Synthesis and Characterization of Diazido–Germanium(IV) and –Tin(IV) Porphyrins. Crystal Structure of Diazido(5,10,15,20-tetra-*p*-tolylporphyrinato)germanium(IV) †

Roger Guilard and Jean-Michel Barbe
Laboratoire de Synthèse et d'Electrosynthese Organométallique, associé au C.N.R.S. (UA 33), Faculté des Sciences 'Gabriel', 6, Boulevard Gabriel, 21100 Dijon, France
Mohamed Boukhris and Claude Lecomte
Laboratoire de Minéralogie et Cristallographie (UA 809), Faculté des Sciences, Centre de 2ème Cycle, B.P. No. 239, 54506 Vandoeuvre-les-Nancy Cedex, France

The synthesis and physico-chemical characterization of diazido–germanium(IV) and –tin(IV) porphyrins by ^{1}H n.m.r., i.r., u.v.–visible, and mass spectroscopy has been carried out. The crystal structure of diazido(5,10,15,20-tetra-*p*-tolylporphyrinato)germanium(IV) is described [tetragonal, space group $I\bar{4}2d$, a = 18.123(1), c = 12.162(2) Å, Z = 4, R = 0.032, R' = 0.034]. The co-ordination polyhedron is an almost perfect octahedron: Ge–N(porphyrin) 1.983(3), Ge–N(azide) 1.963(4) Å.

Metalloporphyrin complexes with metal–nitrogen axial bonds have been shown to be involved in many biological processes[1] and several nitrido- and azido-metalloporphyrins have been described.[2–11] Recently, we reported the synthesis and characterization of some azidogallium(III) porphyrins.[8] Thermal or photolytic decomposition of such complexes could lead to remarkable precursors of conducting polymers. On the other hand, as previously shown for organic azides,[12] azidometalloporphyrins react with nitriles leading to a new class of porphyrin complexes having a tetrazole ring linked to the metal by a nitrogen atom.[13]

We report here the synthesis and spectroscopic characterization of diazido complexes $M^{IV}(por)(N_3)_2$ (M = Sn or Ge) ‡ and the *X*-ray structure determination of $Ge(tptp)(N_3)_2$.

Experimental

Syntheses.—The complexes $Ge(por)Cl_2$[14] and $Sn(por)Cl_2$[15] were obtained using literature methods. The syntheses of $M(por)(N_3)_2$ were performed under argon using Schlenk techniques. All solvents were purified thoroughly and distilled under argon just before use.

Preparation of $M(por)(N_3)_2$ (M = Ge *or* Sn). A solution of $M(por)Cl_2$ (0.74 mmol) in 1,2-dichloroethane (50 cm^3) was refluxed with NaN_3 (15.38 mmol) for 24 h. The mineral salts were removed by suction filtration and the solution evaporated *in vacuo*. The resulting solid was then recrystallized. Yields, recrystallization solvents, and elemental analyses are given in Table 1.

Physical Measurements.—Elemental analyses were performed by the Service Central de Microanalyse du C.N.R.S. Mass spectra were obtained in the electron-impact mode with a Finnigan 3300 spectrometer: ionizing energy 70 eV, ionizing current 0.4 mA, source temperature 250—400 °C. ^{1}H N.m.r. spectra were recorded at 400 MHz on a Bruker WM 400 spectrometer at the Centre de Resonance Magnètique de l'Université de Dijon. Spectra were measured on solutions of complex (3 mg) in $CDCl_3$ (0.5 cm^3) using $SiMe_4$ as internal reference. Infrared spectra were performed with a Perkin-Elmer 580B instrument. Samples were prepared as 1% dispersions in CsI. U.v.–visible spectra were taken on a Perkin-Elmer 559 spectrophotometer.

