instead loss of the reduced diazo molecule and subsequent attack of the "Cp$_2$M" species by excess ligand. Intermediates in hydride insertion reactions were obtained with diazodicarboxylate molecules,[29] but these reactions stopped at the monoinserted product. The title complex therefore represents an important intermediate in model system studies for the reduction of dinitrogen. Further studies are presently underway[30] in an attempt to structurally characterize the unstable first product [Cp$_2$WH(NNHPh)][BF$_4$] in the above insertion reaction, in order to gain a better understanding of the factors favoring the unusual double-insertion reaction.

Acknowledgment. We thank the University of Alberta and the Natural Science and Engineering Research Council of Canada for financial support and Professor Derek Sutton for supplying the crystals and for helpful discussions.

Registry No. $[(\eta^5\text{-}C_5H_5)_2W(H_2NNC_6H_5)][BF_4]$, 73358-24-4.

Supplementary Material Available: Table VI showing the idealized hydrogen parameters and a listing of the observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

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Contribution from Evans Chemical Laboratory,
The Ohio State University, Columbus, Ohio 43210

Substituent Effects in the Control of the Oxidation–Reduction Properties of Metal Ions in Complexes with Macrocyclic Ligands

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The complexes [Ni(Me$_n$[Z]tetraenatoN$_4$)] (Z = 14, 15 or 16) contain dianionic macrocyclic ligands having pairs of charged, unsaturated chelate rings which contain nucleophilic centers. These species have been used to produce a wide variety of substituted derivatives [Ni(Me$_n$E$_m$[Z]tetraenatoN$_4$)] with the substituent ranging from electron-donating alkyl groups to electron-withdrawing nitro groups. The numbers of methyl substituents on the saturated chelate rings (n) have also been varied. The effects of the substituent (E) on the properties of the central metal atom are both large and systematic. Both the position of the d–d electronic band maximum (for the planar Ni^{II} ion) and half-wave potential for the Ni^{2+}/Ni^{3+} couple vary linearly with Hammett substituent constants. The correlations (R) are good and the sensitivities (ρ) large if the substituents are directly attached to the unsaturated chelate ring. Tests with various Hammett σ constants failed to indicate the mode of transmission of the electronic effects. Remote substituents (para-substituted benzoyl groups) gave relatively small effects. Significantly, the sensitivities (ρ values) to both direct and remote substituents were found to be essentially identical with those reported for porphyrin derivatives. Changes in the numbers of methyl groups on the saturated rings produce no effect, supporting the view that both the reduced and oxidized forms of the complexes contain planar nickel. This class of ligands facilitates close control over the electronic properties of the central metal atom.

Introduction

The design and synthesis of small molecules and ions that are capable of performing functions identified with metal-containing natural products are a multifaceted problem.[1,2] The natural products to be mimicked are complicated protein derivatives, and, most generally and somewhat simplistically, the protein provides two principal structural components to the coordination site.[1,2] It provides much of the primary ligand field, thereby determining the electronic properties of the metal ion, and it provides further aspects of the active-site environment. The work described here is concerned with the first set of relationships, the control of the electronic properties of the metal ion. Because heme proteins are involved in oxidation–reduction[3–5] processes, such studies are particularly germane to model heme protein studies. Complexes with synthetic macrocyclic ligands are uniquely convenient for the evaluation of the dependence of oxidation–reduction properties of metal chelates on the detailed structure of the ligand while a given metal ion is maintained in an essentially constant coordination geometry. A variety of kinds of process have been identified depending primarily on the metal ion, the ligand, and the solvent. These include oxidation and reduction of the central metal ion,[6–10] various oxidation and reduction reactions of the ligand,[7–14] and processes which involve both the central metal atom and the ligand.[8] The present study is concerned with the first kind of process, those centered on the metal ion. Complexes of neutral tetraaza macrocycles have dominated earlier studies of this kind. For a large number of such ligands it has been possible to identify electrode processes that are attributable to the same metal ion couple. Perhaps it is an indication of the ligating efficacy of tetraaza macrocycle that the previously rarely observed Ni^{2+}/Ni^{3+} couple has figured most heavily in these studies. The influences of various structural features[6] have been quantitated, including ring size,[6,15,17] degree and arrangement of unsaturation,[6,7,10,16] and alkyl substitution.[9,16]

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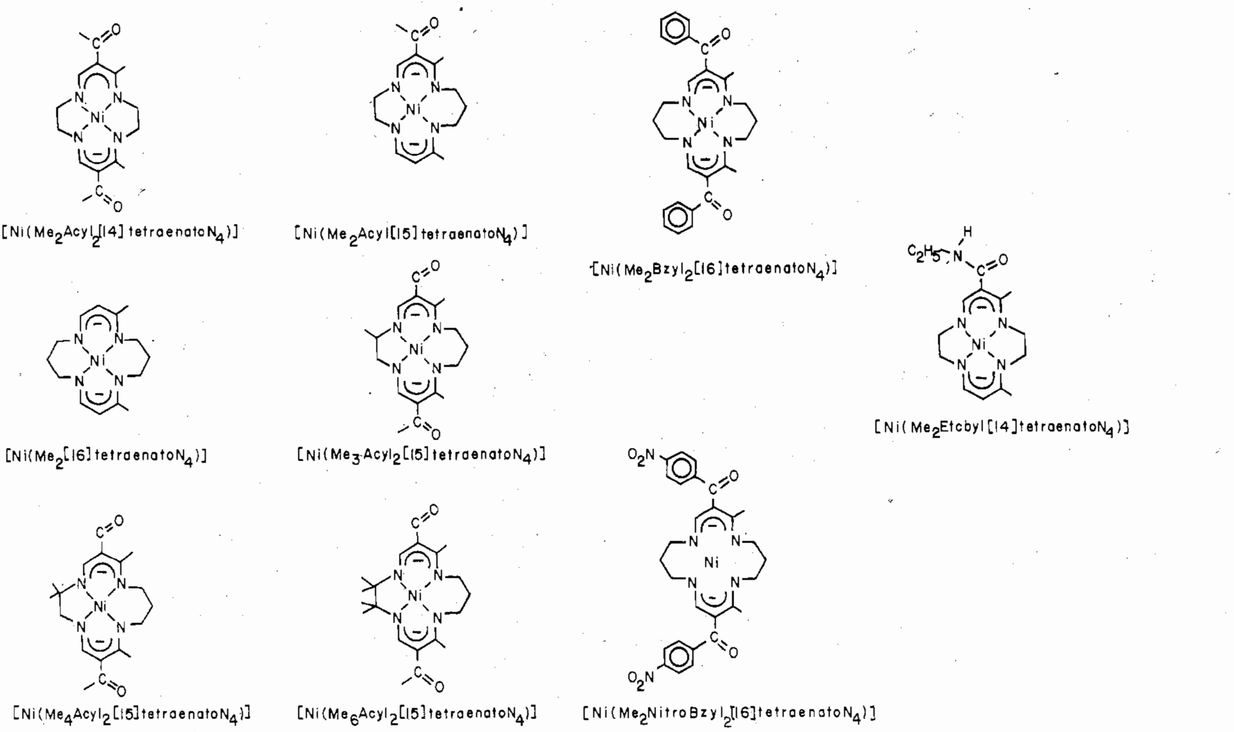


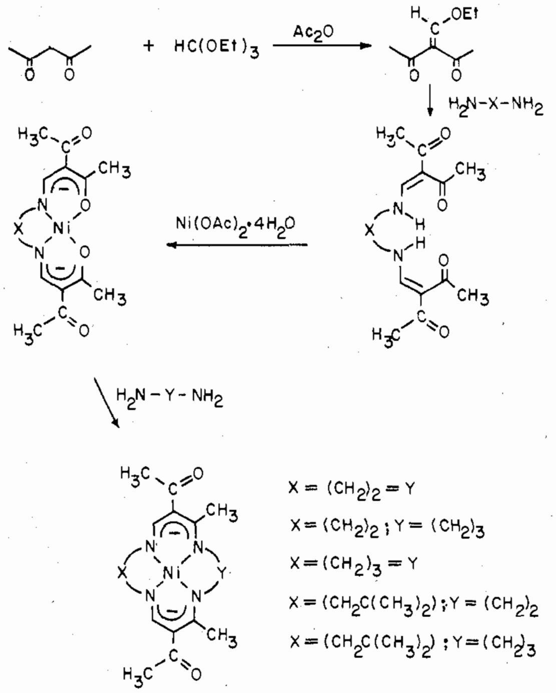
Figure 1. Structures of the nickel(II) complexes of various substituted macrocycles.

Here we report the effects of electronically active ligand substituents on the electronic spectra and electrochemistry of a particularly interesting structural class of macrocyclic complexes. The various ligands of interest are illustrated in Figure 1 along with the abbreviated, nomenclature-derived formulas. In these sample structures, acyl groups occupy substituent locations on the unsaturated, negatively charged chelate rings. By analogy to the structurally similar β-diketonate chelate rings, we refer to these positions as the γ and γ' positions. It is appropriate to acknowledge at the outset that these ligands are of much interest because of their similarities to porphyrins; i.e., both ligands present an N_4 square-planar donor set to the central metal ion and they are both dianionic with charge-delocalized chelate rings. Further, comparisons can be made with the results of work on substituent effects among porphyrin complexes.[18,19] The synthetic macrocycles of Figure 1 were first separated by Jäger,[20,21] and the evolved synthetic procedures[22] permit easy variations in structure, especially ring size variation and differing substitution on the saturated rings. Work with neutral macrocyclic ligands has shown that both structural factors have large effects on the $E_{1/2}$ values for a number of metal ion couples. These ligands are particularly well suited to the development of large numbers of derivatives having substituents on the γ and γ' positions of the unsaturated rings.

Results and Discussion

Synthesis of the New Complexes. The synthetic route to the macrocyclic complexes [Ni(Me$_2$Acyl$_2$[Z]tetraenatoN$_4$)] is shown in Scheme I. Details are presented elsewhere.[22] Scheme I shows that various diamines can be incorporated into the structure to achieve variations in ring size and unsaturated ring substitution (see also Figure 1). The complexes described here span the ring sizes from 14 members through 16 members and involve from zero to four methyl groups on a saturated chelate ring.

