a fragment corresponding to the metal-free tetrakis(cumylphenoxy)phthalocyanines (*m/z* 1355). Again, as in the case of the unsubstituted lead phthalocyanine, this likely is due to the size of the lead and bismuth ions and hence their ease of displacement from their location above the plane of the phthalocyanine nucleus.

The observation of a protonated BiTPc molecule at *m/z* 1562 is of particular importance because it establishes evidence of a Bi(II) compound. Previous to this study, the only evidence for the existence of this compound was an elemental analysis.[29] A FAB spectrum of BiTPc is shown in Figure 4.

Tetra-9,10-phenanthrotetraazaporphyrin. A sample of this compound was presented as an unknown in order to obtain molecular weight information, confirming a novel synthesis.[30] This compound, H_2TPTAP, was run in a neat sulfuric acid matrix as this was the only solvent in which the sample dissolved. A molecular ion at *m/z* 914 and a protonated molecule (*m/z* 915) were observed in the FAB mass spectra. No fragment ions were observed. In addition, like the underivatized phthalocyanines, an isotope cluster was observed at *m/z* 930 corresponding to an oxygen adduct ion. Elemental analyses of this compound were confused by the presence of oxygen until the samples were degassed by heating in vacuo. Exposure to air resulted in readsorption of oxygen according to elemental analysis.[29]

Conclusion

In general, FAB provides a rapid technique for the confirmation of the molecular weight of different series of substituted and unsubstituted phthalocyanines. Fragmentation of the phthalocyanines by FAB is minimal, yielding little structural information. This is in contrast to the FAB results on the "tailed" porphyrins and meso-substituted tetraphenylporphines.[8] However, these phthalocyanines are structurally simple relative to the tailed porphyrins. Because there is no perceptible fragmentation, and sometimes a meager abundance of the molecular ion, the FAB technique is not readily amenable to evaluation of a complete unknown. However, as shown in the case of the tetra-9,10-phenanthrotetraazaporphyrin, FAB can provide evidence confirming proposed identities of phthalocyanines and structurally similar compounds.

Water, oxygen, and dioxygen adduct ions were observed for the unsubstituted phthalocyanines, providing corroborating evidence of an oxygen-phthalocyanine interaction from ESR analyses.[27] Because the metal-free as well as the metal-bound phthalocyanines show these oxygen adduct species, one may conclude that there is no significant oxygen-metal interaction. Instead, this observation implies that the oxygen interaction is with the aromatic macrocycle. Furthermore, the peripherally substituted tetrakis(cumylphenoxy)phthalocyanince do not show such adducts. This may indicate a much weaker interaction of the oxygen on the macrocyclic backbone of the peripherally substituted species.

Acknowledgment. The authors thank Arthur W. Snow of the Naval Research Laboratory for his valuable discussions and for providing the phthalocyanine compounds used in this study. This work was supported by the Office of Naval Research and the Army Chemical Research and Development Center.

Registry No. H_2Pc, 574-93-6; FePc, 132-16-1; CoPc, 3317-67-7; NiPc, 14055-02-8; CuPc, 147-14-8; ZnPc, 14320-04-8; PbPc, 15187-16-3; H_2TPc, 93530-40-6; BeTPc, 93530-41-7; MgTPc, 93530-42-8; MnTPc, 93530-43-9; FeTPc, 93530-44-0; CoTPc, 93530-45-1; NiTPc, 93530-46-2; CuTPc, 93530-47-3; ZnTPc, 93530-48-4; PtTPc, 93530-49-5; PdTPc, 93530-50-8; PbTPc, 93530-51-9; BiTPc, 93530-52-0.

---

(30) Snow, A. W.; Price, T. R. *Synth. Met.* **1984**, *9*, 239-340.

Contribution from the Chemistry Division,
Naval Research Laboratory, Washington, D.C. 20375

Crystal and Molecular Structure of Chloro(phthalocyaninato)gallium(III), Ga(Pc)Cl, and Chloro(phthalocyaninato)aluminum(III), Al(Pc)Cl

KENNETH J. WYNNE[1]

Received April 6, 1984

A single-crystal X-ray diffraction analysis has been carried out on the title compounds to provide a structural basis for the observed conductivity upon doping and the photoconductivity. Ga(Pc)Cl (Pc = phthalocyaninato dianion, $C_{32}H_{20}N_8^{2-}$) crystallizes in the triclinic space group $P\bar{1}$ with the following: $a = 9.301$ (3), $b = 11.272$ (1), $c = 13.143$ (3) Å; $\alpha = 105.46$ (2), $\beta = 105.61$ (2), $\gamma = 96.80$ (2)°; $V = 1252.8$ Å^3. For $Z = 2$ and fw = 617.7 the calculated density is 1.64 g/cm^3. Automated diffractometer intensity data (Enraf-Nonius CAD4) were used to solve the structure. Refinement led to $R_F = 0.036$ and $R_{wF} = 0.042$ for all 3483 unique reflections with $2.8° < 2\theta < 46°$ (Mo Kα radiation). Square-pyramidal coordination exists about Ga with Cl occupying the apex (Ga-Cl = 2.217 (1) Å) and N(1)-N(4) the basal positions: Ga-N(1) = 1.979 (4), Ga-N(2) = 1.981 (4), Ga-N(3) = 1.983 (4), Ga-N(4) = 1.9988 (4) Å. Gallium is 0.439 (1) Å above the least-squares plane formed by N(1)-N(4). The Pc ring is essentially planar; packing gives an interleaved slipped-stacked array in the crystal with an interplanar distance of 3.34 Å. Al(Pc)Cl also crystallizes in the triclinic space group $P\bar{1}$ with the following: $a = 13.776$ (6), $b = 13.775$ (4), $c = 14.059$ (5) Å; $\alpha = 98.36$ (3), $\beta = 108.60$ (3), $\gamma = 90.16$ (3)°; $V = 2498.2$ Å^3. For $Z = 4$ and fw = 579.0 the calculated density is 1.54 g/cm^3. Disorder gave rise to high overall R values: $R_F = 0.137$ and $R_{wF} = 0.164$ for 9454 unique reflections with $2.8° < \theta < 140°$ (Cu Kα radiation). The coordination geometry is square pyramidal as for Ga(Pc)Cl. Bond distances for the nondisordered molecule containing Al(1) are Al(1)-Cl(1) = 2.179 (6), Al(1)-N(1) = 1.961 (12), Al(1)-N(2) = 1.962 (13), Al(1)-N(3) = 1.966 (12), and Al(1)-N(4) = 2.018 (12) Å. Al(1) is 0.410 (6) Å above the basal plane formed by N(1)-N(4).

