Conclusion

The results presented here are consistent with Scheme I, in which a metallocyclopentadiene molecule is the key intermediate in the cyclocotrimerization of two molecules of acetylene and one molecule of olefin to form cyclohexa-1,3-diene derivatives. By judicious choice of an electron-withdrawing metallocycle and an electron-donating olefin it is possible to suppress the competing cyclotrimerization reaction of three molecules of acetylene to obtain a catalytic, stereoselective production of the cyclohexa-1,3-diene.

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Supplementary Material Available: the idealized H atom parameters (Table III), the amplitudes of vibration on individual nonhydrogen atoms (Table IV), and a listing of observed and calculated structure amplitudes (27 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Nagoya University; (b) Northwestern Univesity.
(2) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis", Logos Press, London, 1967, p 30.
(3) P. N. Rylander, "Organic Synthesis with Noble Metal Catalysts", Academic Press, New York, N.Y., 1973, p 191.
(4) J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes", Springer-Verlag, West Berlin and Heidelberg, 1975, p 152.
(5) A. J. Chalk, *J. Am. Chem. Soc.*, **94**, 5928 (1972).
(6) H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **21**, 431 (1970).
(7) Y. Wakatsuki, T. Kuramitsu, and H. Yamazaki, *Tetrahedron Lett.*, 4549 (1974); *J. Am. Chem. Soc.*, **96**, 5284 (1974).
(8) D. M. Singleton, *Tetrahedron Lett.*, 1245 (1973).
(9) A. Carbonaro, A. Greco, and G. Dall'Asta, *Tetrahedron Lett.*, 5129 (1968).
(10) E. H. Huntress, T. E. Lesslee, and J. Bornstein, "Organic Synthesis", Collect. Vol. 4, Wiley, New York, N.Y., 1963, p 329.
(11) T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, *J. Organomet. Chem.*, **65**, 253 (1974).
(12) T. Ito, S. Hasegawa, Y. Takahashi, and Y. Ishii, *J. Chem. Soc., Chem. Commun.*, 629 (1972); *J. Organomet. Chem.*, **73**, 401 (1974).
(13) K. Moseley and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1604 (1971); *J. Chem. Soc., Dalton Trans.*, 169 (1974).
(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(15) Computer programs, sources af atomic scattering factors, and general procedures have been described previously. See, for example, L. Que, Jr., M. A. Brobik, J. A. Ibers, and R. H. Holm, *J. Am. Chem. Soc.* **96**, 4168 (1974).
(16) Supplementary material.
(17) J. T. Mague, *Inorg. Chem.*, **9**, 1610 (1970).
(18) J. T. Mague, *Inorg. Chem.*, **12**, 2649 (1973).
(19) R. G. Gastinger, M. D. Rausch, D. A. Sullivan, and G. J. Palenik, *J. Am. Chem. Soc.*, **98**, 719 (1976).
(20) J. L. Atwood, W. E. Hunter, H. Alt, and M. D. Rausch, *J. Am. Chem. Soc.*, **98**, 2454 (1976).
(21) C. G. Pierpont, H. H. Downs, K. Itoh, H. Nishiyama, and Y. Ishii, *J. Organomet. Chem.*, submitted for publication.
(22) H. S. Aldrich, J. T. Mague, and L. C. Cusachs, *Int. J. Quantum Chem.*, **7**, 239 (1973).
(23) N. C. Baenzinger, G. F. Richards, and J. R. Doyle, *Acta Crystallogr.*, **18**, 924 (1969).
(24) F. P. Boer and J. Flynn, *J. Am. Chem. Soc.*, **93**, 6495 (1971).
(25) F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1754 (1972).
(26) M. R. Churchill and K. K. G. Lin, *J. Am. Chem. Soc.*, **96**, 76 (1974).
(27) J-M. Manoli, A. P. Gaughan, Jr., and J. A. Ibers, *J. Organomet. Chem.*, **72**, 247 (1974).
(28) S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, **14**, *33* (1976).
(29) T. W. Muecke and M. I. Davis, American Crystallographic Association Meeting, March, 1966, Abstract F1.
(30) A. Carbonaro, A. Greco, and G. Dallasta, *Tetrahedron Lett.*, 5129 (1968); *J. Organomet. Chem.*, **20**, 177 (1969).
(31) Y. Akasaki and T. Mukai, *Tetrahedron Lett.*, 1985 (1972).

Cofacial Dimer of a Dihydrooctaaza[14]annulene Complex Containing a Nickel–Nickel Bond and Related Monomeric Complexes

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Abstract: Oxidative dehydrogenation of the bis-α-diimine macrocyclic complex, $[Ni(C_{10}H_{20}N_8)]^{2+}$, under basic conditions results in a four-electron oxidation of the ligand and deprotonation of each six-membered chelate ring to yield a molecular dimeric complex, $[Ni(C_{10}H_{14}N_8)]_2$. A single-crystal x-ray structure analysis (space group $C2/c$; $a = 16.597$ (9), $b = 18.534$ (9), $c = 13.233$ (7) Å; $\cos\beta = -0.8121$ (2); $\rho_{calcd} = 1.718$ g/cm^3, $\rho_{expl} = 1.70$ (2) g/cm^3; $Z = 4$) has revealed an eclipsed cofacial dimeric complex with nickel–nickel bond length of 2.788 (2) Å. The close approach of the eclipsed macrocyclic ligands, 3.00 Å, necessitates ascribing bonding between the two macrocyclic ligands in addition to the metal–metal bond. The dimer units are stacked along the c axis of the unit cell with adjacent dimer units having a nickel–nickel separation of 3.800 (3) Å. The octaaza[14]annulene ligand has a delocalized double-bond arrangement comparable to that expected for an aromatic system. A monomeric isomer of this complex having a syn–anti α-diimine arrangement and C_{2h} molecular symmetry has also been isolated. A comparison of the solid state and solution electronic spectra indicates some interaction in the solid state for the C_{2h} isomer. A crystal structure analysis of the C_{2h} isomer (space group, $P\bar{1}$; $a = 8.433$ (1), $b = 8.408$ (2), $c = 4.860$ (1) Å; $\alpha = 75.94$ (1), $\beta = 68.25$ (1), $\gamma = 81.73$ (1)°; $\rho_{calcd} = 1.632$ g/cm^3, $\rho_{expl} = 1.628$; $Z = 1$) reveals a localized double-bond arrangement. The molecules are packed in a parallel fashion with a Ni–Ni separation of 4.860 Å and interplanar separations of 3.373 Å for adjacent molecules. The nickel–nitrogen distances, 1.784 (1) and 1.820 (1) Å, are unusually short for Ni(II).

The significant role of highly conjugated and completely conjugated macrocyclic ligands in biological processes suggests that highly conjugated synthetic macrocyclic ligands may confer unusual properties on coordinated metals as well. Naturally occurring macrocyclic ligands have nitrogen-to-center (N–Ct) distances in the range of 2.0–2.05 Å,[1] a range compatible with ideal first-row transition metal–nitrogen distances. The N–Ct distance associated with completely conjugated 14-membered macrocyclic ligands are expected to be in the range 1.80–1.90 Å, significantly shorter than

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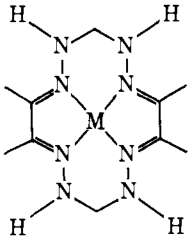
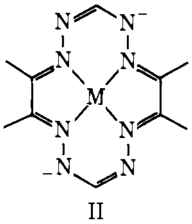
normal metal-nitrogen distances. Reduction of the ligand radius can lead to either of two effects. A metal lying in the plane of the donor atoms can experience strong tetragonal fields leading to unusual electronic states and/or complex reactivity. A metal too large to fit in the plane will be extruded to one side and lead to a preference for five-coordinate structures.

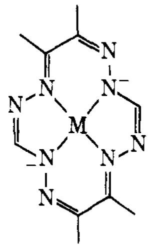
The macrocyclic complexes, I, obtained by the metal-template condensation of 2,3-butanedihydrazone with aldehydes,[2] presented attractive possibilities for conversion to completely conjugated 14-membered macrocyclic ligand complexes. Studies by others have shown that hydrazone ligands are easily deprotonated[3] and it was expected that this would facilitate oxidation of the N-N and N-C linkages of the six-membered chelate rings. A monomeric nickel complex of a tetradentate ligand, closely related to the macrocyclic ligand, I, has been characterized;[4] the structure of a dimeric complex containing a metal-metal bond and an oxidized form of this ligand has been determined.[5]



I



II D_{2h}



III C_{2h}

This paper reports the synthesis and structural characterization of two isomeric nickel(II) complexes of a dihydrooctaaza[14]annulene ligand. The nickel complex of isomer II is an unusual dimeric species with a Ni-Ni bond; structural evidence suggest bonding interaction between the ligands themselves. The other isomer, III, is monomeric although solution and solid-state spectra of this isomer indicate interactions between molecules in the solid state.

The unusual nature of these nickel complexes prompted us to determine the crystal structures of these isomers to (a) determine the metal-nitrogen distances in completely conjugated 14-membered ligands, (b) evaluate the extent of delocalization in the two isomeric octaaza[14]annulene metal complexes, (c) determine the arrangement of double bonds and location of negative charges of systems having a predominantly localized bond structure, (d) determine the nature of the Ni-Ni bond in the dimeric structure, and (e) establish the extent of solid-state intermolecular interaction for the two isomers and to compare these interactions with those of closely related systems such as bis(dimethylglyoximato)nickel(II), Ni(dmg)$_2$.

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.

All 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. 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 MHz spectrometers.

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

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

Warning! The compounds containing perchlorate anions must be regarded as potentially explosive and extremely hazardous. Although we did not experience any difficulty in this regard, the possibility of unprovoked detonation exists and only minimal quantities should be prepared. Storage for time periods greater than 1 week is not recommended.

