cupies four of the six available sites for each iron. It seems clear that making more sites available will lead to larger aggregates, as in the case of the tridentate tacn ligand, which gives rise to an octanuclear complex,[18] and in the case of the bidentate benzoate, which gives rise to an undecanuclear species.[19] The isolation and structural characterization of these iron-oxo aggregates further enhance our understanding of the core nucleation process in ferritin and the bioinorganic chemistry of rust.

Acknowledgment. This work was supported by the National Institutes of Health Grants GM-33162 (L.Q.) and GM-22701 (Eckard Münck). L.Q. thanks the Alfred P. Sloan Foundation for a Research Fellowship (1982-1986) and the National Institutes of Health for a Research Career Development Award (1982-1987). We thank Professor S. J. Lippard and R. L. Rardin for generously providing and analyzing the variable-temperature susceptibility data on [Fe_2(5-Me-HXTA)OH(H_2O)$_2$].

Supplementary Material Available: Listings of H atom and solvent atom parameters, temperature factors, and appropriate least-squares planes for [Fe_2(5-Me-HXTA)OH(H_2O)$_2$] and (pyrrH)$_4$[Fe_4(5-Me-HXTA)$_2$$O_2(OH)_2$] (Tables S1-S6), variable-temperature solid-state susceptibility data on [Fe_2(5-Me-HXTA)OH(H_2O)$_2$] (Table S7), cation-anion packing in (pyrrH)$_4$[Fe_4(5-Me-HXTA)$_2$$O_2(OH)_2$] (Figure S1), temperature dependences of the NMR signals of [Fe_2(5-Me-HXTA)] complex at pH 3 and 4.3, respectively (Figures S2 and S3), and variable-temperature solid susceptibility data on [Fe_2(5-Me-HXTA)OH(H_2O)$_2$] and the best fit (Figure S4) (18 pages). Ordering information is given on any current masthead page.

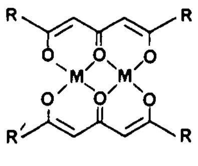
Neutral Bimetallic Macrocyclic Complexes. 1. Investigation of Mono- and Bimetallic Complexes of Tetraiminato Macrocyclic Complexes Derived from 1,3,5-Triketones

M. Himmelsbach, R. L. Lintvedt,* J. K. Zehetmair, M. Nanny, and M. J. Heeg

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received April 16, 1987*

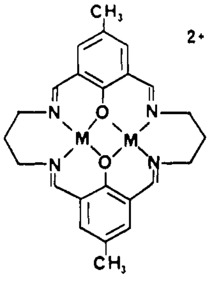
Abstract: The first bimetallic complex of the macrocyclic ligand derived from 1,3,5-triketones and diamines has been synthesized and characterized by single-crystal X-ray diffraction and NMR spectroscopy. It has been determined that the mono- and bimetallic Ni(II) complexes of the macrocyclic ligand formed from ethylenediamine and 2-methyl-3,5,7-octanetrione, $NiH_2(IAA)_2(EN)_2$ and $Ni_2(IAA)_2(EN)_2$, are isomorphous. Both crystallize in the space group $P2_1/c$ ($Z = 2$). For the green platelets of $NiH_2(IAA)_2(EN)_2$: $a = 12.730$ (6), $b = 7.625$ (2), $c = 12.113$ (4) Å; $\beta = 111.40$ (3)°; $V = 1094.8$ (7) Å^3. For the purple platelets of $Ni_2(IAA)_2(EN)_2$: $a = 12.556$ (3), $b = 7.587$ (1), $c = 12.143$ (1) Å; $\beta = 111.09$ (1)°; $V = 1079.2$ (3) Å^3. The bimetallic $Ni_2(IAA)_2(EN)_2$ is highly planar with a Ni-Ni distance of 2.859 (2) Å and angles Ni-O-Ni and O-Ni-O of 101.0 (2)° and 79.0 (2)°, respectively. The structure was also determined for a crystalline disordered mixture of the above mono- and bimetallic products and yielded an average formula $Ni_{1.6}H_{0.8}(IAA)_2(EN)_2$. This structure is isomorphous, with the pure components giving the following cell parameters: $a = 12.646$ (12), $b = 7.609$ (5), $c = 12.131$ (8) Å; $\beta = 111.23$ (6)°; $V = 1088$ (1) Å^3; $Z = 2$. The free ligand, $H_4(IAA)_2(EN)_2$, crystallizes as pale yellow rhombic crystals with space group $C2/c$: $a = 17.649$ (2), $b = 11.036$ (1), $c = 11.659$ (1) Å; $\beta = 97.375$ (8)°; $V = 2251.0$ (4) Å^3; $Z = 4$. Several new macrocylic ligands and their complexes have been prepared and characterized with a Ni(II) template reaction for the triketone-diamine condensation. This includes condensation of benzoyl groups, yielding products that are not accessible except through the template reaction.

The behavior of bimetallic complexes can, in principle, be quite distinct from their monometallic analogues. If metal-metal bonding occurs, the reactivity of this functional group may dominate the observed chemistry. In the absence of metal-metal bonding, characteristic behavior may stem from electronic communication through bridging ligands and/or the spatial proximity of the metal ions. It has been a long-standing interest in this group to examine the properties of bimetallic complexes of triketonate ligands I.[1] In these complexes the metals are maintained by the rigid backbone at a distance that does not permit metal-metal bonding. The metals still interact, however, as the magnetic data indicate; they are antiferromagnetically coupled through the bridging ligands.[2]



I

Another means of developing bimetallic chemistry is through the use of a macrocyclic ligand that incorporates two binding sites. The first example of a ligand of this type was reported by Pilkington and Robson in 1970.[3] Condensation of 2-hydroxy-5-methylisophthalaldehyde and 1,3-diaminopropane and loss of the acidic phenolic protons result in a dianionic ligand, which upon complexation with divalent metal ions yields dicationic, bimetallic macrocyclic complexes II. The dicopper complex of II and the



II

---

(1) (a) Lintvedt, R. L.; Ahmad, N. *Inorg. Chem.* **1982**, *21*, 2356. (b) Heeg, M. J.; Mack, J. L.; Glick, M. D.; Lintvedt, R. L. *Inorg. Chem.* **1981**, *20*, 833. (c) Guthrie, J. W.; Lintvedt, R. L.; Glick, M. D. *Inorg. Chem.* **1980**, *19*, 2949. (d) Kuszaj, J. M.; Tomlonovic, B.; Murtha, D. P.; Lintvedt, R. L.; Glick, M. D. *Inorg. Chem.* **1973**, *12*, 1297.

(2) Glick, M. D.; Lintvedt, R. L. *Prog. Inorg. Chem.* **1976**, *21*, 233.

(3) Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225.

0002-7863/87/1509-8003$01.50/0

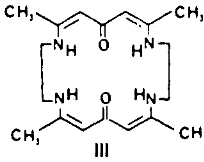
Table I. Elemental Analyses[a]

compd	composition found (calcd)			
	% C	% H	% N	% M
$H_4(IAA)_2(EN)_2$	67.90 (68.01)	9.40 (9.34)	14.37 (14.42)	
$H_4(NAA)_2(EN)_2$	68.10 (68.01)	9.31 (9.34)	14.45 (14.42)	
$H_4(DIA)_2(EN)_2$	70.39 (70.23)	9.93 (9.97)	12.71 (12.60)	
$H_4(IAA)_2(1,2\text{-}PN)_2$	69.20 (69.19)	9.31 (9.68)	13.42 (13.45)	
$NiH_2(IAA)_2(EN)_2$	59.34 (59.35)	7.51 (7.70)	12.55 (12.58)	12.97 (13.19)
$CuH_2(IAA)_2(EN)_2$	58.65 (58.71)	7.46 (7.61)	12.39 (12.45)	14.36 (14.12)
cis & trans $NiH_2(IAA)_2(EN)_2$	59.35 (59.35)	7.51 (7.70)	12.45 (12.58)	13.50 (13.19)
$NiH_2(BAA)_2(EN)_2$	65.38 (65.52)	6.04 (5.89)	10.89 (10.92)	
81% $NiH_2(IAA)_2(EN)_2$/ 19% $Ni(IAA)_2(EN)_2$	58.06 (58.01)	7.56 (7.45)	12.15 (12.30)	15.34 (15.23)
$Ni_2(IAA)_2(EN)_2$	52.73 (52.64)	6.43 (6.43)	11.08 (11.16)	21.96 (23.39)

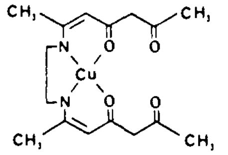
[a] Abbreviations are explained in ref 13.

one-electron-reduced species have been examined both structurally[4] and electrochemically.[5] The electron-transfer behavior of these macrocycles, the dicopper triketonates,[6] and other bimetallic copper complexes[7] is of interest because of the possible relationship to copper-containing proteins and the potential utility of a multielectron redox reagent.

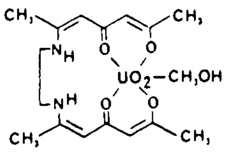
Complexation of macrocyclic Schiff bases derived from 1,3,5-triketones and diamines with divalent metal ions will yield neutral molecules. Such molecules containing interacting metal ions are, apparently, quite rare. Complexation has been attempted for a macrocyclic Schiff base derived from 2,4,6-heptanetrione and 1,2-ethylenediamine, III.[8] Reaction of this macrocycle with copper acetate and uranyl nitrate provided the partially hydrolyzed products, IV and V.[8,9]



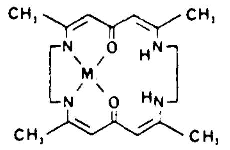
III



IV



V



VI

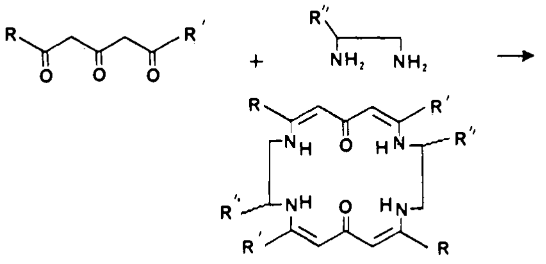
The cyclic monometallic derivatives, VI, are obtained in the case of nickel and cobalt.[9]

Additional monometallic derivatives based on similar macrocycles have also been reported.[10] In contrast to the Robson complexes, it has not been possible previously to isolate bimetallic macrocycles derived from the triketones.

