(D$_2$H$_2$)(DEA), 64413-61-2; CH$_3$OOCCH$_2$Co(D$_2$H$_2$)(DEA), 64413-60-1.

References and Notes

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(2) Abbreviations: RCo(D$_2$H$_2$)(HOH), substituted alkyl(aquo)bis(dimethylglyoximato)cobalt = alkyl(aquo)cobaloxime; DEA, dimethoxyethylamine = aminoacetaldehyde dimethyl acetal.

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Template Condensations: Metal-Ion-Directed Syntheses of Macrocyclic Complexes from 2,3-Butanedione Dihydrazone and Aldehydes or Ketones

SHIE-MING PENG, GUY C. GORDON, and VIRGIL L. GOEDKEN*

The metal-directed condensation of 2,3-butanedione dihydrazone with formaldehyde yields metal complexes of the 14-membered macrocyclic ligand, C$_{10}$H$_{20}$N$_8$, with M = Fe(II), Co(II), Ni(II), or Cu(II). Other aldehydes and ketones, as well as acetals and ketals, condense similarly to give related macrocyclic ligands. The hydrazones of the α-diimine functions have the anti–anti configuration yielding a macrocyclic species with D_{2h} symmetry. Six-coordinate diamagnetic Fe(II) complexes have been obtained with a variety of axial substituents (pyridine, imidazole, ammonia, thiocyanate, and acetonitrile). The Ni(II) complex is diamagnetic and four-coordinate, the Co(II) and Cu(II) complexes exhibit only weak interactions with axial ligands. Oxidation of the Co(II) complex with dioxygen under acidic conditions in acetonitrile yields the Co(III) complex, [Co(C$_{10}$H$_{20}$N$_8$)(CH$_3$CN)$_2$](ClO$_4$)$_3$. The physical and chemical properties of the complexes are compared with other closely related macrocyclic complexes.

Introduction

Most macrocyclic ligand complexes are best prepared with the aid of metal ions as "templates" to direct the steric course of the condensation reactions which ultimately end with ring closure.[1-3] However, important nontemplate syntheses have been developed for a number of important macrocyclic lig-

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ands.[4-7] This paper reports the formation and characterization of octaazabis(α-diimine) macrocyclic complexes of Fe(II), Co(II), Co(III), Ni(II), and Cu(II) from the template condensation of 2,3-butanedione dihydrazone with aldehydes and ketones.

A wide variety of amines, both "free" and coordinated, are known to react with aldehydes to form more complicated amine ligands. The products of these reactions can be of many

different types although the innumerable Schiff base ligands represent the largest class of these ligands. Related types of reactions include the well-known reaction of ammonia with formaldehyde to yield hexamethylenetetramine and the lesser known but similar product I obtained by the condensation of ethylenediamine with formaldehyde.[8] More recent examples of polydentate[9] and macrocyclic ligand[10] syntheses from the reaction of amines with formaldehyde, II and III, are illustrated.

I

II

$$[Ni(en)_3]^{2+} + 4CH_2O + 2NH_3 \longrightarrow$$


III
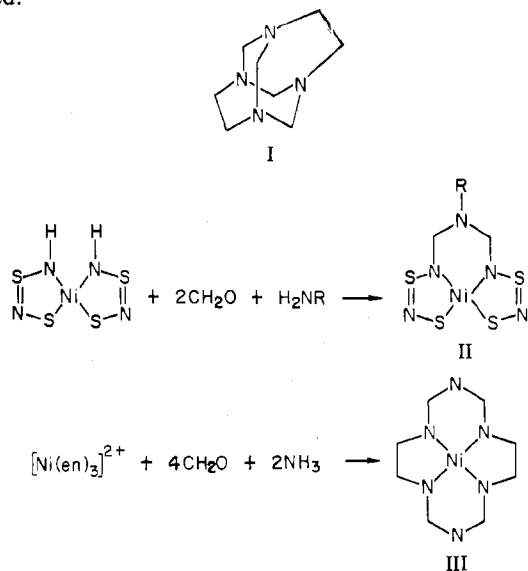
The ring-closure step of a 14-membered ring poses special constraints when the amino group undergoing condensation is to be coordinated in the final product. The nucleophilicity of coordinated amino functions is greatly reduced. Consequently, dissociation must occur prior to the condensation process while still maintaining the stringent stereochemical restraints that govern nucleophilic attack of the carbonyl group. These problems are largely eliminated when the macrocyclization process utilizes functional groups which are not coordinated to the metal ion.

The free amino groups of coordinated 2,3-butanedione dihydrazone are ideally oriented for ring closure by reaction with carbonyl functions to give six-membered chelated rings and ultimately octaaza–14-membered ring macrocyclic complexes, 2,3,9,10-tetramethyl-1,4,5,7,8,11,12,14-octaaza-cyclotetradeca-1,3,8,10-tetraene ligand, IV. This type of reaction closely parallels that reported by Kerwin and Melson in which tetradentate ligands were formed by the condensation of benzil monohydrazone in the presence of Ni(II).[11] In the absence of added carbonyls, the 2,3-butanedione dihydrazone complexes described in an early report by Stoufer and Busch are formed.[12]

Me$_4$[14]1,3,8,10-tetraeneN$_8$

IV
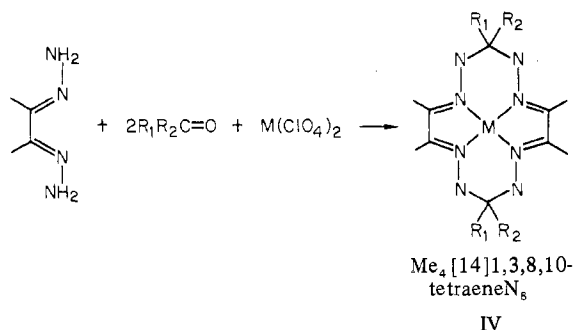
Complexes of type IV were expected to have physical properties very similar to those of the metal complexes of 2,3,-9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (V)[13,14] but to be much more chemically reactive for

Me$_4$[14]1,3,8,10-tetraeneN$_4$ = "TIM"

V
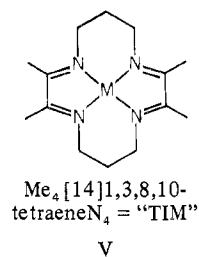
a number of reasons. The six-membered chelate rings of IV contain hydrazone linkages which are more reactive than the 1,3-diaminopropane ring of TIM, V, complexes. In addition, C—N linkages are easier to oxidize than C—C single bonds. Other possible reactions include (a) reduction of the C=N double bonds (The resulting completely saturated complexes should have no particularly unusual physical properties. However, reoxidation of the ligand should occur at the N—N linkages in the six-membered rings yielding a new type of chelate ring.), (b) nucleophilic attack on C=N double bonds, (c) deprotonation of hydrazine protons, (d) further condensation reactions which can occur at the secondary N—H centers. The present study is concerned with the preparation and characterization of these bis(α-diimine) macrocyclic complexes. Some reactions of these complexes have been previously communicated.[15-19]

Experimental Section

All solvents and chemicals used in the experiments were obtained commercially and were of reagent grade. They were used without further purification except for drying with 4A molecular sieves.