Syntheses. $C_4N_4H_{10}$. 2,3-Butanedihydrazone was prepared by the method of Busch and Bailar.[6a]

[Ni($C_{10}H_{20}N_8$)](ClO$_4$)$_2$. Aqueous formaldehyde (38%, 1.61 g, 20 mmol) was added to a solution containing 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-butanedihydrazone was added. Concentrated perchloric acid (1 drop) was added to catalyze the reaction. The reaction proceeded immediately and was essentially complete after 0.5 h at room temperature. Diethyl ether (50 ml) was slowly added to the red-brown solution to induce precipitation of the product. The red-brown product 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($C_{10}H_{14}N_8$)]$_2$. A solution of 200 mg of [Ni($C_{10}H_{20}N_8$)](ClO$_4$)$_2$ in 30 ml of CH$_3$CN was prepared, to which 0.5 ml of pyridine was added. Molecular oxygen was bubbled through the solution for 10 min. The lustrous, black, finely-divided product which precipitated during this period was immediately filtered, washed with CH$_3$CN, and dried in vacuo. The filter cake of the product frequently appears to have a copper-like luster. Yields approach 40%.

Excess oxygen reacts with the product, yielding intense green solutions. These solutions are unstable and slowly darken, yielding undefinable residues that make characterization of the further oxidized species difficult. To avoid the problems associated with the use of dioxygen in the synthesis of [Ni($C_{10}H_{14}N_8$)]$_2$ other oxidants may be used. Either I$_2$ or [Fe(acac)$_3$] (4 equiv) dissolved in CH$_3$CN serve equally well. Oxidants such as *o*-chloranil and 2,3-dichloro-5,6-dicyanobenzoquinone, although capable of introducing additional double bonds into the macrocyclic ligand, produce charge-transfer adducts between an oxidized form of the complex and the oxidant.

Anal. Calcd for [Ni($C_{10}H_{14}N_8$)]$_2$: C, 39.38; H, 4.59; N, 36.76. Found: C, 39.50; H, 4.58; N, 36.65.

[Ni($C_{10}H_{14}N_8$)]. To a solution prepared by dissolving Ni(ClO$_4$)$_2$·6H$_2$O (29 ml, 7.33 g) in acetonitrile (50 ml), 2,3-butanedione (40 mmol, 3.5 g) and formaldehyde (40 mmol, 3.3 g of 37% aqueous solution) were slowly added. Hydrazine (80 mmol, 2.7 g) was added drop by drop to the acetonitrile solution at room temperature under an O$_2$ atmosphere. The reaction is strongly exothermic and the temperature of the solution frequently approaches the boiling point. Thin plate-like orange crystals of [Ni($C_{10}H_{16}N_4$)], a 14π system containing one saturated five-membered ring,[6b] together with red-black crystals of [Ni($C_{10}H_{14}N_8$)] appear within 30 min. The C_{2h} isomer was obtained by allowing the filtrate to stand for 1 day during which time the [Ni($C_{10}H_{16}N_4$)] aerially oxidized to [Ni($C_{10}H_{14}N_4$)]. The crystalline product was filtered, washed with ethanol, and dried in the air.

Anal. Calcd for [Ni($C_{10}H_{14}N_8$)]: C, 39.38; H, 4.59; N, 36.76. Found: C, 39.39; H, 4.56; N, 36.60.

[Cu($C_{10}H_{20}N_8$)Cl(H$_2$O)](ClO$_4$). Formaldehyde, 3.22 g (37% aqueous solution), was added to a solution containing 3.41 g of CuCl$_2$·2H$_2$O in 50 ml of water. Then 4.56 g of solid 2,3-butanedihydrazone was dissolved in the solution and was 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$_2$O was added to precipitate the complex. Shiny, green, plate-like crystals of the product, which crystallized within 1 h, were filtered, washed with a small amount of water, and dried in air (yield about 80%).

Anal. Calcd for [Cu($C_{10}H_{20}N_8$)Cl(H$_2$O)](ClO$_4$): C, 25.61; H, 4.69; N, 23.91. Found: C, 24.93; H, 4.26; N, 23.75.

[Cu($C_{10}H_{14}N_8$)], C_{2h} Isomer. A solution of 200 mg of [Cu($C_{10}H_{20}N_8$)(H$_2$O)Cl](ClO$_4$) and 1 ml of triethylamine was prepared in 10 ml of acetonitrile. Molecular oxygen was then bubbled through the solution for 3 min. The product precipitated as lustrous, flaky yellow-green crystals and was filtered, washed with CH$_3$CN, and dried in vacuo (yield about 30%).

Anal. Calcd for [Cu($C_{10}H_{14}N_8$)], C_{2h} isomer: C, 38.77; H, 4.33; N, 36.19. Found: C, 38.55; H, 4.52; N, 35.72.

X-Ray Structural Determination Details. Crystals of

Table I. Crystal Data for Dihydrooctaaza[14]annulene Complexes of Nickel(II)

Compd	$[Ni(C_{10}H_{14}N_8)]$	$[Ni(C_{10}H_{14}N_8)]_2$
Molecular weight	304.99	609.97
Space group	$P\bar{1}$	$C2/c$
Cell constants		
a, Å	8.433 (1)	15.497 (9)
b, Å	8.408 (2)	18.534 (9)
c, Å	4.860 (1)	13.123 (7)
α, deg	75.94 (1)	90.00 (0)
β, deg	68.25 (1)	144.30 (2)
γ, deg	81.73 (1)	90.00 (0)
No. of reflections used to determine cell constants	34	12
2θ limits, deg	$40 < 2\theta < 80$	$30 < 2\theta < 40$
Z	1	4
ρ_{calcd}, g/cm^3	1.632	1.718
ρ_{exptl}, g/cm^3	1.63 (2)	1.70 (2)
Absorption coefficients, cm^{-1}	21.83	16.46
Crystal dimension, mm	Spherically ground crystal of 0.25 mm dia.	$0.024 \times 0.054 \times 0.23$
Absorption correction	None	None

Table II. Data Collection Details for the Dihydrooctaaza[14]-annulene Complexes of Nickel(II)

Compd	$[Ni(C_{10}H_{14}N_8)]$	$[Ni(C_{10}H_{14}N_8)]_2$
Diffractometer	Picker FACS-1	
Monochrometer (Bragg angle)	None	Graphite (6.093)
Radiation	Cu Kα 1.5418 (Ni filtered)	Mo Kα 0.7106
Takeoff angle	3.0	3.0
Method	θ-2θ	θ-2θ
Scan speed	2°/min	1°/min
Scan width, deg	2.5	1.8
Background time, s	20×2	20×2
Standards	3	3
Av deviation of standards from mean value	1% (random)	4%
2θ limits of data	$0 < 2\theta \leq 125$	$0 < 2\theta < 55$
No. of data collected	1234 (nonstandards)	2077 (unique)
No. of data used in final refinement	961 ($F \geq 2\sigma(F)$)	2077 ($F \geq 0$)

Table III. Structure Determination Details for the Octaaza[14]-annulene Complexes

Compd	$[Ni(C_{10}H_{14}N_8)]$	$[Ni(C_{10}H_{14}N_8)]_2$
Method	Heavy atom Patterson technique	Heavy atom Patterson technique
Heavy atom position from Patterson map	Special position $x = 0.000$ $y = 0.000$ $z = 0.000$	General position $x = 0.015$ $y = -0.001$ $z = 0.041$
Number of cycles used in the full-matrix least-squares refinement	6	6
Model for final cycle of refinement	All non-hydrogen atoms refined using anisotropic thermal parameters and hydrogen atoms refined with isotropic thermal parameters	All non-hydrogen atoms refined using anisotropic thermal parameters and hydrogen atoms included as fixed contributions
Final R_1[a]	2.21%	10.4%
Final R_2	2.73%	6.1%
gof[b]	2.80	2.55
Highest peak in final difference Fourier	0.3 e/Å^3 around Ni atom	1.2 e/Å^3 around Ni atom
Noise level for final difference Fourier	Less than 0.2 e/Å^3	Less than 0.3 e/Å^3
Ratio of observables to variables	8.3:1	12.1:1

[a] $R_1 = \sum[||F_o| - |F_c||]/\sum|F_o|$, $R_2 = (\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2)^{1/2}$. [b] "gof" $= [\sum||F_o| - |F_c||^2]^{1/2}/(N_{obsd} - N_{var})$.

$[Ni(C_{10}H_{14}N_8)]$, C_{2h} isomer, suitable for x-ray structure analyses, were grown by slow evaporation of a nitromethane solution at 95 °C. At lower temperatures thin, plate-like crystals unsuitable for diffraction studies were obtained. Precession photographs of a crystal, ground to a sphere of 0.25-mm diameter, revealed no systematic absences and indicated a triclinic space group. The crystal was transferred to a Picker FACS-1 automated diffractometer for the accurate determination of cell constants and for data collection. These details are presented in Tables I and II.

The dimeric complex, $[Ni(C_{10}H_{14}N_8)]_2$ of D_{2h} symmetry is extremely insoluble in common organic solvents; all attempts to obtain high-quality crystals by recrystallization were futile. The largest crystals obtained, after 2 years of effort, were grown by slow diffusion (24 h) of molecular oxygen into a 10:1 acetonitrile-pyridine solution of $[Ni(C_{10}H_{20}N_8)](ClO_4)_2$. The best crystal available, a very small one of dimensions $0.024 \times 0.054 \times 0.23$ mm, was used for the space group determination, measurement of cell constants, and data collection. Precession photographs revealed the following systematic absences: hkl: $h + k = 2n$, $h0l$: $l = 2n$ ($h = 2n$); $0k0$: ($k = 2n$) indicating $C2/c$ or Cc as possible space groups. (Satisfactory refinement of the structure assuming $C2/c$ as the more probable space group confirmed the former as being correct.) A Picker FACS-1 automated diffractomer was used for the determination of accurate cell constants and for data collection. The crystal data are summarized in Table I and the data collection details are presented in Table II.[7]

The very small crystal size and weak intensities of the data necessitated collecting three equivalent quadrants of data. Equivalent data were merged (with an "R" value of 5.9%) to yield a data set containing 2077 independent reflections. All unique data were used in the solution and refinement of the structure for two reasons. First, the very small crystal size gave rise to weak intensities; all reflections having 2θ values greater than 45° being unobserved. Second, reflections for which $l \neq 2n$ had intensities much weaker than reflections having even l indices because of pseudosymmetry in the structure. Elimination of weak intensities in the refinement could conceivably have biased the structure unwittingly. The estimated standard deviations of bond lengths for this structure are between 0.005 and 0.008 Å, indicating a satisfactory level of refinement. The higher than desirable final R value (Table III) results from the combined effects of small crystal size, weak intensities, and inclusion of all data (including zero net intensities) in the refinement.