Introduction

There has recently been considerable interest in group 3 and 4 phthalocyanines because of the high conductivity of partially oxidized derivatives,[2-4] interesting cofacial polymeric structures,[3-7] and the thermal and hydrolytic robustness of these

---

(1) Address correspondence to the Chemistry Division, Office of Naval Research, Arlington, VA 22217.

(2) Nohr, R. S.; Kuznesof, P. M.; Wynne, K. J.; Kenney, M. E.; Siebenman, P. G. *J. Am. Chem. Soc.* **1981**, *103*, 4371.

(3) Dirk, C. W.; Inabe, T.; Schoch, K. F., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539.

Table I. Experimental Data for the X-ray Diffraction Study of Ga(Pc)Cl and Al(Pc)Cl

	Ga(Pc)Cl	Al(Pc)Cl
	(A) Crystal Parameters	
temp, °C	23 ± 1	23 ± 1
cryst dimens, mm	0.10 × 0.15 × 0.15	0.20 × 0.20 × 0.05
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.301 (3)	13.776 (6)
b, Å	11.272 (1)	13.775 (4)
c, Å	13.143 (3)	14.059 (5)
α, deg	105.46 (2)	98.36 (3)
β, deg	105.51 (2)	108.60 (3)
γ, deg	96.80 (2)	90.16 (3)
V, Å^3	1252.8	2498.2
Z	2	4
mol wt	617.71	579.00
ρ_{calcd}, g/cm^3	1.64	1.54
	(B) Measurement of Data	
radiation	Mo Kα (λ = 0.710 73 Å)	Cu Kα (λ = 1.541 84 Å)
monochromator	graphite crystal, incident beam	
2θ range, deg	2.8-46	2.8-140
scan type	ω-θ	ω-θ
scan speed, deg/min	2-20 (in ω)	2-20 (in ω)
scan range, deg	0.6 + 0.350 tan θ	0.6 + 0.300 tan θ
no. of total reflcns colled	3607	9724
no. of unique reflcns colled	3483	9454
stds	3/41 min; no measurable change	
corrections	Lorentz-polarization empirical absorption extinction	

materials.[2-9] Thus, the cofacially joined metallomacrocyclic polymers $[\mathrm{M(Pc)O}]_n$ (M = Si, Ge; Pc = phthalocyaninato dianion) may be partially oxidized with a variety of reagents, but most commonly I_2, to give stable, conducting materials.[5,6] The isoelectronic group 3 polymers $[\mathrm{M(Pc)F}]_n$ (M = Al, Ga) may also be partially oxidized with I_2[2] or nitrosyl salts,[10,11] and the resulting materials are also highly conducting.

Variations in M and X in partially oxidized $[\mathrm{M(Pc)X}]_n$ structures have provided valuable insight into how factors such as interplanar ring spacing affect electrical, electronic, and optical properties. In order to acquire further knowledge concerning structure–property relationships, chloro–, bromo–, and iodo–phthalocyaninato complexes of Al, Ga, and In were prepared and partially oxidized with nitrosyl salts.[11] High conductivities were observed; e.g., for $[(\mathrm{Ga(Pc)Cl})(\mathrm{BF_4})_{0.7}]$ $\sigma = 3.2\ \Omega^{-1}\ \mathrm{cm}^{-1}$. To provide some insight into the structural basis of this result, the crystal and molecular structure of Ga(Pc)Cl has been determined. The structure of Ga(Pc)Cl is also of interest because of its utility as a crystalline, photoconducting thin film capable of supporting significant positive and negative photopotentials.[12]

As a parallel effort the structure of Al(Pc)Cl has been determined, and the results of both investigations are reported below.

Experimental Section

Ga(Pc)Cl and Al(Pc)Cl were prepared by the method of Kenney.[9]

Ga(Pc)Cl. A purple prismatic crystal of Ga(Pc)Cl having approximate dimensions of 0.10 × 0.15 × 0.15 mm was obtained by sublimation at 570 °C and was mounted on a glass fiber in a random orientation.[13] Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.710 73 Å) on an Enraf-Nonius CAD4 computer-controlled κ-axis diffractometer equipped with a graphite crystal, incident-beam monochromator.[14] Crystal data and other data collection parameters are listed in Table I. A detailed description of the data collection, reduction, solution, and refinement may be found in the supplementary material.

Al(Pc)Cl. The structure of Al(Pc)Cl was determined in a similar manner,[13] with details being available in the supplementary material. A black, platelike crystal grown by sublimation at 500 °C having approximate dimensions of 0.20 × 0.20 × 0.05 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.543 184 Å). Table I lists data collection parameters.

Structure Solution and Refinement

Ga(Pc)Cl. The structure was solved by using the Patterson heavy-atom method, which revealed the position of the Ga atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o|-|F_c|)^2$ and the weight w was $4F_o^2/\sigma^2(F_o^2)$.

The standard deviation on intensities, $\sigma(F_o^2)$, is defined as

$$\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/L_p{}^2$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, L_p is the Lorentz–polarization factor. The parameter p is a factor of 0.050 introduced to downweight intense reflections.

Scattering factors were taken from Cromer and Waber.[14] Anomalous dispersion effects were included in F_c.[15] The values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[16] Only the 2250 reflections giving intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 444 variable parameters and converged (largest parameter shift was 0.04 times its esd) with unweighted and weighted agreement factors of

$$R_F = \sum||F_o| - |F_c||/\sum|F_o| = 0.036$$

$$R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.042$$

The standard deviation of an observation of unit weight was 1.06. The highest peak in the final difference Fourier had a height of 0.40 e/Å^3 with an estimated error based on ΔF[17] of 0.06. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends.

