anisms, unless a radical-forming step is reversible. A separate rate term may exist, however, of the form $k[Cu(SO_4)_n^{2-n}][S(IV)]$. A similar Cu(II) term can contribute significantly to the slower sulfur(IV) reduction of chloroaquoiron(III) complexes, in 1 M chloride media,[36] but was not observed in the sulfur(IV) reduction of sulfatoaquoiron(III) complexes in sulfate media.[6]

Oxidation of sulfur(IV) by a pathway second order in sulfur(IV) is unusual. The previous observation of a second-order path, in the oxidation by chromium(VI), probably involves reaction between a sulfitochromate(VI) ester and a second sulfur(IV) species.[37] Mechanism 7 is similar to that proposed for the chromium system,[37] except for the structure of the intermediate; ester formation by FeL_3^{3+} does not appear possible. A mechanism analogous to 6 could not account for the exact form of the rate law in the chromium system,[37] rate $= k[Cr(VI)][S(IV)]^2[H^+]/(1 + a[S(IV)])$, owing to the small value[35] of Q_{6a}.

Limiting mechanisms 6 and 7, representing approach to the transition state by two sulfur atoms, either in a single species (6), or separately (7), cannot be distinguished by the observations made in this study. The positive entropy of activation appears consistent with either mechanism. If mechanism 6 is correct, then comparatively great reactivity of $S_2O_5^{2-}$ in this system is implied; second-order terms could perhaps be found in other systems, including anion oxidants such as $IrCl_6^{2-}$, for which ion pairs or specific sulfur–ligand interactions are unlikely.

If mechanism 7 is correct, then one can question whether the species $(FeL_3 \cdot S)^{VII}$ is only an ion pair or if a more specific interaction between inner- and outer-sphere ligands exists. An experimental approach to this question would include attempts to detect the complex, or other $ML_3 \cdot S$ complexes, and studies of reaction with other metal ion oxidants, especially highly charged ones. It has been suggested[38] that anion catalysis of the $Fe(H_2O)_6^{2+}$–FeL_3^{3+} reaction may involve specific interaction between a bridging anion and the phenanthroline ligand.

The unexpected results of this work are the suggestions that $S_2O_5^{2-}$, potentially a two- to four-electron reducing agent, may react rapidly in a one-electron step and an alternate possibility that decomposition of $(FeL_3 \cdot S)^{VII}$ to FeL_3^{2+} and S(V) can be accelerated by S(IV).

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Synthesis and Properties of Tetraaza[14]tetraene and Tetraaza[14]hexaene Macrocyclic Complexes

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Abstract: An efficient nontemplate synthesis of the new macrocycle 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (H_2(MeHMe(en)$_2$), **11**) is described. This compound reacts with metal(II) acetates or with other metal(II) salts under conditions of nonaqueous chelation to afford the macrocyclic 12-π complexes M(MeHMe(en)$_2$) (**13**, M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II)), whose electronic properties are consistent with planar coordination. Treatment of the Ni(II) and Cu(II) complexes with 3 equiv of trityl tetrafluoroborate in acetonitrile results in oxidative dehydrogenation, yielding the 15-π cations [M(MeHMe-2,9-diene)]$^+$ (**15**) which were isolated as their tetrafluoroborate salts. Conductivity, spectrophotometric, and epr results indicate that the nickel complex exists in a paramagnetic monomer $\rightleftarrows$ diamagnetic dimer equilibrium in solution. The nickel and copper cations are reduced by sodium borohydride in ethanol to the neutral 16-π complexes M(MeHMe-2,9-diene) (**14**). Voltammetric studies of these complexes in acetonitrile have established the existence of a three-membered electron-transfer series **14** (16-π) $\rightleftharpoons$ **15** (15-π) $\rightleftharpoons$ **16** (14-π). Members of the series are interconverted by reversible one-electron redox processes considered to alter the ligand oxidation level such that the terminal oxidized member, [M(MeHMe-2,8,10-triene)]$^{2+}$ (**16**), contains a $(4n + 2)$-stabilized ring system. 16-π Ni(II) complexes **26** derived from several recently reported dihydrooctaaza[14]annulene macrocycles have been prepared. These and the 16-π Ni(II) complexes **1** were found to undergo two-electron oxidations, presumably yielding the 14-π species **27** and **28**, respectively.

Attempts to relate electronic properties and reactivities of synthetic macrocyclic complexes to those of naturally occurring macrocycles, such as porphyrins and corrins, continue to promote considerable interest in their design and preparation. Work in this area has resulted in substantial progress in the development of cyclization reactions, usually involving metal ions, which have led to a variety of new macrocycles.[1] In addition, development of systematic transformations, particularly hydrogenation and dehydrogenation reac-

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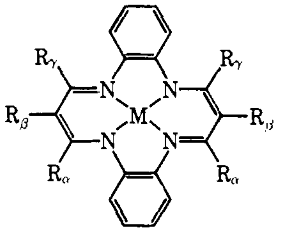
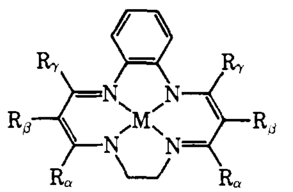
tions, has allowed preparation of species with lesser or greater degrees of unsaturation than the precursor macrocyclic complex.

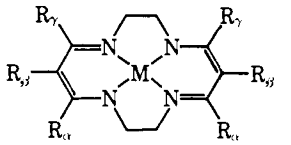
In contrast to the natural macrocycles, which usually contain four conjugated six-membered rings or three six- and one five-membered ring (6-6-6-6 and 6-6-6-5 types, respectively), the majority of synthetic macrocycles are of the 6-5-6-5 type.[2] Their complexes may be organized in terms of the degree of unsaturation of the ligand structure internal to the chelate rings. Known examples range from the completely conjugated 16-π electron system **1**[3–6] to the completely saturated system **6**[7] (and *C*-methyl derivatives thereof[8]) and include the 14-π[9] (**2**), 12-π[9–11] (**3**), 8-π[8,12] (**4**), and 4-π[8,13,14] (**5**) systems. Cis and trans 6-π and 2-π complexes derived from **5** have also been reported.[8,12a] In addition, the neutral complexes **7** with B = phen and en, which have been prepared recently,[15] may be recognized as 14-π and 12-π cases, respectively.



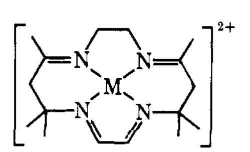
1, M(R$_\gamma$R$_\beta$R$_\alpha$-(phen)$_2$)



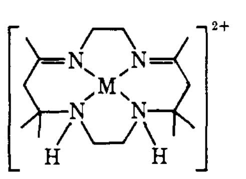
2



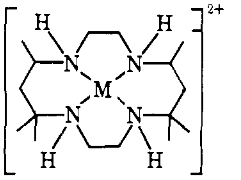
3, M(R$_\gamma$R$_\beta$R$_\alpha$-(en)$_2$)



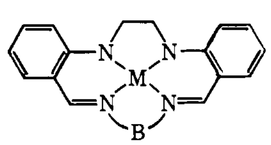
4 (cis, trans)



5 (cis, trans)



6



7

In the course of our examination of electronic properties and chemical reactivities of divalent metal ions in planar or tetragonal N$_4$ environments, we have devised a nontemplate synthesis of the basic macrocycle 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,-6,11,13-tetraene, H$_2$(MeHMe(en)$_2$), and its 12-π metal(II) complexes M(MeHMe(en)$_2$), M = Fe(II)–Zn(II).

This report elaborates our recent account[16] of this work and also describes a new synthetic approach to the dehydrogenation of coordinated ligands which has resulted in the preparation of Ni(II) and Cu(II) complexes of the new 16-π macrocycle ligand 5,7,12,-14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-2,4,6,9,-11,13-hexaene. Spectral and limited magnetic properties are presented for the above complexes and several members of another new class of 16-π M(II)–N$_4$ macrocyclic complexes derived from one type of recently reported dihydro-1,2,4,5,8,9,11,12-octaaza[14]annulenes.[17] Electrochemical and synthetic studies have been carried out on a series of 16-π complexes in order to determine if they can be oxidized to the 14-π level. Species of the latter type would presumably contain a (4*n* + 2)-stabilized macrocycle representing aza analogs of the carbocycle [14]annulene.[18]

Experimental Section

Preparation of Compounds. Ni(HHH(phen)$_2$), Ni(MeHH-(phen)$_2$), and Ni(Me, COMe, H(phen)$_2$) were prepared by published methods.[4,6] Analytical data for new compounds are given in Table I. Spectral and other properties are summarized in Tables II–V. Structural formulas are set out in Scheme I and in the text.