The solution and refinement of each structure was straightforward and presented no difficulties. Pertinent details for both structures are summarized in Table III. The final positional and thermal parameters for $[Ni(C_{10}H_{14}N_8)]$ and $[Ni(C_{10}H_{14}N_8)]_2$ are listed in Tables IV and V, respectively.

Results and Discussion

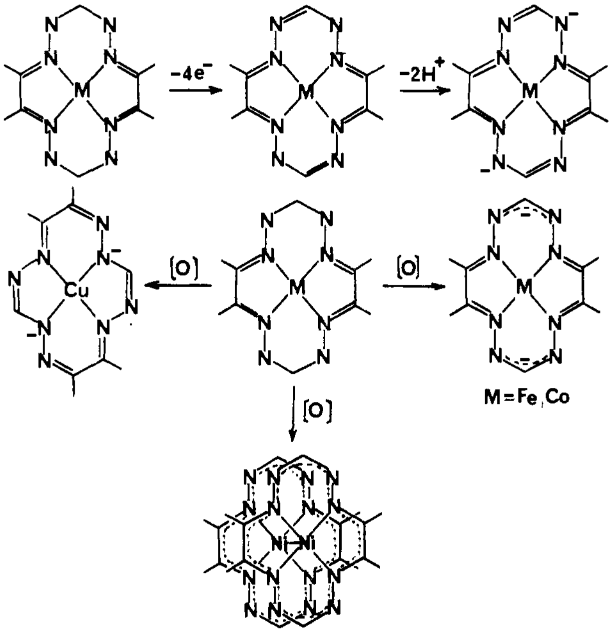
Ligand Oxidation. Under suitable conditions, the octaaza-macrocyclic complexes, I, undergo a sequence of redox reactions in which double bonds are introduced into the six-membered chelate rings via a series of two-electron oxidative de-

Table IV. Final Positional Parameters and Thermal Parameters[a] for $[Ni(C_{10}H_{14}N_8)]$

Atom	X	Y	Z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.0000 (0)	0.0000 (0)	0.0000 (0)	115.1 (8)	87.8 (7)	376.9 (26)	−1.4 (5)	99.4 (11)	−42.7 (10)
N1	−0.0146 (2)	0.2159 (2)	−0.0194 (3)	129 (3)	94 (2)	424 (9)	−3 (2)	−106 (4)	−47 (4)
C1	0.0957 (2)	0.2605 (2)	0.0900 (4)	154 (4)	103 (3)	494 (11)	−18 (3)	−107 (5)	−57 (5)
N2	0.1963 (2)	0.1481 (2)	0.1941 (4)	139 (3)	114 (3)	503 (10)	−20 (2)	120 (4)	−68 (4)
N3	0.1629 (2)	−0.0056 (2)	0.1651 (3)	114 (3)	104 (2)	375 (8)	−4 (2)	−83 (4)	−53 (4)
C2	0.2500 (2)	−0.1367 (2)	0.2583 (4)	113 (3)	134 (3)	325 (9)	3 (2)	−63 (4)	−34 (4)
C3	0.2188 (2)	−0.2994 (2)	0.2376 (4)	143 (3)	125 (3)	392 (10)	13 (3)	−95 (5)	−43 (5)
N4	0.1122 (2)	−0.3381 (2)	0.1281 (3)	152 (3)	84 (2)	448 (19)	9 (2)	−113 (4)	−39 (4)
C4	0.3836 (3)	−0.1216 (3)	0.3838 (5)	144 (4)	175 (4)	528 (13)	0 (3)	−145 (6)	−46 (6)
C5	0.3196 (3)	−0.4452 (3)	0.3573 (6)	226 (5)	139 (4)	660 (15)	37 (3)	−223 (7)	−59 (6)
H1	0.103 (2)	0.373 (2)	0.097 (4)	1.51[b]					
H2	0.381 (3)	−0.014 (3)	0.406 (6)	4.55					
H3	0.495 (3)	−0.155 (3)	0.258 (5)	3.30					
H4	0.368 (3)	−0.197 (3)	0.574 (6)	3.71					
H5	0.447 (3)	−0.430 (3)	0.246 (5)	2.96					
H6	0.287 (3)	−0.540 (3)	0.327 (5)	2.89					
H7	0.298 (3)	−0.452 (3)	0.570 (5)	2.43					

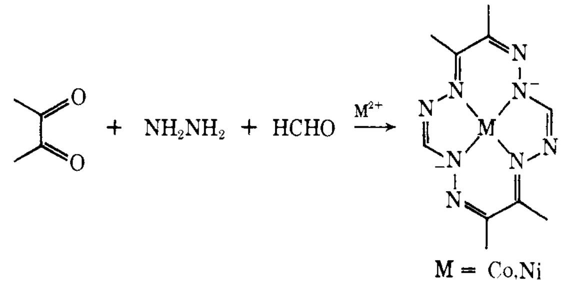
[a] The thermal parameters are of the form exp $[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl) \times 10^{-4}]$. [b] Isotropic thermal parameters.

hydrogenation processes. The remaining highly acidic N–H protons ionize under the reaction conditions, yielding 16π ligand systems of dihydrooctaaza[14]annulene ligands. The oxidation process and some of the types of complexes which have been isolated are illustrated below.



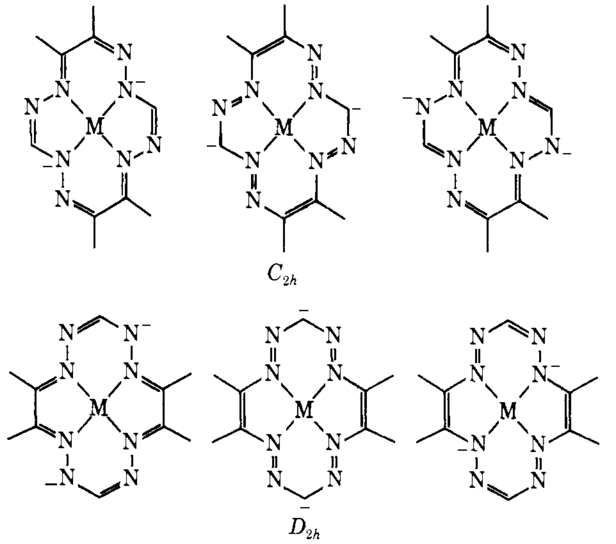
Ligand oxidation of the octaaza-macrocyclic complexes, I, generally occurs under mild conditions, requiring only weak oxidants (O_2, I_2, or $[Fe(acac)_3]$) and a suitable base (triethylamine, pyridine, or *tert*-butoxide anions) to facilitate the oxidation process by removal of a proton from the hydrazine linkages. Attempts using the high potential quinones, chloranil and 2,3-dichloro-5,6-dicyanoquinone, to prepare these complexes were unsuccessful. Although these quinones partially oxidize the ligands, evidence from mass spectroscopic and infrared studies indicated the presence of N–H groups. The products were generally isolated as insoluble 1:1 adducts with the quinone, an undesirable feature from the viewpoint of characterizing the metal complex per se. The use of quinones as oxidants was not pursued further.

Octaazaannulene complexes of C_{2h} symmetry, III, having the syn-anti α-diimine arrangement were obtained by two routes. Those of Co(II) and Ni(II) were obtained from the metal-directed condensation of 2,3-butanedione, hydrazine, and formaldehyde as described in the Experimental Section.[8]



Oxidative dehydrogenation of the Cu(II) complex of I was accompanied by anti-anti to syn-anti isomerization of the α-diimine functions, yielding the C_{2h} isomer of the dihydrooctaaza[14]annulene ligand.

For each dihydrooctaaza[14]annulene isomer, a number of valence isomers may be drawn. Some of the important contributing structures are illustrated below.



Butanedihydrazone has the anti-anti α-diimine arrangement when isolated as indicated by the single NMR resonances of the $-CH_3$ groups and $-NH_2$ groups at 1.85 and 5.5 ppm (δ), respectively. This arrangement is consistent with the observed anti-anti α-diimine configuration of the macrocyclic com-

Table V. Fractional Coordinates and Thermal Parameters[a] for $[Ni(C_{10}H_{14}N_8)]_2$

