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Using a metal template reaction, a series of [14]azaannulenes formed from a β -diketone and an aromatic diamine in the presence of nickel(II) have been synthesized. Attempted cyclizations with bulky β -diketones and certain substituted diamines showed that the cyclization is sensitive to steric effects. At least one of the nickel complexes readily reacts with a series of nucleophilic reagents to give methine-substituted products.

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The use of metal ions for improving the yield of cyclization processes, particularly those based on Schiff base reactions is well documented (1,2). The phenomenon, known as the metal template effect, appears to be a direct consequence of the coordination properties of the added metal ion. Reactive groups, *e.g.*, amine functions in the case of Schiff base reactions, are held in the correct juxtaposition *via* metal coordination such that a high yield of cyclic as opposed to an acyclic structure results. The cyclic compound is usually isolated as its metal complex, and under favorable conditions the compound can be demetallated to yield the free macrocyclic ligand.

A macrocyclic Schiff base which can be synthesized in high yield as its Ni(II) complex from *o*-phenylenediamine and acetylacetone, **1**, is shown in Figure 1. Since the Ni(II) complex of **1**, Ni(II)-**1** (**3**), is susceptible to demetallation yielding the free Schiff base ligand, the cyclic structure is an ideal synthetic candidate for studying porphyrin-like structure-function correlations (4-26). In an effort to introduce useful peripheral substitution on the framework of **1**, we have examined the breadth of the metal-mediated cyclization reaction which produces, **1**, as a function of diamine and β -diketone structure. In addition, we have explored the response of **1** toward electrophilic reagents. The structures reported here for the first time, **2-4**, **9**, **10**, **16**, **18-20**, **25-27**, as well as those already known, **1**, **5-8**, **11-15**, **17**, **21-24**, **28-32** (13,20,21,27-35) are shown in Figure 1.

The Cyclization Reaction.

Reference to Figure 1 will show that the metal-assisted Schiff base cyclization reaction is versatile. Structures **1-10**, **25-27** can be produced in significant yields (up to ~50%) by the reaction of an aromatic 1,2-diamine and a β -diketone in the presence of Ni(II). The nickel complexes that are isolated are intensely green in color and diamagnetic, the latter feature greatly facilitating characterization *via* nmr. As a class, the compounds are unstable toward hot methanolic hydrogen chloride. Purging methanol suspensions of Ni(II)-**1**, **5** and **10** with hydrogen chloride gas followed by workup results in the isolation of

the corresponding metal-free Schiff base (21,22,36). The reaction of the Schiff base with other metal salts under anhydrous conditions results in the reinsertion of the metal ion and the generation of new metal complexes.

Cis and *trans* isomers are possible for five of the newly synthesized compounds **4**, **9**, **10**, **26** and **27**. Nmr spectroscopy confirmed that isomeric mixtures are produced in at least two of the template syntheses. The ^1H nmr of Ni(II)-**9** showed three methine singlets at δ 4.56, 4.68, and 4.75, indicating the presence of the two isomers. In addition, the free ligand **H₂-10**, exhibited a 17° melting point range, and showed a total of 19 resonance lines in its ^{13}C nmr spectrum. Since the *cis* and *trans* isomers of the compound should exhibit 13 and 12 resonance lines respectively, **H₂-10** must exist as a mixture of isomers. No attempt was made to separate the two compounds.

The condensation reaction with Ni(II) appears to be sensitive to steric effects. X-Ray crystallographic studies by Goedken *et al.* (7,8-12,16-19,20,22,32,34) have shown that **1** and its metal complexes are not flat but are in fact saddle shaped. The source of nonplanarity in the structures appears to be the steric interactions which occur between the methyl groups, R_{1-4} and the *ortho* aromatic hydrogens of the Schiff base. We have found that increasing steric bulk at these positions impedes cyclization. For example, 3,5-heptanedione, 4,6-nonanedione, 1-phenyl-2,4-pentanedione, 2-acetylcyclohexanone and 2-acetylcyclopentanone lead to cyclic products, Ni(II)-**2-4**, **26**, **27**, while other more sterically hindered β -diketones do not. Thus, 2,6-dimethyl-3,5-heptanedione and 2,2,6,6-tetramethyl-2,5-heptanedione in the presence of *o*-phenylenediamine and Ni(II) do not form nickel macrocyclic complexes. Furthermore, diamines having substituents which would interact sterically with the methyl groups of Ni(II)-**1**, *e.g.*, 3,4,5-trichloro-*o*-phenylenediamine and 9,10-diaminophenanthrene, also do not lead to cyclic products. However, with one exception, those diamines examined having substituents in only the 4 and 5 positions of the aromatic ring (compounds Ni(II)-**5-10**, **25**) formed macrocyclic compounds. The reaction of 4-nitro-*o*-phenylenediamine with

