

# Synthesis, Characterization, and Structure of Tri- $\mu$ -halogeno-hexacarbonyldirhenate(I) Salts of Monocationic Porphyrin Acids

C. P. Hrung,<sup>1a</sup> M. Tsutsui,\*<sup>1a</sup> D. L. Cullen,<sup>1b</sup> E. F. Meyer, Jr.,<sup>1b</sup>  
and C. N. Morimoto<sup>1c</sup>

Contribution from the Department of Chemistry and Department of Biophysics and Biochemistry, Texas Agricultural Experiment Station, Texas A & M University, College Station, Texas 77843, and Control Data Corporation, Sunnyvale, California 94086. Received February 3, 1978

**Abstract:** Two new compounds,  $\mu$ -(2,3,7,8,12,13,17,18-octaethylporphyrin)-bis[tricarbonylrhenium(I)],  $(C_{36}H_{44}N_4)[Re(CO)_3]_2$ , and a salt of a monocationic porphyrin acid, octaethylporphyrinium tri- $\mu$ -chloro-hexacarbonyldirhenate(I),  $(C_{36}H_{47}N_4)^+[Re_2(CO)_6Cl_3]^-$ , have been synthesized by the reaction of a 2:1 mole ratio of rhenium pentacarbonyl chloride and octaethylporphyrin in refluxing decalin under argon. The structure of the latter was determined from three-dimensional diffractometer data. A total of 10 792 independent reflections were measured. The compound crystallizes in the monoclinic space group  $P2_1/a$  with a unit cell of  $a = 18.140$  (3) Å,  $b = 19.847$  (3) Å,  $c = 13.625$  (2) Å,  $\beta = 111.64$  (2)°. There are four molecules in the unit cell. The structure was solved by heavy-atom methods and refined by least-squares techniques to a conventional  $R$  index of 0.045 for the 5995 reflections having  $I \geq 3\sigma_I$ . The porphyrin monoacid cation has three coplanar pyrrole rings with the plane of the fourth ring tilted by 8.6° from the mean plane of the other three. Evidence indicates that the nitrogen atom in the tilted ring has  $sp^3$  hybridization. The anion consists of two rhenium atoms bridged by three chlorine atoms. Three carbonyl groups complete the octahedral coordination on each metal atom. There is a water molecule of crystallization which is involved in hydrogen bonding with the pyrrole nitrogen atoms of the cation. The salt could also be prepared using a 1.5/1  $Re(CO)_5Cl/H_2OEP$  mixture with  $(H-OEP)Re(CO)_3$  as the other product. Analogous compounds could be made using mesoporphyrin IX dimethyl ester and  $Re(CO)_5Br$ , but the monocationic porphyrin species could not be obtained when *meso*-tetraphenylporphyrin was used.

## Introduction

The metal-carbonyl insertion method<sup>2</sup> has been found useful for the preparation of bimetallic porphyrin complexes of rhodium, rhenium, and technetium.<sup>3,4</sup> Metal carbonyl halides are more reactive reagents than metal carbonyls for the synthesis of bimetallic complexes of porphyrins as well as bimetallic salts of porphyrin acids.<sup>5-8</sup> For example, dimeric rhodium dicarbonyl chloride reacts with porphyrin in benzene at ambient temperature or in boiling chloroform to form a dirhodium porphyrin complex or a dirhodium salt of a porphyrin diacid.<sup>9,10</sup> In the present work it was discovered that dimeric rhenium tetracarbonyl halides are also capable of reacting with porphyrin in refluxing decalin to form a monorhenium or a dirhenium porphyrin complex as well as a salt complex of a porphyrin monoacid.<sup>11</sup> This salt contains an anionic dimeric halocarbonyl rhenium complex, tri- $\mu$ -halogeno-hexacarbonyldirhenate(I). The structure of the salt containing chlorine as the halogen and octaethylporphyrinium monoacid as the cation has been elucidated by several means, primary among them being an X-ray structural analysis. A preliminary communication on this work has been published.<sup>11</sup>

Only a few porphyrin acid structures have been reported. Most of these have been porphyrin diacids. The earlier studies revealed macrocycles with large deviations from planarity, presumably because of the nonbonded interactions between the four imino hydrogen atoms.<sup>7</sup> However, a more recent report on the structure of an  $H_4OEP^{2+}$  salt ( $OEP =$  octaethylporphyrin anion) showed that the macrocycle in that case was nearly planar.<sup>10</sup> Monoacid porphyrin cations are uncommon. Samuels, Shuttleworth, and Stevens<sup>12</sup> reported the preparation of a triiodo derivative of octaethylporphyrin. A later X-ray structure determination, reported by Hirayama et al. in a short communication, revealed that this compound should be formulated as  $(H_3OEP)^+I_3^-$ .<sup>5</sup> While the macrocycle in this case shows some deviations from planarity, the H-H contacts inside the porphyrin "hole" are still too short if the pyrrole nitrogen

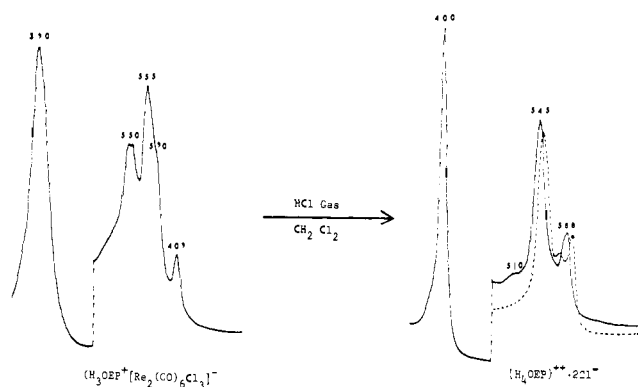
atoms are assumed to be trigonally hybridized. Thus partial  $sp^3$  hybridization of the nitrogen atoms has been proposed for both the monocationic and dicationic octaethylporphyrin salts.<sup>5,10</sup> Such a hybridization would be necessary to explain the proposed hydrogen bonding in the  $H_4OEP^{2+}$  structure.<sup>10</sup>

In all of the porphyrin acid structures so far reported, the data have not been of sufficient quality to examine these suggestions adequately. However, in the present case, crystals of excellent quality were available. Thus in addition to elucidating the nature of the material obtained in the synthetic procedure, a full X-ray analysis promised to shed some light on the nature and conformations of the porphyrin acids.

## Results and Discussion

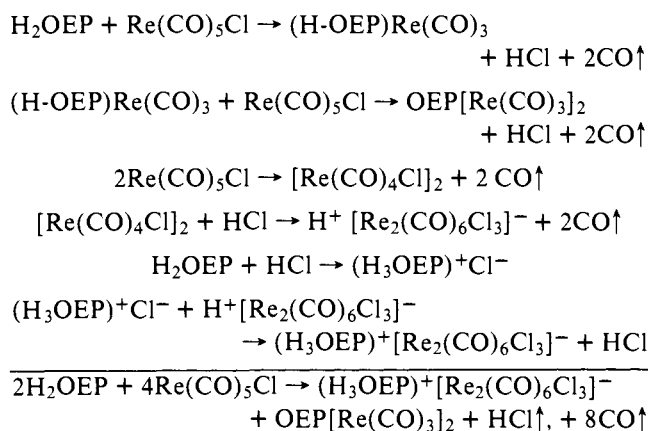
**Monocation Porphyrinium Tri- $\mu$ -halogeno-hexacarbonyldirhenate(I).** Rhenium pentacarbonyl chloride,  $Re(CO)_5Cl$ , and octaethylporphyrin,  $H_2OEP$ , in a 2:1 mole ratio reacted in decalin under argon to form a dirhenium octaethylporphyrin complex,  $OEP[Re(CO)_3]_2$ , and a new compound, I. The structure of the new compound was formulated as  $(H_3OEP)^+[Re_2(CO)_6Cl_3]^-$ , monocation octaethylporphyrinium tri- $\mu$ -chloro-hexacarbonyldirhenate(I), based on elemental analysis, spectroscopic data, and a single-crystal X-ray diffraction analysis.

The new compound I is sensitive to moisture and heat. It is stable in dry methylene chloride, tetrahydrofuran, and ethyl acetate but decomposes immediately in alcohols, acetone, and water to free octaethylporphyrin,  $H_2OEP$ . It can be kept under argon for several days without decomposition in a vacuum desiccator stored in a refrigerator. However, it decomposes gradually in solution at room temperature to dirhenium octaethylporphyrin as indicated by its visible absorption spectrum. This behavior was confirmed by heating a purified sample of I in decalin under argon (Figure 2). After cooling, dirhenium octaethylporphyrin formed in the supernatant while the undecomposed burgundy-colored solid of I remained at the



**Figure 1.** Visible spectra of  $(\text{H}_3\text{OEP})^+[\text{Re}_2(\text{CO})_6\text{Cl}_3]^-$  and  $(\text{H}_4\text{OEP})^{2+}2\text{Cl}^-$ .

#### Scheme I



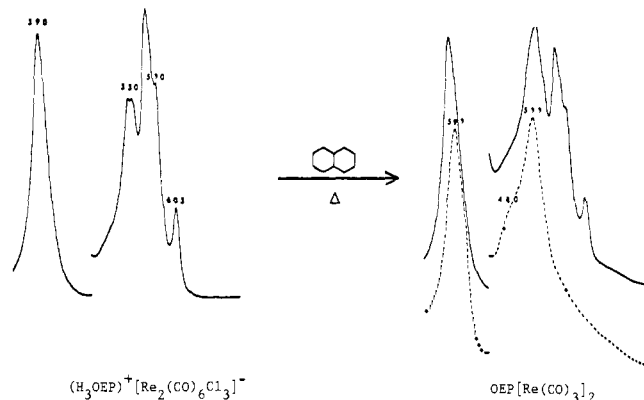
bottom of the reaction flask. The amount of the dirhenium octaethylporphyrin varied with the heating time and temperature, between 100 and 195 °C for 2–10 h. Prolonged heating of I in refluxing decalin for 1–2 days caused further decomposition to monorhenium octaethylporphyrin, (H-OEP)-Re(CO)<sub>3</sub>, as indicated by its visible absorption spectrum.<sup>11</sup>

By reaction of H<sub>2</sub>MPIXDME with stoichiometric quantities of Re(CO)<sub>5</sub>Br or [Re(CO)<sub>4</sub>Br]<sub>2</sub> in refluxing decalin under argon, an analogous salt-like complex of I was prepared: (H<sub>3</sub>MPIXDME)<sup>+</sup>[Re<sub>2</sub>(CO)<sub>6</sub>Br<sub>3</sub>]<sup>-</sup> (II), monocation meso-porphyrinium IX dimethyl ester tri- $\mu$ -bromo-hexacarbonyldirhenate(I). This complex has chemical and spectroscopic properties similar to those of I (Figure 3). Therefore, a structure identical with that of I is proposed for II.

