Synthetic Transformations of Tetraaza Macrocyclic Metal Complexes. Preparation of the Corrinoid and Other Unsaturated Ring Systems by Oxidative Dehydrogenation Reactions of Nickel(II), Copper(II), and Cobalt(II) Macrocycles

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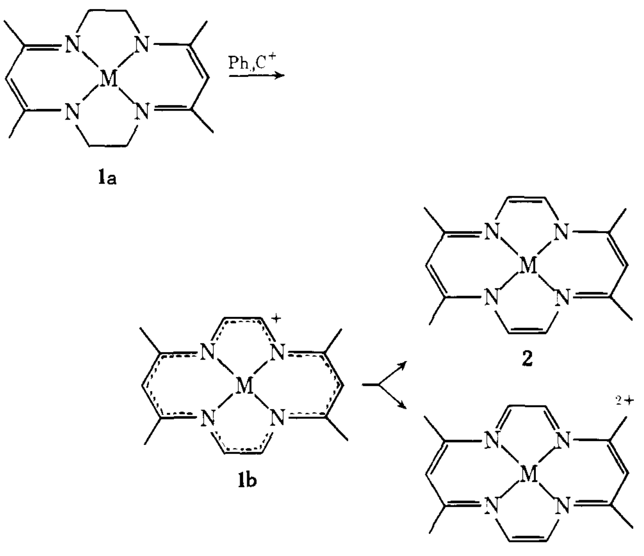
Abstract: Neutral macrocyclic bis(β-iminoamine) Cu(II), Ni(II), and Co(II) complexes containing 14-, 15-, and 16-membered rings undergo oxidative dehydrogenation reactions with trityl ion (Ni) or 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (Cu, Ni, Co) affording complexes with increased ligand π-unsaturation. Complexes with 15- and 16-membered rings afford the 14-π species $[M(Ph_2[15]hexaenatoN_4)]^+$ (**10**, M(II) = Ni, Cu), $[Co(Ph_2[15]hexaenatoN_4)(py)_2]^{2+}$ (**15**), and $[M(Ph_2[16]hexaenatoN_4)]^+$ (**11**, M(II) = Ni, Cu), respectively. From analytical, mass spectrometric, ^1H NMR, and electronic spectral properties complexes of types **10** and **15** were shown to contain the essential corrin inner ring structure present in vitamin B_{12} and its derivatives. Further confirmation of formation of this ring was obtained by electronic spectral comparison of $Co(Ph_2[15]hexaenatoN_4)(CN)_2$ (**16**) and dicyanocobalamin, which contain a common set of axial ligands. Complexes **10**, **15**, and **16** represent the initial examples of synthesis of the 14-π corrin ring nucleus devoid of supporting pyrroline rings. These complexes are prepared by a rather straightforward four-step synthesis, rendering the cobalt complexes accessible in vitamin B_{12} model system studies where a more realistic representation of electronic structure and in-plane coordination than obtainable with current models may be desired.

In order to provide a basis for the interpretation of certain stereochemical, electronic, and reactivity properties of tetraaza macrocyclic metal complexes,[1] we have initiated an investigation of synthetic complexes containing ligand structures with different fused chelate ring size patterns (6-5-6-5, 6-5-6-6, 6-6-6-6) and degrees of π-unsaturation. These patterns correspond to [14]-, [15]-, and [16]-membered ring systems, respectively. Structures equivalent to the inner rings of corrin (6-5-6-6) and porphyrin (6-6-6-6) systems are among those of prime interest. The steps involved in one approach to the synthesis of large ring complexes currently under study in this laboratory[2-4] are the following: (i) nontemplate synthesis of 12-π bis(β-iminoamine) macrocycles containing 14-, 15-, or 16-membered rings; (ii) insertion of metal ion with concomitant removal of two protons and formation of a particular chelate ring size pattern; (iii) oxidative dehydrogenation of these complexes to species with increased ligand unsaturation; (iv) redox reactions affording complexes with different total oxidation levels. The first experiments[2] led to the synthesis of the ligand $H_2(Me_4[14]tetraeneN_4)$[5] and its 6-5-6-5 12-π metal(II) complexes (**1a**), their direct conversion to the 15-π cations **1b** (M = Ni, Cu), and reduction and oxidation to the 16-π and 14-π species **2** and **3**, respectively. The 15-π free radical nature of the nickel cation **1b** has been demonstrated by a detailed EPR study,[9] and strongly supports the previous proposition[2] that the redox reactions in series **1a**–**3** are ligand based. Steps (i)–(iii) have previously been employed in the preparation of unsaturated Fe(II) complexes based on ligands of the Curtis type.[6,7]



1a

1b

2

3

The inability to extend the method affording $H_2(Me_4[14]tetraeneN_4)$ to the formation of larger ring systems led to the development of a second nontemplate synthesis which yielded 14-, 15-, and 16-membered rings in good yield.[3,4] This procedure involved the reactions of the 4-phenyl-1,2-dithiolium cation with primary diamines, yielding initially bis(β-aminothiones). These compounds are readily cyclized by a second equivalent of diamine (ethylenediamine, trimethylenediamine) giving the macrocycles $H_2(Ph_2[14]tetraeneN_4)$, $H_2(Ph_2[15]tetraeneN_4)$, and $H_2(Ph_2[16]tetraeneN_4)$, whose metal(II) complexes **5**, **6**, and **7**, respectively, are set out in Figure 1. These complexes serve as precursors to others with ligand unsaturation exceeding the 12-π level. We have been particularly interested in producing a 14-π 15-membered tetraaza macrocyclic system similar to that present in the basic corrin unit **4**. Here we report the oxidative dehydrogenation reactions of 12-π Cu(II), Ni(II), and Co(II) complexes which afford among their products metallocorrinoid species. Preparative meth-

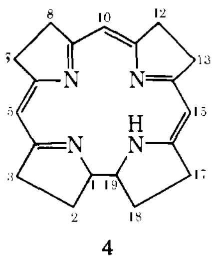


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Table I. Characterization Data for Macrocyclic Complexes

Compound	Calcd, %				Found, %			
	C	H	N	F	C	H	N	F
[Cu(Ph$_2$[15]hexaenatoN$_4$)](PF$_6$) (**10**)	49.16	3.77	9.97	20.29	49.06	4.06	9.88	19.96
[Cu(Ph$_2$[16]hexaenatoN$_4$)](PF$_6$) (**11**)	50.05	4.02	9.73	19.79	49.92	4.13	9.50	19.82
Ni(Ph$_2$[14]hexaenatoN$_4$) (9)	66.54	4.57	14.11		66.19	4.64	14.38	
[Ni(Ph$_2$[14]hexaenatoN$_4$)](BF$_4$) (8)	54.60	3.75	11.58		54.64	3.75	11.58	
[Ni(Ph$_2$[15]hexaenatoN$_4$)](PF$_6$) (10)	49.59	3.80	10.06	20.46	50.04	3.91	9.98	20.05
[Ni(Ph$_2$[16]hexaenatoN$_4$)](PF$_6$) (**11**)	50.47	4.06	9.81	19.96	50.59	4.12	9.70	19.76
[Co(Ph$_2$[15]hexaenatoN$_4$)(py)$_2$](PF$_6$)$_2$ (15)	46.06	3.63	9.77	26.49	46.19	3.78	9.73	26.44
[Co(Ph$_2$[14]tetraenatoN$_4$)(py)$_2$]I$_3$ (**12**)	40.88	3.43	8.94		40.76	3.34	9.24	
[Co(Ph$_2$[15]tetraenatoN$_4$)(py)$_2$]I$_3$ (13)	41.53	3.59	8.81	(39.89)^a	41.60	3.75	8.83	(39.60)^a
[Co(Ph$_2$[16]tetraenatoN$_4$)(py)$_2$]I (14)	57.15	5,08	11.76		57.06	4.99	11.65	
Co(Ph$_2$[15]hexaenatoN$_4$)(CN)$_2$ (16)	64.66	4.56	18.10		64.59	4.57	18.18	

^{a} % I.