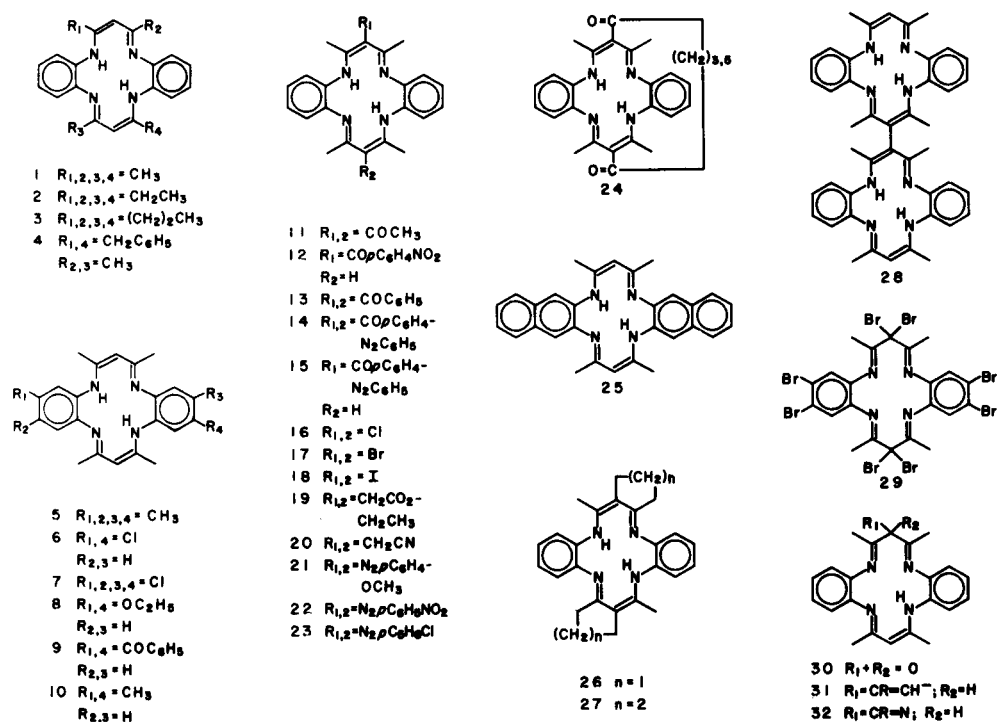
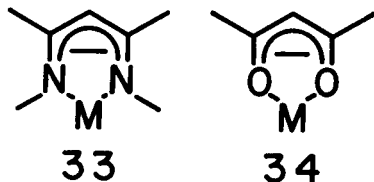


Figure 1. The known structural analogues of **1** are shown. Although the structures of the metal-free ligands are shown, in most cases only the Ni(II) complexes and in a few cases the Co(III) compounds of the ligands are known. Tautomeric forms of **22-23** (**27**), were isolated. Protonated forms of the Ni(II) complexes of **11** and **24** were reported (30). Several variants of structures **31** and **32** have also been reported (13,34).

2,4-pentanedione in the presence of the metal ion did not lead to product formation. Since steric interactions generated by the nitro-compound should not be significantly different than those associated with *o*-phenylenediamine itself, the difference in behavior appears to have an electronic origin.

The Reactivity of the Schiff Base.

The similarity in electronic structure between the coordinated diiminate rings, **33**, of the macrocyclic compounds



shown in Figure 1 and the diketone rings found in metal acetylacetonates, **34**, suggests that both structures should exhibit similar reactivity patterns. Studies by Collman, *et al.*, (37) have shown that metal acetylacetonates readily undergo electrophilic substitution at the methine carbon atom of the diketone moiety. This type of substitution was also found to occur for both Ni(II) and Co(II) com-

plexes of **1**. The condensation of Ni(II)-**1** with aryl acid chlorides, the *N*-halosuccinimides or strong alkylating agents, *e.g.*, ethyl bromoacetate or bromoacetonitrile, yielded the corresponding ketones, **12**, **13**, **24**, halo compounds, **16-18**, and alkyl derivatives, **19**, **20**. However, Ni(II)-**1** was found to be unreactive with a number of alkyl halides and acrylonitrile. As was previously reported (32), subjecting Ni(II)-**1** to nitration conditions lead to ligand oxidation and the formation of the dinuclear complex **28**. The nitro analogue of Ni(II)-**1** has not yet been reported.