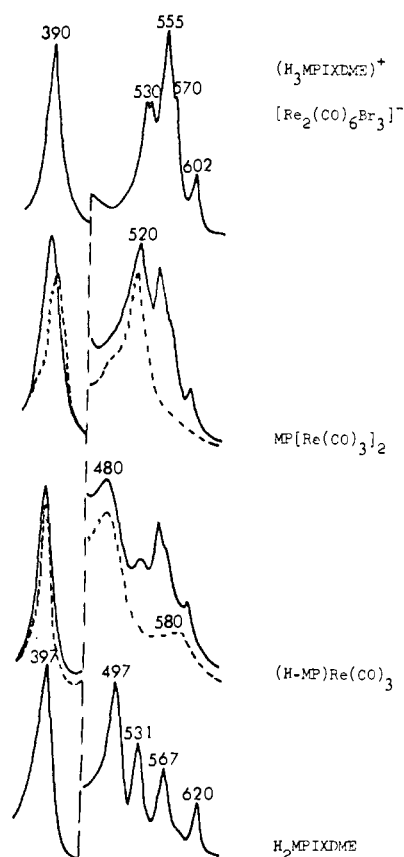
On the basis of the stepwise changes of visible absorption spectra of the reaction mixture and the X-ray crystal structure of I, Scheme I was proposed.

Because of the instability of *meso*-tetraphenylporphine monocation,<sup>6,7</sup> none of the corresponding monocation tetraphenylporphyrinium analogues could be prepared; possible reasons for this instability are outlined by Fleischer.<sup>7</sup>

**X-ray Structural Data.** A preliminary study on the single-crystal X-ray diffraction analysis of I has already been reported.<sup>11</sup> It is an ionic compound with the porphyrin moiety present as a monocationic species, H<sub>3</sub>OEP<sup>+</sup>. In the anionic species [Re<sub>2</sub>(CO)<sub>6</sub>Cl<sub>3</sub>]<sup>-</sup>, the two rhenium ions have octahedral coordination. They are joined by three bridging chlorine atoms. Three carbonyl groups on each metal ion complete the coordination. ORTEP<sup>13</sup> drawings of the compound are shown in Figure 4. Figure 4a also shows the nomenclature for the different types of carbon atoms and the designations for the four rings. A stereoview of the entire formula unit, including a water molecule of crystallization, is shown in Figure 5.



**Figure 2.** Thermal decomposition of  $(\text{H}_3\text{OEP})^+[\text{Re}_2(\text{CO})_6\text{Cl}_3]^-$  to form  $\text{OEP}[\text{Re}(\text{CO})_3]_2$  in refluxing decalin. The latter was isolated after cooling to have absorptions as shown in the dotted line.



**Figure 3.** Repeated scan spectrophotometry showing progress of the formation of  $(\text{H-MP})\text{Re}(\text{CO})_3$ ,  $\text{MP}[\text{Re}(\text{CO})_3]_2$ , and  $(\text{H}_3\text{MPIXDME})^+[\text{Re}_2(\text{CO})_6\text{Br}_3]^-$ .

**A. Cation.** The imino hydrogen atoms appear to be localized on rings A, B, and C. Such a localization was postulated for the H<sub>3</sub>OEP<sup>+</sup> cation as found in the triiodide salt.<sup>5</sup> The hydrogen atoms in that study were not located directly, but the C<sub>a</sub>-N-C<sub>a</sub> angle for one ring was reported as 102° as compared to the values of 109 and 110° for the other two crystallographically independent rings, which presumably bear imino hydrogen atoms. A similar difference is noted in the present case. Bond lengths and angles are tabulated in Table I. Some nonbonded contacts of interest are also shown. Ring D, the pyrroline ring, has a C<sub>a</sub>-N-C<sub>a</sub> bond angle of 105.3 (6)°, while the analogous angles on the other three rings are 110.6 (6), 108.3 (6), and 110.8 (6)°. These values for rings A, B, and D correspond to those tabulated by Hoard<sup>14</sup> for pyrrole rings

Table I. Bond Lengths (Å) and Angles (deg)<sup>a</sup>

A. Cation				B. Anion			
N(1)-C(1)	1.377 (9)	C(1)-N(1)-C(4)	110.6 (6)	Re(1)-Cl(1)	2.517 (2)	Cl(1)-Re(1)-Cl(2)	79.06 (5)
N(1)-C(4)	1.351 (9)	C(6)-N(2)-C(9)	108.3 (6)	Re(1)-Cl(2)	2.501 (2)	Cl(1)-Re(1)-Cl(3)	79.87 (6)
N(2)-C(6)	1.382 (8)	C(11)-N(3)-C(14)	110.8 (5)	Re(1)-Cl(3)	2.493 (2)	Cl(1)-Re(1)-C(37)	171.0 (2)
N(2)-C(9)	1.391 (8)	C(16)-N(4)-C(19)	105.3 (6)	Re(1)-C(37)	1.889 (8)	Cl(1)-Re(1)-C(38)	95.6 (3)
N(3)-C(11)	1.378 (8)	N(1)-C(1)-C(2)	106.4 (6)	Re(1)-C(38)	1.852 (10)	Cl(1)-Re(1)-C(39)	97.1 (2)
N(3)-C(14)	1.363 (8)	N(1)-C(1)-C(20)	125.3 (6)	Re(1)-C(39)	1.877 (8)	Cl(2)-Re(1)-C(37)	94.6 (2)
N(4)-C(16)	1.367 (8)	C(2)-C(1)-C(20)	128.2 (6)	Re(2)-Cl(1)	2.530 (2)	Cl(2)-Re(1)-C(38)	93.8 (2)
N(4)-C(19)	1.364 (8)	C(2)-C(1)-C(20)	128.2 (6)	Re(2)-Cl(2)	2.509 (2)	Cl(2)-Re(1)-C(39)	175.1 (2)
C(1)-C(2)	1.406 (9)	C(1)-C(2)-C(3)	107.9 (6)	Re(2)-Cl(3)	2.501 (2)	Cl(3)-Re(1)-C(37)	92.9 (2)
C(1)-C(20)	1.366 (10)	C(1)-C(2)-C(21)	124.6 (7)	Re(2)-C(40)	1.091 (9)	Cl(3)-Re(1)-C(38)	173.4 (3)
C(2)-C(3)	1.381 (9)	C(3)-C(2)-C(21)	127.5 (7)	Re(2)-C(41)	1.897 (9)	Cl(3)-Re(1)-C(39)	95.7 (2)
C(2)-C(21)	1.496 (9)	C(2)-C(3)-C(4)	107.7 (6)	Re(2)-C(42)	1.867 (9)	C(37)-Re(1)-C(38)	91.2 (3)
C(3)-C(4)	1.407 (9)	C(2)-C(3)-C(23)	126.3 (6)	C(37)-O(1)	1.142 (8)	C(37)-Re(1)-C(39)	88.9 (3)
C(3)-C(23)	1.504 (10)	C(4)-C(3)-C(23)	126.0 (6)	C(38)-O(2)	1.191 (9)	C(38)-Re(1)-C(39)	89.5 (3)
C(4)-C(5)	1.391 (9)	N(1)-C(4)-C(3)	107.2 (6)	C(39)-O(3)	1.138 (8)	Cl(1)-Re(2)-Cl(2)	76.68 (5)
C(5)-C(6)	1.381 (9)	N(1)-C(4)-C(5)	124.6 (6)	C(40)-O(4)	1.158 (9)	Cl(1)-Re(2)-Cl(3)	79.47 (6)
C(6)-C(7)	1.417 (9)	C(3)-C(4)-C(5)	128.1 (7)	C(41)-O(5)	1.125 (8)	Cl(1)-Re(2)-C(40)	96.57 (2)
C(7)-C(8)	1.348 (9)	C(4)-C(5)-C(6)	131.3 (6)	C(41)-O(6)	1.159 (9)	Cl(1)-Re(2)-C(41)	170.9 (2)
C(7)-C(25)	1.523 (10)	N(2)-C(6)-C(5)	123.8 (6)	Re(1)-Re(2)	3.375 (1)	Cl(1)-Re(2)-C(42)	97.5 (3)
C(8)-C(9)	1.410 (9)	N(2)-C(6)-C(7)	107.4 (6)			Cl(2)-Re(2)-Cl(3)	80.37 (6)
C(8)-C(27)	1.516 (9)	C(5)-C(6)-C(7)	128.8 (6)			Cl(2)-Re(2)-C(40)	174.8 (2)
C(9)-C(10)	1.381 (9)	C(6)-C(7)-C(8)	108.2 (6)			Cl(2)-Re(2)-C(41)	95.6 (2)
C(10)-C(11)	1.352 (9)	C(6)-C(7)-C(25)	123.8 (6)			Cl(2)-Re(2)-C(42)	93.9 (3)
C(11)-C(12)	1.435 (9)	C(8)-C(7)-C(25)	128.0 (6)			Cl(3)-Re(2)-C(40)	96.8 (3)
C(12)-C(13)	1.358 (9)	C(7)-C(8)-C(9)	108.8 (6)			Cl(3)-Re(2)-C(41)	92.7 (2)
C(12)-C(29)	1.520 (9)	C(7)-C(8)-C(27)	127.6 (6)			Cl(3)-Re(2)-C(42)	173.9 (3)
C(13)-C(14)	1.421 (8)	C(9)-C(8)-C(27)	123.6 (6)			C(40)-Re(2)-C(41)	88.9 (3)
C(13)-C(31)	1.520 (9)	N(2)-C(9)-C(8)	107.1 (6)			C(40)-Re(2)-C(42)	88.7 (4)
C(14)-C(15)	1.392 (9)	N(2)-C(9)-C(10)	123.5 (6)			C(41)-Re(2)-C(42)	89.9 (3)
C(15)-C(16)	1.392 (9)	C(8)-C(9)-C(10)	129.2 (6)			Re(1)-Cl(1)-Re(2)	83.93 (6)
C(16)-C(17)	1.425 (9)	C(9)-C(10)-C(11)	130.0 (6)			Re(1)-Cl(2)-Re(2)	84.70 (6)
C(17)-C(18)	1.341 (10)	N(3)-C(11)-C(10)	125.6 (6)			Re(1)-Cl(3)-Re(2)	85.02 (6)
C(17)-C(33)	1.495 (10)	N(3)-C(11)-C(12)	105.5 (6)			Re(1)-C(37)-O(1)	177.7 (7)
C(18)-C(19)	1.419 (10)	C(10)-C(11)-C(12)	129.0 (6)			Re(1)-C(38)-O(2)	177.8 (8)
C(18)-C(35)	1.698 (20)	C(11)-C(12)-C(13)	108.7 (6)			Re(1)-C(39)-O(3)	179.2 (7)
C(19)-C(20)	1.407 (10)	C(11)-C(12)-C(29)	123.3 (6)			Re(2)-C(40)-O(4)	179.1 (8)
C(21)-C(22)	1.458 (13)	C(13)-C(12)-C(29)	127.9 (6)			Re(2)-C(41)-O(5)	177.5 (8)
C(23)-C(24)	1.467 (12)	C(13)-C(12)-C(14)	107.9 (6)			Re(2)-C(42)-O(6)	178.7 (8)
C(25)-C(26)	1.449 (12)	C(12)-C(13)-C(14)	107.9 (6)				
C(27)-C(28)	1.480 (13)	C(12)-C(13)-C(31)	128.3 (6)				
C(29)-C(30)	1.486 (11)	C(14)-C(13)-C(31)	123.6 (6)				
C(31)-C(32)	1.472 (10)	N(3)-C(14)-C(13)	107.1 (6)				
C(33)-C(34)	1.472 (12)	N(3)-C(14)-C(15)	125.2 (6)				
C(35)-C(36)	1.262 (18)	C(13)-C(14)-C(15)	127.7 (6)				
N(1)-H(1)	0.62 (7)	C(14)-C(15)-C(16)	129.0 (6)				
N(2)-H(2)	0.84 (7)	N(4)-C(16)-C(15)	124.1 (6)				
N(3)-H(3)	0.62 (8)	N(4)-C(16)-C(17)	110.8 (6)				
N(1)-N(2)	3.002 (9)	C(15)-C(16)-C(17)	125.1 (6)				
N(1)-N(4)	2.908 (9)	C(16)-C(17)-C(18)	105.9 (6)				
N(2)-N(3)	2.940 (9)	C(16)-C(17)-C(33)	125.3 (6)				
N(3)-N(4)	2.945 (9)	C(18)-C(17)-C(33)	128.7 (7)				
N(1)-N(3)	4.226 (8)	C(17)-C(18)-C(19)	108.1 (6)				
N(2)-N(4)	4.113 (9)	C(17)-C(18)-C(35)	127.4 (7)				
C(5)-C(15)	6.782 (10)	C(19)-C(18)-C(35)	122.7 (18)				
C(10)-C(20)	6.883 (10)	N(4)-C(19)-C(18)	109.9 (6)				
		N(4)-C(19)-C(20)	125.2 (7)				
		C(18)-C(19)-C(20)	124.7 (7)				