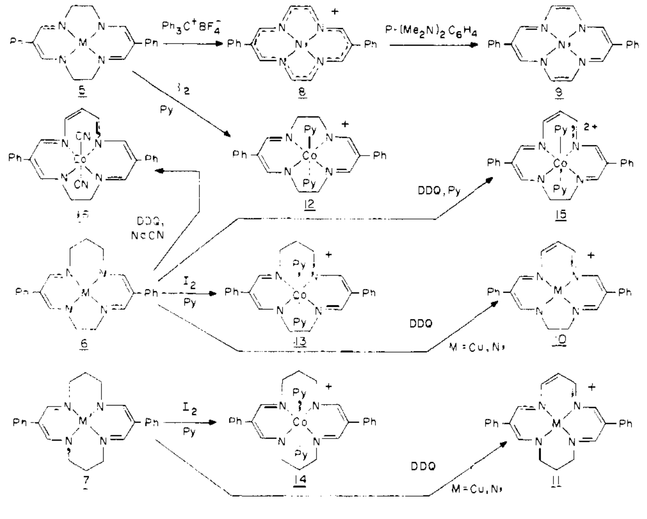


Figure 1. Scheme illustrating synthetic routes from 12-π 6-5-6-5 (**5**), 6-5-6-6 (**6**), and 6-6-6-6 (**7**) complexes to the 14-π corrinoid (**10, 15, 16**), the 14-π (**11**), the 15-π (**8**), and 16-π (**9**) Ni(II), and the bis(pyridine) 12-π Co(III) (**12–14**) complexes.

ods are described in full together with a brief consideration of certain spectroscopic properties. A preliminary account[3] of some of these results has been communicated.

Experimental Section

Preparation of Compounds. The complexes M(Ph$_2$[14]tetraenatoN$_4$), M(Ph$_2$[15]tetraenatoN$_4$), and M(Ph$_2$[16]tetraenatoN$_4$), M = Cu(II), Ni(II), Co(II), were prepared as previously described.[4] 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, Eastman) was recrystallized once from benzene. Ethanol, acetonitrile, and THF were dried, and pyridine was distilled from BaO prior to use. Crystalline vitamin B$_{12}$ was purchased from Nutritional Biochemical Corporation. All other chemicals were of reagent grade quality. All operations were carried out under a nitrogen atmosphere. Melting points were determined in evacuated tubes and are uncorrected. Analytical data for new compounds are collected in Table I.

Copper Complexes. (a) [Cu(Ph$_2$[15]hexaenatoN$_4$)](PF$_6$) (10, M = Cu). To a suspension of 2.0 g (4.8 mmol) of Cu(Ph$_2$[15]tetraenatoN$_4$) in 120 ml of trichloroethylene at 85° was added 4.7 g (21 mmol) of DDQ. The mixture was stirred at this temperature for 10 hr, filtered when hot, and the collected solid dried in vacuo at room temperature. The dark purple solid was partially dissolved in 110 ml of hot ethanol, the suspension filtered, and the hot filtrate treated with a warm solution of 2.0 g (12 mmol) of NaPF$_6$ in 10 ml of ethanol. Upon cooling to room temperature 0.90 g of crude product separated from the red-purple solution. This material was purified by dissolving it in ca. 15 ml of acetone. The filtrate from this solution was heated to 60° and 65 ml of boiling ethanol was added slowly. Gradual cooling afforded 0.53 g (20%) of the salt as brown needles. An analytical sample was obtained by a second recrystallization from acetone-ethanol; mp 245–247°.

(b) [Cu(Ph$_2$[16]hexaenatoN$_4$)](PF$_6$) (11, M = Cu). To a suspension of 1.4 g (3.2 mmol) of Cu(Ph$_2$[16]tetraenatoN$_4$) in 110 ml of trichloroethylene at 85° was added 3.3 g (14 mmol) of DDQ. The mixture was stirred at this temperature overnight and filtered when hot, and the collected solid was thoroughly washed with hot trichloroethylene and dried in vacuo at room temperature. The dark blue solid was partially dissolved in 150 ml of hot ethanol, the suspension filtered, and the hot filtrate treated with a warm solution of 2.0 g (12 mmol) of NaPF$_6$ in 10 ml of ethanol. Upon cooling to room temperature 0.76 g (41%) of pure product separated as purple crystals from the purple solution. The compound can also be recrystallized from acetone-ethanol, mp 259–261°.

Nickel Complexes. (a) [Ni(Ph$_2$[14]hexaenatoN$_4$)](BF$_4$) (8). To a solution of 1.0 g (2.5 mmol) of Ni(Ph$_2$[14]tetraenatoN$_4$) in 30 ml of acetonitrile at 50° was added 2.72 g (8.2 mmol) of trityl tetrafluoroborate. The solution immediately turned from red to dark purple and thereafter purple crystals separated. The reaction mixture was maintained at 50° for 4 hr and then allowed to cool to room temperature. The pure product as purple-brown microcrystals (0.95 g, 79%) was collected by filtration and was washed thoroughly with several portions of cold methanol, mp 264–265° with sublimation. The product should be protected from the atmosphere.

(b) Ni(Ph$_2$[14]hexaenatoN$_4$) (9). To a suspension of 0.85 g (1.8 mmol) of **8** in 30 ml of acetonitrile was added a solution of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine. The latter solution was prepared by suspending 0.42 g (1.8 mmol) of the diamine dihydrochloride in 25 ml of acetonitrile followed by the addition of 0.36 g (3.6 mmol) of triethylamine, stirring, and removing triethylammonium chloride by filtration. Addition of the diamine afforded a deep purple reaction mixture, which was stirred for 3 hr. The product was collected as a red-brown microcrystalline product which was washed thoroughly with acetonitrile until all traces of the purple color were removed; 0.60 g (86%) of pure compound was obtained, mp > 360°. The material was insufficiently soluble for recrystallization; it should be protected from the atmosphere.

