

Transition-Metal Complexes of Superstructured Cyclidene Macrobicycles: Structural Features and Their Chemical Consequences. 1. Complexes of the Unbridged Cyclidene Ligands and of Precursor Ligands

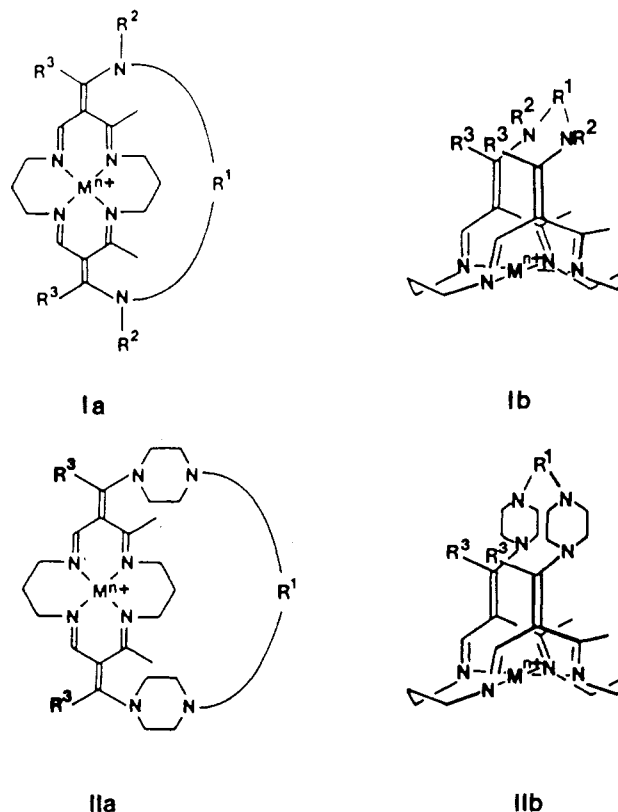
Nathaniel W. Alcock,*† Wang-Kan Lin,† Alan Jircitano,† James D. Mokren,† P. W. R. Corfield,†§ Gordon Johnson,†|| George Novotnak,† Colin Cairns,† and Daryle H. Busch*†

Received March 27, 1986

The cyclidene macrocycle is particularly favorable for (a) the attachment of superstructures and (b) the promotion of dioxygen adduct formation by iron(II) and cobalt(II). Consequently, a number of families of cyclidene derivatives have been developed, including synthetic *lacunar* dioxygen carriers and *vaulted* hosts for inclusion complexation. As the initial phase of full structural characterization of these families of complexes, the syntheses and X-ray structures of seven unbridged complexes are reported and analyzed here. The structures of five of these unbridged complexes show the saddle conformation that is critical to the bridging reaction which produces the cavities in the lacunar and vaulted complexes. Four of these complexes contain the 16-membered parent cyclidene ring while the fifth has a 15-membered ring. The driving force for adoption of the saddle shape is identified with the favored boat and chair conformations of the saturated 6-membered chelate rings. In turn, this causes the unsaturated rings to be thrust upward on the same side of the N_4 coordination plane. Additional boat-shaped distortion of the unsaturated rings is correlated with the π -electron distribution, as revealed by bond lengths. This distribution is strongly influenced by substituents, but it does not closely reflect the formal bond pattern or the net charge. The remaining two structures contain 14-membered and 15-membered cyclidene rings. The 14-membered ring derivative is essentially planar, the only substantial deviations being due to substituents and the skew conformations of the saturated 5-membered chelate rings. In the final structure, the saddle is converted into a Z-conformation by folding one of the unsaturated rings from above to below the N_4 plane. This converts the saturated 6-membered ring into a skew conformation. Both this Z-form and the planar structure are ill-suited to bridge formation. Crystal data: compound 1, $C_{17}H_{24}N_4O_2Ni \cdot 0.5C_3H_5N$, triclinic, $P\bar{1}$, $a = 7.824$ (2) Å, $b = 10.538$ (3) Å, $c = 14.283$ (4) Å, $\alpha = 115.84$ (1)°, $\beta = 112.81$ (2)°, $\gamma = 85.79$ (2)°, $Z = 2$; compound 2, $C_{20}H_{30}N_4O_2Ni$, orthorhombic, $Pnma$, $a = 12.055$ (2) Å, $b = 15.701$ (3) Å, $c = 10.650$ (2) Å, $Z = 4$; compound 3, $C_{18}H_{20}N_4O_2Cl_2Ni$, triclinic, $P\bar{1}$, $a = 10.013$ (1) Å, $b = 11.935$ (2) Å, $c = 11.613$ (2) Å, $\alpha = 108.52$ (1)°, $\beta = 101.18$ (1)°, $\gamma = 103.12$ (1)°, $Z = 2$; compound 4, $C_{16}H_{22}N_4O_2Ni$, monoclinic, $P2_1/n$, $a = 5.253$ (1) Å, $b = 18.047$ (5) Å, $c = 8.682$ (2) Å, $\beta = 107.56$ (2)°, $Z = 2$; compound 5, $C_{19}H_{30}N_4O_10Cl_2Ni$, orthorhombic, $Pbcm$, $a = 8.257$ (7) Å, $b = 13.940$ (11) Å, $c = 22.108$ (14) Å, $Z = 4$; compound 6, $C_{20}H_{34}N_6P_2F_{12}Cu$, monoclinic, $P2_1/m$, $a = 10.480$ (2) Å, $b = 12.148$ (2) Å, $c = 11.958$ (3) Å, $\beta = 91.37$ (2)°, $Z = 2$; compound 7, $C_{34}H_{54}N_{10}P_2F_{12}Cu$, triclinic, $P\bar{1}$, $a = 13.922$ (2) Å, $b = 14.654$ (3) Å, $c = 11.674$ (2) Å, $\alpha = 98.98$ (2)°, $\beta = 104.68$ (1)°, $\gamma = 95.92$ (2)°, $Z = 2$.

Introduction

The macrobicyclic families of cyclidene derivatives produce fascinating complexes having a broad range of structures and functions.¹ The lacunar complexes (structures Ia and Ib) contain small cavities well-suited to binding dioxygen or other small ligands.²⁻⁶ The vaulted complexes (structures IIa and IIb) were designed to participate in host-guest complex formation with organic molecules that might serve as substrates in monooxygenase models.⁷⁻¹¹ These capabilities have been combined to produce the first credible models for the ternary complexes of cytochrome P450, and promoted oxygenations of substrates have been demonstrated.¹² Naturally, the various effects and interactions are strongly dependent on cavity geometry.^{2-6,8-11} In addition, the ring closure reactions leading to formation of the permanent cavities in the lacunar and vaulted species are remarkably facile.¹³⁻¹⁹ The presence of the dominant saddle conformation in the precursor to the crucial ring closure is believed to strongly favor that process, especially as compared to ring closures spanning distant points on such flat structures as porphyrins. This is the initial report in a detailed exploration of the structural foundations for the chemistry of the cyclidene families of compounds. Cavity dimensions and shape, the character of the cavity, and the mutual interactions of the superstructure and its substituents are of principal concern. Here we concentrate on the cyclidene unit itself (structure III).



* To whom correspondence should be addressed.

† University of Warwick.

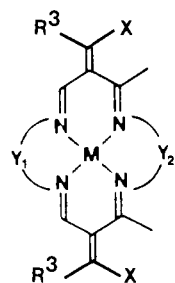
‡ Ohio State University.

§ Chemistry Department, The King's College, Briarcliff Manor, NY 10510.

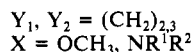
|| Chemistry Department, Kenyon College, Gambier, OH 43022.

(1) Busch, D. H. *Pure Appl. Chem.* **1980**, *52*, 2477.

(2) Stevens, J. C.; Jackson, P. J.; Schammel, W. P.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3283.



III



Compounds

Seven compounds are considered in this paper, and these represent three general classes, which correspond to successive stages in the synthesis of the cyclidene macrocycles, not including the final formation of the vault or lacuna. The first group, (IV, compounds 1–4 in Scheme I) are starting materials, the macrocyclic complexes first reported by Jäger.^{20,21} The charge on the Ni^{2+} ion in these complexes is balanced by the delocalized charges on the ring, resulting in neutral molecules. These Jäger complexes are closer in structure and chemical nature to the cyclidenes (compounds V–XII) than appears from Scheme I, and it is useful to view them as doubly deprotonated hydroxy-cyclidenes. The structural parameters discussed here demonstrate this relationship. The four examples of this class vary principally in the saturated polymethylene linkages, forming 14-, 15-, and 16-membered macrocyclic ligands. In the case of compound 2, the central carbon of one 6-membered saturated chelate ring bears two methyl substituents.

As shown in Scheme I, methylation of a complex from the first group produces one of the second group, the methoxy-cyclidenes (V), for which one structure is available (compound 5). Finally, the methoxy-cyclidenes may be converted into amino-cyclidenes by reaction with primary or secondary amines. Simple amines give unbridged species (VI), while diamines generate lacunar amino-cyclidene complexes (structure VII). The structures of two unbridged amino-cyclidene complexes have been determined (compounds 6 and 7).

Preparative details are provided for those species that have not previously been reported, though the main emphasis in this paper is on their structures. The syntheses generally follow earlier procedures. However, these have been considerably improved with experience, and the preparation of compound 3 is described in detail to illustrate current practice. The unusual difficulties found with compound 7 should also be noted. It was prepared in two stages, initially by using methylamine to generate the unbridged amino-cyclidene ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{CH}_3$). This intermediate then reacted with a pyrazolyl tosylate under strongly basic conditions to give compound 7.

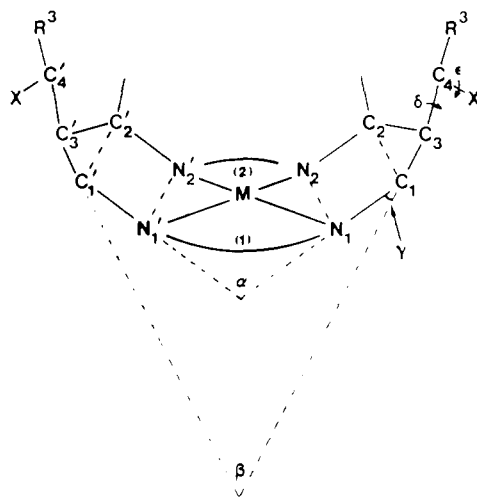
Structural Relationships

The crucial structural observation is immediately obvious from the views of the compounds seen in Figures 1–3. With only two exceptions (compounds 1 and 4, Figure 2), these complexes adopt saddle-shaped conformations, making them well-suited for the formation of lacunar and vaulted complexes by bridging across the crevice. If only the structures of the lacunar complexes were known, their saddle conformation might be attributed to steric stress associated with the bicyclic structures. However, the presence of saddle forms in the unbridged complexes shows unequivocally that this is the preferred conformation.

The crystal packings of these compounds show no dramatic features and have not been studied in detail. Compounds 2, 5, and 6 lie on crystallographic mirror planes, while 4 possesses a center of symmetry.

Dimensions. Table I summarizes a variety of structural parameters that allow detailed comparison of the structures (see structure VIII for a key to the parameters and the generic atom labels). All of the compounds have the four coordinating nitrogen

- (3) Stevens, J. C.; Busch, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 3285.
- (4) Busch, D. H.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Cristoph, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *78*, 5919.
- (5) Herron, N.; Cameron, J. H.; Neer, G. L.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 298.
- (6) Herron, N.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Cameron, J. H.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 6585.
- (7) Takeuchi, K. J.; Busch, D. H.; Alcock, N. *J. Am. Chem. Soc.* **1981**, *103*, 2421.
- (8) Takeuchi, K. J.; Busch, D. H.; Alcock, N. *J. Am. Chem. Soc.* **1983**, *105*, 4261.
- (9) Takeuchi, K. J.; Busch, D. H. *J. Am. Chem. Soc.* **1983**, *105*, 6812.
- (10) Kwik, W.-L.; Herron, N.; Takeuchi, K.; Busch, D. H. *J. Chem. Soc., Chem. Commun.* **1983**, 409.
- (11) Meade, T. J.; Kwik, W.-L.; Herron, N.; Alcock, N. W.; Busch, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 1954.
- (12) Meade, T. J.; Takeuchi, K. J.; Busch, D. H., submitted for publication. Coltrain, B. K. Ph.D. Thesis, The Ohio State University, 1985.
- (13) Schammel, W. P.; Mertes, K. S. B.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1979**, *101*, 1622.
- (14) Schammel, W. P.; Zimmer, L. L.; Busch, D. H. *Inorg. Chem.* **1980**, *19*, 3159.
- (15) Busch, D. H.; Olszanski, D. J.; Stevens, J. C.; Schammel, W. P.; Kojima, M.; Herron, N.; Zimmer, L. L.; Holter, K. A.; Mocak, J. *J. Am. Chem. Soc.* **1981**, *103*, 1472.
- (16) Busch, D. H.; Christoph, G. G.; Zimmer, L. L.; Jackels, S. C.; Grzybowski, J. J.; Callahan, R. W.; Kojima, M.; Holter, K. A.; Mocak, J.; Herron, N.; Chavan, M.; Schammel, W. P. *J. Am. Chem. Soc.* **1981**, *103*, 5107.
- (17) Busch, D. H.; Jackels, S. C.; Callahan, R. W.; Grzybowski, J. J.; Zimmer, L. L.; Kojima, M.; Olszanski, D. J.; Schammel, W. P.; Stevens, J. C.; Holter, K. A.; Mocak, J. *Inorg. Chem.* **1981**, *20*, 2834.
- (18) Korybut-Daszkiwicz, B.; Kojima, M.; Cameron, J. H.; Herron, N.; Chavan, M. Y.; Jircitano, A. J.; Coltrain, B. K.; Neer, G. L.; Alcock, N. W.; Busch, D. H. *Inorg. Chem.* **1984**, *23*, 903.
- (19) Herron, N.; Chavan, M. Y.; Busch, D. H. *J. Chem. Soc., Dalton Trans.* **1984**, 1491.
- (20) Jäger, E. Z. *Anorg. Allg. Chem.* **1966**, *346*, 76.
- (21) Jäger, E. Z. *Anorg. Allg. Chem.* **1968**, *8(30)*, 392.