<sup>a</sup> Some nonbonded distances of interest are also given.

respectively lacking and carrying an N-H bond in free base porphyrins. The value for ring B is intermediate. Reasons for this apparent anomaly will be discussed below.

Unlike the earlier studies, electron density peaks corresponding to the imino hydrogen atoms were found in the present case, thus confirming the localization of hydrogen atoms. No evidence of any electron density corresponding to a hydrogen atom bonded to N(4) (ring D) was found.

Of particular interest is the planarity of the cation. The free base of octaethylporphyrin is essentially planar. The structure of *meso*-tetraphenylporphyrin, H<sub>2</sub>TPP, has been reported as planar in a triclinic crystalline modification<sup>15</sup> and as nonplanar in a tetragonal crystalline modification.<sup>16</sup> Three structures of

divalent cationic porphyrin species have been reported. In the two earlier studies, both of which involved *meso*-substituted porphyrins, the cations are decidedly nonplanar.<sup>7</sup> In these nonplanar species, the symmetry of the cations may be described as S<sub>4</sub>. The nonplanarity of these cations has been postulated as a mechanism for relieving the crowding of the imino hydrogen atoms. In a much more recent study, the H<sub>4</sub>OEP<sup>2+</sup> cation, as observed in a crystalline salt formulated as (H<sub>4</sub>OEP<sup>2+</sup>)[Rh(Cl<sub>2</sub>)(CO)<sub>2</sub>]<sub>2</sub>, is nearly planar.<sup>10</sup>

As in the earlier study,<sup>5</sup> the monovalent H<sub>3</sub>OEP<sup>+</sup> cation in the present work has three of the four pyrrole rings (A, C, D) approximately coplanar. Information on least-squares planes is given in Table II. As is normally found the individual pyrrole

Table II. Least-Squares Planes

	A. Deviations ( $\text{\AA}$ ) from Planes						
	plane 1	plane 2	plane 3	plane 4	plane 5	plane 6	plane 7
N(1)	0.007	-0.027	-0.008	-0.003	-0.298	0.106	0.102
N(2)	0.127	0.027	0.092	0.208	-0.009	0.095	0.183
N(3)	-0.013	-0.027	-0.024	0.109	-0.504	-0.002	-0.016
N(4)	-0.024	0.027	-0.015	0.009	-0.677	0.117	0.013
C(1)	0.040	0.044	0.036	-0.008	-0.373	0.203	0.148
C(2)	0.102	0.082	0.091	0.016	-0.196	0.273	0.243
C(3)	0.050	-0.020	0.026	-0.018	-0.072	0.165	0.199
C(4)	0.035	-0.043	0.008	0.014	-0.094	0.105	0.154
C(5)	-0.107	-0.226	-0.147	-0.100	-0.111	-0.096	0.006
C(6)	0.002	-0.133	-0.042	0.057	0.018	-0.040	0.088
C(7)	-0.189	-0.371	-0.247	-0.105	-0.022	-0.295	-0.107
C(8)	-0.091	-0.266	-0.147	0.036	0.017	-0.225	-0.039
C(9)	0.078	-0.047	0.035	0.204	-0.005	-0.011	0.0112
C(10)	0.094	-0.007	0.058	0.255	-0.108	-0.001	0.095
C(11)	0.052	0.001	0.030	0.213	-0.331	0.000	0.036
C(12)	0.060	0.034	0.045	0.258	-0.444	0.001	0.011
C(13)	0.009	0.024	0.000	0.183	-0.674	-0.002	-0.055
C(14)	-0.041	-0.009	-0.038	0.094	-0.708	0.002	-0.067
C(15)	-0.049	0.027	-0.035	0.054	-0.860	0.057	-0.071
C(16)	-0.023	0.064	-0.004	0.034	-0.830	0.130	-0.016
C(17)	0.004	0.139	0.036	0.033	-0.958	0.221	0.013
C(18)	-0.046	0.082	-0.016	-0.059	-0.946	0.198	-0.005
C(19)	-0.062	0.014	-0.046	-0.073	-0.771	0.135	-0.004
C(20)	-0.007	0.047	0.003	-0.055	-0.603	0.200	0.084
O(7)	2.254	2.228	2.241	2.304	1.844	2.311	2.304

	B. Angles (deg) between Least-Squares Planes					
	plane 2	plane 3	plane 4	plane 5	plane 6	plane 7
plane 1	2.1	0.6	1.9	7.7	2.7	1.4
plane 2		1.5	3.2	9.8	1.5	2.9
plane 3			2.2	8.3	2.2	1.7
plane 4				7.9	4.3	3.2
plane 5					9.8	7.1
plane 6						2.7

C. Equations of Planes <sup>a</sup>	
plane 1 macrocycle: N(1)-N(4), C(1)-C(20)	plane 5 ring B: N(2), C(6)-C(9)
$11.711x + 12.286y - 8.909z = -2.725$	$10.883x + 14.155y - 7.604z = -1.625$
plane 2 N(1)-N(4)	plane 6 ring C: N(3), C(11)-C(14)
$11.992x + 11.703y - 9.197z = -2.854$	$12.296x + 11.627y - 9.032z = -2.812$
plane 3 N(1), N(3), N(4), C(1)-C(5), C(10)-C(20)	plane 7 ring D: N(4), C(16)-C(19)
$11.796x + 12.121y - 8.990z = -2.755$	$11.899x + 12.36y - 8.693z = -2.628$
plane 4 ring A: N(1), C(1)-C(4)	
$11.274x + 12.454y - 9.063z = -2.909$	

<sup>a</sup> All planes are unweighted.  $x$ ,  $y$ ,  $z$  are in monoclinic fractional coordinates.

rings are planar. For rings A, C, and D the interplanar angles between adjacent pyrrole rings are 3.2 and 2.7°. The maximum deviation of an atom in rings A, B, and D from the mean plane of these three rings is 0.09 Å (for C(2)). The fourth ring (B) is tilted by 8.6° from the plane of the other three rings. By way of comparison, this angle is 14° in the triiodide salt. In the current study, interplanar angles between ring B and the adjacent rings are 7.9 and 9.8°.