Due to the additional stability provided by a macrocyclic ligand[11] and the opportunity to study the metals in an N_2O_2 coordination environment, as contrasted to the O_4 environment of the triketonate complexes, we have pursued the synthesis of macrocyclic complexes based on the triketones. This work was initiated in our laboratory some years ago[12] and has led to several interesting results. Use of a template reaction has made possible the synthesis of certain macrocyclic ligands that could not otherwise be prepared. Also, initial efforts to synthesize the bimetallic complexes have resulted in the isolation of mixtures of cocrystallizing mono- and bimetallic macrocyclic complexes. This unusual cocrystallization is described along with the preparation of several macrocyclic ligands and their monometallic derivatives. Most importantly, we report the first synthesis and characterization of bimetallic complexes of this class of macrocyclic ligand.

Results

Ligand Syntheses and Characterization. Macrocyclic ligands that contain two coordination sites have been synthesized by the Schiff base condensation of a triketone with ethylenediamine or 1,2-propylenediamine (eq 1). This condensation reaction proceeds



(eq 1)

R	R′	R″	abbreviation[13]
$CH(CH_3)_2$	CH_3	H	$H_4(IAA)_2(EN)_2$
$CH_2CH_2CH_3$	CH_3	H	$H_4(NAA)_2(EN)_2$
$CH(CH_3)_2$	$CH(CH_3)_2$	H	$H_4(DIA)_2(EN)_2$
$CH(CH_3)_2$	CH_3	CH_3	$H_4(IAA)_2(1,2\text{-}PN)_2$

readily at room temperature, and the products precipitate from solution as yellow microcrystalline solids. Formulation of these compounds as macrocycles is supported by elemental analyses (Table I) and by their mass spectra, which display strong parent ions. Other possible products such as the 2:1 condensation of triketone to diamine or the 1:1 condensation of the diamine across two adjacent carbonyls (to produce a diazepine) are not observed. The macrocycle $H_4(IAA)_2(EN)_2$ has also been characterized by single-crystal X-ray diffraction.

Crystallographic details are found in Table II. Table III contains the fractional atomic coordinates, and the bond lengths and angles are given in Table IV. Figure 1 illustrates the labeling and molecular geometry. A packing diagram is given in the

---

(4) (a) Hoskins, B. F.; McLeod, N. J.; Schaap, H. A. *Aust. J. Chem.* **1976**, *29*, 515. (b) Gagne, R. R.; Henling, L. M.; Kistenmacher, T. J. *Inorg. Chem.* **1980**, *19*, 1226.

(5) (a) Gagnē, R. R.; Koval, C. A.; Smith, T. J.; Cimolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571. (b) Addison, A. W. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 899.

(6) Lintvedt, R. L. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: New York, 1983; p 129–155.

(7) Long, R. C.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1983**, *105*, 1513.

(8) Yano, T.; Ushijima, T.; Sasaki, M.; Kobayashi, H.; Ueno, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2452.

(9) Vigato, P. A.; Vidali, M.; Casellato, U.; Graziani, R.; Benetollo, F. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 595.

(10) Fenton, D. E.; Gayda, S. E. *J. Chem. Soc., Dalton Trans.* **1977**, 2095.

(11) Margerum, D. W.; Cabbiness, D. K. *J. Am. Chem. Soc.* **1969**, *91*, 6540.

(12) Guthrie, J. W. Ph.D. Dissertation, Wayne State University, Detroit, MI, 1985.

(13) The abbreviations employed for the triketones and the macrocyclic derivatives are based on their trivial names: benzoylcetylacetone (H_2BAA), dibenzoylacetone (H_2DBA), isobutyrylacetylacetone (H_2IAA), *n*-butyrylacetylacetone (H_2NAA), diisobutyrylacetone (H_2DIA). The systematic name of the macrocycle $H_4(IAA)_2(EN)_2$ is 5,14-dimethyl-9,18-diisopropyl-1,4,10,13-tetraazacyclooctadeca-5,8,14,17-tetraene-7,16-dione.

Table II. Experimental Crystallographic Data[a,b]

	$Ni_2(IAA)_2(EN)_2$	$Ni_{1.6}H_{0.8}(IAA)_2(EN)_2$	$NiH_2(IAA)_2(EN)_2$	$H_4(IAA)_2(EN)_2$
formula	$Ni_2O_2N_4C_{22}H_{32}$	$Ni_{1.6}O_2N_4C_{22}H_{32.8}$	$NiO_2N_4C_{22}H_{34}$	$O_2N_4C_{22}H_{36}$
MW	501.94	479.27	445.25	388.56
cryst dimens (mm)	0.30 × 0.42 × 0.09	0.30 × 0.26 × 0.04	0.30 × 0.26 × 0.04	0.35 × 0.18 × 0.50
space grp	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
cell dimens				
a, Å	12.556 (3)	12.646 (12)	12.730 (6)	17.649 (2)
b, Å	7.587 (1)	7.609 (5)	7.625 (2)	11.036 (1)
c, Å	12.143 (1)	12.131 (8)	12.113 (4)	11.659 (1)
β, deg	111.09 (1)	111.23 (6)	111.40 (3)	97.375 (8)
V, Å^3	1079.3 (3)	1088 (1)	1094.8 (7)	2251.0 (4)
Z	2	2	2	4
D_{calcd}, g cm^{-3}	1.544	1.463	1.362	1.146
2θ range, deg	3–100	2–45	2–45	3–100
total data colld	1293	1643	1650	1712
no. of obsd, unique data	949, $I_o \geq 2.5\sigma(I)$	962, $I_o \geq 2.5\sigma(I)$	673, $I_o \geq 2.5\sigma(I)$	1256, $I_o \geq 3.0\sigma(I)$
μ, cm^{-1}	23.43 (Cu Kα)	12.99 (Mo Kα)	9.126 (Mo Kα)	5.14 (Cu Kα)
transmissn coeff	1.136–1.673	1.141–1.255	1.034–1.262	0.948–0.693
F_{000}	528	507	476	848
R, R_w	0.050, 0.078	0.051, 0.063	0.077, 0.084	0.034, 0.025

[a] The Ni-containing structures listed herein are all isomorphous. [b] Other experimental details in common are scan method, $\theta/2\theta$; scan range, 1.0° below Kα_1 to 1.0° above Kα_2; scan rate, 2–5 deg/min; bkgd/scan ratio, 0.5; $w = (\sigma_F)^{-2}$.

Table III. Atomic Positional Parameters for $H_4(IAA)_2(EN)_2$

atom	x	y	z
O1	0.30227 (7)	0.3240 (1)	0.6081 (1)
N1	0.3645 (1)	0.4148 (2)	0.4297 (1)
N2	0.2452 (1)	0.1814 (2)	0.7606 (2)
C1	0.3518 (1)	0.4701 (2)	0.3156 (2)
C2	0.4286 (1)	0.3590 (2)	0.4789 (2)
C3	0.4987 (1)	0.3649 (3)	0.4179 (2)
C4	0.4308 (1)	0.2964 (2)	0.5799 (2)
C5	0.3660 (1)	0.2724 (2)	0.6389 (1)
C6	0.3745 (1)	0.1844 (2)	0.7308 (2)
C7	0.3172 (1)	0.1370 (2)	0.7842 (2)
C8	0.3310 (1)	0.0380 (2)	0.8740 (2)
C9	0.4035 (2)	−0.0348 (4)	0.8641 (5)
C10	0.3308 (3)	0.0910 (4)	0.9950 (3)
C11	0.1750 (1)	0.1201 (2)	0.7795 (2)

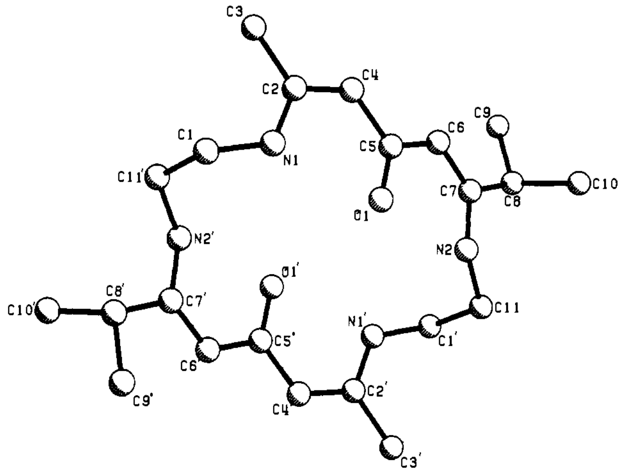


Figure 1. Molecular structure of the ligand $H_4(IAA)_2(EN)_2$.

supplementary material. All atoms occupy general positions in the unit cell. However, the molecule occupies a crystallographic center of symmetry located at ($^1/_4$, $^1/_4$, $^1/_2$).

Unlike the planar conformation of this molecule when it acts as a ligand to one or two metal ions, the free molecule adopts a "step stool" conformation wherein each backbone section of the molecule remains reasonably planar and the two sections are parallel but displaced. The N–C–C–N torsion angle in the ethylenediamine linkage that approaches 0° in the ideal planar molecule here is opened up to 57.9 (3)°. This very different spatial structure has two energetically favorable consequences: the atomic arrangement in the ethylenediamine linkage is now staggered (vs eclipsed in the molecule as ligand), and there is the formation of intramolecular hydrogen bonding between the proton on the nitrogen atom and the central oxygen atom. Intramolecular close contacts are (N1)H1···O1 = 1.904 (18) Å and (N2)H2···O1 = 1.865 (18) Å. There are no intermolecular hydrogen bonds.