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.01517 (7)	−0.00104 (5)	0.40994 (9)	30.2 (8)	12.3 (2)	85.2 (13)	1.5 (4)	27.9 (9)	−1.4 (5)
N1	0.098 (5)	0.0973 (3)	0.3935 (7)	47 (8)	16 (2)	133 (13)	2 (3)	62 (9)	4 (3)
N2	−0.1010 (6)	0.1402 (3)	0.2692 (8)	67 (8)	17 (2)	152 (13)	4 (3)	73 (9)	7 (4)
N3	−0.2656 (5)	0.0387 (3)	0.0905 (7)	50 (6)	22 (2)	104 (11)	11 (3)	48 (8)	19 (4)
N4	−0.1707 (4)	−0.0126 (3)	0.1969 (6)	33 (5)	19 (2)	69 (9)	0 (3)	23 (6)	2 (3)
N5	0.0218 (5)	−0.0996 (3)	0.4128 (7)	52 (8)	14 (2)	92 (12)	1 (3)	49 (9)	−2 (3)
N6	0.1341 (6)	−0.1423 (3)	0.5356 (7)	59 (7)	14 (2)	136 (13)	8 (3)	54 (9)	6 (3)
N7	0.2991 (5)	−0.0408 (3)	0.7153 (7)	34 (6)	21 (2)	112 (11)	3 (3)	37 (7)	2 (4)
N8	0.2030 (4)	0.0106 (3)	0.6081 (6)	31 (5)	16 (2)	86 (9)	2 (3)	26 (6)	0 (4)
C1	−0.2233 (7)	0.1070 (4)	0.1356 (10)	62 (9)	22 (3)	132 (16)	13 (4)	60 (11)	15 (5)
C2	−0.2122 (7)	−0.0822 (4)	0.1498 (9)	46 (8)	20 (2)	89 (14)	−5 (4)	42 (10)	−0 (4)
C3	−0.1043 (7)	−0.1315 (3)	0.2692 (9)	68 (9)	17 (2)	118 (15)	−15 (4)	67 (11)	−23 (5)
C4	0.2560 (7)	−0.1094 (4)	0.6704 (9)	43 (8)	21 (2)	110 (15)	17 (4)	42 (10)	7 (5)
C5	0.2442 (6)	0.0798 (4)	0.6457 (9)	33 (7)	17 (2)	121 (14)	−11 (3)	44 (9)	−10 (4)
C6	0.1361 (7)	0.1295 (4)	0.5250 (10)	72 (9)	14 (2)	160 (17)	−10 (4)	89 (11)	−6 (5)
C7	−0.3588 (7)	−0.1018 (4)	−0.0213 (8)	53 (8)	38 (3)	91 (13)	−14 (4)	45 (9)	−22 (5)
C8	−0.1178 (8)	−0.2114 (4)	0.2455 (10)	104 (10)	20 (2)	217 (17)	−15 (4)	117 (12)	−25 (5)
C9	0.3950 (7)	0.0987 (4)	0.7925 (9)	58 (8)	27 (2)	168 (16)	−21 (3)	68 (10)	24 (5)
C10	0.1530 (8)	0.2087 (4)	0.4]38 (9)	109 (10)	16 (2)	206 (17)	−3 (4)	115 (12)	1 (5)

[a] The thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \times 10^{-4}]$.

plexes that is obtained when 2,3-butanedihydrazone is one of the starting materials. Significantly, other bishydrazone ligands, particularly those derived from cyclic α-diketones, have syn-anti arrangements and lead to macrocyclic complexes of C_{2h} symmetry.[8] Because the macrocyclic condensation reaction employing 2,3-butanedione and hydrazine, rather than 2,3-butanedihydrazone, yields the isomeric product III, both anti-anti and syn-anti configurations of the dihydrazone are probably formed in solution prior to further condensation with formaldehyde and subsequent macrocyclic formation.

The mechanisms responsible for the introduction of the double bonds into the six-membered rings of the macrocyclic complexes, giving the dihydrooctaaza[14]annulene complexes of D_{2h} symmetry, were not investigated. However, the very mild conditions that promote the oxidative dehydrogenation of the ligand indicate an electron-transfer process assisted by an unstable oxidation state of the coordinated metal. Participation of cobalt in the ligand oxidation has been implicated in a separate study where the Co(III) complex of I, $[Co(C_{10}H_{20}N_8)(CH_3CN)_2]^{3+}$, was reduced to Co(I) and an oxidized form of the ligand under basic conditions.[9] The isomerization that accompanies the oxidative dehydrogenation of the Cu(II) complex implicates a role for the metal redox process. The most likely oxidation states of Cu participating in the redox reaction are Cu(I) and Cu(II) rather than Cu(II) and Cu(III) because the hydrazone donor atoms stabilize lower valent states. Cu(I), a d^{10} system, has a much larger ionic radius than Cu(II) and is likely to be displaced a significant distance from the plane of the ligand, or yield significantly longer Cu-N bond distances. Rearrangement to the C_{2h} isomer by anti-anti to syn-anti conversion would be facilitated on two counts: the d^{10} configuration of Cu(I) would stabilize α-diimine chelation less than the other metals studied, and the distortion of ligand by the relatively large radius of Cu(I) would provide some of the activation energy required for the isomerization of the hydrazone linkages.

These oxidative dehydrogenation reactions differ in an important respect from those of most other metal-assisted ligand oxidations of tetraaza-macrocyclic metal complexes. Whereas double bonds are normally introduced into positions α to coordinated nitrogen atoms,[10-12] the added double bonds in our system are β to the coordinated nitrogen atoms. The α positions of the bis α-diimine macrocyclic complexes cannot be further oxidized and the oxidation of the C-N linkages in the six-membered rings is facilitated by the relative ease with which the hydrazone N-H's are deprotonated.

Physical Properties. The extent of ligand unsaturation and the identification of the isomeric type of complex were determined with the aid of ^1H NMR, infrared, and mass spectroscopy. The IR spectra of the octaaza[14]annulene complexes contained no absorptions attributable to N-H groups or of ClO_4^- anions present in the starting compounds. The mass spectra gave parent peaks consistent with $M(C_{10}H_{14}N_8)$ molecular species. A very weak peak at 608 amu in the mass spectrum of the Ni(II) complex of D_{2h} symmetry provided the first evidence for the dimeric formulation.

The IR spectra of the two isomers of the Ni(II) complexes were significantly different from one another[13] and also differed appreciably from the Co(III) complexes having D_{2h} symmetry, which have been structurally characterized.[9b] This suggested different valence isomers for the Co(III) and Ni(II) complexes of D_{2h} symmetry. The IR spectrum of the Cu(II) complex was virtually identical with the Ni(II) complex of C_{2h} symmetry; x-ray powder patterns established the isomorphism of the two complexes. Oxidation of the Cu(II) complex with Ce(IV) yielded a diamagnetic Cu(III) species, $[Cu(C_{10}H_{14}N_8)]^+$. The ^1H NMR spectrum of the methyl region of this species had two singlets of equal intensity at 2.43 and 2.75 ppm (δ), further confirming that an isomerization process accompanied ligand oxidation.

Consider now some other properties of the nickel complexes of stoichiometry $Ni(C_{10}H_{14}N_8)$, having C_{2h} symmetry (III) and D_{2h} symmetry (II). The structure with C_{2h} symmetry is a monomer and has a well-defined NMR spectrum: two distinct methyl group resonances appear at 2.16 and 2.36 ppm (δ) and the CH resonance of the five-membered ring appears at 7.09 ppm (δ). The general properties of this complex are consistent with those of other four-coordinate square-planar nickel(II). However, the solid-state spectrum of this complex is appreciably different from its solution spectrum (Table VI; Figure 1). The absorption maxima of the solid-state spectrum appear about 200 Å lower than of the corresponding solution spectra and suggest electronic interaction between adjacent molecules in the solid state. Solid state interactions have been observed and extensively studied in $Ni(dmg)_2$ and other square-planar d^8 systems. These complexes crystallize in a stacked arrangement with close metal-metal contacts (~3.25 Å), which are attributed to metal-metal interactions

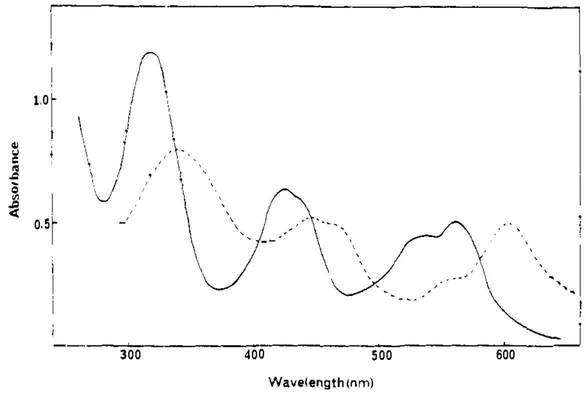


Figure 1. A comparison of the solution and solid-state electronic spectra of [Ni($C_{10}H_{14}N_8$)]: (—) solution spectrum (1.00×10^{-3} M) in $CHCl_3$ with 1-mm cell; (- - - - -) solid state transmittance spectrum taken in hexachlorobutadiene mulls.

Table VI. Electronic Spectra of the [M($C_{10}H_{14}N_8$)] Complexes

Complex	Solvent	Absorption, nm[a]
[Ni($C_{10}H_{14}N_8$)], C_{2h}	CH_3Cl	560 (4.40×10^3), 532 (4.00×10^3), 440 (5.2×10^3, sh), 425 (5.72×10^3), 320 (1.13×10^4)
	Solid state	604, 554, 470, 446, 342.
[Ni($C_{10}H_{14}N_8$)]$_2$, D_{2h}	CH_3Cl	610 (4.4×10^3), 440 (7.0×10^3), 360 (8.9×10^3), 310 (1.16×10^4)
	Solid state	630, 454, 392, 315.
[Cu($C_{10}H_{14}N_8$)], C_{2h}	DMF	407 (8.54×10^3), 386 (8.36×10^3), 335 (7.84×10^3)
	Solid state	424, 400, 340.

[a] Numbers in parentheses are the molar extinction coefficients.

alone.[14-16] The closest Ni–Ni distances in the structure of the C_{2h} isomer are 4.860 Å, and too great for M–M interactions. Thus the solid-state intermolecular interactions are probably either of the M–π (ligand) or π–π ligand nature and not attributable to metal-metal interactions. Similar solution and solid-state spectral characteristics for closely packed molecules having large delocalized electronic systems have been observed.[17]

The dimeric Ni(II) complex is virtually insoluble in all solvents, giving only a faint green color in $CHCl_3$ or CH_2Cl_2. The solution spectra are slightly different from those obtained in the solid state (Figure 2) and suggest extended interactions in the solid state also. Solutions of the complex are unstable and react moderately rapidly with molecular oxygen, decomposing to insoluble undefinable residues. Decomposition also occurs slowly (within hours) in rigorously deoxygenated chlorocarbon solvents, as indicated by irreversible changes in the absorption spectra. The highly insoluble nature of this complex (significantly less soluble than Ni(dmg)$_2$) and the differences of the solution and solid-state spectra suggest the presence of Ni–Ni interaction between dimers in the solid state.