Infrared spectra were recorded on a Beckman IR-10 infrared spectrophotometer in the range of 4000–250 cm^{-1}. Samples were prepared as Nujol or hexachlorobutadiene mulls and the spectra were calibrated with the 2851.5- and 1601.8-cm^{-1} absorptions of polystyrene film. A Beckman RC 16B2 conductivity bridge was used for all conductivity measurements. Ultraviolet and visible spectra were obtained using a Cary Model 14 recording spectrophotometer within the range 10 000–2000 Å. Nuclear magnetic resonance spectra were recorded on either Varian A-60 A or Bruker 270 megacycle spectrometers.

Elemental analyses were performed commercially by Galbraith Laboratories, Inc., Knoxville, Tenn., or Chemalytic, Inc., Tempe, Ariz.

Magnetic susceptibilities of the complexes were measured on a Faraday balance using Hg[Co(NCS)$_4$] as a calibrant. Molar susceptibilities were corrected for diamagnetism of the ligands with Pascal's constants.

Warning! The compounds containing perchlorate anions, particularly the iron compounds, must be regarded as potentially explosive and therefore hazardous. Since the possibility of unprovoked detonation exists, only minimal quantities should be prepared and long term storage (greater than 1 month) is not advised.

Syntheses. C$_4$H$_4$N$_{10}$. 2,3-Butanedione dihydrazone was prepared by the method of Busch and Bailar.[20]

[Ni(C$_{10}$H$_{20}$N$_8$)](ClO$_4$)$_2$. A total of 1.61 g (20 mmol) of 38% aqueous formaldehyde solution was added to a solution of 3.65 g (10 mmol) of Ni(ClO$_4$)$_2$·6H$_2$O in 30 mL of acetonitrile. To this blue solution, 2.28 g (20 mmol) of 2,3-butanedione dihydrazone was added. One drop of concentrated perchloric acid was added to catalyze the condensation reaction. The reaction was essentially complete after 0.5 h at room temperature. Fifty milliliters of diethyl ether was slowly added to the red-brown solution to induce precipitation of the product. The red-brown precipitate was filtered and then recrystallized from acetonitrile (yield about 90%).

Anal. Calcd for [Ni(C$_{10}$H$_{20}$N$_8$)](ClO$_4$)$_2$: C, 23.53; H, 3.92; N, 21.96. Found: C, 23.43; H, 3.86; N, 21.67.

[Ni(C$_{12}$H$_{24}$N$_8$)](ClO$_4$)$_2$ and [Ni(C$_{14}$H$_{28}$N$_8$)](ClO$_4$)$_2$. The procedure followed was the same as above except that acetaldehyde or propionaldehyde were used in place of formaldehyde.

Anal. Calcd for [Ni(C$_{12}$H$_{24}$N$_8$)](ClO$_4$)$_2$: C, 26.78; H, 4.46; N, 20.83. Found: C, 26.60; H, 4.41; N, 21.22.

Anal. Calcd for [Ni(C$_{14}$H$_{28}$N$_8$)](ClO$_4$)$_2$: C, 29.55; H, 5.05; N, 20.53. Found: C, 29.70; H, 4.99; N, 19.79.

An isomeric product of $[Ni(C_{14}H_{28}N_8)](ClO_4)_2$ can be obtained by utilizing acetone in place of propionaldehyde for ring closure. The reaction conditions are similar to those for the formaldehyde condensation except that a stoichiometric amount of acetone (20 mm) must be used. An excess results in the formation of the stable tris(α-bis(azine))nickel(II) complex. The condensation reaction occurs at a slower rate with ketones and the reaction mixture must be allowed to stand at room temperature for 12 h to obtain a reasonable yield, approximately 60%. The identical product is obtained if 2,2-dimethoxypropane is substituted for acetone. However, the reaction with 2,2-dimethoxypropane occurs at a faster rate than with ketones and is virtually complete within 1 h at room temperature.

Anal. Calcd for $Ni(C_{14}H_{28}N_8)(ClO_4)_2$, acetone condensation product: C, 30.05; H, 4.85; N, 19.75. Found: C, 29.70; H, 4.99; N, 19.79.

$[Ni(C_{20}H_{36}N_8)](ClO_4)_2$. The procedure followed was similar to that for $[Ni(C_{10}H_{20}N_8)](ClO_4)_2$, except that cyclohexanone was used instead of formaldehyde.

Anal. Calcd: C, 37.13; H, 5.58; N, 17.35. Found: C, 37.34; H, 5.58; N, 17.51.

$[Ni(C_{10}H_{20}N_8)]Cl_2$. A total of 1.61 g (20 mmol) of 38% aqueous formaldehyde solution was added to a constantly stirred solution (30 mL of a 2:1 mixture of H_2O and acetonitrile) containing 2.37 g (10 mmol) of $NiCl_2 \cdot 6H_2O$ and 2.28 g (20 mmol) of butanedione dihydrazone. The solution was left standing overnight during which time the dark brown product precipitated. The product was filtered and washed by CH_3CN dried in air. Yield was 80%.

Anal. Calcd: C, 31.41; H, 5.23; N, 29.32. Found: C, 31.48; H, 4.47; N, 29.93.

$[Ni(C_{10}H_{20}N_8)](PF_6)_2$. A solution of 3.26 g of NH_4PF_6 in 5 mL of H_2O was added to a solution of 3.82 g of $[Ni(C_{10}H_{20}N_8)]Cl_2$ in 10 mL of H_2O. The brown-orange product precipitated immediately. The product was filtered, washed with H_2O, and dried in air. Yield was virtually quantitative.

Anal. Calcd: C, 19.97; H, 3.22; N, 18.64. Found: C, 19.97; H, 3.33; N, 18.78.

$[Co(C_{10}H_{20}N_8)](ClO_4)_2$. The procedure used was similar to that followed for the analogous Ni complex, but the reaction was carried out under a nitrogen atmosphere.

Anal. Calcd for $[Co(C_{10}H_{20}N_8)](ClO_4)_2$: C, 23.53; H, 3.92; N, 21.96; Cl, 13.92. Found: C, 23.42; H, 4.11; N, 21.44; Cl, 13.07. (Yield was about 90%.)