Metal coordination is not a requirement for electrophilic substitution of the cyclic Schiff base. The free ligand, **1**, has been shown to react with certain aryl acid chlorides and with diazonium salts, to give γ -substituted macrocyclic products **14**, **15**, **21-23**. The reaction of **1** with excess bromine leads to the unusual macrocyclic structure **29**, or to the dibrominated derivative **17** under more mild conditions (31). However, **1** does not display the wide range of reactivity with electrophiles that its nickel complex evidences. Attempts to alkylate **1** with ethyl bromoacetate under conditions similar to those successful for the alkylation of Ni(II)-**1** resulted in decomposition of the macrocyclic framework. It thus appears that the coor-

Table I
Elemental Analyses

Compound No.	Empirical Formula	Carbon %		Hydrogen %		Nitrogen %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Ni(II)-2	C ₂₆ H ₃₀ N ₄ Ni	68.30	68.23	6.61	6.82	12.25	12.22
Ni(II)-3	C ₃₀ H ₃₆ N ₄ Ni	70.19	70.17	7.46	7.65	10.91	10.83
Ni(II)-4	C ₃₄ H ₃₀ N ₄ Ni	73.80	73.55	5.46	5.61	10.12	10.07
Ni(II)-9	C ₃₆ H ₃₀ N ₄ O ₂ Ni	70.95	70.75	4.96	5.04	9.19	9.18
Ni(II)-10	C ₂₄ H ₂₆ N ₄ Ni	67.16	67.28	6.10	6.21	13.05	13.06
H ₂ -10	C ₂₄ H ₂₆ N ₄	77.38	77.15	7.58	7.79	15.04	15.03
Ni(II)-16 (a)	C ₂₂ H ₂₀ N ₄ Cl ₂ Ni·0.5CCl ₄	55.43	55.33	4.22	4.16	11.72	11.49
Ni(II)-17 (b)	C ₂₂ H ₂₀ N ₄ Br ₂ Ni·CCl ₄	46.21	45.81	3.51	3.44	9.75	9.54
H ₂ -17 (c)	C ₂₂ H ₂₂ N ₄ Br ₂	56.62	52.58	4.41	4.48	11.15	10.98
Ni(II)-19	C ₃₀ H ₃₄ N ₄ O ₄ Ni	62.85	62.74	5.98	5.95	9.77	9.79
Ni(II)-20	C ₂₆ H ₂₄ N ₆ Ni	65.16	64.08	5.05	5.24	17.54	17.15
Ni(II)-25	C ₃₀ H ₂₆ N ₄ Ni	71.88	71.59	5.22	5.24	11.17	10.99
Ni(II)-26	C ₂₆ H ₂₆ N ₄ Ni	68.90	68.81	5.78	5.93	12.36	12.34
Ni(II)-27	C ₂₈ H ₃₀ N ₄ Ni	69.88	69.85	6.28	6.37	11.64	11.54

(a) Calcd. for Cl: 16.32. Found: 16.55. (b) Calcd. for Br: 27.82. Found: 27.94. (c) Calcd. for Br: 31.82. Found: 31.74.

minated metal ion of Ni(II)-1 protects the potentially nucleophilic nitrogen centers from attack, allowing only the methine carbons to be susceptible to substitution reactions.

EXPERIMENTAL

Unless otherwise noted all materials were reagent grade and were used without further purification. Proton and ¹³C magnetic resonance spectra were obtained using a Varian T-60A or CFT-20 NMR spectrometer equipped with 5 mm probes. Chemical shifts are reported relative to tetramethylsilane. Unless otherwise noted infrared spectra were recorded as Nujol or Halocarbon mulls with potassium bromide plates on Beckman Acculab-6 or 4220 spectrophotometers. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, Tennessee. The analytical data are collected in Table I. Low resolution mass spectra (70 eV) were obtained from the Cornell University Chemistry Department Mass Spectrometry Facility, Ithaca, New York.

5,7,12,14-Tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-1) (20-22,36).

To 500 ml. of degassed methanol was added nickel(II) acetate tetrahydrate (50.0 g.), 2,4-pentanedione (40.3 g.), and *o*-phenylenediamine (43.5 g.). The reaction mixture was refluxed under nitrogen for 48 hours. After cooling in an ice bath, the dark-violet crystalline solid which formed was removed by filtration, washed thoroughly with cold methanol, and vacuum dried to yield 29.4 g. of product (36.5%); ¹H nmr (carbon tetrachloride): δ 2.05 (s, 12, CH₃), 4.70 (s, 2, methine), 6.48 (s, 8, aromatic); ir: (cm⁻¹) 1545, 1530 (diiminate), 750 (aromatic); ms: m/e (relative intensity) 403 (11.0), 402 (46.6), 401 (26.0), 400 (100.0), 200 (11.2).