Although the dimeric complex is diamagnetic in the solid state, all samples investigated gave a moderately strong sharp isotropic ESR signal with a half-width of 20 G, $g = 2.001$, which persists over the 77–300 K temperature range. The source of this ESR signal is not understood, but probably is indicative of unpaired spin density delocalized over the ligand π system. It may arise from a small impurity of a 15π-electron cationic species similar in nature to one characterized for a closely related system.[18] It should be noted that a large number of diamagnetic phthalocyanines, including free phthalocyanines, give sharp isotropic signals with $g = 2.0037$.[19]

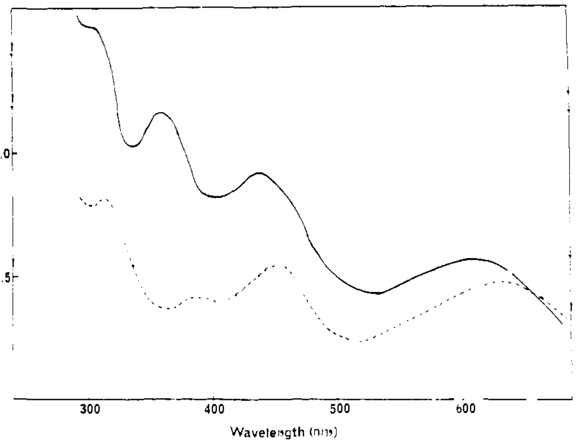


Figure 2. A comparison of the solution and solid-state electronic spectrum of [Ni($C_{10}H_{14}N_8$)$_2$]: (—) solution spectrum taken in $CHCl_3$; (- - - - -) solid-state transmittance spectrum taken in a hexachlorobutadiene mull.

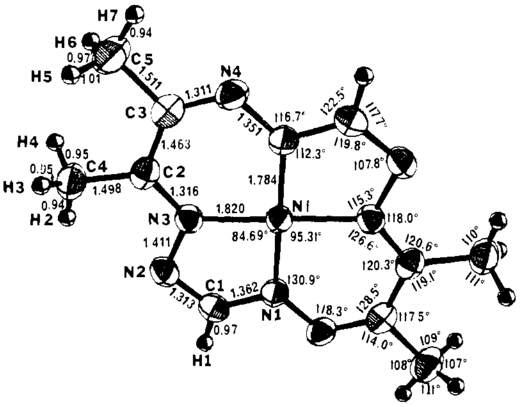


Figure 3. Molecular structure and labeling scheme for [Ni($C_{10}H_{14}N_8$)]. The left side of the drawing shows the bond lengths and the right hand side illustrates selected bond angles. The estimated standard deviations are as follows: Ni–N distances, 0.001 Å; C–C and C–N distances, 0.002–0.003 Å; C–H distances, 0.02 ÅA, angles involving Ni, 0.06°; angles involving nonhydrogen light atoms, 0.1°.

Structure of Ni($C_{10}H_{14}N_8$), the C_{2h} Isomer. The crystal structure of the C_{2h} isomer consists of discreet monomeric units of Ni($C_{10}H_{14}N_8$) containing four-coordinate square-planar Ni(II) packed parallel in the triclinic lattice. The final positional and thermal parameters of the C_{2h} complex are listed in Table IV. The molecular structure and labeling scheme of [Ni($C_{10}H_{14}N_8$)] together with the distances and angles are presented in Figure 3. Several features of this structure are especially noteworthy: (1) The Ni–N distances of 1.784 (1) and 1.820 (1) Å are unusually short, (2) the 16π-electron ligand contains essentially localized double bonds, and (3) the interplanar separation of adjacent molecules is 3.373 Å. Most of these structural details were discussed in a preliminary communication[20] and only those aspects associated with the packing of the molecules will be considered here.

The packing arrangement of the molecules is significant; two perspectives are shown in Figure 4. The molecules of adjacent planes are staggered to minimize the nonbonding interactions and lie parallel to the $10\bar{1}$ plane, giving an interplanar separation of 3.373 Å and a Ni–Ni separation of 4.860

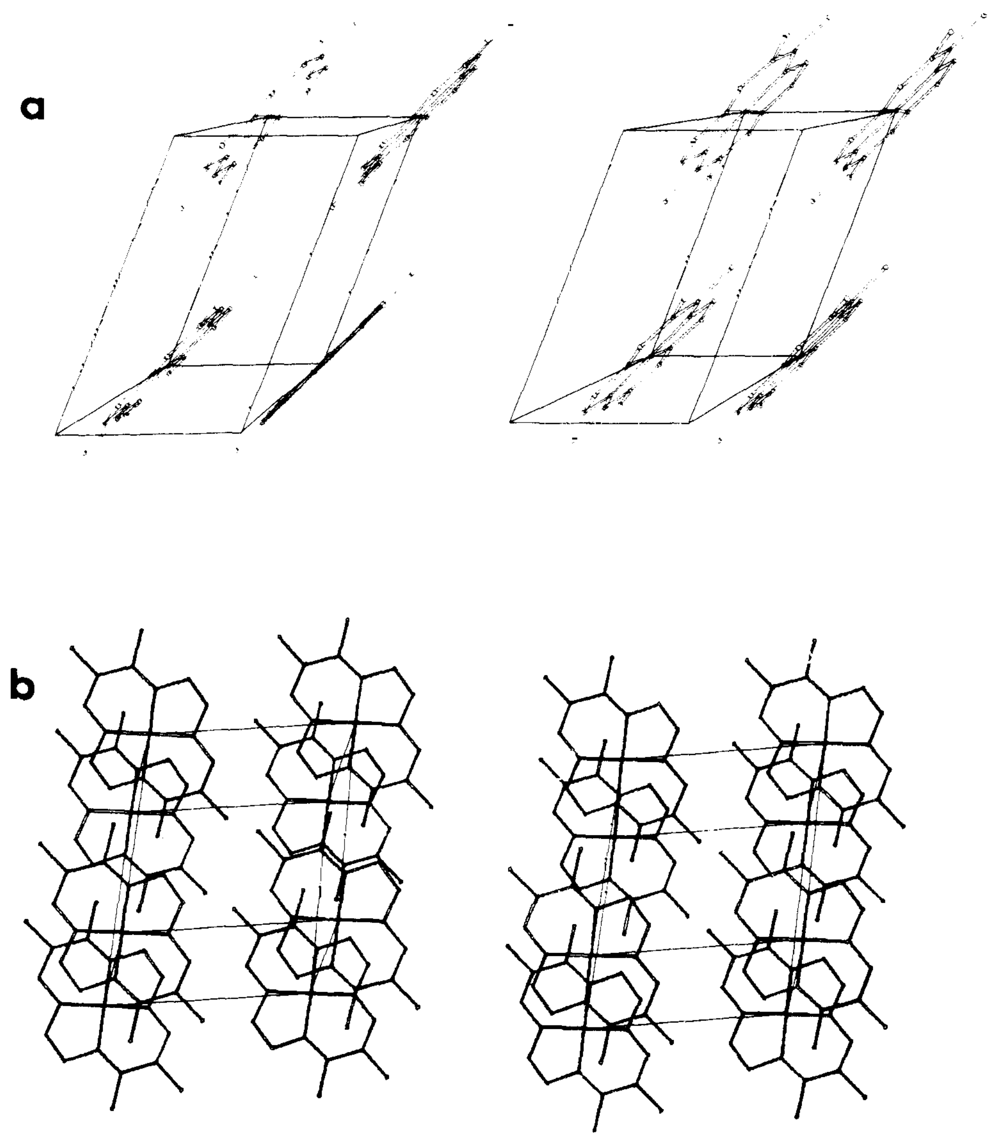


Figure 4. Two stereoscopic views illustrating the packing of the $[Ni(C_{10}H_{14}N_8)]$ molecules in the unit cell: (a) illustrates the parallel arrangement of the molecules in the cell; (b) presents a view perpendicular to the coordination plane and illustrates the staggered arrangement of the atoms in adjacent planes.

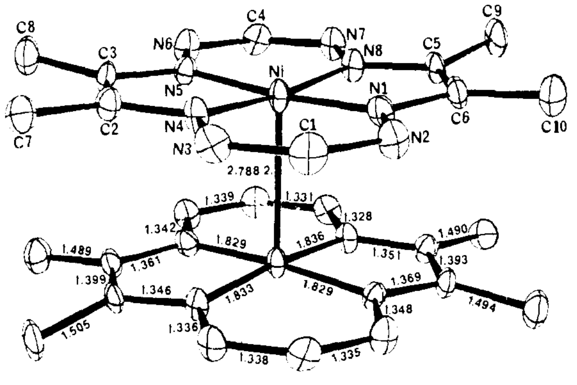


Figure 5. A drawing of the $[Ni(C_{10}H_{14}N_8)]_2$ dimer together with selected interatomic distances. The estimated standard deviations of bond lengths are: Ni–N distances, 0.005 Å; N-N, C–N, and C–C distances, 0.006-0.008 Å.

Å. The interplanar separation, 3.373 Å, is comparable to that of graphite, 3.35 Å.[21] The packing of the molecules bears no similarity to that of $Ni(dmg)_2$.[14] The molecules of $Ni(dmg)_2$ are stacked directly over one another, but are rotated by 90° to minimize nonbonding repulsions of the methyl groups. The Ni-Ni separation of $Ni(dmg)_2$, 3.245 Å, is equivalent to the interplanar separation.

Structure of $[Ni(C_{10}H_{14}N_8)]_2$, a Dimer of D_{2h} Symmetry. The structure of $[Ni(C_{10}H_{14}N_8)]_2$ consists of a dimeric macrocyclic complex containing a Ni-Ni bond with the dimeric units stacked along the *c* direction of the unit cell. The dimer structure and labeling scheme of $[Ni(C_{10}H_{14}N_8)]_2$, together with the bond distances, are presented in Figure 5; the bond angles are listed in Table VII.

A number of unusual features in addition to the Ni-Ni bond warrant emphasis. These are (1) an eclipsed arrangement for the two macrocyclic ligands of the dimer; (2) a very short interplanar separation, 3.00 Å, between the ligands of the dimer; (3) apparent complete delocalization of the double bonds of the macrocyclic ligand; and (4) a stacked arrangement of the dimers, in which the nickel atoms form a chain down the *c* axis of the unit cell. These aspects will now be elaborated upon in detail.