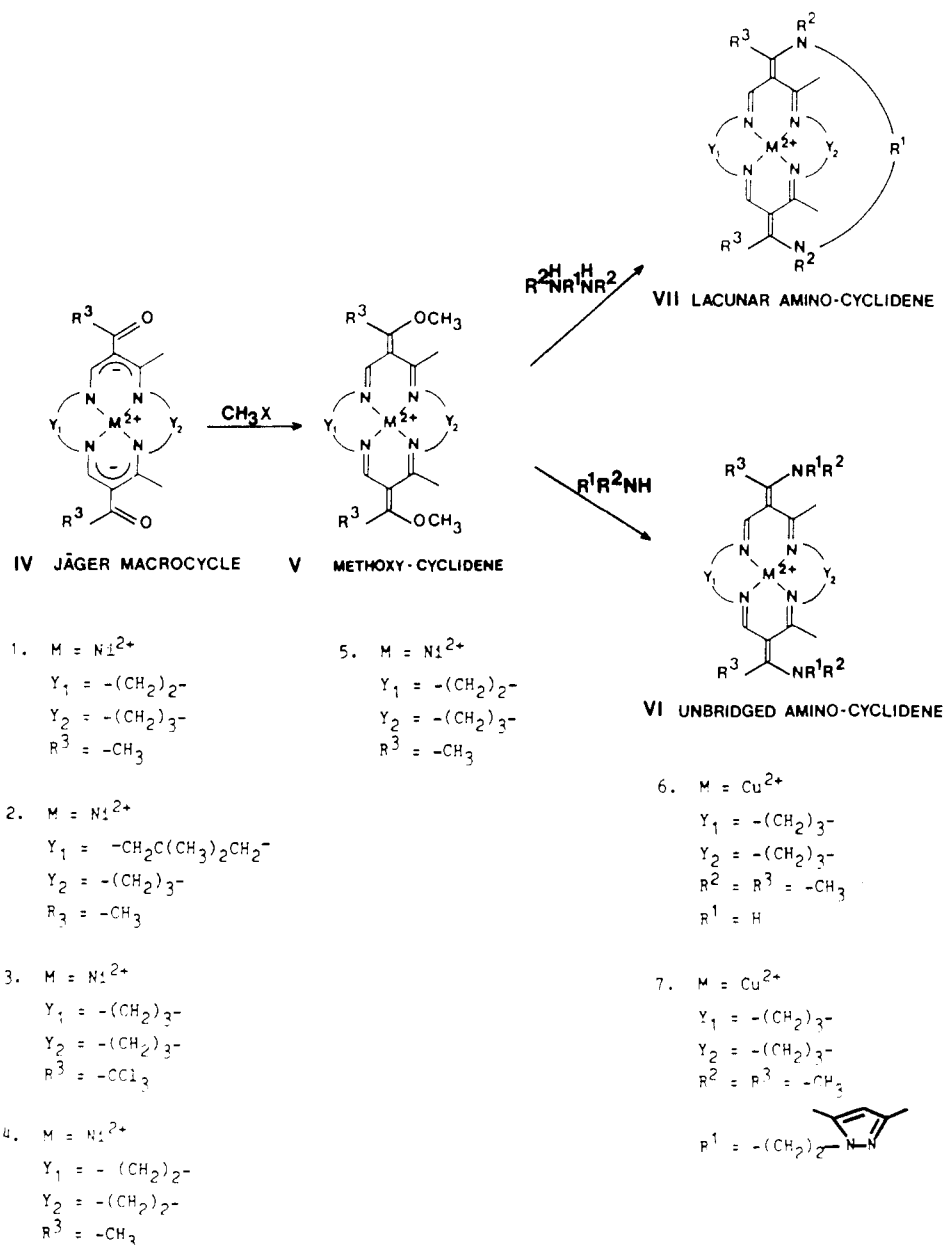


VIII

key to parameters and atom identification: α , angle between equivalent $\{\text{N}_1\text{N}_2\text{C}_1\text{C}_3\}$ planes; β , angle between equivalent $\{\text{C}_1\text{C}_2\text{C}_3\}$ planes; γ , angle between $\{\text{N}_1\text{N}_2\text{C}_1\text{C}_2\}$ and $\{\text{C}_1\text{C}_2\text{C}_3\}$ planes ($=0.5(\beta - \alpha)$); dihedral angle δ , bond $\text{C}_3\text{--C}_4$; dihedral angle ϵ , bond $\text{C}_4\text{--X}$

atoms coplanar, with the metal atoms virtually in the plane (maximum deviation 0.09 Å). The Cu–N distances are slightly greater than the Ni–N distances, as expected for d^9 and d^8 electronic configurations. The lengths of the bonds in the unsaturated chelate ring ($\text{M--N}_1\text{--C}_1\text{--C}_3\text{--C}_2\text{--N}_2$) and to the attached

Scheme I

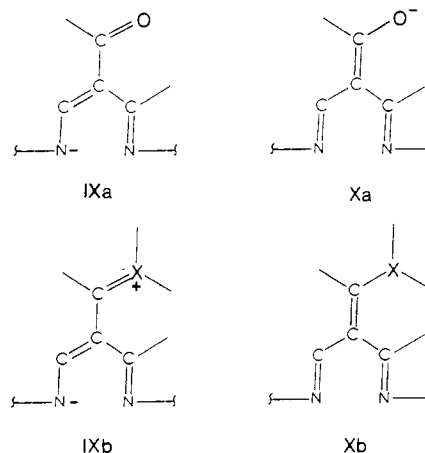


atoms (C₃-C₄ and C₄-X) show irregularities that are surprising at first. However, they can be understood when it is recognized that the formal bonding representations usually used for the cyclidene structure actually conceal significant charge delocalization.

The canonical forms shown in structures IX and X contribute to comparable extents in all seven of the compounds whose structures are reported here, irrespective of whether they are charged (IXa and Xa) or neutral (IXb and Xb). The N₁-C₁ and N₂-C₂ distances are similar in all seven compounds, and their values indicate considerable double-bond character (cf.: typical N-C single bond, 1.48 Å; typical N=C double bond, 1.27 Å). The C₁ (or C₂)-C₃ distances are also shorter than single C-C bonds; they show a slight variation (considered below). The C₃-C₄ (noncyclic) bond lengths also vary somewhat. That in the methoxy-cyclidene complex is the shortest, while the longest bonds are found in the Jäger complexes, 1, 2, and 4. This reverses the trend in the bonds from C₁ and C₂ to C₃. The C₄-X bonds in the Jäger compounds correspond to ketonic C=O, but the C₄-X bonds in compounds 5-7 are substantially shortened (C-O = 1.33 Å and C-N = 1.32 Å) compared to the other bonds formed by these atoms (O-C = 1.43 Å and N-C = 1.47-1.48 Å).

The short C₃-C₄ bond of the methoxy-cyclidene compound (5)

indicates that it has the largest contribution from canonical form X. Clearly the electronegativity of the two-coordinate oxygen atom



canonical forms for (a) anionic species and (b) neutral species, with forms IXa and IXb also having alternatives with the single and double bonds to N, etc. interchanged

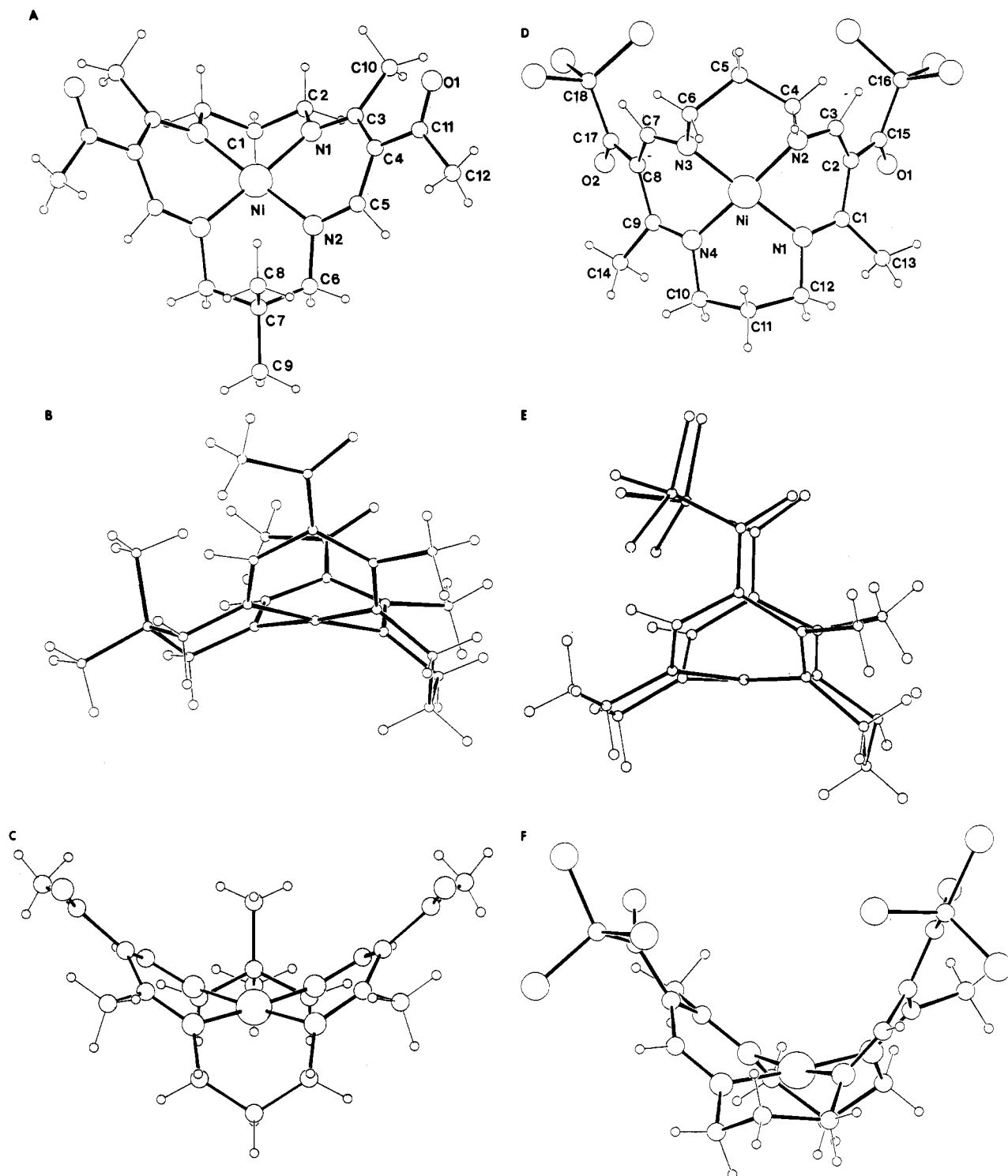


Figure 1. Views and atomic numbering of (A-C) molecule 2, which lies on a crystallographic mirror plane, and (D-F) molecule 3.

causes its lone pair of electrons to be less available for interaction with the unsaturated ring than are the nitrogen lone pairs of compounds 6 and 7. Among the Jäger compounds, compound 3 shows the greatest contribution from X. Indeed the presence of the electron-withdrawing $R^3 = CCl_3$ group has made the corresponding dimensions of this Jäger complex indistinguishable from those of the amino-cyclidene compound 6.

Rotation about the C_3-C_4 bond (angle δ in Table I) would be expected to reduce its double-bond character, but up to the maximum observed angle of 42° (compound 7), no such effect is seen.