Final positional parameters for Ga(Pc)Cl are given in Table II. A listing of positional and thermal parameters and their esd's for all

---

(4) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1551.

(5) Nohr, R. S.; Wynne, K. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1210.

(6) Swift, D. R. Ph.D. Thesis, Case Western Reserve University, 1970.

(7) Kroenke, W. J.; Sutton, L. E.; Joyner, R. D.; Kenney, M. E. *Inorg. Chem.* **1963**, *2*, 1064.

(8) Esposito, J. N.; Lloyd, J. E.; Kenney, M. E. *Inorg. Chem.* **1966**, *5*, 1979.

(9) Linsky, J. P.; Paul, T. R.; Nohr, R. S.; Kenney, M. E. *Inorg. Chem.* **1980**, *19*, 3131.

(10) Brant, P.; Nohr, R. S.; Wynne, K. J.; Weber, D. *Mol. Cryst. Liq. Cryst.* **1982**, *81*, 255.

(11) Weber, D. C.; Brant, P.; Nohr, R. S.; Haupt, S. G.; Wynne, K. J. *J. Phys., Colloq. C-3, Suppl. No. 6 (Orsay, Fr.)* **1983**, *44*, 639.

(12) (a) Mezza, T. M.; Linkous, C. L.; Shepard, V. R.; Armstrong, N. R.; Nohr, R.; Kenney, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *124*, 311. (b) Linkous, C. L.; Klofta, T.; Armstrong, N. R. *J. Electrochem. Soc.*, in press. (c) Rieke, P. C.; Linkous, C. L.; Armstrong, N. R. *J. Phys. Chem.* **1984**, *88*, 1351. (d) Rieke, P. C.; Armstrong, N. R. *J. Am. Chem. Soc.* **1984**, *106*, 47. (e) Buttner, W.; Rieke, P.; Armstrong, N. R. *J. Electrochem. Soc.*, in press.

(13) Structure determinations were performed by the crystallographic staff of the Molecular Structure Corp. All calculations were performed on a PDP-11/45 computer using the Enraf-Nonius Structure Determination Package as well as private programs of the Molecular Structure Corp.

(14) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(15) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(16) Cromer, D. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(17) Cruickshank, D. W. J. *Acta Crystallogr.* **1949**, *2*, 154.

(18) Brown, D. S., Einstein, F. W. B., Tuck, D. G. *Inorg. Chem.* **1969**, *8*, 14.

(19) Restivo, R.; Palenik, G. J. *J. Chem. Soc., Dalton Trans.* **1972**, 341.

(20) Beran, G.; Carty, A. J.; Patel, H. A.; Palenik, G. J. *J. Chem. Soc. D* **1970**, 222.

Table II. Positional Parameters and Their Esd's for Ga(Pc)Cl[a]

	x	y	z
Ga	0.06053 (6)	0.18339 (5)	0.20496 (4)
Cl	−0.0585 (1)	0.3141 (1)	0.2937 (1)
N(1)	0.2672 (4)	0.2209 (3)	0.3129 (3)
N(2)	0.1486 (4)	0.2834 (3)	0.1248 (3)
N(3)	−0.1002 (4)	0.0938 (3)	0.0614 (3)
N(4)	0.0183 (4)	0.0305 (3)	0.2490 (3)
N(5)	0.3923 (4)	0.3880 (3)	0.2642 (3)
N(6)	−0.0600 (4)	0.2325 (3)	−0.0458 (3)
N(7)	−0.2227 (4)	−0.0780 (3)	0.1067 (3)
N(8)	0.2331 (4)	0.0749 (3)	0.4146 (3)
C(1)	0.3857 (5)	0.3174 (4)	0.3280 (4)
C(2)	0.2831 (5)	0.3723 (4)	0.1707 (4)
C(3)	0.2899 (5)	0.4482 (4)	0.0990 (4)
C(4)	0.3971 (6)	0.5508 (5)	0.1089 (4)
C(5)	0.3711 (6)	0.6047 (5)	0.0260 (4)
C(6)	0.2432 (6)	0.5605 (5)	−0.0658 (4)
C(7)	0.1347 (6)	0.4573 (5)	−0.0760 (4)
C(8)	0.1607 (5)	0.4027 (4)	0.0071 (4)
C(9)	0.0717 (5)	0.2989 (4)	0.0252 (4)
C(10)	−0.1399 (5)	0.1378 (4)	0.0291 (4)
C(11)	−0.2844 (5)	0.0648 (4)	−0.1060 (4)
C(12)	−0.3733 (6)	0.0739 (5)	−0.2051 (4)
C(13)	−0.5099 (6)	−0.0097 (5)	−0.2586 (4)
C(14)	−0.5571 (5)	−0.1022 (5)	−0.2150 (4)
C(15)	−0.4689 (5)	−0.1119 (4)	−0.1164 (4)
C(16)	−0.3305 (5)	−0.0259 (4)	−0.0621 (4)
C(17)	−0.2148 (5)	−0.0074 (4)	0.0424 (4)
C(18)	−0.1142 (5)	−0.0600 (4)	0.2015 (4)
C(19)	−0.1169 (5)	−0.1388 (4)	0.2718 (4)
C(20)	−0.2266 (6)	−0.2405 (5)	0.2618 (4)
C(21)	−0.1980 (6)	−0.2976 (5)	0.3426 (4)
C(22)	−0.0638 (6)	−0.2559 (5)	0.4306 (4)
C(23)	0.0453 (6)	−0.1542 (4)	0.4424 (4)
C(24)	0.0141 (5)	−0.0965 (4)	0.3605 (4)
C(25)	0.0998 (5)	0.0107 (4)	0.3443 (4)
C(26)	0.3109 (5)	0.1723 (4)	0.3998 (5)
C(27)	0.4591 (5)	0.2398 (4)	0.4725 (4)
C(28)	0.5506 (6)	0.2271 (5)	0.5699 (4)
C(29)	0.6894 (6)	0.3087 (5)	0.6217 (4)
C(30)	0.7377 (6)	0.3966 (5)	0.5760 (4)
C(31)	0.6488 (6)	0.4091 (4)	0.4789 (4)
C(32)	0.5080 (5)	0.3303 (4)	0.4284 (4)

[a] A listing of positional and thermal parameters and their esd's for all atoms, including the hydrogens, is available in Table II-S of the supplementary material.

atoms, including hydrogens, is available in supplementary Table II-S, as are values of observed and calculated structure factor amplitudes (Table IX-S).