5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,12-tetraene, H$_2$(MeHMe(en)$_2$) (11) and Its Metal(II) Complexes, M(MeHMe(en)$_2$) (13). H$_2$(MeHMe(en)$_2$). To a solution of 30.0 g (0.30 mol) of 4-aminopent-3-en-2-one[19] in 200 ml of dry dichloromethane was added 57.0 g (0.30 mol) of triethyloxonium tetrafluoroborate dissolved in 150 ml of dry dichloromethane. The solution was stirred at room temperature under an atmosphere of dry nitrogen for 30 min. Ethylenediamine (9.0 g, 0.15 mol), freshly distilled from sodium hydroxide, was added dropwise with stirring over a 30-min period. The solution was stirred for an additional 3 hr at room temperature during which time a white solid formed. Dichloromethane was removed under reduced pressure and replaced with 400 ml of absolute methanol. To this solution was added 16.2 g (0.30 mol) of sodium methoxide in 150 ml of methanol and thereafter an additional 9.0 g (0.15 mol) of ethylenediamine was immediately introduced. The reaction was allowed to proceed for 4 hr with stirring during which time ammonia was evolved. Removal of the methanol under reduced pressure, followed by extraction of the residue with hot absolute ethanol, yielded a first crop of cream-colored platelets from the cooled extract. A second crop was obtained by extraction of the residue with chloroform and removal of this solvent under reduced pressure. The two crops were combined and recrystallized from *ca.* 1800 ml of absolute ethanol to afford 13.0–13.2 g (35–35.5%) of pure product as cream-colored platelets. The product is best stored in a dry nitrogen atmosphere. Molecular weight: calcd, 248; found, 244 (osmometry, toluene solution). The mass spectrum revealed an intense parent ion peak at *m/e* 248.

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Table I. Characterization Data for Macrocyclic Ligand and Complexes

Compound	Mp,[a] °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
H$_2$(MeHMe(en)$_2$)	226–228	67.70	9.74	22.56	67.83	9.70	22.65
[H$_4$(MeHMe(en)](BF$_4$)$_2$	175–180	36.22	6.08	14.08	36.34	6.05	13.68
Fe(MeHMe(en)$_2$)	340–343	55.64	7.34	18.54	55.67	7.07	18.33
Co(MeHMe(en)$_2$)	>360	55.08	7.26	18.35	54.63	7.06	18.24
Ni(MeHMe(en)$_2$)	331–334	55.12	7.27	18.36	55.15	7.15	18.32
[Ni(H(MeHMe(en)$_2$))](BF$_4$)	247–251	42.69	6.04	14.22	43.15	6.03	14.31
[Ni(MeHMe-2,9-diene)](BF$_4$)[b]	262–263	43.24	4.93	14.41	43.64	4.80	14.54
Ni(MeHMe-2,9-diene)	310–312 dec	55,86	6.03	18.61	55.89	5.96	18.58
Ni(Me$_2$(ch)oaa)	273–275	49.90	5.76	29.10	50.08	5.93	29.29
Ni(Et$_2$(ch)oaa)	257–259	52.33	6.34	27.12	52.22	6.55	27.14
Cu(MeHMe(en)$_2$)	298–299	54.26	7.16	18.08	54.29	7.09	18.18
[Cu(MeHMe-2,9-diene)](BF$_4$)	255–256	42.81	4.62	14.26	43.25	4.83	14.41
Cu(MeHMe-2,9-diene)	320–322	54.98	5.93	18.31	55.08	6.10	18.31
Zn(MeHMe(en)$_2$)	266–268	53.94	7.11	17.97	54.23	6.76	17.96

[a] Sealed tube, uncorrected. [b] Calculated for [Ni(MeHMe-1-ene)](BF$_4$): C, 43.02; H, 5.41; N, 14.33.

Table II. Pmr Data for Macrocycles and Complexes

Compound	Solvent	Chemical shifts, ppm
H$_2$(MeHMe(en)$_2$)	CDCl$_3$	−1.95 (Me), −3.51 (CH$_2$), −4.58 (CH), −11.6[a] (NH)
[H$_4$(MeHMe(en))](BF$_4$)$_2$[b]	py-d_5	−2.36[c] (Me), −3.83[d] (CH$_2$), −5.49 (CH), −8.80[a] (NH)
Ni(MeHMe(en)$_2$)	CDCl$_3$	−1.90 (Me), −3.12 (CH$_2$), −4.58 (CH)
[Ni(H(MeHMe(en)$_2$))](BF$_4$)	DMSO-d_6	−2.01 (Me), −2.14 (Me), −3.40[d] (CH$_2$), −4.19 (CH), −4.92 (NH)
Zn(MeHMe(en)$_2$)[e]	CHCl$_3$	−1.97 (Me), −3.52 (CH$_2$), −4.47 (CH)
H$_2$(Me$_2$(ch)oaa)	CDCl$_3$	−1.65[d] (β-CH$_2$), −2.10 (Me), −2.32[d] and −2.70[d] (α-CH$_2$), −17.4 (NH)
H$_2$(Et$_2$(ch)oaa)	CDCl$_3$	−1.18[f] (Me), −1.65[d] (β-CH$_2$), −2.30[d] and −2.72[d] (α-CH$_2$), −2.50[f] (CH$_2$), −17.2 (NH)
Ni(Me$_2$(ch)oaa)	CDCl$_3$	−1.67[d] (β-CH$_2$), −2.09 (Me), −2.50[d] and −2.85[d] (α-CH$_2$)
Ni(Et$_2$(ch)oaa)	CDCl$_3$	−1.13[f] (Me), −1.70[d] (β-CH$_2$), −2.48[d] and −2.88[d] (α-CH$_2$), −2.56[f] (CH$_2$)

[a] Center of broad peak. [b] A second small peak in the (CH) region at −5.21 ppm (relative intensity ~10%) indicates the presence of a second conformation in solution or an impurity of similar structure. [c] Center of two overlapping singlets. [d] Center of a complex multiplet. [e] Spectrum taken in CHCl$_3$ because of loss of (CH) signal due to exchange in CDCl$_3$. [f] Centers of triplet and quartet of ethyl groups, J_{HH} = 7.5 Hz.

Table III. Magnetic and Electronic Spectral Data

Compound	μ_{eff} (BM)[a]	λ_{max}, cm^{-1} (ϵ)[b]
H$_2$(MeHMe(en)$_2$)[c]		30,200 (sh, 5800), 32,600 (28,700), 33,100 (sh, 25,200)
Zn(MeHMe(en)$_2$)[c]	dia	~18,500 (sh, 70), ~25,100 (sh, 1400), ~28,300 (sh, 10,100), 30,300 (17,000)
Fe(MeHMe(en)$_2$[d]	3.95	7690 (87), ~10,100 (sh, 140)
Co(MeHMe(en)$_2$)[d]	2.06	10,870 (45), ~17,000 (sh, ~280), ~19,600 (sh, 790), ~21,500 (sh, 1290), ~23,200 (sh, ~1700), 25,800 (5230), ~27,800 (sh, 4200), 32,200 (7700), 37,500 (9130)
Ni(MeHMe(en)$_2$)$_2$[c,g]	dia	17,900 (227), 21,500 (sh, 1200), 23,600 (sh, 3700), 24,950 (6090), ~30,400 (sh, ~4400), 34,500 (15,200), ~38,900 (sh, ~10,300)
[Ni(H(MeHMe(en)$_2$))](BF$_4$)[e]	dia	18,700 (186), 21,600 (sh, 140), ~24,400 (sh, ~550), 25,400 (sh, 1250), 28,100 (9930), 29,100 (sh, 8300), 36,300 (5060), 38,600 (6080)
[Ni(MeHMe-2,9-diene)](BF$_4$)[f,h]	dia	7500 (565), 11,100 (2320), ~13,800 (sh, 1900), ~16,600 (sh, 1400), 18,800 (1740), ~21,700 (sh, 2600), ~23,500 (sh, 3200), 27,200 (12,400), 30,100 (11,100), 34,000 (23,100), 34,700 (sh, 22,100)
Ni(MeHMe-2,9-diene)[c,g]	dia	14,500 (195), 15,800 (175), ~17,300 (sh, 120), 21,100 (3620), 22,700 (3560), 27,500 (18,500), 28,700 (17,000), 33,100 (20,300), 36,800 (22,300)
H$_2$(Et$_2$(ch)oaa)[c]		31,100 (24,100), 39,500 (30,400)
Ni(Et$_2$(ch)oaa)[c]	dia	17,080 (3770), ~17,900 (sh, 3380), ~22,200 (sh, 5200), 22,700 (5730), 30,800 (12,300), ~37,900 (sh, 11,900)
Cu(MeHMe(en)$_2$)[c,g]	1.78	16,200 (111), 20,900 (sh, 220), 22,500 (sh, 330), 24,700 (sh, 790), 27,700 (sh, 5900), 29,500 (21,800), 30,200 (sh, 13,000), 33,200 (10,300), ~40,000 (sh, ~12,500)
[Cu(MeHMe-2,9-diene)](BF$_4$)[f]	1.11	12,740 (1890), ~14,820 (sh, 2190), 15,400 (2230), ~17,600 (sh, 1300), 21,600 (1110), ~23,100 (sh, 1380), ~27,500 (sh, 13,400), 29,200 (21,900), 32,100 (19,000), 33,800 (21,400), ~34,800 (sh, 19,500), 37,000 (17,600)
Cu(MeHMe-2,9-diene)[c,g]	1.78	15,100 (170), 16,600 (160), 21,000 (3240), 22,200 (3810), ~23,500 (sh, 2750), ~26,000 (sh, 5850), 28,700 (32,700), ~29,500 (sh, 29,600), ~33,500 (sh, 11,800), 35,400 (17,300), ~43,000 (sh, 28,000)

[a] Solid state, ~25°; dia = diamagnetic. [b] Apparent values, uncorrected for underlying absorption. [c] Chloroform solution. [d] DMF solution. Due to extreme air sensitivity of the Fe(II) complex, a reproducible spectrum at >10,500 cm^{-1} was not obtained. [e] Methanol solution. [f] Acetonitrile solution. [g] Reproducible spectra were not obtained at <14,000 cm^{-1} because of decomposition in ir lamp beam. [h] c = 9.5 × 10^{-4} M.