Saddle Conformation. In Table I, angles α , β , and γ and distances C_3-C_3' , C_4-C_4' , and $X-X'$ measure the extent to which

the molecules take up a saddle conformation. If discussion is reserved on compounds 1 and 4, the bulk of the compounds fall into two somewhat different groups: 2, 5, and 7 on the one hand, and 3 and 6 on the other. The latter are rather more highly bowed. This is recognized most clearly from the side views in the figures. The saddle shape results from a combination of two effects. (i) In the six-membered saturated chelate rings, either the boat or the chair conformation forces the C-N bonds in these rings to be parallel but to be at an angle to the {NNNN} plane. The {NCCN} planes of these saturated chelate rings make angles of $22-37^\circ$ with the {NNNN} planes. (ii) The four nitrogen atoms coordinated to the metal have essentially planar environments because of the partial double-bond character of the N-C₁ and

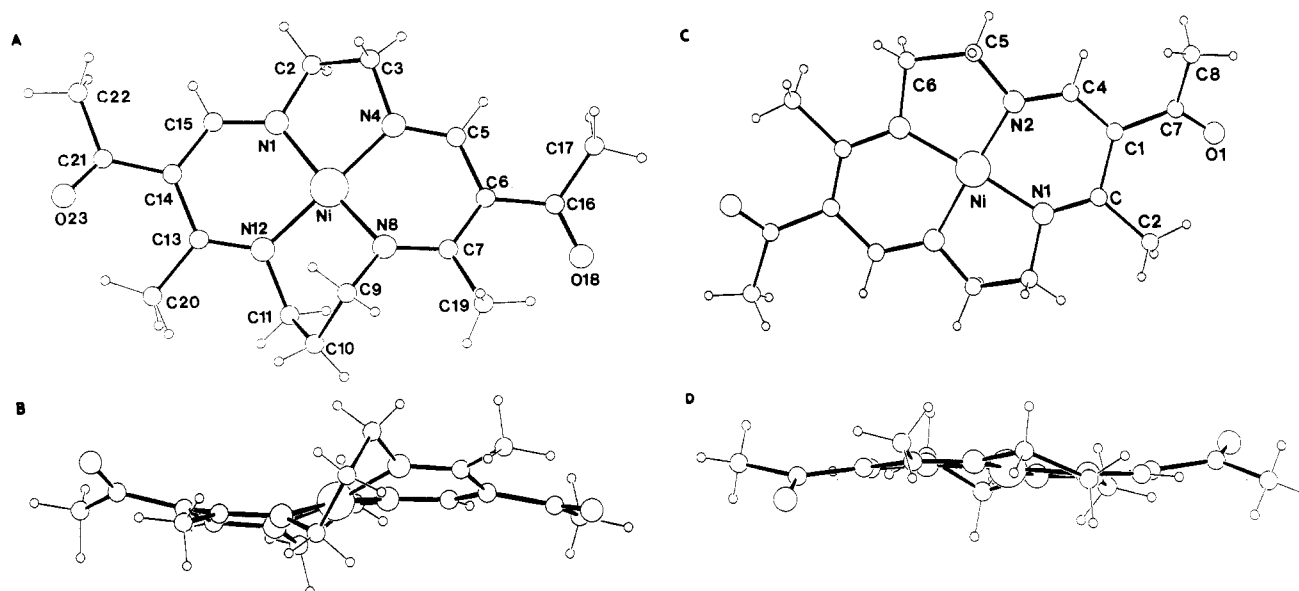


Figure 2. Views and atomic numbering of (A, B) molecule 1 and (C, D) molecule 4, which lies on an inversion center.

Table I. Structural Parameters^a

	1	2	3	4	5	6	7
type	Jäger	Jäger	Jäger	Jäger	methoxy	amino	amino
metal; M-N dist, Å	Ni; 1.86	Ni; 1.89	Ni; 1.88	Ni; 1.857	Ni; 1.88	Cu; 1.95	Cu; 1.98
dev of M from {NNNN} plane, Å	0.01	0.05	0.09	0.00	0.05	0.09	0.09
bond lengths							
N-C ₁ /C ₂ , Å	1.31	1.31	1.29	1.31	1.28	1.29	1.30
C ₁ /C ₂ -C ₃ , Å	1.42	1.42	1.44	1.42	1.46	1.44	1.42
C ₃ -C ₄ , Å	1.47	1.46	1.42	1.47	1.36	1.42	1.43
heteroatom (X)	O	O	O	O	O	N	N
C ₄ -X, Å	1.21	1.22	1.22	1.22	1.33	1.32	1.31
saddle angles and dist							
α, deg	...	110.3	93.9	...	110.0	95.0	110.3
β, deg	...	76.9	48.0	...	60.1	48.7	74.4
γ, deg	12.5	15.7	22.9	6.9	25.0	23.2	18.0
C ₃ -C ₃ , Å	6.48	5.77	5.18	6.55	5.47	5.29	5.83
C ₄ -C ₄ , Å	9.33	7.93	6.50	9.47	6.71	6.50	7.88
X-X, Å	10.72	8.58	6.85	11.02	7.23	6.39	7.95
pyramidity of ligand N atoms (dev of N from {MCC} plane), Å	0.06	0.02	0.06	0.02	0.07	0.07	0.03
side rings							
size, conformation ^b							
ring 1	5, skew	6, C	6, C	5, skew	5, half-skew	6, C	6, C
ring 2	6, skew	6, B	6, B	5, skew	6, B	6, B	6, B
angle of depression between {NNNN} and {NNCC} plane ^c							
ring 1	1.0 ^c	28.3 ^d	29.8	8.9 ^c	26.1 ^c	26.9	22.2
ring 2	20.9	37.4	37.4	10.4 ^c	32.5	35.0	30.6
dev of C ₄ from {C ₁ C ₂ C ₃ } plane, Å	0.09	0.24	0.09	0.00	0.07	0.03	0.22
dihedral angles							
δ, deg	22.3; 11.4	18.3	6.4; 11.6	22.2	7.5	20.3	41.7; 41.9
ε, deg					7.6	6.5	-174.7; -26.8

^a Averaged where appropriate; distances have esd's <0.01, and angles have esd's <0.5°, except for compound 7, whose esd's are 0.02 Å and 1.0°. See structure VIII for atom identifications. ^b Legend: B, boat; C, chair. ^c 5-membered ring. ^d gem-Me₂. ^e The average angle between the {NNNN} and {N₁N₂C₁C₂} planes for 1 is 21.8°, corresponding to α = 136.4°, if the deviations added rather cancelled, and for 4 is 5.6°, corresponding to α = 169.9°.

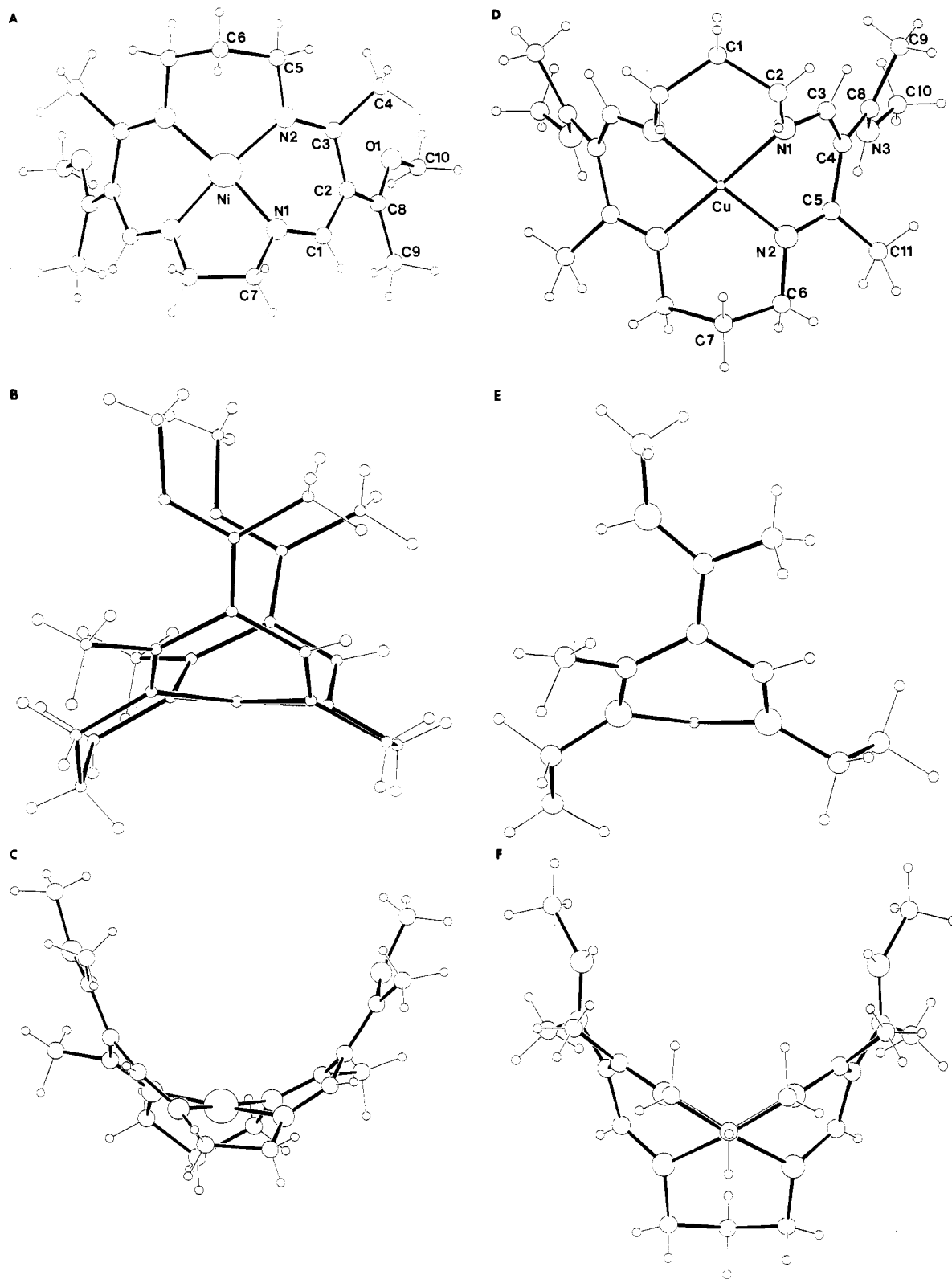
Table II. Correlation of Angle γ and Bond Lengths C₁/C₂-C₃ and C₃-C₄

	5	6	3	7	2	1	4
type	methoxy	amino	Jäger	amino	Jäger	Jäger	Jäger
γ, deg	25.0	23.2	22.9	18.0	15.7	12.5	6.9
C ₁ /C ₂ -C ₃	1.458 (4)	1.437 (8)	1.435 (3)	1.415 (15)	1.420 (3)	1.422 (3)	1.417 (2)
C ₃ -C ₄	1.364 (4)	1.412 (8)	1.419 (3)	1.425 (15)	1.455 (3)	1.467 (3)	1.469 (2)