Al(Pc)Cl. The structure was solved by direct methods. From 450 reflections (minimum E of 2.12) and 4275 relationships, a total of 64 phase sets were produced. A total of 40 atoms were located from an E map prepared from the phase set with probability statistics: absolute figure of merit = 1.06; residual = 10.27; ψ_0 = 2.960. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were not included in the calculations. The structure was refined as for Ga(Pc)Cl. The factor p introduced to downweight intense reflections was set to 0.060.

Only the 2165 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 443 variable parameters and converged (largest parameter shift was 0.90 times its esd) with unweighted and weighted agreement factors as defined above of $R_F = 0.137$ and $R_{wF} = 0.164$. The standard deviation of an observation of unit weight was 3.02. The highest peak in the final difference Fourier had a height of 1.01 e/Å^3 with an estimated error based on ΔF^{17} of 0.24. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends.

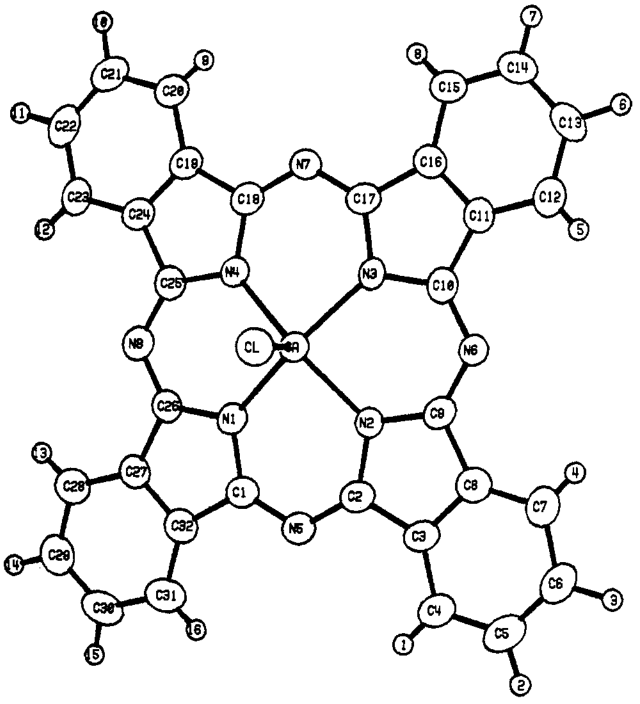


Figure 1. The Ga(Pc)Cl molecule with atoms labeled.

Table III. Interatomic Distances (Å) with Esd's[a]

	A. Ga(Pc)Cl		
Ga–Cl	2.217 (1)	N(4)–C(18)	1.378 (6)
Ga–N(1)	1.979 (4)	N(4)–C(25)	1.369 (6)
Ga–N(2)	1.981 (4)	N(5)–C(1)	1.309 (6)
Ga–N(3)	1.983 (4)	N(5)–C(2)	1.321 (6)
Ga–N(4)	1.988 (4)	N(6)–C(9)	1.316 (6)
N(1)–C(1)	1.386 (6)	N(6)–C(10)	1.328 (6)
N(1)–C(26)	1.381 (6)	N(7)–C(17)	1.315 (6)
N(2)–C(2)	1.383 (6)	N(7)–C(18)	1.325 (6)
N(2)–C(9)	1.381 (6)	N(8)–C(25)	1.316 (6)
N(3)–C(10)	1.385 (6)	N(8)–C(26)	1.331 (6)
N(3)–C(17)	1.386 (6)		
	B. Al(Pc)Cl		
Al(1)–Cl(1)	2.179 (6)	N(4)–C(25)	1.43 (2)
Al(1)–N(1)	1.961 (12)	N(4)–C(32)	1.41 (2)
Al(1)–N(2)	1.962 (13)	N(5)–C(1)	1.53 (2)
Al(1)–N(3)	1.966 (12)	N(5)–C(32)	1.28 (2)
Al(1)–N(4)	2.018 (12)	N(6)–C(8)	1.34 (2)
N(1)–C(1)	1.51 (2)	N(6)–C(9)	1.34 (2)
N(1)–C(8)	1.45 (2)	N(7)–C(16)	1.29 (2)
N(2)–C(9)	1.459 (15)	N(7)–C(17)	1.41 (2)
N(2)–C(16)	1.46 (2)	N(8)–C(24)	1.37 (2)
N(3)–C(17)	1.35 (2)	N(8)–C(25)	1.33 (2)
N(3)–C(24)	1.46 (2)		

[a] Distances to and within the peripheral phenyl groups may be found in the supplementary material.

Limited observed data were obtained as a result of disorder in the Al(Pc)Cl structure. One molecule was found to be translationally disordered and was refined as two half-molecules with some atoms weighted at 1.0, where they approximate positins for both half-molecules. The disorder gave high overall R values since not all atoms in the disordered molecule could be located. Due to the disorder and the limited data, many atoms also refined to somewhat incorrect positions. Refinement attempts in space group $P1$ did not resolve the disorder. The positional and thermal parameters and esd's for the 108 atoms used in the refinement are available as supplementary material in Table X-S, along with values of observed and calculated structure factor amplitudes (Table XV-S), temperature factor expressions (B's; Table XVI-S), and a stereoview of the disordered unit cell (Figure 4-S).

Discussion

Ga(Pc)Cl. The crystal consists of discrete chloro(phthalocyaninato)gallium(III) molecules of approximately D_{4h} symmetry as shown in Figure 1, which also indicates the numbering scheme.