Scheme I. Preparative Scheme for Jäger Macrocycles



The macrocyclic complexes produced according to Scheme I have acetyl groups on the γ and γ' positions. These materials can be converted into powerful nucleophiles by removal of the acetyl substituents. This can be accomplished by two routes: The first is removal of the acetyl groups along with the central nickel(II) ion followed by reintroduction of the metal ion.[23] This route is important in that it allows introduction of other metal ions into the basic ligand framework. The second is

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Table I. Elemental Analyses and Mass Spectral Data for a Series of Substituted Macrocyclic Complexes $[Ni(Me_nE_2[Z]tetraenatoN_4)]$[a]

	no. of methyl		$Z = 14$				$Z = 15$				$Z = 16$			
substituents (E)	groups		C	H	N	m/e	C	H	N	m/e	C	H	N	m/e
2 $CH_2CH_2CO_2C_2H_5$	2	calcd	55.37	7.18	11.74	476	56.23	7.39	11.41	490	57.05	7.58	11.09	504
		found	55.17	7.36	11.76	476	56.16	7.30	11.35	490	56.88	7.64	10.80	504
$COCH_3$, H	2	calcd	52.70	6.32	17.56	318	54.09	6.66	16.82	332	55.36	6.97	16.14	346
		found	52.54	6.29	17.47	318	54.18	6.59	16.73	332	55.66	7.06	15.97	346
$CONHC_2H_5$, H	2	calcd	51.76	6.66	20.12	347								
		found	51.90	6.82	20.17	347								
2 $CONHC_2H_5$	2	calcd					52.68	6.98	19.40	432	53.71	7.21	18.79	446
		found					52.52	7.11	19.56	432	53.60	7.14	19.07	446
2 CONH-α-nap	2	calcd	66.36	5.24	13.66	614	66.79	5.45	13.35	628	67.20	5.64	13.06	642
		found	66.22	5.19	13.72	445	66.66	5.62	13.79	459	67.10	5.67	12.96	304
2 $COCH_2CH_2CO_2CH_3$	2	calcd	52.30	5.99	11.09	504	53.20	6.21	10.79	518	54.06	6.42	10.51	532
		found	52.15	5.67	11.10	504	53.07	6.12	10.88	518	54.09	6.45	10.31	532
2 $COC_6H_4CH_3$	2	calcd	65.52	5.89	10.92	512	66.06	6.12	10.63	526	66.56	6.33	10.35	540
		found	65.39	5.83	10.92	512	65.93	6.03	10.47	526	66.76	6.22	9.95	540
2 COC_6H_5	2	calcd	64.36	5.40	11.55	484	67.54[b]	5.85[b]	10.61[b]	498	65.52	5.89	10.91	512
		found	64.23	5.42	11.40	484	67.50	5.64	10.24	498	65.32	5.89	10.89	512
2 $COC_6H_4NO_2$	2	calcd	54.29	4.21	14.61	574	55.03	4.45	14.26	588	53.02[c]	4.50[c]	13.02[c]	602
		found	54.17	4.45	14.81	574	55.34	4.21	14.42	588	52.61	5.05	12.93	602
2 NO_2	2	calcd					previously synthesized				42.56	5.10	21.27	394
		found									42.67	5.26	20.95	394
2 $COCH_3$	3	calcd	54.43	6.45	14.94	374	55.56	6.73	14.40	388				
		found	54.37	6.57	14.74	374	55.56	6.94	14.21	388				
2 $CO_2C_2H_5$	3	calcd	previously synthesized				previously synthesized				46.45	5.85	12.38	516
		found									46.68	5.72	12.29	516

[a] Refer to Figure 1 for details of structures. [b] This value is calculated for two benzenes of solvation for every three molecules of complex. [c] This value is calculated for one methylene chloride of solvation for every two molecules of complex.

selective removal of only the acetyl groups. The unsubstituted complexes will react with a variety of electrophiles to produce derivatives that are substituted at the γ and γ' positions. Scheme II summarizes these procedures along with the group of electrophilic reagents that were examined. Consequently, the electronic properties of the substituent groups can be varied from the electron-donating alkyl substituent, which results from the Michael addition of ethyl acrylate, to the highly electron-withdrawing nitro group.

The electrophilic substitution reactions were typically performed with a large excess of the electrophile, and this usually produced disubstituted macrocyclic complexes. In contrast, by closer control of the reaction stoichiometry monosubstituted products could also be isolated. All of the complexes prepared via these reaction schemes were characterized by elemental analyses and by mass and infrared spectral data (Tables I and II). In addition, since the products were all diamagnetic, square-planar Ni(II) complexes, nuclear magnetic resonance measurements were employed for further characterization, but these studies will be the subject of a separate report.

Synthetic problems were encountered only in attempts to prepare $[Ni(Me_2Nitro_2[14]tetraenatoN_4)]$. The reaction conditions which were attempted are detailed elsewhere.[19] Exactly the same reaction conditions which proved successful in preparing both the 15- and 16-membered ring homologues did not afford pure $[Ni(Me_2Nitro_2[14]tetraenatoN_4)]$.

Because of the nature of the interpretations that will be offered for these series of complexes, the data for the dinitro derivative of the 14-membered ring complex are of considerable importance. This is true because the nitro group represents the extreme in electron-withdrawing strength from among the substituents studied here. Therefore some of the properties of this still unknown material will be predicted from those of certain well-characterized, closely similar substances.

The predictions of the position of the band maximum of the d–d transition and the $E_{1/2}$ value of the first oxidation reaction of $[Ni(Me_2Nitro_2[14]tetraenatoN_4)]$ were made by comparing the properties of seven known compounds (Table III). The predicted values for $[Ni(Me_2Nitro_2[14]tetraenatoN_4)]$ are underlined. They were made on the following bases: (1) Methyl substitution on the saturated chelate rings has no effect on the position of the band maximum for the d–d transition. The desired complex differs only in degree of methyl substitution from $[Ni(Me_4Nitro_2[14]tetraenatoN_4)]$, which was first synthesized by Hipp.[24] On this basis the predicted value of ν_{dd} is 20 000 cm^{-1}. (2) The prediction of the $E_{1/2}$ value is more complicated. A comparison of complexes of the same ring size having similar substituents at the γ and γ' positions but differing only in methyl substitution on one of the saturated chelate rings forms the basis of this prediction. For the 14-membered diacetylated species the difference between the dimethyl and the tetramethyl complexes is 30 mV with the tetramethyl complex exhibiting the higher potential. Exactly

Scheme II. Reactivity of Jäger Macrocyclic Nickel(II) Complexes toward Various Electrophiles

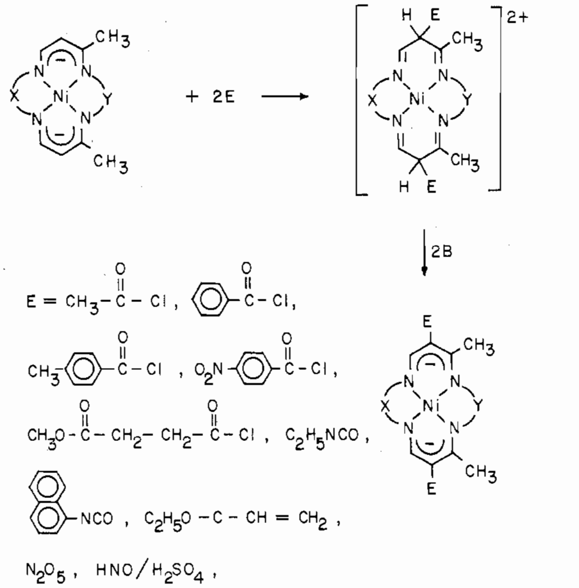

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Table II. Selected Infrared Frequencies for a Series of Substituted Macrocyclic Complexes [Ni(Me$_n$E$_2$[Z]tetraenatoN$_4$)]^a

substituents (E)	no. of methyl groups (n)	ring size (Z)	medium	abs max, cm^{-1} (assignt)
2 $CH_2CH_2CO_2C_2H_5$	2	14	KBr pellet	1725 ($CO_2C_2H_5$), 1595 (diiminato rings)
		15	$CDCl_3$ solution	1722 ($CO_2C_2H_5$), 1590 (diiminato rings)
		16	KBr pellet	1720 ($CO_2C_2H_5$), 1590 (diiminato rings)
$COCH_3$, H	2	14	KBr pellet	1630 ($COCH_3$), 1580 (br, diiminato rings)
		15	$CDCl_3$ solution	1620 ($COCH_3$), 1572 (br, diiminato rings)
		16	KBr pellet	1618 ($COCH_3$), 1575 (diiminato rings)
$CONHC_2H_5$, H	2	14	KBr pellet	3280 (br, NH), 1610 (CONH), 1595 (br, diiminato rings), 1520
2 $CONHC_2H_5$	2	15	Nujol mull	3290 (br, NH), 1615 (CONH), 1580 (diiminato rings)
		16	KBr pellet	3260 (br, NH), 1613 (CONH), 1585 (diiminato rings), 1530
2 CONH-α-nap	2	14	Nujol mull	3180 (br, NH), 1620 (CONH), 1595 (diiminato rings), 1520
		15	Nujol mull	3150 (br, NH), 1622 (CONH), 1599 (diiminato rings), 1515
		16	KBr pellet	3210 (br, NH), 1625 (CONH), 1595, 1580 (diiminato rings), 1510
2 $CO_2C_2H_5$	2	14	KBr pellet	1670 ($CO_2C_2H_5$), 1590 (diiminato rings), 1500
		15	KBr pellet	1665 ($CO_2C_2H_5$), 1590 (diiminato rings), 1505
		16	Nujol mull	1680 ($CO_2C_2H_5$), 1595 (diiminato rings)
2 $COC_6H_4CH_3$	2	14	KBr pellet	1620 (CO), 1595 (aroyl group), 1560 (diiminato rings)
		15	Nujol mull	1632 (CO), 1606 (aroyl group), 1530 (br, diiminato rings)
		16	KBr pellet	1610 (CO), 1600 (aroyl group), 1550 (diiminato rings)
2 COC_6H_5	2	14	KBr pellet	1610 (CO), 1595 (aroyl group), 1565 (diiminato rings)
		15	Nujol mull	1621 (CO), 1600 (aroyl group), 1570 (br, diiminato rings)
		16	KBr pellet	1610 (CO), 1595, 1575 (aroyl group), 1540 (diiminato rings)
2 $COC_6H_4NO_2$	2	14	KBr pellet	1610 (CO), 1590 (aroyl group), 1550 (diiminato rings)
		15	Nujol mull	1620 (CO), 1600 (aroyl group), 1562 (br, diiminato rings)
		16	KBr pellet	1615 (CO), 1600 (aroyl group), 1560 (diiminato rings)
2 $COCH_2CH_2CO_2CH_3$	2	14	KBr pellet	1740 (CO_2CH_3), 1640 (CO), 1590 (diiminato rings)
		15	Nujol mull	1729 (CO_2CH_3), 1620 (CO), 1581 (diiminato rings)
		16	KBr pellet	1725 (CO_2CH_3), 1630 (CO), 1580 (diiminato rings)
2 NO_2	2	15	Nujol mull	1601 (diiminato rings), 1510 (NO_2)
		16	KBr pellet	1610 (diiminato rings), 1520 (NO_2)
2 $COCH_3$	3	14	KBr pellet	1625 ($COCH_3$), 1580 (diiminato rings)
		15	KBr pellet	1625 ($COCH_3$), 1580 (diiminato rings), 1515

[a] For details of structures refer to Figure 1.