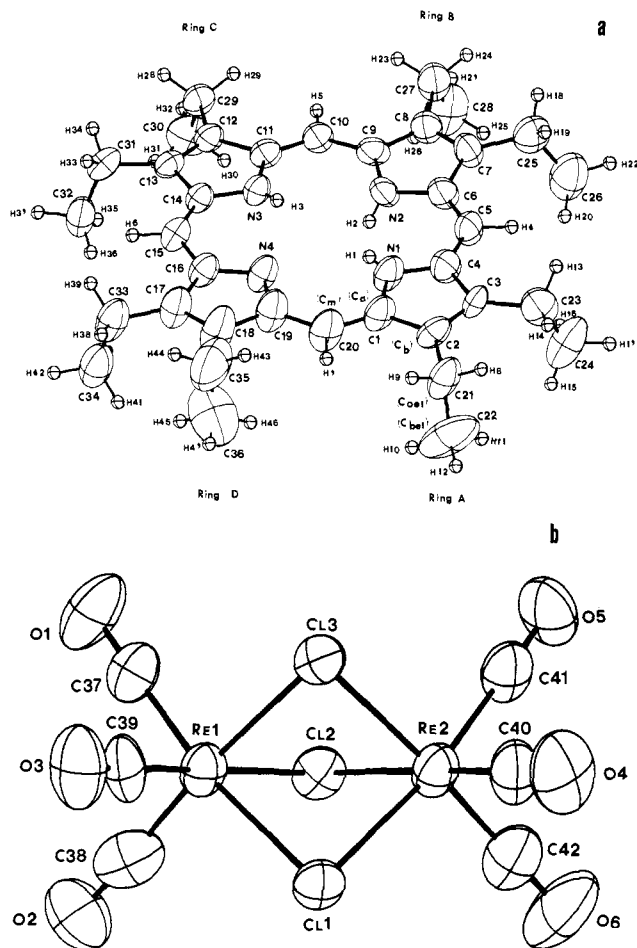
It is believed that this deviation from planarity is due in part to the tight H-H contacts of the imino hydrogens. Ring B, the one which is not coplanar, bears the imino hydrogen atom which comes in closest contact with the other two imino hydrogen atoms. However, this deviation from planarity is still not sufficient to relieve the tight contacts completely. In the present case, the H-H contacts are still ~1.5–1.6 Å if we assume trigonal hybridization and a N-H bond length of 1.0 Å. The minimum H-H nonbonded contact is usually taken to be 1.9–2.0 Å.<sup>17</sup>

In both the H<sub>4</sub>OEP<sup>2+</sup> salt<sup>10</sup> and in the triiodide salt of

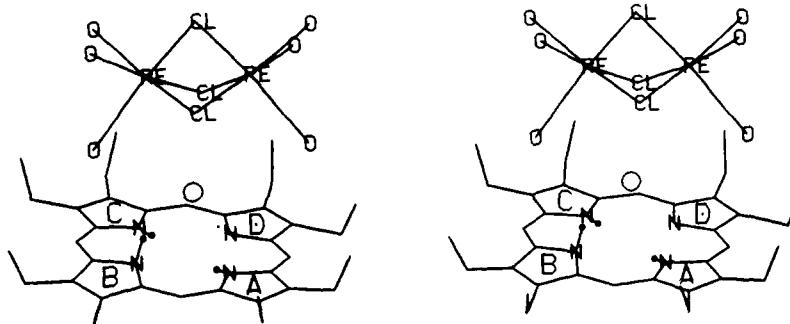
H<sub>3</sub>OEP<sup>+</sup>,<sup>5</sup> sp<sup>3</sup> hybridization of the nitrogen atoms has been postulated. Such a hybridization would be advantageous for a number of reasons. Most importantly, such a hybridization would relieve the tight H-H contacts. A second reason would be to explain the hydrogen-bonding arrangement found in some of these compounds.

In the case of the H<sub>4</sub>OEP<sup>2+</sup> salt,<sup>10</sup> hydrogen bonds are postulated between the pyrrole nitrogen atoms and one of the chlorine atoms of the anion. For this to occur, the N-H bonds need to point more or less directly toward the chlorine atoms, as would be the case if there were sp<sup>3</sup> hybridization of the nitrogen atoms.

In the triiodide salt of H<sub>3</sub>OEP<sup>+</sup>,<sup>5</sup> no hydrogen bonding is reported. In the present case there is hydrogen bonding between the pyrrole nitrogen atoms and the water molecule of solvation. Intermolecular contacts between pyrrole nitrogen atoms and the oxygen atom of the water molecule are shown schematically in Figure 6. N...O distances are 2.97, 2.99, and 3.05 Å for N(1), N(2), and N(4), respectively. These are short



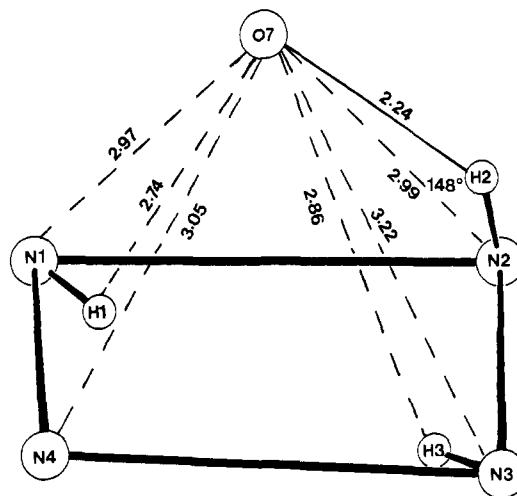
**Figure 4.** (a) ORTEP<sup>13</sup> drawing of the porphyrin cation, H<sub>3</sub>OEP<sup>+</sup>. Numbering scheme is shown. Shown in parentheses are the designations for the various types of carbon atoms. The thermal ellipsoids are drawn for 50% probability, except those of the hydrogen atoms, which are not drawn to scale. H(21) and H(40) are hidden behind C(26) and C(34), respectively. (b) ORTEP drawing of the complex anion.



**Figure 5.** A stereoview of the formula unit of (H<sub>3</sub>OEP)<sup>+</sup>[Re<sub>2</sub>(CO)<sub>6</sub>Cl<sub>3</sub>]<sup>-</sup>·H<sub>2</sub>O. The water of crystallization is illustrated by a large circle. Imino hydrogen atoms are indicated by small circles. Other hydrogen atoms have been omitted. The notation of the pyrrole rings is shown. Note the tilt of ring B with respect to the macrocycle.

enough to be considered hydrogen-bonding distances. The fourth N ... O distance (N(3) ... O(7)) is 3.22 Å, probably too long to be considered a hydrogen bond. There are also fairly short intermolecular distances between the water molecule and two of the chlorine atoms of the anion (O(7)-Cl(1), 3.43 Å; O(7)-Cl(2), 3.46 Å) but these are probably too long to be considered O-H ... Cl hydrogen bonds.

Thus, there are at least three hydrogen bonds involving the water molecule. At least one of the hydrogen bonds should involve an imino hydrogen atom, especially since N(4) has no hydrogen atom of its own and yet is implicated in the hydrogen bonding scheme. The observed hydrogen atom positions would



**Figure 6.** Schematic drawing showing the significant contacts between the porphyrins cation and the oxygen atom of the water of crystallization. The lines between nitrogen atoms signify the planes of the macrocycle. Of the hydrogen atoms shown, it is believed that only H(2) is involved in hydrogen bonding. This is indicated by a solid line between H(2) and O(7). The N(2)-H(2)-O(7) bond angle is also shown.

indicate that N(2) has at least some degree of sp<sup>3</sup> hybridization, whereas N(1) and N(3) are trigonally hybridized. H(1) and H(3) are 0.13 (7) and 0.04 (7) Å, respectively, out of planes defined by the pyrrole rings to which they are bonded. The bond angles also indicate trigonal hybridization. On the other hand H(2) is 0.68 (7)° out of the plane of ring B in the direction of the water molecule. The N(2)-H(2) ... O(7) angle is 148°. It is presumed that the hydrogen atoms of the water molecule are involved in the other two hydrogen bonds. However, these hydrogen atoms could not be located. This is not surprising in view of the difficulty of locating hydrogen atoms in the presence of heavy metal ions. There is also a possibility the positions of these atoms may be disordered. If N(2) is a sp<sup>3</sup>-hybridized atom, the problem of tight H-H

contacts is also eliminated. The three observed H-H contacts are 2.62 (H(1)-H(2)), 3.00 (H(1)-H(3)), and 2.34 Å (H(2)-H(3)). If the hydrogen atom positions are given idealized values (assuming sp<sup>3</sup> hybridization for N(2), trigonal hybridization for N(1) and N(3), and a N-H bond length of 1.0 Å) the corresponding H-H contacts are 2.22, 2.23, and 2.19 Å.

A caveat should be observed here. The accuracy of the hydrogen atom positions is quite low. For example, the N-H observed bond lengths in this case are certainly underestimated and the angles involving H(2) differ considerably from ideal values. Thus the observed hydrogen atom positions should be

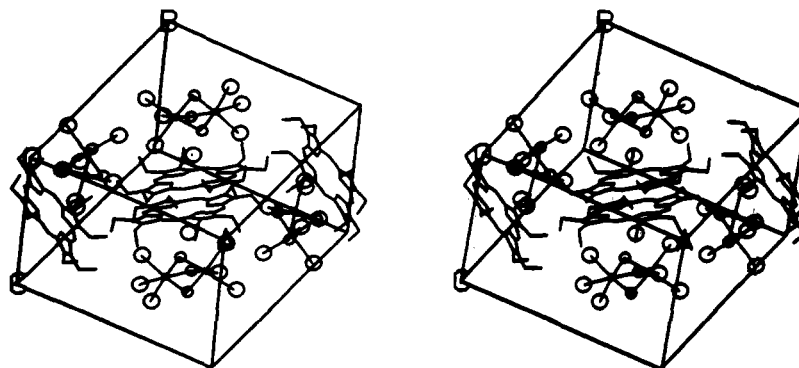


Figure 7. Stereoview of the packing in the unit cell. Circles of increasing size represent rhenium, chlorine, and oxygen atoms, respectively.

viewed as merely an indication of the nature of the nitrogen atom hybridization. However, other supportive geometric evidence for the suggested hybridization is available.

