Synthesis, Properties, and Crystal Structure of Octaethylporphin Bis[*cis*-dicarbonyldichlororhodate(I)] $[oepH_4]^{2+}2[RhCl_2(CO)_2]^-$ and Some New Reactions of Co(oep) Derivatives

By **Engin Çetinkaya, Alan W. Johnson, Michael F. Lappert,*** **George M. McLaughlin,** and **Kenneth W. Muir,** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

Octaethylporphin, oepH$_2$, and $[RhCl(CO)_2]_2$ react in hot chloroform to form a complex, which has been shown by chemical analysis, spectroscopic studies, and *X*-ray analysis to be $[oepH_4]^{2+}2\{cis\text{-}[RhCl_2(CO)_2]\}^-$. Crystals are tetragonal, space group *P*4/*n*, *Z* = 4, with cell dimensions *a* = 24·604(3) and *c* = 8·231(1) Å. The structure has been refined by Fourier and least-squares methods to *R* 0·089 for 1439 diffractometric intensity data. A novel feature of the structure is the essential planarity of the $[oepH_4]^{2+}$ dication. Other new complexes to have been prepared are Co(oep)(PR$_3$)$_2$, $[Co(oep)(PR_3)_2]^+Br^-$, and Co{N:C(CF$_3$)$_2$}(oep).

STUDIES on metalloporphyrins[1] have recently been extended to second- and third-row transition elements. Syntheses frequently employ the free base, symbolised pH$_2$, and a suitable metal carbonyl complex. Compounds described in the literature include derivatives of rhenium(I),[2] ruthenium(II),[3] rhodium(I),[4-6] rhodium(II),[5] and rhodium(III).[5-7]

The rhodium complexes have been obtained from di-μ-chloro-tetracarbonyldirhodium(I), $[RhCl(CO)_2]_2$) and the appropriate porphyrin. Thus, mesoporphyrin IX diethyl ester in hot glacial acetic acid afforded Rh^I(me-pdee);[4] *N*-methyloctaethylporphin in benzene at ambient temperature gave (Meoep)$[Rh^ICl(CO)_2]_2$, formulated schematically as (I), which upon heating yielded MeRh^{III}(oep);[7] octaethylporphin in benzene at ambient temperature gave $H^+[oep{\cdot}Rh^I_2(CO)_4Cl]^-$, formulated schematically as (II), and ClRh^{III}(oep),2H$_2$O, which upon treatment with methyl-lithium furnished MeRh^{III}(oep);[6] and tetraphenylporphin in hot glacial acetic acid afforded ClRh^{III}(tpp),H$_2$O and Rh^{II}(tpp), which was reduced by hydrogen to HRh(tpp),2H$_2$O.[5] We now report different findings yet again, using octa-

---

[1] *Cf.*, T. E. Falk, 'Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964; E. B. Fleischer, *Accounts Chem. Res.*, 1970, **3**, 105.

[2] D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Amer. Chem. Soc.*, 1971, **93**, 2548.

[3] J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 2141, and references therein.

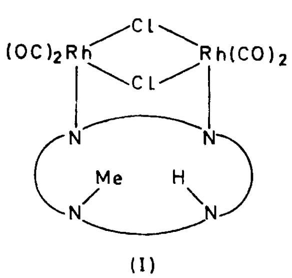
[4] N. Sadasivan and E. B. Fleischer, *J. Inorg. Nuclear Chem.*, 1968, **30**, 591.

[5] B. R. James and D. V. Stynes, *J. Amer. Chem. Soc.*, 1972, **94**, 6225.

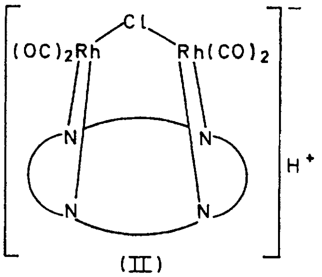
[6] Z. Oshida, H. Ogoshi, T. Omura, E. Watanabe, and T. Kurosaki, *Tetrahedron Letters*, 1972, 1077.

[7] H. Ogoshi, T. Omura, and Z. Oshida, *J. Amer. Chem. Soc.*, 1973, **95**, 1666.

ethylporphin, oepH_2, in hot chloroform, to afford a salt-like complex $[oepH_4]^{2+}2\{cis\text{-}[RhCl_2(CO)_2]\}$. Our original objective was to synthesise rhodium–oep derivatives for comparison with their cobalt analogues. We therefore also record some new data on the latter. It was expected that the attachment to the metal of ligating atoms with nuclear spin might be useful spectroscopically: hence we prepared some ^{31}P- and ^{19}F-containing complexes of cobalt.

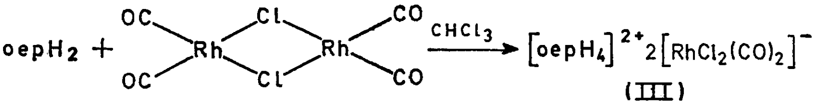


(I)



(II)

Reaction of Octaethylporphin, $oepH_2(C_{36}H_{46}N_4)$, *with Di-μ-chloro-tetracarbonyldirhodium*(I) *in Hot Chloroform, and Identification of* $[oepH_4]^{2+}2\{cis\text{-}[RhCl_2(CO)_2]\}^-$.—When an equimolar mixture was heated in chloroform under reflux for 7 h, dark purple needles of compound (III) were obtained, and shown by total analysis to be $C_{40}H_{48}Cl_4N_4O_4Rh_2$. The structure of the compound was deduced to be $[oepH_4]^{2+}2[RhCl_2(CO)_2]^-$ from the stoicheiometry of equation (1), spectroscopic data, and finally a single-crystal *X*-ray analysis (see later). It is evident from equation (1) that there is participation of 2 mol of hydrogen chloride, which must derive from solvent chloroform. It is known that $[RhCl(CO)_2]_2$ reacts with HCl in the presence of a base to yield $[RhCl_2(CO)_2]^-$.[8] The chloroform solution of (III) has the red colour typical[9] of diacid porphyrin species; the visible spectrum of this solution (Table 1) is extremely similar to that of $[oepH_4]^{2+}2Cl^-$ in chloroform and is distinctly different from that of chloroform solutions of either $oepH_2$ or of rhodium mesoporphyrin diethyl ester, Rh(Mepdee).[4] When ethanol is added to the chloroform solution of (III) the visible spectrum reverts to that of $oepH_2$; by contrast, metalloporphyrins are demetallated with difficulty, *e.g.* by use of strong mineral acid.[1]



(III)

(1)

TABLE 1

Absorption spectra ($\lambda_{max.}$/nm) of various porphyrin derivatives in chloroform

Compound	α (I)	β (II)	Soret	α (I)/β (II) intensity
Rh(Mepdee)	546	512	398	1·5
$[oepH_4]^{2+}2[RhCl_2(CO)_2]^-$	592	548	411	0·4
$[oepH_4]^{2+}2Cl^-$	622	558	415 [403sh]	0·3
$oepH_2$	598 567	534	498 417	

In the mass spectrum of (III) a parent ion is not observed, but the most abundant peak (534) corresponds to $oepH_2^+$.