$[Co(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_3$. A total of 0.5 mL of perchloric acid was added to a solution of 2.1 g of $[Co(C_{10}H_{20}N_8)](ClO_4)_2$ in 25 mL of acetonitrile. Molecular oxygen was bubbled through the solution for 10 min. The color of the solution changed from orange-brown to dark brown. After the brown product slowly crystallized, it was filtered, washed with acetonitrile, and dried in air. Yield was 80%.

Anal. Calcd: C, 24.29; H, 3.76; N, 20.24; Cl, 15.40. Found: C, 23.48; H, 3.47; N, 19.22; Cl, 14.58.

$[Cu(C_{10}H_{20}N_8)Cl(H_2O)](ClO_4)$. Formaldehyde, 3.22 g of a 38% aqueous solution, was added to a solution containing 3.41 g of $CuCl_2 \cdot 2H_2O$ in 50 mL of water. Then 4.56 g of 2,3-butanedione dihydrazone was added as a solid and the solution stirred for 5 min. The solution turned dark green as the reaction proceeded. An aqueous solution of 5 g of $NaClO_4$ and 0.3 mL of $HClO_4$ in 10 mL of H_2O was then added to precipitate the complex. The complex which separated as shiny green plates was filtered, washed with a small amount of water, and dried in air.

Anal. Calcd for $Cu(C_{10}H_{20}N_8)Cl(H_2O)(ClO_4)$: C, 25.61; H, 4.69; N, 23.91. Found: C, 24.93; H, 4.26; N, 23.75. (Yield was about 80%.)

$[Fe(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_2$. A solution containing 3.22 g of 38% aqueous formaldehyde solution and 3.44 g of 2,3-butanedione was added to a solution of 7.27 g of $Fe(ClO_4)_2 \cdot 6H_2O$ in 100 mL of acetonitrile. Then 2.6 g of anhydrous hydrazine was added dropwise. The red solution was filtered at this point to remove insoluble residues. The solution was stoppered and placed in a refrigerator for 12 h during which time the product crystallized. The product was filtered, washed with ethanol, and air-dried.

Anal. Calcd for $[Fe(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_2$: C, 28.53; H, 4.54; N, 23.77. Found: C, 29.49; H, 4.52; N, 23.92. (Yield was about 50%.)

$[Fe(C_{10}H_{20}N_8)L_2](ClO_4)_2$, L = C_5H_5N, NH_3, or $C_3H_4N_2$. A large excess of L (40 mmol) was added to a solution of 1.2 g (2 mmol) of

Scheme I
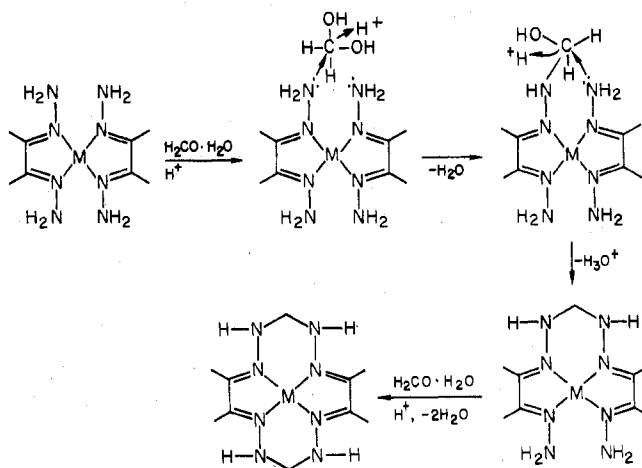
$[Fe(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_2$ in 30 mL of acetonitrile. The color of solution changed from brown to red immediately. Anhydrous diethyl ether was added slowly to induce precipitation of the product. The red product was filtered and washed with a 3:1:1 mixture of diethyl ether, acetonitrile, and L. Yield was 70–80%.

Anal. Calcd for $[Fe(C_{10}H_{20}N_8)(C_5H_5N)_2](ClO_4)_2$: C, 36.09; H, 4.51; N, 21.05. Found: C, 35.19; H, 4.54; N, 20.60.

$[Fe(C_{10}H_{20}N_8)(NCS)_2]$. A solution of 0.82 g of NaNCS in 10 mL of CH_3CN was added to a solution containing 1.45 g of $[Fe(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_2$ in 20 mL of CH_3CN. The red precipitate formed immediately. The product was filtered, washed with CH_3CN, and dried in air. Yield was quantitative.

Anal. Calcd: C, 33.18; H, 4.61; N, 32.26. Found: C, 33.49; H, 4.52; N, 32.09.

$[Ni(C_{10}H_{18}N_8)]$. Triethylamine, 0.5 mL, was added to a deaerated solution of 200 mg of $[Ni(C_{10}H_{20}N_8)](ClO_4)_2$ in 15 mL of CH_3CN. The red-orange solution changed to an intense dark red color upon mixing the reagents. The air-sensitive product, which began precipitating within minutes, was filtered after 0.5 h under a nitrogen atmosphere, washed with anhydrous ethanol, and dried in vacuo.

Anal. Calcd for $[Ni(C_{10}H_{18}N_8)]$: C, 38.87; H, 5.83; N, 36.28. Found: C, 38.85; H, 5.35; N, 36.40.

Results and Discussion

Product Formation and Isolation. Octaazabis(α-diimine) macrocyclic complexes were prepared by reacting 2 equiv of 2,3-butanedione dihydrazone with 2 equiv of the appropriate aldehyde or ketone in the presence of 1 equiv of the appropriate divalent transition metal (M = Cu^{II}, Ni^{II}, Co^{II}). The cyclization process is acid catalyzed, but large excesses of acid destroy the complexes. The sequence of steps leading to the formation of the macrocyclic complexes are undoubtedly complicated and were not pursued. However, a plausible series of reactions consistent with the known reactions of amines with carbonyl functions or acetals is presented in Scheme I. Aldehydes and ketones which readily form hydrates react much faster than those which do not.[21] Similar pathways are envisaged for acetals and ketals which react at least an order of magnitude faster than the parent aldehyde or ketone. In the presence of large excesses of ketones or aromatic aldehydes, stable α-bis(azines) are formed which have little tendency to undergo further condensation reactions.

Condensation reactions with the following carbonyl-containing compounds led to successful macrocyclic synthesis with Ni(II): formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, acetone, and cyclohexanone. Other potentially attractive carbonyls for which the attempted macrocyclic syntheses were unsuccessful included anthrone, anthraldehyde, benzophenone, and 9-fluorenone. Attempts to obtain macrocyclic complexes by substitution of other α-diketones in place of 2,3-butanedione (glyoxal, o-benzoquione, or phenanthrenequinone) were unsuccessful. Glyoxal forms a dihydrazone,

but efforts to carry out analogous template condensations with formaldehyde invariably led to polymer formation. *o*-Benzoquinone, as well as its substituted derivatives, has sufficiently high redox potentials to oxidize hydrazine and prevent formation of dihydrazones.