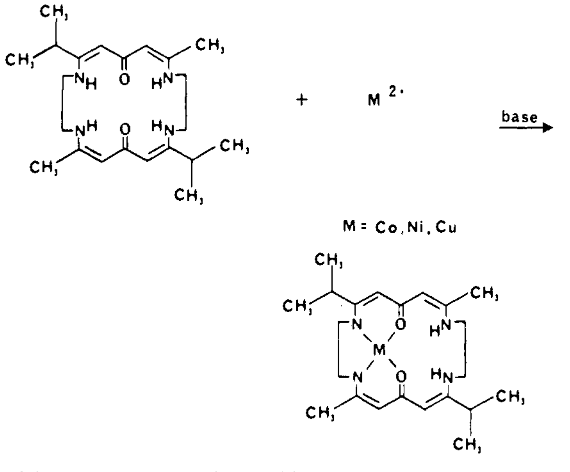
Table IV. Bond Lengths (Å) and Bond Angles (deg) for $H_4(IAA)_2(EN)_2$

	Bond Lengths		
O1–C5	1.271 (2)	C2–C4	1.361 (2)
N1–C1	1.455 (2)	C4–C5	1.432 (3)
N1–C2	1.350 (3)	C5–C6	1.440 (2)
N2–C7	1.356 (3)	C6–C7	1.358 (3)
N2–C11	1.453 (3)	C7–C8	1.512 (3)
C1–C11′	1.520 (3)	C8–C9	1.528 (5)
C2–C3	1.505 (3)	C8–C10	1.527 (4)
	Bond Angles		
O1–C5–C4	120.9 (1)	C2–C4–C5	125.0 (2)
O1–C5–C6	121.1 (2)	C3–C2–C4	119.8 (2)
N1–C1–C11′	112.9 (2)	C4–C5–C6	118.0 (2)
N1–C2–C3	118.4 (2)	C5–C6–C7	126.0 (2)
N1–C2–C4	121.8 (2)	C6–C7–C8	122.2 (2)
N2–C7–C6	120.1 (2)	C7–N2–C11	126.6 (2)
N2–C7–C8	117.7 (2)	C7–C8–C9	112.9 (2)
N2′–C11′–C1	112.7 (2)	C7–C8–C10	110.1 (2)
C1–N1–C2	126.9 (2)	C9–C8–C10	111.9 (3)

The best plane describing the independent backbone section, atoms N1, O1, N2, C2, C4–C7, is 2.601 Å from the parallel symmetry-related plane described by atoms N1′, O1′, N2′, C2′, C4′–C7′ (supplementary material). These backbone sections are slightly folded along the O1–C5 axis at an angle of 12.2 (3)°. The O···N bite distances are normal (N1···O1 = 2.668 (2), N2···O1 = 2.667 (2) Å), but the N···N bite distance is larger than for the complexed ligand (N1···N2′ = 2.949 (2) Å) due to the larger torsion angle in the ethylenediamine linkage. The lone pairs on the nitrogen atoms are oriented exo to the macrocycle.

Many tautomers can be drawn for this molecule that satisfy the valences for all atoms. In the crystal structure analysis, the hydrogen atoms were well-defined in a difference Fourier map and their positions and temperature factors refined. On the basis of hydrogen atom placement, the keto amine form with both hydrogens bound to the nitrogens best describes the tautomer present. The pattern of C–C lengths in the backbone is short–long–long–short, which also supports this assignment. However, the general planarity throughout the backbone and the bond lengths themselves imply some degree of delocalization.

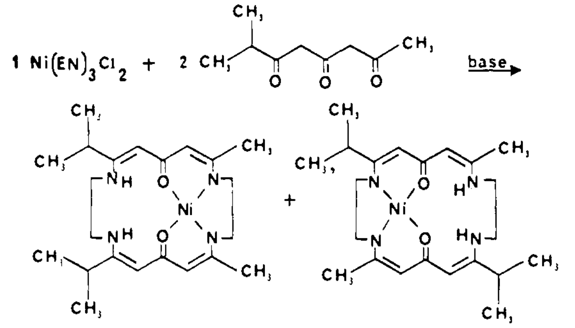
Monometallic Complexes. When the free ligand $H_4(IAA)_2(EN)_2$ is reacted with several first-row transition metals in 1:1 stoichiometry, the mononuclear macrocycle is formed (eq 2). The products of this reaction are crystalline compounds, which for



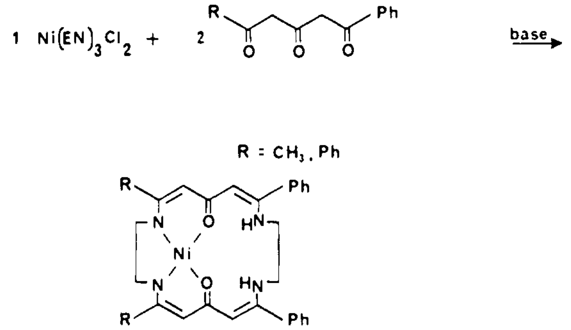
(eq 2)

nickel and copper are isolated in good yield. The cobalt macrocycle is very air-sensitive, even as a solid, and decomposes rapidly. Under identical conditions no reaction was found to occur with zinc. The IR spectra of these products are primarily due to ligand bands and therefore are very similar; however, they are indicative of metal coordination. A broad composite band centered at 1584 cm^{-1} in the free ligand ($C{=}O\cdots H$, $C{=}C$) is no longer present, while sharp absorptions are observed about 1640 and 1515 cm^{-1} ($C\overset{\cdots}{-}O$, $C{=}C$). These bands show only slight shifts as the nature of the metal ion is changed. Similar observations have been noted for the metal β-diketonates.[14] In addition, a weak N–H stretch is observed for these complexes about 3200 cm^{-1}, and a strong absorption occurs between 790 and 770 cm^{-1} (=C—H). All three compounds display an intense parent ion in the mass spectrum. Elemental analyses for the nickel and copper complexes of $H_4(IAA)_2(EN)_2$ appear in Table I. Nickel complexes of the remaining macrocyclic ligands have also been synthesized; characterization data are given in the Experimental Section.

A crystallographic structural determination was carried out on the nickel complex $NiH_2(IAA)_2(EN)_2$. The molecular geometry of $NiH_2(IAA)_2(EN)_2$, shown in Figure 2, illustrates the nearly planar arrangement of the macrocycle. The molecule occupies a crystallographic inversion center. The molecular stacking is shown in Figure 3. Packing forces and the symmetry of the ligand allow the metal coordination site to alternate randomly throughout the lattice, producing a 1:1 disorder. Because of this, each metal site was treated with a partial occupancy factor of 0.5, and half-weighted nickel ions are placed in each coordination site in Figures 2 and 3. Due to this disorder, the bond angles and bond lengths represent an appropriately weighted average of those found in the metal site and the vacant site. Crystallographic information is given in Table II. Positional parameters are given in Table V. Structure factors, thermal parameters, hydrogen atom parameters, and selected bond angles and distances have been deposited as supplementary material.



(eq 3a)



(eq 3b)

Template Reaction. The use of a template reaction provides a synthetic route to several additional mononuclear nickel complexes. Reaction of tris(ethylenediamine)nickel dichloride, $Ni(EN)_3Cl_2$, and the corresponding triketone in refluxing methanol affords the products shown in eq 3. When the unsymmetrical triketone 7-methyl-2,4,6-octanetrione (H_2IAA) is used in this reaction, the isolated product is a mixture of structural isomers (eq 3a). The ^{1}H NMR spectrum indicates the composition of this mixture to be a 55:45 ratio of cis to trans isomers. On the basis of ^{1}H NMR data, the cis isomer is assigned to have the nickel ion in the dimethyl end. The chemical shift of the isopropyl proton, $CH(CH_3)_2$, in the free ligand is 2.57 ppm (trans isomer). For the trans mononuclear complex, the resonance for this proton occurs at 2.85 ppm in the metal end and 2.49 ppm in the uncomplexed site. A resonance at 2.50 ppm in the cis complex implies the $CH(CH_3)_2$ protons are remote from the metal. Another unsymmetrical triketone, 1-phenyl-1,3,5-hexanetrione (H_2BAA), provides only the cis isomer (eq 3b). Assignment of the nickel ion to the dimethyl end is again consistent with the ^{1}H NMR data. Finally, the symmetrical triketone 1,5-diphenyl-1,3,5-pentanetrione (H_2DBA) produces the macrocyclic complex with all phenyl substituents (eq 3b). Changing the reaction stoichiometry to 1:1 to achieve bimetallic products does not influence the reaction, as only the monometallic compound is formed.

Macrocyclic products have not been isolated, however, when the triketone contains *tert*-butyl substituents. Presumably, steric effects predominate, and no condensation is observed.

Cocrystallization of Mono- and Bimetallic Complexes. Our initial attempts to prepare the bimetallic nickel macrocycle resulted in the isolation of mixtures of mono- and bimetallic species. Dropwise addition of the ligand $H_4(IAA)_2(EN)_2$ into a solution containing an excess of metal salt yielded the monometallic macrocycle and a second component in varying amounts. Formulation of this component as the bimetallic macrocycle was based on the ^{1}H NMR and mass spectral data. The ^{1}H NMR of one mixture is shown in Figure 4b. The monometallic complex is identified by comparison with an authentic spectrum (Figure 4a). The second component is found to have higher symmetry than $NiH_2(IAA)_2(EN)_2$ as fewer resonances and only one isopropyl doublet occur; in addition, no new NH resonances are found, suggesting that both coordination sites are filled. The mass spectrum of this mixture displays a parent ion for both $NiH_2(IAA)_2(EN)_2$ and $Ni_2(IAA)_2(EN)_2$. For a given mixture, the composition was determined from the ^{1}H NMR to be 80% $NiH_2(IAA)_2(EN)_2$ and 20% $Ni_2(IAA)_2(EN)_2$. This assignment was confirmed by elemental analysis, which showed a best fit for 81% $NiH_2(IAA)_2(EN)_2$ and 19% $Ni_2(IAA)_2(EN)_2$ (Table I).

Efforts to isolate the bimetallic complex from these mixtures were unsuccessful. Column chromatography of the two products on various supports led to the decomposition of the bimetallic species. Fractional recrystallization also failed to resolve the two macrocycles. Upon recrystallization of these mixtures, only one crystal form was observed while spectral data still showed two components. Since it was expected that the bimetallic complex would be a planar molecule, like the monometallic complex, this suggested that the two compounds were cocrystallizing. A single-crystal structure determination demonstrated this supposition was correct. Although isomorphous with the monometallic macrocycle $NiH_2(IAAA)_2(EN)_2$, the occupancy factor of each independent metal ion was 0.78 (contrast to an occupancy of 0.5 for the metal sites in the monometallic compound). The value of 0.78 corresponds to a composition of 44% $NiH_2(IAA)_2(EN)_2$ and 56% $Ni_2(IAA)_2(EN)_2$. Crystallographic information is given

---

(14) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978; p 249–251.