First, the Ni-Ni bond length, 2.788 (2) Å, although comparable to the σ-bond Co–Co distance of 2.794 Å in the $[Co(CN)_5]^{3-}$ dimer,[22] cannot account for all the structural features observed in this dimer molecule (vide infra). A mo-

Table VII. Interatomic Angles (deg) for $[Ni(C_{10}H_{18}N_8)]_2$

Ni′-Ni-Ni″	169.48 (5)	N6-N5-C3	118.5 (6)
Ni′-Ni-N1	93.5 (2)	N5-N6-C4	116.9 (6)
Ni′-Ni-N4	93.2 (2)	N8-N7-C4	117.3 (5)
Ni′-Ni-N5	92.7 (2)	N1-N8-N7	127.6 (4)
Ni′-Ni-N8	93.8 (2)	Ni-N8-C5	113.9 (4)
N1-Ni-N4	94.4 (2)	N7-N8-C5	118.5 (5)
N1-Ni-N5	173.8 (2)	N2-C1-N3	135.3 (6)
N1-Ni-N8	85.1 (2)	N4-C2-C3	113.5 ()
N4-Ni-N5	85.0 (2)	N4-C2-C7	121.6 (6)
N4-Ni-N8	173.0 (2)	C3-C2-C7	124.7 (6)
N5-Ni-N8	94.8 (2)	N5-C3-C2	113.4 (6)
Ni-N1-N2	128.3 (4)	N5-C3-C8	121.2 (6)
Ni-N1-C6	114.2 (4)	C2-C3-C8	125.3 (6)
N2-N1-C6	117.4 (6)	N6-C4-N7	135.3 (6)
N1-N2-C1	116.3 (6)	N8-C5-C6	114.2 (5)
N4-N3-C1	117.8 (5)	N8-C5-C9	120.8 (6)
Ni-N4-N3	127.5 (4)	C6-C5-C9	124.5 (6)
Ni-N4-C2	114.2 (4)	N1-C6-C5	112.7 (6)
N3-N4-C2	118.3 (5)	N1-C6-C10	121.9 (7)
Ni-N5-N6	127.8 (4)	C5-C6-C10	125.3 (6)
Ni-N5-C3	113.8 (4)		

Table VIII. Closest Contacts within Dimer[a] and between Dimers[b]

Within dimers	Å	Between dimers	Å
Ni-Ni′	2.788 (2)	Ni-Ni″	3.800 (3)
N1-N5′	2.985 (7)	N1-N1″	3.508 (12)
N2-N6′	3.024 (10)	N2-C6″	3.410 (10)
N3-N7′	3.018 (9)	N3-C5″	3.479 (9)
N4-N8′	3.011 (8)	N4-N8″	3.606 (8)
C1-C4′	3.002 (12)	N5-N5″	3.707 (12)
C2-C5′	3.132 (11)	N5-C3″	3.637 (10)
C3-C6′	3.146 (11)	N6-C3″	3.615 (10)
C8-C10′	3.454 (12)	N7-C7″	3.581 (10)
C7-C9	3.509 (11)	N7-C2″	3.793 (10)
		C1-C5″	3.453 (11)
		C1-C6″	3.415 (12)
		C1-C9″	3.702 (11)
		C1-C10″	3.696 (12)
		C4-C7″	3.490 (11)
		C4-C2″	3.671 (11)

[a] These atoms are related by center of symmetry which is between the Ni-Ni bond. [b] These atoms are related by a twofold axis approximately parallel to the Ni-N1 bond.

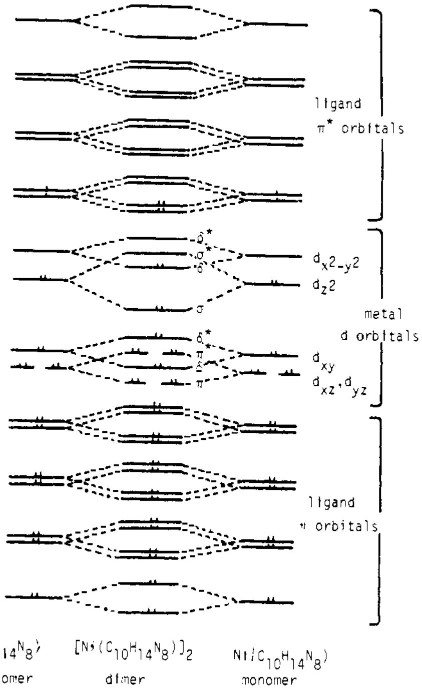


Figure 6. A qualitative molecular orbital diagram accounting for the Ni-Ni bond and the eclipsed ligand conformation. The π orbitals of the ligand have been separated from the metal "d" orbitals for clarity of presentation.

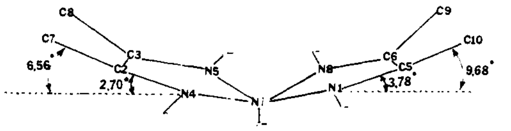


Figure 7. Schematic drawing of a selected fragment illustrating the extent to which the five-membered chelate rings are bent back by the repulsions of the methyl groups in the $[Ni(C_{10}H_{14}N_8)]_2$ dimer.

lecular orbital scheme to account only for the M-M bond in this structure would include orbitals ($d_{x^2-y^2}$) of the proper symmetry for a δ bond as well. Nickel-nickel bonds are not common, although a number have been characterized in recent years. All have bridging N-donor or S-donor ligands with Ni-Ni bond lengths ranging from 2.38 to 2.81 Å.[23-28] The shorter Ni-Ni distances are observed in structures for which nonbonding repulsions of the ligands are minimal and indicate a moderately strong δ bond in addition to the σ bond. The structure most closely related to ours contains a dianionic quadridentate N-donor ligand and has a Ni-Ni bond length of 2.81 Å.[23]

The displacement of the Ni atoms 0.104 Å from the N_4 donor atom plane toward one another indicates a reasonably strong Ni-Ni bond. The bonding between the nickel atoms can be viewed as involving a strong σ bond and a weak δ bond (Figure 6). Upon facial approach of two monomeric units, a splitting of the d_{z^2} and $d_{x^2-y^2}$ orbitals into bonding and antibonding orbitals will occur; occupation of the bonding set by a d^8 electron system results in the aforementioned bond scheme.

The eclipsed arrangement of the macrocyclic ligands of the dimer maximizes rather than minimizes nonbonding interactions between the two ligands. Although highly delocalized systems such as porphyrins, phthalocyanines, chlorophyll, and related systems have attractive π-π interactions leading to aggregation in solution, a staggered arrangement of the atoms minimizing nonbonding repulsions is preferred.[29] Attractive interaction between the two macrocyclic moieties, in addition to a Ni-Ni σ bond, must be present to account for the eclipsed conformation of the dimer units.

The interplanar separation between the least-squares plane defined by the two macrocyclic rings is 3.00 Å. The distances between atoms of the macrocyclic ligands within the dimer having the closest contacts are listed in Table VIII. Obvious nonbonding repulsions of the four methyl groups, as indicated by separation of 3.45 and 3.51 Å for atoms C(8) and C(10)′ and C(7)-C(9)′, respectively, prevent closer approach of the ligands and, to some extent, the Ni atoms. The effect of the repulsive interactions of the methyl groups leads to a slightly saddle-shaped ligand. This is barely noticeable in Figure 5 and schematically illustrated in Figure 7. The planes defined by the four atoms of the five-membered chelate rings are tipped by approximately 3° relative to the N_4 donor plane because of the CH_3 interactions. A list of dihedral angles of various multiple atom defined planes with the N_4 donor atom plane is given in Table IX.

The close interplanar separation cannot be accounted for solely by the Ni-Ni bonding. The 3.00-Å separation between ligands within a dimer is in a modestly repulsive range for

Table IX. Angles between N_4 Donor Atom Plane and Other Selected Planes

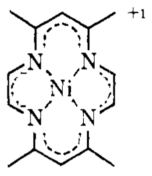
Atoms defining plane	Intersection angle with N_4 plane, deg
N4-C2-C3-N5	2.70
N1-C6-C5-N8	3.78
C7-C2-C3-C8	6.56
C9-C5-C6-C10	9.68
N5-N6-C4-N7-N8	0.38
N4-N3-C1-N2-N1	0.29
N4-Ni-N5	4.60
N1-Ni-N8	4.60

nonbonding interactions.[30] To place the close approach of the two ligands in context, the interplanar distance for graphite is 3.35 Å,[21] but the closest C-C approach is only 3.62 Å because of the staggered arrangement of the carbon atoms of adjacent sheets. The interplanar separation of $[Ni(C_{10}H_{14}N_8)]_2$ is smaller than the interplanar distance of 3.14 Å for tetracyanoquinonedimethane of the TTF-TCNQ metallic conducting compound,[31] or the 3.28-Å separation of the tight donor-acceptor complex formed between perylene and pyromellitic dianhydride.[32] These latter structures also have a staggered arrangement of the atoms of adjacent planes to minimize nonbonding repulsive interactions. To consider an even more extreme case, the distance between the benzene rings of [2.2]paracyclophane is 3.09 Å,[33] for which the strain energy is considerable, 31 kcal/mol.[34] Low-temperature x-ray analyses of that structure revealed a slight twisting of the benzene rings, approximately 6°, to minimize the repulsive interactions.[35]

If the only attractive interaction of the Ni dimer were through the Ni-Ni bonds, the peripheral atoms of the macrocyclic rings should have a larger separation than those more centrally located, e.g., the four-coordinated nitrogen atoms. In fact, the atoms located on the periphery of the six-membered chelate rings, i.e., C(1) and C(4), are separated by 3.02 Å, and not bent away from one another as expected for the repulsive interactions at that distance.