Table III

	1	2	3	4	5	6	7
formula	$C_{17}H_{24}N_4O_2Ni \cdot 0.5C_3H_3N$	$C_{20}H_{30}N_4O_2Ni$	$C_{18}H_{20}N_4O_2Cl_4Ni$	$C_{16}H_{22}N_4O_2Ni$	$C_{19}H_{30}N_4O_{10}Cl_2Ni$	$C_{20}H_{34}N_6P_2F_{12}Cu$	$C_{34}H_{54}N_{10}P_2F_{12}Cu$
space group	triclinic	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic	triclinic
a , Å	7.824 (2)	12.055 (2)	10.013 (1)	5.253 (1)	8.257 (7)	10.480 (2)	13.922 (2)
b , Å	10.538 (3)	15.701 (3)	11.935 (2)	18.047 (5)	13.940 (11)	12.148 (2)	14.654 (3)
c , Å	14.283 (4)	10.650 (2)	11.613 (2)	8.682 (2)	22.108 (14)	11.958 (3)	11.674 (2)
α , deg	115.84 (1)	90	108.52 (1)	90	90	90	98.98 (2)
β , deg	112.81 (2)	90	101.18 (1)	107.56 (2)	90	91.37 (2)	104.68 (1)
γ , deg	85.79 (2)	90	103.23 (1)	90	90	90	95.92 (2)
U , Å ³	970.5	2015.8	1227	786	2545	1521.92	2250.2
M_r	414.67	417.25	595.81	361.1	604.09	712.08	956.35
Z	2	4	2	2	4	2	2
$D_{\text{crist.}}$, g cm ⁻³	1.42	1.375	1.61	1.52	1.58	1.55	1.410
$D_{\text{meas.}}$, g cm ⁻³	1.43		1.58		1.57	1.55	
radiation	Cu K α	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α
λ , Å	1.5418	0.71069	0.71069	0.71069	0.71069	0.71069	0.71069
μ , cm ⁻¹	15.8	9.84	14.60	12.5	10.32	9.517	6.69
syst absences	none	$0kl, k+l=2n+1$ $hko, h=2n+1$	none	$h0l, l=2n+1$ $0k0, k=2n+1$	$h0l, l=2n+1$ $0kl, k=2n+1$	$0k0, k=2n+1$	none
no. of total reflexions	3165	2231	5735	2055	3778	3665	7461
no. of reflexions with $I/I(\sigma) \geq 3.0$	2717	1794	4794	1405	2228	2968	4669
scan type	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
$2\theta_{\text{max}}$, deg (in 2θ)	128	55	55	55	60	55	48
scan range, deg (in 2θ) ^a	2.5	-1.0, +1.1	-1.0, +1.0	-1.1, +1.25	2.2	-1.25, +0.77	-1.0, +1.0
scan speed, min ⁻¹	2.0	2.0-24.0	2.0-24.0	4.0-29.0	2.0	0.65-5.0	4.0-24.0
bkgd at each end ^b	20 s	0.50/ST	0.5/ST	0.5/ST	20 s	0.5/ST	0.5/ST
frequency of stds	375	100	100	200	500	100	100
abs cor	Gaussian	no	Gaussian	Gaussian	Gaussian	no	no
transmission range	0.90-0.75	not recorded	not recorded	0.76-0.59	not recorded	not recorded	not recorded
cryst dimens, mm	$0.07 \times 0.10 \times 0.30$	$0.2 \times 0.2 \times 0.4$	$0.38 \times 0.30 \times 0.40$	$0.40 \times 0.23 \times 0.67$	$0.5 \times 0.25 \times 0.35$	$0.20 \times 0.50 \times 0.60$	$0.20 \times 0.21 \times 0.55$
weighting scheme	statistical	statistical	statistical + modifier	statistical	statistical	statistical	statistical
R	0.031	0.030	0.035	0.030	0.045	0.086	0.084
R_w	0.045	0.033	0.036	0.035	0.054	0.096	0.106
max peak on final ΔF map, e Å ⁻³	0.5	0.33	0.56	0.5	0.5	1.66	1.57
table for coordinates	IV	VI	VIII	X	XII	XIV	XVI
table for bond lengths and angles	V	VII	IX	XI	XIII	XV	XVII

^a Legend: -, below $K\alpha_1$; +, above $K\alpha_2$. ^b ST = scan time.



N-C₂ bonds. This is shown by the small deviations of these atoms from the planes through the adjacent atoms ($\{MCC\}$ planes). As a result, the N-C₁ (or C₂) bonds are forced upward by the depression below the $\{N\text{NNN}\}$ plane of the N-C bonds in the saturated rings. This leads to the saddle conformation.

The saturated chelate rings show systematic differences in that ring 2 (the one closest to the X groups) is invariably boat-shaped, while ring 1 has a chair conformation (except for the five-membered rings in structures 1 and 4). Simultaneously, ring 2 is

depressed below the $\{M\text{NNNN}\}$ plane considerably more than is ring 1. These differences probably reflect the greater repulsion from the methyl groups in the vicinity of ring 2, as compared to that from the hydrogen atoms in juxtaposition to ring 1. Although the pattern for this series of unbridged species is uniform, the selection in favor of the boat form for ring 2 and the chair form for ring 1 is not very substantial. The 25 structures that have been completed on bridged species include boat-boat and chair-chair structures as well as the boat-chair arrangement shown

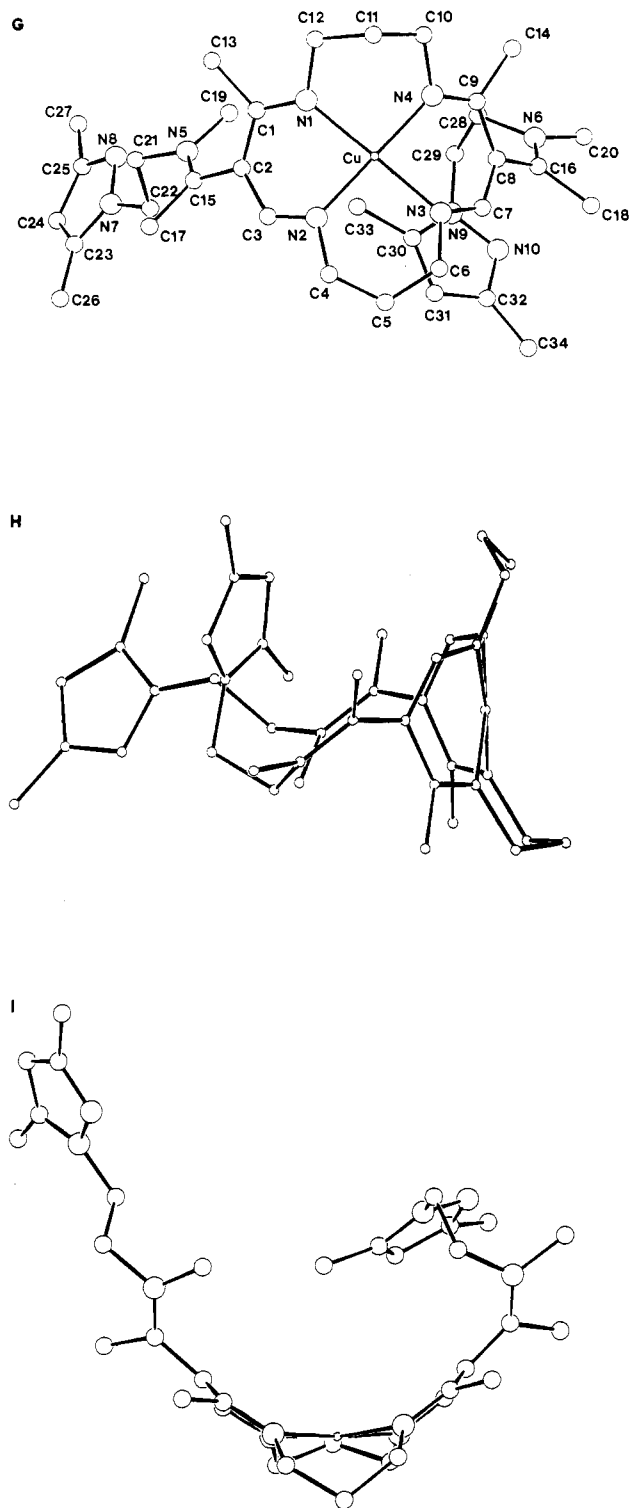


Figure 3. Views and atomic numbering of (A–C) cation **5** and (D–F) cation **6**, which lie on crystallographic mirror planes, and (G–I) cation **7** (omitting hydrogen atoms).

here. There is, however, no case in which the location of the boat and chair conformation is reversed.²⁻¹⁹

We find no obvious rationale for the two groups having saddle angles $\alpha \cong 110^\circ$ and $\alpha \cong 94^\circ$, respectively. The occurrence of the smaller angle for compounds **3** and **6** continues the close correspondence between structural parameters for these two compounds. It is suspected that this angle is relatively "soft" and that it may be affected by various steric constraints, including unidentifiable packing influences.

The conformations of the two complexes of 15-membered macrocycles present as intriguing contrast. Compound **5** has the saddle shape that is typical of the 16-membered derivatives with the 5-membered saturated chelate ring departing from planarity to much the same extent as the 6-membered rings. The C–C bond of this ring is eclipsed, a conformation required to harmonize with the boat form of the 6-membered chelate ring on the opposite side of the macrocycle. The two conformations force the two unsaturated chelate rings to lie on the same side of the {NNNN} plane and produce a saddle shape.

In contrast, the overall conformation of compound **1** is Z-shaped and both the 5- and 6-membered chelate rings have skew conformations. These conformations thrust the two unsaturated chelate rings onto opposite sides of the {NNNN} plane. In this case, the 5-membered ring has its preferred conformation while the 6-membered ring has a less favored form. The diverse behavior would seem to reflect the fact that the two sizes of rings cannot simultaneously achieve their favored conformations in these macrocyclic systems. The {N₁N₂C₁C₂} planes are still bent out of the {NNNN} planes for these two structures, but the angles are smaller than in the other compounds.

The precise energy effects that lead compound **1** to adopt the Z-form and **5** the saddle form are not easily identified. That compounds **1** and **5** have different electron delocalization patterns is suggested, for example, by differences in N–C₁(or C₂) bond lengths. This may affect the balance between the alternatives of unfavorable conformations for the 5-membered or for the 6-membered ring. This is very different from the 16-membered macrocycle, in which both saturated chelate rings can simultaneously adopt optimum conformations. By implication, 14-membered ring systems should resemble compound **1** rather than compound **5**.

Indeed, this expectation is borne out by the structure of compound **4**, the only 14-membered macrocycle derivative in this study. The two saturated 5-membered chelate rings are skew in form, and the net effect is that the unsaturated chelate rings are essentially coplanar with the N₄ plane. The significance of this structural feature to synthetic chemistry is immediate. The appending of the bridging groups should be less efficient and long chains should be required to span between the planar points of attachment to the parent cyclidene ring. Attempts to produce lacunar versions of [14]cyclidenes²² and studies on other reactions of the 14-membered Jäger complex confirm²³ this conclusion.

Thus, the canting of the unsaturated chelate rings results from the conformational constraints of the saturated 6-membered chelate rings. This combines with the trigonal-planar coordination spheres of the ligating nitrogen atoms to produce the saddle shape. The depth of the crevice is strongly affected by the conformations of the unsaturated rings. These are invariably boat-shaped, with the top {C₁C₂C₃} plane making an angle of 15–25° with the {N₁N₂C₁C₂} plane. This bowing must result from the need to reduce the angle strain in the 6-membered ring, particularly that caused by the large metal atom, whose limiting bond angles are 90°, rather than 120°. This is to be expected in any 6-membered ring, but the effect is surprisingly large on portions of the rings that are expected to be fully conjugated and therefore planar.

A close examination of the structural parameters shows a precise inverse correlation between the interplanar dihedral angle {N₁N₂C₁C₂}/C₁C₂C₃, γ , and the C₁(or C₂)–C₃ bond length and, therefore, a direct correlation with the C₃–C₄ bond length (listed in order of decreasing γ in Table II). Thus, the extent of this bending and the relief of the angle strain in the ring depends strongly, but inversely, on the amount of double-bond character in the C₁(or C₂)–C₃ bond but not on the formal type of the compound (IV–VI in Scheme I). Preliminary study of the bridged cyclidenes shows that this strong electronic effect on steric pa-

(22) Shaw, R.; Nosco, D. L.; Busch, D. H., unpublished results.

(23) Riley, D. P.; Stone, J. A.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 767.

Table IV. Fractional Atomic Coordinates for Compound 1 Non-Hydrogen Atoms ($\times 10^4$)

atom	x	y	z
Ni	2897.5 (5)	1267.4 (3)	709.2 (2)
N(1)	1969 (3)	265 (2)	-840 (1)
C(2)	1357 (4)	-1234 (2)	-1266 (2)
C(3)	2643 (4)	-1675 (2)	-385 (2)
N(4)	2907 (3)	-483 (2)	707 (1)
C(5)	2936 (3)	-717 (2)	1538 (2)
C(6)	3283 (3)	321 (2)	2646 (2)
C(7)	4112 (3)	1721 (2)	3026 (2)
N(8)	4147 (2)	2161 (2)	2300 (1)
C(9)	5308 (3)	3491 (2)	2704 (2)
C(10)	4117 (4)	4676 (2)	2651 (2)
C(11)	2303 (4)	4122 (2)	1605 (2)
N(12)	2556 (3)	3003 (2)	607 (1)
C(13)	2532 (3)	3281 (2)	-215 (2)
C(14)	2432 (3)	2143 (3)	-1284 (2)
C(15)	1978 (3)	740 (3)	-1540 (2)
C(16)	2849 (3)	-113 (2)	3380 (2)
C(17)	2689 (5)	-1607 (3)	3107 (3)
O(18)	2567 (3)	720 (2)	4207 (2)
C(19)	5116 (5)	2642 (3)	4286 (2)
C(20)	2532 (5)	4790 (3)	-65 (3)
C(21)	2627 (4)	2377 (4)	-2182 (2)
C(22)	2124 (5)	1180 (5)	-3343 (3)
O(23)	3271 (5)	3488 (3)	-2033 (2)