The i.r. spectrum of (III) has a broad band at 3180 cm^{-1}, attributed to N–H stretching, which would, of course, be absent in a metalloporphyrin. There is no strong absorption at *ca.* 350 cm^{-1}, typical of metalloporphyrins and assigned to ν(M–N) coupled to porphyrin skeletal deformation modes.[10] Instead absorption bands characteristic of the $[RhCl_2(CO)_2]^-$ anion[8] are present (see Table 2).

Reactions Involving Cobaltoporphyrins.—Treatment of octaethylporphincobalt(II), Co(oep),[11] with the tertiary phosphines, PMe_2Ph or $PMePh_2$, gave black crystalline six-co-ordinate species [equation (2)]. Similarly, octaethylporphincobalt(III) bromide, $[Co(oep)]^+Br^-$ (*cf.* ref. 12) reacted with tertiary phosphines to give the corresponding $[Co(oep)(PR_3)_2]^+Br^-$.

$$Co(oep) + 2PR_3 \longrightarrow Co(oep)(PR_3)_2 \qquad (2)$$

TABLE 2

I.r. data (cm^{-1}) on $[RhCl_2(CO)_2]^-X^+$ species [a]

X	ν(CO)	δ(RhCO)	ν(RhC)	ν(RhCl)
$[Bu^n{}_4N]^+$ [b]	2058, 1974	619, 496	456	320, 290
$[Ph_4As]^+$ [b]	2060, 1975	617, 495		318, 290
$\frac{1}{2}[oepH_4]^{2+}$	2060, 1975	619, 490	462	320, 285

[a] In Nujol. [b] See ref. 8.

In an attempt to replace the bromide by a dimethylamido-group, bromo-octaethylporphin(pyridine)-cobalt(III) (*cf.* ref. 12), CoBr(oep)py, was treated with dimethylamidolithium. A strong smell of pyridine was noticed, but Co(oep) was the only product isolated. Although dimethylamidolithium did not react with $[Co(oep)]^+Br^-$, there was a reaction with a ketimide [equation (3)]. In compound (IV), the ν(CN) region

$$Li\{N{:}C(CF_3)_2\} + [Co(oep)]^+Br^- \longrightarrow Co\{N{:}C(CF_3)_2\}(oep) \qquad (3)$$

(IV)

---

[8] L. M. Vallarino, *Inorg. Chem.*, 1965, **4**, 161.

[9] A. Stone and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1968, **90**, 2735.

[10] L. J. Boucher and J. J. Katz, *J. Amer. Chem. Soc.*, 1967, **89**, 1340; H. Ogoshi, N. Masai, Z. Yoshida, J. Takemoto, and K. Nakamoto, *Bull. Chem. Soc. Japan.*, 1971, **44**, 49.

[11] H. Fischer and W. Neumann, *Annalen*, 1932, **494**, 225.

[12] A. W. Johnson and I. T. Kay, *J. Chem. Soc.*, 1960, 2979.

typical of ketimides (1600—1700 cm^{-1})[13] is obscured by bands due to ν(C⁚C) and ν(CN) of the porphyrin ring. The ^{19}F n.m.r. spectrum of (IV) contains a broad signal at 70·5 p.p.m. (relative to $CFCl_3$). When compound (IV) was treated with diethylamine, in the expectation of obtaining Co(oep)NEt_2 by bis(trifluoromethyl)methylamine elimination, only Co(oep) was isolated. Numerous transition-metal complexes of the ligand N⁚C$(CF_3)_2$ have been reported,[14] but none previously with cobalt.

CRYSTALLOGRAPHIC STUDIES

Crystal Data.—$C_{40}H_{48}Cl_4N_4O_4Rh_2$, M = 996·5. Tetragonal, a = 24·604(3), c = 8·231(1) Å (21 °C), U = 4983 Å^3, D_m = 1·39 g cm^{-3} (by flotation), Z = 4, D_c = 1·328, $F(000)$ = 2024. Space group $P4/n$. Mo-K_α radiation, λ = 0·71069 Å, μ(Mo-K_α) = 9·0 cm^{-1}.

Crystals of (III) are usually twinned and a single crystal suitable for *X*-ray analysis was obtained only with difficulty. Approximate unit-cell dimensions, the Laue group, and the extinctions ($hk0$ when $h + k = 2n + 1$) caused by the space-group symmetry were derived from Weissenberg and precession photographs.

Final values of the unit-cell parameters and the intensities of 3672 independent reflections for which θ(Mo-K_α) $\leqslant$22° were measured on a computer-controlled Hilger and Watts Y 290 four-circle diffractometer by methods already described in detail.[15] The θ—2θ scan technique was used in conjunction with molybdenum radiation, a graphite monochromating crystal, and a pulse-height analyser. Each reflection was scanned in 40 steps of 0·01° in θ, counting for 2·5 s at each step; at each extreme of the scan stationary-crystal stationary-counter background counts were measured for 20 s. During the experiment the stability of the crystal and counting system was monitored by remeasuring periodically the intensities of two strong reflections; these showed no fluctuation greater than ±2% of their mean values.

Integrated intensities and their standard deviations were derived in the usual manner[15] and Lorentz and polarisation factors were applied. The crystal used to measure the intensities was needle shaped, with dimensions 0·15 × 0·15 × 0·47 mm; a test calculation indicated that the transmission factors were constant to within 1% and accordingly no absorption corrections were applied.

A total of 1439 reflections (39% of those measured) for which $I \geqslant 3\sigma(I)$ were used in the analysis.

Structure Analysis.—The position of the rhodium atom was deduced from a Patterson synthesis and those of the other non-hydrogen atoms from subsequent difference syntheses.