Important bond distances and angles for Ga(Pc)Cl are contained in Tables III and IV, respectively, while a complete set of data is available as supplementary material (Tables III-S and IV-S). Distances of selected atoms from a least-squares

Table IV. Interatomic Angles (deg) with Esd's

	A. Ga(Pc)Cl[a]		
Cl–Ga–N(1)	103.1 (1)	Ga–N(3)–C(17)	125.8 (3)
Cl–Ga–N(2)	102.8 (1)	C(10)–N(3)–C(17)	106.8 (4)
Cl–Ga–N(3)	102.4 (1)	Ga–N(4)–C(18)	125.2 (3)
Cl–Ga–N(4)	102.9 (1)	Ga–N(4)–C(25)	125.5 (3)
N(1)–Ga–N(2)	87.3 (2)	C(18)–N(4)–C(25)	108.1 (4)
N(1)–Ga–N(3)	154.5 (2)	C(1)–N(5)–C(2)	122.9 (4)
N(1)–Ga–N(4)	87.3 (2)	C(9)–N(6)–C(10)	122.8 (4)
N(2)–Ga–N(3)	87.1 (2)	C(17)–N(7)–C(18)	122.2 (4)
N(2)–Ga–N(4)	154.3 (2)	C(25)–N(8)–C(26)	122.5 (4)
N(3)–Ga–N(4)	87.0 (2)	N(1)–C(1)–N(5)	127.3 (5)
Ga–N(1)–C(1)	125.8 (3)	N(1)–C(26)–N(8)	126.7 (4)
Ga–N(1)–C(26)	126.1 (3)	N(2)–C(2)–N(5)	127.4 (5)
C(1)–N(1)–C(26)	107.0 (4)	N(2)–C(9)–N(6)	127.4 (5)
Ga–N(2)–C(2)	125.1 (3)	N(3)–C(10)–N(6)	126.8 (4)
Ga–N(2)–C(9)	125.7 (3)	N(3)–C(17)–N(7)	127.3 (5)
C(2)–N(2)–C(9)	107.5 (4)	N(4)–C(25)–N(8)	128.2 (5)
Ga–N(3)–C(10)	125.8 (3)	N(4)–C(18)–N(7)	128.0 (5)
	B. Al(Pc)Cl[b]		
Cl(1)–Al(1)–N(1)	102.7 (4)	N(1)–Al(1)–N(3)	154.7 (6)
Cl(1)–Al(1)–N(2)	100.7 (4)	N(1)–Al(1)–N(4)	88.0 (5)
Cl(1)–Al(1)–N(3)	102.4 (4)	N(2)–Al(1)–N(3)	84.9 (5)
Cl(1)–Al(1)–N(4)	102.1 (4)	N(2)–Al(1)–N(4)	157.2 (5)
N(1)–Al(1)–N(2)	86.8 (5)	N(3)–Al(1)–N(4)	90.4 (5)

[a] Angles within the peripheral phenyl groups may be found in the supplementary material. [b] Angles within the peripheral phenyl groups and the macrocyclic ring are of decreased accuracy and may be found in the supplementary material.

Table V. Distances from the Least-Squares Plane Formed by Coordinated Nitrogens N(1)–N(4)[a]

Ga(Pc)Cl		Al(Pc)Cl	
	Atoms in Plane		
N(1)	−0.002 (4)	N(1)	−0.016 (15)
N(2)	0.002 (4)	N(2)	0.019 (16)
N(3)	−0.002 (4)	N(3)	−0.017 (16)
N(4)	0.002 (4)	N(4)	0.015 (15)
	Other Atoms		
Ga	−0.439 (1)	Al(1)	0.410 (6)
Cl	−2.657 (1)	Cl(1)	2.588 (5)
N(5)	0.044 (4)	N(5)	−0.031 (16)
N(6)	0.041 (4)	N(6)	−0.093 (19)
N(7)	0.022 (4)	N(7)	−0.147 (16)
N(8)	0.079 (4)	N(8)	0.012 (17)
C(1)	0.046 (5)	C(1)	0.097 (22)
C(9)	0.026 (5)	C(8)	−0.021 (19)
C(10)	0.024 (5)	C(9)	−0.059 (17)
C(17)	0.023 (5)	C(16)	−0.118 (19)
C(18)	0.019 (5)	C(17)	−0.066 (18)
C(25)	0.064 (5)	C(24)	−0.129 (25)
C(26)	0.052 (5)	C(25)	0.101 (19)
		C(32)	−0.062 (20)

[a] Constants and orthogonalized coordinates for the planes defined above, as well as a number of other least-squares planes, are available in the supplementary material.

plane through the coordinated nitrogen atoms are shown in Table V. Supplementary Table V-S contains a listing of 10 least-squares planes through various sets of atoms.

The coordination about Ga is square pyramidal, with four Pc nitrogen atoms (N(1)–N(4)) at the basal apices and Cl occupying the remaining apex. Gallium is centered 0.439 (1) Å above the plane formed by the four coordinated nitrogen atoms (Table V). The virtually identical values for the Cl–Ga–N and cis and trans N–Ga–N bond angles demonstrates the regularity of the coordination geometry. Although square-pyramidal geometry is known for indium in the related In(TPP)Cl[21] (TPP = 5,10,15,20-tetraphenylporphinato dianion), this is the first time it has been observed for gallium. The position of Ga above the Pc plane results from a combination of steric and electronic effects not operative in Ga(Pc)F, where Ga is coplanar with the Pc ring and octahedral geometry results from F bridging.[5]

The Ga–Cl and Ga–N bond distances in Ga(Pc)Cl are unexceptional. The Ga–Cl distance of 2.217 (1) Å may be compared with 2.265 (1) Å for octahedral $[GaCl_2(bpy)_2]^+$ and 2.171 (2) and 2.162 (2) Å for tetrahedral $[GaCl_4]^-$ in $[GaCl_2(bpy)_2][GaCl_4]$.[19] Three different Ga–Cl bond lengths, 2.235 (3), 2.329 (3), and 2.403 (2) Å, were found for octahedral $GaCl_3$(terpy).[20] From these limited data a correlation of increasing bond lengths with increasing coordination number is noted. The Ga–N bond lengths for Ga(Pc)Cl, which range from 1.979 (4) to 1.988 (4) Å, are slightly longer than those for Ga(Pc)F (1.969 (2) and 1.970 (2) Å).[5] This lengthening stems from the out-of-plane position of Ga in Ga(Pc)Cl. The Ga–N bond lengths observed here are shorter than those for complexes containing nonmacrocyclic ligands (2.1–2.2 Å).[19–21]