Table V. Bond Distances (Å) and Angles (deg) for Compound 1

N(1)-C(2)	1.464 (3)	C(9)-C(10)	1.514 (3)
C(2)-C(3)	1.507 (3)	C(10)-C(11)	1.518 (3)
C(3)-N(4)	1.460 (3)	C(11)-N(12)	1.476 (3)
N(4)-C(5)	1.305 (3)	N(12)-C(13)	1.322 (3)
C(5)-C(6)	1.406 (3)	C(13)-C(14)	1.449 (3)
C(6)-C(7)	1.436 (3)	C(14)-C(15)	1.397 (3)
C(7)-N(8)	1.317 (3)	C(15)-N(1)	1.301 (3)
N(8)-C(9)	1.483 (3)	Ni-N(8)	1.884 (2)
Ni-N(1)	1.835 (2)	Ni-N(12)	1.889 (2)
Ni-N(4)	1.843 (2)		
C(16)-C(6)	1.462 (3)	C(16)-O(18)	1.219 (3)
C(16)-C(17)	1.512 (3)	C(13)-C(20)	1.508 (3)
C(7)-C(19)	1.513 (3)		
C(21)-C(14)	1.470 (3)	C(21)-O(23)	1.208 (4)
C(21)-C(22)	1.496 (5)		
N(1)-Ni-N(4)	85.4 (1)	N(8)-Ni-N(12)	93.5 (1)
N(4)-Ni-N(8)	90.7 (1)	N(12)-Ni-N(1)	91.1 (1)
Ni-N(1)-C(2)	114.1 (1)	Ni-N(8)-C(7)	127.9 (1)
Ni-N(1)-C(15)	125.8 (2)	C(7)-N(8)-C(9)	120.3 (2)
C(15)-N(1)-C(2)	119.7 (2)	N(8)-C(9)-Cn10	111.3 (2)
N(1)-C(2)-C(3)	105.8 (2)	C(9)-C(10)-O(11)	111.1 (2)
C(2)-C(3)-N(4)	105.6 (2)	C(10)-C(11)-N(12)	112.3 (2)
Ni-N(4)-C(5)	125.6 (1)	Ni-N(12)-C(13)	128.0 (2)
Ni-N(4)-C(3)	114.0 (1)	Ni-N(12)-C(11)	111.6 (1)
C(3)-N(4)-C(5)	120.0 (2)	C(11)-N(12)-C(13)	120.4 (2)
N(4)-C(5)-C(6)	126.0 (2)	N(12)-C(13)-C(14)	120.7 (2)
C(5)-C(6)-C(7)	119.6 (2)	C(13)-C(14)-C(15)	119.7 (2)
C(6)-C(7)-N(8)	121.1 (2)	C(14)-C(15)-N(1)	126.9 (2)
Ni-N(8)-C(9)	111.8 (1)	N(12)-C(13)-C(20)	120.1 (2)
C(6)-C(6)-C(16)	117.3 (2)	C(14)-C(13)-C(20)	119.2 (2)
C(7)-C(6)-C(16)	123.0 (2)	C(13)-C(14)-C(21)	123.7 (2)
C(6)-C(16)-C(17)	119.8 (2)	C(15)-C(14)-C(21)	116.4 (2)
C(6)-C(16)-O(18)	123.2 (2)	C(14)-C(21)-C(22)	120.3 (3)
C(17)-C(16)-O(18)	117.0 (2)	C(14)-C(21)-O(23)	123.7 (3)
C(6)-C(7)-C(19)	118.7 (2)	C(22)-C(21)-O(23)	115.9 (3)
N(8)-C(7)-C(19)	119.9 (2)		

rameters is also present in these systems, though deviations are produced by the steric constraints imposed by the bridges.

As one moves further from the metal atom, in these open, unconstrained systems, the atoms C_4 are essentially coplanar with the plane $\{C_1C_2C_3\}$, as expected. Again bridging affects this, as does the extra bulk of the substituents in compound 7. Thus, the most direct measures of saddle width, the distances $C_3-C_{3'}$, and $C_4-C_{4'}$, depend on the two angles α and β (or, equivalently, α and

Table VI. Fractional Atomic Coordinates for Compound 2 Non-Hydrogen Atoms ($\times 10^4$)

atom	x	y	z
Ni	4983.8 (3)	2500.0	828.3 (3)
N(1)	4670 (2)	3369 (1)	2021 (2)
N(2)	5371 (2)	3365 (1)	-314 (2)
O(1)	7177 (2)	5231 (1)	2521 (2)
C(1)	3016 (3)	2500	2447 (4)
C(2)	3660 (2)	3280 (2)	2786 (3)
C(3)	5285 (2)	4049 (1)	2209 (2)
C(4)	6048 (2)	4338 (1)	1275 (2)
C(5)	5901 (2)	4048 (1)	32 (2)
C(6)	5170 (2)	3287 (1)	-1669 (2)
C(7)	5686 (3)	2500	-2254 (3)
C(8)	5390 (4)	2500	-3658 (3)
C(9)	6938 (3)	2500	2065 (4)
C(10)	5065 (2)	4588 (2)	3348 (2)
C(11)	6835 (2)	5026 (1)	1482 (2)
C(12)	7277 (2)	5513 (2)	367 (2)

Table VII. Bond Distances (Å) and Bond Angles (deg) for Compound 2

Ni-N(1)	1.902 (2)	N(1)-C(3)	1.315 (3)
Ni-N(2)	1.882 (2)	N(2)-C(5)	1.302 (3)
N(1)-C(2)	1.472 (3)	C(3)-C(4)	1.428 (3)
N(2)-C(6)	1.469 (3)	C(4)-C(5)	1.411 (3)
C(2)-C(1)	1.495 (3)	C(3)-C(10)	1.504 (3)
C(6)-C(7)	1.517 (3)	C(4)-C(11)	1.455 (3)
C(7)-C(8)	1.538 (5)	C(11)-C(12)	1.509 (3)
C(7)-C(9)	1.523 (5)	C(11)-O(1)	1.224 (3)
N(1)-Ni-N(2)	87.8 (1)	C(3)-C(4)-C(5)	118.0 (2)
N(1)-Ni-N(1')	91.7 (1)	C(3)-C(4)-C(11)	123.5 (2)
N(2)-Ni-N(2')	92.4 (1)	C(5)-C(4)-C(11)	117.6 (2)
Ni-N(1)-C(2)	117.8 (2)	C(4)-C(5)-N(2)	126.3 (2)
Ni-N(1)-C(3)	124.9 (2)	N(2)-C(6)-C(7)	113.8 (2)
C(2)-N(1)-C(3)	117.3 (2)	C(6)-C(7)-C(8)	107.7 (2)
Ni-N(2)-C(5)	122.3 (2)	C(6)-C(7)-C(9)	110.6 (2)
Ni-N(2)-C(6)	122.3 (1)	C(8)-C(7)-C(9)	111.0 (3)
C(5)-N(2)-C(6)	115.3 (2)	C(6')-C(7)-C(6)	109.1 (3)
C(2)-C(1)-C(2')	110.1 (3)	C(6')-C(7)-C(8)	107.7 (2)
C(1)-C(2)-N(1)	111.9 (2)	C(6')-C(7)-C(9)	110.6 (2)
N(1)-C(3)-C(4)	121.0 (2)	C(4)-C(11)-C(12)	119.2 (2)
N(1)-C(3)-C(10)	118.8 (2)	C(4)-C(11)-O(1)	123.5 (2)
C(4)-C(3)-C(10)	119.7 (2)	C(12)-C(11)-O(1)	117.3 (2)

Table VIII. Fractional Coordinates for Compound 3 Non-Hydrogen Atoms ($\times 10^4$)

atom	x	y	z
Ni	3703.4 (3)	2552.4 (3)	2290.9 (3)
N(1)	2498 (2)	3553 (2)	2487 (2)
N(2)	4428 (2)	3178 (2)	4061 (2)
N(3)	4835 (2)	1493 (2)	2101 (2)
N(4)	2766 (2)	1761 (2)	537 (2)
C(1)	1742 (3)	3609 (2)	3282 (2)
C(2)	2093 (3)	3170 (3)	4292 (2)
C(3)	3539 (3)	3220 (3)	4730 (2)
C(4)	5944 (3)	3426 (3)	4704 (3)
C(5)	6426 (3)	2301 (4)	4276 (3)
C(6)	6339 (3)	1905 (3)	2856 (3)
C(7)	4235 (3)	329 (2)	1438 (2)
C(8)	2818 (3)	-202 (2)	587 (2)
C(9)	2270 (3)	559 (2)	-15 (2)
C(10)	2444 (3)	2531 (2)	-184 (2)
C(11)	3099 (3)	3889 (2)	649 (3)
C(12)	2346 (3)	4241 (2)	1641 (2)
C(13)	645 (3)	4281 (3)	3266 (3)
C(14)	1225 (3)	-40 (3)	-1322 (3)
C(15)	1030 (3)	2823 (3)	4873 (3)
C(16)	1469 (4)	-2633 (4)	6159 (3)
C(17)	1984 (3)	-1448 (3)	279 (3)
C(18)	2657 (3)	-2309 (3)	829 (3)
O(1)	-243 (2)	2625 (3)	4448 (2)
O(2)	728 (2)	-1933 (2)	-350 (2)
Cl(1)	2272 (1)	1447 (1)	6017 (1)
Cl(2)	-43 (1)	2225 (2)	6670 (1)
Cl(3)	2657 (1)	4040 (1)	7361 (1)
Cl(4)	3299 (1)	-1671 (1)	2507 (1)
Cl(5)	4064 (1)	2601 (1)	189 (1)
Cl(6)	1342 (1)	-3740 (1)	399 (1)

Table IX. Bond Distances (Å) and Angles (deg) for Compound 3

Ni-N(1)	1.880 (1)	Ni-N(3)	1.873 (1)
Ni-N(2)	1.871 (2)	Ni-N(4)	1.885 (2)
N(1)-C(1)	1.298 (3)	C(8)-C(9)	1.450 (2)
N(1)-C(12)	1.474 (2)	C(8)-C(17)	1.420 (2)
N(2)-C(3)	1.290 (3)	C(9)-C(14)	1.503 (4)
N(2)-C(4)	1.469 (3)	C(10)-C(11)	1.504 (3)
N(3)-C(6)	1.467 (3)	C(11)-C(12)	1.498 (4)
N(3)-C(7)	1.283 (2)	C(15)-C(16)	1.577 (4)
N(4)-C(9)	1.296 (2)	C(15)-O(1)	1.210 (3)
N(4)-C(10)	1.473 (2)	C(16)-Cl(1)	1.760 (3)
C(1)-C(2)	1.445 (3)	C(16)-Cl(2)	1.754 (3)
C(1)-C(13)	1.501 (3)	C(16)-Cl(3)	1.770 (3)
C(2)-C(3)	1.419 (3)	C(17)-C(18)	1.575 (2)
C(2)-C(15)	1.419 (3)	C(17)-O(2)	1.223 (3)
C(4)-C(5)	1.498 (3)	C(18)-Cl(4)	1.773 (3)
C(5)-C(6)	1.543 (5)	C(18)-Cl(5)	1.768 (2)
C(7)-C(8)	1.427 (3)	C(18)-Cl(6)	1.753 (2)
N(2)-Ni-N(1)	88.3 (1)	C(7)-C(8)-C(9)	117.6 (1)
N(4)-Ni-N(1)	90.9 (1)	C(7)-C(8)-C(17)	122.2 (2)
N(3)-Ni-N(2)	91.7 (1)	C(9)-C(8)-C(17)	120.2 (2)
N(3)-Ni-N(4)	88.8 (1)	N(4)-C(9)-C(8)	119.6 (2)
Ni-N(1)-C(1)	122.8 (1)	N(4)-C(9)-C(14)	120.3 (2)
Ni-N(1)-C(12)	117.9 (1)	C(8)-C(9)-C(14)	120.0 (2)
C(1)-N(1)-C(12)	119.2 (2)	N(4)-C(10)-C(11)	110.3 (2)
Ni-N(2)-C(3)	118.7 (2)	C(10)-C(11)-C(12)	110.6 (2)
Ni-N(2)-C(4)	122.5 (2)	C(11)-C(12)-N(1)	111.1 (1)
C(3)-N(2)-C(4)	117.9 (2)	C(2)-C(15)-C(16)	119.9 (2)
C(6)-N(3)-C(7)	118.0 (1)	C(2)-C(15)-O(1)	125.3 (3)
Ni-N(3)-C(6)	122.0 (1)	C(16)-C(15)-O(1)	114.8 (2)
Ni-N(3)-C(7)	119.1 (1)	C(15)-C(16)-Cl(1)	112.3 (2)
Ni-N(4)-C(9)	121.6 (1)	C(15)-C(16)-Cl(2)	110.3 (2)
Ni-N(4)-C(10)	118.6 (1)	C(15)-C(16)-Cl(3)	110.1 (2)
C(9)-N(4)-C(10)	119.4 (2)	Cl(1)-C(16)-Cl(2)	107.5 (2)
N(1)-C(1)-C(2)	119.6 (2)	Cl(1)-C(16)-Cl(3)	109.6 (2)
N(1)-C(1)-C(13)	120.2 (2)	Cl(2)-C(16)-Cl(3)	106.9 (2)
C(2)-C(1)-C(13)	119.7 (2)	C(8)-C(17)-C(18)	119.7 (2)
C(1)-C(2)-C(3)	117.3 (2)	C(8)-C(17)-O(2)	125.9 (2)
C(1)-C(2)-C(15)	119.2 (2)	C(18)-C(17)-O(2)	114.4 (1)
C(3)-C(2)-C(15)	123.2 (2)	C(17)-C(18)-Cl(4)	112.6 (2)
C(2)-C(3)-N(2)	124.9 (2)	C(17)-C(18)-Cl(5)	110.4 (2)
N(2)-C(4)-C(5)	112.6 (2)	C(17)-C(18)-Cl(6)	109.4 (2)
C(4)-C(5)-C(6)	110.8 (2)	Cl(4)-C(18)-Cl(5)	109.4 (1)
N(3)-C(6)-C(5)	109.4 (2)	Cl(4)-C(18)-Cl(6)	106.9 (1)
N(3)-C(7)-C(8)	124.6 (1)	Cl(5)-C(18)-Cl(6)	108.0 (1)