The structure was refined by the method of full-matrix least squares. The function minimised was $\Sigma w\Delta^2$, where $\Delta = ||F_o| - |F_c||$; weights w were taken as the reciprocals of the variances of $|F_o|$ as previously described.[15] Scattering factors were taken from ref. 16, except for those of rhodium[17] and hydrogen.[18] Values of $\Delta f'$ and $\Delta f''$ from ref. 19 were used to correct the structure factors for the anomalous scattering of the rhodium atom.

The structure thus obtained consisted of a porphyrin nucleus situated at a crystallographic centre of symmetry and a $[RhCl_2(CO)_2]^-$ anion at a general position in the unit cell. Refinement of the positional and isotropic temperature factors of the non-hydrogen atoms gave values of R and R' of 0·13 and 0·16, respectively. Introduction of anisotropic temperature parameters for the atoms of the complex anion reduced R and R' to 0·090 and 0·134. The contributions of the hydrogen atoms, except for those attached to nitrogen and methyl carbon atoms, were now included in the structure-factor calculations; the positions of these atoms were chosen to be consistent with the known stereochemistry of tetrahedrally and trigonally hybridised carbon atoms and were not refined; for all hydrogen atoms a temperature factor U 0·08 Å^2 was assumed. This refinement converged with R 0·089 and R' 0·133.

At this stage there were still substantial discrepancies between F_o and F_c for many low-angle reflections. These could not be ascribed to malfunction of the diffractometer since the diffractometric intensities were in good agreement with those on the preliminary Weissenberg and precession photographs. Moreover, the poor agreement between the observed and calculated densities had already led us to suspect that the crystals contained solvent. A difference synthesis revealed regions of diffuse positive density with maximum function values in the range 0·9—1·3 e A^{-3} situated close to the symmetry axes at $\pm\frac{1}{4},\frac{1}{4},z$. These diffuse peaks did not correspond to any recognisable chemical entity. Their closest approach to an atom of the porphyrin nucleus or complex anion was that of 3·7 Å to C(92). After a number of trial calculations four atoms were introduced into the refinement; they were assigned oxygen scattering factors and fixed isotropic U parameters of 0·16 Å^2. Adjustment of their positional parameters and occupancies, together with the positional and thermal parameters of the atoms of the porphyrin nucleus and anion, led to final values of R and R' of 0·077 and 0·114, respectively, and to particularly noticeable improvement in the structure factor agreement at low angle.

Although it was apparent that the structural model for the disordered atoms was still inadequate, the analysis was now terminated. The refinement had not permitted the disordered species to be identified. Chemical analysis of the sample from which the *X*-ray data crystal was taken gave results identical to those obtained originally.

The final difference map contained function values ranging from 0·4 to −0·3 e Å^{-3} apart from five regions close to the sites of the disordered atoms where function values ranged from 0·7 to 1·2 e Å^{-3}. Analysis of the variation of $w\Delta^2$ as a function of $|F_o|$ and sin θ/λ indicated that the weighting scheme was satisfactory. Final atomic parameters and a selection of functions derived from them are presented in Tables 3—5. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20923 (2 pp.).* Views of the structure are shown in Figures 1—3.

---

* See Notice to Authors No. 7 in *J.C.S. Dalton*, **1973**, Index issue. (Items less than 10 pp. are sent as full size copies.)

[13] M. F. Lappert, J. McMeeking, and D. E. Palmer, *J.C.S. Dalton*, 1973, 151.

[14] B. Çetinkaya, M. F. Lappert, and J. McMeeking, *J.C.S. Dalton*, 1973, 1975.

[15] K. W. Muir, *J. Chem. Soc.* (*A*), 1971, 2663.

[16] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[17] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[18] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[19] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

The computer programs used were C. K. Johnson's ORTEP, the ATLAS version of Dr. J. M. Stewart's *X*-Ray '70 system, the Hilger and Watts software package for the Y 290 diffractometer, and the HILGA data processing program of M. A. Bush, K. W. Muir, and D. White.

TABLE 3

Atomic parameters with standard deviations in parentheses

(*a*) Fractional co-ordinates ($\times 10^4$) and isotropic temperature parameters (A^2 $\times 10^3$) origin at $\bar{1}$

Atom	*x*	*y*	*z*	*U*
Rh	391(1)	−1626(1)	332(2)	*
Cl(1)	173(2)	−917(2)	−1495(5)	*
Cl(2)	−511(2)	−1922(2)	308(8)	*
O(1)	1522(7)	−1271(7)	207(29)	*
O(2)	637(10)	−2494(8)	2613(22)	*
C(1A)	1073(10)	−1423(9)	284(31)	*
C(2A)	538(11)	−2142(8)	1716(28)	*
N(1)	641(4)	−129(4)	1633(12)	39(3)
N(2)	−550(4)	−375(4)	1569(13)	49(3)
C(1)	108(6)	−602(5)	3736(18)	48(4)
C(2)	575(5)	−393(5)	3090(17)	42(4)
C(3)	1115(6)	−399(6)	3826(19)	56(4)
C(4)	1464(6)	−141(6)	2851(19)	59(5)
C(5)	1174(5)	22(5)	1404(17)	44(4)
C(6)	1379(5)	293(5)	92(18)	48(4)
C(7)	−1095(5)	−460(5)	1273(17)	39(4)
C(8)	−1300(6)	−757(6)	2641(17)	52(4)
C(9)	−893(6)	−843(6)	3720(18)	55(4)
C(10)	−408(6)	−609(5)	3057(17)	47(4)
C(31)	1225(6)	−673(7)	5479(21)	75(5)
C(32)	1275(7)	−1252(8)	5354(24)	102(6)
C(41)	2085(8)	−12(8)	3179(24)	97(6)
C(42)	2382(9)	−522(9)	2931(26)	121(8)
C(81)	−1885(7)	−955(7)	2764(21)	82(6)
C(82)	−1953(9)	−1439(9)	1841(28)	128(8)
C(91)	−920(7)	−1125(7)	5429(22)	82(5)
C(92)	−757(9)	−1665(9)	5274(29)	132(8)

(*b*) Anisotropic temperature factors (A^2 $\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	110(1)	55(1)	55(1)	10(1)	0(1)	6(1)
Cl(1)	75(3)	61(3)	49(2)	3(2)	−1(2)	11(2)
Cl(2)	134(5)	88(4)	136(5)	−30(3)	51(4)	13(4)
O(1)	127(14)	152(15)	212(19)	6(13)	−37(17)	−13(15)
O(2)	345(28)	118(15)	156(17)	17(17)	−38(18)	64(13)
C(1A)	127(21)	97(16)	101(18)	16(16)	−51(21)	−14(14)
C(2A)	228(27)	49(13)	99(18)	7(16)	−7(18)	10(13)

(*c*) Fractional co-ordinates ($\times 10^4$), population parameters ($\times 10^3$,) and site symmetries of disordered atoms

Atom	*x*	*y*	*z*	Population parameter	Site-symmetry
O(3)	$\frac{1}{4}$	$\frac{1}{4}$	4903(108)	330(10)	4
O(4)	$-\frac{1}{4}$	$\frac{1}{4}$	4070(79)	288(14)	2
O(5)	2492(18)	1804(19)	2711(55)	307(23)	1
O(6)	$-\frac{1}{4}$	$\frac{1}{4}$	0	349(10)	$\bar{4}$

* Anisotropic temperature factors were used for these atoms, in the form: $\exp\,(-2\pi^2\Sigma\Sigma U_{ij}h_ih_ja_i^*a_j^*)$.