Table IV. Conductivity Data for Acetonitrile Solutions at 25° [a]

Compound	Λ_0 ohm^{-1} cm^2 equiv^{-1}	A Calcd	A Found
$(n\text{-}Bu_4N)(BF_4)$	163	350[b]	362
$[Ni(H(MeHMe(en)_2))](BF_4)$	167	352[b]	369
$[Ni(MeHMe\text{-}2,9\text{-}diene)](BF_4)$	179	748[c]	580
$[Cu(MeHMe\text{-}2,9\text{-}diene)](BF_4)$	167	352[b]	355

[a] The cell was calibrated with 0.01 *N* KCl in distilled water. Measurements were made at four–six concentrations in the range 5×10^{-3}–1×10^{-4} *M*. [b] Calcd for 1:1 electrolyte. [c] Calcd for 2:1 electrolyte. Value for 1:1 electrolyte is 362.

Table V. Polarographic Data for Nickel and Copper Complexes

Complex	Solvent	Couple[a]	$E_{1/2}$, V	i_d/C[b] (μA/m*M*)	Slope, mV $\lvert E_{3/4} - E_{1/4}\rvert$
$Ni(MeHMe\text{-}2,9\text{-}diene)$	CH_3CN	$0 \rightleftharpoons +1$	+0.11	−29	64
		$+1 \rightleftharpoons +2$	+0.70	−24	54
$[Ni(MeHMe\text{-}2,9\text{-}diene)](BF_4)$	CH_3CN	$0 \rightleftharpoons +1$	+0.10	33	59
		$+1 \rightleftharpoons +2$	+0.70	−26	52
$Cu(MeHMe\text{-}2,9\text{-}diene)$	CH_3CN	$0 \rightleftharpoons +1$	−0.04	−25	58
		$+1 \rightleftharpoons +2$	+0.50	−26	73
$[Cu(MeHMe\text{-}2,9\text{-}diene)](BF_4)$	CH_3CN	$0 \rightleftharpoons +1$	−0.07	26	60
		$+1 \rightleftharpoons +2$	+0.50	−25	57
$Ni(MeHMe(en)_2)$	DMF	$0 \rightleftharpoons +1$	+0.11	−14	64
$Ni(MeHMe(NH)_2)_2$	DMF	$0 \rightleftharpoons +1$	+0.18	−12	52
$Cu(MeHMe(en)_2)$	DMF	$0 \rightleftharpoons +1$	+0.17	−15	61
$Zn(MeHMe(en)_2)$	CH_3CN	$0 \rightleftharpoons +1$	+0.23	−22	86
$Ni(MeHH(phen)_2)$	DMSO	$-1 \rightleftharpoons 0$	−1.63	7.0	61
		$0 \rightleftharpoons +2$	+0.58	−17	55
$Ni(HHH(phen)_2)$	DMSO	$-1 \rightleftharpoons 0$	−1.66	8.0	64
		$0 \rightleftharpoons +2$ (?)	+0.65	−12	74
$Ni(Me, COMe, H(phen)_2)$	CH_3CN	$-1 \rightleftharpoons 0$	−1.48	25	62
		$0 \rightleftharpoons +1$	+0.94	−24	68
		$+1 \rightleftharpoons +2$	+1.14	−24	73
$Ni(Me_2(ch)oaa)$	CH_2Cl_2	$-1 \rightleftharpoons 0$	−1.20	25	57
		$0 \rightleftharpoons +2$[c]	+1.26	−43	71
$Ni(Et_2(ch)oaa)$	CH_2Cl_2	$-1 \rightleftharpoons 0$	−1.24	23	61
		$0 \rightleftharpoons +2$[c]	+1.25	−40	65

[a] Notation used indicates number of electrons transferred but does not necessarily imply strict electrochemical reversibility. [b] Comparison data for one-electron transfer: $[Ni(tdt)_2]^{2-} \rightleftharpoons [Ni(tdt)_2]^- + e^-$, i_d/C (μA/m*M*) = 25 (CH_3CN); 12 (DMF); 6.8 (DMSO); 18 (CH_2Cl_2). [c] The total oxidation waves of these complexes appear to be comprised of two overlapping processes. The $E_{1/2}$ and slope values given are for the more anodic component and the i_d/C values are given for the total oxidative diffusion current. In each case, the less positive portion of the wave has a diffusion current of *ca.* ≤ 40% of the total and appears to be markedly irreversible.

2,11-Diimonium-4,9-dimethyl-5,8-diazadodeca-3,9-diene Tetrafluoroborate (10). This compound was obtained by isolating the white solid formed during 3 hr of stirring as described in the preceding preparation. This material was collected by filtration under dry nitrogen and recrystallized from *ca.* 800 ml of absolute methanol to yield 18–20 g (31–35%) of pure product. No attempt was made to recover additional product from the filtrate. The product is hydrolytically unstable and should be handled under a dry nitrogen atmosphere.

$H_2(MeHMe(en)_2)$ from 10 and Ethylenediamine. Sodium (0.46 g, 20 mmol) was dissolved in 100 ml of absolute methanol under a dry nitrogen atmosphere. To this solution was added 3.98 g (10 mmol) of **10** followed immediately by 0.60 g (10 mmol) of ethylenediamine. The reaction solution was stirred for 3 hr at room temperature while ammonia was evolved. Removal of methanol under reduced pressure followed by extraction of the residue with 200 ml of hot absolute ethanol and cooling of the extract solution yielded white crystals. Recrystallization from absolute ethanol afforded 1.3 g (52%) of crystalline product identified by melting point and pmr as $H_2(MeHMe(en)_2)$.

$M(MeHMe(en)_2)$, M = Fe(II), Co(II). These complexes were prepared by the nonaqueous chelation reaction in *tert*-butyl alcohol which has been described in detail previously.[20] Tetraalkylammonium tetrahalometalate(II) salts were employed as the anhydrous metal(II) source. Due to the slowness of the reactions at room temperature, they were conducted at 50° for 12–48 hr. At the conclusion of the reactions the solvent was removed under reduced pressure and the product extracted with and recrystallized from dry, degassed xylene under nitrogen atmosphere. The cobalt(II) complex was isolated as an orange-red crystalline solid which is apparently stable to dry air; it is air-sensitive in solution. The iron(II) complex was obtained as a brick-red solid which is sensitive to atmospheric oxygen in both solid and solution phases. Yields of the two purified complexes were *ca.* 50%.

$M(MeHMe(en)_2)$, M = Ni(II), Cu(II). Reaction of hot ethanolic solutions containing equimolar proportions of $H_2(MeHMe(en)_2)$ and the appropriate metal(II) acetate hydrate afforded the desired complexes in crystalline form. The nickel(II) complex was further purified by recrystallization from dry xylene and was isolated as red-brown needles. The copper(II) complex was recrystallized under nitrogen from dry degassed xylene and was obtained as emerald green platelets. Yields of purified products were 80–95%.

$Zn(MeHMe(en)_2)$. This complex was synthesized by nonaqueous chelation[21,22] by utilizing *n*-butyllithium in tetrahydrofuran (distilled under a nitrogen atmosphere from lithium aluminum hydride). To a solution of 6 mmol of $H_2(MeHMe(en)_2)$ in 200 ml of THF maintained at −20° was added 2 equiv of a 1.6 *M* *n*-butyllithium solution in *n*-hexane under a dry nitrogen atmosphere. Tetraethylammonium tetrachlorozincate(II) (6 mmol) was added and the reaction mixture stirred at room temperature for 6 days. Removal of the solvent under reduced pressure followed by extraction of the product with and recrystallization from dry degassed xylene yielded golden brown platelets in 65% yield. The product was dried *in vacuo* for 12 hr before analysis. The compound is sensitive to moisture and should be stored under a dry nitrogen atmosphere.