1,8-Dihydro-5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradeca-4,6,11,13-tetraene (H₂-1).

Demetallation of Ni(II)-1 was accomplished according to the method described by Goedken (36). A stirred suspension of Ni(II)-1 (15.0 g.) in absolute ethanol (1 l.) was treated with excess anhydrous hydrochloric acid until the turquoise-colored ligand tetrachloronickelate salt precipitated. The reaction mixture was cooled to about 0° and filtered. The solid was washed sparingly with cold ethanol and vacuum dried. The ligand salt was metathesized to the hexafluorophosphate form by adding a solution of ammonium hexafluorophosphate (16.2 g.) in water (~15 ml.) to a well-stirred solution of the tetrachloronickelate salt (18.0 g.) in water (200

ml.). The resulting suspension was filtered, the solid washed with water and vacuum dried. A suspension of the dry hexafluorophosphate salt (11.4 g.) in methanol (150 ml.) was treated with triethylamine (6 ml.) to afford a yellow precipitate. The suspension was filtered, washed with methanol, and vacuum dried to yield 10.0 g. of metal-free, neutral ligand (59% from Ni(II)-1); ¹H nmr (carbon tetrachloride): δ 2.12 (s, 12, CH₃), 4.73 (s, 2, methine), 6.85 (s, 8, aromatic), 12.00 (s, 2, NH); ¹³C nmr (deuteriochloroform): ppm 20.7 (CH₃), 97.8 (methine), 122.8, 123 (aromatic), 138 (aromatic CN), 158.8 (imine CN); ir: (cm⁻¹) 1616 (C=N), 746, 737 (aromatic).

5,7,12,14-Tetraethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-2).

Methane (175 ml.), 3,5-heptanedione (6.36 g.), *o*-phenylenediamine (5.90 g.) and nickel(II) acetate tetrahydrate (6.79 g.) were reacted as described above for 56 hours to yield 1.73 g. of product (15.2%); ¹H nmr (carbon tetrachloride): δ 1.20 (t, 12, CH₃), 2.42 (q, 8, CH₂), 4.80 (s, 2, CH), 6.47 (s, 8, aromatic); ir: (cm⁻¹) 1557, 1529 (diiminate), 1420, 745 (aromatic); ms: m/e (relative intensity) 460 (8.6), 458 (45.8), 457 (35.3), 456 (100.0), 228 (13.6).

5,7,12,14-Tetra-*n*-propyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-3).

Methanol (100 ml.), nickel acetate tetrahydrate (4.61 g.), 4,6-nonanedione (5.79 g.) and *o*-phenylenediamine (4.01 g.) were reacted as described above for 84 hours to yield 1.20 g. of product (12.6%); ¹H nmr (carbon tetrachloride): δ 1.02 (t, 12, CH₃), 1.60 (m, 8, CH₂), 2.35 (q, 8, CH₂), 4.83 (s, 2, methine), 6.52 (s, 8, aromatic); ir: (cm⁻¹) 1539, 1521 (diiminate), 1420, 742 (aromatic); ms: m/e (relative intensity) 515 (15.0), 514 (44.2), 513 (37.5), 512 (100.0), 82 (42.9), 80 (44.3), 79 (16.1).

5,12-Dibenzyl-7,14-dimethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-4).

Methanol (40 ml.), nickel acetate tetrahydrate (3.95 g.), 1-phenyl-2,4-pentanedione (5.60 g.), and *o*-phenylenediamine (3.44 g.) were reacted as described above for 3d to yield 3.59 g. of product (40.8%). An analytical sample was obtained by chromatography of the crude material (0.95 g.) on alumina using methylene chloride as the eluant. The rapidly-eluting green solution was evaporated to dryness under reduced pressure, and the residual glassy solid triturated with 15 ml. of ether for 2 hours. The resulting slurry was filtered and the solid dried in vacuum to obtain 0.85 g. of a dark-green finely powdered material (91%); ¹H nmr (carbon tetrachloride): δ (2.03 (s, 6, CH₃), 3.78 (s, 4, CH₂), 4.68 (s, 2, methine), 6.49 (m,

6, aromatic), 7.25 (s, 10, aromatic); ir: (cm^{-1}) 1537 (diiminate), 1465, 1409, 750 (aromatic); ms: m/e (relative intensity) 556 (9.9), 555 (19.2), 554 (41.9), 553 (41.8), 552 (100.0), 276 (6.9), 44 (27.1).