(c) [Ni(Ph$_2$[15]hexaenatoN$_4$)](PF$_6$) (10, M = Ni). This compound was prepared from 2.0 g (4.8 mmol) of Ni(Ph$_2$[15]tetraenatoN$_4$) in a manner similar to that for its copper analog. The initial solid was washed with three 20-ml portions of hot trichloroethylene and dried. Isolation of the salt followed by recrystallization yielded 0.51 g (19%) of brown microcrystals. Final purification was achieved by a second recrystallization from acetone-ethanol, mp 248–250°.

(d) [Ni(Ph$_2$[16]hexaenatoN$_4$)](PF$_6$) (11, M = Ni). To a suspension of 2.1 g (4.8 mmol) of Ni(Ph$_2$[16]tetraenatoN$_4$) in 100 ml of trichloroethylene at 85° was added 5.3 g (23 mmol) of DDQ. Stirring was continued at this temperature for 8 hr. The solid collected by filtration of the hot solution was washed with three 30-ml portions of hot trichloroethylene, dried, and converted to the hexafluorophosphate salt by the method employed for the copper analog using 2.8 g (17 mmol) of NaPF$_6$ in 40 ml of ethanol added dropwise to the hot red-purple ethanol filtrate. The product (1.30 g, 60%) was obtained as a green microcrystalline solid. Recrystallization from acetone-ethanol yielded the salt as green needles which were dried in vacuo for 24 hr at 140°, mp 269–270°.

Cobalt Complexes. (a) [Co(Ph$_2$[14]tetraenatoN$_4$)(py)$_2$]I$_3$ (12). To a suspension of 1.3 g (3.3 mmol) of Co(Ph$_2$[14]tetraenatoN$_4$) in 50 ml of THF at ~25° was added 20 ml of a 0.5 *N* solution of I_2 (9.9 mmol) in pyridine. The reaction mixture turned from red to brown-green and was stirred for 3 hr. The product was collected as a brown crystalline solid and dried in vacuo yielding 2.6 g (83%). An analytical sample was obtained as black needles after recrystallization from acetonitrile, mp 205–207°.

(b) **$[Co(Ph_2[15]tetraenatoN_4)(py)_2]I_3$ (13).** The preceding preparation was followed giving the product in 80% yield as green-black crystals. Recrystallization from pyridine–ethanol afforded an analytical sample, mp 180–182°.

(c) **$[Co(Ph_2[16]tetraenatoN_4)(py)_2]I$ (14).** The same procedure as above was employed but with 1 equiv of iodine/Co. The green crystalline product was isolated in 60% yield following recrystallization from pyridine–THF, mp 239–241°.

(d) **$[Co(Ph_2[15]hexaenatoN_4)(py)_2](PF_6)_2$ (15).** To a solution of 1.0 g (2.4 mmol) of $Co(Ph_2[15]tetraenatoN_4)$ in 120 ml of benzene (80°) was added a benzene solution of 2.4 g (11 mmol) of DDQ. The reaction mixture was stirred at 80° for 10 hr and filtered when hot, and the collected dark purple solid was dried in vacuo at room temperature. This material was partially dissolved in 120 ml of hot ethanol and the suspension filtered. To the hot filtrate was added 0.38 g (4.8 mmol) of pyridine followed by slow addition of a solution of 2.0 g (12 mmol) of $NaPF_6$ in 15 ml of ethanol. Upon cooling 0.90 g (43%) of essentially pure product separated from the brown solution. Recrystallization from acetone–ethanol and acetonitrile–ethanol afforded black crystals, mp 262–263°.

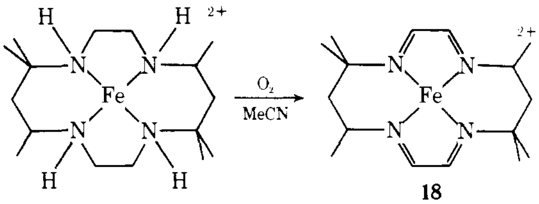
(e) **$[Co(Ph_2[15]hexaenatoN_4)(CN)_2]$ (16).** To a solution of 1.0 g (2.4 mmol) of $Co(Ph_2[15]tetraenatoN_4)$ in 120 ml of benzene at 80° was added a benzene solution of 2.4 g (11 mmol) of DDQ. The reaction mixture was stirred at 80° for 10 hr and filtered when hot, and the collected dark purple solid was dried in vacuo at ambient temperature. This material was partially dissolved in 120 ml of hot ethanol and the suspension filtered. To the hot filtrate was added 0.26 g (5.3 mmol) of sodium cyanide dissolved in a small amount of water. Upon cooling the reaction mixture was filtered. The filtrate was allowed to stand at ambient temperature for 5 days during which time the pure product separated from the green solution as red crystals (0.31 g, 28%), mp 164–165°.

Mass Spectra. High-resolution mass spectra were determined using a CEC 21-11B double-focusing spectrometer employing photoplate recording and operating at 70 eV. Tabulated below are the principal peaks in the parent ion regions of four macrocyclic complexes with assigned isotopic composition and observed and calculated exact masses for monopositive ions given in that order. $[Ni(Ph_2[16]hexaenatoN_4)](PF_6)$: $^{12}C_{24}{}^{1}H_{22}{}^{14}N_4{}^{58}Ni$, 424.116, 424.120; $^{12}C_{23}{}^{13}C^{1}H_{22}{}^{14}N_4{}^{58}Ni$, 425.122, 425.123; $^{12}C_{24}{}^{1}H_{22}{}^{14}N_4{}^{60}Ni$, 426.115, 426.118. $[Ni(Ph_2[15]hexaenatoN_4)](PF_6)$: $^{12}C_{23}{}^{1}H_{20}{}^{14}N_4{}^{58}Ni$, 410.103, 410.104; $^{12}C_{22}{}^{13}C^{1}H_{20}{}^{14}N_4{}^{58}Ni$, 411.102, 411.107; $^{12}C_{23}{}^{1}H_{20}{}^{14}N_4{}^{60}Ni$, 412.104, 412.102. $[Ni(Ph_2[14]hexaenatoN_4)]$: $^{12}C_{22}{}^{1}H_{18}{}^{14}N_4{}^{58}Ni$, 396.088, 396.088; $^{12}C_{21}{}^{13}C^{1}H_{18}{}^{14}N_4{}^{58}Ni$, 397.091, 397.092; $^{12}C_{22}{}^{1}H_{18}{}^{14}N_4{}^{60}Ni$, 398.086, 398.086; $^{12}C_{21}{}^{13}C^{1}H_{18}{}^{14}N_4{}^{60}Ni$, 399.089, 399.090. $[Co(Ph_2[15]hexaenatoN_4)(CN)_2]$: $^{12}C_{23}{}^{1}H_{21}{}^{14}N_4{}^{59}Co$, 412.123, 412.122 ($M - 2^{12}C^{14}N$); $^{12}C_{24}{}^{1}H_{18}{}^{14}N_5{}^{59}Co$, 435.089, 435.089 ($M - 3 - {}^{12}C^{14}N$); $^{12}C_{24}{}^{1}H_{20}{}^{14}N_5{}^{59}Co$, 437.105, 437.105 ($M - 1 - {}^{12}C^{14}N$); $^{12}C_{23}{}^{13}C^{1}H_{20}{}^{14}N_5{}^{59}Co$, 438.106, 438.108 ($M - 1 - {}^{13}C^{14}N$); $^{12}C_{25}{}^{1}H_{19}{}^{14}N_6{}^{59}Co$, 462.103, 462.100 ($M - 2$).