The Fe(II) macrocyclic complexes could not be prepared directly from 2,3-butanedione dihydrazone. All attempts using it led initially to the formation of the stable tris(2,3-butanedione dihydrazone)iron(II) complexes. Subsequent reaction with formaldehyde yielded a three-dimensional quadricyclic encapsulating ligand, an aspect discussed in a separate paper.[15] To prevent the complete encapsulation of the metal a different synthetic method was developed that involved the addition of 4 equiv of hydrazine to an acetonitrile solution containing 1 equiv of Fe(ClO$_4$)$_2$·6H$_2$O, 2 equiv of 2,3-butanedione, and 2 equiv of formaldehyde. This latter method of octaaza-macrocyclic ligand synthesis was successful only for the Fe(II) complexes. With, Co(II) and Ni(II), these conditions led to the isolation of dihydrooctaaza[14]annulene complexes, VI.[16,22]

VI
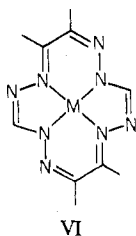
All attempts to synthesize the octaazabis(*α*-diimine) complexes of Mn(II) and Zn(II) failed. The octahedral tris(2,3-butanedione dihydrazone)metal complexes were found to undergo condensation reactions with formaldehyde under conditions similar to those described for macrocyclic formation of the other metals. However, these condensation reactions stopped short of macrocyclic ring formation. The infrared spectra of condensation products clearly indicated the presence of uncoordinated –NH$_2$ groups (ν_{NH_2} 3390, 3300, 3200, 1630 cm^{-1}) and the NMR spectra of the Zn(II) product displayed two types of –CH$_3$ resonances, 1.87 and 2.06 ppm (δ), consistent with the noncyclic tetradentate ligand VII.
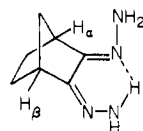
VII
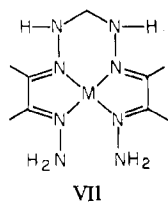
The failure of the Zn(II) and Mn(II) systems to undergo complete cyclization is attributed to the larger radius associated with d^5 and d^{10} electron systems. Idealized models of these macrocyclic ligands, assuming standard C=N, N—N, and C—N distances indicate a preferred center-to-nitrogen distance of approximately 1.90–1.92 Å. While this distance is compatible with observed metal–nitrogen distances for Cu(II) complexes and for low-spin Fe(II), Co(II), and Ni(II), it is significantly shorter than observed for most Zn(II) and Mn(II) distances. Zn(II)–N distances are near 2.08 Å;[23] those of Mn(II)–N are around 2.27 Å.[24] Thus, the minimum distance required for linkage of the two dangling amino groups with a –CH$_2$– group is probably exceeded by the uncyclized quadridentate complexes, VII.
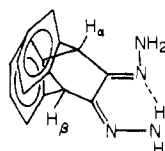
General Properties. The octaazabis(*α*-diimine) macrocyclic ligands are strong-field ligands and promote spin pairing whenever possible. Thus the Ni(II), Co(III), and Fe(II) complexes are diamagnetic, while the Co(II) complex and Cu(II) complex have magnetic moments of 1.9 μ_B, characteristic of one unpaired electron.

Table I. ^{1}H NMR Spectra of Some Dihydrazones

| Compd	Solvent	Chemical shift
(NH$_2$N=CH)$_2$	CD$_3$CN	CH 7.35 (s, 2), NH$_2$ 5.8 (b, 4)
(NH$_2$N=CCH$_3$)$_2$	CD$_3$CN	CH$_3$ 1.85 (s, 6), NH$_2$ 5.5 (b, 4)
(CH$_3$NHN=CCH$_3$)$_2$	CD$_3$CN	CCH$_3$ 1.94 (s, 6), NCH$_3$ 3.04 (s, 6), NH 4.59 (b, 2)
	CDCl$_3$^{a}	H$_\alpha$, H$_\beta$ 2.78, 330
	CDCl$_3$^{a}	H$_\alpha$, H$_\beta$ 4.83, 5.44

^{a} From ref 22.

These macrocyclic ligand complexes do not have the remarkable stability in strong acidic media that is characteristic of their tetraaza counterparts. In solutions containing strong acids, the ligands fragment liberating solvated M^{n+} species. The nature of the decomposition products was not pursued. The reactions of these octaaza–macrocyclic complexes with oxidizing and reducing agents are discussed elsewhere.[17,19,25]

The possibility of syn–anti and anti–anti isomerization among the free dihydrazone ligands and their octaaza complexes was considered. Both isomers of 2,3-butanedione

VIII   IX
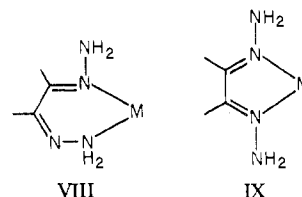
dihydrazone are capable of forming metal chelates with the syn–anti configuration forming six-membered chelate rings, VIII, while the anti–anti configuration yields five-membered *α*-diimine chelate rings, IX.

The syn–anti configuration of a number of cyclic 1,2-dihydrazones was observed by Baldwin and co-workers.[22] However, the NMR spectrum of 2,3-butanedione dihydrazone indicates the anti–anti configuration. The pertinent NMR data are presented in Table I.

The π-acceptor property of the *α*-diimine moieties enhances their chelating tendency with metals of significant π-donor tendency. Therefore the cyclization products of IX obtained from condensation of 2,3-butanedione dihydrazone with aldehydes are expected to yield products having the symmetrical anti–anti structure of IV.

Characterization of the Macrocyclic Complexes. Infrared Spectra. The infrared spectra of the complexes, [M-(C$_{10}$H$_{20}$N$_8$)L$_2$](ClO$_4$)$_2$, are all very similar to one another and support the ligand structure proposed in IV. The most diagnostic absorption bands are the N—H and C=N stretching modes, as well as those attributable to free perchlorate anions. Some of the representative N—H and C=N stretching frequencies are tabulated in Table II. There were no other absorption bands present which could be assigned to uncondensed functional groups, e.g., as –NH$_2$ or C=O, of the starting materials.