Table X. Fractional Atomic Coordinates for Compound 4 Non-Hydrogen Atoms ($\times 10^4$)

atom	x	y	z
Ni	5000	5000	5000
N(1)	4485 (4)	4007 (1)	4325 (2)
N(2)	6840 (4)	5219 (1)	3568 (2)
O(1)	5191 (4)	3210 (1)	-103 (2)
C(1)	5073 (4)	3672 (1)	3127 (3)
C(2)	4740 (7)	2843 (1)	2968 (4)
C(3)	6242 (4)	4064 (1)	2075 (3)
C(4)	7156 (4)	4794 (1)	2417 (3)
C(5)	8104 (5)	5948 (1)	3817 (3)
C(6)	6463 (5)	6445 (1)	4534 (3)
C(7)	6540 (5)	3731 (1)	596 (3)
C(8)	8571 (6)	4043 (2)	-136 (3)

γ). The size of α is dominant, producing the broadest saddles in compounds 2 and 7, while the value of γ for compound 5 leaves its saddle hardly wider than those of compounds 3 and 6. For compound 1, the Z-shape leads to a C_3-C_3 distance little different from those in the other compounds, but thereafter, the distances are much greater as the two unsaturated rings extend away from each other.

The X-X' distance between the heteroatoms is particularly important in the bridged systems, as this often represents the overall width of the cavity fairly well. This distance is somewhat affected by rotation about the C_3-C_4 bond, δ , though this movement is generally approximately orthogonal to the X-X'

Table XI. Interatomic Distances (Å) and Angles (deg) for Compound 4^a

Ni-N(1)	1.879 (2)	Ni-N(2)	1.835 (2)
Ni-N(1a)	1.879 (2)	Ni-N(2a)	1.835 (2)
N(1)-C(1)	1.318 (3)	N(1)-C(6a)	1.481 (3)
N(2)-C(4)	1.309 (3)	N(2)-C(5)	1.462 (3)
O(1)-C(7)	1.223 (3)	C(1)-C(2)	1.509 (3)
C(1)-C(3)	1.433 (4)	C(3)-C(7)	1.469 (3)
C(3)-C(4)	1.402 (3)	C(5)-C(6)	1.503 (4)
C(6)-N(1a)	1.481 (3)	C(7)-C(8)	1.508 (4)
N(1)-Ni-N(2)	92.9 (1)	N(1)-Ni-N(1a)	180.0 (1)
N(2)-Ni-N(1a)	87.1 (1)	N(1)-Ni-N(2a)	87.1 (1)
N(2)-Ni-N(2a)	180.0 (1)	Ni-N(1)-C(1)	129.6 (2)
Ni-N(1)-C(6a)	111.3 (1)	C(1)-N(1)-C(6a)	118.8 (2)
Ni-N(2)-C(4)	127.3 (2)	Ni-N(2)-C(5)	113.8 (2)
C(4)-N(2)-C(5)	118.9 (2)	N(1)-C(1)-C(2)	118.6 (2)
N(1)-C(1)-C(3)	121.6 (2)	C(2)-C(1)-C(3)	119.5 (2)
C(1)-C(3)-C(4)	121.0 (2)	C(1)-C(3)-C(7)	122.3 (2)
C(4)-C(3)-C(7)	116.7 (2)	N(2)-C(4)-C(3)	126.6 (2)
O(1)-C(7)-C(3)	123.3 (2)	N(2)-C(5)-C(6)	107.8 (2)
C(3)-C(7)-C(8)	119.4 (2)	C(5)-C(6)-N(1a)	107.5 (2)
		O(1)-C(7)-C(8)	117.2 (2)

^aAtoms indicated by (a) are related by the molecular center of symmetry to the corresponding ones.

Table XII. Fractional Atomic Coordinates for Compound 5 Non-Hydrogen Atoms ($\times 10^4$)

atom	x	y	z
Coordination Sphere			
Ni	518 (1)	1445.7 (4)	2500
N(1)	-938 (3)	1951 (2)	1945 (1)
N(2)	1786 (3)	920 (2)	1868 (1)
C(1)	-1431 (4)	1471 (3)	1487 (2)
C(2)	-583 (4)	638 (2)	1264 (1)
C(3)	1169 (4)	573 (2)	1382 (2)
C(4)	2242 (6)	171 (4)	886 (2)
C(5)	3573 (4)	919 (3)	1932 (2)
C(6)	4132 (7)	1406 (4)	2500
C(7)	-1823 (5)	2812 (3)	2157 (2)
C(8)	-1420 (4)	-77 (3)	982 (2)
C(9)	-3184 (5)	-52 (4)	831 (2)
C(10)	-1368 (8)	-1722 (4)	638 (3)
O(1)	-599 (3)	-879 (2)	865 (1)
Perchlorate Groups			
Cl(1)	5895 (2)	2500	0
O(11)	4910 (10)	1810 (10)	240 (10)
O(12)	7370 (10)	2170 (10)	-130 (10)
O(13)	5310 (20)	2680 (20)	-580 (10)
O(14)	6050 (30)	3300 (10)	320 (10)
Cl(2)	2994 (2)	3995 (1)	2500
O(20)	2716 (5)	5000 (2)	2500
O(21)	2320 (14)	3519 (5)	2000 (3)
O(22)	4632 (10)	3859 (8)	2500
O(23)	3913 (17)	3712 (6)	2002 (4)
O(24)	1696 (15)	3545 (11)	2500

direction. Thus, the ordering of the X-X' distances tends to be the same as that of the C_3-C_4 distances.

The other dihedral angle listed in Table I, ϵ , is again of particular importance in the bridged species, in that it controls the orientation of the bridging R^1 groups. The only substantial departure from zero (R^2 and R^3 eclipsed) among the unbridged species is found for compound 7, where, as Figure 3H shows, one pyrazole group (R^1) is turned in and the other is turned out. Despite this orientational distinction, the two groups still point upwards (Figure 3I), corresponding to the "lid-on" form of cavity among the lacunar complexes.^{24,25}

(24) Busch, D. H.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. W.; Christoph, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5919.

(25) Herron, N.; Nosco, D. L.; Busch, D. H. *Inorg. Chem.* **1983**, *22*, 2970.

Table XIII. Bond Distances (Å) and Angles (deg) for Compound 5^a

Ni-N(1)	1.856 (3)	Ni-N(2)	1.893 (3)
N(1)-C(1)	1.280 (4)	C(3)-C(4)	1.516 (5)
N(1)-C(7)	1.481 (4)	C(3)-N(2)	1.286 (4)
C(1)-C(2)	1.443 (5)	N(2)-C(5)	1.482 (4)
C(2)-C(3)	1.472 (5)	C(5)-C(6)	1.499 (5)
C(2)-C(8)	1.364 (5)	C(7)-C(7')	1.519 (10)
C(8)-C(9)	1.495 (5)	O(1)-C(10)	1.427 (6)
C(8)-O(1)	1.333 (4)		
N(1)-Ni-N(2)	91.0 (1)	C(4)-C(3)-N(2)	120.8 (3)
N(1)-Ni-N(1')	82.7 (2)	C(3)-N(2)-C(5)	118.3 (3)
N(2)-Ni-N(2')	95.1 (2)	C(3)-N(2)-Ni	123.0 (2)
Ni-N(1)-C(1)	122.1 (2)	C(5)-N(2)-Ni	118.7 (3)
Ni-N(1)-C(7)	114.8 (3)	N(2)-C(5)-C(6)	112.7 (4)
C(1)-N(1)-C(7)	121.0 (3)	C(5)-C(6)-C(5')	113.6 (5)
N(1)-C(1)-C(2)	122.4 (3)	C(7)-C(7)-N(1)	108.4 (2)
C(1)-C(2)-C(3)	117.8 (3)	C(2)-C(8)-C(9)	125.4 (3)
C(1)-C(2)-C(8)	119.9 (3)	C(2)-C(8)-O(1)	116.4 (3)
C(3)-C(2)-C(8)	122.2 (3)	C(9)-C(8)-O(1)	118.1 (4)
C(2)-C(3)-C(4)	118.0 (4)	C(8)-O(1)-C(10)	122.2 (4)
C(2)-C(3)-N(2)	120.9 (3)		

^a Primed atoms are related to unprimed atoms by the mirror plane.**Table XIV.** Fractional Coordinates of Non-Hydrogen Atoms for Compound 6 ($\times 10^4$)

atom	x	y	z
Cu	4767.6 (9)	2500.0	3567.6 (8)
N(1)	5386 (4)	1349 (4)	2589 (4)
N(2)	3995 (4)	1351 (4)	4487 (4)
N(3)	1269 (5)	-132 (6)	2576 (6)
C(1)	6635 (9)	2500	1297 (8)
C(2)	6594 (6)	1454 (6)	1977 (6)
C(3)	4593 (6)	595 (5)	2281 (5)
C(4)	3448 (5)	326 (5)	2840 (5)
C(5)	3362 (5)	545 (5)	4026 (5)
C(6)	4054 (6)	1467 (5)	5698 (5)
C(7)	4782 (9)	2500	6043 (7)
C(8)	2448 (7)	-173 (5)	2211 (6)
C(9)	2640 (9)	-728 (8)	1118 (8)
C(10)	122 (9)	-663 (10)	2078 (10)
C(11)	2686 (7)	-226 (6)	4753 (6)
P(1)	9977 (3)	2500	4340 (4)
P(2)	3097 (3)	2500	9271 (3)
F(11)	8597 (13)	2500	4683 (21)
F(12)	11235 (9)	2500	3790 (13)
F(13)	9985 (7)	1249 (5)	4358 (10)
F(14)	10421 (34)	2500	5446 (13)
F(15)	9472 (19)	2500	3198 (19)
F(21)	2008 (9)	1700 (9)	9449 (12)
F(22)	2827 (14)	2500	8103 (10)
F(23)	4170 (10)	1720 (10)	9196 (13)
F(24)	3336 (11)	2500	10314 (9)

Table XV. Bond Distances (Å) and Angles (deg) for Compound 6^a

Cu-N(1)	1.942 (5)	C(1)-C(2)	1.515 (9)
Cu-N(2)	1.967 (5)	C(3)-C(4)	1.425 (8)
N(1)-C(2)	1.481 (8)	C(4)-C(5)	1.455 (9)
N(1)-C(3)	1.287 (8)	C(4)-C(8)	1.412 (9)
N(2)-C(5)	1.294 (7)	C(5)-C(11)	1.504 (9)
N(2)-C(6)	1.449 (8)	C(6)-C(7)	1.522 (8)
N(3)-C(8)	1.332 (9)	C(8)-C(9)	1.494 (12)
N(3)-C(10)	1.472 (12)		
N(1)-Cu-N(2)	88.6 (2)	N(1)-C(3)-C(4)	124.9 (5)
N(1)-Cu-N(1')	92.0 (3)	C(3)-C(4)-C(5)	119.2 (5)
N(2)-Cu-N(2')	90.3 (3)	C(3)-C(4)-C(8)	118.2 (6)
Cu-N(1)-C(2)	122.3 (4)	C(5)-C(4)-C(8)	122.6 (5)
Cu-N(1)-C(3)	117.7 (4)	N(2)-C(5)-C(4)	121.1 (5)
C(2)-N(1)-C(3)	118.3 (5)	N(2)-C(5)-C(11)	119.6 (6)
Cu-N(2)-C(5)	120.7 (4)	C(4)-C(5)-C(11)	118.9 (5)
Cu-N(2)-C(6)	118.7 (4)	N(2)-C(6)-C(7)	111.3 (6)
C(5)-N(2)-C(6)	120.5 (5)	C(6)-C(7)-C(6')	111.1 (8)
C(8)-N(3)-C(10)	127.8 (8)	N(3)-C(8)-C(4)	119.6 (7)
C(2)-C(1)-C(2')	114.3 (8)	N(3)-C(8)-C(9)	117.5 (7)
N(1)-C(2)-C(1)	111.8 (6)	C(4)-C(8)-C(9)	122.8 (6)