X-*Ray Data Collection, Structure Solution, and Refinement.*—A suitable crystal of $Ge(tptp)(N_3)_2$ was obtained from recrystallization of the complex in toluene. Preliminary Weissenberg photographs along the c axis revealed $\frac{4}{m}mm$ symmetry and systematic absences (hkl, $h + k + l = 2n + 1$; hhl, $2h + 1 = 4n + 1$) led to the possible space group $I4_1md$ or $I\bar{4}2d$. The nature of the four-fold axis was established on the diffrac-

Table 1. Yields, recrystallization solvents, and elemental analyses for $M(por)(N_3)_2$ complexes

Complex	Yield (%)	Recrystallization solvent[a]	Molecular formula	Analysis[b] (%) C	H	N
$Ge(oep)(N_3)_2$	79	C	$C_{36}H_{44}GeN_{10}$	62.4 (62.7)	6.2 (6.45)	19.4 (20.3)
$Ge(tptp)(N_3)_2$	84	A	$C_{48}H_{36}GeN_{10}$	69.0 (68.7)	3.6 (3.65)	16.1 (18.2)
$Ge(tmtp)(N_3)_2$	81	A	$C_{48}H_{36}GeN_{10}$	69.3 (68.7)	3.8 (3.65)	16.5 (18.2)
$Sn(oep)(N_3)_2$	89	C	$C_{36}H_{44}N_{10}Sn$	58.7 (58.8)	6.3 (6.05)	17.5 (19.05)
$Sn(tptp)(N_3)_2$	89	A	$C_{48}H_{36}N_{10}Sn$	65.8 (66.15)	4.2 (4.15)	14.7 (16.05)
$Sn(tmtp)(N_3)_2$	79	A–B (1:1)	$C_{48}H_{36}N_{10}Sn$	67.0 (66.15)	4.1 (4.15)	15.1 (16.05)

[a] A = Toluene, B = heptane, C = 1,2-dichloroethane. [b] Calculated values are given in parentheses.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ Abbreviations: por = unspecified porphyrinate(2−), tptp = 5,10,15,20-tetra-*p*-tolylporphyrinate(2−), tpp = 5,10,15,20-tetraphenylporphyrinate(2−), py = pyridine, oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2−), tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinate(2−).

tometer (Enraf-Nonius CAD4F) showing no particular extinction on 001. Hence, the crystal structure was solved in the $I\bar{4}2d$ space group. Experimental conditions and crystal data are given in Table 2. The data reduction was made with the SDP package.[16] The crystal structure was solved by the heavy-atom method, the germanium lying on the (0, 0, 0) $\bar{4}$ axis. Subsequent Fourier syntheses revealed all atoms including H. All the non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically.[17] At the end of the least-squares process, the reliability factors were $R = 0.032$; $R' = 0.034$, goodness of fit = 1.35, $w = [\sigma^2(F) + 0.0085F^2]^{-1}$. Final fractional atomic co-ordinates of the non-hydrogen atoms are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, remaining bond distances and angles.