Physical Measurements. Electronic spectra were recorded on a Cary Model 14 or 17 spectrophotometer. ^{1}H NMR spectra were obtained on a Varian HA-100 or Hitachi Perkin-Elmer R22 90-MHz spectrometer; chemical shifts are relative to TMS internal reference. EPR measurements were made on a Varian E-9 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer.

Results and Discussion

Following attainment of a synthetic method for 14-, 15-, and 16-membered macrocycles and their metal(II) complexes[4] **5–7** (Figure 1), efforts have been directed toward the development of oxidative dehydrogenation reactions effecting an increase in ligand π-unsaturation. Such reactions have figured prominently in synthetic macrocyclic chemistry and numerous recent examples are available.[2,7,10-20] These include formation of an unsaturated ligand from a saturated precursor (e.g., **17** (0-π) → **18** (8-π),[7] $[Ru(en)_3]^{2+} \rightarrow [Ru(en)_2(NHCHCHNH)]^{2+}$[15]) and an increase in the degree of unsaturation (e.g., **19**(4-π) → **20** (8-π)[10,14]), and exemplify reactions of the general type **21** → **22** whereby a saturated coordinated secondary amine is converted to an imine. Inasmuch as the minimum ligand unsaturation sought in this work was 14-π or greater, our approach has been to prepare complexes with a level of π-unsaturation (12-π) consistent with feasible direct synthesis in good yield and then to subject these species to oxidative dehydrogenation. In this approach the desired minimum transformation is formation of C–C unsaturation vinylogous to a coordinated imino or amido nitrogen, **23** → **24**, with the initial substrate lacking an N–H proton. Previous examples of the introduction of C–C unsaturation, or C–N unsaturation in rings without coordinated -NH- groups, in macrocyclic complexes are relatively rare.[11,17,20] Among these examples is **25** → **26**[20] affording the "dibenzocorromin" complex $[Co(dbc)(py)_2]^{2+}$, which has been described as a corrin analog. It and corresponding M = Ni(II) and Cu(II) complexes have also been obtained directly by template synthesis.[21]



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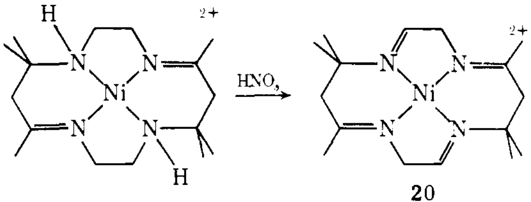

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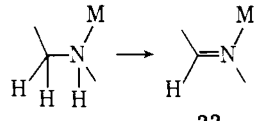

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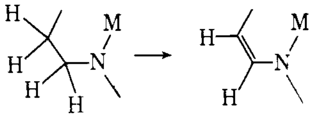

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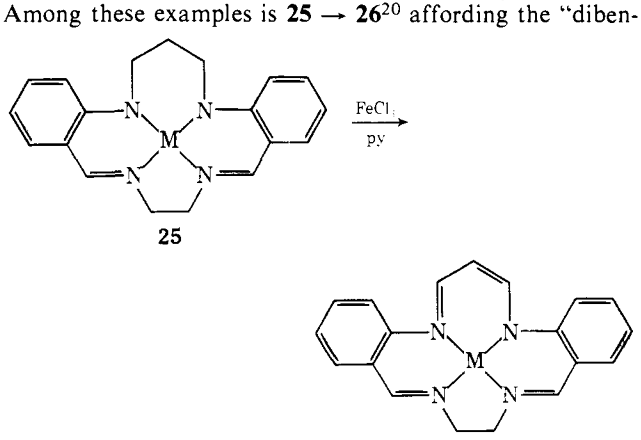

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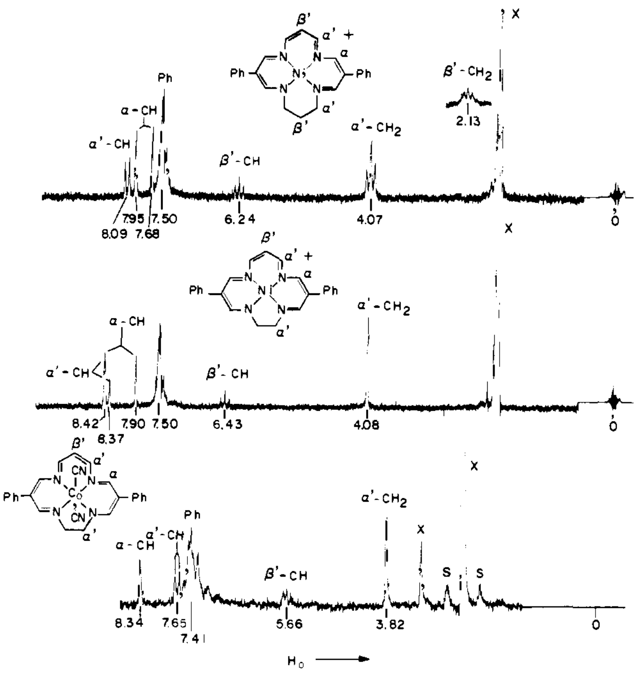


Figure 2. ^1H NMR specta: (upper) $[Ni(Ph_2[16]hexaenatoN_4)]^+$ in CD_3CN with insert showing β'-CH_2 resonance in CD_3NO_2; (middle) $[Ni(Ph_2[15]hexaenatoN_4)]^+$ in CD_3CN; (lower) $[Co(Ph_2[15]hexaenatoN_4)(CN)_2]$ in DMSO-d_6. Chemical shifts are in parts per million from TMS; s = side band. Integrations are consistent with the indicated assignments; coupling constants are ~7 Hz.

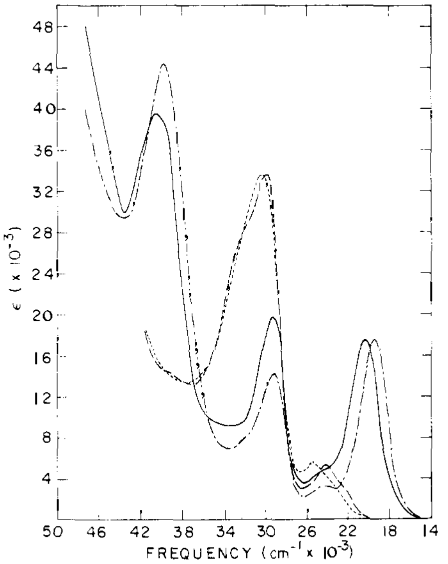


Figure 3. Electronic spectra of nickel complexes: — —, $Ni(Ph_2[15]tetraenatoN_4)$ in chloroform; —, $[Ni(Ph_2[15]hexaenatoN_4)](PF_6)$ in acetonitrile; - - -, $Ni(Ph_2[16]tetraenatoN_4)$ in chloroform; —•—•, $[Ni(Ph_2[16]hexaenatoN_4)](PF_6)$ in acetonitrile.