It is therefore proposed that significant bonding interaction exists between the macrocyclic ligands themselves. Figure 6 illustrates a qualitative molecular orbital scheme that accounts for both the metal-metal bonding and close approach of the eclipsed ligands. The octaaza[14]annulene ligands are 16 π-electron systems. Disregarding the fact that a coordinated metal in a heteroatom annulene vitiates using a Huckel MO formulation for annulene ligands, the following analysis can be made. Of the 16π electrons of the octaaza[14]annulene ligand, 14 are in bonding MO's and the remaining two are in π^* orbitals. The facial approach of two monomeric units leads to a splitting of all the π levels, as observed for the π orbitals of the benzene rings in paracyclophane.[36] If antibonding orbitals are occupied, as in the case of the octaaza[14]annulene ligands, the splitting of the antibonding orbitals and population of the lower set would lead to a net stabilization and formation of two weak δ bonds between the macrocyclic ligands. An imperfect analogy of this bonding scheme may be made with the phenomena of eximer formation of aromatic molecules. For example, excitation of pyrene, which has an interplanar separation of 3.53 Å[37] in the crystal, yields an eximer with a binding energy of 9.2 kcal/mol[38] and an equilibrium separation of approximately 3.3 Å.[39]

Holm and co-workers have synthesized very closely related 15π and 16π 14-membered tetraaza-macrocyclic complexes, V, via oxidative dehydrogenation of ethylenediamine derived chelate rings. The cationic 15π system, a very well-characterized complex, exhibits monomer-dimer equilibrium in solution and is diamagnetic in the solid state.[40]



V

15-π system

If the bonding scheme depicted is valid, the following predictions can be made. First, the 15π-electron cationic species, V, will exist as a Ni-Ni dimer in the solid state with an eclipsed ligand configuration, but with a greater ligand-ligand separation than observed in our dimer.[41] Holm's 16π-electron system, [Ni(MeHMe-2,9-diene)], although not as well characterized because of its extreme insolubility, is predicted to be dimeric with a Ni-Ni distance and ligand-ligand separation comparable to those observed in our Ni dimer. The extreme insolubility suggests that Holm's 16π system possesses a stacked structure similar to ours or to that of $Ni(dmg)_2$ with extended lattice interactions. Cobalt(II) complexes of the 16π-electron systems of either the D_{2h} isomer of $C_{10}H_{14}N_8{}^{2-}$ or of Holm's (MeHMe-2,9-diene) ligand are predicted to be dimers having a Co-Co bond and eclipsed ligand configurations.

The proposed bonding scheme removes much of the antibonding character from the two π^* electrons of each ligand and transforms the octaaza[14]annulene ligand from a 16-π "antiaromatic" system toward a 14-π aromatic one. This provides rationalization for the extensive delocalization observed in the ligands of the dimer. The average C-C and C-N distances in the five-membered rings, 1.396 and 1.357 Å, are very close to the accepted C-C distances of benzene and the aromatic C-N distance of pyridine, 1.35 Å. The N-N and C-N distances of the six-membered chelate rings are also intermediate between those expected for single and double bonds. This degree of delocalization is much more extensive than that observed in the Ni C_{2h} structure, III and Figure 3, which has an alternating double-bond arrangement and in the Co(III) structure.[9] The unsaturation in the latter complex is limited to discreet α-diimine functions of the five-membered chelate rings and to a three-atom N-C-N allylic type system isolated by single N-N bonds of the six-membered chelate ring.

The N-C-N angles of the six-membered chelate rings reflect the differences in double-bond character. For the allylic-type system of the Co(III) complex, the angles are unusually wide, 140.0 (2)°,[9] and decrease to 135.3 (6)° in the dimeric Ni(II) complex. When the N-C-N linkage is incorporated into a five-membered chelate ring, as in the Ni(II) complex of C_{2h} symmetry, the angle decreases to 119.8 (1)°. The changes occurring in the N-C-N angles are reflected in the adjacent N-N-C angles, which have an average value of 115.6° in the Co(III) complex and 117.1° for the dimeric Ni complex. The angle of the N-N-C linkage decreases markedly to 107.8 (1)° when incorporated into a five-membered ring of the Ni(II) C_{2h} isomer.

The average Ni-N distance for the dimer, 1.832 (5) Å, is shorter than normal, but still longer than observed in the C_{2h} monomeric isomer for which the Ni-N distance, 1.781 (1) Å, is the shortest reported Ni-N (amine) distance. The Ni-N distances in both these structures are significantly shorter than the average Co(III)-N distances, 1.866 (2) Å, of the same macrocyclic ligand.[9]

The packing arrangement of the dimer molecules (Figure 8) is significant. The adjacent dimers are related by a crystallographic twofold axis passing between the dimer molecules, and are stacked along the *c* unit cell direction. The closest contacts between dimer molecules are listed in Table VIII, with the shortest distances, 3.41 Å, corresponding to normal van der

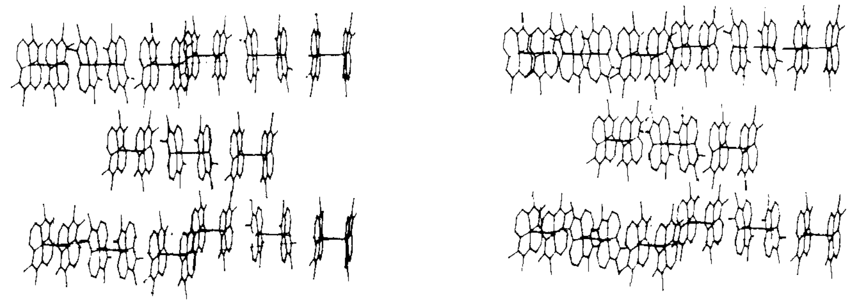


Figure 8. A stereoscopic view of the unit cell contents of $[Ni(C_{10}H_{14}N_8)]_2$ illustrating the stacked nature of the dimers.

Waals separations for structures of this type. The separation between Ni atoms of adjacent dimer molecules is 3.800 Å. Movement of the Ni atoms within a dimer by only 0.50 Å from each other would lead to a new dimer with equivalent Ni–Ni distance, but with the macrocyclic ligands rotated by 90° with respect to one another. In the absence of δ bonding and attractive ligand–ligand interaction, this latter arrangement appears to be more favorable because repulsive interactions within the dimer would be minimized. The stacked nature of the structure and possible attractive interaction between dimers analogous to that for $Ni(dmg)_2$ may account for the extreme insolubility of the complex.

Heretofore, it has been assumed that the structure consist of Ni(II) and dianionic ligands. The possibility of intramolecular electron transfer between Ni(II) and the macrocyclic ligand to give an electronic arrangement other than a formal Ni(II)–16π-electron system has been considered. The following combinations of Ni oxidation state and π electrons yield a neutral molecule: Ni(III)–17π electrons, Ni(I)–15π electrons, and Ni(0)–14π-electrons. The Ni(III)–17π-electrons is unreasonable for a number of reasons. It is unlikely that a species containing Ni(III) coordinated to four hydrazine linkages would have long term stability, or be oxygen sensitive. The charge separation between the metal and the highly conjugated ligand is also unlikely. The resultant d^7 system, while capable of forming a Ni–Ni bond, would not have the potential for δ-bond formation, as required to account for the eclipsed ligand arrangement.

The Ni(I)–15π-electron scheme can be eliminated, since the resulting d^9 configuration for Ni would place a single electron in the $d_{x^2-y^2}$ orbital. Although a weak δ interaction might be possible, it would be much too weak to overcome the repulsive ligand–ligand interactions produced from a 3.00-Å interplanar separation. Even in the $[Cu(OAc)_2 \cdot H_2O]_2$ dimer, where the Cu–Cu distance is 2.64 Å,[42,43] only partial electron pairing occurs at room temperature, $\mu_{eff} = 1.4\ \mu_B$, with the first excited triplet, $^3B_{1g}$, lying some 300 cm^{-1} above the ground state, $^1A_{1g}$.[44] The Ni(0)–14π-electron distribution, while consistent with the "aromatic" type delocalization observed in the ligand, would not account for the Ni–Ni bond and the close distance between the ligands. The radius associated with Ni(0) is expected to be significantly larger than for Ni(II) and should be reflected in longer Ni–N distances than observed or to a greater displacement of the metal from the plane of the ligand than observed.

The vexing question as to why the $Ni(C_{10}H_{14}N_8)$ complex of D_{2h} symmetry forms a dimer, whereas the isomeric C_{2h} complex is monomeric, remains. It would appear that the different tendencies towards dimer formation are related to the charge distribution within the complex. For the C_{2h} structures, the negative charges of the ligand are primarily localized on the nitrogen atoms coordinated to the metal, whereas for the D_{2h} monomeric structure, e.g., $[Co(C_{10}H_{14}N_8)(CH_3)(NH_2NHCH_3)]$, the negative charges are delocalized over three atom linkages removed several angstroms from the metal center.[9] For the C_{2h} structures, the Coulombic attraction between the dipositive metal and the negative charges on the adjacent nitrogen atoms will alter the energy levels of Figure 6, particularly the π^* levels, such that the net bonding interactions between the ligands may be effectively eliminated.

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Supplementary Material Available: A list of structure factor amplitudes and coordinates of the hydrogen atoms used in the structural refinement and the infrared spectra of the isomeric octaaza[14]annulene complexes (14 pages). Ordering information is given on any current masthead page. Note: The structure factor amplitudes of $Ni(C_{10}H_{14}N_8)$ monomer, C_{2h} isomer, were published previously in the microfilm version of *J. Am. Chem. Soc.*, **95**, 5773 (1973).

References and Notes

(1) J. L. Hoard, *Science*, **174**, 1295 (1971); E. B. Fleischer, *Acc. Chem. Res.*, **3**, 105 (1970).

(2) V. L. Goedken and S.-M. Peng, *J. Chem. Soc., Chem. Commun.*, 62 (1973). Full details of the synthesis and properties of these complexes will be published elsewhere, submitted for publication.