Table III. Comparison of Nitrated and Acetylated 14- and 15-Membered Ring Complexes^a

compd	no. of methyl groups	ν_{dd},^{b} cm^{-1} × 10^3	^{1}H NMR, ppm^c	$E_{1/2}$,^{d} V
[Ni(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)]	2	19.7	7.68	0.19
[Ni(Me$_4$Acyl$_2$[14]tetraenatoN$_4$)]	4	19.7	7.60 7.67	0.22
[Ni(Me$_2$Nitro$_2$[14]tetraenatoN$_4$)]	2	20.0^e	8.45^e	0.45^e
[Ni(Me$_4$Nitro$_2$[14]tetraenatoN$_4$)]	4	20.0	8.41 8.45	0.54
[Ni(Me$_2$Acyl$_2$[15]tetraenatoN$_4$)]	2	19.3	7.63	0.22
[Ni(Me$_4$Acyl$_2$[15]tetraenatoN$_4$)]	4	19.4	7.47	0.25
[Ni(Me$_2$Nitro$_2$[15]tetraenatoN$_4$)]	2	19.8	8.29	0.42
[Ni(Me$_4$Nitro$_2$[15]tetraenatoN$_4$)]	4	20.0	8.23	0.51

[a] For details of structures refer to Figure 1. [b] Transitions obtained in chloroform solution. [c] Chemical shifts obtained in $CDCl_3$ and are listed from internal tetramethylsilane. [d] Potentials for the nickel(II) oxidation were obtained in dimethylformamide with 0.1 M tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte vs. an Ag/$AgNO_3$ reference electrode. [e] Values predicted as indicated in text.

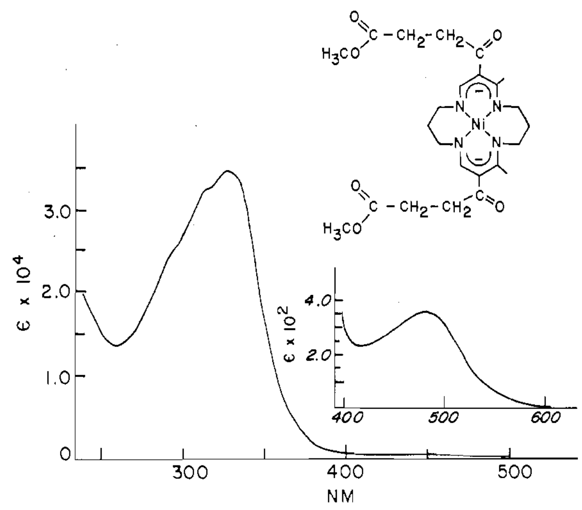

Figure 2. Typical ultraviolet–visible spectrum in chloroform solution.

the same separation and relative order are observed for the corresponding 15-membered ring homologues. The dinitro, 15-membered ring compounds show the same trend but a large separation between the potentials of the dimethyl and tetramethyl complexes (90 mV). Since the diacetylated complexes show exactly the same potential separation due to the methyl substitution pattern, independent of ring size, the assumption is made that the dinitro derivatives will exhibit the same behavior. Therefore $E_{1/2}$ is predicted to be +0.45 V for [Ni(Me_2Nitro_2[14]tetraenatoN_4)]; this corresponds to a value which is 90 mV lower than the potential for [Ni(Me_4Nitro_2[14]tetraenatoN_4)]. These predicted values will be used in discussions that follow.

Electronic Spectra. Visible and ultraviolet spectra of the entire series of complexes were obtained on the 10^{-4}–10^{-5} M solutions in chloroform over the range from 12 500 to 41 000 cm^{-1}. Figure 2 shows the spectrum of [Ni(Me_2Mesuc_2[16]tetraenatoN_4)] where Mesuc represents the methyl ester of the succinyl derivative. These types of complexes show several band maxima in the ultraviolet region of the spectrum with extinction coefficients in the range from 3000 to 40 000 M^{-1} cm^{-1} which agree with assignment of the bands as representing charge-transfer transitions. The spectra also exhibit a broad transition in the visible region with an extinction coefficient on the order of 100–500 which resembles the d–d transitions of other square-planar Ni(II) complexes.[25] The data for the substituted 14-, 15-, and 16-membered ring derivatives are shown in Tables IV–VI, respectively. The most striking feature of the data is the variation of the position of the band maximum for the d–d transition. For all three ring sizes, an increase in the electron-withdrawing strength of the substituent groups results in an increase in the energy of the band maximum.

The dependence on the electronic properties of the substituent groups was examined by means of Hammett substituent constants.[26–28] For each series of substituted complexes of the same ring size linear correlation is found when the observed d–d band maxima are graphed vs. the sum of the Hammett constants of the substituent groups (Figure 3). The linearity of this relationship is important because it demonstrates that this property of the central metal ion is affected directly by the electronic properties of the substituent group. The correlation of the data with various types of Hammett constants was examined, and the results are summarized in Table VII. The correlation coefficient (R) indicates the linearity of the correlation (ideally, R = 1.00), while the slope

Table IV. Electronic Absorption Bands for the 14-Membered Ring Derivatives [Ni(Me_nE_2[14]tetraenatoN_4)][a,b]

substituents (E)	no. of methyl groups	ν_{dd}, cm^{-1} × 10^3 (ϵ)	other transitions: ν, cm^{-1} × 10^3 (ϵ)
2 CH_2CH_2-$CO_2C_2H_5$	2	17.59 (274)	23.72 (6450), 33.11 (16 800), 37.45 (15 000)
2 H	2	17.83	
CONHnap, H	2	18.47	23.39 (4230), 25.28 (9440), 29.61 (21 800), 34.08 (42 000)
$CONHC_2H_5$, H	2	18.52 (358)	23.26 (2940), 25.03 (6670), 26.32 (4500), 34.42 (27 100)
$COCH_3$, H	2	18.80 (262)	25.79 (5380), 29.41 (13 400), 34.78 (14 600), 38.39 (11 400)
2 $CO_2C_2H_5$	2	19.95	
2 $COCH_3$	2	19.69	
2 $COCH_3$	3	19.74 (392)	29.28 (27 700), 35.27 (12 500), 40.32 (10 700)
2 $COCH_3$	4	19.69	
2 $COCH_3$	6	19.72 (531)	29.54 (37 000), 35.27 (17 000), 40.16 (22 900)
2 COC_6H_4-CH_3	2	19.65 (614)	27.17 (24 300), 35.03 sh (22 600), 39.89 (37 100)
2 COC_6H_5	2	19.61 (578)	27.36 (23 500), 37.17 (26 900)
2 COC_6H_4-NO_2	2		21.93 sh, 24.27 sh, 26.18 sh, 29.29 (23 400), 35.84 (41 000)
2 $COCH_2CH_2$-CO_2CH_3	2	19.84 (7.86)	29.15 (37 500), 35.25 (20 000)
2 NO_2	4	20.02	

[a] For details of structures refer to Figure 1. [b] Spectra were obtained for 10^{-3}–10^{-4} M solutions in chloroform.

Table V. Electronic Absorption Bands for the 15-Membered Ring Derivatives [Ni(Me_2E_2[15]tetraenatoN_4)][a,b]

substituents (E)	ν_{dd}, cm^{-1} × 10^3 (ϵ)	other transitions: ν, cm^{-1} × 10^3 (ϵ)
2 $CH_2CH_2CO_2C_2H_5$	17.02 (224)	22.35 (3320), 25.00 (4570)
2 H[c]	17.15	
$COCH_3$, H	18.32 (197)	24.24 sh (4020), 25.97 (6670), 29.89 (16 240)
2 CONHnap	18.66 (285)	24.24 sh (4160), 29.50 (27 750)
2 $CONHC_2H_5$	18.42 (294)	23.98 (3400), 25.58 (4600), 27.17 (3800)
2 $CO_2C_2H_5$[c]	19.18	
2 $COCH_3$[c]	19.30	
2 $COC_6H_4CH_3$	19.31 (421)	27.40 (25 600)
2 COC_6H_5	19.27 (433)	27.51 (25 650)
2 $COC_6H_4NO_2$		20.30 (106 700), 24.04 (28 160)
2 $COCH_2CH_2CO_2CH_3$	19.38 (344)	29.76 (35 560)
2 NO_2	19.80 (922)	24.04 (38 870)

[a] For details of structures refer to Figure 1. [b] Spectra were obtained for 10^{-3}–10^{-4} M solutions in chloroform. [c] Complexes were prepared prior to this work.

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Table VI. Electronic Absorption Bands for the 16-Membered Ring Derivatives $[Ni(Me_2E_2[16]tetraenatoN_4)]$[a, b]

substituents (E)	ν_{dd}, $cm^{-1} \times 10^3$ (ϵ)	other transitions: ν, $cm^{-1} \times 10^3$ (ϵ)
2 $CH_2CH_2CO_2C_2H_5$	17.81 (369)	26.04 (15 800), 32.79 (10 700), 40.98 (27 800)
2 H	17.95	
$COCH_3$, H	17.66 (102) 20.20 (383)	26.11 (8400), 30.44 (34 000), 33.44 (26 500)
2 CONHnap	20.20 (347)	29.50 (261 000), 35.34 (209 000)
2 $CONHC_2H_5$	20.00 (308)	28.29 (7500), 33.56 (13 900), 35.46 (16 000), 39.84 (11 300)
2 $CO_2C_2H_5$	20.45 (256)	29.50 (9200), 32.70 (23 600), 35.65 (24 900), 40.49 (14 800)
2 $COCH_3$	20.77	
2 $COC_6H_4CH_3$	20.79 (317)	29.33 (22 700)
2 COC_6H_5	20.75 (365)	29.42 (27 700)
2 $COC_6H_4NO_2$		25.49 sh, 31.35 (31 900), 36.63 (31 800)
2 $COCH_2CH_2CO_2CH_3$	20.92 (368)	30.43 (34 600), 31.72 (32 300), 34.01 (24 600)
2 NO_2	23.38 (589)	25.16 (27 100), 27.25 (29 500)

[a] For details of structures refer to Figure 1. [b] Spectra were obtained for 10^{-3}–10^{-4} M solutions in chloroform.