^a Primed atoms are related to unprimed atoms by the mirror plane.**Table XVI.** Fractional Atomic Coordinates of Non-Hydrogen Atoms for Compound 7 ($\times 10^4$)

atom	x	y	z
Cu	2049.2 (11)	3352.7 (9)	4383.5 (12)
P(1)	2719 (4)	-819 (3)	6960 (3)
P(2)	-2136 (3)	6264 (2)	225 (3)
F(11)	2229 (11)	-1284 (8)	7817 (11)
F(12)	3192 (13)	-363 (8)	6136 (13)
F(13)	1690 (12)	-607 (13)	6288 (15)
F(14)	2486 (15)	-1714 (8)	6078 (11)
F(15)	2884 (15)	108 (8)	7801 (11)
F(16)	3652 (11)	-1114 (14)	7596 (17)
F(21)	-2247 (7)	5813 (6)	1340 (7)
F(22)	-1488 (8)	5506 (7)	-117 (11)
F(23)	-1154 (9)	6879 (9)	1001 (9)
F(24)	-2010 (7)	6693 (6)	-911 (7)
F(25)	-3076 (8)	5592 (9)	-550 (9)
F(26)	-2747 (11)	7011 (8)	572 (13)
N(1)	1600 (7)	4426 (6)	3632 (8)
N(2)	793 (8)	3257 (7)	4852 (8)
N(3)	2436 (7)	2238 (6)	5031 (7)
N(4)	3229 (6)	3351 (6)	3733 (7)
N(5)	-1289 (7)	3605 (6)	1194 (8)
N(6)	3294 (7)	737 (6)	1650 (8)
N(7)	-3619 (7)	2420 (7)	-1104 (9)
N(8)	-3362 (8)	2539 (7)	-2129 (9)
N(9)	1194 (7)	137 (6)	1044 (8)
N(10)	1424 (7)	-721 (6)	1273 (8)
C(1)	662 (8)	4449 (7)	3033 (9)
C(2)	-140 (8)	3835 (8)	3152 (9)
C(3)	24 (9)	3403 (8)	4173 (10)
C(4)	672 (12)	2871 (11)	5940 (12)
C(5)	1049 (11)	1935 (10)	5939 (12)
C(6)	2137 (11)	2000 (10)	6113 (11)
C(7)	2803 (8)	1624 (7)	4441 (10)
C(8)	3201 (8)	1699 (7)	3464 (9)
C(9)	3536 (7)	2606 (7)	3252 (9)
C(10)	3786 (9)	4275 (8)	3708 (12)
C(11)	3397 (9)	5090 (8)	4376 (13)
C(12)	2387 (10)	5217 (8)	3648 (13)
C(13)	453 (9)	5261 (8)	2393 (11)
C(14)	4356 (9)	2712 (8)	2648 (11)
C(15)	-1137 (9)	3713 (8)	2371 (10)
C(16)	3405 (8)	874 (7)	2811 (10)
C(17)	-2023 (10)	3737 (10)	2876 (12)
C(18)	3828 (10)	126 (8)	3458 (11)
C(19)	550 (10)	3470 (10)	572 (11)
C(20)	3696 (11)	-10 (9)	1025 (12)
C(21)	-2307 (9)	3558 (8)	364 (11)
C(22)	-2808 (10)	2534 (8)	-2 (11)
C(23)	-4597 (10)	2077 (9)	-1328 (13)
C(24)	-4976 (10)	1954 (10)	-2561 (14)
C(25)	-4202 (10)	2272 (8)	-3014 (11)
C(26)	-5053 (13)	1883 (13)	-383 (17)
C(27)	-4203 (15)	2312 (9)	-4318 (13)
C(28)	2569 (10)	1191 (8)	852 (10)
C(29)	1626 (10)	524 (8)	202 (10)
C(30)	692 (9)	533 (9)	1808 (11)
C(31)	595 (9)	103 (9)	2559 (11)
C(32)	1054 (9)	854 (8)	2205 (10)
C(33)	336 (11)	1444 (8)	1728 (14)
C(34)	1168 (11)	-1700 (9)	2711 (12)

Experimental Section

Syntheses. (6,14-Diacetyl-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,6,12,14-tetraenato(2-)- κ^4 N)nickel(II),²⁶ [NiAc₂Me₂[15]tetraenatoN₄] (1). This complex was prepared according to Jäger²¹ and recrystallized from pyridine as small red plates.

(3,11-Diacetyl-2,7,7,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2-)- κ^4 N)nickel(II), [NiAc₂Me₄[16]tetraenatoN₄] (2). This complex was synthesized according to previously published methods.²⁷ Recrystallization by slow evaporation from acetonitrile gave orange needles of the analytically pure product.

Preparation of Compound 3. First Intermediate: (N,N'-Trimethylenebis(2-acetyllethylideneamino)(2-))nickel(II), Ni-16-LTD. This acyclic complex was prepared by using a modification of the procedure of Riley,²⁷ the only difference being the additional presence of 2 equiv of sodium hydroxide in the reaction mixture.

Table XVII. Bond Distances (Å) and Angles (deg) for Compound 7

Cu-N(1)	1.99 (2)	N(10)-C(31)	1.35 (2)
Cu-N(2)	1.96 (1)	C(1)-C(2)	1.41 (2)
Cu-N(3)	1.97 (2)	C(1)-C(13)	1.52 (2)
Cu-N(4)	1.98 (2)	C(2)-C(3)	1.42 (2)
N(1)-C(1)	1.32 (2)	C(2)-C(15)	1.43 (2)
N(1)-C(12)	1.51 (2)	C(4)-C(5)	1.52 (2)
N(2)-C(3)	1.27 (2)	C(5)-C(6)	1.47 (2)
N(2)-C(4)	1.51 (2)	C(7)-C(8)	1.40 (2)
N(3)-C(6)	1.50 (2)	C(8)-C(9)	1.44 (2)
N(3)-C(7)	1.27 (2)	C(8)-C(16)	1.42 (2)
N(4)-C(9)	1.31 (2)	C(9)-C(14)	1.49 (2)
N(4)-C(10)	1.49 (2)	C(10)-C(11)	1.55 (2)
N(5)-C(15)	1.32 (2)	C(11)-C(12)	1.49 (2)
N(5)-C(19)	1.41 (2)	C(15)-C(17)	1.50 (2)
N(5)-C(21)	1.48 (2)	C(16)-C(18)	1.51 (2)
N(6)-C(16)	1.31 (1)	C(21)-C(22)	1.53 (2)
N(6)-C(20)	1.46 (2)	C(23)-C(24)	1.38 (2)
N(6)-C(28)	1.48 (2)	C(23)-C(26)	1.45 (3)
N(7)-N(8)	1.36 (2)	C(24)-C(25)	1.39 (2)
N(7)-C(22)	1.45 (2)	C(25)-C(27)	1.53 (2)
N(7)-C(23)	1.35 (2)	C(28)-C(29)	1.50 (3)
N(8)-C(25)	1.33 (2)	C(30)-C(31)	1.39 (2)
N(9)-C(29)	1.43 (2)	C(30)-C(33)	1.50 (2)
N(9)-C(30)	1.36 (2)	C(31)-C(32)	1.39 (2)
N(9)-N(10)	1.38 (2)	C(32)-C(34)	1.46 (2)
N(1)-Cu-N(2)	86.9 (4)	C(5)-C(4)-N(2)	110.3 (12)
N(2)-Cu-N(3)	92.5 (4)	C(4)-C(5)-C(6)	113.6 (12)
N(3)-Cu-N(4)	87.2 (4)	C(5)-C(6)-N(3)	111.9 (10)
N(4)-Cu-N(1)	92.9 (4)	N(3)-C(7)-C(8)	128.4 (10)
Cu-N(1)-C(1)	123.9 (7)	C(7)-C(8)-C(9)	120.2 (9)
Cu-N(1)-C(12)	118.1 (7)	C(7)-C(8)-C(16)	118.3 (10)
C(1)-N(1)-C(12)	117.7 (9)	C(9)-C(8)-C(16)	120.8 (10)
Cu-N(2)-C(3)	122.0 (9)	N(4)-C(9)-C(8)	120.2 (10)
Cu-N(2)-C(4)	123.5 (8)	N(4)-C(9)-C(14)	119.6 (9)
C(3)-N(2)-C(4)	113.9 (11)	C(8)-C(9)-C(14)	119.4 (9)
Cu-N(3)-C(6)	120.7 (8)	N(4)-C(10)-C(11)	111.2 (11)
Cu-N(3)-C(7)	120.9 (8)	C(10)-C(11)-C(12)	110.3 (10)
C(6)-N(3)-C(7)	117.5 (10)	N(1)-C(12)-C(11)	110.8 (10)
Cu-N(4)-C(9)	125.5 (7)	C(2)-C(15)-N(5)	120.4 (12)
Cu-N(4)-C(10)	118.0 (7)	N(5)-C(15)-C(17)	118.8 (10)
C(9)-N(4)-C(10)	116.5 (10)	C(2)-C(15)-C(17)	120.7 (11)
C(15)-N(5)-C(19)	125.6 (10)	N(6)-C(16)-C(8)	122.9 (10)
C(15)-N(5)-C(21)	121.8 (11)	N(6)-C(16)-C(18)	116.4 (10)
C(19)-N(5)-C(21)	112.6 (9)	C(8)-C(16)-C(18)	120.7 (10)
C(16)-N(6)-C(20)	122.6 (10)	N(5)-C(21)-C(22)	108.5 (10)
C(16)-N(6)-C(28)	121.3 (10)	N(7)-C(22)-C(21)	109.4 (10)
C(20)-N(6)-C(28)	114.9 (9)	N(7)-C(23)-C(24)	105.0 (13)
N(8)-N(7)-C(22)	117.3 (10)	N(7)-C(23)-C(26)	122.8 (12)
N(8)-N(7)-C(23)	112.3 (10)	C(24)-C(23)-C(26)	132.2 (13)
C(22)-N(7)-C(23)	129.6 (12)	C(23)-C(24)-C(25)	107.2 (11)
N(7)-N(8)-C(25)	105.3 (11)	C(24)-C(25)-N(8)	110.1 (12)
N(10)-N(9)-C(29)	117.1 (10)	N(8)-C(25)-C(27)	120.3 (13)
N(10)-N(9)-C(30)	111.8 (10)	C(24)-C(25)-C(27)	129.6 (12)
C(29)-N(9)-C(30)	130.3 (10)	N(6)-C(28)-C(29)	111.1 (10)
N(9)-N(10)-C(32)	104.9 (10)	N(9)-C(29)-C(28)	110.6 (9)
N(1)-C(1)-C(2)	121.0 (10)	N(9)-C(30)-C(31)	105.7 (11)
N(1)-C(1)-C(13)	118.0 (10)	N(9)-C(30)-C(33)	122.4 (13)
C(2)-C(1)-C(13)	120.1 (10)	C(31)-C(30)-C(33)	131.8 (14)
C(1)-C(2)-C(3)	120.4 (9)	C(30)-C(31)-C(32)	106.7 (12)
C(1)-C(2)-C(15)	123.1 (10)	N(10)-C(32)-C(31)	110.9 (11)
C(3)-C(2)-C(15)	115.9 (11)	N(10)-C(32)-C(34)	120.6 (12)
C(2)-C(3)-N(2)	127.0 (12)	C(31)-C(32)-C(34)	128.5 (13)

Second, Third, and Fourth Intermediates: (3,11-Diacetyl-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2-)- κ^4N)nickel(II), $[\text{Ni}(\text{Ac}_2\text{Me}_2[16]\text{tetraena}N_4)]$, (4,10-Dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene- κ^4N)nickel(II) Hexafluorophosphate, $[\text{Ni}(\text{H}_2\text{Me}_2[16]\text{tetraena}N_4)](\text{PF}_6)_2$, and (4,10-Dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2-)- κ^4N)nickel(II), $[\text{Ni}(\text{Me}_2[16]\text{tetraena}N_4)]$. The compounds were synthesized by previously reported methods.^{27,28}

(3,11-Bis(trichloroacetyl)-4,10-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato(2-)- κ^4N)nickel(II) (3). Trichloroacetyl chloride (24.6 mL, 0.22 mol) was dissolved in 50 mL of ether and added dropwise to a solution of $[\text{Ni}(\text{Me}_2[16]\text{tetraena}N_4)]$ (33.4 g; 0.11 mol) and 30.7 mL (0.22 mol) of tetraethylamine in 1000 mL of ether at room temperature. A yellow precipitate formed immediately on mixing the reactants. After addition was complete, the crude product was collected by filtration, washed with water (200 mL), and dried in vacuo. The solid was dissolved in chloroform and loaded on a neutral-alumina chromatography column. The absorbed yellow band was eluted with chloroform, and the eluate was concentrated. Precipitation of the pure product occurred on addition of ethanol, and the yellow solid was filtered and dried in vacuo (yield 76%). Recrystallization from chloroform-ethanol gave golden yellow rods.