RESULTS AND DISCUSSION

Chemical analysis and the visible and i.r. spectra of (III) are consistent with its formulation as $[\text{oepH}_4]^{2+}$-$2[\text{RhCl}_2(\text{CO})_2]^-$.

Crystal structure analysis of (III) reveals a planar porphyrin nucleus and square planar *cis*-$[\text{RhCl}_2(\text{CO})_2]^-$ complex anions. Hydrogen atoms were not located in the analysis and it is therefore uncertain whether the porphyrin nucleus in the crystal is that of a diacid or a free base. Furthermore, the solid also contains a disordered species which gives rise to four electron density peaks each containing a total of *ca.* 2—3 electrons. We have not been able to identify this species either by chemical or *X*-ray analysis. Partial solvation of crystalline $[\text{oepH}_4]^{2+}2[\text{RhCl}_2(\text{CO})_2]^-$ by chloroform is consistent with the *X*-ray data, but not with chemical or spectroscopic analysis. However, because hydrogen atoms were not located and because direct chemical

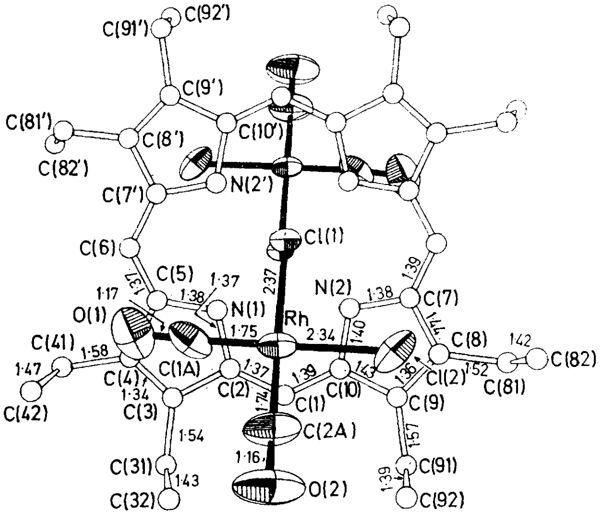


FIGURE 1 The octaethylporphin cation viewed along the normal to the plane of the nitrogen atoms. The two nearest neighbour $[\text{RhCl}_2(\text{CO})_2]^-$ anions are shown. The atomic numbering and some bond lengths are also indicated. The thermal ellipsoids enclose 30% of probability

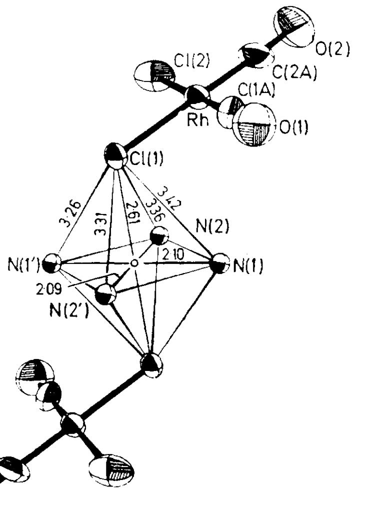


FIGURE 2 A view of the spatial relationship between the nearest anions and the nitrogen atoms of the porphyrin nucleus. Selected non-bonded distances are indicated. The thermal ellipsoids enclose 30% of probability

evidence for the nature of the disordered species is lacking, the *X*-ray analysis could also be interpreted in terms of another formulation of the solid, $[\text{oepH}_2]\cdot 2[\text{RhCl}_2(\text{CO})_2]^-\cdot 2X^+$, where X^+ is a cation containing light atoms such as NH_4^+ or H_3O^+. However, we reject this formulation, not only on analytical grounds but because generation of such a cation in stoicheiometric amounts from a reaction mixture containing oepH_2, $[\text{RhCl}(\text{CO})_2]_2$, and chloroform seems implausible. Moreover, the presence of oepH_4^{2+} in chloroform solutions of (III) is clearly indicated by the visible spectrum.