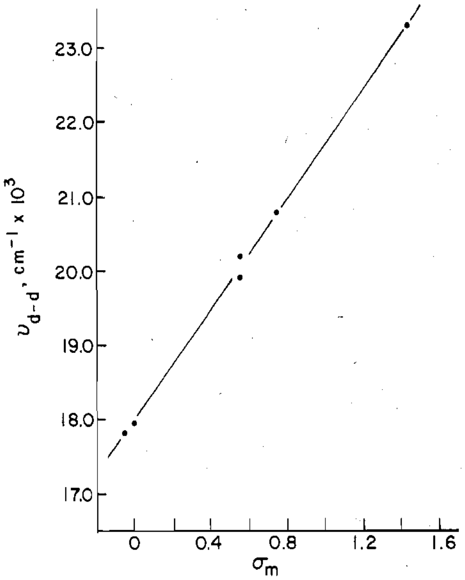

Figure 3. Plot of d–d transition vs. σ_m for a series of substituted 16-membered ring complexes.

of the line (ρ) gives an indication of the sensitivity of the property being examined to the electronic properties of the substituent groups. The *R* values obtained are typical of this type of correlation. For the various substituent constants examined there is no indication that one set of constants gives a much better correlation than any of the others. Therefore no conclusions about how the electronic effects might be transmitted (inductive vs. resonance) are warranted from these data.

From the ρ values for any given substituent constant, the 16-membered ring derivatives seem to exhibit the greatest sensitivity toward the electronic properties of the substituent groups. The 14- and 15-membered rings show similar but lower sensitivities. The differences observed may be due to conformational differences of the various ring sizes due to some structural effect. Both the 14- and 15-membered ring complexes have at least one 5-membered saturated chelate ring. This may cause a rigidity in the structure which limits the sensitivities of compounds having these ring sizes. On the other hand the 16-membered ring complexes may be more flexible since they have no 5-membered saturated chelate rings and therefore might be able to adopt different conformations.

Table VII. Correlations of ν_{dd} with Hammett Constants

ring size	Hammett const	slope (ρ) ± std dev	*R*
14	σ_m	1.73 ± 0.25	0.945
	σ_p	1.55 ± 0.14	0.977
	σ_p^-	0.99 ± 0.08	0.975
15	σ_m	2.00 ± 0.25	0.953
	σ_p	1.77 ± 0.14	0.980
	σ_p^-	1.13 ± 0.09	0.976
17	σ_m	3.70 ± 0.12	0.997
	σ_p	3.11 ± 0.23	0.984
	σ_p^-	1.69 ± 0.26	0.924

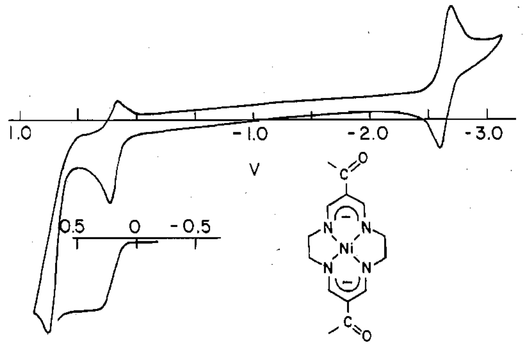

Figure 4. Electrochemistry of $[Ni(Me_2Acyl_2[14]tetraenatoN_4)]$ in DMF vs. an $Ag/AgNO_3$ reference electrode.

Electrochemistry. Electrochemical measurements were performed on 10^{-3}–10^{-4} M solutions of the substituted complexes in dimethylformamide. For direct comparison of the values obtained, the conditions under which the experiments were performed were kept as constant as possible throughout the entire series of complexes. Tetra-*n*-butylammonium tetrafluoroborate (0.1 M) was used as the supporting electrolyte. The working electrode was a platinum-disk electrode, and the reference electrode was a silver wire immersed in a 0.1 M solution of silver nitrate in dimethylformamide. Both cyclic voltammetric and rotating platinum electrode voltammograms were measured.

Figure 4 illustrates a typical cyclic voltammogram for one of the series of complexes. The three electrode processes usually observed were previously assigned to electrochemical reactions:[9] (1) the quasi-reversible reduction at very negative potential was assigned to the Ni^{2+}/Ni^{1+} couple, (2) the relatively well-behaved oxidation at around 0 V was assigned to the Ni^{2+}/Ni^{3+} couple, and (3) the oxidation at higher potential, which is strictly irreversible, was assigned to a ligand oxidation. As stated in the Introduction we are concerned about control of the M^{2+}/M^{3+} oxidation potential for various series of macrocyclic complexes. Consequently, the process that usually occurs at around 0 V is of most interest.

Tables VIII–X show the $E_{1/2}$ values obtained from RPE voltammograms of the electrode processes for all of the 14-, 15-, and 16-membered ring complexes. The most interesting feature of the entire set of data is the variation of the first oxidation potential for these complexes. With reference to complexes of the same ring size, as the electron-withdrawing power of the substituent group is increased, the Ni^{2+}/Ni^{3+} oxidation becomes more difficult. This implies that the sub-

Table VIII. Electrochemical Data for a Series of Substituted 14-Membered Ring Complexes $[Ni(Me_nE_2[14]tetraenatoN_4)]^{a,b}$

	no. of	oxidation		reduction	
substituents (E)	methyl groups	$E_{1/2}$, V	Δ,[c] mV	$E_{1/2}$, V	Δ,[c] mV
2 $CH_2CH_2CO_2C_2H_5$	2	−0.40	70	−3.08	80
		+0.45	75		
2 H	2	−0.36	75		
CONHnap, H	2	−0.25	60	−2.88	110
		+0.59	65		
$CONHC_2H_5$, H	2	−0.27	65		
		+0.52	70		
$COCH_3$, H	2	−0.135	71	−2.835	92
		+0.63	87		
2 $CO_2C_2H_5$	2	+0.19[d]			
2 $COCH_3$	2	+0.19[d]			
2 $COCH_3$	3	+0.22	75	~−2.7	abs[f]
		+0.79	irr[e]		
2 $COCH_3$	4	+0.22[d]			
2 $COCH_3$	6	+0.235	60	~−2.7	abs
		+0.83	irr		
2 $COC_6H_4CH_3$	2	+0.17	75	~−2.6	irr
		+0.71	90		
2 COC_6H_5	2	+0.19	66	−2.52	70
		+0.73	85	−2.695	80
2 $COC_6H_4NO_2$	2	+0.24	75	−1.45	80
		+0.75	100	−2.10	110
2 $COCH_2CH_2CO_2CH_3$	2	+0.195	70	−2.61	80
		+0.81	110		
2 NO_2	4	+0.54	75		

[a] For details of structures refer to Figure 1. [b] Potentials were obtained with use of a rotating platinum disk electrode in dimethylformamide containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate vs. the Ag/$AgNO_3$ reference electrode. [c] $\Delta = E_{3/4} - E_{1/4}$. [d] Values not available. [e] Irreversible. [f] Absorption at electrode.

Table IX. Electrochemical Data for a Series of Substituted 15-Membered Ring Complexes $[Ni(Me_2E_2[15]tetraenatoN_4)]^{a-c}$

	oxidation		reduction	
substituents (E)	$E_{1/2}$, V	Δ, mV	$E_{1/2}$, V	Δ, mV
2 $CH_2CH_2CO_2C_2H_5$	−0.39	85	−2.92	195
	+0.29	irr		
2 H	−0.36	irr	−2.85	120
	+0.39	irr		
$COCH_3$, H	−0.14	irr	−2.64	90
	+0.51	irr		
2 CONHnap	+0.03	65	−2.59	100
	+0.55	irr		
2 $CONHC_2H_5$	−0.03	65	−2.67	80
	+0.61	80		
2 $CO_2C_2H_5$	+0.22	70		
2 $COCH_3$	+0.22	70		
2 $COC_6H_4CH_3$	+0.19	60	−2.44	100
	+0.63	irr		
2 COC_6H_5	+0.21	55	−2.42	95
	+0.64	irr		
2 $COC_6H_4NO_2$	+0.31	80	−1.47	80
	+0.79			
2 $COCH_2CH_2CO_2CH_3$	+0.22	55	−2.50	120
	+0.66			
2 NO_2	+0.42	60	−2.00	80
	+1.04	irr	−2.6	irr

[a] For details of structures refer to Figure 1. [b] Potentials were obtained with use of a rotating platinum disk electrode in dimethylformamide containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate vs. an Ag/$AgNO_3$ reference electrode. [c] $\Delta = E_{3/4} - E_{1/4}$; irr = irreversible.

stituent groups directly affect the electron density on the metal atom even though they must transmit their effect through the charge-delocalized chelate ring. With an increase in the electron-withdrawing power of the substituent groups, less electron density resides on the chelate ring, which would in turn result in less electron density on the central metal atom.

Table X. Electrochemical Data for a Series of Substituted 16-Membered Ring Complexes $[Ni(Me_2E_2[16]tetraenatoN_4)]^{a,b}$

	oxidation		reduction	
substituents (E)	$E_{1/2}$, V	Δ,[c] mV	$E_{1/2}$, V	Δ,[c] mV
2 $CH_2CH_2CO_2C_2H_5$	−0.35	75	−2.83	175
	+0.23	60		
2 H	−0.31	55		
$COCH_3$, H	−0.04	55	−2.50	75
	+0.78	125		
2 $CONHC_2H_5$	+0.02	75	~−2.6	irr
	+0.64	150		
2 CONHnap	+0.11	65	−2.46	75
	+0.53	85		
2 $CO_2C_2H_5$	+0.32	60	~−2.5	irr
	~+0.65	irr		
2 $COCH_3$	+0.40	65	−2.39	70
	~+0.6	irr		
2 $COC_6H_4CH_3$	+0.29	65	−2.31	100
	+0.63	105		
2 COC_6H_5	+0.31	65	−2.28	80
	+0.60	80		
2 $COC_6H_4NO_2$	+0.38	70	−1.48	75
	+0.76	85	−2.12	115
2 $COCH_2CH_2CO_2CH_3$	+0.335	60	−2.39	70
	+0.615	100		
2 NO_2	+0.53	80	−1.97	65
	~+1.0	irr	−2.64	70

[a] For details of structures refer to Figure 1. [b] Potentials were obtained with use of a rotating platinum disk electrode in dimethylformamide containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate vs. an Ag/$AgNO_3$ reference electrode. [c] $\Delta = E_{3/4} - E_{1/4}$; irr = irreversible.