Dihydro-1,2,4,5,8,9,11,12-octaaza[14]annulenes, $H_2(R_2(ch)_2oaa)$ and Their Nickel(II) Complexes, $Ni(R_2(ch)_2oaa)$ (26). $H_2(R_2(ch)_2$-, oaa), R = Me, Et. Both of these compounds have been reported recently[17] but preparative details were not given. The methyl derivative was obtained by the following method. 1,2-Cyclo-

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(20) R. H. Holm, F. Röhrscheid, and G. W. Everett, Jr., *Inorg. Syn.*, 11, 72 (1968).

(21) W. R. McClellan and R. E. Benson, *J. Amer. Chem. Soc.*, **88**, 5165 (1966).

(22) D. H. Gerlach and R. H. Holm, *ibid.*, **91**, 3457 (1969).

hexanedione dihydrazone (2.5 g, 18 mmol) dissolved in 100 ml of absolute ethanol was added to a solution of 2.9 g (18 mmol) of triethyl orthoacetate in 50 ml of absolute ethanol containing 1 drop of concentrated sulfuric acid. The mixture was heated at *ca.* 60° for 24 hr under nitrogen. Red crystals appeared after 7 hr. The reaction mixture was cooled and the red crystalline product collected by filtration. After drying for 1 hr *in vacuo* 0.6 g (21%) of product was obtained. The ethyl derivative was prepared by an analogous procedure employing triethyl orthopropionate. A red crystalline product was obtained in 16% yield. The two compounds were identified by their melting points and pmr spectra.[17]

Ni(R$_2$(ch)$_2$oaa), R = Me, Et. To a solution of 1.5 mmol of the free base in 175 ml of hot absolute ethanol was added 0.38 g (1.5 mmol) of nickel acetate tetrahydrate in 50 ml of hot absolute ethanol. The violet solid which separated was collected and air-dried. The complexes were purified by recrystallization from 1:1 v/v toluene-*n*-heptane and were isolated in 74–78% yield as violet crystals.

[Ni(H(MeHMe(en)$_2$))](BF$_4$) (12). In attempts to prepare complexes derived from the neutral macrocycle **11**, reactions of it and nickel(II) salts were carried out under several different conditions. Salts of the 1:1 type were obtained; the following procedure was the most reliable. H$_2$(MeHMe(en)$_2$) (3.0 g, 12 mmol) was dissolved in 100 ml of degassed absolute ethanol under a nitrogen atmosphere and 7.8 g (12 mmol) of tetraethylammonium tetrabromonickelate(II) in 100 ml of degassed absolute ethanol added. The reaction mixture was refluxed for 24 hr and filtered when hot in the absence of air. To the warm filtrate was added 2.7 g of sodium tetrafluoroborate in 50 ml of hot degassed methanol. Upon cooling red crystals separated. This material was purified by repeated (3–4 times) recrystallization from a degassed 1:1 v/v mixture of absolute methanol–ethanol under a nitrogen atmosphere. The product was obtained as deep red platelets (1.5 g, 31%), which should be protected from the atmosphere.

Reaction Products of Ni(MeHMe(en)$_2$). (a) [Ni(MeHMe-2,9-diene)](BF$_4$) (15, M = Ni). The following operations were carried out under a nitrogen atmosphere. To a solution of 4.0 g (13 mmol) of Ni(MeHMe(en)$_2$) in 30 ml of dry degassed acetonitrile was added 13.6 g (39 mmol + 5% excess) of trityl tetrafluoroborate.[23] The solution was heated at ~50° for 5 hr. During this time the solution became dark green and then dark green crystals separated. After cooling overnight a quantity of green-black crystals and a small amount of yellowish white crystals (triphenylmethane) were collected by filtration. The latter were removed by washing with degassed absolute ethanol. Purification was accomplished by two recrystallizations from ~450 ml of 1:1 v/v mixture of dry degassed acetonitrile–ethanol. The yield of green-black needles was 2.5 g (48%). The compound should be protected from the atmosphere.

(b) Ni(MeHMe-2,9-diene) (14, M = Ni). The following operations were carried out under a nitrogen atmosphere. [Ni(MeHMe-2,9-diene)](BF$_4$) (0.50 g, 1.3 mmol) was suspended in 25 ml of degassed absolute ethanol and 49 mg (1.3 mmol) of sodium borohydride was added. The mixture was stirred at room temperature for 4 hr. During the first 20 min, rapid gas evolution and a change in solution color from green to golden brown occurred. The microcrystalline solid which separated was collected and dried *in vacuo*. The pure complex was obtained by two recrystallizations from *ca.* 300 ml of dry degassed xylene (green solution) and isolated as copper-colored platelets, which were dried *in vacuo* overnight yielding 0.33 g (85%) of product.

Reaction Products of Cu(MeHMe(en)$_2$). (a) [Cu(MeHMe-2,9-diene)] (BF$_4$) (15, M = Cu). The following operations were carried out under a nitrogen atmosphere. To a solution of 4.0 g (13 mmol) of Cu(MeHMe(en)$_2$) in 30 ml of dry degassed acetonitrile was added 13.6 g (39 mmol + 5% excess) of trityl tetrafluoroborate.[23] The mixture was stirred at ~50° for 8 hr. It turned dark red-brown almost immediately and after *ca.* 30 min, a dark green color developed and dark green crystals began to separate. At the end of the reaction period the mixture was cooled and filtered to yield large green-black crystals, which were washed with ~50 ml of absolute ethanol and twice recrystallized from 500 ml of a 1:1 v/v mixture of dry degassed acetonitrile–ethanol. Additional crops were isolated in both recrystallizations by reducing the volume of the filtrate. A total of 1.7–2.1 g (34–41%) of green-black crystals was obtained. The product should be protected from the atmosphere.

(b) Cu(MeHMe-2,9-diene) (14, M = Cu). The following operations were carried out under a nitrogen atmosphere. [Cu(MeHMe-2,9-diene)](BF$_4$) (0.40 g, 1.0 mmol) was suspended in 30 ml of degassed absolute ethanol and 39 mg (1.0 mmol) of sodium borohydride added. The mixture was stirred at room temperature for 6 hr. During the first 30 min, vigorous gas evolution took place and the crystals of the starting material were converted to a brown microcrystalline solid. The mixture was filtered and the brown solid collected was dried *in vacuo*. Three recrystallizations from ~300 ml of dry degassed xylene afforded 0.24 g (78%) of pure product as brown platelets, which were dried *in vacuo* at 80° for 3 days. The product should be protected from the atmosphere.

Physical Measurements. Electronic spectral data were obtained using a Cary Model 14 spectrophotometer. Magnetic measurements were made by the Faraday method using HgCo(NCS)$_4$ and Ni(en)$_3$S$_2$O$_3$ as calibrants. A Mechrolab Model 302 osmometer operating at 37° was used for molecular weight measurements in solutions prepared from dry toluene. A Princeton Applied Research Model 170 electrochemistry system was employed for electrochemical measurements. The usual polarographic measurements were carried out using a rotating platinum electrode as the working electrode. Solutions were $\sim 10^{-3}$ *M* in complex and 0.10 *M* in tetra-*n*-butylammonium perchlorate as the supporting electrolyte in dichloromethane solution and 0.05 *M* tetra-*n*-butylammonium tetrafluoroborate as the supporting electrolyte in other solvents. All potentials were determined at 25° *vs.* a saturated calomel reference electrode. Pmr spectra were obtained on either a Varian HR-100 or a Hitachi Perkin-Elmer R-20B spectrometer using TMS as an internal standard. Conductivity measurements were made using as the solvent acetonitrile which had been distilled from calcium hydride under a nitrogen atmosphere and a Serfass conductivity bridge. Solutions were thermostated at 25.0 ± 0.2° during the measurements.

Mass Spectra. Low-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D spectrometer operating at 70 eV. High-resolution mass spectra were determined using a CEC21-11B double-focusing spectrometer employing photoplate recording and operating at 70 eV. Tabulated below are the principal peaks in the parent ion region of the high-resolution spectra of Ni(MeHMe-2,9-diene) and Cu(MeHMe-2,9-diene). Given in the tabulation are the assigned isotopes and the observed and calculated exact masses for each. The following approximate masses together with the observed (calculated) relative intensities were obtained under low resolution in the parent ion region of Ni(MeHMe-2,9-diene): 300, 100 (100); 301, 19 (17); 302, 43 (40); 303, 9 (8); 304, 8 (6); 306, 2 (2).