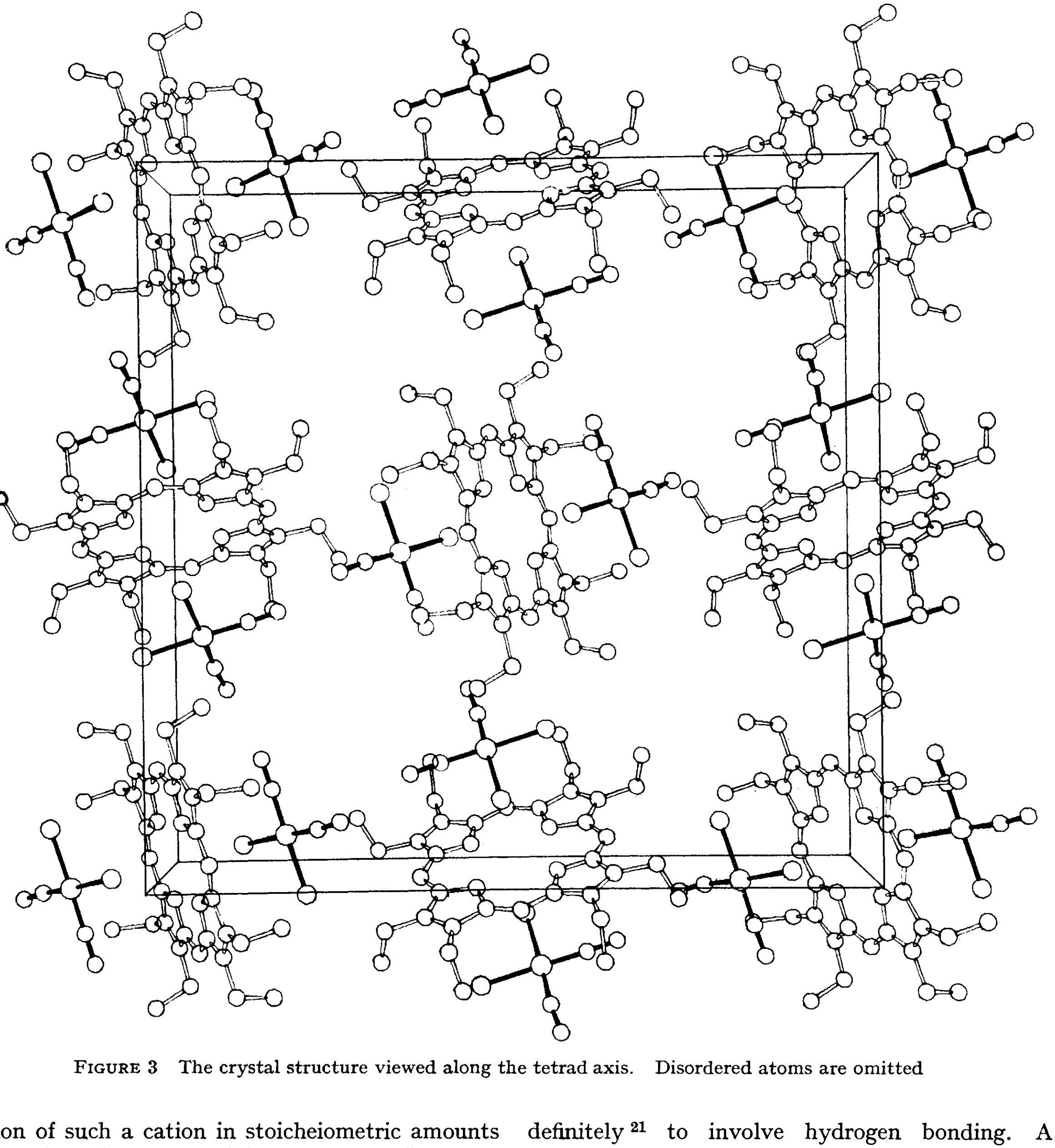


FIGURE 3 The crystal structure viewed along the tetrad axis. Disordered atoms are omitted

The Crystal Structure.—Each porphyrin nucleus is associated with two complex anions (Figure 2). The contacts between the four porphyrin nitrogen atoms and Cl(1) of the anion are in the range 3·26—3·42 Å, and these are short enough to permit hydrogen bonding of the type N–H ··· Cl. The mean N ··· Cl distance in such hydrogen bonds is *ca.* 3·21 Å[20] and a N ··· Cl contact of 3·27 Å has been shown by neutron diffraction definitely[21] to involve hydrogen bonding. A disordered arrangement of hydrogen atoms is possible since there are eight N ··· Cl contacts in each $[\text{oepH}_4]^{2+}$-$2[\text{RhCl}_2(\text{CO})_2]^-$ unit but only four hydrogen atoms. Direct electrostatic attraction between the chlorine and nitrogen atoms may also be involved. The dihedral angle between the co-ordination plane of the rhodium

---

[20] G. C. Pimental and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960, pp. 293—295.

[21] W. C. Hamilton and S. J. La Placa, *Acta Cryst.*, 1968, **B24**, 1147.

TABLE 4

(*a*) Bond lengths (Å) with standard deviations in parentheses

Rh–Cl(1)	2·365(4)	C(1)–C(2)	1·367(19)
Rh–Cl(2)	2·335(6)	C(1)–C(10)	1·388(20)
Rh–C(1A)	1·752(25)	C(5)–C(6)	1·366(20)
Rh–C(2A)	1·744(21)	C(6)–C(7′)	1·385(20)
O(1)–C(1A)	1·168(31)	Mean	1·377(10)
O(2)–C(2A)	1·163(28)		
		C(3)–C(31)	1·542(23)
N(1)–C(2)	1·373(17)	C(4)–C(41)	1·583(25)
N(1)–C(5)	1·377(17)	C(8)–C(81)	1·523(23)
N(2)–C(7)	1·378(17)	C(9)–C(91)	1·570(23)
N(2)–C(10)	1·397(18)	Mean	1·555(14)
Mean	1·381(9)		
		C(31)–C(32)	1·434(25)
C(2)–C(3)	1·460(20)	C(41)–C(42)	1·467(30)
C(4)–C(5)	1·444(21)	C(81)–C(82)	1·421(29)
C(7)–C(8)	1·435(20)	C(91)–C(92)	1·394(29)
C(9)–C(10)	1·431(20)	Mean	1·429(16)
Mean	1·443(10)		
C(3)–C(4)	1·337(21)		
C(8)–C(9)	1·357(21)		
Mean	1·347(15)		

Co-ordinates of primed atoms are derived from those of corresponding atoms in Table 3 by the transformation $\bar{x}, \bar{y}, \bar{z}$.

(*b*) Bond angles (°) with standard deviations in parentheses

Cl(1)–Rh–Cl(2)	90·5(2)	C(1)–C(2)–C(3)	127(1)
Cl(1)–Rh–C(1A)	89·6(8)	C(4)–C(5)–C(6)	127(1)
Cl(1)–Rh–C(2A)	178·4(8)	C(8)–C(7)–C(6′)	128(1)
Cl(2)–Rh–C(1A)	177·7(8)	C(1)–C(10)–C(9)	128(1)
Cl(2)–Rh–C(2A)	88·6(9)	Mean	127·4(7)
C(1A)–Rh–C(2A)	91·4(12)		
		C(2)–C(3)–C(31)	122(1)
C(2)–N(1)–C(5)	111(1)	C(5)–C(4)–C(41)	124(1)
C(7)–N(2)–C(10)	110(1)	C(7)–C(8)–C(81)	123(1)
Mean	110·4(8)	C(10)–C(9)–C(91)	124(1)
		Mean	123·4(7)
N(1)–C(2)–C(3)	105(1)		
N(1)–C(5)–C(4)	106(1)	C(3)–C(31)–C(32)	113(1)
N(2)–C(7)–C(8)	106(1)	C(4)–C(41)–C(42)	107(2)
N(2)–C(10)–C(9)	107(1)	C(8)–C(81)–C(82)	110(2)
Mean	106·2(6)	C(9)–C(91)–C(92)	109(2)
		Mean	109·6(13)
C(2)–C(3)–C(4)	109(1)		
C(3)–C(4)–C(5)	108(1)	C(4)–C(3)–C(31)	129(1)
C(7)–C(8)–C(9)	109(1)	C(3)–C(4)–C(41)	128(2)
C(8)–C(9)–C(10)	108(1)	C(9)–C(8)–C(81)	127(1)
Mean	108·6(7)	C(8)–C(9)–C(91)	129(1)
		Mean	128·1(7)
N(1)–C(2)–C(1)	128(1)		
N(1)–C(5)–C(6)	126(1)	C(2)–C(1)–C(10)	128(1)
N(2)–C(7)–C(6′)	126(1)	C(5)–C(6)–C(7′)	127(1)
N(2)–C(10)–C(1)	125(1)	Mean	127·5(9)
Mean	126·4(7)		