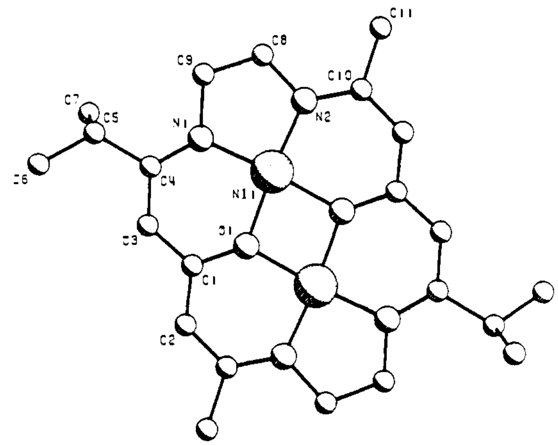
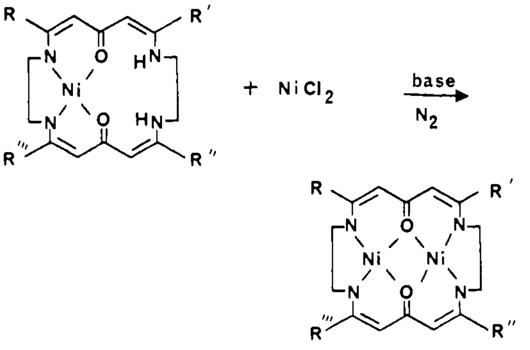


Figure 2. Molecular structure of $NiH_2(IAA)_2(EN)_2$. Each of the shaded metal sites represents 50% occupancy due to the 1:1 disorder observed. This figure is also an appropriate description of the isomorphous structures $Ni_2(IAA)_2(EN)_2$—with each metal site fully occupied—and $Ni_{1.6}H_{0.8}(IAA)_2(EN)_2$—with fractional occupancy.

in Table II. Once again, bond distances and angles represent appropriately weighted averages for occupied and unoccupied sites and are not listed separately.

Bimetallic Complexes. Formation of the bimetallic nickel complex was accomplished cleanly when the monometallic species was utilized as the starting material. The mononuclear complex was treated with anhydrous nickel chloride and base, in dilute solution, and refluxed for 48 h under N_2 (eq 4). The microcrystalline products obtained from these reactions proved to be the desired bimetallic macrocycles; the complexes that have been synthesized (thus far) are listed in eq 4. The bimetallic species are easily identified by their mass spectra and the ^1H NMR data. The diamagnetic character of these complexes is demonstrated by the ^1H NMR spectrum of $Ni_2(IAA)_2(EN)_2$, the trans isomer, in Figure 4c. Lack of NH protons implies both coordination sites are filled, and the occurrence of only one resonance for each type of proton indicates both halves of the molecule are equivalent.



(eq 4)

		product
R = R″ = $CH(CH_3)_2$	R′ = R‴ = CH_3	$Ni_2(IAA)_2(EN)_2$, trans isomer
R = R‴ = CH_3	R′ = R″ = $CH(CH_3)_2$	$Ni_2(IAA)_2(EN)_2$, cis isomer
R = R″ = $CH_2CH_2CH_3$	R′ = R‴ = CH_3	$Ni_2(NAA)_2(EN)_2$
R = R′ = R″ = R‴	R‴ = $CH(CH_3)_2$	$Ni_2(DIA)_2(EN)_2$
R = R‴ = CH_3	R′ = R″ = Ph	$Ni_2(BAA)_2(EN)_2$

An important consideration was determined to be the use of dilute solutions to prevent cocrystallization of the starting material and product. For $NiH_2(IAA)_2(EN)_2$, coprecipitation with $Ni_2(IAA)_2(EN)_2$ appears to lower the effective solubility of the mononuclear species and prevent the complexation reaction from proceeding to completion. The bimetallic complexes are found to be less stable than their mononuclear derivatives; decomposition takes place upon standing in solution or upon exposure to water. In addition to the requirement for reasonably dry solvents and reagents, the synthesis of these compounds was best accomplished in an inert atmosphere.

Table V. Positional Coordinates for Metal Complexes

atom	*x*	*y*	*z*
		$NiH_2(IAA)_2(EN)_2$	
Ni1	0.9776 (3)	0.1523 (4)	0.9415 (3)
O1	0.9030 (8)	−0.0115 (12)	0.9880 (7)
N2	1.0644 (11)	0.3087 (14)	0.8889 (9)
N1	0.8451 (10)	0.2923 (14)	0.8688 (9)
C1	0.8001 (14)	−0.0257 (19)	0.9749 (10)
C2	0.7580 (12)	−0.1767 (20)	1.0228 (12)
C3	0.7176 (11)	0.1073 (19)	0.9137 (11)
C4	0.7455 (14)	0.2571 (18)	0.8658 (11)
C5	0.6461 (12)	0.3889 (17)	0.8043 (12)
C6	0.5470 (14)	0.3789 (21)	0.8417 (12)
C7	0.6090 (12)	0.3626 (19)	0.6688 (12)
C8	0.9833 (13)	0.4351 (20)	0.8060 (13)
C9	0.8812 (13)	0.4532 (21)	0.8310 (12)
C10	0.8300 (14)	−0.3043 (18)	1.0924 (11)
C11	0.7748 (12)	−0.4408 (19)	1.1451 (12)
		$Ni_{1.6}H_{0.8}(IAA)_2(EN)_2$	
Ni1	0.9766 (1)	0.1599 (1)	0.9386 (1)
O1	0.9017 (4)	−0.0118 (6)	0.9877 (4)
N2	1.0604 (5)	0.3157 (8)	0.8883 (5)
N1	0.8487 (5)	0.2952 (7)	0.8673 (5)
C1	0.7936 (5)	−0.0269 (9)	0.9724 (5)
C2	0.7598 (6)	−0.1765 (10)	1.0209 (6)
C3	0.7188 (5)	0.1050 (9)	0.9116 (6)
C4	0.7440 (6)	0.2596 (10)	0.8638 (6)
C5	0.6478 (6)	0.3884 (9)	0.8019 (6)
C6	0.5460 (7)	0.3771 (11)	0.8416 (7)
C7	0.6076 (6)	0.3612 (10)	0.6670 (7)
C8	0.9879 (7)	0.4440 (11)	0.8089 (7)
C9	0.8796 (6)	0.4614 (11)	0.8272 (7)
C10	0.8271 (6)	−0.3059 (9)	1.0888 (6)
C11	0.7753 (6)	−0.4434 (11)	1.1406 (7)
		$Ni_2(IAA)_2(EN)_2$	
Ni1	0.9762 (1)	0.1634 (1)	0.9372 (1)
O1	0.9029 (3)	−0.0124 (5)	0.9880 (3)
N2	1.0595 (4)	0.3204 (6)	0.8897 (5)
N1	0.8498 (4)	0.2987 (6)	0.8668 (5)
C1	0.7925 (5)	−0.0289 (8)	0.9714 (5)
C2	0.7607 (6)	−0.1777 (9)	1.0205 (6)
C3	0.7196 (5)	0.1066 (8)	0.9106 (6)
C4	0.7448 (5)	0.2601 (9)	0.8634 (5)
C5	0.6478 (6)	0.3879 (9)	0.8020 (6)
C6	0.5454 (6)	0.3756 (9)	0.8406 (7)
C7	0.6070 (6)	0.3612 (9)	0.6664 (6)
C8	0.9899 (6)	0.4550 (10)	0.8112 (6)
C9	0.8776 (6)	0.4671 (10)	0.8238 (6)
C10	0.8284 (6)	−0.3093 (8)	1.0872 (6)
C11	0.7737 (6)	−0.4467 (10)	1.1396 (7)

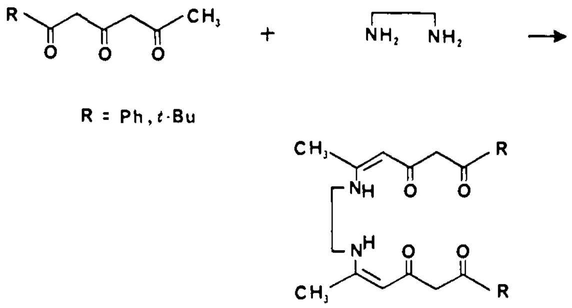
The molecular structure of $Ni_2(IAA)_2(EN)_2$ has also been determined and is isomorphous with $NiH_2(IAA)_2(EN)_2$. Both metal ions reside in a square-planar environment (Figure 2), and the macrocycles stack in an identical fashion (Figure 3). Both N_2O_2 sites are occupied, and full-occupancy factors (1.0) for Ni are used. Crystallographic information is listed in Table II. Fractional atomic coordinates are listed in Table V. Bond angles and bond distances are given in Table VI. The least-squares planes and deviations table is deposited in the supplementary material.

Discussion

The ligand syntheses described in eq 1 afford only the desired macrocyclic products when R and R′ are relatively simple aliphatic groups. Under these conditions, acyclic products formed by the condensation of one diamine and two triketones are not observed. When the nature of the R groups is changed, however, these acyclic compounds are obtained as the only products. For instance, when bulky groups are employed, such as phenyl or *tert*-butyl, the isolated products are the acyclic Schiff bases (eq 5).[15-17] For

---

(15) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P.; Kuszaj, J. M. *Inorg. Chem.* **1976**, *15*, 1633.



