alkyl Grignard reagents in the presence of [*n*-Bu$_3$PCuI]$_4$, followed by treatment of the reaction intermediate with isopropyl alcohol.[8]

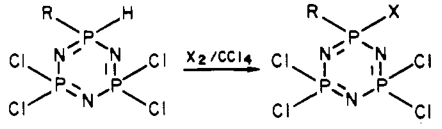


I II

The principal objectives of this present work were to answer the following questions. (1) Can the hydrogen atom bound to phosphorus in compound II (the apparent cause of the air and moisture instability of these molecules) be replaced by chlorine to yield monoalkylpentachlorocyclotriphosphazenes? These compounds are inaccessible by other routes. (2) Could other halogen atoms (such as bromine or iodine) be attached to the phosphazene ring via replacement of the hydrogen atom in compounds II, and, if so, what would be the air or moisture sensitivity and thermal stability of these new mixed halophosphazenes? And, finally, (3) how would the presence of the different halogen atoms on the phosphazene ring affect the reactivities of these compounds?

Results and Discussion

The Synthesis Reaction. When hydridophosphazenes (II)



II

III, X = Cl
IV, X = Br
V, X = I

were allowed to react with an excess of halogen (chlorine, bromine, or iodine) in tetrachloromethane, the hydrogen atom was replaced cleanly and smoothly by the halogen to yield a new class of 1-halo-1-alkyltetrachlorocyclotriphosphazenes (III, IV, or V). These compounds possess an alkyl group and the added halogen atom (chlorine, bromine, or iodine) linked to the same phosphorus atom. The range of compounds III–V, where R = CH$_3$, C$_2$H$_5$, *n*-C$_3$H$_7$, *n*-C$_4$H$_9$, *i*-C$_3$H$_7$, and *t*-C$_4$H$_9$, were prepared.

General Characteristics of Alkylpentachlorocyclotriphosphazenes, N$_3$P$_3$Cl$_5$R (III). The reaction of hydridophosphazenes (II) with elemental chlorine provides the most effective general synthetic route for the formation of alkylpentachlorocyclotriphosphazenes (III). All these compounds are air- and moisture-stable, volatile products. Where R = CH$_3$, C$_2$H$_5$, or *n*-C$_3$H$_7$, they are white crystalline compounds. When R = *i*-C$_3$H$_7$, *n*-C$_4$H$_9$, or *t*-C$_4$H$_9$, they are colorless oils at 25 °C. In a recent paper[4,5] we have shown that these monoalkylpentachlorocyclotriphosphazenes (III) are "monomers" for the formation of a new class of high molecular weight poly(organophosphazenes) which contain phosphorus–carbon bonds.

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(1) For a previous paper in this series see: Allcock, H. R.; Greigger, P. P.; Wagner, L. J.; Bernheim, M. Y. *Inorg. Chem.* **1981**, *20*, 716.
(2) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(3) Allcock, H. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 147.
(4) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Macromolecules*, **1979**, *12*, 1014.
(5) Allcock, H. R.; Ritchie, R. J.; Harris, P. J. *Macromolecules*, **1980**, *13*, 1332.
(6) Ritchie, R. J.; Harris, P. J.; Allcock, H. R. *Inorg. Chem.* **1980**, *19*, 2483.
(7) Harris, P. J.; Allcock, H. R. *J. Am. Chem. Soc.* **1978**, *100*, 6512.
(8) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.

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