1,8-Dihydro-5,7,12,14-tetramethylbis-4,5-dimethylbenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradeca-4,6,11,13-tetraene (H_2 -5) (21).

Ni(II)-5 (21) was synthesized in analogous fashion to Ni(II)-1. The demetallation procedure was performed in similar fashion to that reported below for H_2 -10 in 64% yield; ^1H nmr (carbon tetrachloride): δ 2.17 (s, 12, CH_3), 2.37 (s, 12, CH_3), 4.17 (s, 2, methine), 6.90 (s, 4, aromatic), 12.70 (s, 2, NH); ^{13}C nmr (deuteriochloroform): ppm 19.5, 20.5 (CH_3), 97.5 (methine), 124.1 (3,4-phenyl), 130.8 (2,5-phenyl), 136.3 (1,6-phenyl), 158.4 (imine CN).

5,7,12,14-Tetramethyl-di-4-benzoylbenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-9).

Methanol (100 ml.), nickel(II) acetate tetrahydrate (5.0 g.), 2,4-pentanedione (4.0 g.), 3,4-diaminobenzophenone monohydrochloride (10.0 g.), and ammonium hydroxide (3 ml.) were reacted as described above for 48 hours to yield 0.80 g. of product (7%); ^1H nmr (carbon tetrachloride): δ 1.90 (s), 1.95 (s) (12H, CH_3), 4.56 (s), 4.68 (s), 4.75 (s), (2, methine), 6.27-7.73 (m, 16, phenyl); ir: 1645 (C=O), 1545, 1530 (diiminate).

5,7,12,14-Tetramethyl-di-4-methylbenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-10).

Methanol (500 ml.), nickel(II) acetate tetrahydrate (13.0 g.), 2,4-pentanedione (30.0 g.), 3,4-diaminotoluene (36.6 g.) and ammonium hydroxide (3 ml.) were reacted as described above for 48 hours, to yield 51.9 g. of product (22%); ^1H nmr (carbon tetrachloride): δ 2.02 (s, 12, CH_3), 2.12 (s, 6, CH_3), 4.65 (s, 2, methine), 6.33 (s, 6, aromatic); ir: (cm^{-1}) 1545, 1535 (diiminate), 870, 810 (aromatic).

1,8-Dihydro-5,7,12,14-tetramethyl-di-4-methylbenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradeca-4,6,11,13-tetraene (H_2 -10).

Ni(II)-10 (20.0 g.) in methanol (100 ml.) was treated with hydrogen bromide in a fashion analogous to H_2 -1. The demetallated ligand was isolated as the white dihydrobromide salt and treated with excess triethylamine in methanol to afford a mixture of desired product (~90%) and the starting material (~10%). The above treatment was repeated once more to completely strip Ni(II) from the organic framework and yield 8.0 g. (46.1%) of product. Recrystallization from acetonitrile yielded an analytical sample; m.p. 178-195°; ^1H nmr (carbon tetrachloride): δ 2.17 (s, 12, CH_3), 2.37 (s, 6, aromatic CH_3), 4.17 (s, 2, methine), 6.90 (s, 6, aromatic), 12.70 (s, 2, NH); ^{13}C nmr (deuteriochloroform): ppm 20.8, 21.1 (CH_3), 97.6, 97.8, 97.9 (methine), 122.6, 122.8, 123.4, 123.5, 123.6 (CH, aromatic), 132.5, 132.6 (CCH_3 , aromatic), 135.6, 136.0, 138.5, 138.9 (CN, aromatic), 158.3, 158.6, 158.9 (imine CN); ir: (cm^{-1}) 1620 (C=N), 752 (aromatic); ms: m/e (relative intensity) 373 (34.1), 372 (100.0) M^+ , 357 (49.1), 221 (46.6).

6,13-Dichloro-5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-16).

N-Chlorosuccinimide (1.9 g.) was added to 250 ml. of a cold (-17°) carbon tetrachloride solution containing 1.0 g. of Ni(II)-1. After 35 minutes, the reaction mixture was filtered and the filtrate evaporated under reduced pressure to dryness. The residue was chromatographed on a 50 \times 50 mm alumina column using carbon tetrachloride as the eluant. The fraction which passed through the column was collected and evaporated to dryness under reduced pressure to yield 1.0 g. of the desired product (87%); ^1H nmr (carbon tetrachloride): δ 2.25 (s, 12, CH_3), 6.53 (s, 8, aromatic); ir: (cm^{-1}) 1530 (diiminate), 750 (aromatic).