(eq 5)

these triketones, the 2:1 condensation product is obtained independent of the reaction stoichiometry. If a triketone with two bulky substituents is used, such as 1,5-diphenyl-1,3,5-pentanetrione (H_2DBA), no reaction occurs. The kinetic influence of sterically hindered ketones on condensation reactions has long been recognized in organic chemistry.[18,19] The rate of reaction at these carbon centers is much slower and often requires more forcing conditions and/or the use of a catalyst. These effects are also observed for the β-diketones where, in addition, condensation at one carbonyl appears to deactivate the adjacent center. Macrocycle formation usually does not occur without the presence of a metal ion.[20]

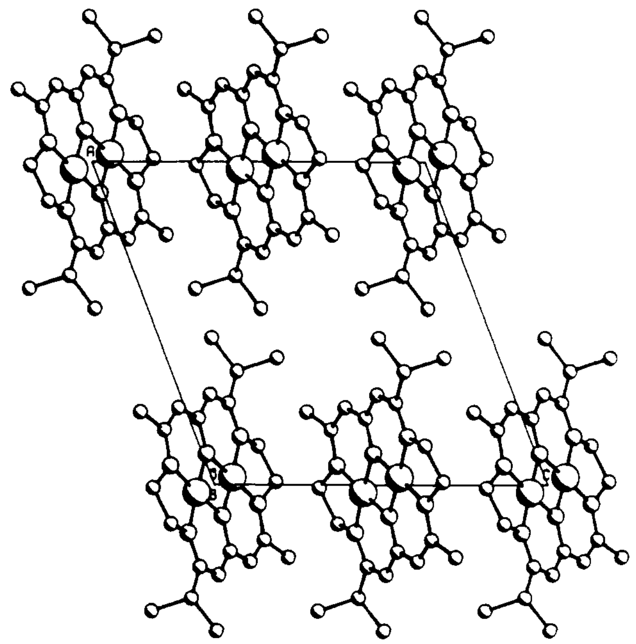
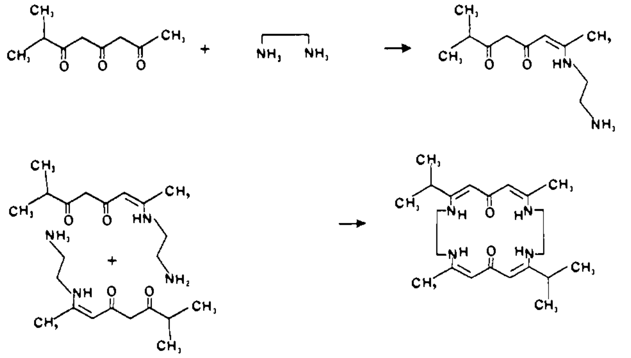


Figure 3. Molecular stacking for $NiH_2(IAA)_2(EN)_2$.

Table VI. Distances (Å) and Angles (deg) in $Ni_2(IAA)_2(EN)_2$

	Bond Distances		
M–O1	1.848 (4)	C4–C5	1.525 (9)
M–O1′	1.857 (4)	C4–N2′	1.337 (8)
M–N1	1.811 (5)	C5–C6	1.520 (10)
M–N2	1.824 (5)	C5–C7	1.553 (7)
O1–C1	1.333 (7)	C8–C9	1.475 (10)
N1–C8	1.454 (8)	C10–C11	1.510 (10)
N2–C9	1.469 (9)	C10–N1	1.335 (8)
C1–C2	1.400 (9)	O1–O1′	2.357 (8)
C1–C3	1.398 (8)	O1–N1	2.734 (6)
C2–C10	1.371 (9)	O1–N1	2.718 (6)
C3–C4	1.384 (9)	N1–N2	2.552 (7)
	Bond Angles		
O1–M–N1	95.6 (2)	N2–C4′–C3′	122.8 (6)
O1–M–O1′	79.0 (2)	N2–C9–C8	110.0 (6)
N1–M–N2	89.1 (2)	N1–C10–C2	123.5 (6)
N2–M–O1′	96.2 (2)	N1–C10–C11	118.3 (6)
M–O1–M	101.0 (2)	O1–C1–C2	116.8 (5)
M–O1–C1	129.3 (4)	O1–C1–C3	117.3 (6)
M–N1–C8	113.0 (4)	C1–C3–C4	129.4 (6)
M–N1–C10	125.3 (4)	C3–C4–C5	118.4 (6)
M–N2–C4′	125.0 (4)	C4–C5–C6	115.2 (6)
M–N2–C4	122.5 (5)	C4–C5–C7	109.6 (5)
N1–C8–C9	110.3 (6)		
	Metal–Metal Distances		
M–M		2.859 (2)	

Scheme I



For the triketones utilized in this reaction (eq 1), three are unsymmetrical molecules and can give rise to cis and trans isomers of the macrocycle. For $H_4(IAA)_2(EN)_2$ and $H_4(NAA)_2(EN)_2$, only the trans isomer has been identified. A plausible explanation of how this might take place is presented in Scheme I. For steric reasons, condensation at the methyl end should be more facile than at the other two carbonyls. If the first step proceeds quantitatively, prior to any competing condensations, the intermediate formed can only react in one fashion to produce a macrocycle (giving the trans isomer). For $H_4(IAA)_2(1,2\text{-}PN)_2$, the alkyl groups on the triketone are assumed to be trans by analogy to $H_4(IAA)_2(EN)_2$ and $H_4(NAA)_2(EN)_2$. In this molecule a second factor is the methyl group on the diamine, which can lead to both structural isomers (methyl groups cis or trans) and stereoisomers (methyl groups up or down). The NMR data do indicate that several isomers are present, although these are not assigned. In contrast to the triketones and β-diketones, which can exist as a mixture of keto and enol tautomers, these Schiff base macrocycles show only one tautomeric form by ^1H NMR. The presence of four vinylic protons and four NH protons (about 11 ppm[21]) indicates the tautomeric form shown in eq 1. Previous workers have also observed only one tautomer for several acyclic Schiff base derivatives of the β-diketones.[22] The crystallographic determination carried out for $H_4(IAA)_2(EN)_2$ supports the tautomeric assignment. One acidic proton is located on each nitrogen and refines in that position. In addition, only one proton is found on each of the backbone carbons C4 and C6. The folded structure shown in Figure 1 permits hydrogen bonding between the acidic proton on each pyramidal nitrogen and the adjacent carbonyl. One interesting aspect of this structure is the bond distances, which indicate that some delocalization does occur in the free ligand. The bond lengths between C2–C4 (1.361 Å) and C6–C7 (1.358 Å) are somewhat longer than a typical[36b] carbon–carbon double bond (1.337 Å). Correspondingly, the lengths for the adjacent bonds C4–C5 (1.432 Å) and C5–C6 (1.440 Å) are somewhat shorter than a typical carbon–carbon single bond (1.541 Å). The C2–N1 (1.350 Å) and C7–N2 (1.356 Å) distances are also shorter than expected for a carbon–nitrogen single bond (1.472 Å). These values and the general planarity of the atoms indicate that the ligand may best be described with some contribution from the

---

(16) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P. *Inorg. Chem.* **1976**, *15*, 1646.

(17) Lintvedt, R. L.; Tomlonovic, B. K.; Fenton, D. E.; Glick, M. D. *Adv. Chem. Ser.* **1976**, *No. 150*, 407.

(18) Reeves, R. L. In *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Wiley: New York, 1966; Chapter 12.

(19) Newman, M. S. *J. Am. Chem.* **1950**, *72*, 4783.

(20) Lindoy, L. F.; Busch, D. H. In *Preparative Inorganic Reactions*; Jolly, W. L., Ed.; Wiley: New York, 1971; Vol. 1, p 30–32.

(21) Enolic protons in the parent triketones are found between 14 and 16 ppm.

(22) Dudek, G. O.; Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 2099.

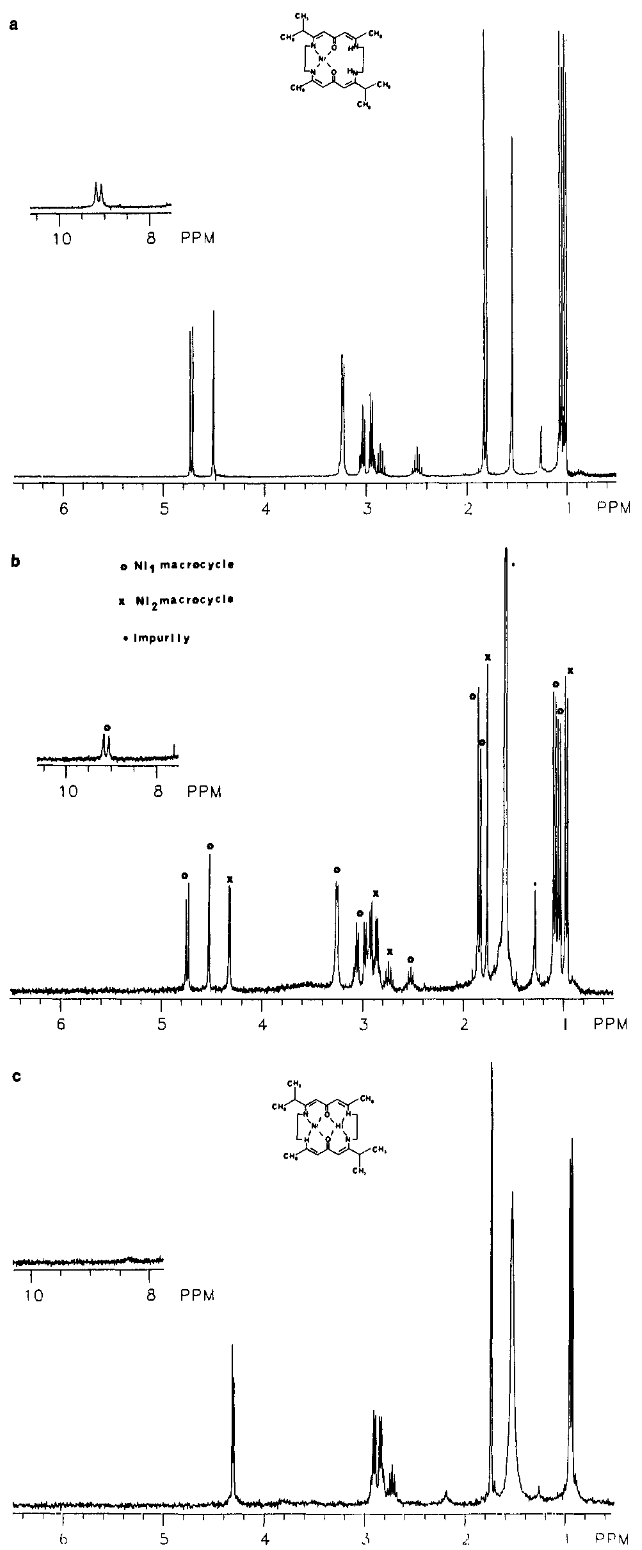
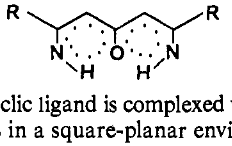


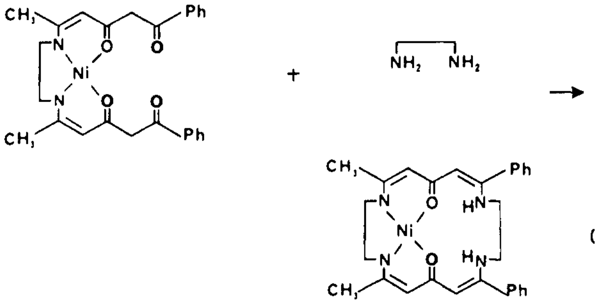
Figure 4. 300-MHz NMR spectra (in $CDCl_3$) of (a) the mononuclear Ni complex, (b) a mixture of mono- and binuclear complexes, and (c) the binuclear complex.

delocalized six-membered rings formed by hydrogen bonding (shown below).