Ni(MeHMe-2,9-diene)		
Ion$^+$	Obsd	Calcd
$^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{58}Ni$	300.0857	300.0884
$^{12}C_{13}{}^{13}C_1{}^{1}H_{18}{}^{14}N_4{}^{58}Ni$	301.0901	301.0918
$^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{60}Ni$	302.0828	302.0863
$^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{61}Ni$	303.0851	303.0841
$^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{62}Ni$	304.0791	304.0814
$^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{64}Ni$	306.0799	306.0811
Cu(MeHMe-2,9-diene)		
Ion$^+$	Obsd	Calcd
$^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{63}Cu$	305.0806	305.0829
$^{12}C_{13}{}^{13}C_1{}^{1}H_{18}{}^{14}N_4{}^{63}Cu$	306.0832	306.0863
$^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{65}Cu$	307.0826	307.0809
$^{12}C_{13}{}^{13}C_1{}^{1}H_{18}{}^{14}N_4{}^{65}Cu$	308.0855	308.0843

Results and Discussion

Synthesis of Macrocycle and Complexes. Jager[3,6,9,10] has demonstrated that macrocyclic complexes **1–3** can be prepared by reactions between the tetradentate β-ketoamine complexes **17** (M = Ni, Cu) and primary diamines. The occurrence or extent of reaction appears to be significantly dependent upon the nature of R$_\beta$. Cyclization reactions involving aliphatic diamines

17

1 (B = B' = *o*-C$_6$H$_4$)
2 (B = *o*-C$_6$H$_4$; B' = (CH$_2$)$_2$)
3 (B = B' = (CH$_2$)$_{2,3}$)

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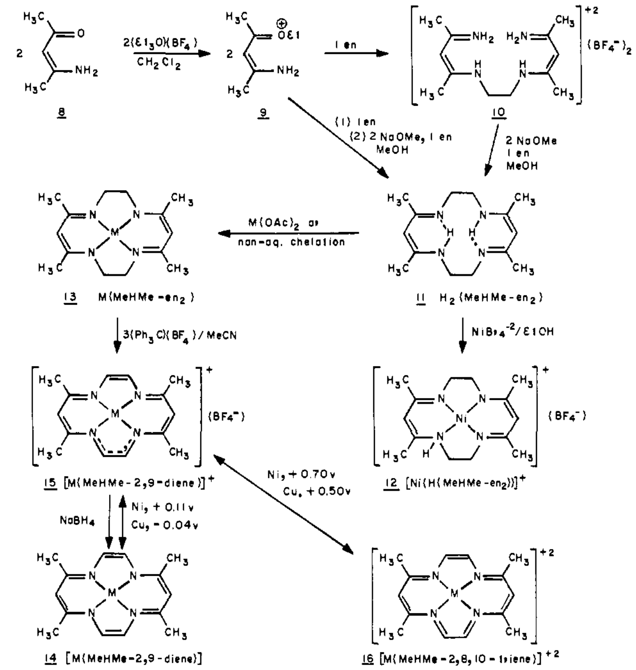
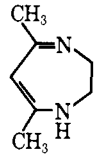
(23) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

fail unless R_β = COR or COOR. For example, we have found that refluxing bis(acetylacetone)ethylenediimine–metal(II) complexes in neat ethylenediamine for up to 2 days did not result in cyclization. In related work Bamfield[11] has found that ring closure can be effected with analogs of **17** derived from 2-hydroxymethylenecyclohexa-1,3-dione but not from 2-hydroxymethylenecyclohexanone. Closure can be accomplished by reaction of *o*-phenylenediamine and **17** with or without carbonyl-containing groups at the β positions.[6] In the latter case strongly forcing conditions are required. We have confirmed the synthesis[6] of Ni(MeHH(phen)$_2$) using molten *o*-phenylenediamine as the reaction medium.

In view of the failure of the above template reactions to yield macrocyclic complexes lacking functional groups, a nontemplate method of synthesis was developed. The reactions employed are set out in Scheme I. Preparation of the macrocycle 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene (H$_2$(MeHMe(en)$_2$), **11**) was first accomplished by a reaction sequence in which intermediates were not isolated. Alkylation of the β-ketoamine **8** yielded the *O*-ethyl cation **9**, a dichloromethane solution of which was treated with 1 equiv of ethyenediamine and subsequently with 2 equiv of sodium methoxide and a second equivalent of diamine. Straightforward work-up afforded the pure macrocycle in 35% average yield. Molecular weight determination by osmometry in toluene solution and by mass spectrometry provides the necessary demonstration that the product is not the monomer 2,3-dihydro-5,7-dimethyl-1,4-diazepine[24] which has structure **18** in weakly polar media.[25] Ultraviolet and pmr spectral data (*cf.* Tables II and III) are consistent with those reported for noncyclic β-iminoamines[25b,26–28] and thus support structure **11**. In particular the strongly deshielded resonance of the NH proton (−11.6 ppm) is indicative of the existence of hydrogen-bonded chelate rings. The course of the reaction has been investigated by isolating the product formed from **9** and the first equivalent of ethylenediamine. The 1:2 salt **10** was obtained in 31–35% yield. The exact tautomeric structure of the cation is uncertain. Reaction of the salt with 2 equiv of base and 1 equiv of diamine gave the macrocycle **11** in 52% yield. These results indicate that the macrocycle is formed by two nucleophilic reactions. The first involves attack of the amine nucleophile at the–COEt carbon of **9** and is analogous to similar reactions of alkylated β-ketoamine cations with amines and hydrosulfide ion to afford β-iminoamines[28] and β-aminothiones.[22] The second reaction is an analogous nucleophilic attack on the neutral base obtained from **10**, resulting in displacement of ammonia by the stronger base ethylenediamine and concomitant ring closure. No attempt has been made to isolate any products other than **11** which may have been formed in this reaction.

Scheme I. Synthesis of the Macrocycle **11** and Its Derivative Ni and Cu Complexes.





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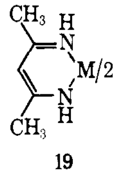
The neutral 12-π complexes M(MeHMe(en)$_2$) (**13**) are readily obtained from the macrocycle by reaction with the metal(II) acetate (Ni(II), Cu(II)) or by nonaqueous chelation (Fe(II), Co(II), Zn(II)). As a class they are moderately soluble in weakly polar solvents. The ligand structure requires an essentially planar M–N$_4$ geometry, although this stereochemistry is apparently preferred on an electronic basis inasmuch as McGeachin's sterically unencumbered bis(β-iminoaminato) complexes **19** (M(MeHMe-(NH)$_2$)$_2$), M = Co(II), Ni(II), Cu(II), are planar in the solid and solution phases.[28] Magnetic and ligand field spectral data for the M(MeHMe(en)$_2$) complexes of these metal ions (Table III) are closely comparable with those of types **2** and **3**,[9] **7**[15] (B = CH$_2$CH$_2$), and **19**.[28] All Co(II) complexes are low spin and exhibit a d–d band near 11,000 cm^{-1}. The lowest energy ligand field transition occurs at 16,200 and 17,900 cm^{-1} for the spin doublet Cu(II) and diamagnetic Ni(II) complexes, respectively. Fe(MeHMe(en)$_2$) is of particular interest for it is one of the few well-characterized, apparently four-coordinate ferrous complexes. Its magnetic moment of 3.95 BM in the solid phase is consistent with an S = 1 ground state and finds analogy with the value (3.89 BM) at ambient temperature for Fe(II) phthalo-



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[24] G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1139 (1940); D. Lloyd and D. R. Marshall, *J. Chem. Soc.*, 2597 (1956).

[25] (a) H. A. Staab and F. Vögtle, *Chem. Ber.*, **98**, 2701 (1965); (b) E. Daltrozzo and K. Feldman, *Ber. Bunsenges. Phys. Chem.*, **72**, 1140 (1968).

[26] J. E. Parks and R. H. Holm, *Inorg. Chem.*, **7**, 1408 (1968).

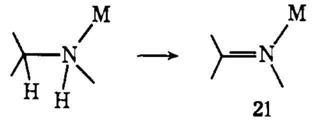
[27] C. L. Honeybourne and G. A. Webb, *Spectrochim. Acta, Part A*, **25**, 1075 (1969).

[28] S. G. McGeachin, *Can. J. Chem.*, **46**, 1903 (1968).

cyanine, whose electronic structure has been deduced to be $(xz,yz)^4(xy)^1(z^2)^1$ from magnetic anisotropy measurements.[29] Related measurements have not as yet been performed on Fe(MeHMe(en)$_2$) and its electronic ground state remains to be established. Both this complex and Co(MeHMe(en)$_2$) are markedly oxygen sensitive in solution and this behavior is currently under investigation.

Transformations of M(MeHMe(en)$_2$). One of our principal interests in macrocyclic tetraaza complexes of the 6-6-6-6, 6-6-6-5, and 6-5-6-5 types containing one or more saturated rings is concerned with their transformation into species whose conjugated ligand structures are related to those of natural macrocycles such as porphyrins and corrins. Although the 6-5-6-5 complexes **13** do not reproduce the ring-size patterns found in the biological ligands, they serve as feasible starting points for development of the desired reactions. These complexes lack the possibly interfering functional groups R_β = COR, COOR present in **3**.[3,6,9,10] Double dehydrogenations of each of their dimethylene bridges result in a fully conjugated and, hence, presumably stable 16-π ligand system. Such 16-π complexes, which have been obtained previously only as the di-*o*-phenyllene bridged species **1**, have in addition the potentiality of generating a three-membered electron transfer series whose terminal oxidized member could have a 14-π $(4n + 2)$ stabilized ligand structure.