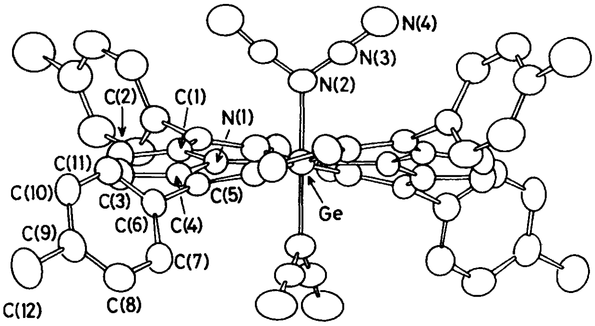

Figure 1. Molecular structure of $Ge(tptp)(N_3)_2$

Table 2. Experimental conditions and crystal data for $Ge(tptp)(N_3)_2$

Formula	$C_{48}H_{36}GeN_{10}$
M	825.2
System, space group	Tetragonal, $I\bar{4}2d$
a/Å	18.123(1)
c/Å	12.162(2)
U/Å^3	3 994(3)
Z	4
D_c/g cm^{-3}	1.37
Radiation	Mo-K_α (λ = 0.710 69 Å, graphite monochromatized)
$\sin\theta/\lambda_{max.}$ (Å^{-1})	0.72
Scan speed (θ/° min^{-1})	$2 < \theta < 33$
Scan range (°)	0.95 + 0.4 tanθ
Aperture (mm)	3 + 1.0 tanθ
Take-off angle (°)	3
h, k, l limits	$-25 < h < 0, 0 < k < 25, 0 < l < 17$
Number of measurements	2 333
Number of unique reflections (N)	1 548, 989 [$I < 3\sigma(I)$]
Agreement factor $R_i(F)$ between symmetry-related reflections	0.023
Corrections	Lorentz polarization
Number of parameters (N_p)	149
N/N_p	6.6
Δ/σ (max.)	0.21 for z of C(12)

Results and Discussion

The reaction of $M(por)Cl_2$ with NaN_3 in 1,2-dichloroethane leads easily to the formation of $M(por)(N_3)_2$; yields are in the range 79—89%. Characterization of these latter compounds

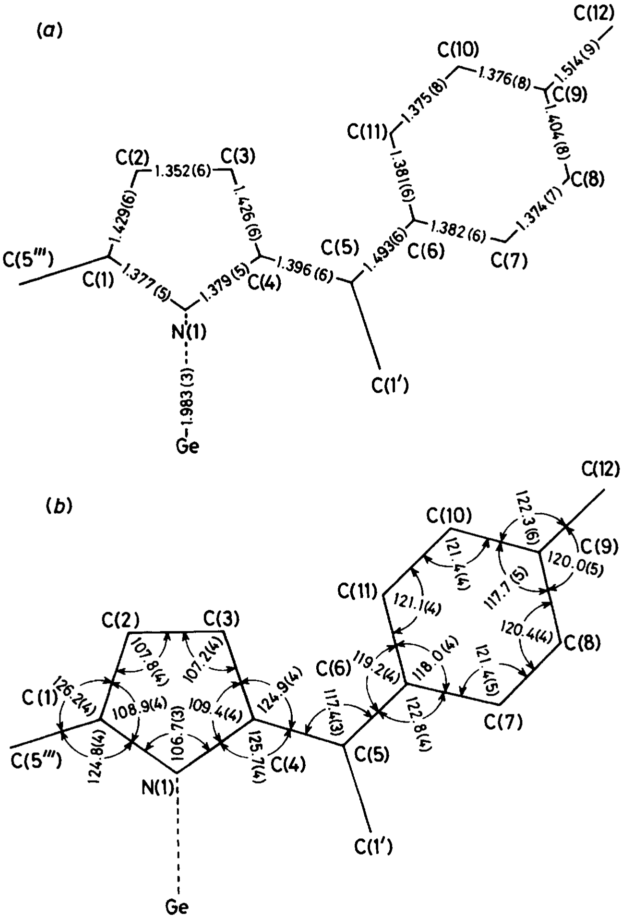

Figure 2. (a) Bond distances, (b) bond angles

Table 3. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Ge	0.500	0.500	0.500	C(11)	0.248 7(3)	0.625 3(3)	0.686 0(4)
N(1)	0.400 1(2)	0.455 3(2)	0.499 7(3)	C(12)	0.044 2(4)	0.668 7(6)	0.708 9(8)
N(2)	0.500	0.500	0.661 5(3)	N(3)	0.533 4(4)	0.459 4(4)	0.715 9(6)
C(1)	0.334 8(2)	0.489 5(3)	0.527 1(3)	N(4)	0.566 7(7)	0.442 1(7)	0.774 6(8)
C(2)	0.276 8(3)	0.436 1(3)	0.525 6(4)	H(21)	0.234(4)	0.442(3)	0.544(5)
C(3)	0.305 9(2)	0.371 4(2)	0.491 1(4)	H(31)	0.283(3)	0.327(3)	0.482(3)
C(4)	0.383 3(2)	0.382 6(2)	0.477 7(3)	H(71)	0.195(3)	0.571(3)	0.446(5)
C(5)	0.326 7(2)	0.565 2(2)	0.544 4(3)	H(81)	0.085(4)	0.614(4)	0.508(6)
C(6)	0.254 0(2)	0.594 5(2)	0.582 4(3)	H(101)	0.182(4)	0.666(4)	0.805(5)
C(7)	0.190 9(3)	0.591 0(3)	0.519 1(4)	H(111)	0.289(3)	0.629(2)	0.727(4)
C(8)	0.124 2(3)	0.616 2(3)	0.557 8(5)	H(121)	0.008(6)	0.669(5)	0.658(7)
C(9)	0.118 7(3)	0.645 8(3)	0.664 2(5)	H(123)	0.047(4)	0.623(4)	0.751(7)
C(10)	0.182 3(3)	0.650 8(4)	0.725 5(4)				