A comparison of the spectra of the octaazabis(*α*-diimine)macrocyclic complexes with those of the closely related divalent metal complexes of Me$_4$[14]1,3,8,10-tetraeneN$_4$[13,14]

Table II. Pertinent Infrared Absorptions of $[M(C_{10}H_{20}N_8)L_2](ClO_4)_n$

|	Absorptions, cm^{-1}	
Compd	(N–H)	(C=N)
$[Fe(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_2$	3260 s^a	1600 s
$[Co(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_3$	3230 s	1608 s
$[Co(C_{10}H_{20}N_8)](ClO_4)_2$	3280 s	1608 s
$[Ni(C_{10}H_{20}N_8)](ClO_4)_2$	3240 s	1605 s
$[Cu(C_{10}H_{20}N_8)Cl(H_2O)](ClO_4)$	3290 s	1615 s

^{a} s = strong.

reveals some differences in the C=N stretching frequency region of the spectrum. The C=N stretching vibration is absent or very weak in all the iron(II) complexes of Me$_4$-[14]1,3,8,10-tetraene and has been attributed to delocalization of the "d" electron density onto the π^* orbitals of the α-diimine.[14] However, the intensity and position of the C=N stretching frequency of our octaazabis(α-diimine)bis(acetonitrile)iron(II) complex are strong and sharp and are one indication of the difference in dipole strength of the hydrazone C=N as compared to the α-diimine C=N bond.

NMR Spectra. The ^{1}H NMR spectral data of the diamagnetic complexes are presented in Table III. The methyl resonances of the 2,3-butanedione dihydrazone linkage occur in the vicinity of 2.0–3.0 ppm (δ) and appear as singlets confirming the symmetrical D_{2h} structure of IV. There was no observable coupling between the protons of these methyl groups and the N–H protons of the six-membered rings. Homoallylic couplings of the –CH$_3$ protons with those of the –CH$_2$ protons of the six-membered chelate rings have been reported for the closely related Me$_4$[14]1,3,8,11-tetraene complexes of Co(III).[13,14]

The –CH$_2$ groups of the six-membered chelate rings exhibit a triplet in the vicinity of 4.5 ppm due to the coupling with the hydrogen atoms of the adjacent nitrogen atoms. The N–H resonances appear as a broad band near 6.5 ppm, the broad nature of absorption attributable to the combined effects of the quadrupole moment of nitrogen, rapid exchange of N–H protons, and motion of these protons (resulting from configuration inversion about the nitrogen atom) in the anisotropic magnetic field created by the square-planar coordination environment of the metal ions. The methylene resonances are also braoder than usual, half-width 4 Hz, and attributable to rapid equilibrium between the two conformers depicted below

and to the anisotropic nature of the magnetic field of a low-spin d^8 system.
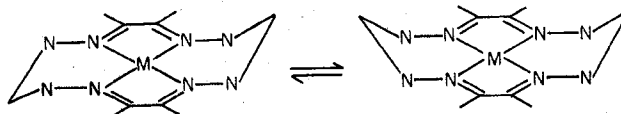
The interconversion between the two conformers is rapid since it can be achieved either by rotation about the carbon–nitrogen bonds or by inversion about the nitrogen centers. Exchanging one hydrogen atom of the –CH$_2$ group for another group leads to two stereoisomers, syn and anti, as indicated below.
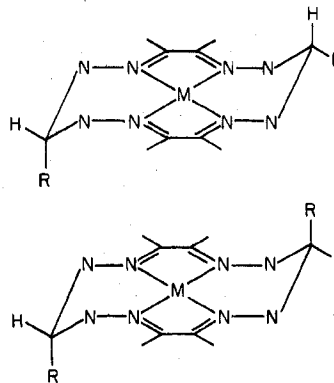
The nickel(II) complex having a methyl group on each carbon atom of the six-membered ring contained only two distinguishable types of methyl groups in the ^{1}H NMR spectrum. The methyl groups derived from the α-diimine chelate rings appeared as a singlet at 2.25 ppm (δ) and the methyl groups of the six-membered rings appeared as a doublet at 1.51 ppm. This implies rapid interconversion between axial and equatorial methyl groups, a process facilitated by inversion of the N-atom configuration and that if both syn and anti isomers are present, their difference in chemical shift is too small to be resolvable.

The macrocyclic complexes with an ethyl substituent on the carbon atom of the six-membered rings gave a considerably more complicated spectrum. The methyl groups attached to the five-membered chelate rings appeared as a sharp singlet at 2.22 ppm. The methyl resonance of the ethyl group gave

Table III. ^{1}H NMR Data for Octaazabis(α-diimine) Macrocyclic Complexes

		Chemical shift, ppm	
Complex	Solvent	Five-membered ring	Six-membered ring
$[Ni(C_{10}H_{20}N_8)](ClO_4)_2{}^a$ (formaldehyde)	CD$_3$CN	–CH$_3$ 2.15 (s,^{b} 12)	–CH 4.51 (t, J = 5.0,^{c} 4), NH 6.78 (b, 4)
$[Ni(C_{10}H_{20}N_8)]Cl_2$ (formaldehyde)	D$_2$O	–CH$_3$ 2.25 (s, 12)	–CH$_2$ 4.50 (b, 4), NH exchanges with D$_2$O
$[Ni(C_{10}H_{18}N_8)]^0$ (formaldehyde)	(CD$_3$)$_2$NCHO	–CH$_3$ 2.18 (s, 6), 2.23 (s, 6)	–CH$_2$ 4.60 (b, 4), NH 8.15 (2)
$[Ni(C_{12}H_{24}N_8)](ClO_4)_2$ (acetaldehyde)	CD$_3$CN	–CH$_3$ 2.22 (s, 12)	–CH$_3$ 1.51 (d, J = 6.7, 6), –CH 4.56 (b, 2), –NH 6.26 (b, 4)
$[Ni(C_{14}H_{24}N_8)](ClO_4)_2$ (propionaldehyde)	CD$_3$CN	–CH$_3$ 2.25 (s, 12)	–CH$_3$ 0.93–1.26 (m, 6), –CH$_2$ 1.8–2.2 (m, 4), –CH 4.2–4.7 (m, 2), –NH 6.0–6.5 (b, 4)
$[Ni(C_{14}H_{28}N_8)](ClO_4)_2$ (acetone)	CD$_3$CN	–CH$_3$ 2.27 (s, 12)	–CH$_3$ 1.70 (12), –NH 6.25 (b, 4)
$[Ni(C_{20}H_{36}N_8)](ClO_4)_2$ (cyclohexanone)	CD$_3$CN	–CH$_3$ 2.29 (s, 12)	–CH$_2$ 1.56, 2.15 (b, 20), –NH 6.12 (b, 4)
$[Co(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_2$	CD$_3$NO$_2$	–CH$_3$ 2.94 (s, 12)	–CH$_2$ 5.16 (b, 4), –NH exchanges with CD$_3$NO$_2$, CH$_3$CN 2.21 (s, 6)
$[Fe(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_2$ (formaldehyde)	CD$_3$CN and D$_2$O	–CH$_3$ 2.51 (s, 12)	–CH$_2$ 4.43 (s, 4), –NH exchange with D$_2$O, CH$_3$CN (free) 1.97 (s, 6)