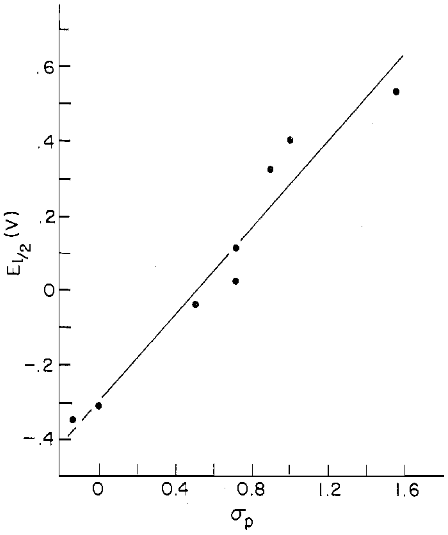

Figure 5. Plot of $E_{1/2}$ vs. σ_p for a series of substituted 16-membered ring complexes.

Since oxidation is the removal of an electron from the oxidized species, the more electron density that is removed from the central metal ion as a result of the electronic properties of the substituent groups the harder it should be to perform the oxidation. This is exactly the behavior that is observed.

To quantify the observed variation, we applied the same treatment used for the spectrochemical data to the electrochemical data. Figure 5 shows a graph of the first oxidation potentials vs. the σ_p constant for a series of substituted 16-membered ring derivatives. The observed linear correlation is quite useful since this type of relationship readily allows both extrapolation and interpolation. The problem of tuning the Ni^{2+}/Ni^{3+} oxidation potential is thereby simplified to merely reading from the linear graph the electronic properties of the substituent groups which are needed to attain any desired oxidation potential and referring to a standard table of Ham-

Table XI. Correlations of First Oxidation Potentials with Hammett Constants for the Synthetic Complexes

ring size	Hammett const	slope (ρ) ± std dev	R
14	σ_m	0.63 ± 0.06	0.977
	σ_p	0.54 ± 0.04	0.985
	σ_p^-	0.35 ± 0.03	0.969
15	σ_m	0.59 ± 0.06	0.968
	σ_p	0.52 ± 0.04	0.982
	σ_p^-	0.33 ± 0.03	0.975
16	σ_m	0.67 ± 0.09	0.941
	σ_p	0.58 ± 0.06	0.965
	σ_p^-	0.34 ± 0.04	0.957

Table XII. Correlation of First Oxidation Potentials with Hammett Constants for Substituted Benzoyl Derivatives

ring size	Hammett const	slope (ρ) ± std dev	R
14	σ_p	0.035 ± 0.004	0.994
15	σ_p	0.064 ± 0.001	0.999
16	σ_p	0.047 ± 0.002	0.999

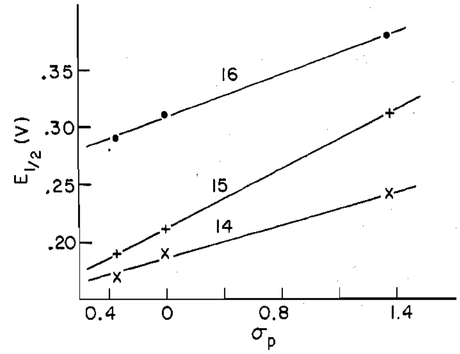

Figure 6. Plot of $E_{1/2}$ of substituted benzoyl derivatives vs. σ_p.

mett substituent constants to choose the appropriate substituents that would result in those electronic properties.

The R values listed in Table XI indicate linear correlations that are typical for such analyses. Again the correlations with various Hammett constants provide no conclusions as to a predominance of a resonance or inductive mode of electronic transmission in these systems. Further, the ρ values indicate that there is no ring size effect in the case of the electrochemical data. It is not clear why a ring size effect is observed for the spectrochemical data when none is seen for the electrochemical data.

Effect of Remote Substitution. A series of complexes was also examined to assess substituent effects at a more remote position with respect to the metal atom. This remote substitution was achieved by placing substituents at the para position of a benzoyl group. Three-membered series were examined for each ring size, the nitro, the methyl, and the unsubstituted derivatives (Table XII). The R values (Table XII) calculated from the linear correlations indicate a very good agreement with the calculated least-squares line. A ring-size effect is evident for this series of data by examining the ρ values (Figure 6). These slopes indicate that the 15-membered ring is more sensitive to substituent effects at this remote site followed by the 16-membered ring with the 14-membered ring exhibiting the least sensitivity. This may be the result of the overall planarity allowed by each ring size between the charge-delocalized chelate ring and the substituted π system of the benzoyl group.

Relative Sensitivity to Substituent Effects of Synthetic Macrocycles and Porphyrins. It is interesting and informative to compare the effects of substituents in these complexes with those observed for substituted porphyrins. Kadish and Morrison[18] examined remote substituent effects in porphyrin complexes by substituting various groups at the para position of the phenyl rings of tetraphenylporphyrin. The reaction constant, ρ, they obtained for the first oxidation process was +0.07 V. This was shown to be relatively insensitive to the central metal ion. The effect of direct substitution on the porphyrin ring was also evaluated by Kadish and Morrison[19] in studies involving the β positions of octaethylporphyrin. They obtained a reaction constant of +0.50 V for the first oxidation. Table XIII compares these effects for the porphyrin ring with those seen for the 15-membered-ring complexes reported here. The comparison between these two macrocyclic systems is astonishing. Both show essentially the same sensitivity with respect to remote and direct substitution on the periphery of the macrocycle. The close similarity in behavior is even more surprising in view of the fact that the oxidations for the two series have different centers. For the porphyrins it is ligand centered while for the nickel Jäger complexes it is metal ion centered. The similarity probably relates to the fact that in both macrocycles the substitution effects are transmitted from γ positions, through charge-delocalized six-member chelate rings.

Table XIII. Comparison of Substituent Effects for Porphyrins and the Synthetic Macrocycles (V)

substitution	[Ni(Me$_2$E$_2$[15]-tetraenatoN$_4$)]	porphyrin
direct	+0.52	+0.50[19]
remote	+0.064	+0.07[18]

Substitution of Other Positions of the Macrocycle. To assess the possibility of exerting further control over the properties mentioned thus far, we attempted substitution at positions other than on the γ- and γ'-carbons of the unsaturated six-membered chelate ring. For other macrocyclic systems methyl substitution proved to exert a large effect upon $E_{1/2}$ values exhibited by the complexes.[9] Methyl substitution on the saturated linkages in the complexes discussed here can easily be accomplished by simply substituting various diamines in Scheme I. This was realized by substituting 1,2-diaminopropane, 1,2-diamino-2-methylpropane, and 2,3-diamino-2,3-dimethylbutane for ethylenediamine in the second reaction of Scheme I to produce complexes having one, two, and four methyl groups on a five-membered saturated chelate ring. Analytical, mass spectral, and infrared data are listed for these complexes in Tables I and II. As a clear illustration of the effect of methyl substitution Table XIV shows spectrochemical and electrochemical data for these complexes as compared to the previously discussed materials that have no methyl substituents on their saturated chelate ring. It is obvious that methyl substitution for these complexes has no systematic effect upon the properties examined. This insensitivity is consistent with the steric origin suggested for alkyl group effects in other systems.[9] It was previously suggested that both the oxidized and reduced forms of [Ni(Me$_n$E$_m$[Z]tetraenatoN$_4$)] contain square-planar nickel. It appears that previously observed effects of alkyl substituents on saturated chelate rings arise from steric interaction with axial ligands.[6]

Experimental Section

General Data. Synthetic procedures on the nickel complexes were performed on the bench top under a blanket of nitrogen which had been passed through an aqueous solution of chromium(II) to remove oxygen unless otherwise noted. Reagent grade solvents stored for several days over molecular sieves were employed. Standard drying procedures[29] were employed for solvents used for electrochemistry. Nitrogen was bubbled through the dry solvent for 15 min to remove traces of oxygen. Triethylamine, ethylenediamine, 1,2-diaminopropane,

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(29) Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1970; pp 116–121.

Table XIV. Effect of Methyl Substitution on Electrochemical and Spectrochemical Behavior for the Derivatives [Ni(Me$_n$Ac$_2$[*Z*]tetraenatoN$_4$)]^a

no. of methyl groups	ring size (*R*)	$E_{1/2}$,^{b} V oxidation	$E_{1/2}$,^{b} V reduction	ν_{dd}, cm^{-1} × 10^3 (ϵ)	other transitions: ν, cm^{-1} × 10^3 (ϵ)^c
2	14	+0.19		19.69	
3	14	+0.22 (Δ = 75 mV) +0.79 (irr)	~−2.7 (abs)	19.74 (392)	29.28 (27 700), 35.27 (12 500), 40.32 (10 700)
4	14	+0.22		19.69	
6	14	+0.235 (Δ = 60 mV) +0.83 (irr)	~−2.7 (abs)	19.72 (531)	29.54 (37 000), 35.27 (17 000), 40.16 (22 900)
2	15	+0.22		19.30	
3	15	+0.24 (Δ = 70 mV) +0.71 (irr)	~−2.5 (abs)	19.42 (318)	29.85 (33 400), 38.31 (18 900)
4	15	+0.25		19.38	
6	15	+0.25		19.63	

^{a} For details of structure refer to Figure 1. ^{b} Potentials were obtained with use of a rotating platinum disk electrode in dimethylformamide containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate vs. an Ag/AgNO$_3$ reference electrode. $\Delta = E_{3/4} - E_{1/4}$; irr = irreversible; abs = absorption at electrode. ^{c} Spectra were obtained for 10^{-3}–10^{-4} M solutions in chloroform.

and 1,3-diaminopropane were all distilled under nitrogen from KOH prior to use. β-(Carbomethoxy)propionyl chloride was prepared via a procedure in ref 30 and was distilled prior to use. *p*-Methylbenzoyl chloride was produced via the action of thionyl chloride on *p*-toluic acid. This and other acid chlorides were distilled prior to use. N$_2$O$_5$ was prepared by the reaction procedure of Caesar and Goldfrank[31] and was stored in a refrigerator as a chloroform solution. All other chemicals were reagent grade and used without purification.