The maximum distance of any atom in the Pc ring from the least-squares plane defined by the coordinated nitrogen atoms N(1)–N(4) is 0.079 (4) Å for N(8). The Pc ring is therefore essentially planar, as found in the free acid[22,23] and many metal complexes.[24–26]

Intermolecular contacts (Table VII-S) are for the most part normal and approximate those expected on the basis of the sum of van der Waals radii.[27] However, compared to the van der Waals Cl–H distance of 3.0 Å,[27] one shortened Cl–H contact to a β-hydrogen in each 2-iminoisoindolinato moiety is observed. The Cl–H(3) contact is closest (2.75 (5) Å), followed by others to H(7), H(11), and H(15), which are only slightly shortened (2.85 (5)–2.92 (5) Å). This weak hydrogen bonding is expected to result in slightly longer C–H bonds. While the longest C–H bond (C(6)–H(3), 1.04 (5) Å) could be a consequence of Cl–H(3) hydrogen bonding, hydrogen-bonding effects are effectively masked by an overall trend for longer C–H$_\beta$ bonds (0.94 (5)–1.04 (5) Å) than C–H$_\alpha$ bonds (0.83 (5)–0.95 (4) Å). Thus, the remaining hydrogen-bonded C–H$_\beta$ distances (to H(7), H(11), and H(15); 0.94 (5)–0.96 (5) Å) are in the range of non-hydrogen-bonded C–H$_\beta$ distances (0.96 (7)–1.02 (5) Å).

Figure 2 shows a stereoview of the unit cell and reveals the molecular packing. Along the *c* axis are parallel stacks of "slipped disks", which form layers in the *a*–*c* plane. The layers are interleaved along the *b* axis, with the direction of the Ga–Cl bond reversing by 180° in going from layer to layer. The closest intermolecular ring spacing (3.34 Å)[28] occurs through this interleaving between layers along the *b* axis. This distance may be visualized by inspection of Figure 2. There is one molecule to the left of center of the unit cell and another related to the first by an inversion center down the *b* axis. The 3.34 Å interplanar distance is that from a least-squares plane defined by N(1)–N(4) on the first molecule, to the adjacent aromatic carbon atoms in the second molecule. The interplanar ring spacing of 3.34 Å is close to the van der Waals value of 3.4 Å[27] but considerably shorter than the 3.872 (2) Å distance observed for the linear, F-bridged, cofacial array in Ga(Pc)F. The interplanar ring spacing for Ga(Pc)Cl is

---

[21] Ball, R. G.; Lee, K. M.; Marshall, A. G.; Trotter, J. *Inorg. Chem.* **1980**, *19*, 1463.

[22] Robertson, J. M. *J. Chem. Soc.* **1936**, 1195.

[23] Hoskins, B. F.; Mason, S. A.; White, J. C. B. *J. Chem. Soc. D* **1969**, 554.

[24] Robertson, J. M.; Woodward, I. *J. Chem. Soc.* **1937**, 219.

[25] Brown, C. J. *J. Chem. Soc. A* **1968**, 2488.

[26] Brown, C. J. *J. Chem. Soc. A* **1968**, 2494.

[27] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

[28] The intermolecular ring spacing was determined by calculating the distance from the least-squares plane (N(1)–N(4)) of one molecule to the corresponding plane in an adjacent molecule along the *b* axis (Table VI-S).

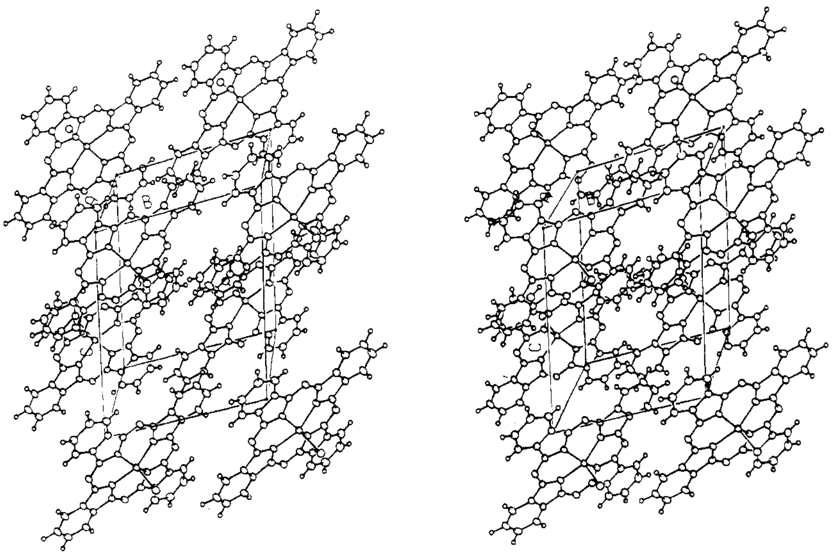


Figure 2. Stereoscopic view of the Ga(Pc)Cl unit cell.

between the values observed for CuPc (3.28 Å), where partial, intermolecular, Cu–N coordination results in a short spacing,[26] and PtPc (3.57 Å), which has a longer intermolecular spacing but a large central atom.[25]

Al(Pc)Cl. The structure consists of two unique, discrete chloro(phthalocyaninato)aluminum(III) molecules. One molecule was found to be translationally disordered and was refined as two half-molecules with some atoms weighted at 1.0, where they approximate positions for both half-molecules. The disorder gave high overall *R* values since not all atoms in the disordered molecule could be located. Due to the disorder and the limited data many atoms also refined to somewhat incorrect positions, and the discussion below concerns only the Al(Pc)Cl molecule containing Al(1).