The systematic transformation of a parent macrocyclic tetraaza complex into species with greater or lesser degrees of unsaturation was first achieved by Curtis.[12a] By dehydrogenation and hydrogenation reactions he was able to transform the *cis*- and *trans*-tetraazadiene complexes **5** into their tetraazatetraene (**4**) and fully saturated analogs, respectively. This work,[12a] together with other investigations,[33–37a] has demonstrated that coordinated secondary amines[37b] may be oxidatively dehydrogenated to imines (**20** → **21**). A similar approach was attempted in this work.



(1)

20 **21**

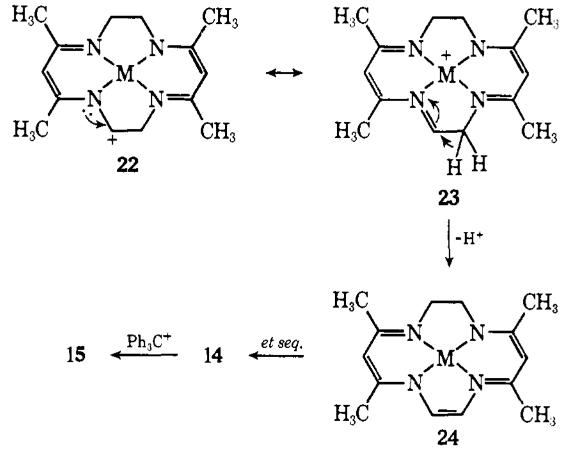
Reaction of the macrocycle **11** with Ni(II) in the absence of base afforded, instead of the anticipated dipositive complex cation, the monoprotonated species **12** (Scheme I). Analytical results, nmr data (Table II), and conductivity in acetonitrile (Table IV) are consistent with the indicated formulation. Attempts to effect the conversion **20** → **21** with several different oxidizing agents were not successful.

Attention was then directed to reactions involving loss of hydrogen, either as H$^+$ or H$^-$ or both, from the five-membered rings of the complexes **13**, which do not contain coordinated secondary amines. The ultimately successful reactions were suggested by the work of Bonthrone and Reid,[38] who found that additional conjugation could be introduced into certain unsaturated hydrocarbons by the reaction sequence 2 and 3. Hydride abstraction by the strongly electrophilic trityl

$$\text{-CHRCHR}'\text{-} + \text{Ph}_3\text{C}^+ \longrightarrow [\text{-CHRCR}'\text{-}]^+ + \text{Ph}_3\text{CH} \qquad (2)$$

$$[\text{-CHRCR}'\text{-}]^+ \longrightarrow \text{-RC=CR}'\text{-} + \text{H}^+ \qquad (3)$$

cation affords a resonance-stabilized carbonium ion which undergoes proton elimination resulting in the formation of a carbon–carbon double bond. As indicated in Scheme I, reaction of M(MeHMe(en)$_2$), M = Ni(II) and Cu(II), with 3 equiv of trityl tetrafluoroborate in acetonitrile effects dehydrogenation of the five-membered chelate rings. The overall process may be interpreted in terms of reactions 2 and 3, in which case the cation **22** → **23** is initially formed and then eliminates a proton resulting in the species **24**. Repetition of the sequence would generate the fully conjugated complex **14**, which is oxidized to the cation **15** by the third equivalent of trityl cation.[39] The cationic species **15**, [M(MeHMe-2,9-diene)]$^+$, were isolated in the form of their crystalline tetrafluoroborate salts. Upon treatment with sodium borohydride in ethanol, the cations were smoothly reduced to the corresponding neutral complexes **14**, M(MeHMe-2,9-diene), which were obtained in yields of *ca.* 80% after purification. The conversion of M(MeHMe(en)$_2$) (12-π) to M(MeHMe-2,9-diene) (16-π) is one of the few examples of



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(29) C. G. Barraclough, R. L. Martin, S. Mitra, and R. C. Sherwood, *J. Chem. Phys.*, **53**, 1643 (1970). There are few magnetic data reported for Fe(II)–N$_4$ chelates. Moments of Fe(II) tetraphenylporphin have been claimed to be 0 BM[30] (benzonitrile solution) and 4.75 BM[31] (solid) implying S = 0 and 2 in the two different phases. The only other Fe(II) complex with a moment similar to that of Fe(MeHMe(en)$_2$) is bis(monothioacetylacetone)ethylenediimine–Fe(II)[32] (3.80 BM).

(30) A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, **92**, 2982 (1970).

(31) H. Kobayashi, M. Shimizu, and I. Fujita, *Bull. Chem. Soc. Jap.*, **43**, 2335 (1970).

(32) D. M. C. Wei and S. C. Cummings, Abstracts of Papers, 162nd National Meeting of the American Chemical Society, Sept 1971, INOR-136.

(33) V. L. Goedken, Abstracts of Papers, 162nd National Meeting of the American Chemical Society, Sept 1971, INOR-150.

(34) E. Ochiai and D. H. Busch, *Inorg. Chem.*, **8**, 1798 (1969).

(35) E. K. Barefield and D. H. Busch, *ibid.*, **10**, 108 (1971).

(36) E. G. Vassian and R. K. Murmann, *ibid.*, **6**, 2043 (1967).

(37) (a) J. C. Dabrowiak, F. V. Lovecchio, V. L. Goedken, and D. H. Busch, Abstracts of Papers, 162nd National Meeting of the American Chemical Society, Sept 1971, INOR-140. (b) Recently the oxidative dehydrogenation of a coordinated primary amine has been reported: B. C. Lane, J. E. Lester, and F. Basolo, *Chem. Commun.*, 1618 (1971).

(38) W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959).

(39) The individual steps 13 → (22, 23) → 24 → 14 are suggested by analogy to reactions 2 and 3;[38] studies of separate reaction steps have not been carried out. In particular, the proposed intermediate 24 has not been isolated. It is noted that the initial complexes 13, like 14, possess rather low polarographic half-wave potenials (Table V) and their oxidation by trityl cation could be the first step in the reaction sequence instead of hydride abstraction as shown. Reaction of 13 with 2 equiv of trityl tetrafluoroborate also afforded the cation 15 in *ca.* 30% yield. If the above sequence is correct, this result indicates that under the preparative conditions employed, the effective rate of oxidation of 14 is comparable to or exceeds the rate of hydride abstraction from 13 by trityl cation.

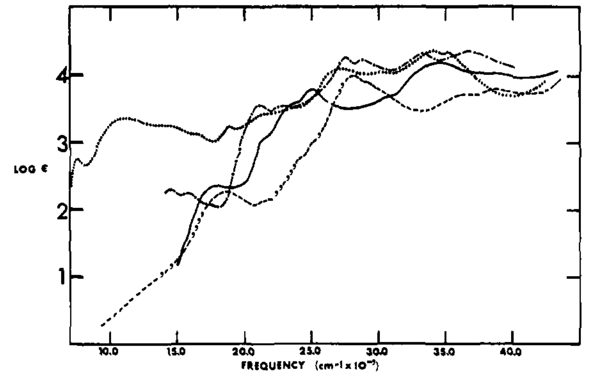


Figure 1. Electronic spectra of nickel complexes: (——) Ni(MeHMe(en)$_2$) (**13**) in chloroform; (– – – –) [Ni(H(MeHMe(en)$_2$))](BF$_4$) (**12**) in methanol; (-··-) Ni(MeHMe-2,9-diene) (**14**) in chloroform; (····) [Ni(MeHMe-2,9-diene)](BF$_4$) (**15**) in acetonitrile (9.5 × 10^{-4} *M*). Spectra of **13** and **14** could not be obtained below *ca.* 14,000 cm^{-1} due to photolytic decomposition.