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were obtained as either Nujol mulls or KBr pellets. They were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer. Mass spectra were run by Mr. Richard Weisenberger with an MS-9 mass spectrometer at 70 eV. Ultraviolet, visible, and near-infrared spectra were obtained in chloroform solution with use of matched 1-cm quartz cells. They were recorded on a Varian Instruments Cary Model 17D recording spectrophotometer.

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 XY 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.

Syntheses of Nickel Complexes. 3-(Ethoxymethylidene)-2,4-pentanedione. A 2-L one-necked, round-bottomed flask with a ground-glass joint is charged with 498 mL (3 mol) of triethyl orthoformate, 546 mL (6 mol) of acetic anhydride, and 309 mL (3 mol) of 2,4-pentanedione. This mixture is refluxed under nitrogen for approximately 0.5 h, at which time the temperature has dropped to 100–105 °C. The solution is distilled under house vacuum until the temperature reaches 115 °C, and this forerun is discarded. The vacuum distillation is continued. The temperature rapidly rises to 155–160 °C, and a yellowish liquid is collected. The distillation is stopped when the distillate begins to darken, yielding 300–330 g of a yellow oil (65–70%). *Caution*! The vapors filling the system immediately after completion of the distillation are extremely combustible. Several accidents have occurred in these laboratories when air was admitted back into the system after vacuum distillation. For avoidance of this problem the system should initially be brought back to atmospheric pressure by flushing the system with nitrogen after it has cooled for 5 or 6 min. If longer cooling periods are employed, the dark residue that remains in the flask hardens and becomes extremely difficult to wash out of the flask with chloroform. When this procedure has been followed, no ignitions of the flammable vapors have occurred.

3,3′-[Trimethylenebis(iminomethylidene)]bis(2,4-pentanedione) and 3,3′-[Ethylenebis(iminomethylidene)]bis(2,4-pentanedione). These materials were both synthesized by the procedure of Riley.[22,23] A typical procedure involves adding 1.92 mol of either 1,3-propanediamine or ethylenediamine dissolved in 800 mL of absolute ethanol to a solution of 3.84 mol of 3-(ethoxymethylidene)-2,4-pentanedione dissolved in 2.5–3 L of absolute ethanol. The addition should take approximately 1 h. During the addition the reaction vessel is cooled by immersing it in a water–ice bath. After the addition is complete, the mixture is stirred for approximately 30 min while it is cooled with the water–ice bath. The precipitate which forms during the addition is filtered and air-dried overnight. A typical yield is 70% on the basis of starting 3-(ethoxymethylidene)-2,4-pentanedione.

3,3′-[Trimethylenebis(iminomethylidene)]bis(2,4-pentanedionato)nickel(II) (Ni-16-LTD), 3,3′-[Ethylenebis(iminomethylidene)]bis(2,4-pentanedionato)nickel(II) (Ni-14-LTD), (6,13-Diacetyl-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,8,11,13-tetraenato)nickel(II) ([Ni(Me$_2$Acyl$_2$[14]tetraenatoN$_4$)]), and (7,15-Diacetyl-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato)nickel(II) ([Ni(Me$_2$Acyl$_2$[16]tetraenatoN$_4$)]). All of these materials were prepared by the procedure described by Riley.[22,23]

(6,14-Diacetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato)nickel(II) ([Ni(Me$_2$Acyl$_2$[15]tetraenatoN$_4$)]). To 50 g (0.149 mol) of Ni-14-LTD in a single-necked, 1-L round-bottomed flask are added 50 mL (0.60 mol) of dry 1,3-diaminopropane (dried over and distilled from potassium hydroxide), 100 mL of dimethyl sulfoxide (dried over 4-Å Linde molecular sieves), and 400 mL of xylene. A Dean-Starke trap is attached to the flask with a condenser, and the system is flushed with nitrogen and heated in an oil bath maintained at 160–180 °C. During the reflux period the color of the mixture changes to a dark red and a lower layer appears in the Dean-Starke trap. After 22–25 mL of liquid has been collected in this lower layer, the reaction is allowed to cool. The cooled reaction mixture is filtered, and the crystallite solid is washed thoroughly with xylene and dried in a vacuum oven overnight. The mother liquor and washings can be taken to dryness to obtain another crop of the material. The final crop can be recrystallized in boiling xylene. The total yield from both crops is 44.5–47.3 g (80–85%).

(6,13-Diacetyl-2,7,12-trimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)nickel(II) ([Ni(Me$_3$Acyl$_2$[14]tetraenatoN$_4$)]). The synthesis of the necessary linear tetradentate nickel(II) complex is exactly the same as for Ni-14-LTD except that 1,2-diaminopropane is substituted for ethylenediamine. However, the ring closure is different for this material. To a slurry of 20 g (0.057 mol) of the corresponding linear tetradentate nickel complex in 75 mL of xylene and 25 mL of Me$_2$SO (both solvents were dried over molecular sieves for at least 1 week) is added 4–5 mL of freshly distilled ethylenediamine. The water azeotrope is removed by using a Dean-Starke trap, similar to the procedure for [Ni(Me$_2$Acyl$_2$[15]tetraenatoN$_4$)]. This mixture is refluxed under nitrogen until 12 mL of H$_2$O has been extracted. The reaction mixture is then allowed to cool. When cool, the precipitate is isolated by filtration. This precipitate is a mixture of the desired product and unreacted starting material. This mixture can be separated with a chromatographic column of 2–3 in. of neutral alumina with chloroform as the eluant. The fastest moving band contains unreacted starting material, and the slowest moving band is the desired product. The second band is collected and rotary evaporated to dryness. The resulting orange powder is recrystallized from a 50/50 mixture of ethanol/chloroform. The yield is 8.4 g (38%).

(6,13-Diacetyl-2,2,7,12-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)nickel(II) ([Ni(Me$_4$Acyl$_2$[14]tetraenatoN$_4$)]). This material was prepared by using a method published by Hipp;[24] yield 35–45%.

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(30) "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, p 169.

(31) Caesar, G. V.; Goldfrank, M. *J. Am. Chem. Soc.* **1946**, *68*, 372.

(6,13-Diacetyl-2,2,3,3,7,12-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)nickel(II) ([Ni(Me$_6$Acyl$_2$[14]tetraenatoN$_4$)]). This complex is synthesized[22] by a procedure analogous to that for [Ni(Me$_4$Acyl$_2$[14]tetraenatoN$_4$)], as published by Hipp.[24] Substitution of 2,3-diamino-2,3-dimethylbutane in place of ethylenediamine yields the corresponding linear tetradentate complex. The closure step is performed with a slurry of 20 g (0.015 mol) of the linear tetradentate complex in 50 mL of dry ethylenediamine. This slurry is refluxed for 1 h and then allowed to cool. Then 100 mL of distilled H_2O is added and the mixture is cooled overnight in the refrigerator. The solid is filtered; it is then dissolved in chloroform and the solution is dried by stirring for at least 1 h with anhydrous sodium sulfate. The sodium salt is filtered, and absolute ethanol is added to the solution. Rotary evaporation of the mixture to a volume of 10–15 mL yields 8.2 g (40%) of the desired complex.

(6,14-Diacetyl-2,7,13-trimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato)nickel(II) ([Ni(Me$_3$Acyl$_2$[15]tetraenatoN$_4$)]). The synthesis of the nickel linear tetradentate complex is described earlier during the procedure for [Ni(Me$_3$Acyl$_2$[14]tetraenatoN$_4$)]. The desired compound can be made by using exactly the same procedure as for [Ni(Me$_6$Acyl$_2$[14]tetraenatoN$_4$)] except that 50 mL of 1,3-diaminopropane is used in the ring-closure step instead of the corresponding amount of ethylenediamine, yielding 50–60% of [Ni(Me$_3$Acyl$_2$[15]tetraenatoN$_4$)].

(7,12-Dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)nickel(II) ([Ni(Me$_2$[14]tetraenatoN$_4$)]), (7,13-Dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato)nickel(II) ([Ni(Me$_2$[15]tetraenatoN$_4$)]), and (8,14-Dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato)nickel(II) ([Ni(Me$_2$[16]tetraenatoN$_4$)]). Procedure I. These materials can be synthesized by the procedure described by Riley.[22] This is a two-step procedure with a lower overall yield than procedure II. Overall yields based on starting diacetylated nickel(II) complexes are 20–25%.

Procedure II. In a 1-L single-necked flask are combined 0.05 mol of the corresponding diacetylated complex, 0.16 mol of *p*-toluenesulfonic acid monohydrate, and 250 mL of methanol. The mixture is maintained at reflux under nitrogen for 40–45 min during which time the solution becomes dark. The solution is then cooled in a dry ice/acetone bath, and a solution of 0.2 mol of sodium hydroxide in 100 mL of methanol is added under nitrogen. The solution is removed from the cold bath and stirred under nitrogen for 30 min. A greenish red solution and precipitate result. Care must be taken not to expose the solution to air during the workup. The methanol is removed by evaporation to dryness, and 50–100 mL of dry benzene is added. This slurry is taken to dryness to remove any traces of methanol, and 100 mL of dry benzene is added. The resulting slurry is filtered through a pad of Celite filter aid. About 100 mL of dry benzene is used to aid in the transfer of product and in the washing of the sodium tosylate. The benzene filtrate is concentrated to about 50 mL total solution volume. This solution is then chromatographed on a column approximately 2 in. in diameter with use of 2–3 in. of activity grade 1 neutral alumina and with benzene as the eluant. The fastest moving band is the desired product. This band is collected, and the benzene is evaporated. The resulting solid is recrystallized from absolute ethanol under an inert atmosphere, yielding 10–12 g (65–75%) of a red-black solid. Note: All solutions of these materials are air sensitive so care should be taken not to expose them to the atmosphere.