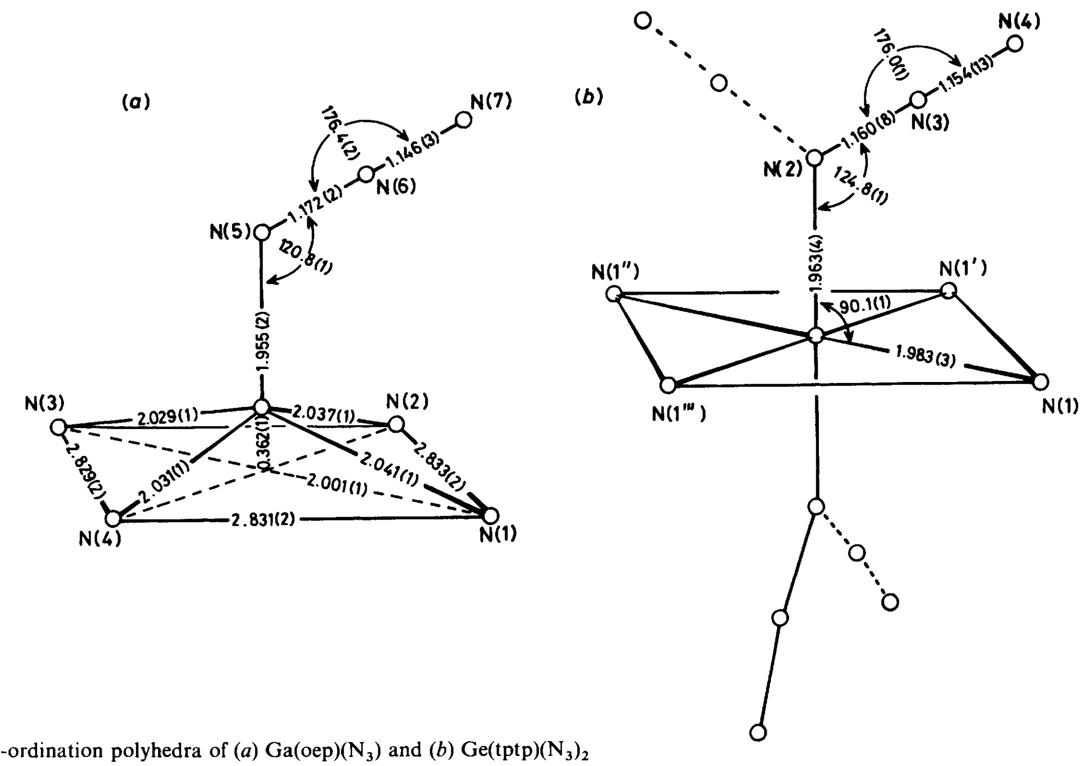

Figure 3. Co-ordination polyhedra of (*a*) Ga(oep)(N_3) and (*b*) Ge(tptp)$(N_3)_2$