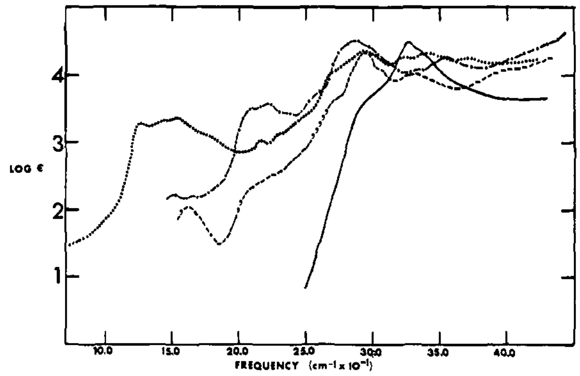
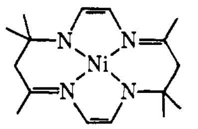


Figure 2. Electronic spectra of the macrocycle **11** and copper complexes: (——) H$_2$(MeHMe(en)$_2$) (**11**) in chloroform; (– – – –) Cu(MeHMe(en)$_2$) (**13**) in chloroform; (-··-) Cu(MeHMe-2,9-diene) (**14**) in chloroform; (····) [Cu(MeHMe-2,9-diene)](BF$_4$) in acetonitrile. Spectra of **13** and **14** could not be obtained below *ca.* 14,000 cm^{-1} due to photolytic decomposition.

introduction of carbon–carbon unsaturation in chelate rings and is the only instance of formation of a fully conjugated ligand system by this means. Of the two previous examples,[1b,36] the transformation of the dipositive *trans*-Ni(II) tetraene **4** under basic conditions to the corresponding neutral complex,[1b] formulated here as the 12-π species **25**, is the more closely related to the present work.



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Properties of M(MeHMe-2,9-diene) and [M(MeHMe-2,9-diene)]$^+$. Magnetic and electronic spectral results are given in Table III and Figures 1 and 2. The neutral macrocyclic complexes M(MeHMe-2,9-diene) were isolated as brown crystalline solids, which are only slightly soluble in weakly polar solvents yielding green solutions. Low solubility precluded determination of solution molecular weights and measurement of the pmr spectrum of the diamagnetic nickel complex. Confirmatory evidence for the formulation of these complexes as the fully conjugated 16-π species **14** has been obtained from their high-resolution mass spectra (*cf.* Experimental Section). The complexes are monomeric in the vapor phase and in each case the most intense spectral peaks are those of the molecular ions ($^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{58}Ni$ and $^{12}C_{14}{}^{1}H_{18}{}^{14}N_4{}^{63}Cu$). The nickel complex was also examined under low-resolution conditions and the observed and calculated relative intensities of isotope peaks in the molecular ion region were found to be in satisfactory agreement. The electrochemical studies described below reveal that the nickel and copper complexes **14** and **15** may be interconverted by reversible one-electron redox reactions, thereby demonstrating that these species differ only in total oxidation level. Electronic spectral comparisons of the complexes **13** and **14** of each metal reveal a number of differences, the most significant of which is the greater absorbance of the fully conjugated species in the near-infrared region.

The cationic complexes [M(MeHMe-2,9-diene)]$^+$, **15**, were obtained as green-black tetrafluoroborate salts, which are moderately soluble in polar solvents such as acetonitrile, DMF, and DMSO, affording intense green solutions. Their electronic spectra are markedly different from the neutral species **14**. Pronounced absorbance was found in the near-infrared, and no photochemical instability was detected. The origin of the magnetic moment of the solid copper complex (1.11 BM) is unknown at present and could result from intermolecular antiferromagnetic spin coupling or distribution over intramolecular spin singlet and triplet states. The most nearly analogous known complex, Cu(tetraphenylporphine)$^+$, has a moment of 2.88 BM in solution,[30] indicating a triplet spin state. Solubility limitations prevented accurate magnetic measurements in solution. [Ni(MeHMe-2,9-diene)](BF$_4$) was found to be diamagnetic in the solid state at room temperature. Because the cation is an odd-electron species, this result implies spin pairing possibly through dimer or polymer formation in the solid state. The nature of this complex in solution was investigated by the conductivity and spectral measurements; solution magnetic studies could not be performed because of solubility restrictions.

The degree of association *n* of an electrolyte A_nB_n may be determined from measurement of the equivalent conductivity (Λ_e) as a function of concentration.[40] The slope *A* obtained from a plot of the Onsager limiting law $\Lambda_0 - \Lambda_e = A\sqrt{c}$ is characteristic of a particular *n* value in a given solvent. Conductivity data obtained from measurement of acetonitrile solutions (5 × 10^{-3}–1 × 10^{-4} *M*) of three complexes prepared in this work and (n-Bu$_4$N)(BF$_4$) as a standard 1:1 electrolyte are given in Table IV. A comparison of calculated and observed *A* values[41] reveals that tetra-

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[40] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

[41] Values of Λ_0 were determined by extrapolation of plots of Λ_e *vs.* $\sqrt{c}$. The slopes *A* were obtained from these plots. Theoretical values of *A* were calculated for the electrolyte types (A$^+$) (B$^-$) (1:1) and ($A_2{}^{2+}$)(B$^-$)$_2$ (2:1) from the limiting law expression using constants appropriate to acetonitrile.[42] In the calculation of *A* for the 2:1 case the equivalent ionic conductance $\lambda_0{}^-$ of tetrafluoroborate in acetonitrile was taken as 108.5 ohm^{-1} cm^2 equiv^{-1} [43] and $\lambda_0{}^+$ was determined by difference, $\Lambda_0 = \lambda_0{}^- + \lambda_0{}^+$. Solubility limitations prevented measurement of solutions of the complexes **15** with concentrations greater than *ca.* 5 × 10^{-3} *M*.

[42] P. Walden and E. J. Birr, *Z. Phys. Chem.*, **144**, 269 (1929); J. F. Coetzee and G. P. Cunningham, *J. Amer. Chem. Soc.*, **87**, 2529 (1965).

[43] H. L. Yeager and B. Kratochvil, *J. Phys. Chem.*, **73**, 1963 (1969).

fluoroborate salts of the nickel complex **12** and the copper complex **15** behave as simple 1:1 electrolytes. The observed value of *A* for [Ni(MeHMe-2,9-diene)]-(BF_4) is, however, intermediate between the values calculated for 1:1 and 2:1 electrolytes found in this and other[44] conductivity studies in acetonitrile. Spectral studies of this compound in acetonitrile over the same concentration interval used in the conductivity measurements reveal definite departure from Beer's law and isosbestic points at 18,500 and 22,000 cm^{-1}. No spectral changes were observed at concentrations above *ca.* 2.0×10^{-3} *M*. Similar spectral behavior is encountered in 3:1 v/v DMF-acetone solutions, whose epr spectra reveal a signal of $\langle g \rangle = 2.002$, assigned to the spin-doublet monomer, with no resolved hyperfine splitting (peak-to-peak width 5.5 G). The spectrum of a frozen solution (*ca.* −100°) consists of a single signal with no detectable anisotropy. From these preliminary results it is considered likely that $[Ni(MeHMe\text{-}2,9\text{-}diene)]^+$ exists in a paramagnetic monomer $\rightleftharpoons$ diamagnetic dimer equilibrium. Preliminary analysis indicates that the spectrum shown in Figure 1 corresponds to *ca.* <10% monomer present.

Polarographic Results. (a) $[M(MeHMe\text{-}2,9\text{-}diene)]^z$ Complexes. Synthesis of the fully conjugated complexes **14** immediately raised the possibility that they would be subject to two one-electron oxidations, producing a heretofore unknown three-membered electron transfer series terminating in species with a 14-π (4*n* + 2)-stabilized ligand system. The polarographic data in Table V and the cyclic voltammograms shown in Figure 3 indicate that the nickel and copper complexes each undergo two well-separated reversible or quasi-reversible one-electron oxidations in acetonitrile solution. Further, the cations **15** exhibit both a one-electron oxidation and a one-electron reduction at half-wave potentials within 30 mV of the corresponding processes of the neutral complexes.[45] Slopes of the polarographic waves of the cations correspond very closely to the theoretical value of 56 mV for a reversible one-electron transfer. No other waves were observed in the potential interval of *ca.* −2.0 to +2.0 V. These results lead to the formulation of the following three-membered electron transfer series (*cf.* Scheme I) in which the redox processes are proposed to effect

$$\begin{tikzcd}
\underset{16\text{-}\pi}{[M(MeHMe\text{-}2,9\text{-}diene)]^0} \arrow[r, shift left] & \underset{15\text{-}\pi}{[M(MeHMe\text{-}2,9\text{-}diene)]\cdot^+} \arrow[l, shift left] \arrow[d, shift left] \\
 & \underset{14\text{-}\pi}{[M(MeHMe\text{-}2,8,10\text{-}triene)]^{2+}} \arrow[u, shift left]
\end{tikzcd}$$

changes in total oxidation levels of the macrocyclic ligands with the metals retaining a formal M(II) oxidation state. The epr data for the nickel cation described above are consistent with a π-radical description. The dipositive cations **16** have not yet been isolated. In terms of previous considerations[46] the series is considered "complete" in that its limits are defined by the terminal reduced and oxidized forms of the ligand system in combination with a stable valence state of the metals employed. It is limited to three members rather than the five found for the similarly complete series $[M(C_6H_4(NH)_2)_2]^z$ [46] and $[Pt(R_2NCS\text{-}NNPh)_2]^z$ [47] ($z = -2$ to $+2$), whose greater redox capacity arises from combinations of different oxidation states of separate ligands coordinated to the same metal.