[6,13-Bis(2′-carbethoxyethyl)-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato]nickel(II) ([Ni(Me$_2$Carbetet$_2$[14]tetraenatoN$_4$)]), [6,14-Bis(2′-carbethoxyethyl)-7,18-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato]nickel(II) ([Ni(Me$_2$Carbetet$_2$[15]tetraenatoN$_4$)]), and [7,15-Bis(2′-carbethoxyethyl)-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato]nickel(II) ([Ni(Me$_2$Carbetet$_2$[16]tetraenatoN$_4$)]). A solution of 10 mmol of ethyl acrylate in 2.5 mL of methylene chloride and 10 mL of absolute ethanol is added dropwise to a solution of 3.5 mmol of the appropriate unsubstituted nickel complex in 20 mL of methylene chloride and 40 mL of absolute ethanol. The addition is performed while the solution is stirred under a blanket of nitrogen. After the addition is complete (30 min), the mixture is allowed to stir for about 24 h. The solvents are removed, and the residue is taken into an inert-atmosphere dry lab facility. The residue is dissolved in benzene and filtered through a pad of Celite. The benzene is removed to produce a red oily material. This oil can be solidified and recrystallized from either absolute ethanol or heptane to obtain 25–35% yield of the corresponding substituted complex.

(6-Acetyl-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)nickel(II) ([Ni(Me$_2$Acyl[14]tetraenatoN$_4$)]) and (6-Acetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato)nickel(II) ([Ni(Me$_2$Acyl[15]tetraenatoN$_4$)]). In a 250-mL round-bottomed flask is added 0.04 mol of *p*-toluenesulfonic acid monohydrate to a slurry of 14 mmol of the corresponding diacetylated nickel complex in 100 mL of methanol. This mixture is refluxed for 10 min under nitrogen. The mixture is rapidly cooled to dry ice/acetone temperature. Once cool, the acid is neutralized with a solution of 0.05 mol of sodium hydroxide dissolved in 100 mL of methanol. (During the cooling and neutralization procedures the solution is stirred vigorously.) The stirring is continued for an additional 30 min at room temperature. The solvent is then removed, and the solid is taken into an inert-atmosphere dry lab facility. Care must be taken not to expose the neutralized solution to oxygen. Inside the inert-atmosphere dry lab facility the residue is dissolved in hot benzene and filtered through a pad of Celite. The volume is then reduced. The mixture is chromatographed on a column of 2–3 in. of activity grade 1 neutral alumina with a 90/10 benzene/acetonitrile mixture as the eluant. The first green band which elutes is the corresponding unsubstituted nickel complex. The orange-red second band is the desired material. The orange-red material can be recrystallized from diethyl ether to obtain a 55–65% yield of the desired complex.

(7-Acetyl-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato)nickel(II) ([Ni(Me$_2$Acyl[16]tetraenatoN$_4$)]). Prior to use, acetyl chloride was distilled (bp 51 °C). Under high-dilution conditions 0.25 g of freshly distilled acetyl chloride (3.5 mmol) in 500 mL of diethyl ether is added very slowly (over a period of 3 h) to a solution of 1 g of [Ni(Me$_2$[16]tetraenatoN$_4$)] (3.3 mmol) and 4 mL of triethylamine (29 mmol) in 400 mL of diethyl ether. The reaction vessel is maintained under a blanket of nitrogen and stirred during the addition which should take 4 h. After the addition, the solution is allowed to stir additionally for 1 h. The solvent is removed, and the resulting residue is taken into an inert-atmosphere dry lab facility. It is dissolved in hot benzene and filtered through a pad of Celite. The volume of the benzene solution is reduced to 1 or 2 mL, and the light orange powder that separates is filtered. The powder was identified as [Ni(Me$_2$Acyl$_2$[16]tetraenatoN$_4$)]. The dark red benzene solution is chromatographed on a column of 2 in. of activity grade 1 alumina with acetonitrile as the eluant. The desired material moves very rapidly through the column. The acetonitrile is removed, and the red powder is recrystallized from diethyl ether, yielding 0.62 g (54%).

[6,13-Bis(α-naphthylcarbamoyl)-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)nickel(II) ([Ni(Me$_2$Napcbyl$_2$[14]tetraenatoN$_4$)]), [6,14-Bis(α-naphthylcarbamoyl)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato]nickel(II) ([Ni(Me$_2$Napcbyl$_2$[15]tetraenatoN$_4$)]), and [7,15-Bis(α-naphthylcarbamoyl)-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato]nickel(II) ([Ni(Me$_2$Napcbyl$_2$[16]tetraenatoN$_4$)]). These complexes are prepared by adding 7 mmol of α-naphthyl isocyanate to a solution of 3.4 mmol of the corresponding unsubstituted nickel complex in 30 mL of methylene chloride. This mixture is allowed to stir for approximately 3 h under a blanket of nitrogen. During this time a precipitate forms. The mixture is filtered, yielding 75–85% of the desired disubstituted complex.

[6,14-Bis(ethylcarbamoyl)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato]nickel(II) ([Ni(Me$_2$Etcbyl$_2$[15]tetraenatoN$_4$)]) and [7,15-Bis(ethylcarbamoyl)-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato]nickel(II) ([Ni(Me$_2$Etcbyl$_2$[16]tetraenatoN$_4$)]). For the preparation of either of these complexes 0.1 mol of ethyl isocyanate is added to a solution of 3.4 mmol of the corresponding unsubstituted nickel complex in 50 mL of benzene. This mixture is stirred under nitrogen for 24 h. The precipitate which forms is filtered from the reaction mixture and dissolved in a minimum amount of chloroform. The chloroform solution is chromatographed on a short column (~1 in.) of activity grade 1 neutral alumina with chloroform as the eluant. The red band is collected. Recrystallizing the resulting solids from 50/50 mixture of methylene chloride/heptane results in 75–80% of the desired complex. The complexes must be thoroughly dried as they tend to crystallize as solvates.

[6-(Ethylcarbamoyl)-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato]nickel(II) ([Ni(Me$_2$Etcbyl[14]tetraenatoN$_4$)]). An 8-mL portion of ethyl isocyanate (0.10 mol) is added to a solution of 1.9 g of [Ni(Me$_2$[14]tetraenatoN$_4$)] (6.5 mmol) in

50 mL of dry benzene. The mixture is stirred and refluxed under nitrogen for ~3 h. The solvent is removed, and the residue is dissolved in 15–20 mL of chloroform. The solution is chromatographed on a column of 2 in. of activity grade 1 neutral alumina with chloroform as the eluant. The slower moving reddish band is the desired product. The faster moving green band is unreacted starting material. The desired product can be recrystallized from a 50/50 mixture of methylene chloride and heptane. The yield is 0.7 g (47%) of unreacted starting material and 0.9 g (40%) of the desired product.

[6,13-Bis(*p*-methylbenzoyl)-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato]nickel(II) ([Ni(Me$_2$(MeBzyl)$_2$[14]tetraenatoN$_4$)]), [6,14-Bis(*p*-methylbenzoyl)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato]nickel(II) ([Ni(Me$_2$(MeBzyl)$_2$[15]tetraenatoN$_4$)]), and [7,15-Bis(*p*-methylbenzoyl)-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato]nickel(II) ([Ni(Me$_2$(MeBzyl)$_2$[16]tetraenatoN$_4$)]). Prior to use *p*-methylbenzoyl chloride is distilled (bp 233 °C). Then 8.6 mmol of freshly distilled *p*-methylbenzoyl chloride is added to a solution of 3.4 mmol of the corresponding unsubstituted nickel complex and 14.4 mmol of triethylamine in 40 mL of methylene chloride and 40 mL of benzene. The mixture is stirred and refluxed under nitrogen for 5 h. The solvent is removed, and the residue is dissolved in 50 mL of hot chloroform and filtered through a pad of Celite. The volume is reduced, and the solution is chromatographed on a short column of activity grade 1 neutral alumina (~1 in.) with chloroform as the eluant. The desired compounds move fairly slowly on this column, but the unwanted contaminants stick tenaciously to the very top of the alumina. The orange band is collected, the chloroform is removed, and the compound is dried thoroughly, yielding 60–70% of the desired complex. Recrystallization is not necessary to obtain an analytically pure sample.

(6,13-Dibenzoyl-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)nickel(II) ([Ni(Me$_2$Bzyl$_2$[14]tetraenatoN$_4$)]), (6,14-Dibenzoyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato)nickel(II) ([Ni(Me$_2$Bzyl$_2$[15]tetraenatoN$_4$)]), and (7,15-Dibenzoyl-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato)nickel(II) ([Ni(Me$_2$Bzyl$_2$[16]tetraenatoN$_4$)]). Freshly distilled (bp 194 °C) benzoyl chloride (8.6 mmol) is added to a solution of 3.4 mmol of the corresponding unsubstituted nickel complex and 14.4 mmol of triethylamine in 40 mL of methylene chloride and 40 mL of benzene. The mixture is refluxed and stirred under nitrogen for 2 h. The solvent is removed, and the residue is dissolved in 50 mL of hot benzene. This solution is filtered through a pad of Celite. The benzene is removed by evaporation, and the solid is dissolved in a minimum amount of chloroform. The solution is chromatographed on a 1-in. column of activity grade 1 neutral alumina with chloroform as the eluant. The red-orange band is collected. The complexes can be recrystallized from benzene or 50/50 methylene chloride/heptane to result in 55–65% of the desired complexes. Care should be taken to thoroughly dry the material as it tends to crystallize as a solvate.

[6,13-Bis(*p*-nitrobenzoyl)-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato]nickel(II) ([Ni(Me$_2$(NitroBzyl)$_2$[14]tetraenatoN$_4$)]), [6,14-Bis(*p*-nitrobenzoyl)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato]nickel(II) ([Ni(Me$_2$(NitroBzyl)$_2$[15]tetraenatoN$_4$)]), and [7,15-Bis(*p*-nitrobenzoyl)-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato]nickel(II) ([Ni(Me$_2$(NitroBzyl)$_2$[16]tetraenatoN$_4$)]). *p*-Nitrobenzoyl chloride (8.6 mmol) is added to a solution of 3.4 mmol of the corresponding unsubstituted nickel complex and 14.4 mmol of triethylamine in 25 mL of methylene chloride and 25 mL of benzene. This mixture is stirred and refluxed under nitrogen for 2 h. The solvent is then removed, and the residue is dissolved in a minimum amount of chloroform. The solution is chromatographed on a short column (~1 in.) of activity grade 1 neutral alumina with chloroform as the eluant. The dark red band is collected. The solvent is removed, and the complexes can be recrystallized from a 50/50 mixture of methylene chloride/heptane yielding 60–70% of the desired complexes. These complexes must be thoroughly dried as they tend to crystallize as solvates.