The  $C_a-N-C_a$  angle in ring B ( $108.3(6)^\circ$ ) is significantly less than that found in rings A and C ( $110.6(6)$  and  $110.8(5)^\circ$ ). In an N-substituted porphyrin, ethoxycarbonylmethyloctaethylporphyrin,<sup>18</sup> the only reported structure which could serve as a valid comparison, the  $C_a-N-C_a$  angle is  $107^\circ$  on the pyrrole ring which has the substituent on the nitrogen atom. There is little doubt that the nitrogen atom in this ring has  $sp^3$  hybridization. On the other hand, the angle is  $109^\circ$  in the ring in which the nitrogen atom is trigonally hybridized and bears a hydrogen atom. Unfortunately the standard deviations in this compound make it difficult to assess the significance of these differences. However, as previously noted, the angle in ring B is significantly smaller than that found in free base porphyrins for pyrrole rings carrying a N-H bond, yet significantly larger than that found in rings lacking a N-H bond.<sup>14</sup>

The  $C_a-N$  bond lengths provide inconclusive evidence for this hybridization scheme. One would expect a bond length of  $\sim 1.41$  Å if  $sp^3$  hybridization were present, as opposed to  $\sim 1.38$  Å if there were trigonal hybridization.<sup>4,18</sup> The  $C_a-N$  distances are slightly longer in ring B than in the other rings, but this difference is not statistically significant. Given the esd of  $\sim 0.01$  Å in a bond length, it is not unexpected that a difference, if there is one, cannot be observed.

The average  $C_a-C_b$  distance of  $1.42(1)$  Å is somewhat shorter than the usual  $1.44$  Å, but once again it is difficult to judge the statistical significance of the difference. The  $C_b-C_b$  distances fall within the range tabulated by Hoard.<sup>14</sup> With the exception of the  $C_a-C_m-C_a$  angles, other bond parameters in the macrocyclic skeleton agree well with those tabulated. These angles are larger than expected, especially those involving atoms in ring B. Angles of  $125-127^\circ$  are normally found.<sup>14</sup> Opening of the  $C_a-C_m-C_a$  angle would further increase the distance between the hydrogen atoms. In an oxodipyrromethene where pyrrole rings bear imino hydrogen atoms, the angle is  $133^\circ$ , presumably to relieve the close H-H contacts.<sup>19</sup> Since ring D does not bear an imino hydrogen atom, the need for an extension of the  $C_a-C_m-C_1$  angle is eliminated and the angles involving this ring are smaller.

The values for terminal C-C bonds are unusually short. This is a common observation for octaethylporphyrin complexes and is probably due to thermal shortening. Previous experience has shown that when these bond distances are corrected for thermal motion assuming a "riding" model, more reasonable values are obtained.<sup>20</sup> However, thermal shortening does not completely explain the short C(35)-C(36) distance. This is undoubtedly short because of the unusually long C(18)-C(35) distance. No explanation for this long bond length is readily available. The large thermal ellipsoids and standard deviations for C(35) and C(36) may indicate some disorder, but attempts to resolve this

Table III. Intermolecular Contacts (Å)  $\leq 3.5$  Å<sup>f</sup>

Cl(2)-O(7)	3.43	O(1)-C(33) <sup>a</sup>	3.47
Cl(3)-O(7)	3.47	O(1)-C(34) <sup>a</sup>	3.20
C(38)-O(7)	3.46	C(5)-C(31) <sup>b</sup>	3.45
N(1)-O(7)	2.97*	C(27)-C(33) <sup>b</sup>	3.47
N(2)-O(7)	2.99*	O(1)-C(24) <sup>c</sup>	3.30
N(3)-O(7)	3.22	O(2)-O(4) <sup>d</sup>	3.09
N(4)-O(7)	3.05*	O(3)-C(21) <sup>e</sup>	3.38
O(2)-C(10)	3.19		
O(2)-C(11)	3.24		
O(6)-C(36)	3.42		

<sup>a</sup>  $-x, -y, -z$ . <sup>b</sup>  $-x, -y, 1-z$ . <sup>c</sup>  $-1/2+x, 1/2-y, -1+z$ . <sup>d</sup>  $-1/2+x, 1/2-y, z$ . <sup>e</sup>  $1/2-x, 1/2+y, -1+z$ . <sup>f</sup> Superscripts denote the following equivalent positions relative to positions given in Table V. No superscript indicates that only the identity transformation has been made. Asterisks indicate hydrogen-bonding distances.

possible disorder failed. This bond length was long in separate refinements using both the copper and molybdenum radiation data (see Experimental Section).

**B. Complex Anion.** The preparative,<sup>21-26</sup> mechanistic,<sup>27,28</sup> and spectroscopic<sup>29-31</sup> properties of halocarbonyls of rhenium(I) have been extensively studied in the past. Four series of halocarbonyl anions of rhenium(I) besides the one found in this study have been reported:  $[\text{Re}(\text{CO})_3\text{X}_3]^{2-}$ ,  $[\text{Re}(\text{CO})_4\text{X}_2]^-$ ,  $[\text{Re}_2(\text{CO})_7\text{X}_3]^-$ , and  $[\text{Re}_2(\text{CO})_6\text{X}_4]^{2-}$ .<sup>32-34</sup> The structures of these anions were deduced from infrared spectroscopic data.

The preparation of  $[\text{Re}(\text{CO})_6\text{Cl}_3]^-$  is mentioned only briefly in a review article.<sup>35</sup> The structures of two compounds containing this anion have recently been reported.<sup>36</sup> These are of the type  $[\text{Re}(\text{CO})_3\text{X}_3][(\text{CO})_3\text{Re}(\text{arene})]$ . In one compound  $\text{X} = \text{Br}$  and the arene is toluene, whereas in the other  $\text{X} = \text{Cl}$  and the arene is hexamethylbenzene. In the anion in the present work the average Re-Cl distance is  $2.51(1)$  Å, the average Re-C distance is  $1.88(2)$  Å, while the average C-O distance is  $1.15(2)$  Å. These numbers agree well with those found in the arene complexes. The Re-C and C-O distances also agree with those found in  $\text{TPP}[\text{Re}(\text{CO})_3]_2$ .<sup>4</sup> The Re(1)-Re(2) distance of  $3.375(1)$  Å is too long to postulate any sort of direct metal-metal interactions. None would be expected.

**C. Molecular Packing.** A stereoview of the packing in the unit cell is shown in Figure 7. The reason for all eight terminal carbon atoms being pointed in one direction with respect to the porphyrin ring is apparent from this figure. With this arrangement steric interactions with the porphyrin cation related by a center of symmetry are avoided. This was also observed in *N*-ethoxycarbonylmethyloctaethylporphyrin.<sup>18</sup> The interplanar separation between the cation and its centrosymmetrically related nearest neighbor is  $3.4$  Å, which is the approximate layer separation in graphite. However, there are no

unusually close contacts between atoms in the two macrocycles. A listing of the intermolecular contacts  $\leq 3.5$  Å is given in Table III. With the obvious exception of the hydrogen-bonding distances between the cation and the water molecule, and with the possible exception of the Cl(2)-O(7) and Cl(3)-O(7) distances which, though unlikely, may correspond to weak O-H...Cl hydrogen-bonding distances, none of these contacts is expected to have any significant effect on the observed structure.

### Experimental Section

**Materials.** Octaethylporphyrin, H<sub>2</sub>OEP, was purchased from Strem Chemical Co.; dirhenium decacarbonyl, Re<sub>2</sub>(CO)<sub>10</sub>, and rhenium pentacarbonyl chloride, Re(CO)<sub>5</sub>Cl, were purchased from Pressure Chemical Co.; decahydronaphthalene (decalin) was purchased from J. T. Baker Chemical Co., treated with concentrated sulfuric acid, neutralized with sodium bicarbonate solution, washed with distilled water, dried over anhydrous calcium chloride overnight, filtered, and further dried over sodium wire; finally it was distilled under vacuum and stored in a Schlenk tube under argon before use. Other organic solvents were reagent grade chemicals, dried over type 4A molecular sieve and distilled under argon before use.

Rhenium pentacarbonyl bromide, Re(CO)<sub>5</sub>Br, and dimeric rhenium tetracarbonyl bromide, [Re(CO)<sub>4</sub>Br]<sub>2</sub>, were prepared by literature procedures.<sup>37-39</sup>

**Physical Measurements.** Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Visible spectra were measured with a Cary 14 spectrophotometer. Infrared spectra were measured with a Beckman IR-8 spectrophotometer. Mass spectra were obtained on a CEC-21-104 mass spectrometer. Proton magnetic resonance spectra were obtained using Varian T-60 spectrometers.

**Monocation Octaethylporphyrinium Tri- $\mu$ -chloro-hexacarbonyl-dirhenate(I), (H<sub>3</sub>OEP)<sup>+</sup>[Re<sub>2</sub>(CO)<sub>6</sub>Cl<sub>3</sub>]<sup>-</sup> (I).** A mixture of 95 mg (0.26 mmol) of Re(CO)<sub>5</sub>Cl and 65.5 mg (0.13 mmol) of H<sub>2</sub>OEP was refluxed in decalin under argon. The progress of the reaction was followed by visible spectroscopy. The reaction was complete after 20 h of refluxing. The decalin solution was then allowed to stand at room temperature. A large quantity of burgundy-colored crystals was collected by centrifugation and washed with decalin and *n*-pentane. Finally, the crude product was recrystallized from dichloromethane/cyclohexane to give 84 mg (0.07 mmol) of dark red crystals (I), mp 215–220 °C. Anal. Calcd for Re<sub>2</sub>C<sub>42</sub>H<sub>47</sub>N<sub>4</sub>O<sub>6</sub>Cl<sub>3</sub>: Re, 31.50; N, 4.74; Cl, 8.98. Found: Re, 26.25; N, 4.81; Cl, 8.91. The supernatant contained only dirhenium octaethylporphyrin complex, OEP[Re(CO)<sub>3</sub>]<sub>2</sub>, as indicated by its visible spectrum. About 55 mg (0.05 mmol) of the dirhenium octaethylporphyrin complex was isolated from the supernatant solution.