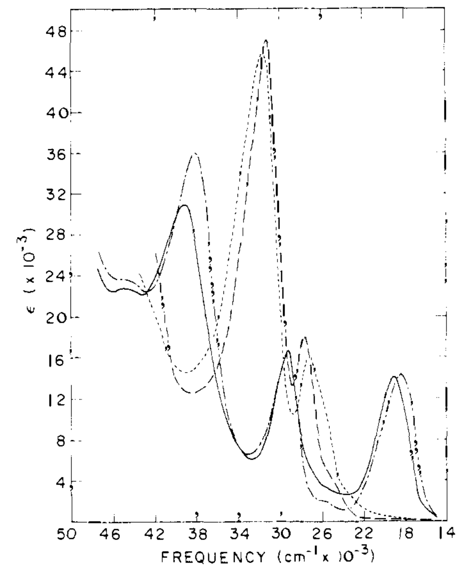


Figure 4. Electronic spectra of copper complexes: — —, $Cu(Ph_2[15]tetraenatoN_4)$ in chloroform; —, $[Cu(Ph_2[15]hexaenatoN_4)](PF_6)$ in acetonitrile; - - -, $Cu(Ph_2[16]tetraenatoN_4)$ in chloroform; —•—•, $[Cu(Ph_2[16]hexaenatoN_4)](PF_6)$ in acetonitrile.

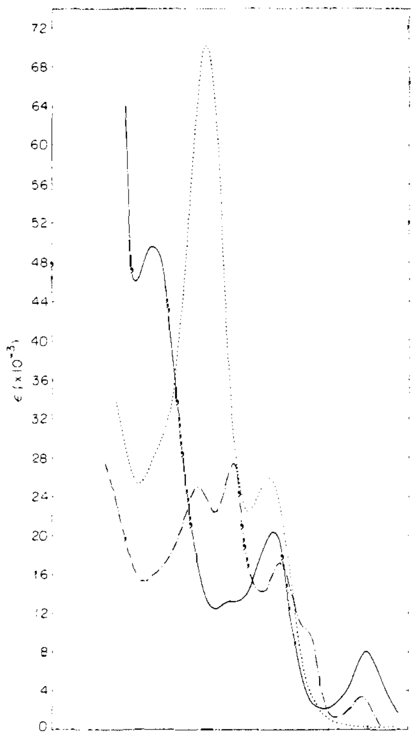


Figure 5. Electronic spectra of cobalt complexes: —•—•, $Co(Ph_2[15]tetraenatoN_4)$ in dichloromethane; • • •, $[Co(Ph_2[15]tetraenatoN_4)(py)_2]I_3$ in acetonitrile; —, $[Co(Ph_2[15]hexaenatoN_4)(py)_2](PF_6)_2$ in acetonitrile.

Synthetic Transformations. The results of oxidative dehydrogenation and pyridine complexation reactions on the precursor complexes **5–7** are summarized in Figure 1. The structures of these complexes follow from those of their fully characterized parent macrocycles.[4] Analytical data for new compounds are given in Table I and ^1H NMR and electronic spectral information are available in Figures 2–6 and Tables II and III.

(a) **Nickel Complexes.** Having previously established the reaction sequence **1a** → **1b** → **2, 3,** similar transformations were investigated with $Ni(Ph_2[14]tetraenatoN_4)$ (**5**, M = Ni). Treatment of this complex with slightly more than 3 equiv of trityl tetrafluoroborate in acetonitrile afforded the monocation $[Ni(Ph_2[14]hexaenatoN_4)]^+$ (**8**) as its BF_4^- salt in 79% yield. This compound was readily reduced with N,N,N',N'-tetramethyl-p-phenylenediamine in acetonitrile to the neutral complex, $Ni(Ph_2[14]hexaenatoN_4)$ (**9**, 87%). Both of these compounds proved to be insufficiently soluble for NMR and polarographic measurements; the latter method was used to establish the existence of the 14-π dication **3**.[2] The formulations of **8** and **9** as 15-π and 16-π complexes, respectively, are based on analytical results, electronic spectra (Table II) which are qualitatively similar to

Table II. Electronic Spectral Data

Complex	λ_{max}, cm^{-1} (ϵ)[a]
$Ni(Ph_2[14]tetraenatoN_4)$[b] (5)	~18,200 (sh, 500), ~20,300 (sh, 1500), 23,300 (5150), 29,100 (27,400), 32,100 (25,400)
$[Ni(Ph_2[14]hexaenatoN_4)](BF_4)$[c] (8)	~16,900 (sh, 2000), 20,400 (4660), ~21,300 (sh, 4500), 26,600 (9920), ~29,700 (sh, 14,800), 33,600 (23,600)
$Ni(Ph_2[14]hexaenatoN_4)$[b] (9)	20,300 (4990), 21,200 (5120), 26,000 (8780), ~37,000 (sh, 8500), 32,500 (27,000)
$Ni(Ph_2[15]tetraenatoN_4)$[b] (6)	~22,200 (sh, 3000), 24,000 (5440), 29,800 (33,500), ~32,500 (sh, 26,900)
$Ni(Ph_2[16]tetraenatoN_4)$[b] (7)	~23,200 (sh, 3400), 25,300 (5630), 30,200 (33,600)
$[Ni(Ph_2[15]hexaenatoN_4)](PF_6)$[c] (10)	20,400 (17,500), ~24,200 (sh, 5000), 29,200 (19,700), 40,400 (39,400)
$[Ni(Ph_2[16]hexaenatoN_4)](PF_6)$[c] (11)	19,400 (17,500), 24,300 (3260), 29,000 (14,400), 39,700 (44,300)
$Cu(Ph_2[15]tetraenatoN_4)$[b] (6)	~24,700 (sh, 3600), 27,600 (17,900), 31,300 (47,000)
$Cu(Ph_2[16]tetraenatoN_4)$[b] (7)	~23,800 (sh, 3000), 27,200 (16,100), 31,600 (45,800)
$[Cu(Ph_2[15]hexaenatoN_4)](PF_6)$[c] (10)	19,100 (14,100), ~25,300 (sh, 3100), 29,200 (16,700), 39,000 (30,900), 44,800 (22,800)
$[Cu(Ph_2[16]hexaenatoN_4)](PF_6)$[c] (11)	18,400 (14,300), ~25,600 (sh, 1840), 29,200 (16,700), 38,000 (35,900), 44,900 (23,600)
$Co(Ph_2[15]tetraenatoN_4)$[d] (6)	18,700 (3400), ~24,200 (sh, 10,300), 27,000 (17,300), 31,600 (27,500), 35,200 (25,000)
$Co(Ph_2[16]tetraenatoN_4)$[d] (7)	18,600 (2660), 23,500 (7110), 27,000 (14,700), 31,700 (31,300), 35,100 (32,600), 38,500 (29,000)
$[Co(Ph_2[15]tetraenatoN_4)(py)_2]I_3$[b] (13)	28,100 (25,800), 34,500 (70,200)[f]
$[Co(Ph_2[16]tetraenatoN_4)(py)_2]I$[b] (14)	20,200 (614), 25,800 (6320), 33,200 (26,100), 40,600 (36,600)
$[Co(Ph_2[15]hexaenatoN_4)(py)_2](PF_6)_2$[b] (15)	18,300 (8100), 27,500 (20,500), ~32,200 (sh, 13,200), 39,700 (49,700)
$[Co(Ph_2[15]hexaenatoN_4)(CN)_2]$[e] (16)	15,300 (13,400), 16,600 (11,600), ~17,800 (sh, 7500), ~24,400 (sh, 4000), 26,400 (14,300), ~27,800 (sh, 7900), 29,600 (6310), 30,800 (7240), 32,000 (6800), 36,800 (28,500)