^{a} Carbonyl used to form macrocyclic ligand is indicated in parentheses under the complex. ^{b} Key: s = singlet, d = doublet, t = triplet, m = multiplet, and b = broad. ^{c} J in Hz.
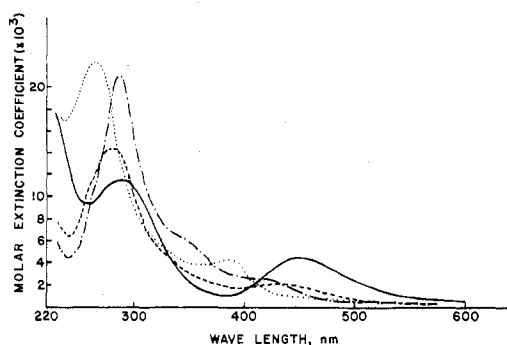
Figure 1. Electronic spectra of representative octaazabis(α-diimine) macrocyclic complexes, $[M(C_{10}H_{20}N_8)]^{n+}$, in acetonitrile: (—) $[Fe(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_2$, (---) $[Co(C_{10}H_{20}N_8)](ClO_4)_2$, (···) $[Co(C_{10}H_{20}N_8)(CH_3CN)_2](ClO_4)_3$, (-···-) $[Ni(C_{10}H_{20}N_8)](ClO_4)_2$.

Table IV. Electronic Spectra of Octaazabis(α-diimine) Macrocyclic Complexes

Complex	Solvent	Absorption[a]
$[Ni(C_{10}H_{20}N_8)](ClO_4)_2$	CH_3CN	430 (sh,[b] 2.50×10^3), 350 (sh, 6.05×10^3), 286 (2.17×10^4)
$[Ni(C_{10}H_{18}N_8)]^0$	CH_3CN	500 (1.03×10^4), 450 (sh, 5.0×10^3)
$[Ni(C_{12}H_{24}N_8)](ClO_4)_2$	CH_3CN	430 (sh, 2.63×10^3), 350 (sh, 6.24×10^3), 287 (2.16×10^4)
$[Ni(C_{14}H_{28}N_8)](ClO_4)_2$	CH_3CN	430 (sh, 2.68×10^3), 350 (sh, 6.57×10^3), 289 (2.37×10^4)
$[Ni(C_{10}H_{20}N_8)]Cl_2$	H_2O	430 (sh, 2.13×10^3), 350 (sh, 5.70×10^3), 286 (2.22×10^4)
	Solid state	610, 445
$[Co(C_{10}H_{20}N_8)](ClO_4)_2$	CH_3CN	442 (2.17×10^3), 281 (1.44×10^4)
	CH_3NO_2	440 (2.16×10^3), 280 (1.44×10^4)
$[Co(C_{10}H_{20}N_8)(CH_3CN)_2]$-$(ClO_4)_3$	CH_3CN	389 (4.48×10^3), 264 (2.24×10^4)
$[Fe(C_{10}H_{20}N_8)(CH_3CN)_2]$-$(ClO_4)_2$	CH_3CN	448 (4.41×10^3), 290 (1.17×10^4), 225 (1.81×10^4)
$[Fe(C_{10}H_{20}N_8)(C_5H_5N)_2]$-$(ClO_4)_2$	CH_3CN[c]	525 (4.70×10^3), 418 (3.20×10^3), 370 (sh, 5.66×10^3)
$[Fe(C_{10}H_{20}N_8)(C_3H_4N_2)_2]$-$(ClO_4)_2$	CH_3CN[c]	548 (5.99×10^3), 287 (1.23×10^4), 240 (sh, 1.27×10^4)
$[Fe(C_{10}H_{20}N_8)(NH_3)_2]$-$(ClO_4)_2$	CH_3CN[c]	551 (4.09×10^3), 292 (1.29×10^4), 241 (1.13×10^4)
$[Cu(C_{10}H_{20}N_8)Cl(H_2O)]$-$(ClO_4)$	CH_3CN	610 (2.17×10^2), 297 (1.45×10^4), 240 (1.10×10^4)
	CH_3NO_2	612 (2.10×10^2)[d]
	H_2O	595 (3.20×10^2), 292 (1.43×10^4), 230 (sh, 1.05×10^4)

[a] Band maxima in nm, molar extinction coefficient in parentheses. [b] Shoulder. [c] Tenfold excess axial ligand added to repress dissociation. [d] Higher energy bands are obscured by nitromethane absorption.

two distinct overlapping triplets in the 0.93–1.26 ppm region and the methylene resonances gave overlapping multiplets (quartets) in the 1.8–2.2 ppm vicinity. This argues for, albeit weakly, a reduction in the rate of axial–equatorial interchange of the ethyl groups giving two conformers on the NMR time scale.

Electronic Spectra. The visible and UV spectra of octaazabis(α-diimine) macrocyclic complexes are given in Table IV and Figure 1. The electronic spectra of these intensely colored complexes are dominated by intense charge-transfer absorptions ($\epsilon_{max} = 10^3$–10^4) in the visible and UV portions of the spectra. The spectra are tabulated for identification purposes only; no detailed assignments will be made due to the overlap of ligand field and charge-transfer absorptions. Generally, the lowest energy bands of the spectra for Ni(II), Co(II), Co(III), and Fe(II) are d $\rightarrow$ π^* charge-transfer bands which have been extensively studied and characterized in other α-diimine complexes.[26] The back-donation tendency varies from metal to metal and follows the order Fe(II) > Co(II) $\sim$ Ni(II) > Co(III). The lowest energy transition of Cu(II) complex at 610 nm is probably a d–d transition as indicated by an extinction coefficient ($\epsilon_{max} = 217$) that is only slightly higher than expected. The intense absorption bands in the near-UV spectra of complexes arise form π–π^* transitions of the ligands, slightly perturbed by the presence of the metal ions.

The coordination numbers for some of the Co(II), Ni(II), and Cu(II) complexes are not readily ascertainble since interactions of these macrocyclic complexes with axial ligands are relatively weak. For weak axial ligation, the perturbations on the electronic states of the metal are minor and not diagnostic of coordination number. Differences of spectra obtained in the solid state in solution can be due to factors other than changes in coordination number.