The new complex I was also prepared by heating H<sub>2</sub>OEP and Re(CO)<sub>5</sub>Cl in a 1:1.5 mole ratio in decalin under argon for approximately 5 h. The supernatant contained only the monorhenium octaethylporphyrin complex, (H-OEP)Re(CO)<sub>3</sub>, as indicated by its visible absorption spectrum. When equimolar quantities of H<sub>2</sub>OEP and Re(CO)<sub>5</sub>Cl were refluxed in decalin under argon for approximately 3 h, only the monorhenium octaethylporphyrin complex was formed.

Compound I has visible absorptions in dichloromethane at 390 (Soret band), 530, 555, 570, and 602 nm. The visible spectrum is extremely similar to that of monocation octaethylporphyrinium triiodide, (H<sub>3</sub>OEP)<sup>+</sup>·I<sub>3</sub><sup>-</sup> (the only previously known porphyrin monocation salt),<sup>5</sup> and is distinctly different from that of the dication salt, (H<sub>4</sub>OEP)<sup>2+</sup>·2Cl<sup>-</sup> (Figure 1).<sup>6</sup> When ethanol is added to the dichloromethane solution of I, the visible spectrum reverts to that of metal free octaethylporphyrin H<sub>2</sub>OEP. The infrared spectrum of I in the solid state (KBr pellet) has two broad peaks at 3350 and 3375 cm<sup>-1</sup> attributed to stretching vibrations of the two chemically independent N-H bonds, and three strong metal-carbonyl stretching bands at 1950, 2020, and 2050 cm<sup>-1</sup>. The far-infrared spectrum of I (in Nujol) has two broad metal-halide stretching peaks at 200 and 250 cm<sup>-1</sup>. The <sup>1</sup>H NMR solution of I in deuteriochloroform shows two sharp peaks at  $\delta$  1.90 (t) and 4.20 (q) for the ethyl substituents and two broad peaks at  $\delta$  10.70 and -3.50 for the bridged methine protons and the pyrrolic N-H protons, respectively.

**Monocation Mesoporphyrinium IX Dimethyl Ester Tri- $\mu$ -bromohexacarbonyl-dirhenate(I), (H<sub>3</sub>MPIXDME)<sup>+</sup>[Re<sub>2</sub>(CO)<sub>6</sub>Br<sub>3</sub>]<sup>-</sup> (II).** The

**Table IV.** Crystal Data for (C<sub>36</sub>H<sub>47</sub>N<sub>4</sub>)<sup>+</sup>[Re<sub>2</sub>(CO)<sub>6</sub>Cl<sub>3</sub>]<sup>-</sup>·H<sub>2</sub>O<sup>a</sup>

$a = 18.140$ (3) Å	mol wt = 1200.6
$b = 19.847$ (3) Å	$Z = 4$
$c = 13.625$ (2) Å	$d_{\text{calcd}} = 1.75$ g/cm <sup>3</sup>
$\beta = 111.64$ (2)°	$\mu = 58.4$ cm <sup>-1</sup> (Mo K $\alpha$ radiation)
$V = 4559$ Å <sup>3</sup>	
systematic absences:	$h0l$ ( $h$ odd); $0k0$ ( $k$ odd)
space group:	$P2_1/a$

<sup>a</sup> Estimated standard deviation of least significant figures shown in parentheses.

reaction was carried out in essentially the same manner as that described above, with rhenium pentacarbonyl bromide, Re(CO)<sub>5</sub>Br, substituted for Re(CO)<sub>5</sub>Cl as the metal source. A 120-mg sample of H<sub>2</sub>MPIXDME (0.21 mmol) and 180 mg (0.44 mmol) of Re(CO)<sub>5</sub>Br in about 20 mL of decalin were heated under argon in an oil bath. The reaction was observed to proceed at a temperature of ca. 120 °C and the progress of the reaction was followed by visible absorption spectroscopy. A stepwise change in the absorption spectra (Figure 3) and a continuous change of color in the reaction mixture was observed. After 5 h of heating, the decalin solution was cooled to room temperature. A large quantity of burgundy-colored substance crystallized out and was collected by centrifugation, washed with decalin and *n*-pentane, and finally recrystallized from ethyl acetate/cyclohexane/dichloromethane to give 186 mg (0.14 mmol) of dark red crystals (II), mp 180–185 °C. Anal. Calcd for Re<sub>2</sub>C<sub>42</sub>H<sub>43</sub>N<sub>4</sub>O<sub>10</sub>Br<sub>3</sub>: C, 36.63; H, 3.13; Re, 27.10; N, 4.07; Br, 17.82. Found: C, 35.74; H, 3.26; Re, 29.74; N, 4.31; Br, 19.58. The supernatant contained only the dirhenium mesoporphyrin complex, MP[Re(CO)<sub>3</sub>]<sub>2</sub>, as indicated by its visible absorption spectrum. About 75 mg (0.067 mmol) of the dirhenium mesoporphyrin complex was isolated from the supernatant solution.

Compound II can also be prepared in essentially the same manner as that described above, with dimeric rhenium tetracarbonyl bromide, [Re(CO)<sub>4</sub>Br]<sub>2</sub>, substituted for Re(CO)<sub>5</sub>Br as the metal source. H<sub>2</sub>MPIXDME (198 mg, 0.33 mmol) and [Re(CO)<sub>4</sub>Br]<sub>2</sub> (304 mg, 0.40 mmol) were mixed in about 20 mL of decalin and heated under argon in an oil bath. The reaction was observed to proceed at a temperature of ca. 105 °C and the progress of the reaction was followed by visible absorption spectroscopy.

**Attempted Preparation of meso-Tetraphenylporphyrin Monocation Salt.** The reaction of stoichiometric quantities of Re(CO)<sub>5</sub>Cl with H<sub>2</sub>TPP in refluxing decalin under argon, in a manner similar to that used in preparing the salt-like complex I, resulted in a mixture of the meso-tetraphenylporphyrin dication salt, (H<sub>4</sub>TPP)<sup>2+</sup>·2Cl<sup>-</sup>, and the monorhenium tetraphenylporphyrin complex, (H-TPP)Re(CO)<sub>3</sub>.

**X-ray Study.** The crystals of complex I were grown from a solvent pair of dichloromethane and cyclohexane (1:1) in a Schlenk tube which was kept slightly open in a vacuum desiccator over blue Drierite under argon atmosphere and stored in a refrigerator for 5 days.

The crystals of I grew as parallelepipeds elongated along  $c$  and bounded by {110}. The crystal chosen for intensity measurements measured  $0.23 \times 0.34 \times 0.44$  mm. The crystal was mounted in a capillary at an arbitrary orientation,<sup>40</sup> but with the  $c$  axis approximately parallel to the spindle axis. The crystal has remained stable for over 2 years in contact with mother liquor in a sealed capillary.

Crystal data are listed in Table IV. Cell dimensions were determined by least squares, minimizing the differences between observed and calculated  $2\theta$  values. Twenty-four Cu K $\alpha$  ( $\lambda = 1.54178$  Å) reflections, all having  $2\theta$  in the range 50–52.5°, were measured at both + and - $2\theta$ . A Syntex-Datex automated diffractometer equipped with a graphite monochromator was used. The systematic absences uniquely determined the space group as  $P2_1/a$ .

A set of intensity data was collected on the Datex-Syntex diffractometer using Cu K $\alpha$  radiation, using the  $\theta$ - $2\theta$  method. A total of 4946 independent reflections were measured out to ca. 100° in  $2\theta$ , the machine limit. Of these 3463 were considered observed and were used in the analysis. They were corrected for absorption effects using a Gaussian integration method.

From these data the structure was elucidated, which provided the basis for the preliminary communication.<sup>11</sup> However, for a number of reasons it was decided to re-collect the data using Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). At the machine limit of 100° in  $2\theta$ , a large percentage of the reflections still had intensities which were considered

Table V. Fractional Coordinates and Thermal Motion Parameters Derived from the Least-Squares Refinement<sup>a</sup>