Figure 3 shows the Al(Pc)Cl molecule containing Al(1) and the numbering scheme. Important bond distances and angles for Al(1)(Pc)Cl are contained in Tables III and IV, respectively, while a complete set of data for Al(1)- and Al(2)–Al(3)-containing molecules is available as supplementary material (Tables XI-S and XII-S). Table V shows distances relative to a least-squares plane including N(1)–N(4), while a complete listing of data for six least-squares planes may be found in supplementary Table XIII-S.

As for the Ga(Pc)Cl structure, the coordination geometry about Al in Al(Pc)Cl is square pyramidal with Al being 0.410 (6) Å above the least-squares plane formed by N(1)–N(4) (Table IV). The Pc macrocycle is essentially planar, with some minor buckling. Structures containing pentacoordinate aluminum are rare, and those that are known, including bis(2-methyl-8-quinolinlato)aluminum(III)[29] and bis(trimethylamine)–alane,[30] have trigonal-bipyramidal geometry. The presence of the rigid Pc macrocycle has resulted in the first example of square-pyramidal geometry for Al(III).

The apical Al(1)–Cl bond distance is 2.179 (6) Å. Comparison with the terminal Al–Cl distances found for tetrahedrally coordinated Al in $[AlCl_4]^-$ (2.121 (2)–2.134 (2) Å),[31] $[AlCl_2(CH_3)_2N]^2$ (2.088 (3), 2.123 (3) Å),[32] $S_2N_2{\cdot}2AlCl_3$ (2.083 (3)–2.124 (3) Å),[33] and $W(\eta^2\text{-}HC{\equiv}COAlCl_3)(CO)[P(CH_3)]_3Cl$ (2.117 (2)–2.122 (2) Å)[34] and for octahedrally coordinated Al in $[AlCl_2(py)_4]^+$ (2.278 (3), 2.280 (3) Å)[31] reveals an increase in Al–Cl bond distance with coordination number.

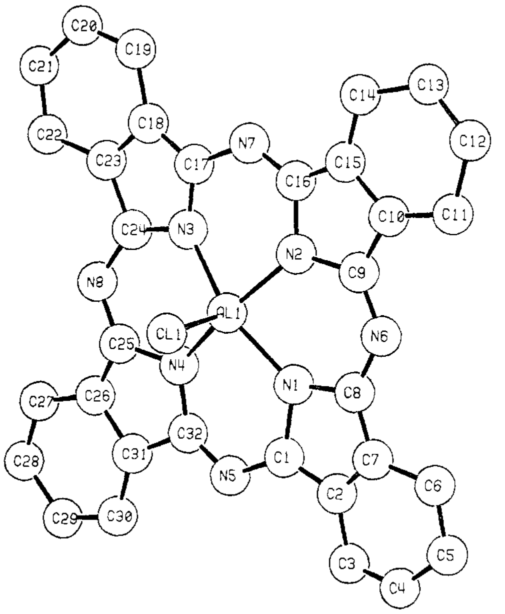


Figure 3. The Al(Pc)Cl molecule with atoms labeled.

The Al–N distances of 1.961–2.018 (12) Å follow a similar pattern, being longer than four-coordinate Al–N bonds (1.91–1.96 Å)[32,33] but shorter than six-coordinate Al–N bonds (2.06–2.08 Å).[31] The trigonal-bipyramidal structures noted above[29,30] provide exceptions to this trend, having apical Al–N bonds equal to or longer than those found in six-coordinate structures.

Conclusion

An important criterion for charge transport in an organic solid is the arrangement of molecules in close spacial proximity. In the pristine state this condition is met in Ga(Pc)Cl by an interleaved "slipped disk" structure that provides intermolecular contact (3.34 Å) approximating the van der Waals value (3.4 Å). This feature of the structure is interesting, as the steric encumbrance caused by the Ga–Cl group was expected to cause an increased interplanar spacing similar to that found for PtPc (3.57 Å).[26]

---

(29) Kushi, Y.; Fernando, Q. *J. Chem. Soc. D* **1969**, 555.

(30) Heitsch, C. W.; Nordman, C. E.; Parry, R. W. *Inorg. Chem.* **1963**, *2*, 508.

(31) Pullmann, P.; Hensen, K.; Bats, J. W. *Z. Naturforsch., B.: Inorg. Chem. Org. Chem.* **1982**, *37B*, 1312.

(32) Ahmed, A.; Schwarz, W.; Hess, H. *Acta Crystallogr., Sect. B* **1977**, *B33*, 3574.

(33) Thewalt, U.; Burger, M. *Angew. Chem.* **1982**, *94*, 646.

(34) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1983**, *22*, 41.

While the structures of the conducting, partially oxidized materials[11] derived from Ga(Pc)Cl are not known, the intermolecular contact in the pristine material is probably closely related to those in the doped materials and rationalizes the high conductivity observed.

Finally, in view of the similarity of the Pc and TPP macrocyclic ligands and the biological importance of the latter,[35] it is useful to compare the displacement above the macrocyclic ring for structures known in group 3. The most closely related structures (with displacements) to Al(Pc)Cl (0.410 (6) Å) and Ga(Pc)Cl (0.439 (1) Å) are those for In(TPP)Cl[21] (0.61 Å) and Tl(TPP)Cl[36] (0.74 Å). Depsite the difference in the macrocyclic ligands, the trend toward increased displacement with increased size is apparent.

Acknowledgment. The author wrote this paper while a Visiting Scholar in the Department of Chemical Engineering, Stanford University, and a Visiting Scientist at the IBM Research Laboratory, San Jose, and he gratefully acknowledges the generous hospitality provided. The author thanks M. Kenney, Case Western Reserve University, and J. M. Troup and M. W. Extine, Molecular Structure Corp., for stimulating discussions, R. Nohr for the preparation of samples of Ga(Pc)Cl and Al(Pc)Cl, and the Office of Naval Research for financial support.

Registry No. Ga(Pc)Cl, 19717-79-4; Al(Pc)Cl, 14154-42-8.