When the macrocyclic ligand is complexed with a divalent metal ion, the metal resides in a square-planar environment (Figure 2). For the d^8 nickel ion, this result in a diamagnetic complex. For copper, with a d^9 configuration, the complex is paramagnetic; the measured susceptibility of 1.81 μ_B (23 °C) is quite typical of copper in this environment.[23] The N_2O_2 coordination of copper is confirmed by the solution EPR spectrum. Splitting due to copper ($I = {}^3/_2$) gives rise to four lines, with each of the two high-field lines showing an additional five-line pattern due to nitrogen ($I = 1$). The air sensitivity of the cobalt complex is not surprising in view of the number of cobalt(II) compounds known to react with molecular oxygen. For several related cobalt complexes, the metal ion was found to mediate oxidation of the ligand backbone to form a new complex containing one or two carbonyls.[24-26] It is not known whether the oxidation of $CoH_2(IAA)_2(EN)_2$, which leads to decomposition, involves oxidation of the ligand backbone, oxidation of the metal, or formation of oxygen adducts. Only one fragment has been identified in this oxidation process; that is the parent triketone H_2IAA. The remaining products have not proven to be tractable.

The template reaction has provided an alternate route to the monometallic derivatives, some of which are unavailable by direct ligand synthesis. In the presence of the nickel(II) ion, both the cis and trans isomers of $NiH_2(IAA)_2(EN)_2$ are formed (eq 3a). In contrast, only the trans isomer of the macrocyclic ligand is produced in the organic Schiff base reaction (eq 1). The absence of steric effects in this template process suggested that other macrocycles might be synthesized that contain bulkier terminal substituents. Indeed, when the triketones with phenyl substituents are reacted with the nickel salt, the corresponding mononuclear complexes are produced (eq 3b). Formation of these macrocycles indicates the metal ion activates the benzoyl carbon toward condensation. Further confirmation of this is given by the fact that condensation will also take place for the metal complex $NiH_2(BAA)_2(EN)$ (eq 6), whereas condensation will not occur for the free ligand $H_4(BAA)_2(EN)$.



(eq 6)

A unique aspect of this chemistry was the discovery of cocrystallization of $NiH_2(IAA)_2(EN)_2$ and $Ni_2(IAA)_2(EN)_2$. Cocrystallization is known in analytical chemistry where it has been a rare and troublesome problem in gravimetric analysis.[27] Cocrystallization most commonly occurs in ionic systems where similar cations or anions may substitute in the lattice of a host complex. Recently, the cocrystallization of four diastereoisomers of a cationic cobalt complex has been reported.[28] For neutral species, this phenomenon is seldom ever observed; however, the planar nature of both $NiH_2(IAA)_2(EN)_2$ and $Ni_2(IAA)_2(EN)_2$ and their similarity permit the formation of "mixed" crystals. Crystallographic studies of the "pure" crystals of each component demonstrated that they are isomorphous. Thus, this represents an unusual situation where two products (the mono- and bimetallic derivatives) are isomorphous and, therefore, so are all mixtures of the two. As one would expect under these conditions, separations are very difficult. This phenomenon undoubtedly explains our great frustration in attempts to prepare the bimetallic com-

---

(23) Hasty, E. F.; Colburn, T. J.; Hendrickson, D. N. *Inorg. Chem.* **1973**, *12*, 2414.

(24) Lintvedt, R. L.; Ranger, G.; Ceccarelli, C. *Inorg. Chem.* **1985**, *24*, 456.

(25) Durham, B.; Anderson, T. J.; Switzer, J. A.; Endicott, J. F.; Glick, M. D. *Inorg. Chem.* **1977**, *16*, 271.

(26) Weiss, M. C.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 3389.

(27) Vogel, A. I. *Quantitative Inorganic Analysis*; Wiley: New York, 1961; pp 110-111.

(28) Jones, P.; Vagg, R. S.; Williams, P. A. *Inorg. Chem.* **1984**, *23*, 4110.

plexes of the macrocycle derived from 2,4,6-heptanetrione (DIACAC), M$_2$(DIACAC)$_2$(EN)$_2$.[12] Complexes of this ligand are much less soluble than those of H$_4$(IAA)$_2$(EN)$_2$ and exhibit no tendency to form single crystals. These facts, together with the varying composition of mono- and bimetallic mixtures depending upon synthetic conditions, made characterization very difficult. The crystallizability of the NiH$_2$(IAA)$_2$(EN)$_2$/Ni$_2$(IAA)$_2$(EN)$_2$ system was a necessary criterion for understanding this perplexing characterization problem. On the basis of these results, it is now obvious that complete conversion to the bimetallic product must take place before the solubility of any product is exceeded in order to avoid isolation of inseparable mixtures.

Synthesis of the bimetallic complexes proved to be very sensitive to the reaction conditions. Efforts to synthesize the dinuclear compounds from the free ligand H$_4$(IAA)$_2$(EN)$_2$ and an excess of a nickel salt led to the coprecipitation of NiH$_2$(IAA)$_2$(EN)$_2$ and Ni$_2$(IAA)$_2$(EN)$_2$. The dinuclear compounds could be cleanly prepared only when the monometallic complex was utilized as the starting material. In order to circumvent cocrystallization of the starting material and product, it was necessary to use quite dilute solutions. In addition, precautions were required to prevent hydrolysis of the bimetallic species as they proved to be easily decomposed by water. The instability of these bimetallic compounds compared to the monometallic analogues indicates complexation of the second metal promotes hydrolysis and might explain why they have not previously been isolated. Several clear examples of the promotion of hydrolysis by metal ion binding have recently been reported.[29] So far, our efforts to prepare heterobimetallic complexes of nickel with cobalt or copper, as well as attempts to prepare a homobimetallic copper complex, have all been unsuccessful. In addition, we have not been able to synthesize a mono- or bimetallic complex of zinc. A comparison of the ionic radii of these four-coordinate, divalent metal ions shows that nickel is the smallest ion.[30] Our observations imply that the cavity provided by these macrocyclic ligands may be too small to accommodate the larger ions in a bimetallic, planar complex. In the bimetallic complexes, II, prepared by Pilkington and Robson, propylenediamine ligands were used to provide a larger cavity. A nitrogen–nitrogen bite distance of 2.94 Å is found in the copper complex of II compared to a bite distance of 2.55 Å in Ni$_2$(IAA)$_2$(EN)$_2$. Significantly, homobimetallic complexes of II for nickel, copper, and zinc have all been isolated. Our current efforts are directed toward the synthesis of macrocycles with an expanded cavity.

Experimental Section

Reagent-grade methanol was stored over 3A molecular sieves. Prior to use, tetrahydrofuran was distilled from sodium benzophenone ketyl. All other solvents were reagent grade and were used without further purification. Ethylenediamine was stirred over barium oxide and then distilled under nitrogen from sodium wire. Tris(ethylenediamine)nickel(II) chloride dihydrate, Ni(EN)$_3$Cl$_2$·2H$_2$O,[31] and anhydrous nickel chloride[32] were prepared according to published methods. The triketones were synthesized according to the general method of Miles, Harris, and Hauser.[33] Condensation of an appropriate 1,3-diketone and an ester was carried out in refluxing tetrahydrofuran with sodium hydride as the base. The triketones 1-phenyl-1,3,5-hexanetrione (H$_2$BAA)[13] and 1,5-diphenyl-1,3,5-pentanetrione (H$_2$DBA) are solids, which were isolated by recrystallization. The remaining triketones, 7-methyl-2,4,6-octanetrione (H$_2$IAA), 2,4,6-nonanetrione (H$_2$NAA), and 2,8-dimethyl-3,5,7-nonanetrione (H$_2$DIA), are high-boiling liquids, which were isolated by vacuum distillation. The Schiff base 1,14-diphenyl-5,10-dimethyl-6,9-diazatetradeca-4,11-diene-1,3,12,14-tetrone (H$_4$(BAA)$_2$EN)[15] and its nickel complex (NiH$_2$(BAA)$_2$EN)[16] were prepared as previously reported.

Ligand Syntheses. H$_4$(IAA)$_2$(EN)$_2$. Ethylenediamine (0.85 mL, 13 mmol) was dissolved in 150 mL of methanol. The triketone H$_2$IAA (2.0 mL, 12 mmol) was added dropwise in 50 mL of methanol, and the reaction mixture was stirred for 4 h. A light yellow solid crystallized from solution as the volume of solvent was reduced. Yield: 1.7 g 71%. Mp: 231–233 °C. MS (*m*/*e*): M$^+$, 388. ^{1}H NMR (CDCl$_3$, δ): 11.1 (s, 2, NH), 10.8 (s, 2, NH), 4.80 (s, 2, =CH), 4.79 (s, 2, =CH), 3.34 (m, 8, NCH$_2$CH$_2$N), 2.57 (septet, 2, C*H*(CH$_3$)$_2$), 1.88 (s, 6, CH$_3$), 1.11 (d, 12, CH(C*H*$_3$)$_2$). IR (KBr pellet, cm^{-1}): 3090 (N–H); 1584 (C=O···H, C=C); 801, 785, 714 (=C—H, N—H).

The other three macrocyclic ligands were synthesized in an analogous manner starting with 2.0 mL of the triketone and a stoichiometric amount of the diamine.

H$_4$(**DIA**)$_2$(**EN**)$_2$. Yield: 1.2 g, 57%. Mp: 285 °C. MS (*m*/*e*): M$^+$, 444. ^{1}H NMR (CDCl$_3$, δ): 11.1 (s, 4, NH), 4.85 (s, 4, =CH), 3.36 (m, 8, NCH$_2$CH$_2$N), 2.59 (septet, 4, C*H*(CH$_3$)$_2$), 1.11 (d, 24, CH(C*H*$_3$)$_2$). IR (KBr pellet, cm^{-1}): 3086 (N–H); 1586 (C=O···H, C=C); 806, 719(=C—H, N—H).