Table 4. Mass spectral data for M(por)$(N_3)_2$ complexes

Complex	*m*/*e*	Relative intensity (%)	Fragmentation pattern
Sn(oep)$(N_3)_2$	652	65.97	$[Sn(oep)]^{\bullet +}$
	694	100.00	$[Sn(oep)N_3]^+$
	723	2.81	$[Sn(oep)(N_3)N_2H]^{\bullet +}$
Sn(tptp)$(N_3)_2$	788	52.46	$[Sn(tptp)]^{\bullet +}$
	802	2.54	$[Sn(tptp)N_3]^+$
	830	100.00	$[Sn(tptp)N_3]^+$
	844	0.48	$[Sn(tptp)(N_3)N]^+$
Sn(tmtp)$(N_3)_2$	788	58.94	$[Sn(tmtp)]^{\bullet +}$
	802	2.36	$[Sn(tmtp)N]^+$
	830	100.00	$[Sn(tmtp)N_3]^+$
	845	0.52	$[Sn(tmtp)(N_3)NH]^+$
Ge(oep)$(N_3)_2$	606	9.66	$[Ge(oep)]^{\bullet +}$
	620	4.20	$[Ge(oep)N]^+$
	634	5.04	$[Ge(oep)N_2]^+$
	648	100.00	$[Ge(oep)N_3]^+$
	662	0.42	$[Ge(oep)(N_3)N]^+$
Ge(tptp)$(N_3)_2$	742	14.56	$[Ge(tptp)]^{\bullet +}$
	756	5.94	$[Ge(tptp)N]^+$
	784	100.00	$[Ge(tptp)N_3]^+$
	798	0.34	$[Ge(tptp)(N_3)N]^+$
Ge(tmtp)$(N_3)_2$	742	13.11	$[Ge(tmtp)]^{\bullet +}$
	756	14.86	$[Ge(tmtp)N]^+$
	784	100.00	$[Ge(tmtp)N_3]^+$
	798	0.58	$[Ge(tmtp)(N_3)N]^+$
	813	0.29	$[Ge(tmtp)(N_3)N_2H]^{\bullet +}$

Table 5. Infrared data (cm^{-1}) for M(por)$(N_3)_2$ complexes

Complex	$\nu_{asym}(N_3)$	$\nu_{sym}(N_3)$	$\delta(N_3)$	$\nu(M-N_3)$
Sn(oep)$(N_3)_2$	2 060	1 285	655	375
Sn(tptp)$(N_3)_2$	2 060	1 285	665	390
Sn(tmtp)$(N_3)_2$	2 060	1 280	660	380
Ge(oep)$(N_3)_2$	2 080	1 290	675	415
Ge(tptp)$(N_3)_2$	2 080	1 290	675	400
Ge(tmtp)$(N_3)_2$	2 080	1 285	675	415

was achieved on the basis of mass spectral data, i.r., u.v.–visible, and ^1H n.m.r. data.

Mass spectral data show that the most abundant ion is always the monoazido ion $[M(por)N_3]^+$ whereas the molecular peak is never detected. The abstraction of a nitrogen molecule from the starting compound and/or $[M(por)N_3]^+$ is also observed for most of the complexes. Mass spectral results are listed in Table 4.

Usually, i.r. spectra of organometallic azido complexes

Table 6. U.v.–visible data of $M(por)(N_3)_2$ complexes

Complex	Absorptions λ/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})						
	N(0,0)	*B*(1,0)	*B*(0,0)	*Q*(2,0)	*Q*(1,0)	*Q*(0,0)	
$Sn(oep)(N_3)_2$[a]	354 (4.13)	387 (6.47)	408 (31.92)	499 (0.23)	538 (1.86)	577 (1.44)	
$Sn(tptp)(N_3)_2$[b]		408 (4.64)	430 (47.70)	524 (0.35)	564 (1.64)	605 (1.62)	627 (0.38)
$Sn(tmtp)(N_3)_2$[b]		406 (4.10)	429 (52.00)	522 (0.34)	563 (1.82)	603 (1.41)	627 (0.37)
$Ge(oep)(N_3)_2$[a]	345 (3.27)	388 (5.77)	408 (37.87)	496 (0.21)	536 (1.78)	573 (1.58)	
$Ge(tptp)(N_3)_2$[b]		405 (4.67)	427 (50.02)	519 (0.37)	560 (1.94)	601 (1.37)	
$Ge(tmtp)(N_3)_2$[b]		405 (4.51)	427 (51.32)	518 (0.34)	559 (1.81)	599 (1.35)	

[a] Recorded in CH_2Cl_2. [b] Recorded in toluene.