Supplementary Material Available: A detailed experimental section, listings of positional and thermal parameters and esd's (Tables II-S (Ga) and X-S (Al)), bond distances and angles (Tables III-S–V-S (Ga) and XI-S and XII-S (Al)), least-squares planes (Tables VI-S (Ga) and XIII-S (Al)), intermolecular contacts (Tables VII-S (Ga) and XIV-S (Al)), temperature factors (Table VIII-S (Ga) and XVI-S (Al)), and observed and calculated structure factor amplitudes (Tables IX-S (Ga) and XV-S (Al)), and a stereoview of the unit cell of Al(Pc)Cl (Figure 4-S) (95 pages). Ordering information is given on any current masthead page.

---

(35) Perutz, M. F. *Sci. Am.* **1978**, *239*, 92.

(36) Henrick, K.; Matthews, R. W.; Tasker, P. A. *Inorg. Chem.* **1977**, *16*, 3293.

Contribution from the Department of Chemistry,
University of Minnesota, Minneapolis, Minnesota 55455

Synthesis and Structural Characterization of Rhodium(I) and Iridium(I) Complexes of the Asymmetric Tetradentate PPNN Ligand 2,2′-Bis[[*o*-(diphenylphosphino)benzylidene]amino]-6,6′-dimethylbiphenyl

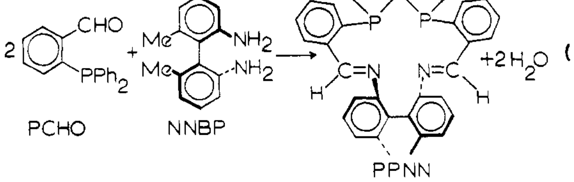
TRICIA L. MARXEN, BRIAN J. JOHNSON, PER V. NILSSON, and LOUIS H. PIGNOLET*

Received March 26, 1984

The new asymmetric ligand 2,2′-bis[[*o*-(diphenylphosphino)benzylidene]amino]-6,6′-dimethylbiphenyl, PPNN, was synthesized by the Schiff base reaction of *o*-(diphenylphosphino)benzaldehyde with 2,2′-dimethyl-6,6′-diaminobiphenyl. The *d* and *l* optical isomers of PPNN were also synthesized by the above reaction using the resolved enantiomers of 2,2′-dimethyl-6,6′-diaminobiphenyl. Specific and molecular rotations ($[\alpha]^{25}{}_D$, $[M]^{25}{}_D$ ($CHCl_3$)) for *d*-PPNN and *l*-PPNN were +198, 1493° and −193, −1457°, respectively. Rh(I) and Ir(I) complexes of PPNN were synthesized by the reactions of PPNN with $[Rh(1,5\text{-cyclooctadiene})Cl]_2$ and $Ir(PPh_3)_2(N_2)Cl$, respectively, using CH_2Cl_2 as solvent. Both complexes were isolated in good yield as BPh_4 salts. The single-crystal X-ray structures of racemic $[Rh(PPNN)]BPh_4$ and $[Ir(PPNN)]BPh_4$ were determined. The two compounds are essentially isostructural. Crystal parameters for Rh: $P\bar{1}$, a = 13.473 (2) Å, b = 13.506 (2) Å, c = 17.424 (3) Å, α = 100.20 (1)°, β = 98.17 (1)°, γ = 91.41 (1)°, Z = 2, R (R_w) = 0.034 (0.047) for 6168 observations [$F_o^2 \geq 3\sigma(F_o^2)$]. Crystal parameters for Ir: $P\bar{1}$, a = 13.48 (1) Å, b = 13.551 (3) Å, c = 17.438 (8) Å, α = 100.28 (3)°, β = 98.00 (5)°, γ = 91.38 (4)°, Z = 2, R (R_w) = 0.055 (0.064) for 4483 observations [$F_o^2 \geq 2\sigma(F_o^2)$]. Both compounds have approximately square-planar P_2N_2 coordination core geometries with average Rh–P and Ir–P distances of 2.222 (1) and 2.244 (3) Å and with average Rh–N and Ir–N distances of 2.106 (3) and 2.09 (1) Å, respectively. The PPNN ligand is tetradentate in both complexes, and the twisted substituted biphenyl group imposes an asymmetry on the entire complex. The reactions of these complexes with CO and H_2 have been studied.

Introduction

In recent years there has been intense interest in the design and use of chiral transition-metal complexes for asymmetric catalysis.[1-5] The vast majority of these complexes have involved the use of chiral bidentate phosphines as ligands and Rh(I) as the metal. In very few cases have complex tetradentate chiral ligands been employed although such ligands should provide more stereochemically rigid complexes.[6] Higher optical yields may result from catalysts that use such ligands because a rigid arrangement of bulky substituents around the metal center should prevent significant changes in the asymmetric environment during the course of the catalytic cycle. In this paper we report the synthesis of the new tetradentate chiral ligand 2,2′-bis[[*o*-(diphenylphosphino)benzylidene]amino]-6,6′-dimethylbiphenyl, PPNN, from the reaction of *o*-(diphenylphosphino)benzaldehyde with (*R*)- or (*S*)-2,2′-dimethyl-6,6′-diaminobiphenyl as shown in eq 1.



(1)

The rhodium(I) and iridium(I) complexes, $[Rh(PPNN)]BPh_4$ (**1**) and $[Ir(PPNN)]BPh_4$ (**2**), have been synthesized and characterized. Single-crystal X-ray diffraction analyses were carried out on both racemic complexes in order to determine their stereochemistry and because the reactivity of the com-

---

(1) Brown, J. M.; Chaloner, P. A. In "Homogeneous Catalysis with Metal Phosphine Complexes"; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; Chapter 4, p 137.

(2) Oliver, J. D.; Riley, D. P. *Organometallics* **1983**, *2*, 1032.

(3) Halpern, J. *Science* (*Washington, D.C.*) **1982**, *217*, 401 and references therein.

(4) MacNeil, P. R.; Roberts, N. K.; Bosnich, B. *J. Am. Chem. Soc.* **1981**, *103*, 2273.

(5) Vineyard, B. D.; Knowles, W. S.; Sabacky, M. J.; Bachman, G. L.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5946.

(6) Brunner, H.; Rahman, A. F. M. M. *Chem. Ber.* **1984**, *117*, 710.

0020-1669/84/1323-4663$01.50/0 © 1984 American Chemical Society