H$_4$(IAA)$_2$(**1,2-PN**)$_2$. Yield: 1.4 g, 53%; a mixture of isomers. Mp: 256–260 °C. MS (*m*/*e*): M$^+$, 416. ^{1}H NMR (CDCl$_3$, δ): 11.0 (4, NH), 4.75 (4, =CH), 3.8 (2, NC*H*(CH$_3$)CH$_2$N), 3.3 (4, NCH(CH$_3$)C*H*$_2$N), 2.6 (2, C*H*(CH$_3$)$_2$), 1.9 (6, CH$_3$), 1.2 (6, NCH(C*H*$_3$)CH$_2$N), 1.1 (12, CH(C*H*$_3$)$_2$). IR (KBr pellet, cm^{-1}): 3055 (N–H); 1589 (C=O···H, C=C); 801, 719 (=C—H, N—H).

Monometallic Complexes. NiH$_2$(IAA)$_2$(EN)$_2$. The macrocyclic ligand H$_4$(IAA)$_2$(EN)$_2$ (0.58 g, 1.5 mmol) was dissolved in 75 mL of dichloromethane, and the solution was added to nickel chloride hexahydrate (0.36 g, 1.5 mmol) in 150 mL of methanol. Triethylamine (3 mL, 0.02 mol) was pipetted into solution, and the mixture was refluxed for 24 h. The volume of solvent was reduced, and the solution was filtered to afford a green microcrystalline solid. Yield: 0.47 g, 70%. Mp: >300 °C. MS (*m*/*e*): M$^+$ (base peak), 444. ^{1}H NMR (CDCl$_3$, δ): 9.17 (s, 1, NH), 9.05 (s, 1, NH), 4.73 (s, 1, =CH), 4.70 (s, 1, =CH), 4.50 (s, 2, =CH), 3.22 (m, 4, NCH$_2$CH$_2$N), 2.98 (m, 4, $\overline{\mathrm{NiNCH_2CH_2N}}$), 2.85 (septet, 1, C*H*(CH$_3$)$_2$), 2.49 (septet, 1, C*H*(CH$_3$)$_2$), 1.01 (d, 6, CH(C*H*$_3$)$_2$). IR (KBr pellet, cm^{-1}): 3205 (N–H); 1645, 1518 (C$\overset{\cdots}{-}$O, C=C); 1419 (CH$_3$); 785 (=C—H).

The remaining monometallic complexes were synthesized in a similar fashion.

CuH$_2$(IAA)$_2$(EN)$_2$. The copper macrocycle was obtained as a brown microcrystalline solid. Yield: 55%. Mp: 277–278 °C. MS (*m*/*e*): M$^+$ (base peak), 449. EPR (toluene, 23 °C): $g = 2.09 \pm 0.02$, $A(\mathrm{Cu}) = (90 \pm 2) \times 10^{-4}$ cm^{-1}, $a(\mathrm{N}) = (14 \pm 2) \times 10^{-4}$ cm^{-1}. IR (KBr pellet, cm^{-1}): 3169 (N–H); 1637, 1513 (C$\overset{\cdots}{-}$O, C=C); 1410 (CH$_3$); 788 (=C—H). Magnetic susceptibility (23 °C): 1.81 ± 0.05 μ_B.

CoH$_2$(IAA)$_2$(EN)$_2$. The cobalt complex was prepared under N$_2$ and isolated as a red-orange microcrystalline solid. IR and mass spectral data were obtained immediately on a fresh sample. MS (*m*/*e*): M$^+$ (base peak), 445. IR (KBr pellet, cm^{-1}): 3222 (N–H); 1645, 1518 (C$\overset{\cdots}{-}$O, C=C); 1414 (CH$_3$); 793 (=C—H).

NiH$_2$(**NAA**)$_2$(**EN**)$_2$. Yield: 68%. MS (*m*/*e*): M$^+$ (base peak), 444. ^{1}H NMR (CDCl$_3$ δ): 9.12 (s, 1, NH), 9.05 (s, 1, NH), 4.66 (s, 1, =CH), 4.63 (s, 1, =CH), 4.45 (s, 1, =CH), 4.44 (s, 1, =CH), 3.20 (s, 4, NCH$_2$CH$_2$N), 2.95 (m, 4, $\overline{\mathrm{NiNCH_2CH_2N}}$), 2.12 (t, 2, C*H*$_2CH_2CH_3$), 2.03 (t, 2, C*H*$_2CH_2CH_3$), 1.82 (s, 3, CH$_3$), 1.79 (s, 3, CH$_3$), 1.46 (m, 4, CH$_2$C*H*$_2CH_3$), 0.91 (t, 6, CH$_2CH_2$C*H*$_3$). IR (KBr pellet, cm^{-1}): 3231 (N–H); 1644, 1517 (C$\overset{\cdots}{-}$O, C=C); 1421 (CH$_3$); 782 (=C—H).

NiH$_2$(**DIA**)$_2$(**EN**)$_2$. Yield: 64%. MS (*m*/*e*): M$^+$ (base peak), 500. ^{1}H NMR (CDCl$_3$, δ): 9.13 (s, 2, NH), 4.78 (s, 2, =CH), 4.54 (s, 2, =CH), 3.23 (m, 4, NCH$_2$CH$_2$N), 3.00 (s, 4, $\overline{\mathrm{NiNCH_2CH_2N}}$), 2.85 (septet, 2, C*H*(CH$_3$)$_2$), 2.50 (septet, 2, C*H*(CH$_3$)$_2$), 1.07 (d, 12, CH(C*H*$_3$)$_2$), 1.02 (d, 12, CH(C*H*$_3$)$_2$). IR (KBr pellet, cm^{-1}): 3218 (N–H); 1639, 1519 (Co· ·O, C=C); 1425 (CH$_3$); 787 (=C—H).

NiH$_2$(IAA)$_2$(1,2-PN)$_2$. Yield: 74%; a mixture of isomers. MS (*m*/*e*): M$^+$ (base peak), 472. ^{1}H NMR (CDCl$_3$, δ): 9.2 (2, NH), 4.7 (2, =CH), 4.5 (2, =CH), 3.7 (1, NCH(CH$_3$)CH$_2$N), 3.3 (2, NCH(CH$_3$)CH$_2$N), 3.1 (1, $\overline{\mathrm{NiNC\mathit{H}(CH_3)CH_2N}}$), 2.8 (1, CH(CH$_3$)$_2$), 2.7 (2, $\overline{\mathrm{NiNCH(CH_3)C\mathit{H}_2N}}$), 2.5 (1, C*H*(CH$_3$)$_2$), 1.8 (6, CH$_3$), 1.3 (6, NCH(C*H*$_3$)CH$_2$N), 1.1 (12, CH(C*H*$_3$)$_2$). IR (KBr pellet, cm^{-1}): 3205 (N–H); 1636, 1514 (Co$\overset{\cdots}{-}$O, C=C); 1418 (CH$_3$); 785 (=C—H).

Template Reaction. Ni(EN)$_3$Cl$_2$·2H$_2$O (5 mmol) and the appropriate triketone (10 mmol) were dissolved in 150–200 mL of methanol. Triethylamine (3 mL) was added, and the solution was refluxed for 24 h. The solution was cooled to 0 °C and then filtered to obtain the monometallic complex.

NiH$_2$(IAA)$_2$(EN)$_2$. Yield: 62%; a 55:45 mixture of cis to trans isomers. Recrystallization from dichloromethane/methanol provides the cis isomer as the major constituent (70–90%). ^{1}H NMR (CDCl$_3$, δ, cis isomer): 9.17 (s, 2, NH), 4.70 (s, 2, =CH), 4.50 (s, 2, =CH), 3.24 (m, 4, NCH$_2$CH$_2$N), 2.95 (s, 4, $\overline{\mathrm{NiNCH_2CH_2N}}$), 2.50 (septet, 2, C*H*-

---

(29) (a) Groves, J. T.; Olson, J. R. *Inorg. Chem.* **1985**, *24*, 2715. (b) Groves, J. T.; Dias, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 1033.

(30) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

(31) State, H. M. *Inorg. Synth.* **1960**, *6*, 200.

(32) Pray, A. R. *Inorg. Synth.* **1957**, *5*, 153.

(33) Miles, M. L.; Harris, T. M.; Hauser, C. R. *J. Org. Chem.* **1965**, *30*, 1007.

$(CH_3)_2$), 1.82 (d, 6, CH_3), 1.06 (d, 12, $CH(CH_3)_2$). Elemental analysis is found in Table I.

NiH_2(**BAA**)$_2$(**EN**)$_2$. Yield: 29%; cis isomer. MS (*m/e*): M$^+$ (base peak), 512. ^{1}H NMR ($CDCl_3$, δ): 8.96 (s, 2, NH), 7.30 (s, 10, Ph), 4.79 (s, 2, =CH), 4.66 (s, 2, =CH), 3.04 (s, 4, $\overline{NiNCH_2CH_2N}$), 2.98 (m, 4, NCH_2CH_2N), 1.87 (s, 6, Ch$_3$). IR (KBr pellet, cm^{-1}): 3210 (N–H); 1637, 1513 ($C\overset{-}{-}O$, C=C); 1412 (CH_3); 772 (=C—H); 1484, 977, 703 (Ph). Elemental analysis is found in Table I. This compound was also prepared by slurrying $NiH_2(BAA)_2(EN)$ (0.7 g, 1.6 mmol) and 100 mL of methanol followed by the addition of ethylenediamine (0.30 mL, 4.5 mmol) and triethylamine (3 mL, 0.02 mol). The solution was refluxed for 24 h and then cooled to 0 °C. The brown microcrystalline product was filtered from solution. Yield: 0.20 g, 25%.

NiH_2(**DBA**)$_2$(**EN**)$_2$. Yield: 2%. MS (*m/e*): M$^+$, 636. ^{1}H NMR ($CDCl_3$, δ): 9.16 (s, 2, NH), 7.31 (s, 20, Ph), 4.84 (s, 2, =CH), 4.71 (s, 2, =CH), 3.04 (s, 4, NCH_2CH_2N), 2.67 (s, 4, $\overline{NiNCH_2CH_2N}$). IR (KBr pellet, cm^{-1}): 1630, 1513 ($C\overset{-}{-}O$, C=C); 1416 (CH_3); 765 (=C—H); 1479, 701 (Ph).