6,13-Dibromo-5,6,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-17) (31).

N-Bromosuccinimide (2.35 g.) was added to a stirred carbon tetrachloride solution containing Ni(II)-1 (1 g. in 200 ml.). After 15 minutes, the reaction mixture was vacuum filtered and the filtrate evaporated

under reduced pressure to dryness. The residue which remained was chromatographed on a 50 \times 50 mm alumina column using carbon tetrachloride as the eluant. The fraction that passed through the column was collected and evaporated to dryness under reduced pressure to yield 1.29 g. (90%) of the green-colored complex; ^1H nmr (carbon tetrachloride): δ 2.32 (s, 12, CH_3), 6.48 (s, 8, aromatic); ir: (cm^{-1}) 1520 (diiminate), 742 (aromatic).

1,8-Dihydro-6,13-dibromo-5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradeca-4,6,11,13-tetraene (H_2 -17) (31).

N-Bromosuccinimide (5.5 g.) was suspended in 300 ml. of carbon tetrachloride, and H_2 -1 (3.0 g.) was added. The suspension was stirred and brought to reflux for a period of 45 minutes. After this time the reaction mixture was vacuum filtered to remove any insoluble material and the filtrate was evaporated to an oil using reduced pressure. Methanol (250 ml.) was added to the oily residue and after agitation a yellow solid resulted. The product was further purified by dissolution in carbon tetrachloride followed by the slow addition of methanol until crystallization occurred. The yield was 1.8 g. (42%); ^1H nmr (carbon tetrachloride): δ 2.38 (s, 12, CH_3), 6.94 (s, 8, aromatic), 13.60 (s, 2, NH); ^{13}C nmr (deuteriochloroform): ppm 22.0 (CH_3), 95.3 (methine), 124.2 (aromatic), 128.3 (aromatic), 138.6 (CN aromatic), 159.6 (imine CN); ir: (cm^{-1}) 1595 (C=N), 1550 (C=C), 749 (aromatic); ms: m/e (relative intensity) 504 (6.2), 502 (8.7), 501 (4.6), 400 (6.6), M^+ , 424 (37.8), 423 (100), 422 (40.2), 421 (100).

6,13-Diiodo-5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-18).

N-Iodosuccinimide (1.1 g.) was added to a solution containing 0.66 g. of Ni(II)-1, 175 ml. of carbon tetrachloride and 25 ml. of methylene chloride. The green reaction mixture was allowed to stir at room temperature for 45 minutes. After this time the reaction mixture was filtered and the filtrate evaporated to dryness under reduced pressure. The crude product was chromatographed on a 25 \times 100 mm alumina column using carbon tetrachloride as the eluant. The leading edge of the first band was collected, approximately 100 ml. of eluant. Evaporation of this fraction is dryness under reduced pressure yielded 100-200 mg. of the diiodo complex. The product was found to be unstable towards disproportionation and therefore characterized immediately; ^1H nmr (carbon tetrachloride): δ 2.46 (s, 12, CH_3), 6.50 (s, 8, aromatic); ir: (cm^{-1}) 1505 (diiminate), 740 (aromatic).

6,13-Di-(ethyl-2-acetate)-5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-19).

To 50 ml. of dry acetonitrile containing 1.00 g. of Ni(II)-1 was added 8.35 g. of ethyl bromoacetate. The mixture was refluxed for 14 hours under dry nitrogen, cooled, and the bulk of the solvent removed under reduced pressure to afford a dark-green tar. To this residue was added 50 ml. of petroleum ether and the mixture triturated for 3 hours. The resulting suspension was filtered, and the green solid washed with 10 ml. of petroleum ether and vacuum dried. The solid was dissolved in ~10 ml. of 1:1 dichloromethane-acetonitrile and chromatographed on a 20 \times 200 mm alumina column using dichloromethane as the eluant. A fast-moving dark-green band separated from dark-brown and olive-green immobile bands near the top of the column. The green solution was collected and the bulk of the solvent removed under reduced pressure and vacuum dried. Traces of dichloromethane were removed by trituration of the solid in 25 ml. of pentane. The slurry was filtered, and the finely divided green solid vacuum dried to afford 0.87 g. (61%) of the dialkylated product. ^1H nmr (carbon tetrachloride): δ 1.30 (t, 6, CH_2CH_3), 2.11 (s, CH_3), 3.23 (s, 4, CH_2), 4.14 (q, 4, CH_2CH_3), 6.45 (s, 8, aromatic); ir: (cm^{-1}), 1715 (CO), 1530 (diiminate), 735 (aromatic); ms: m/e (relative intensity) 574 (29.2), 573 (21.9), 572 (63.5), M^+ , ^{58}Ni , 501 (42.8), 500 (31.9), 499 (100.0), 214 (34.7), 213 (46.9).