Table 7. Proton n.m.r. data* for $M(por)(N_3)_2$ complexes

Complex	R^1	R^2	Protons of R^1	Protons of R^2
$Sn(oep)(N_3)_2$	H	Et	s, 4, 10.58	t, 24, 2.05 q, 16, 4.23
$Sn(tptp)(N_3)_2$	*p*-MeC_6H_4	H	s, 12, 2.73 d, 8, 7.62 d, 8, 8.19	s, 8, 9.25
$Sn(tmtp)(N_3)_2$	*m*-MeC_6H_4	H	s, 12, 2.66 m, 8, 7.68 M, 8, 8.12	s, 8, 9.25
$Ge(oep)(N_3)_2$	H	Et	s, 4, 10.42	t, 24, 2.00 q, 16, 4.21
$Ge(tptp)(N_3)_2$	*p*-MeC_6H_4	H	s, 12, 2.71 d, 8, 7.58 d, 8, 8.12	s, 8, 9.16
$Ge(tmtp)(N_3)_2$	*m*-MeC_6H_4	H	s, 12, 2.63 m, 8, 7.65 M, 8, 8.06	s, 8, 9.16

* Data given as multiplicity, intensity, δ/p.p.m. M = Undefined signal.

exhibit three vibration modes for N_3 groups which are the asymmetrical stretching (1 950—2 150 cm^{-1}), the symmetrical stretching (1 250—1 350 cm^{-1}), and the N_3 bending mode (600—700 cm^{-1}).[18] These last vibration modes also appear in the present series of complexes (see Table 5). The asymmetrical stretching mode is observed at 2 060 and 2 080 cm^{-1} for tin and germanium complexes respectively in good agreement with the corresponding frequencies for gallium porphyrins.[8] Such a band is observed at 1 997 and 2 000 cm^{-1} in $Mn(tpp)(N_3)_2$[3] and $Fe(tpp)(N_3)(py)$[6] respectively. This decrease in frequency can be explained by π bonding between the filled metal *d* orbital and the π^* orbital of the nearest nitrogen atom.[19] Such an interaction cannot be involved for the non-transition metal porphyrins $M(por)(N_3)_x$ for which the asymmetrical stretching frequencies are very close to those of inorganic azides.[20,21] So the non-transition metal–azide bond exhibits greater ionic character, as in $Tl(C_2H_5)_2{}^+N_3{}^-$.[22] The symmetrical stretching (1 280—1 290 cm^{-1}) and the bending modes (655—675 cm^{-1}) are in the expected range. Lower frequency metal–azide stretching modes are also detected at 375—390 cm^{-1} for the tin complexes and 400—415 cm^{-1} for the germanium series.

The u.v.–visible data for these azide complexes are similar to those of the corresponding dichloro derivatives and exhibit characteristic electronic spectra of 'normal' metalloporphyrins. All the absorption bands are just slightly blue shifted (1—3 nm) with respect to the starting materials (Table 6).

Hydrogen-1 n.m.r. data are given in Table 7. The spectra of the octaethylporphyrin complexes exhibit a quartet for the methylenic protons, which would indicate the presence of two azido groups linked to the metal in a symmetrical *trans* arrangement. Such an arrangement is also provided by the spectra of tetra-*p*-tolylporphyrins which show doublets for *ortho* and *meta* phenyl protons. ^1H N.m.r. data reveal a slight deshielding of *meso* protons and β-pyrrole protons with respect to the spectra of the corresponding dichloro complexes. This is in agreement with the greater electron withdrawing character of the azide group.