ATOM	X	Y	Z	U(11)	U(22)	U(33)	U(12)	U(13)	U(23)
RE(1)	0.12959(2)	0.19521(2)	0.16057(3)	435(1)	517(2)	626(2)	-46(3)	299(2)	-21(3)
RE(2)	0.29168(2)	0.09642(2)	0.21983(3)	486(2)	524(2)	642(2)	21(3)	165(3)	-99(3)
CL(1)	0.2647(1)	0.2022(1)	0.3048(2)	51(1)	52(1)	57(1)	-17(2)	22(2)	-21(2)
CL(2)	0.1539(1)	0.0741(1)	0.2135(2)	56(1)	49(1)	61(1)	-19(2)	31(2)	-6(2)
CL(3)	0.2143(1)	0.1635(1)	0.0594(2)	56(1)	64(1)	52(1)	2(2)	35(2)	-2(2)
N(1)	0.2259(4)	0.0536(4)	-0.3240(5)	37(4)	69(5)	60(4)	17(7)	-13(6)	-14(7)
N(2)	0.0801(4)	0.1398(4)	-0.4103(5)	42(3)	85(5)	39(3)	15(7)	29(5)	-13(7)
N(3)	0.0168(4)	0.0529(3)	-0.5976(5)	38(3)	64(4)	40(3)	-8(6)	5(5)	-7(6)
N(4)	0.1633(4)	-0.0275(3)	-0.5147(5)	48(4)	43(4)	63(4)	9(6)	0(6)	-4(7)
C(1)	0.2888(5)	0.0102(5)	-0.3049(7)	38(4)	63(5)	60(5)	18(8)	-9(8)	-7(9)
C(2)	0.3468(4)	0.0300(4)	-0.2082(7)	32(4)	61(5)	65(5)	3(8)	4(7)	7(9)
C(3)	0.3164(4)	0.0831(4)	-0.1693(6)	37(4)	56(5)	46(4)	-20(7)	-2(7)	-18(8)
C(4)	0.2412(5)	0.0987(5)	-0.2448(6)	52(4)	69(5)	49(4)	6(9)	24(7)	-41(9)
C(5)	0.1892(5)	0.1490(5)	-0.2402(6)	47(4)	75(6)	43(4)	12(9)	10(7)	-17(8)
C(6)	0.1155(5)	0.1678(5)	-0.3111(6)	45(4)	76(6)	49(4)	28(8)	24(6)	-5(9)
C(7)	0.0609(5)	0.2144(5)	-0.2971(6)	52(4)	78(6)	46(4)	33(8)	24(7)	-21(8)
C(8)	-0.0029(5)	0.2174(4)	-0.3087(6)	47(4)	68(5)	57(5)	22(8)	30(7)	-13(8)
C(9)	0.0065(4)	0.1702(5)	-0.4596(6)	35(4)	80(6)	48(4)	27(8)	26(6)	13(8)
C(10)	-0.0467(4)	0.1512(4)	-0.5576(6)	34(4)	71(5)	44(4)	25(8)	10(6)	0(9)
C(11)	-0.0437(4)	0.0993(4)	-0.6204(6)	35(4)	60(5)	52(4)	13(8)	20(6)	4(8)
C(12)	-0.1002(4)	0.0803(4)	-0.7218(6)	34(4)	67(5)	44(4)	1(7)	15(6)	0(9)
C(13)	-0.0729(4)	0.0248(4)	-0.7558(6)	34(4)	55(5)	46(4)	-10(7)	16(6)	4(8)
C(14)	0.0015(4)	0.0073(4)	-0.6775(6)	38(4)	48(4)	45(4)	0(7)	14(6)	0(7)
C(15)	0.0523(5)	-0.0445(4)	-0.6811(6)	48(4)	48(4)	51(4)	-13(8)	11(7)	1(8)
C(16)	0.1271(5)	-0.0607(4)	-0.6081(7)	48(4)	42(4)	62(5)	0(8)	17(7)	-3(9)
C(17)	0.1761(5)	-0.1138(4)	-0.6200(8)	52(5)	57(5)	77(6)	39(8)	-10(9)	-28(9)
C(18)	0.2404(6)	-0.1143(5)	-0.5305(9)	65(6)	66(5)	111(8)	71(9)	-57(12)	-57(11)
C(19)	0.2328(6)	-0.0611(5)	-0.4653(8)	60(5)	63(5)	78(6)	33(9)	-6(10)	-29(10)
C(20)	0.2916(5)	-0.0423(5)	-0.3684(8)	49(5)	76(6)	81(6)	54(9)	-19(9)	-25(11)
C(21)	0.4271(5)	-0.0013(5)	-0.1596(8)	52(5)	74(6)	80(6)	13(10)	-21(10)	-22(11)
C(22)	0.4862(6)	0.0320(7)	-0.1918(14)	50(6)	110(10)	255(16)	29(13)	58(16)	-1(22)
C(23)	0.3572(5)	0.1192(5)	-0.0664(7)	62(5)	97(7)	65(5)	41(11)	23(9)	7(11)
C(24)	0.3916(7)	0.1844(7)	-0.0767(11)	89(8)	102(9)	115(9)	-36(15)	-17(15)	-24(15)
C(25)	0.0749(5)	0.2522(5)	-0.1946(8)	55(5)	86(7)	75(6)	15(10)	22(9)	4(11)
C(26)	0.1273(7)	0.3095(6)	-0.1793(10)	92(8)	92(8)	119(9)	11(13)	37(13)	-53(14)
C(27)	-0.0751(5)	0.2625(5)	-0.4128(7)	61(5)	90(6)	69(6)	27(10)	24(9)	-24(10)
C(28)	-0.0636(7)	0.3285(6)	-0.4557(10)	91(8)	102(8)	102(9)	69(14)	-12(14)	9(15)
C(29)	-0.1749(5)	0.1205(5)	-0.7804(7)	32(4)	95(6)	60(5)	24(9)	7(7)	-29(10)
C(30)	-0.1644(6)	0.1702(5)	-0.9559(8)	67(6)	90(7)	90(6)	74(10)	38(10)	57(11)
C(31)	-0.1094(5)	-0.0116(4)	-0.8559(7)	41(4)	63(5)	63(5)	-15(8)	9(7)	1(9)
C(32)	-0.0744(6)	0.0068(5)	-0.9380(7)	83(6)	82(6)	61(5)	-38(11)	37(9)	-43(10)
C(33)	0.1596(6)	-0.1551(5)	-0.7175(8)	61(6)	63(6)	83(7)	20(10)	-7(10)	-23(11)
C(34)	0.1841(6)	-0.1190(6)	-0.7948(9)	64(6)	89(7)	103(9)	23(11)	4(11)	-66(12)
C(35)	0.3073(9)	-0.1776(9)	-0.4844(10)	163(11)	217(14)	81(8)	-190(19)	58(15)	-39(18)
C(36)	0.3570(10)	-0.1500(8)	-0.5161(11)	246(15)	115(11)	134(10)	4(22)	170(18)	17(18)
C(37)	0.0347(5)	0.1783(5)	0.0446(7)	54(5)	67(6)	70(5)	-3(9)	31(8)	14(9)
C(38)	0.0735(6)	0.2119(4)	0.2474(7)	96(6)	53(5)	69(5)	-59(9)	29(9)	-11(9)
C(39)	0.1205(5)	0.2866(5)	0.1224(7)	45(4)	68(6)	103(6)	25(8)	62(7)	-7(10)
C(40)	0.3942(5)	0.1217(5)	0.2252(8)	55(5)	60(5)	99(7)	9(9)	22(9)	-34(10)
C(41)	0.2964(5)	0.0201(5)	0.1386(7)	49(5)	59(5)	83(6)	-11(9)	7(9)	-28(10)
C(42)	0.3400(6)	0.0468(5)	0.3435(8)	76(6)	56(5)	89(7)	-14(10)	3(11)	-9(11)
O(1)	-0.0212(4)	0.1670(4)	-0.0272(6)	61(4)	107(5)	107(6)	-34(8)	-35(8)	18(9)
O(2)	0.0356(4)	0.2237(4)	0.3005(5)	103(4)	108(5)	113(4)	3(8)	142(6)	-51(8)
O(3)	0.1156(4)	0.3419(3)	0.0587(6)	103(5)	53(4)	154(6)	32(7)	87(8)	25(8)
O(4)	0.4561(4)	0.1377(4)	0.2273(7)	56(4)	113(6)	163(6)	-44(8)	69(7)	-54(10)
O(5)	0.2993(4)	-0.0237(3)	0.0877(6)	85(4)	73(4)	121(5)	1(7)	52(7)	-32(7)
O(6)	0.3703(5)	0.0150(4)	0.4191(6)	140(7)	99(6)	104(6)	28(11)	-36(11)	61(10)
O(7)	0.1882(4)	0.1236(3)	0.4706(5)	79(4)	79(4)	81(4)	-2(7)	73(5)	0(7)
H(1)	0.193(3)	0.049(3)	-0.358(4)	40					
H(2)	0.100(3)	0.149(3)	-0.456(4)	40					
H(3)	0.046(3)	0.052(3)	-0.555(4)	40					

<sup>a</sup>In this and subsequent tables estimated standard deviations for the least significant figure are in parentheses. The Debye-Waller factor is defined as  $T = \exp[-2\pi^2(U_{11}a^2h^2 + U_{22}b^2k^2 + U_{33}c^2l^2 + U_{12}a*b*hk + U_{13}a*c*hl + U_{33}b*c*kl)]$ . The values for  $U$  have been multiplied by  $10^3$ , except for those of Re, which have been multiplied by  $10^4$ . For those atoms refined isotropically, the values for  $B$  (multiplied by a factor of 10) are given in the column labeled  $U_{11}$ . Isotropic temperature factors are defined by  $T = \exp[-B(\sin^2 \theta)/\lambda^2]$ .

to be observed. Collection of the data to a higher  $\sin \theta/\lambda$  limit would increase the accuracy of the structural parameters. Also, the high linear absorption coefficient for Cu  $K\alpha$  radiation ( $119.5 \text{ cm}^{-1}$ ) introduces a large systematic error which an absorption correction could only approximately correct. Low-order reflections are the most affected by absorption effects. It is these same reflections which contain a significant contribution from the scattering power of the hydrogen atoms. One of the hopes of this study was to locate the imino hydrogen atoms. In the presence of rhenium and chlorine atoms, which have a high scattering power, locating the hydrogen atoms would require a good set of data as free from systematic error as possible.

Therefore the data were recollected on a Syntex P2<sub>1</sub> diffractometer using Mo  $K\alpha$  radiation. The same crystal was used. Intensity data for 10 792 unique reflections ( $2\theta_{\text{max}} = 55^\circ$ ,  $(\sin \theta/\lambda)_{\text{max}} = 0.65$ ) were obtained; the  $\omega$  scan method was employed with a scan range of  $0.6^\circ$ . The scan rate varied from  $2^\circ/\text{min}$  to  $12^\circ/\text{min}$ , depending on the number of counts accumulated in a rapid preliminary scan. The intensities were normalized to counts/min. Background measurements were taken at both ends of the scan with  $\omega$  displaced by  $0.7^\circ$  from the  $K\alpha$  peak; each measurement was made for one-half of the scan time. The intensities of the four standard reflections were monitored after every 89 reflections. Only statistical variations were observed and no corrections were applied.