Cocrystallization of Mixtures. $H_4(IAA)_2(EN)_2$ (0.37 g, 0.95 mmol) and triethylamine (3 mL, 0.02 mol) were dissolved in 50 mL of dichloromethane, and the solution was added dropwise to a methanol solution (100 mL) of nickel chloride hexahydrate (0.87 g, 3.7 mmol). The solution was stirred at room temperature for ca. 30 min before a green microcrystalline solid was filtered from solution. Yield: 0.33 g. MS (*m/e*): M$^+$ ($NiH_2(IAA)_2(EN)_2$), 444; M$^+$ ($Ni_2(IAA)_2(EN)_2$), 500. Purple crystals obtained upon recrystallization from several solvents (benzene, toluene, tetrahydrofuran) showed two components by ^{1}H NMR (Figure 4b). Integration corresponded to 80% $NiH_2(IAA)_2(EN)_2$ and 20% $Ni_2(IAA)_2(EN)_2$. Elemental analysis indicated 81% $NiH_2(IAA)_2(EN)_2$ and 19% $Ni_2(IAA)_2(EN)_2$ (Table I).

Bimetallic Complexes. The appropriate monometallic complex (0.20 mmol) was dissolved in dichloromethane (150 mL) and methanol (100 mL) under nitrogen. Anhydrous nickel chloride (0.065 g, 0.050 mmol) was introduced, and after dissolution, triethylamine (1.5 mL, 0.01 mol) was syringed into solution. The mixture was refluxed for 48 h and then cooled to 0 °C. A purple-brown microcrystalline solid was filtered from solution.

Ni_2(**IAA**)$_2$(**EN**)$_2$. Yield: 0.070 g, 71%. MS (*m/e*): M$^+$ base peak)[1] 500. ^{1}H NMR ($CDCl_3$, δ): 4.32 (s, 2, =CH), 4.29 (s, 2, =CH), 2.86 (m, 8, $\overline{NiNCH_2CH_2N}$), 2.72 (septet, 2, $CH(CH_3)_2$), 1.74 (s, 6, CH_3), 0.96 (d, 12, $CH(CH_3)_2$). IR (KBr pellet, cm^{-1}): 1547, 1463 ($C\overset{-}{-}O$, C=C); 1420, 1339 (CH_3); 777 (=C—H). A mixture of *cis*- and *trans*-$NiH_2(IAA)_2(EN)_2$ obtained from the template reaction was treated as above. The cis isomer of $Ni_2(IAA)_2(EN)_2$ was isolated by recrystallization from benzene. ^{1}H NMR ($CDCl_3$), δ): 4.32 (s, 2, =CH), 4.27 (s, 2, =CH), 2.90 (s, 4, $NiNCH_2CH_2N$), 2.84 (s, 4, $NiNCH_2CH_2N$), 2.74 (septet, 2, $CH(CH_3)_2$), 1.74 (s, 6, CH_3), 0.96 (d, 12, $CH(CH_3)_2$). Elemental analysis is found in Table I.

Ni_2(**NAA**)$_2$(**EN**)$_2$. Yield: 0.073 g, 72%. MS (*m/e*): M$^+$ (base peak)[1] 500. ^{1}H NMR ($CDCl_3$, δ): 4.25 (s, 2, =CH), 4.23 (s, 2, =CH), 2.86 (m, 8, $\overline{NiHCH_2CH_2N}$), 2.00 (t, 4, $CH_2CH_2CH_3$), 1.74 (s, 6, CH_3), 1.40 (sextet, 4, $CH_2CH_2CH_3$), 0.92 (t, 6, $CH_2CH_2CH_3$). IR (KBr pellet, cm^{-1}): 1544, 1468 ($C\overset{-}{-}O$, C=C); 1407, 1347 (CH_3); 769 (=C—H).

Ni_2(**DIA**)$_2$(**EN**)$_2$. Yield: 0.073 g, 65%. MS (*m/e*): M$^+$ (base peak)[1] 556. ^{1}H NMR ($CDCl_3$, δ): 4.34 (s, 4, =CH), 2.87 (s, 8, $\overline{NiHCH_2CH_2N}$), 2.71 (septet, 4, $CH(CH_3)_2$), 0.96 (d, 24, $CH(CH_3)_2$). IR (KBr pellet, cm^{-1}): 1547, 1459 ($C\overset{-}{-}O$, C=C); 1409, 1328 (CH_3); 778 (=C—H).

Ni_2(**BAA**)$_2$(**EN**)$_2$. Yield: 0.085 g, 75%. MS (*m/e*): M$^+$ (base peak)[1] 568. ^{1}H NMR ($CDCl_3$, δ): 7.30 (m, 10, Ph), 4.32 (s, 2, =CH), 4.24 (s, 2, =CH), 2.90 (s, 4, $\overline{NiHCH_2CH_2N}$), 2.44 (s, 4, $\overline{NiNCH_2CH_2N}$), 1.78 (s, 6, CH_3). IR (KBr pellet, cm^{-1}): 1493, 1465 ($C\overset{-}{-}O$, C=C); 1408, 1348 (CH_3); 772 (=C—H); 703 (Ph).

Physical Measurements. Elemental analyses were provided by Galbraith Laboratories, Knoxville, TN. Mass spectral data were obtained on a Kratos MS-80 RFA, equipped with a DCI probe, run under EI conditions (60 eV). The NMR spectra were recorded on a Nicolet QE-300-MHz FT instrument. A Nicolet 20DX FT IR was used to obtain infrared spectra. The EPR data were recorded on a Varian E-109 instrument. Magnetic susceptibility was determined by the Faraday method on a Cahn RG electrobalance with a Varian V-4004 electromagnet.

X-ray Crystallography for $H_4(IAA)_2(EN)_2$. Crystals of $O_2N_4C_{22}H_{36}$ were pale yellow and rhombic. Crystallization was from benzene. Data were collected on a Nicolet P2$_1$ diffractometer using Cu Kα radiation (λ = 1.541 78 Å) and a Ni filter. Three standard reflections measured periodically fluctuated less than 2%, and the subsequent decay correction was negligible. Empirical absorption corrections and a systematic correction for secondary extinction were applied.[34] The structure was solved[35] by direct methods; hydrogen atoms were placed in observed positions and refined isotropically. All non-hydrogen atoms were described anisotropically. Refinement was by full matrix. At convergence the maximum shift was $<0.1\sigma$, and the largest peaks on a ΔF map were ±0.1 e Å^{-3}. Final R values were $R = 0.034$ and $R_w = 0.025$ for observed reflections. Neutral-atom scattering factors were from ref 36a. Other details are given in Table II.

X-ray Crystallography for $NiH_2(IAA)_2(EN)_2$ and $Ni_{1.6}H_{0.8}(IAA)_2(EN)_2$. Crystals of $NiO_2N_4C_{22}H_{34}$ and $Ni_{1.6}O_2N_4C_{22}H_{32.8}$ are violet and diamond shaped. Crystallization from benzene yields isomorphous crystals. Data were collected on a Nicolet P2$_1$ diffractometer using Mo Kα radiation (λ = 0.710 69 Å) and a graphite crystal monochromator. Absorption corrections were carried out with the program ABSORB.[37] The structures were solved by direct methods. Hydrogen atoms were placed in calculated positions and were not refined. All non-hydrogen atoms were described anisotropically. Refinement was by full matrix. At convergence the maximum shift was $<0.1\sigma$, and the largest peaks on a ΔF map were ±0.4 e Å^{-3}. Final R values were $R = 0.077$ and $R_w = 0.084$ for $H_2Ni(IAA)_2(EN)_2$ and $R = 0.051$ and $R_w = 0.063$ for $H_{0.8}Ni_{1.6}(IAA)_2(EN)_2$ for observed reflections. Neutral-atom scattering factors were from ref 36. Other details are given in Table II.

X-ray Crystallography for $Ni_2(IAA)_2(EN)_2$. Crystals of $Ni_2O_2N_4C_{22}H_{32}$ were violet, diamond shaped, and isomorphous with those of $H_2Ni(IAA)_2(EN)_2$ and $H_{0.8}Ni_{1.6}(IAA)_2(EN)_2$. Crystallization was from chloroform. Data were collected on a Nicolet P2$_1$ diffractometer with Cu Kα (λ = 1.541 78 Å) and a Ni filter. Refinement was identical with that used for the previously described structures. At convergence the maximum shift was 0.1σ, and the largest peaks on the ΔF map were ±0.7 e Å^{-3}. Final R values were $R = 0.050$ and $R_w = 0.078$ for observed reflections. Other details are given in Table II.

Acknowledgment is made to the National Science Foundation (Grant CHE841-19100) for the purchase of Syntex automated diffractometer and to the U.S. Air Force (Grant N00014-84-G-0211) for the purchase of a QE-300 multinuclear magnetic resonance spectrometer. The National Science Foundation is also acknowledged (Grant CHE8300251) as is the Petroleum Research Fund, administered by the American Chemical Society, for the general support of this research.

Supplementary Material Available: Listings of thermal parameters and hydrogen atom parameters for each of the structures, torsion angles and a packing diagram for $H_4(IAA)_2(EN)_2$, selected bond distances and angles for $NiH_2(IAA)_2(EN)_2$ and $Ni_{1.6}H_{0.8}(IAA)_2(EN)_2$, and least-squares planes and deviations for $H_4(IAA)_2(EN)_2$ and $Ni_2(IAA)_2(EN)_2$ (14 pages); listings of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

---

(34) The SHELX correction for secondary extinction is $F_c(\mathrm{corr}) = F_c\,(1 - 0.001xF_c^2/(\sin\theta))$. The parameter x refined to 0.006 15 in this structure.

(35) Computations were performed by using SHELX76 and SHELXTL: Sheldrick, G. M. SHELX76, University Chemical Laboratory, Cambridge, England, 1976. Sheldrick, G. M. SHELXTL, University of Gottingen, Federal Republic of Germany, 1978.

(36) (a) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV (Present distributor D. Reidel, Dordrecht). (b) *International Tables for X-ray Crystallography*; D. Reidel: Dordrecht, 1983; Vol. III, p 276

(37) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsee's program for data reduction; (2) MULTAN, a version of Germain and Woolfson's multiple-tangent-formula method; (3) FORDAP, A. Zalkin's Fourier program; (4) ABSORB, D. L. Templeton's program for absorption correction; (5) ORFLS, ORFEE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function and error program; (6) HFINDR, A. Zalkin's program for calculating idealized hydrogen atom positions.

(38) DeMeulenaar, J.; Tompa, J. *Acta Crystallogr.* **1965**, *19*, 1014.

(39) Templeton, L. K.; Templeton, D. H. American Crsytallography Association Meeting, Storrs, CT; Abstract E-10.

(40) Alcock, N. W. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1969**, *A25*, 518.