The Co(II) complex, although prepared from acetonitrile solution, contains no axial ligands other than possible perchlorate anions. Perchlorate anions are well known to coordinate under special conditions (normally the absence of stronger ligands), but such interactions normally manifest themselves by a splitting of the antisymmetric Cl–O stretching mode due to reduced symmetry of the coordinated species. No such splitting of the ClO_4^- absorption band at 1100 cm^{-1} was observed. Any interaction of the ClO_4^- anion with the axial sites is therefore very weak; the extent of this interaction cannot be determined without a full single-crystal x-ray study. Structural studies of a number of macrocyclic Co(II) complexes have shown that Co(II)–axial ligand distances are generally long and span a considerable range. The Co(II)–axial nitrogen distances in two porphyrin complexes, Co-

(TPP)(pip)$_2$[27] and Co(OEP)(1-MeIm)[28] are 2.44 and 2.15 Å, respectively. Two closely related diaquo macrocyclic complexes of Co(II), $[Co(Me_6[14]4,11\text{-dieneN}_4)(H_2O)_2](BF_4)_2$[29] and $[Co([14]tetraeneN_4)(H_2O)](ClO_4)_2$,[30] have Co-O$_{(H_2O)}$ distances of 2.482 and 2.289 Å, respectively. It is doubtful that a Co(II)–O$_{(ClO_4^-)}$ distance of the former would sufficiently perturb the ClO_4^- to be distinguishable from other distortions from T_d symmetry produced by lattice effects.

The electronic spectra of $[Co(C_{10}H_{20}N_8)](ClO_4)_2$ taken as transmission spectra in the solid state and in CH_3NO_2 and CH_3CN solvents are very similar (Table IV) and indicate minimal, if any, interaction of the solvent with the axial sites. ESR spectra of the Co(II) complex in acetonitrile-dimethylformamide glasses at –110 °C reveal hyperfine coupling indicative of the coordination of one molecule of CH_3CN. The addition of pyridine to these solutions produces hyperfine coupling diagnostic of two coordinated pyridine molecules. However, these low-temperature results are not necessarily diagnostic of coordination numbers at higher temperature. For weakly bound ligands the $T\Delta S$ term at higher temperatures overrides the ΔH term of bond formation and leads to species with lower coordination numbers.

The Ni(II) complex, $[Ni(C_{10}H_{20}N_8)]Cl_2$, is a diamagnetic, almost black appearing crystalline solid as opposed to the

orange-brown four-coordinate perchlorate complex. Dissociation of the Cl anions occurs in aqueous solution giving solutions having conductances characteristic of 2:1 electrolytes in water and with spectra identical with that of the perchlorate complex. Transmission spectra of the solid compound, however, have a very intense charge-transfer absorption across much of the visible range of the spectrum, with a new absorption band appearing at 610 nm.

Reactivity. The Cu(II), Ni(II), Co(II), and Co(III) complexes undergo intense color changes due to deprotonation of the macrocyclic ligand in the presence of amine bases such as pyridine and triethylamine. Similar N–H deprotonation reactions have been observed with other metal complexes containing hydrazone linkages. For the Ni(II) complex, triethylamine is sufficiently basic to remove two protons and leads to the formation of the molecular complex, [Ni(C$_{10}$-H$_{18}$N$_8$)]^0. The C=N stretching frequency of this compound, 1510 cm^{-1}, is reduced significantly from its dicationic precursor, 1616 cm^{-1}. The NMR spectrum contains two methyl resonances at 1.95 and 2.47 ppm (δ). These observations support the loss of N—H rather than methylene C—H protons. The C=N stretching frequencies, together with the changes in the electronic spectra (lowering of energy of charge-transfer bands and increased intensity) indicate that the loss of these protons is accompanied by increased delocalization which includes the deprotonated hydrazine linkage.
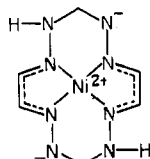
The deprotonated macrocyclic complexes are very susceptible to ligand dehydrogenation reactions with dioxygen, double bonds being introduced into the six-membered chelate rings. The nature of the oxidized products is highly dependent upon the coordinated metal and includes isomerized, oxidized ligands with Cu(II), octaazaannulene complexes of Co(III), and a dimeric species containing a Ni–Ni bond for the Ni(II) complex.[16,19,23]

Axial Ligand Substitution of the Co(III) and Fe(II) Complexes. Generally, axial ligand substitution is slow for Co(III) macrocyclic complexes and relatively faster for low-spin Fe(II) complexes. The exchange of coordinated CH$_3$CN with free acetonitrile of [Co(Me$_4$[14]1,3,8,10-tetraeneN$_8$)(CH$_3$CN)$_2$]$^{3+}$ and related complexes can be readily followed by NMR techniques. The chemical shift of the coordinated CH$_3$CN, 2.21 ppm (δ), in CD$_3$NO$_2$ is substantially shifted from the value of free CH$_3$CN, 1.97 ppm. The intensity of the methyl protons of the coordinated CH$_3$CN decreases slowly after CD$_3$CN is added to the Co(III) solutions. Under the conditions employed (e.g., large excess of added CD$_3$CN), the rate of intensity decrease of the methyl signals of the coordinate CH$_3$CN is equal to the rate of exchange between coordinated and free CH$_3$CN. The pseudo-first-order rate constant for CH$_3$CN exchange reaction of the octaazacobalt(III) macrocyclic complex is 8×10^{-3}. There was no detectable exchange between coordinated CH$_3$CN and free CH$_3$CN in the closely related [Co(Me$_4$[14]1,3,8,10-tetraeneN$_4$)(CH$_3$CN)$_2$]$^{3+}$ species, even after the solutions had been standing 2 weeks, setting an upper limit of 10^{-7} for the exchange rate.

Although the reasons for the profound differences of 10^4 in exchange rates of these closely related systems are not well understood, the exchange rates demonstrate the considerable influence of subtle variations in macrocyclic ring structure on the lability of the axial site ligands. The hydrazone linkages with their lone electron pair of the octaazabis(α-diimine)

complexes appear to have a strong influence on the spectra and reactivity properties of these compounds. The factors contributing to the rates of axial substitution of Co(III) complexes are still not well understood. For example, although the reactivity patterns of cobalamins (vitamin B$_{12}$ derivatives) parallel those of cobaloximes to a surprising degree,[31,32] the cobalamins are 10^7 times more labile.[33]

The CH$_3$CN of [Fe(Me$_4$[14]1,3,8,10-tetraeneN$_8$)-(CH$_3$CN)$_2$]$^{2+}$ exchanges completely in the time required to prepare the samples and measure the NMR spectra, approximately 1–2 min. Attempts to measure the NMR spectra of this complex in CD$_3$NO$_2$, a very weakly coordinating solvent, containing small amounts of CD$_3$CN were unsuccessful because of complex decomposition in this solvent.