(*c*) Selected non-bonded contacts (Å) within the limits of the contact radii: Rh, 2·5; Cl, 2·1; O, N, C, 1·9 Å; contacts involving disordered atoms are not included

Cl(1) · · · N(1)	3·423(11)	Cl(1) · · · N(1′)	3·264(11)
Cl(1) · · · N(2)	3·362(12)	Cl(1) · · · N(2′)	3·313(11)
N(1) · · · N(2)	2·992(15)	N(1) · · · N(2′)	2·922(15)
C(1) · · · Cl(1$^{\mathrm{I}}$)	4·005(15)	C(82) · · · Cl(2$^{\mathrm{III}}$)	3·804(23)
C(31) · · · Cl(1$^{\mathrm{I}}$)	3·642(16)	C(31) · · · O(2$^{\mathrm{IV}}$)	3·523(24)
C(32) · · · C(1$^{\mathrm{I}}$)	3·842(19)	C(32) · · · O(2$^{\mathrm{IV}}$)	3·776(27)
C(91) · · · Cl(1$^{\mathrm{I}}$)	3·728(18)	C(42) · · · O(2$^{\mathrm{IV}}$)	3·691(28)
C(92) · · · Cl(1$^{\mathrm{I}}$)	3·961(23)	C(41) · · · Rh$^{\mathrm{V}}$	4·291(19)
C(1) · · · C(1$^{\mathrm{II}}$)	3·659(19)	C(42) · · · Rh$^{\mathrm{V}}$	3·644(21)
C(9) · · · C(3$^{\mathrm{II}}$)	3·704(21)	C(41) · · · Cl(2$^{\mathrm{V}}$)	3·984(20)
C(91) · · · C(4$^{\mathrm{II}}$)	3·672(23)	C(42) · · · Cl(2$^{\mathrm{V}}$)	4·063(23)
C(81) · · · Cl(2$^{\mathrm{III}}$)	3·728(18)	O(1) · · · O(2$^{\mathrm{V}}$)	3·699(28)

Roman numeral superscripts refer to the following co-ordinate transformations:

I	$x, y, 1 + z$	IV	$\tfrac{1}{2} + y, -x, 1 - z$
II	$-x, -y, 1 - z$	V	$\tfrac{1}{2} + y, -x, -z$
III	$\tfrac{1}{2} - y, x, z$		

atom and that of the porphyrin nucleus is 25° and the closest approaches between atoms of the cation and those of the anion in the [oepH$_4$]$^{2+}$2[RhCl$_2$(CO)$_2$]$^-$ units, excluding those between Cl(1) and the nitrogen atoms, represent normal van der Waals contacts, as do non-bonded contacts between atoms in different units [Table 4(*c*)]. The units are packed so as to leave channels *ca.* 5 Å in diameter (Figure 3). The unidentified solvent molecules may lie in these channels, which are large enough to contain chloroform molecules. Contacts between atoms of the cation or anion and those of the solvent molecule are greater than normal van der Waals distances, the shortest being C(92) · · · O(5) 3·7 Å.

TABLE 5

Least-squares planes. Equations of planes are in the form $Px + Qy + Rz = S$. Deviations (Å) of atoms from the planes are in square brackets

	P	*Q*	*R*	*S*
Plane (1):				
N(1), C(2)—(5)	−4·967	21·671	3·630	−0·012
[N(1) 0·008, C(2) 0·002, C(3) −0·013, C(4) 0·017, C(5) −0·015]				
Plane (2):				
N(2), C(7)—(10)	−5·303	21·208	3·777	0·086
[N(2) 0·003, C(7) 0, C(8) −0·004, C(9) 0·006, C(10) −0·006]				
Plane (3):				
N(1), N(2), N(1′), N(2′)	−4·668	21·701	3·550	0
[N(1) 0, N(2) 0, N(1′) 0, N(2′) 0, C(1) −0·031, C(2) −0·024, C(3) −0·029, C(4) 0·024, C(5) −0·003, C(6) 0·026, C(7) −0·035, C(8) −0·098, C(9) −0·091, C(10) −0·045, C(31) −0·087, C(41) 0·130, C(81) −0·212, C(91) −0·084]				
Plane (4):				
Rh, Cl(1), Cl(2), C(1A), C(2A), O(1), O(2)	−4·710	15·070	6·313	2·433
[Rh 0·007, Cl(1) 0·025, Cl(2) −0·029, C(1A) −0·037, C(2A) 0·034, O(1) −0·069, O(2) 0·024]				

Angles (°) between the planes:

(1)–(2)	1·48	(1)–(4)	24·15
(1)–(3)	0·99	(2)–(4)	22·90
(2)–(3)	2·45	(3)–(4)	24·86

The Complex Anion.—The non-crystallographic symmetry of the *cis*-[RhCl$_2$(CO)$_2$]$^-$ anion is close to C_{2v} and the rhodium co-ordination is square-planar; the angles subtended at the metal by mutually *cis*-ligand donor atoms do not differ significantly from 90° and deviations of the donor atoms from the mean plane of the anion are <0·04 Å. The carbonyl groups are linear and the C–O bonds are equal, mean 1·17(2) Å. The Rh–C bond lengths are also equal; their mean [1·75(2) Å] agrees well with the corresponding value [1·72(3) Å] in [Bu$^n{}_4$N]$^+$*cis*-[RhCl$_2$(CO)$_2$]$^-$;[22] both values are appreciably shorter than that [1·90(4) Å] in [Rh(f$_6$fos)$_2$]$^+$*cis*-[RhCl$_2$(CO)$_2$]$^-$ [f$_6$fos = $\mathrm{\overline{CF_2(CF_2)_2{\cdot}C(PPh_2){:}C}{\cdot}PPh_2}$], where disorder of