Only the 5995 reflections with  $I \geq 3\sigma_I$  were used in the analysis. The standard deviation  $\sigma_I$  was determined in terms of the statistical variances of the counts as  $\sigma_I^2 = \sigma_I^2(\text{count}) + 0.03I^2$  where  $\sigma_I^2(\text{count})$  is the standard deviation based solely on counting statistics.

Absorption corrections were made to the data using a  $\psi$  scan technique, observing the change of intensity of the 52 $\bar{1}$  reflection. The minimum intensity observed for this reflection was 62% of the maximum. A scan of several other reflections gave similar results. Structure factors were calculated in the usual way assuming a 50% ideally perfect—50% ideally imperfect monochromator mounted in a parallel orientation.

**Determination and Refinement of the Structure.** Because there are four molecules in the unit cell of space group  $P2_1/a$ , no crystallographic symmetry is imposed on the molecule. The positions of the rhenium atoms were found from a Patterson synthesis, using the data collected with Cu  $K\alpha$  radiation. The positions of the remaining 56 nonhydrogen atoms were found from a series of difference Fourier maps. Included among these atoms was a peak attributable to a water molecule of crystallization.

Least-squares refinements using block diagonal and finally full-matrix methods were carried out. The function minimized was  $\sum w(F_o - F_c)^2$  where  $w = 1/\sigma_F^2$ . Refinement using the Cu  $K\alpha$  data was not



carried beyond the stage where isotropic temperature factors were used. At this stage  $R = \sum \|F_o\| - |F_c| / \sum F_o$  was 0.106.

Further refinement utilized the Mo K $\alpha$  data. The thermal parameters of the nonhydrogen atoms were refined anisotropically. The large number of parameters required refining the formula unit in blocks, alternately refining the anion and then the cation and water molecule.

After several cycles of refinement,  $\Delta F$  syntheses were calculated in an effort to locate hydrogen atoms. The three imino hydrogen atoms were thus found. Peaks corresponding to these three atoms were 0.3–0.4 e/Å<sup>3</sup>. However, many of the hydrogens on the peripheral atoms were not located or were in chemically unreasonable positions. The positional parameters of the imino hydrogen atoms were refined. The thermal parameters for these three atoms were not refined, but were set at  $B = 4.0 \text{ \AA}^2$ , as was the case for all hydrogen atoms. Idealized positions for the other hydrogen atoms were calculated except for those on the water molecule. A C–H bond length of 1.0 Å and a staggered configuration for the methyl hydrogens were assumed. The contributions from these were added to the calculated structure factors but the positions were not refined. However, before the final cycles of refinement, new positions were calculated and used. The refinement converged with  $R = 0.046$  and  $R_w = (\sum w \|F_o\| - |F_c| / \sum w F_o^2)^{1/2} = 0.047$ . The final value of the standard deviation of an observation of unit weight, defined as  $|\sum w \|F_o\| - |F_c||^2 / (N_o - N_v)^{1/2}$ , was 1.72 for  $N_o = 5995$  reflections and  $N_v = 532$  variables. In the last cycle of refinement all shifts were considerably less than one standard deviation. There were five peaks on the final difference Fourier which were above 1 e/Å<sup>3</sup>. These were all close to the rhenium atoms. Neither they nor any other peak in the final difference Fourier were believed to have any physical significance.

Correction for anomalous dispersion was made for all nonhydrogen atoms.<sup>41</sup> Scattering factors were from ref 42. The rhenium and chlorine atoms were assumed to be in the zero ionization state. No evidence of secondary extinction was found.

The structure was solved and the initial refinement performed on the IBM 360/65 and its successor at Texas A&M, the Amdahl 470 v/6. Most of the programs used have been listed elsewhere.<sup>43,44</sup> In addition the data collection and data reduction programs used for the molybdenum data are those supplied by Syntex Analytical Instruments. Most of the final refinements and calculations were performed on a PDP 11/40 computer using an Enraf-Nonius structure determination package (SDP).

The final positional and thermal parameters for the nonhydrogen atoms and the three imino hydrogen atoms are given in Table V. The final calculated positions of the other hydrogen atoms are given in Table VI. Tables VII and VIII contain the root mean square components of thermal displacement along the principal axes of the thermal ellipsoids and the observed and calculated structure factors, respectively. Tables VI–VIII are available as supplementary material.

**Acknowledgment.** The authors wish to thank Professor Shinzi Kato for many helpful and stimulating discussions. We wish to acknowledge support of this research project by the Office of Naval Research, the Robert A. Welch Foundation (A-328), and the Texas Agricultural Experiment Station (H-1668). In the later phases support was also given by the National Institutes of Health (AM20051) and the National Science Foundation (CHE76-15557).

**Supplementary Material Available:** Tables VI–VIII containing the calculated hydrogen atom positions, the root mean square components along the principal axes of the thermal ellipsoids, and observed and

calculated structure factors (29 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) (a) Department of Chemistry, Texas A&M University; (b) Department of Biochemistry and Biophysics, Texas A&M University; (c) Control Data Corporation.
- (2) M. Tsutsui, M. Ichikawa, F. Vohwinkel, and K. Suzuki, *J. Am. Chem. Soc.*, **88**, 854 (1966).
- (3) H. Ogoshi, J. Setsune, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, **97**, 6461 (1975).
- (4) M. Tsutsui, C. P. Hsung, D. Ostfeld, T. S. Srivastava, D. L. Cullen, and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, **97**, 3952 (1975).
- (5) N. Hirayama, A. Takenaka, Y. Sasada, E. Watanabe, H. Ogoshi, and Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, 330 (1974).
- (6) H. Ogoshi, E. Watanabe, and Z. Yoshida, *Tetrahedron*, **29**, 3241 (1973).
- (7) A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, **90**, 2735 (1968).
- (8) F. Hibbert and K. P. P. Hunte, *J. Chem. Soc., Chem. Commun.*, 728 (1975).
- (9) A. Takenaka, Y. Sasada, H. Ogoshi, T. Omura, and Z. Yoshida, *Acta Crystallogr., Sect. B*, **31**, 1 (1975).
- (10) E. Cetinkaya, A. W. Johnson, M. F. Lappert, G. M. McLaughlin, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1236 (1974).
- (11) (a) C. P. Hsung, M. Tsutsui, D. L. Cullen, and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, **98**, 7878 (1976); (b) C. P. Hsung, Dissertation, Texas A&M University, 1975.
- (12) E. Samuels, R. Shuttleworth, and T. S. Stevens, *J. Chem. Soc. C*, 145 (1968).
- (13) C. K. Johnson, "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., revised 1965.
- (14) J. L. Hoard in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, see especially p 337.
- (15) S. Silvers and A. Tulinsky, *J. Am. Chem. Soc.*, **89**, 3331 (1967).
- (16) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Am. Chem. Soc.*, **86**, 1938 (1964).
- (17) O. Ermer and J. D. Dunitz, *Chem. Commun.*, 178 (1971).
- (18) G. M. McLaughlin, *J. Chem. Soc., Perkin Trans. 2*, 136 (1974).
- (19) D. L. Cullen, P. S. Black, E. F. Meyer, Jr., D. A. Lightner, G. B. Quistad, and C. S. Pak, *Tetrahedron*, **33**, 477 (1977).
- (20) D. L. Cullen and E. F. Meyer, Jr., *Acta Crystallogr., Sect. B*, **32**, 2259 (1976).
- (21) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958).
- (22) B. N. Storhoff, *J. Organomet. Chem.*, **43**, 197 (1972).
- (23) D. Vitali and F. Calderazzo, *Gazz. Chim. Ital.*, **102**, 587 (1972).
- (24) F. Calderazzo and D. Vitali, *Coord. Chem. Rev.*, **16**, 13 (1975).
- (25) R. Colton and J. E. Garrard, *Aust. J. Chem.*, **26**, 529 (1973).
- (26) R. Colton and J. E. Garrard, *Aust. J. Chem.*, **26**, 1781 (1973).
- (27) F. Zingales, U. Sartorelli, F. Canziani, and M. Ravelli, *Inorg. Chem.*, **6**, 154 (1967).
- (28) F. Zingales, U. Sartorelli, and A. Trovati, *Inorg. Chem.*, **6**, 1246 (1967).
- (29) M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).
- (30) W. A. McAllister and A. L. Marston, *Spectrochim. Acta, Part A*, **27**, 523 (1971).
- (31) M. S. Wrighton, D. L. Morse, and L. Pdungsap, *J. Am. Chem. Soc.*, **97**, 2073 (1975).
- (32) E. W. Abel, I. S. Butler, M. C. Ganorkar, C. R. Jenkins, and M. H. B. Stiddard, *Inorg. Chem.*, **5**, 25 (1966).
- (33) M. J. Hawkes and A. P. Ginsberg, *Inorg. Chem.*, **8**, 2189 (1969).
- (34) R. Colton and J. E. Knapp, *Aust. J. Chem.*, **25**, 9 (1972).
- (35) H. C. Lewis and B. N. Storhoff, *J. Organomet. Chem.*, **43**, 38 (1972).
- (36) R. L. Davis and N. C. Baenziger, *Inorg. Nucl. Chem. Lett.*, **13**, 475 (1977).
- (37) W. Hieber and H. Schuler, *Z. Anorg. Allg. Chem.*, **243**, 164 (1939).
- (38) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).
- (39) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958).
- (40) E. F. Meyer, Jr., *J. Appl. Crystallogr.*, **6**, 45 (1973).
- (41) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
- (42) D. T. Cromer and J. T. Waber in "International Tables for X-ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., Kynoch Press, Birmingham, England, 1974, pp 72–101.
- (43) D. L. Cullen, E. F. Meyer, Jr., and K. M. Smith, *Inorg. Chem.*, **16**, 1179 (1977).
- (44) D. L. Cullen, E. F. Meyer, Jr., F. Eivazi, and K. M. Smith, *J. Chem. Soc., Perkin Trans. 2*, 259 (1977).