An ORTEP plot of $Ge(tptp)(N_3)_2$ is shown in Figure 1. The germanium atom lies on the (0,0,0) $\bar{4}$ crystallographic axis. Hence the two azido groups occupy four positions deduced from the $\bar{4}$ symmetry. The bond distances and angles in the macrocycle are displayed in Figure 2; the co-ordination polyhedra of $Ge(tptp)(N_3)_2$ and $Ga(oep)(N_3)$[8] are compared in Figure 3. The co-ordination polyhedron of the germanium atom is an almost perfect octahedron [Ge–N(1) 1.983(3), Ge–N(2) 1.963(4) Å; N(1)–Ge–N(2) 90.1(1)°]. The metal–axial nitrogen bond angle is larger in the germanium derivative (124.8 *vs.* 120.8°); in both structures the azido group departs slightly from linearity (N–N–N *ca.* 176°). The Ge–N(porphyrin) distance [1.983(3) Å] is equal to that found in $Ge(oep)F_2$ [1.986(3) Å].[23] The bond distances and angles in the macrocycle are normal and the porphyrin ring has a very strong 'ruffled' structure like $Ge(oep)F_2$.[23]

References

1. J. T. Groves and T. Takahashi, *J. Am. Chem. Soc.*, 1983, **105**, 2073.
2 B. C. Schardt, F. J. Hollander, and C. L. Hill, *J. Am. Chem. Soc.*, 1982, **104**, 3964.
3 M. J. Camenzind, F. J. Hollander, and C. L. Hill, *Inorg. Chem.*, 1983, **22**, 3776.
4 H. Ogoshi, E. Watanabe, Z. Yochida, J. Kincaid, and K. Nakamoto, *J. Am. Chem. Soc.*, 1973, **95**, 2845
5 I. A. Cohen, *Ann. N.Y. Acad. Sci.*, 1973, **206**, 453.
6 K. M. Adams, P. G. Rasmussen, W. R. Scheidt, and K. Hatano, *Inorg. Chem.*, 1979, **18**, 1892.
7 W. J. Kruper, jun., Ph.D. Thesis, University of Michigan, 1981.
8 A. Coutsolelos, R. Guilard, A. Boukhris, and C. Lecomte, *J. Chem. Soc., Dalton Trans.*, 1986, 1779.
9 J. W. Buchler and C. Dreher, *Z. Naturforsch., Teil B*, 1984, **39**, 222 and refs. therein.
10 D. A. Summerville and I. A. Cohen, *J. Am. Chem. Soc.*, 1976, **98**, 1747.

11 W. R. Scheidt, D. A. Summerville, and I. A. Cohen, *J. Am. Chem. Soc.*, 1976, **98**, 6623.

12 G. L'abbé, *Chem. Rev.*, 1969, **69**, 345.

13 R. Guilard, S. S. Gerges, A. Tabard, P. Richard, M. El Borai, and C. Lecomte, *J. Am. Chem. Soc.*, 1987, **109**, 7228.

14 J. E. Maskasky and M. E. Kenney, *J. Am. Chem. Soc.*, 1973, **95**, 1443.

15 A. H. Corwin and O. D. Collins, III, *J. Org. Chem.*, 1962, **27**, 3060.

16 SDP Structure Determination Package, Enraf Nonius, Delft, Netherlands, 1977.

17 G. M. Sheldrick, SHELX, program for crystal structure determination, University of Göttingen, West Germany, 1976.

18 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley and Sons, New York, 1978.

19 W. R. Scheidt, 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1978, vol. 3, p. 463.

20 D. Forster and W. DeW. Horrocks, jun., *Inorg. Chem.*, 1966, **5**, 1510.

21 J. L. Bryant, *J. Chem. Phys.*, 1964, **40**, 3195.

22 E. Maslowsky, jun., 'Vibrational Spectra of Organometallic Compounds,' 2nd edn., Wiley and Sons, New York, 1978.

23 R. Guilard, J. M. Barbe, A. Boukhris, C. Lecomte, J. E. Anderson, Q. Y. Xu, and K. M. Kadish, *J. Chem. Soc., Dalton Trans.*, 1988, 1109.

Received 15*th July* 1987; *Paper* 7/1268