6,13-Di-(2-acetonitrile)-5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecahexaenatonickel(II) (Ni(II)-20).

To 100 ml. of acetonitrile containing 1.00 g. of Ni(II)-1 was added 6.00 g. of bromoacetonitrile. The mixture was refluxed under nitrogen for 20

hours, cooled, and the solvent removed under reduced pressure. The residue was suspended in about 10 ml. of dichloromethane to which was added 1 ml. of triethylamine. The resultant solution was loaded onto a 20 × 200 mm alumina column prepared with dichloromethane, and dichloromethane used as the eluant. A broad green band quickly separated from a brown immobile band near the top of the column. The green solution was evaporated under reduced pressure and the residue vacuum dried. The residue was washed with methanol (40 ml.), filtered, and vacuum dried to yield 0.67 g. of the desired product (56%) as a dark-green powder; ¹H nmr (deuteriochloroform): δ 2.21 (s, 12, CH₃), 3.35 (s, 4, CH₂), 6.59 (s, 8, aromatic); ir: (cm⁻¹), 2245 (C≡N), 1535 (diiminate), 730 (aromatic); ms: m/e (relative intensity) 480 (43.3), 479 (31.1), 478 (100.0) 453 (27.7), 441 (19.2), 440 (18.9), 439 (42.6), 438 (20.0).

5,7,12,14-Tetramethyl-di-2,3-naphtho[b,i][1,4,8,11]tetraazacyclotetradeca-hexaenatonickel(II) (Ni(II)-25).

Methanol (40 ml.), nickel(II) acetate tetrahydrate (6.3 g.), 2,4-pentanedione (2.5 g.), 2,3-diaminonaphthalene (4.0 g.) and ammonium hydroxide (2 ml.) were reacted as described above for 48 hours to yield 1.04 g. of product (12%). An analytical sample was obtained by recrystallization from acetonitrile. ¹H nmr (carbon tetrachloride): δ 2.22 (s, 12, CH₃), 4.85 (s, 2, methine), 6.85 (s, 4; 1,4-naphthyl), 7.07-7.30 (m, 8, naphthyl); ir: (cm⁻¹) 1545, 1528 (diiminate), 870, 750 (aromatic).

5,12-Dimethyldicyclopentyl[e,f]dibenzo[b,i]tetraazacyclotetradeca-hexaenatonickel(II) (Ni(II)-26).

Methanol (65 ml.), nickel acetate tetrahydrate (4.64 g.), 2-acetyl-cyclopentanone (4.70 g.), and *o*-phenylenediamine (4.03 g.) were reacted as described above for 3d to yield 4.29 g. of product (50.8%); ¹H nmr (carbon tetrachloride): δ 1.77 (m, 4, β CH₂), 1.98 (s, 6, CH₃), 2.57 (m, 8, α CH₂), 6.40 (m, 8, aromatic); ir: (cm⁻¹), 1551 (diiminate), 747 (aromatic); ms: m/e (relative intensity) 455 (14.2), 454 (41.8), 453 (38.4), 452 (100.0), 451 (28.9), 226 (15.1), 225 (13.4).

5,12-Dimethyldicyclohexyl[e,f]dibenzo[b,i][1,4,8,11]tetraazacyclotetra-decahexaenatonickel(II) (Ni(II)-27).

Methanol (160 ml.), nickel(II) acetate tetrahydrate (9.1 g.), 2-acetyl-cyclohexanone (10.3 g.), *o*-phenylenediamine (7.9 g.) and ammonium hydroxide (2 ml.) were reacted as described above for 24 hours to yield 2.87 g. of product (11%); ¹H nmr (carbon tetrachloride): δ 1.45-1.72 (m, 8, β CH₂), 1.98 (s, 6, CH₃), 2.30-2.72 (m, 8, α CH₂), 6.38 (s, 8, aromatic); ir: (cm⁻¹), 1540 (diiminate), 745 (aromatic); ms: m/e (relative intensity) 482 (2.1), 481 (1.6), 480 (4.5), M⁺, 404 (6.8), 403 (12.1), 402 (40.7), 401 (25.1), 400 (100.0), 200 (10.16).