[a] Apparent values, uncorrected for underlying absorption. [b] Chloroform solution. [c] Acetonitrile solution. [d] Dichloromethane solution. [e] $DMSO-H_2O$ (9:1 v/v). [f] Both spectral bands of this compound arise in part from triiodide absorptions; cf. A. I. Popov and R. F. Swensen, *J. Am. Chem. Soc.*, 77, 3724 (1955).

Table III. Comparison of Principal Electronic Absorption Bands in Ni(II) and Co(III) Corrinoid Complexes

Complex	λ_{max}, nm					Ref
Ni(II)[a]	ν_1	ν_2		ν_3		
1,19-Dimethyl-Crn[b,c]	244	304	317	428		23
1,8,8,13,13-Pentamethyl-5-cyano-Crn[b,d]	240(sh)	302	320	440		20, 29
1,7,8,12,13,19-Hexamethyl-Crn[b]	245	306	319	435		30
1,3,7,13,17,19-Hexamethyl-8,12-diethyl-Crn[b]	245	306	319	435		30
10[e]	248	342		490		*h*
$Co^{III}(CN)_2$		γ		β	α	
1,19-Dimethyl-Crn (27)	269	356	490	524	563	23
1,2,2,7,7,12,12-Heptamethyl-Crn (28)	268	353	487	521	559	21
Cobyrinic acid heptamethyl ester[f]		363	~490	534	571	22
Dicyanocobalamin[g]	280	368	508	544	583	*h*
16[g]	272	379	562	602	654	*h*

[a] For spectra of other substituted Ni(II) corrins cf. H. H. Inhoffen, J. Ullrich, H. A. Hoffman, G. Klinzman, and R. Scheu, *Justus Liebigs Ann. Chem.*, 738, 1 (1970). [b] ClO_4^- salt. [c] CH_2Cl_2. [d] Ethanol. [e] Acetonitrile. [f] Benzene. [g] $DMSO-H_2O$ (9:1 v/v). [h] This work.

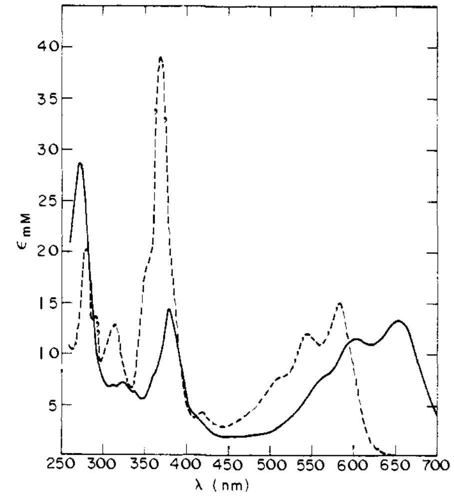


Figure 6. Electronic spectra of $[Co(Ph_2[15]hexaenatoN_4)(CN)_2]$ in 9:1 v/v $DMSO-H_2O$, —; dicyanocobalamin in 9:1 v/v $DMSO-H_2O$ containing 0.01 *M* KCN, - - -. Extinction coefficients in the latter spectrum are based on molecular weight of 1702: D. C. Hodgkin, *Fortschr. Chem. Org. Naturst.*, 15, 167 (1958).

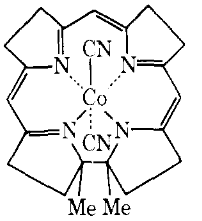
those of **1b** and **2**,[2] and the high resolution mass spectrum of **9** which shows prominent parent ion peaks with calculated and observed *m/e* values for the various isotopic species in excellent agreement. In addition, the cation **8** shows a strong EPR signal in solution with ⟨*g*⟩ = 2.01, peak-to-peak line width of 9 G, and no well-resolved hyperfine splitting. The course of the reaction yielding **8** is presumably similar to that giving **1b** from **1a**, for which a mechanism has been tentatively proposed.[2]

Attempted extension of the dehydrogenation reactions to the larger 6-5-6-6 and 6-6-6-6 ring systems using trityl tetrafluoroborate was not successful. Some indication of reaction was obtained with $Ni(Ph_2[15]tetraenatoN_4)$ (**6**) and $Ni(Ph_2[16]tetraenatoN_4)]$ (**7**) but product isolation was not achieved. However, the desired transformations were effected by use of the high-potential quinone 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) which has found extensive application in the dehydrogenation of organic compounds.[22]

Reaction of **6** and **7** with excess DDQ in hot trichloroethylene afforded the monocations $[Ni(Ph_2[15]hexaenatoN_4)]^+$ (**10**) and $[Ni(Ph_2[16]hexaenatoN_4)]^+$ (**11**) (Figure 1), respectively, isolated as their hexafluorophosphate salts. Yields were 19% (**10**) and 60% (**11**) after purification. Structural assignments are based primarily on the ^{1}H NMR spectra set out in Figure 2. When compared with the spectra of precursors **6** and **7**,[4] these spectra indicate the retention of a saturated five-membered ring in **10** and one saturated six-membered ring in **11**, and reveal a low-field doublet and triplet, assigned to the α'-H and β'-H protons of unsaturated six-membered rings. Electronic spectral differences between reactants and products (Table II, Figure 3) suggest an extended π-system in the latter. The prominent ligand-based transition at ca. 30,000 cm^{-1} in the spectra of **6** and **7** is absent in the spectra of **10** and **11**. These two complexes have very similar spectra, indicating they both possess essentially the same ligand chromophore, and are characterized by a low energy band near 20,000 cm^{-1} and two additional intense features at ca. 29,000 and 40,000 cm^{-1}. High-resolution mass spectra of the salts of **10** and **11** provide some additional evidence for the formulations of the cations. These spectra contain peaks assignable to $C_{23}H_{20}N_4Ni^+$ and $C_{24}H_{22}N_4Ni^+$, presumably resulting from the loss of a proton from **10** and **11**, respectively, under volatilization conditions followed by ionization in the spectrometer. These results together with the analytical data are considered to demonstrate that reaction of DDQ with **6** and **7** results in a 12-π → 14-π ligand transformation and formation of **10** and **11**. The structures of these complexes contain the essential inner ring π-system of the corrin unit **4** and its metal complexes but are slightly modified by phenyl substitution at positions corresponding to 5 and 15 in the corrin.