[6,13-Bis(methylsuccinoyl)-7,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato]nickel(II) ([Ni(Me$_2$Mesuc$_2$[14]tetraenatoN$_4$)]), [6,14-Bis(methylsuccinoyl)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato]nickel(II) ([Ni(Me$_2$Mesuc$_2$[15]tetraenatoN$_4$)]), and [7,15-bis(methylsuccinoyl)-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato]nickel(II) ([Ni(Me$_2$Mesuc$_2$[16]tetraenatoN$_4$)]). Freshly distilled (bp 82 °C (11 mm)) β-(carbomethoxy)propionyl chloride (8.7 mmol) dissolved in 25 mL of methylene chloride is added dropwise to a solution of 3.4 mmol of the corresponding unsubstituted nickel complex and 14.4 mmol of triethylamine in 50 mL of methylene chloride. The addition should take about 30 min and should be accompanied by stirring under a protective nitrogen atmosphere. After the addition is complete, the mixture is stirred additionally for 1 h. The solvent is then removed, and the dark residue is dissolved in 50 mL of hot benzene and filtered through a pad of Celite. The benzene is then removed. The 14-membered ring derivative is chromatographed on a short column (~1 in.) of activity grade 1 neutral alumina with acetone as eluant. The red band is collected. For the 15- and 16-membered ring derivatives, recrystallization from methanol is sufficient to obtain analytically pure samples. By use of this reaction sequence 65–75% yields are obtained.

(6,14-Dinitro-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato)nickel(II) ([Ni(Me$_2$(NO$_2$)$_2$[15]tetraenatoN$_4$)]). The unsubstituted complex (1 g, 0.002 67 mol) is dissolved in 25 mL of glacial acetic acid and 1.0 mL (1.01 g, 0.008 01 mol) of concentrated nitric acid. The solution is stirred for about 30 s, and to this is added a cold solution of 0.54 g (0.008 18 mol) of potassium hydroxide in 10 mL water to which a 50-mL scoop of ice has been added. The mixture is stirred until the ice melts and then filtered. The yellow product is washed thoroughly with water and dried by suction. It is then chromatographed on a short column of deactivated alumina (30 g of grade 1 alumina + 2.25 mL of water) with chloroform to elute. The eluant is then slowly evaporated, yielding yellow crystals. These are recrystallized from chloroform; yield 0.51 g (50%).

(7,15-Dinitro-8,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,7,13,15-tetraenato)nickel(II) ([Ni(Me$_2$(NO$_2$)$_2$[16]tetraenatoN$_4$)]). In a good hood, 1 g of [Ni(Me$_2$[16]tetraenatoN$_4$)] (3.3 mmol) is dissolved in 75 mL of hot chloroform. To this solution is added a three- to fourfold excess of N$_2$O$_5$ as prepared by the procedure of Caesar and Goldfrank.[31] The hot solution is allowed to stir for approximately 10 min. It is filtered, and the solvent is removed by rotary evaporation. The residue is dissolved in a minimum amount of chloroform. The solution is chromagraphed on a short column (~1 in.) of activity grade 1 neutral alumina with chloroform as the eluant. The orange-yellow band is collected, and the solution is taken to dryness. The resulting orange-yellow powder is a mixture of the desired complex and a complex in which only one acetyl group has been replaced with a nitro group. The dinitro derivative can be obtained from this mixture by slurrying the orange-yellow powder in warm 3 M hydrochloric acid. The slurry is stirred for about 0.5 h and then filtered. This serves to protonate the material which still has an acetyl group present, thereby making it water soluble. The dinitro derivative is not affected. The yellow solid obtained from this procedure can be recrystallized from a 50/50 mixture of chloroform/absolute ethanol, yielding 0.36 g (33%) of a bright yellow powder.

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Registry No. Ni(Me$_2$Carbetet$_2$[14]tetraenatoN$_4$), 74466-31-2; Ni(Me$_2$Carbetet$_2$[15]tetraenatoN$_4$), 74466-32-3; Ni(Me$_2$Carbetet$_2$[16]tetraenatoN$_4$), 74466-33-4; Ni(Me$_2$Acyl[14]tetraenatoN$_4$), 74466-34-5; Ni(Me$_2$Acyl[15]tetraenatoN$_4$), 74482-21-6; Ni(Me$_2$Acyl[16]tetraenatoN$_4$), 74466-35-6; Ni(Me$_2$Etcbyl[14]tetraenatoN$_4$), 74466-36-7; Ni(Me$_2$Etcbyl$_2$[15]tetraenatoN$_4$), 74466-37-8; Ni(Me$_2$Etcbyl$_2$[16]tetraenatoN$_4$), 74466-38-9; Ni(Me$_2$Napcbyl$_2$[14]tetraenatoN$_4$), 74466-39-0; Ni(Me$_2$Napcbyl$_2$[15]tetraenatoN$_4$), 74482-40-9; Ni(Me$_2$Napcbyl$_2$[16]tetraenatoN$_4$), 74466-40-3; Ni(Me$_2$Mesuc$_2$[14]tetraenatoN$_4$), 74466-46-9; Ni(Me$_2$Mesuc$_2$[15]tetraenatoN$_4$), 74466-49-2; Ni(Me$_2$Mesuc$_2$[16]tetraenatoN$_4$), 74466-41-4; Ni(Me$_2$(MeBzyl)$_2$[14]tetraenatoN$_4$), 74466-47-0; Ni(Me$_2$(MeBzyl)$_2$[15]tetraenatoN$_4$), 74466-50-5; Ni(Me$_2$(MeBzyl)$_2$[16]tetraenatoN$_4$), 74466-42-5; Ni(Me$_2$Bzyl$_2$[14]tetraenatoN$_4$), 20123-02-8; Ni(Me$_2$Bzyl$_2$[15]tetraenatoN$_4$), 74466-48-1; Ni(Me$_2$Bzyl$_2$[16]tetraenatoN$_4$), 74466-43-6; Ni(Me$_2$(NitroBzyl)$_2$[14]tetraenatoN$_4$), 74466-45-8; Ni(Me$_2$(NitroBzyl)$_2$[15]tetraenatoN$_4$), 74466-51-6; Ni(Me$_2$(NitroBzyl)$_2$[16]tetraenatoN$_4$), 74466-44-7; Ni(Me$_2$(NO$_2$)$_2$[16]tetraenatoN$_4$), 74466-52-7; Ni(Me$_3$Acyl$_2$[14]tetraenatoN$_4$), 74466-53-8; Ni(Me$_3$Acyl$_2$[15]tetraenatoN$_4$), 74466-54-9; Ni(Me$_3$(CO$_2$C$_2$H$_5$)$_2$[16]tetraenatoN$_4$), 74482-41-0; Ni(Me$_2$-

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Synthesis of Superstructure Ligands Using a Novel Methyl Vinyl Ether Functional Group

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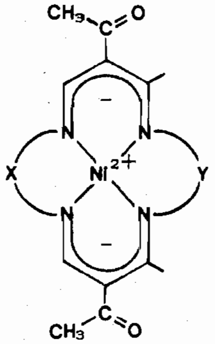
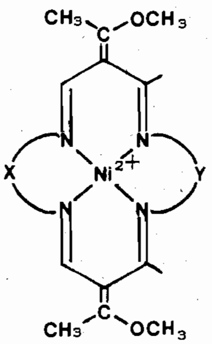
The presence of reactive peripheral functional groups facilitates the synthesis of macrocyclic ligands having superstructure components, designed to mimic the behaviors of biological molecules. The macrocyclic complexes $[Ni[(MeOEthi)_2Me_2[X]tetraeneN_4]]^{2+}$ (X = 14, 15, 16) contain an unusual peripheral conjugated methyl vinyl ether functional group that readily undergoes addition–elimination reactions, especially with amines. This reaction has been used to produce many derivatives whose structures differ either in macrocycle ring size or in the nature of R and R′ on the amine NHRR′. In this way four classes of pendant groups have been produced: (a) those having only small unreactive substituents such as CH_3 or H, (b) large hydrophobic groups such as decyl or naphthyl, (c) additional ligating groups like pyridine, and (d) hydrophilic groups exemplified by an 11-aminoundecanoic acid derivative.

Introduction

In order to develop certain classes of models for biological systems, it is highly useful to have access to functional groups appended to macrocyclic ligands. These functional groups provide points of attachment for superstructures designed to facilitate certain biomimetic properties in the metal complexes of the product ligands.[1,2] One such system of complexes involves those species originally synthesized by Jäger.[3,4] This unique class of structures is shown in structure I.



I

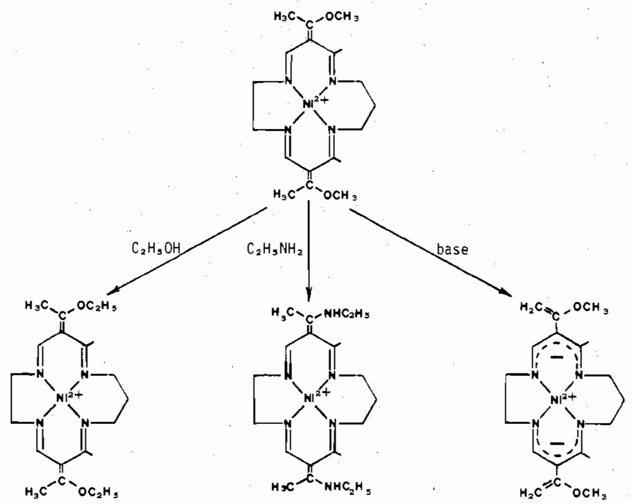


II

X, Y = $(CH_2)_{2,3}$

This species fits the requirements for a suitable starting structure for the synthesis of appropriate ligands since the products can be obtained in reasonable yields from readily available starting materials, the structures bear some useful similarities to porphyrins (four nitrogen donors with substantial unsaturation and delocalization), and they contain functional groups on the ligand periphery. A preliminary communication from these laboratories showed that this species can be alkylated[5] to yield compounds of structure II. Alkylation occurs at the oxygen atoms (formerly of the acetyl groups) as verified by a crystal structure determination.[5] This produces rather novel vinyl ether substituents on the periphery of the unsaturated six-membered chelate rings. These substituents are selectively reactive toward nucleophiles as seen in Scheme I.

Scheme I



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