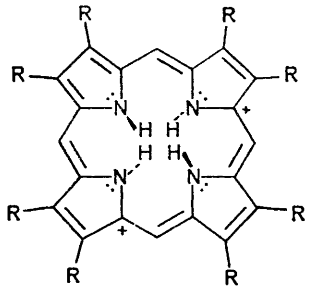
---

[22] C. K. Thomas and J. A. Stanko, *Inorg. Chem.*, 1971, **10**, 566.

the complex anion is suspected.[23] The Rh–C distances in (III) and in $[Bu^n_4N]^+$*cis*-$[RhCl_2(CO)_2]^-$, when compared with values of 1·81 Å in $[RhCl(CO)_2]_2$ [24] and 1·847(7) Å in $[RhCl(CO)(SO_2)(PPh_3)_2]$,[25] suggest that in $[RhCl_2(CO)_2]^-$ there is considerable rhodium–carbonyl back donation. The Rh–Cl distances [2·365(4) and 2·335(6) Å] in (III) differ by 0·030(7) Å, the longer bond being to the chlorine atom involved in hydrogen bonding. Both values are in good agreement with those in $[Bu^n_4N]^+$*cis*-$[RhCl_2(CO)_2]^-$ [2·345(6) Å] and $[Rh(f_6fos)_2]^+$-*cis*-$[RhCl_2(CO)_2]^-$ [2·35(1) Å].[22,23]

The Porphyrin Dication.—Chemically equivalent bond lengths and interbond angles in the $[oepH_4]^{2+}$ dication agree to well within the standard deviations derived from the least-squares matrix. Mean bond lengths and interbond angles found here are in excellent agreement with corresponding values [9] found in the diacid forms of tetraphenyl- and tetrapyridyl-porphin, and with the means suggested independently by Hoard [26] and by Fleischer [1] as appropriate for free-base or metallated porphyrins. For example, the root-mean-square difference between $[oepH_4]^{2+}$ and Hoard's values [26] for the four types of bond in the porphyrin nucleus is 0·003 Å. The largest discrepancy is in the interbond angle at the methine bridge which is 127·5° in $[oepH_4]^{2+}$, 120 and 123° respectively in the diacid forms of tetraphenyl- and tetrapyridyl-porphin,[9] where the bridgehead carbon atom carries an aromatic substituent, and 124° (Hoard [26]) or 126° (Fleischer [1]) in free-base and metallated porphyrins. The mean CH_2–CH_3 bond length [1·429(16) Å] in the ethyl side-chains of $[oepH_4]^{2+}$ is significantly shorter than the accepted value (1·54 Å) for a C(sp^3)–C(sp^3) single bond, suggesting that the positional parameters of the methyl and methylene carbon atoms may be in error; this would not be surprising in view of their large temperature factors.

The $[oepH_4]^{2+}$ skeleton, excluding the ethyl substituents, is essentially planar; the maximum deviation of an atom of the porphyrin nucleus from the plane of the four nitrogen atoms is 0·1 Å (Table 5); the pyrrole rings are accurately planar and the dihedral angles between the plane of the nitrogen atoms and those of the two independent pyrrole rings are respectively 1·0 and 2·5°. Minor deviations from planarity in free-base porphyrins are not uncommon; thus in the triclinic [27] and tetragonal [28] forms of tetraphenylporphin the maximum displacements of atoms from the mean planes of the porphyrin nuclei are respectively 0·16 and 0·38 Å, whereas porphin is planar to ±0·03 Å.[29] However, in the diacid forms of tetraphenyl- and tetrapyridyl-porphin [9] the maximum displacements are respectively 1·16 and 0·92 Å, and the pyrrole rings are inclined at 33 and 28° to the respective mean nuclear planes. It has therefore been argued that in all porphyrin diacids substantial departures from planarity will be found as a consequence of steric crowding of the inner hydrogen atoms.[9] In $[oepH_4]^{2+}$ trigonal hybridisation of the nitrogen atoms would imply that the hydrogen atoms lie in the nuclear plane with H · · · H non-bonded contacts of *ca.* 1·6 Å; the minimum non-bonded contact between hydrogen atoms is usually taken to be 1·9—2·0 Å.[30] In $[oepH_4]^{2+}$ the steric strain between hydrogen atoms could be relieved if the N–H bonds were inclined 20° or more to the plane of the nitrogen atoms; such an arrangement would also lead to stronger N–H · · · Cl hydrogen bonding (see Figure 2). Such a deformation is not unprecedented; in metallated porphyrins the metal atom may deviate by up to 0·5 Å from the plane of the nitrogen atoms [1] and in a synthetic corrin it has been suggested [31] that out-of-plane displacements of the inner hydrogen atoms help to relieve steric strain. Electronic factors may facilitate such out-of-plane deformations in $[oepH_4]^{2+}$ since canonical structures such as (V) may be written in which the nitrogen atoms are tetrahedrally hybridised and the peripheral carbon skeleton carries an 18 electron π-system. If non-centrosymmetric structures such as (V) are important in the present case some disorder of the inner hydrogen atoms would be implied.



(V) R = Et

We are as yet unable to explain why in $[oepH_4]^{2+}$ steric strain is relieved mainly by out-of-plane displacements of the hydrogen atoms, whereas in the diacid forms of tetraphenyl- and tetrapyridyl-porphin buckling of the entire porphyrin nucleus occurs. It may well be significant that the position, size, and electronic nature of the substituents in $[oepH_4]^{2+}$ are different from those in the tetraphenyl- and tetrapyridyl-porphin diacids. Further structural studies on diacid porphyrin species are clearly desirable.

---

[23] F. W. B. Einstein and C. R. S. M. Hampton, *Canad. J. Chem.*, 1971, **49**, 1901.

[24] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1961, **83**, 1762.

[25] K. W. Muir and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1921.

[26] J. L. Hoard, ' Structural Chemistry and Molecular Biology,' eds. A. Rich and N. Davidson, Freeman, London, 1968, pp. 573—594.

[27] S. J. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, 1967, **89**, 3331.

[28] M. J. Hamor, T. J. Hamor, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1964, **86**, 1938.

[29] A. Stone and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1968, **90**, 2735.

[30] O. Ermer and J. D. Dunitz, *Chem. Comm.*, 1971, 178.

[31] H. R. Harrison, O. J. R. Hodder, and D. C. Hodgkin, *J. Chem. Soc.* (*B*), 1971, 640.