(b) **Copper Complexes.** Upon reaction with DDQ the Cu(II) 12-π complexes Cu(Ph$_2$[15]tetraenatoN$_4$) and Cu(Ph$_2$[16]tetraenatoN$_4$) are converted to monocation complexes, which were isolated as hexafluorophosphate salts. Yields of purified salts of **10** and **11** were 20 and 41%, respectively. The electronic spectra of these complexes (Figure 4) contain a three-band system sufficiently similar in energies and intensities to the Ni(II) analogs to establish the presence of the same 14-π ligand chromophore. Despite repeated attempts the Cu(II) analog of **8** could not be obtained from the reaction of Cu(Ph$_2$[14]tetraenatoN$_4$) with trityl tetrafluoroborate.

(c) **Cobalt Complexes.** The low-spin Co(II) complexes of **5–7** are readily oxidized by iodine in the presence of pyridine to afford in good yield the corresponding transdipyridine Co(III) cations **12–14** (Figure 1), isolated as their iodide or triiodide salts. Complex **14** proved inert to DDQ in refluxing benzene, possibly because of the insolubility of its salt. Reactions of **5–7** with DDQ and no added complexing ligand were complicated by oxidation to Co(III)[23] and tractable products were not obtained. However, the reaction of Co(Ph$_2$[15]tetraenatoN$_4$) (**6**) with excess DDQ in benzene gave a dark purple solid which upon treatment with pyridine and NaPF$_6$ in ethanol produced a brown-black crystalline salt in 43% yield. This compound is soluble in polar organic solvents such as acetonitrile, DMSO, and DMF giving purple solutions. The complex cation has been identified as the corrinoid species [Co(Ph$_2$[15]hexaenatoN$_4$)(py)$_2$]$^{2+}$ (**15**) from its ^{1}H NMR spectrum. This spectrum is clearly related to that of the Ni(II) complex **10** (Figure 2) and in acetone-d_6 consists of signals at 4.61 (α'-CH$_2$, s), 6.61 (β'-CH, t), and 10.7 ppm (α'-CH, d). Phenyl, pyridine, and α-CH resonances occur in a complicated multiplet at ~7-9 ppm. In view of the apparent absence of a vitamin B$_{12}$ or other corrinoid derivative containing axial py-Co(III)-py ligation, further evidence for the presence of a corrinoid ring system was sought by preparation of a complex containing the NC-Co(III)-CN unit, as in dicyanocobalamin and the synthetic corrins of Eschenmoser[24-26] and Johnson.[27] The latter contain saturated hydrocarbon fragments as pyrroline rings which form the overall corrin structure **4** and are exemplified by the di- and heptamethyl dicyano corrin complexes **27**[27] and **28**,[25] respectively. Reaction of **6**



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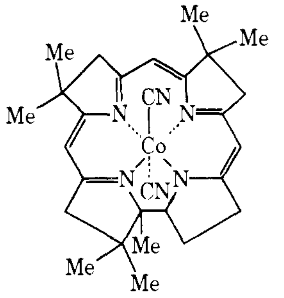

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with DDQ in benzene followed by addition of aqueous sodium cyanide to an ethanol solution of the isolated reaction product afforded the neutral red crystalline dicyano complex [Co(Ph$_2$[15]hexaenatoN$_4$)(CN)$_2$] (**16**, Figure 1) in moderate yield (28%). Inasmuch as the syntheses of both **15** and **16** were performed under anaerobic conditions, the quinone apparently effects both 12π → 14π ligand oxidative dehydrogenation and Co(II) → Co(III) oxidation in the presence of ligands (py, CN$^-$) capable of stabilizing the higher metal oxidation state. [Co(Ph$_2$[15]hexaenatoN$_4$)(CN)$_2$] is soluble in DMF, DMSO, and pyridine giving blue solutions. In the solid state it exhibits a weak but sharp CN stretch at 2117 cm^{-1}. Corresponding values for **28**[25] and dicyanocobalamin[28] are 2118 and 2119 cm^{-1}, respectively. The ^{1}H NMR spectrum of the complex in DMSO-d_6 (Figure 2) is consistent with structure **16**; one of the two inequivalent α-CH proton resonances is contained in the multiplet centered at about 7.4 ppm. The mass spectrum of the compound does not reveal a parent ion but does contain an intense peak at *m/e* 412 corresponding to M − 2CN as well as several other peaks assignable to ions resulting from loss of hydrogen and CN. In their mass spectral examination of the synthetic corrin **27** Johnson and Overend[27] did not detect a parent ion. They did find ions corresponding to loss of hydrogen and CN (M − 4 − 2CN) and further observed that dehydrogenation of metal corrin complexes in the mass spectrometer appears to be a general phenomenon. Our results are consistent with this statement. The electronic spectra of dicyano Co(III) corrins are particularly characteristic and are considered in the following section together with the spectrum of **16**.

Electronic Spectral Properties. The spectral results obtained in Figures 3–6 and summarized in detail in Table II are presented in order to substantiate the presence of a 14-π chromophore arising from oxidative dehydrogenation reactions of Cu(II), Ni(II), and Co(II) complexes of the 12-π types **5–7**. Specific assignments of bands are not warranted here. Several recent theoretical attempts to assign corrin spectra have been published,[29,30] and theory and spectral data for cobalt corrins are summarized elsewhere.[31,32] As noted above and is clearly evident from inspection of Figures 3–5, the oxidized complexes exhibit spectra quite different from their 12-π precursors. An intense three-band pattern is developed and no ligand field transitions can be detected from ca. 14,000 cm^{-1} to higher energies. The complexes [M(Ph$_2$[15]hexaenatoN$_4$)]$^+$ (**10**, M = Ni(II), Cu(II)), [M(Ph$_2$[16]hexaenatoN$_4$)]$^+$ (**11**, M = Ni(II), Cu(II)), and [Co(Ph$_2$[15]hexaenatoN$_4$)(py)$_2$]$^{2+}$ (**15**) all display three intense features occurring in the ranges 18,300-20,400 (546-490, ν_1), 27,500-29,200 (364-342, ν_2), and 38,000-40,400 cm^{-1} (263-248 nm, ν_3). The spectra of the Ni(II) complexes **10** and **11** may be compared to published spectral data and figures for variously substituted synthetic Ni(II) corrins.[24,27,33,34] Representative data for the most intense bands are included in Table III.[35] A similar three-band system is present in the spectra of these complexes but with these differences compared to **10** and **11**: (i) the central feature consists of two (or more[24]) bands at ca. 305 and 320 nm (ν_2) whereas the corresponding band in **10** and **11** near 345 nm exhibits only a slight broadening or weak shoulder on the high energy side (Figure 3); (ii) ν_2 and ν_3 bands are substantially red shifted in the latter complexes compared to the synthetic corrins. Synthetic Cu(II) corrins have not been reported. However, the high degree of spectral similarity between the Cu(II) and Ni(II) complexes **10** and **11** (Figures 3 and 4) assures the presence of identical ligand chromophores. In addition, the Cu(II) complexes of several vitamin B_{12} derivatives[36] exhibit spectra rather similar to those of **10** and **11**. Although possibly fortuitous because of the sensitivity of Co(III) corrin spectra to the nature of axial ligands,[31,32] the spectrum of **15** (Figure 5) has several features in common with the vitamin B_{12} spectrum. The two prominent bands of the latter in the near-uv-visible region (α-, γ-bands) occur at 547 (ϵ_α 8300) and 361 nm (ϵ_γ 27,500) in aqueous solution.[37] Noting that the axial ligands in vitamin B_{12} (CN and 5,6-dimethylbenzimidazole) and **15** (2py) are different, it is perhaps more appropriate to compare **15** with pyridylcobalamin (λ_γ 360 nm[38]).