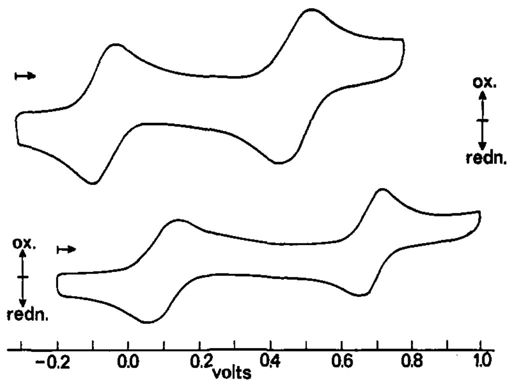

Figure 3. Cyclic voltammograms of the complexes **14** in acetonitrile: upper, Cu(MeHMe-2,9-diene); lower, Ni(MeHMe-2,9-diene). The voltammograms were recorded at a sweep rate of 0.50 V/sec using a stationary platinum electrode.

The redox behavior of the complexes **14**, **15**, and **16** contrasts with that of Ni(II) and Cu(II) complexes of types **5** and **6**. The latter usually exhibit single-electron oxidation and reduction processes,[48] but these are characterized by potentials which are more anodic and much more cathodic than those which interrelate members of the above series. In these cases the ligands lack independent redox capacity and the processes may be reasonably interpreted as M(II) → M(I) and M(II) → M(III).[48]

(b) Related 16-π Systems. In an attempt to assess the generality of the 16-π $\rightleftharpoons$ 14-π electron transfer series, the polarographic behavior of two other systems related to the fully conjugated complexes **14** have been investigated. The octaaza[14]annulene complexes **26**[49] and the di-*o*-phenylene bridged complexes **1** potentially can be oxidized to the M(II) 14-π dications **27** and **28**, respectively. Polarographic results for a

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(44) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968); A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, 6, 458 (1967).

(45) Cyclic voltammetric studies of $[Ni(MeHMe\text{-}2,9\text{-}diene)](BF_4)$ in acetonitrile have established the reversibility of the oxidation and reduction processes of the cation. Polarographic wave slopes are then not consistent with a reversible two-electron transfer per dimeric unit. Diffusion currents given in Table V for this complex were calculated using monomeric formula weights. This procedure accords with the conductivity and spectrophotometric data if a rapid monomer $\rightleftharpoons$ dimer equilibrium obtains and only the monomer is electroactive in the potential range employed. In other solvents and with different supporting electrolytes some evidence has been obtained for redox processes involving one-electron per dimeric unit. These processes are currently under investigation.

(46) A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966).

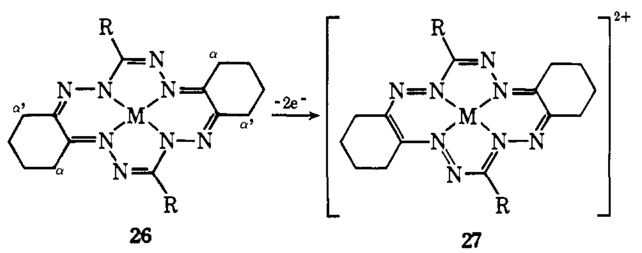
(47) C. E. Forbes, A. Gold, and R. H. Holm, *Inorg. Chem.*, 10, 2479 (1971).

(48) (a) D. C. Olson and J. Vasilevskis, *ibid.*, **8**, 1611 (1969); (b) D. C. Olson and J. Vasilevskis, *ibid.*, 10, 463 (1971); (c) D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *ibid.*, 10, 1739 (1971). For related results of Cu(II) 6-6-5-5 tetraaza macrocycles, *cf.* L. F. Lindoy, N. E. Tokel, L. B. Anderson, and D. H. Busch, *J. Coord. Chem.*, 1, 7 (1971).

(49) In the initial report of the synthesis of metal-free octaazaannulenes,[17a] a structure was proposed which, upon deprotonation, would afford neutral metal(II) complexes of D_{2h} symmetry. Pmr studies of a variety of these macrocycles and their Ni(II) complexes have established a C_{2h} structure,[50] as shown in **26**. The inequivalence of the α- and α′-methylene groups required by this structure but absent in the D_{2h} case is revealed by the pmr data in Table II for several free bases and their complexes. More recently the C_{2h} structure has been recognized,[17b] but no supporting evidence for it was presented.

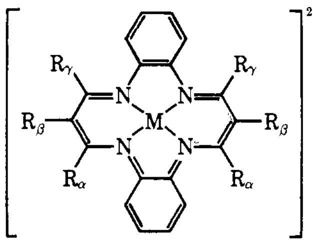
(50) J. E. Baldwin, R. H. Holm, R. E. Harper, J. Huff, S. Koch, and T. J. Truex, *Inorg. Nucl. Chem. Lett.*, **8**, 393 (1972).

number of Ni(II) complexes are given in Table V.



26 **27**

Anodic processes are observed in each case. With the exception of Ni(Me, COMe, H(phen)$_2$) these processes correspond to apparent two-electron oxidations, most of which are at best quasi-reversible as judged by wave slopes. The results do imply that the oxidations **26** → **27** and **1** → **28**, the possibility of which was recognized earlier by Jager,[6] can be effected. No chemical oxidations of **1** and **26** have been attempted. Unlike **14** each of these complexes undergoes a one-electron reduction at potentials somewhat less negative than those required for the Ni(II) → Ni(I) reduction of species **5** and **6**.



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(c) M(MeHMe(en)$_2$) Complexes. For the purpose of comparison with the fully conjugated complexes **14**, the polarographic behavior of M(MeHMe(en)$_2$), M = Ni(II), Cu(II), and Zn(II), has been investigated. Results are given in Table V. These complexes do not reduce at potentials down to *ca.* −2.0 V but do undergo apparent one-electron oxidations at slightly positive potentials. No other anodic waves were observed. Due to the quite low potentials of these processes and their near-independence of metal ion, they are associated with oxidation of the ligand π system rather than with M(II) → M(III).[48] This interpretation is supported by the occurrence of similar slightly anodic oxidations with Ni(MeHMe(NH)$_2$)$_2$ (**19**, Table V) and [Ni(MeHMe(NCH$_2$CH$_2$NHMe)$_2$)]$^+$,[48a] which also contain delocalized β-iminoaminato chelate ring systems. The close correspondence of half-wave potentials between the oxidation of M(MeHMe(en)$_2$) and the first anodic process of M(MeHMe-2,9-diene) may indicate that they are related. In view of this, it should be emphasized that the representation **15** (Scheme I) for [M(MeHMe-2,9-diene)]$^+$ is only one of a number of simple formulations depicting the delocalized nature of the 15-π ligand system.

Further examples of the nontemplate synthesis of tetraaza macrocyles and additional results dealing with the preparation, reactivity, solution behavior, and electronic properties of complexes of the types **14**, **15**, and **16** will be reported subsequently.

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Phosphonitrilic Compounds. XIV.[1] Basic Hydrolysis of Aryloxy- and Spiroarylenedioxycyclophosphazenes[2]

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Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received July 28, 1971*

Abstract: Bis(aryloxy)cyclophosphazenes, $[NP(OAr)_2]_3$, and spirocyclic arylenedioxycyclophosphazenes, $(NPO_2Ar)_3$, have been hydrolyzed in basic 25 vol % water in diglyme. For the bis(aryloxy) derivatives, the ease of hydrolytic removal of the first aryloxy group in $[NP(OR)_2]_3$ from phosphorus is in the order OR = p-$NO_2C_6H_4O$– > m-$NO_2C_6H_4O$– > o-$NO_2C_6H_4O$– ≫ C_6H_5O– > p-$CH_3C_6H_4O$–. For the spirocyclic derivatives, the rate of cleavage of the first aryloxy–phosphorus bond is in the order $[NP(O_2C_6H_4\text{-}1,2)]_3 > [NP(O_2C_{10}H_6\text{-}2,3)]_3 \gg [NP(O_2C_{12}H_8\text{-}2,2')]_3$ and $[NP(O_2C_{12}H_6\text{-}1,8)]_3$. The mechanisms of these reactions are discussed, and comparisons are made with related phosphate ester hydrolyses.

Aryloxycyclo- and polyphosphazenes, $[NP(OAr)_2]_n$, and spirocyclic phosphazenes, $[NP(O_2Ar)]_3$ or $[NP(O_2Ar)]_4$, occupy an important place in phosphorus–nitrogen chemistry. Aryloxycyclophosphazenes, such as $[NP(OAr)_2]_3$ or $[NP(OAr)_2]_4$, are among the most thermally and oxidatively stable phosphorus

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[1] Part XIII: H. R. Allcock, R. L. Kugel, and E. G. Stroh, *Inorg. Chem.*, 11, 1120 (1972).

[2] Preliminary report of parts of this work have appeared: H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.*, 91, 3102 (1969); *Chem. Commun.*, 580 (1970).