Registry No. [Ni(Me$_4$[14]1,3,8,10-tetraeneN$_8$)](ClO$_4$)$_2$, 60086-90-0; [Ni(C$_{12}$H$_{24}$N$_8$)](ClO$_4$)$_2$, 64057-23-4; [Ni(C$_{14}$H$_{28}$-N$_8$)](ClO$_4$)$_2$, 64082-10-6; [Ni(C$_{14}$H$_{28}$N$_8$)](ClO$_4$)$_2$, acetone condensation product, 64082-17-3; [Ni(C$_{20}$H$_{36}$N$_8$)](ClO$_4$)$_2$, 64057-10-9; [Ni(Me$_4$[14]1,3,8,10-tetraeneN$_8$)]Cl$_2$, 64057-11-0; [Ni(Me$_4$[14]-1,3,8,10-tetraeneN$_8$)](PF$_6$)$_2$, 64057-12-1; [Co(Me$_4$[14]1,3,8,10-tetraeneN$_8$)](ClO$_4$)$_2$, 60086-91-1; [Co(Me$_4$[14]1,3,8,10-tetraeneN$_8$)(CH$_3$CN)$_2$](ClO$_4$)$_3$, 64057-14-3; [Cu(Me$_4$[14]1,3,-8,10-tetraeneN$_8$)Cl(H$_2$O)](ClO$_4$), 60119-39-3; [Fe(Me$_4$[14]1,3,-8,10-tetraeneN$_8$)(CH$_3$CN)$_2$](ClO$_4$)$_2$, 60086-92-2; [Fe(Me$_4$[14]1,-3,8,10-tetraeneN$_8$)(C$_5$H$_5$N)$_2$](ClO$_4$)$_2$, 64057-16-5; [Fe(Me$_4$[14]-1,3,8,10-tetraeneN$_8$)(NH$_3$)$_2$](ClO$_4$)$_2$, 64057-18-7; [Fe(Me$_4$[14]1,-3,8,10-tetraeneN$_8$)(C$_3$H$_4$N$_2$)$_2$](ClO$_4$)$_2$, 64057-20-1; [Fe(Me$_4$[14]-1,3,8,10-tetraeneN$_8$)(NCS)$_2$], 64057-21-2; [Ni(C$_{10}$H$_{18}$N$_8$)], 64056-97-9; formaldehyde, 50-00-0; 2,3-butanedione dihydrazone, 40480-39-5; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; acetone, 67-64-1; cyclohexanone, 108-94-1; VII (M = Zn), 64056-98-0.

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# M₂(CO)₆(ligand) Complexes

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We present a systematic molecular orbital study of the electronic structure of complexes containing the $M_2(CO)_6$ binuclear transition-metal fragment bonded to a variety of ligands. These include acetylene, two carbonyls, C_4R_4 (the ferroles), C_6R_6 (flyover bridges), cyclobutadiene, dienes, azulene, cyclooctatetraene, pentalene, tetramethyleneethane, cycloheptatrienyl, hexatrienes, and other π-electron systems. The orientational preferences of these ligands are analyzed in detail. Some inferences are drawn on their reactivity, as well as the possible stability of some as yet unsynthesized complexes.

Dimers with the formula $M_2(CO)_6$(ligand), shown schematically in **1**, frequently crop up in transition-metal chemistry.

1
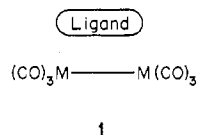
The ligands of primary interest are unsaturated organic molecules, ranging from acetylene to azulene. The number and variety of such complexes are remarkable. Several structural classes are discernible, each exemplified below by a single structure.[1] There are complexes with simple ligands such as acetylenes[2,3] (**2**), ferrole complexes of type **3**,[4,5]

2   **3**

4   **5**
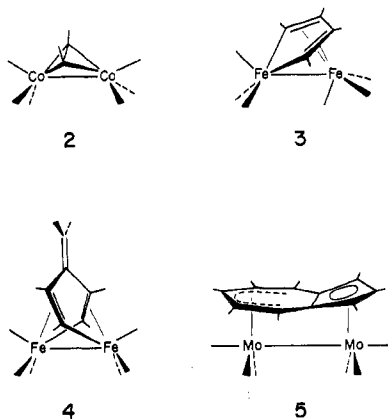
"flyover" bridges such as **4**,[6] and "picnic-table" compounds of type **5**.[7] This list does injustice to the beauty and complexity of the full range of compounds in which the $M_2(CO)_6$ unit appears. Other complexes, and some discussion of bonding and structural trends, are given in several recent review articles.[8,9]

One feature common to all these molecules is the metal–metal-bonded $M_2(CO)_6$ unit. A study of the orbitals and bonding capabilities of such $M_2(CO)_6$ fragments should aid in understanding the structures and, perhaps, the chemistry of these molecules. This approach is a natural extension of earlier work on metal carbonyl fragments[10] and MCp₂ fragments.[11] We begin with a development of the valence

orbitals of $Fe_2(CO)_6$, Fe being chosen as a typical transition metal, followed by a brief look at other related fragments, and then a discussion of bonding patterns with various ligands.

All calculations are of the extended Hückel type, and the parameters used are discussed in Appendix I. The reader should be aware that the extended Hückel procedure has well-known deficiencies. The conclusions drawn in this paper should be viewed as being only indicative of bonding trends and not as definitive statements of fact.

Orbitals of M₂(CO)₆

A typical geometry of the $Fe_2(CO)_6$ fragment is shown in **6**. It is perhaps most readily considered as arising from the

6
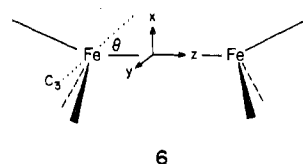
combination of two $Fe(CO)_3$ fragments. In these calculations a local C_3 axis is retained for each $Fe(CO)_3$ unit, with a C–Fe–C angle of 95°, Fe–C 1.74 Å, and C–O 1.13 Å. With these held constant, and the additional constraint of C_{2v} symmetry, the $Fe_2(CO)_6$ fragment has only two degrees of freedom: the metal–metal distance R and the angle of tilt θ, defined as the angle between the local C_3 axis and the metal–metal bond.

The orbitals of $Fe_2(CO)_6$ can be built up by interacting the orbitals of the two $Fe(CO)_3$ fragments. Figure 1 shows the resulting orbitals when the $Fe(CO)_3$ fragments[10] are brought together in D_{3h} symmetry ($\theta = 0°$). Of the six metal-type orbitals of $Fe(CO)_3$ the lower three (heavily involved in Fe–CO back-bonding) hardly interact at all, and in $Fe_2(CO)_6$ they form a low-lying nest of six orbitals. However, the upper three orbitals of $Fe(CO)_3$ interact strongly to form six "valence" orbitals of the $Fe_2(CO)_6$ fragment. Only five of them are available for bonding with ligands, as the highest (a_2'', σ^*) is too strongly antibonding to be used.

To make the $Fe_2(CO)_6$ fragment resemble the "sawhorse" geometry that is found in many of the crystal structures, θ must be increased from 0° to nearly 60°. (A sawhorse with a perfectly linear spine, O–C–Fe–Fe–C–O, has θ equal to 58.357° when the CO–Fe–CO angle is 95°.) This lowers the