(6,13-Diacetyl-5,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato(2-)- κ^4N)nickel(II), $[\text{Ni}(\text{Ac}_2\text{Me}_2[14]\text{tetraena}N_4)]$ (4). This complex was synthesized according to Jäger²¹ by the same method used to prepare compound 1. It was recrystallized from pyridine as deep red plates.

(6,14-Bis(1-methoxyethylidene)-7,13-dimethyl-1,4,8,12-tetraazacyclopentadeca-4,7,12,15-tetraene- κ^4N)nickel(II) Perchlorate (5). The preparation of this complex has been reported previously.²⁹ Recrystallization from acetone gave yellow prisms.

(2,12-Dimethyl-3,11-bis(1-(methylamino)ethylidene)-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene- κ^4N)copper(II) Hexafluorophosphate, $[\text{Cu}(\text{MeNEthi})_2\text{Me}_2[16]\text{tetraena}N_4](\text{PF}_6)_2$ (6). The synthesis of the nickel(II) complex and its ligand salt have been described elsewhere.^{14,15,17} $[\text{H}_2(\text{MeNEthi})_2\text{Me}_2[16]\text{tetraena}N_4](\text{PF}_6)_3\text{Cl}$ (0.62 g; 0.74 mmol) and copper(II) acetate hydrate (0.15 g; 0.74 mmol) were slurried in 20 mL of methanol. On addition of sodium acetate trihydrate (0.40 g; 2.22 mmol), all the solids dissolved to give a deep red solution. This solution was stirred at room temperature for ca. 5 min and filtered through Celite. Slow evaporation of solvent yielded a deep red crystalline product (yield 0.40 g, 76%). Recrystallization from acetonitrile-ethanol gave deep red platelike prisms.

Preparation of Compound 7. First Intermediate: 3,5-Dimethyl-1-(2-hydroxyethyl)pyrazole (A). (2-Hydroxyethyl)hydrazine (12.31 g; 0.162 mol) was dissolved in 40 mL of methanol and cooled to ca. 10 °C. 2,4-Pentanedione (16.2 g; 0.162 mol) was likewise cooled and added dropwise over ca. 10 min to the methanolic hydrazine solution (*Caution!* exothermic reaction). The reaction mixture was stirred in an ice bath for ca. 20 min and then slowly heated to reflux temperature, where it was maintained for ca. 12 h. The mixture was allowed to cool to room temperature and concentrated to remove methanol and water. Addition of diethyl ether caused precipitation of the desired product (yield 16.9 g, 74%).

Second Intermediate: 2-(3,5-Dimethyl-1H-pyrazolyl)ethyl *p*-Toluenesulfonate (B). Tosylation of A was carried out by using previously published methods¹⁵ (yield 62%).

Third Intermediate: (3,11-Bis(1-[(2-(3,5-dimethyl-1H-pyrazolyl)ethyl)methylamino]ethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene- κ^4N)nickel(II) Hexafluorophosphate (C). $[\text{Ni}(\text{MeNEthi})_2\text{Me}_2[16]\text{tetraena}N_4](\text{PF}_6)_2$ (4.0 g; 5.63 mmol) was dissolved in 200 mL of acetonitrile under a nitrogen atmosphere. This solution was treated with sodium (0.26 g, 11.3 mmol) in 10 mL of absolute methanol, and the deep red reaction mixture was heated to reflux. A solution of B (17.99 g, 61.1 mmol) in 200 mL of acetonitrile was added dropwise over 12-18 h, and the reaction mixture was refluxed until the pH of the contents had dropped to ca. 6.5. (This pH was estimated by periodically withdrawing small aliquots of the reaction mixture, diluting with an equal volume of water, and measuring with a combination glass/calomel electrode.) The reaction mixture was cooled, filtered, and concentrated to an oil. Redissolution in a small amount of acetonitrile was followed by alumina chromatography using acetonitrile as the eluant. Two separations were found to be necessary to purify the crude product to a sufficient degree. The final eluant was again concentrated to an oil and dissolved in ca. 100 mL of hot methanol. (A few drops of acetonitrile were added to effect complete dissolution.) Slow cooling gave a yellow crystalline product, which could be recrystallized from methanol-acetonitrile by the same method (yield 2.95 g, 55%).

Compound 7. The complex was synthesized by demetalation of this yellow product and subsequent insertion of copper. The removal of nickel(II) was carried out according to known procedures,^{15,17} and insertion of copper(II) used the same experimental procedure as that described for compound 6. Recrystallization from acetonitrile-ethanol gave deep red blocks.

Crystal Structure Analyses. Data were taken on the products of the

(26) κ^4N denotes coordination to four nitrogen donors. See: Sloan, T. E.; Busch, D. H. *Inorg. Chem.* **1978**, *17*, 2043.

(27) Riley, D. P.; Busch, D. H. *Inorg. Synth.* **1978**, *18*, 36.

(28) Streeky, A. J.; Pillsbury, D. G.; Busch, D. H. *Inorg. Chem.* **1980**, *19*, 3148.

(29) Corfield, P. W. R.; Mokren, J. D.; Hipp, C. J.; Busch, D. H. *J. Am. Chem. Soc.* **1973**, *95*, 4465.

final recrystallization noted above, at room temperature (20 °C) for octants $+h, \pm k, \pm l$, $+h, +k, \pm l$, and $+h, +k, +l$ for triclinic, monoclinic, and orthorhombic crystals, respectively. Crystal data are given in Table IIIa and data collection and refinement information in Table IIIb. Coordinates and bond distances and angles are given in Tables IV-XVII and numbering systems are given in Figures 1-3. Much additional data are available in the supplementary material. Compounds 1 and 5 were studied with a Picker FACS-III diffractometer (B-filter), 6 was studied with an Enraf-Nonius CAD4 diffractometer (graphite monochromator), and the remainder were studied on Syntex P₂ diffractometers (graphite monochromator). For compound 5 the principal crystallographic information is in ref 31. $\theta/2\theta$ scans were used throughout. For all compounds scattering factors and anomalous dispersion factors were taken from ref 30. Final refinement was by large-block least-squares methods, using anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were refined for all except compound 2.

Final computing for compounds 1-3 and 5 used a local version of ORFLS, CRYM, and XRAY-72 on an IBM 370 computer; for compound 4, SHELXTL was used on a Data General DG30 computer.

For all except compound 1, the structure was solved by Patterson methods. For compound 1 superposition was used, based on the nickel position, to reveal all the atoms of the complex. The pyridine in this complex is disordered about a center of symmetry.

(30) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(31) Mokren, J. D. Ph.D. Thesis, The Ohio State University, 1974; *Diss. Abstr. Int.*, B 1975, 35(11), 5313.

For compound 2 the systematic absences indicate either space group *Pnma* or *Pn2₁a*. The former implies that the molecule lies on a crystallographic mirror plane. The first was initially selected and shown to be correct by successful refinement. A similar choice exists for compounds 5 and 6, and in both cases, the centrosymmetric space group is found. For compound 5 the cation and one [ClO₄] group lie on a mirror plane, the other anion being on a twofold axis. For compound 6 the cation and both anions lie on mirror planes. The molecule of compound 4 lies on an inversion center.

In compounds 6 and 7 the relatively large residual electron density is attributed to highly disordered solvent.

Acknowledgment. Support of this research by the National Science Foundation and the National Institutes of Health is gratefully acknowledged. The Ohio State University and the University of Warwick collaboration has been supported by a NATO travel grant.

Supplementary Material Available: Listings of anisotropic thermal parameters and H atom coordinates for compounds 1-4, relationships between original and present numbering for compound 5, anisotropic thermal parameters and H atom coordinates for compounds 5-7, and dimensions of PF₆⁻ groups in compounds 6 and 7 (17 pages); listings of structure factors for compounds 2-4, 6, and 7 (173 pages). Ordering information is given on any current masthead page. Structure factors for compounds 1 and 5 are included in ref 31. Order No. 75-11,400 from University Microfilms, Ann Arbor, MI.

Notes

Contribution from Ames Laboratory—DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Structure of $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CS})]\text{PF}_6$, a Comparison of M-CS and M-CO Bonding

James W. Richardson, Jr., Robert J. Angelici, and Robert A. Jacobson*

Received August 14, 1986

From the time of the preparation and structural determination of the first transition-metal thiocarbonyl complex,¹ it was recognized that M-CS bond distances are shorter than corresponding M-CO distances, as initially established for (PPh₃)₂(Cl)Rh(CS), 1.787 (10) Å, and (PPh₃)₂(Cl)Rh(CO), 1.86 Å.² This M-CS bond shortening and a variety of spectroscopic data have been interpreted to indicate that, in general, CS is a stronger π -accepting ligand than CO, a conclusion with which there is general agreement.³⁻⁶ However, Andrews⁷ suggested, on the basis of $\nu(\text{CS})$ and $\nu(\text{CO})$ infrared stretching frequency trends, that the π -acceptor/ σ -donor ratio varies more for the CS ligand than for CO as the electron richness of the metal is varied. In electron-rich complexes, CS has a higher π -acceptor/ σ -donor ratio than CO, but in electron-poor systems CO has a higher π -acceptor/ σ -donor ratio. This crossover occurs when $\nu(\text{CO})$ force constants for the CO ligand are greater than 17.1 mdyn/Å. This argument suggests that if π -donation from the metal is the most important factor

determining M-CS bond distances, M-CO distances should be longer than M-CS distances in electron-rich complexes, but the reverse would be true in electron-poor systems. Up to this point, all accurate X-ray structural determinations of complexes where M-CO and M-CS bond distance comparisons can be made are for electron-rich complexes where k_{CO} is less than 17.1 mdyn/Å. In this paper, we report the structure of the cationic complex $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CS})^+$, whose k_{CO} value is 17.4 mdyn/Å.⁷

Experimental Section

The complex $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CS})]\text{PF}_6$ (1) was prepared and crystallized as described previously.⁸

X-ray Crystallographic Analysis. A crystal of the title compound was mounted on a glass fiber, positioned on a goniometer head, and then placed on a four-circle diffractometer designed and built at Ames Laboratory.⁹ The crystal was cooled to 143 K, and 10 independent reflections selected from preliminary ω -oscillation programs were used as input to an automatic indexing program.¹⁰ The resulting reduced cell scalars indicated monoclinic symmetry. Unit cell parameters were determined by a least-squares refinement of tuned 2θ values for 12 independent reflections ($24 < 2\theta < 39^\circ$). The space group *C2/c* was selected on the basis of the observed extinctions hkl ($h + k = 2n + 1$) and $h0l$ ($l = 2n + 1$) and a statistical test indicating the presence of a center of symmetry. Equivalent data were averaged ($R_{\text{av}} = 0.040$), yielding 2320 unique observed reflections. Crystallographic data are given in Table I.

All non-hydrogen atom positions, except those for two fluorine atoms and one carbonyl oxygen, were found from a sharpened Patterson map by using the Patterson analysis computer program ALCAMPS.¹¹ The remaining atoms were found from subsequent electron density map calculations. The positional and anisotropic thermal parameters for the non-hydrogen atoms were refined by a combination of block-matrix/full-matrix least-squares calculations.¹² Hydrogen atom positions and

(1) Baird, M. C.; Wilkinson, G. *Chem. Commun.* 1966, 267.

(2) de Boer, J. L.; Rogers, D.; Skapskii, A. C.; Troughton, R. G. *H. Chem. Commun.* 1966, 756.

(3) Butler, I. S.; Fenster, A. E. *J. Organomet. Chem.* 1974, 66, 161.

(4) Yaneff, P. V. *Coord. Chem. Rev.* 1977, 23, 183.

(5) Butler, I. S. *Acc. Chem. Res.* 1977, 10, 359.

(6) Broadhurst, P. V. *Polyhedron* 1985, 4, 1801.

(7) Andrews, M. A. *Inorg. Chem.* 1977, 16, 496.

(8) Dombek, B. D.; Angelici, R. J. *Inorg. Synth.* 1977, 17, 100.

(9) Rohrbaugh, W. J.; Jacobson, R. A. *Inorg. Chem.* 1974, 13, 2535.

(10) Jacobson, R. A. *J. Appl. Crystallogr.* 1976, 9, 115.

(11) Richardson, J. W., Jr. Ph.D. Dissertation, Iowa State University, Ames, IA, 1984.