EXPERIMENTAL

Materials.—$[RhCl(CO)_2]_2$,[32] $LiNMe_2$,[33] Co(oep),[11] $[Co(oep)py]^+Br^-$ (this and the following compound were prepared as [12] for the corresponding cobalt aetioporphyrin I analogues), $[Co(oep)]^+Br^-$ (*cf*. ref. 12), PMe_2Ph,[34] $PMePh_2$,[34] and $Li\{N{:}C(CF_3)_2\}$ [35] were prepared and purified by established procedures. Octaethylporphin was a generous gift from Professor H. H. Inhoffen.

Preparation of Complex (III).—Octaethylporphin (0·534 g, 1 mmol) and di-μ-chloro-tetracarbonyldirhodium(I) (0·390 g, 1 mmol) were heated under reflux in chloroform (160 ml) for 7 h at 115—130 °C. The solution was filtered and evaporated to 30 ml. Addition of warm hexane (80 ml) to the warm chloroform solution afforded dark red crystals of (III), *octaethylporphinbis*[cis-*dichlorodicarbonylrhodate*(I)] (0·456 g, 46%) (Found: C, 49·4; H, 5·1; N, 5·3; O, 6·2. $C_{40}H_{48}Cl_4N_4O_4Rh_2$ requires C, 48·2; H, 4·8; N, 5·6; O, 6·4%). I.r. absorption bands (cm^{-1}) (Nujol): 3180w,br, 2060vs, 1975vs,br, 1505m, 1312w, 1260w, 1212w, 1148m, 1100m, 1055s, 1015m, 958s, 899w, 873m, 848w, 820w, 675w, 668w, 619s, 490s, 462m, 320s, and 285s.

Volatiles were removed from the filtrate by evaporation to dryness. The residue was dissolved in chloroform (*ca*. 4 ml) and this was passed through an alumina column. Crystallisation, from chloroform with hexane at −20 °C, gave a dark red powder (0·222 g) (Found: C, 60·8; H, 6·2; N, 7·7%).

Reaction of Octaethylporphincobalt(III) *Bromide with Bis*(*trifluoromethyl*)*methylamidolithium*.—The bromide (0·671 g, 1 mmol) was added to a solution of the lithium reagent (1·2 mmol) in tetrahydrofuran (50 ml). The mixture was stirred at 20 °C for 1½ h, whereafter the volatiles were removed *in vacuo*. The dark red residue was dissolved in benzene (40 ml) and was filtered. The filtrate was evaporated to dryness and the residue recrystallised (Et_2O, 60 ml, −20 °C) to yield *bis*[(*trifluoromethyl*)*methyleneamido*](*octaethylporphin*)*cobalt*(III) (0·423 g, 56%) (Found: C, 62·2; H, 6·1; N, 9·4. $C_{39}H_{44}CoF_6N_5$ requires C, 62·0; H, 5·8; N, 9·3%); $\nu_{max.}$ (cm^{-1}) (Nujol): 1559w, 1312m, 1285s, 1270s, 1223m, 1203s, 1178s, 1145w, 1120m, 1059sh, 1054s, 1015s, 989s, 955s, 945sh, 921w, 850vs, 750s, 727w, 715vs, 700sh, 693m, 668sh, 665s, 527m, and 367m.

Reaction of Octaethylporphincobalt(III) *Bromide with Tertiary Phosphines*.—Methyldiphenylphosphine (1 ml) was added under nitrogen to the bromide (0·875 g, 1·3 mmol) in chloroform (25 ml), and the mixture heated under reflux for 1 h. Solvent was evaporated *in vacuo*, and excess of phosphine removed by washing with degassed ether. The residue was dried and recrystallised (tetrahydrofuran–C_6H_{14}) to obtain bright black needles of *octaethylporphinbis*(*methyldiphenylphosphine*)*cobalt*(III) *bromide* (1·057 g, 76%), m.p. 168° (Found: C, 70·1; H, 6·7; N, 5·4. $C_{62}H_{70}BrCoN_4P_2$ requires C, 69·5; H, 6·5; N, 5·2%); $\nu_{max.}$ (cm^{-1}) (Nujol): 1282m, 1270w, 1220w, 1140w, 1086w,br, 1050m, 1015m, 990m, 955s, 900sh, 894m, 881s, 826s, 748s, 735sh, 732m, 700w, 689s, 508vs, 450m, and 370w.

By a similar procedure, the bromide (0·221 g, 0·378 mmol) and phenyldimethylphosphine (*ca*. 0·5 ml) afforded bright black crystals of *octaethylporphinbis*(*phenyldimethylphosphine*)*cobalt*(III) *bromide* (0·234 g, 75%), m.p. 182 °C (Found: C, 66·2; H, 7·2; N, 6·0. $C_{52}H_{66}BrCoN_4P_2$ requires C, 65·9; H, 7·0; N, 5·9%); $\nu_{max.}$ (cm^{-1}): 1283m, 1270w, 1222m, 1140m, 1110m, 1064s, 1055s, 1020s, 995m, 960sh, 950s, 905vs, 850w, 840sh, 830s, 750vs, 719m, 692s, 488s, 425w, and 372m.

Reaction of Octaethylporphincobalt(II) *with Methyldiphenylphosphine*.—By a similar procedure octaethylporphincobalt(II) (0·148 g, 0·25 mmol) and the phosphine (*ca*. 0·3 ml) yielded bright black crystals of octaethylporphinbis(methyldiphenylphosphine)cobalt(II) (0·190 g, 77%), m.p. 158 °C (Found: C, 73·1; H, 7·2; N, 6·0. $C_{62}H_{70}CoN_4P_2$ requires C, 75·1; H, 7·1; N, 5·7%); $\nu_{max.}$ (cm^{-1}): 1270s, 1226m, 1146s, 1112w, 1052s, 1018s, 992s, 960s, 905m, 893sh, 886s, 830m, 753sh, 745s, 740sh, 695s, 690sh, 509vs, 445w, and 377m.

We thank Drs. D. J. Cardin and B. Çetinkaya for useful discussions, Engelhard, Ltd. for a loan of rhodium, and the S.R.C. for their support.

[3/1841 *Received*, 4*th September*, 1973]

---

[32] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1437.

[33] U. Wannagat and H. Niederprüm, *Chem. Ber.*, 1961, **94**, 1540.

[34] B. Heaton, D.Phil. Thesis, University of Sussex, 1967.

[35] W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, 1965, **30**, 1398.