(3) B. Chiswell and F. Lions, *Inorg. Chem.*, **3**, 490 (1964); F. Lions and D. V. Martin, *J. Am. Chem. Soc.*, **80**, 3858 (1958); J. F. Geldard and F. Lions, *ibid.*, **84**, 2262 (1962); *Inorg. Chem.*, **2**, 270 (1963).

(4) O. A. Gansow, R. J. Olcott, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 5470 (1967).

(5) N. A. Bailey, T. A. James, J. A. McCleverty, E. D. McKenzie, R. D. Moore, and J. M. Worthington, *J. Chem. Soc., Chem. Commun.*, 681 (1972).

(6) (a) D. H. Busch and J. C. Bailar, *J. Am. Chem. Soc.*, **78**, 1137 (1956). (b) The incompletely oxidized species, $[Ni(C_{10}H_{16}N_8)]$, was erroneously reported as being an isomer of $[Ni(C_{10}H_{14}N_8)]$ having C_s symmetry in preliminary communications (ref 2 and V. Goedken and S.-M. Peng, *Adv. Chem. Ser.*, **No. 150** (1976)). The mass spectrum of $[Ni(C_{10}H_{16}N_8)]$ yields a parent peak corresponding to that expected for $[Ni(C_{10}H_{14}N_8)]$. The facile conversion of $[Ni(C_{10}H_{16}N_8)]$ to the isomer of $[Ni(C_{10}H_{14}N_8)]$ having C_{2h} symmetry was initially interpreted as syn–anti isomerization rather than a redox process.

(7) The raw data were reduced to intensities (I) and estimated errors (σ_I) using

$$I = S - [(t_s/2t_B)(B_1 + B_2)]$$

where S = peak scan counts, B_1, B_2 = background counts at each end of the scan, t_s, t_B = peak and background scan time, and

$$\sigma_I = [S + [(t_s,2t_B)^2(B_1 + B_2)] + K^2(S + [(t_s/2t_B)(B_1 + B_2)])^2]^{1/2}$$

where K = instability constant (0.02). The I's and σ_I's were converted to relative structure factors (F) and estimated errors (σ) using

$$F = (I/\mathrm{Lp})^{1/2}$$

$$\sigma = [I + \sigma_I/\mathrm{Lp}]^{1/2} - (I/\mathrm{Lp})^{1/2}$$

where Lp are Lorentz and polarization factors

$$1/\mathrm{Lp} = \frac{-(\sin 2\theta)(1 + \cos^2 2\theta_m)}{(\cos^2 2\theta + \cos^2 2\theta_m)}$$

where θ_m = Bragg angle. Computations were performed by IBM 360 or 370 computer with the aid of the following programs: Zalkin's FORDAP Fourier program, Busing and Levy's ORFFE function and error program, and Ibers NUCLS least-squares program. Plots of the structures were drawn with the aid of C. K. Johnson's ORTEP. Neutral atom scattering factors were taken from D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968); hydrogen atom scattering factors were taken from "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962. Anomalous scattering corrections were applied to heavy atoms and were taken from D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(8) Very similar complexes having the C_{2h}, syn–anti α-diimine structure have been prepared by first preparing the free ligand by the condensation of other α-diketones with ortho esters: J. E. Baldwin, R. H. Holm, R. W. Harper, J. Huff, S. Koch, and T. J. Truex, *Inorg. Nucl. Chem. Lett.*, **8**, 393 (1972).
(9) (a) V. L. Goedken and S. M. Peng, *J. Chem. Soc., Chem. Commun.*, 914 (1974); (b) *ibid.*, 258 (1975).
(10) N. F. Curtis, *Chem. Commun.*, 881 (1966).
(11) V. L. Goedken and D. H. Busch, *J. Am. Chem. Soc.*, **94**, 7355 (1972).
(12) E. K. Barefield and D. H. Busch, *Inorg. Chem.*, **10**, 108 (1971).
(13) The infrared spectra have been deposited in the microfilm addition, see paragraph at the end of the paper regarding supplementary material.
(14) L. E. Godycki and R. E. Rundle, *Acta Crystallogr.*, **6**, 487 (1953).
(15) G. Basu, G. M. Cook, and R. L. Belford, *Inorg. Chem.*, **3**, 1361 (1964).
(16) L. V. Interrante, Ed., "Extended Interactions Between Metal Ions in Transition Metal Complexes", No. 5, American Chemical Society Symposium Series, Washington, D.C., 1974.
(17) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, N.Y., 1970, p 525.
(18) T. J. Truex and R. H. Holm, *J. Am. Chem. Soc.*, **94**, 4529 (1972).
(19) R. Neiman and D. Kivelson, *J. Chem. Phys.*, **35**, 161 (1961).
(20) V. L. Goedken and S. M. Peng, *J. Am. Chem. Soc.*, **95**, 5773 (1973).
(21) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Wiley-Interscience, New York, N.Y., 1972, p 288.
(22) L. Brown, K. Raymond, and S. Goldberg, *J. Am. Chem. Soc.*, **94**, 7664 (1972); G. Simon, A. Adamson, and L. Dahl, *ibid.*, **94**, 7654 (1972).
(23) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 697 (1969).
(24) O. Jarcow, H. Schultz, and R. Nast, *Angew. Chem.*, **82**, 43 (1970).
(25) M. Corbett and B. Hoskins, *Chem. Commun.*, 1602 (1969).
(26) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 1106 (1969).
(27) N. Bailey, T. James, J. McCleverty, E. McKenzie, R. Moore, and Worthington, *J. Chem. Soc., Chem. Commun.*, 681 (1972).
(28) L. Sacconi, C. Mealli, and D. Gatteschi, *Inorg. Chem.*, **13**, 1985 (1974).
(29) J. J. Katz and J. R. Norris, *Curr. Top. Bioenerg.*, **5**, 41 (1973); T. M. Cotton, A. D. Trifunac, K. Ballschmiter, and J. J. Katz, *Biochim. Biophys. Acta*, **368**, 181 (1974).
(30) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.*, **19**, 531 (1968).
(31) T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 471 (1973).
(32) J. C. Boyens and F. H. Herbstein, *J. Phys. Chem.*, **69**, 2160 (1965).
(33) C. J. Brown, *J. Chem. Soc.*, 3265 (1953).
(34) R. H. Boyd, *Tetrahedron*, **22**, 119 (1966).
(35) K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. R. Soc. London, Ser. A*, **255**, 82 (1960).
(36) R. Gleiter, *Tetrahedron Lett.*, 4453 (1969).
(37) Reference 17, p 317.
(38) J. B. Birks, M. D. Lumb, and I. H. Munro, *Proc. R. Soc. London, Ser. A*, **280**, 289 (1964).
(39) J. B. Birks and A. A. Kazzaz, *Proc. R. Soc. London, Ser. A.*, **304**, 291 (1968).
(40) M. Millar and R. H. Holm, *J. Am. Chem. Soc.*, **97**, 6052 (1975).
(41) The crystal structure of this compound has recently been determined and found to consist of an eclipsed cofacial dimer very similar to ours, but with a slightly greater Ni–Ni and ligand–ligand separation. S.-M. Peng, R. H. Holm, M. Millar, and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 8037 (1976).
(42) E. L. Sutton, *Chem. Soc., Spec. Publ.*, **No. 11**, 1 (1958).
(43) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1953).
(44) B. Bleany and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

Photochemical Generation of Stable *o*-Xylylene Derivatives by the Electrocyclic Ring Opening of Some Polycyclic Benzocyclobutene Derivatives

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Abstract: Simple substituted derivatives of *o*-xylylene **1** which are stable and characterizable in fluid solution at room temperature in the absence of oxygen are generated by the irradiation of the polycyclic benzocyclobutenes **2b**, **3b**, and **12** in 3-methylpentane glass (77 K). The photochemical ring opening requires rigid media and may involve a successive absorption of two photons by the starting materials. The similarity of the UV and emission spectra of **5b**, in which the chromophore is restricted to coplanarity, with those of the parent *o*-xylylene **1** suggests that **1** is close to planar. The regular vibrational progression of ca. 1500 cm^{-1} seen in the absorption spectrum of **5b** indicates a general increase in the lengths of the C=C bonds in the excited state. While **5b** shows no tendency to thermally reclose upon standing at room temperature, irradiation at 350 nm either in rigid media or in fluid solution leads to a rapid nonstereospecific reclosure to regenerate the benzocyclobutene derivatives **2b** and **3b**.

Introduction

The nature of the electronic states of *o*-xylylene (*o*-quinodimethane, **1**) coupled with the high chemical reactivity of the parent and its simple derivatives continues to attract considerable attention.[2,14] In the present paper, we report the preparation and characterization of some simple polycyclic derivatives of *o*-xylylene by photolysis of the corresponding benzocyclobutene derivatives. The cyclic substituents: (1) provide structural rigidity to facilitate spectral analysis, (2) prevent the thermal reclosure of the corresponding benzocyclobutene derivative by a symmetry preferred conrotatory process,[3] and (3) inhibit dimerization by sterically hindering both faces of the reactive *o*-xylylene moiety. The electrocyclic photochemical reactions employed are mechanistically intriguing in that they proceed in rigid but not in fluid solution and may involve a stepwise two-photon process.

Results

The unsaturated endo derivative **2a** was prepared as described by Nenitzescu.[4] Consistent with the assigned endo geometry was the observed doublet ($J = 3.5$ Hz) for the protons H_a in the NMR.[5] The saturated derivative **2b** was easily produced by hydrogenation of **2a** over PtO_2. The unsaturated exo derivative **3a**[6] was the major product of the in situ reaction of benzyne generated from *o*-bromofluorobenzene with norbornadiene. The NMR spectrum of **3a** showed the corresponding protons H_b at τ 6.88 (vs. 6.34 for H_a in **2a**) as a slightly broadened singlet. The saturated exo derivative **3b** was again produced by catalytic hydrogenation.

Preliminary indications that **2** and **3** are precursors to the rigid, strained *o*-xylylenes **5** come from thermolysis experiments. For example, gas-phase pyrolysis of either **2a** or **3a** leads to the isolation of the same tetracyclic adduct **4** in good yield.[7]