As a final and sensitive electronic spectral test for the existence of a chromophore of the corrinoid type produced by oxidative dehydrogenation, [Co(Ph$_2$[15]hexaenatoN$_4$)(CN)$_2$] (**16**) was prepared. Its spectrum and that of dicyanocobalamin are compared in a common solvent, 9:1 v/v DMSO-H$_2$O, in Figure 6, Spectral data for **16** are given in Table II and spectral comparisons, which include synthetic dicyano Co(III) corrins[24-27] (e.g., **27** and **28**), are available in Table III. The spectra in Figure 6 reveal red shifts of the absorption bands of **16** above ca. 300 nm and differences in relative intensities compared to dicyanocobalamin. The spectrum of the latter is essentially identical with those reported in aqueous solution[31,39] except that extinction coefficients are larger, possibly due to an incorrect molecular weight.[31] It is observed that the spectra of **16** and dicyanocobalamin exhibit a near band-for-band correspondence, with the three features in the α–β spectral region strikingly similar in band contour and intensities.

Electronic spectral properties of **10, 11, 15,** and **16**, together with analytical, mass spectrometric, and ^{1}H NMR data, demonstrate the existence of a corrinoid ring system. These complexes represent the initial examples of the synthesis of the 14-π corrin ring nucleus devoid of supporting pyrroline rings. The principal electronic differences between these species and vitamin B_{12}, its derivatives, and purely synthetic corrins occur in relative band intensities and a rather general low energy shift of intense bands in the corrinoid complexes prepared in this work. To this extent these complexes are considered to contain a mildly perturbed corrin chromophore. Inasmuch as the intense absorptions of corrin complexes above 300 nm (Table III) are considered to arise from π-π^* transitions of the 14-π ligand chromophore,[29-32] the presence of two phenyl substituents may result in a somewhat extended π-system and lower transition energies. Additionally, there may be differences in deviations from corrin ring coplanarity in the synthetic species obtained here[40] and vitamin B_{12} and its derivatives, whose corrin nuclei are usually buckled.[31,42,43] The corrinoid complexes in Figure 1 are obtained by a rather straightforward four-step synthesis,[3,4] rendering them equally or more accessible than other synthetic corrins such as **27** and **28** which contain the entire corrin ring pattern **4.** Consequently, with suitable variation of axial ligands and oxidation states the cobalt complexes should serve as useful vehicles in B_{12} model systems where a more realistic representation of electronic structure and in-plane coordination than obtains with current models[32] may be desired. Lastly, oxidative dehydrogenation reactions of the type utilized here should be applicable to other 12-π bis(β-ketoamine) complexes,[44] some of which are conveniently obtained in large quantities by metal template reactions.

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Lamellar Compounds of Graphite with Transition Metals. Graphite as a Ligand

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Abstract: Lamellar compounds of chromium, molybdenum, tungsten, iron, cobalt, nickel, manganese and copper with graphite were obtained and their structure, magnetic properties, and Mössbauer spectra were studied. Molybdenum was shown to form sandwich type π-complexes with graphite, similar to dibenzenemolybdenum, in which graphite acts as an aromatic π-ligand. Arguments were presented suggesting that in graphite compounds with iron, cobalt, and nickel some part of the metal forms weak complexes with graphite.

Carbon atoms in graphite are well known to be arranged in layers, and each layer is a regular hexagonal net of carbon atoms (Figure 1). The C–C distances in a layer are 1.41 Å which is close to the bond length in aromatic hydrocarbons. The interlayer spacing is equal to 3.35 Å which corresponds to van der Waals interaction. Such difference in layer and interlayer bond types makes possible formation of lamellar compounds of graphite (LCG)—the products of insertion of different substances into the interlayer space. At present LCG with alkali and alkali earth metals, acids, halogens, and metal chlorides are described.[1-9] The number of carbon layers of graphite per each layer of inserted substance in an LCG is usually called the stage of LCG (Figure 2). The bonding between an inserted substance and a carbon net of graphite depends on the compound inserted and is known to be of either charge transfer or van der Waals type.

However, if a carbon net of graphite is considered as an infinite aromatic molecule, the formation of another type of LCG, namely, complexes of graphite with transition metals, could be expected. In these complexes the carbon net of graphite should act as a polynuclear aromatic ligand. In accordance with Sidgwick's rule, zero-valent metals of group VI (Cr, Mo, W) form stable bis(arene) complexes. Thus, LCG with these metals can be expected to have a bis(arene) structure. Similar bisarenic complexes could also be expected for Mn(I), Fe(II), Co(III), etc. π-Complexes of allylic and olefinic types should be possible in the case of zero-valent Fe, Co, Ni, Mn, and Cu. Formation of such π-complexes would require localization of a certain number of bonds in the conjugated graphite system at the expense of some resonance energy. However, this loss might be compensated by the energy of complex formation. Actually examples are well known in which a metal atom breaks the conjugation system of benzene producing allylic complexes.[10] However, zero-valent metal LCG could *a priori* have another structure with only weak van der Waals interaction between metal atoms and graphite layers or that of the charge transfer complex type.

The present paper deals with the synthesis of LCG with transition metals iron, cobalt, nickel, chromium, molybdenum, tungsten, manganese, and copper and with a study of their structure by X-rays, Mössbauer spectroscopy, and magnetic measurements.

Transition metal LCG were prepared by reduction of the metal chloride LCG ($FeCl_3$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $MnCl_2$, $CuCl_2$, $MoCl_5$, WCl_6, $CrCl_3$). Reduction by means of different reducing agents, hydrogen, sodium borohydride, lithium aluminum hydride, sodium in liquid ammonia, and aromatic anion-radicals (Li, Na, and K naphthalenide and diphenylide and sodium benzophenone ketyl), has been studied.

Reduction of the $FeCl_3$ LCG by sodium in liquid ammonia has been previously described by Klotz and Schneider;[11] reduction of $FeCl_3$ to Fe(0) is reported to take place. Later Knappwost and Metz[12-14] confirmed this result and studied magnetic properties of Fe LCG. According to their data iron is not chemically bonded to carbon nets of graphite in the compounds obtained.

Experiments and Results

Starting Compounds. The starting compounds were $MoCl_5$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $MnCl_2$, WCl_6, $CrCl_3$, and $CuCl_2$ LCG of a definite stage and good regularity.