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REFERENCES AND NOTES

- (1) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).
- (2) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
- (3) Ni(II)-1 and its analogues contain the dideprotonated (dianionic) form of the macrocyclic ligand.
- (4) D. R. Neves, J. C. Dabrowiak, *Inorg. Chem.*, **15**, 139 (1976).
- (5) W. H. Woodruff, R. W. Pastor, and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **98**, 7999 (1976).
- (6) L. A. Nafie, R. W. Pastor, J. C. Dabrowiak, and W. H. Woodruff, *ibid.*, **98**, 8007 (1976).
- (7) M. C. Weiss, B. Bursten, S.-M. Peng, and V. L. Goedken, *ibid.*, **98**, 8021 (1976).
- (8) F. C. McElroy, J. C. Dabrowiak, and D. J. Macero, *Inorg. Chem.*, **16**, 947 (1977).
- (9) V. L. Goedken and Y.-A. Park, *J. Chem. Soc., Chem. Commun.*, 214 (1975).
- (10) V. L. Goedken, S.-M. Peng, J. Molin-Norris, and Y. A. Park, *J. Am. Chem. Soc.*, **98**, 8391 (1976).
- (11) V. L. Goedken, J. J. Pluth, S.-M. Peng, and B. Bursten, *ibid.*, **98**, 8014 (1976).
- (12) V. L. Goedken, S.-M. Peng, and Y.-A. Park, *ibid.*, **96**, 284 (1974).
- (13) M. C. Weiss and V. L. Goedken, *ibid.*, **98**, 3389 (1976).
- (14) M. C. Weiss and V. L. Goedken, *J. Chem. Soc., Chem. Commun.*, 531 (1976).
- (15) L. G. Bell and J. C. Dabrowiak, *ibid.*, 512 (1975).
- (16) G. C. Gordon, P. W. DeHaven, M. C. Weiss, and V. L. Goedken, *J. Am. Chem. Soc.*, **100**, 1003 (1978).
- (17) M. C. Weiss and V. L. Goedken, *Inorg. Chem.*, **18**, 819 (1979).
- (18) P. W. DeHaven and V. L. Goedken, *ibid.*, **18**, 827 (1979).
- (19) V. L. Goedken, *ibid.*, **18**, 274 (1979).
- (20) E. G. Jaeger, *Z. Anorg. Chem.*, **264**, 177 (1969).
- (21) F. A. L'Epplatenier and A. Pugin, *Helv. Chim. Acta*, **58**, 917 (1975).
- (22) V. L. Goedken, J. A. Molin-Case, and Y. A. Whang, *J. Chem. Soc., Chem. Commun.*, 337 (1973).
- (23) M. Tsutsui, R. L. Bobsein, G. Cash, and R. Pettersen, *Inorg. Chem.*, **18**, 758.
- (24) D. J. Olszanski and G. A. Melson, *Inorg. Chim. Acta*, **23**, L4-6 (1977).
- (25) A. Pezeshk, F. T. Greenaway, J. C. Dabrowiak and G. Vincow, *Inorg. Chem.*, **17**, 1717 (1978).
- (26) D. H. Busch, *Acc. Chem. Res.*, **11**, 392 (1978).
- (27) D. P. Fisher, F. C. McElroy, D. J. Macero and J. C. Dabrowiak, *Inorg. Nucl. Chem. Letters*, **12**, 435 (1976).
- (28) F. C. McElroy, and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **98**, 7112 (1976).
- (29) D. P. Fisher, V. Piermattie, and J. C. Dabrowiak, *ibid.*, **99**, 2811 (1977).
- (30) J. Eilmes and E. Sledziewska, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, **26**, 441 (1978).
- (31) G. P. Ferrara and J. C. Dabrowiak, *Inorg. Nucl. Chem. Letters*, **14**, 31 (1978).
- (32) G. P. Ferrara and J. C. Dabrowiak, *ibid.*, **14**, 223 (1978).
- (33) J. C. Dabrowiak, D. P. Fisher, F. C. McElroy, and D. J. Macero, *Inorg. Chem.*, **18**, 2304 (1979).
- (34) M. C. Weiss, G. C. Gordon, and V. L. Goedken, *J. Am. Chem. Soc.*, **101**, 857 (1979).
- (35) J. D. Goddard, *Inorg. Nucl. Chem. Letters*, **13**, 555 (1977).
- (36) V. L. Goedken, *Inorg. Synth.*, in press.
- (37) J. P. Collman, in "Transition Metal Chemistry", Vol. 2, Marcel Dekker, Inc., New York, New York **1966**, p. 35-45.