Inorg. Chem. **1988**, *27*, 1287–1291

Contribution from the Department of Chemistry, Institut Le Bel,[1]
Universite Louis Pasteur, 67070 Strasbourg, France

Synthesis, Structure, and Spectroscopic Properties of the Reduced and Reduced Protonated Forms of Lutetium Diphthalocyanine

Mehdi Moussavi, Andrē De Cian, Jean Fischer, and Raymond Weiss*

Received June 10, 1987

The synthesis of the bis(phthalocyaninato)lutetium(III) derivatives [LuPc$_2$][Na$\subset$18c.6] (**1**, $C_{76}H_{56}N_{16}NaLu$; 18c.6 = 18-crown-6), [LuPc$_2$][NBu$_4$] (**2**, $C_{80}H_{68}N_{17}Lu$), and [LuHPc$_2$] (**3**, $C_{64}H_{33}N_{16}Lu$) is reported. These compounds were characterized by electronic and ^{1}H NMR spectroscopy. The mass spectrum of [LuHPc$_2$] (**3**) shows a difference of one mass unit from that of [LuPc$_2$]. **2** crystallizes with two DMF molecules of solvation in the triclinic system, with a = 22.390 (8) Å, b = 15.371 (6) Å, c = 11.590 (4) Å, α = 109.35 (2)°, β = 95.33 (2)°, γ = 92.54 (2)°, Z = 2, and space group $P\bar{1}$. **3** belongs to the orthorhombic system, with a = 10.567 (3) Å, b = 50.683 (9) Å, c = 8.849 (3) Å, Z = 4, and space group $P2_12_12_1$. The crystals of **2** contain sandwich-type anions [LuPc$_2$]$^-$ in which the lutetium is, as in [LuPc$_2$], eightfold coordinated by the isoindole nitrogens (N$_{iso}$) of two staggered phthalocyanine rings. The mean value of the Lu–N$_{iso}$ bond distances with one ring is 2.374 (2) Å whereas the average value of the Lu–N$_{iso}$ bond lengths with the other ring is 2.392 (2) Å. A sandwich-type structure is also present in the [LuHPc$_2$] molecules (**3**). The mean value of the Lu–N$_{iso}$ bond lengths with one ring is 2.366 (4) Å and with the other ring is 2.376 (4) Å. The acidic hydrogen of [LuHPc$_2$] could not be located. It is most probably linked to a methine nitrogen and disordered over both rings.

Introduction

The lutetium diphthalocyanine complexes have generated a great deal of interest recently, mainly due to their attractive electrochromic properties.[2-4] We already have shown that the green form of [LuPc$_2$] has a sandwich structure in which one phthalocyanine ring is oxidized in a radical cation Pc(−1).[5] So far, it is not clear whether the unpaired spin present in this complex is localized on one phthalocyanine ring or delocalized over both rings. However, the intrinsic semiconducting properties[6] found recently for this green derivative are probably more in favor of a delocalized system. We have now isolated and studied the blue reduced, protonated form [LuHPc$_2$][7] and several compounds containing the reduced form [LuPc$_2$]$^-$ of the green species [LuPc$_2$]. In this paper we report the synthesis and characterization of these complexes.

Experimental Section

Materials. Dicyanobenzene, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),[8] and chlorobenzene were obtained from EGA; lutetium (III) acetate hydrate was obtained from Johnson-Mathey Co., tetrabutylammonium perchlorate, hydrazine hydrate and sodium hydride (55%–60% dispersion in oil) were obtained from Fluka, and dimethylformamide was obtained from Rhone-Poulenc. The green form of lutetium diphthalocyanine [LuPc$_2$] was prepared by using Lu(OAc)$_3$(H$_2$O)$_x$ following published procedures.[5]

Methods. Spectra were obtained on the following instruments: electronic spectra on a Cary 210 instrument; mass spectra on a Varian MAT 311A apparatus with data system SS 100MS (direct insertion, ion source at 250 °C, field ion desorption mode) at the Institut für Anorganische Chemie Technische Hochschule Darmstadt, FRG; ^{1}H NMR spectra on a Bruker FY200 instrument.

Synthesis of [LuPc$_2$][Na$\subset$18c] (1). To [LuPc$_2$] (80 mg, 6.7 × 10^{-2} mmol) in chlorobenzene (50 mL) were added NaH (dispersion in oil) (880 mg, 18 mmol) and 18-crown-6 (80 mg, 0.31 mmol) in distilled and degassed chlorobenzene (50 mL). The mixture thus obtained was stirred for 15 h. The Turkish blue of the starting solution slowly turned dark blue. Filtration under argon, followed by concentration under vacuum and addition of pentane, yielded blue crystals with red reflections of [LuPc$_2$][Na$\subset$18c.6] (**1**).

Table I. Crystallographic Data

formula	$C_{86}H_{82}N_{19}O_2Lu$	$C_{64}H_{33}N_{16}Lu$
mol wt	1588.7	1200.0
cryst syst	triclinic	orthorhombic
a, Å	22.390 (8)	10.567 (3)
b, Å	15.371 (6)	50.683 (9)
c, Å	11.590 (4)	8.849 (3)
α, deg	109.35 (2)	90
β, deg	95.33 (2)	90
γ, deg	92.54 (2)	90
V, Å^3	3735	4739
Z	2	4
D_{calcd}, g/cm^3	1.41	1.68
μ, cm^{-1}	29.56	44.08
space group	$P\bar{1}$	$P2_12_12_1$
radiation	Cu(graphite monochromated)	
cryst size, mm	0.35 × 0.28 × 0.23	0.22 × 0.12 × 0.04
scan mode	flying step scan	
scan angle, deg	0.90 + 0.14 tan θ	0.95 + 0.14 tan θ
step width, deg	0.05	0.05
scan speed, deg s^{-1}	0.024	0.024
θ limits, deg	3/57	3/57
octants	$\pm h, \pm k, l$	$h, k, \pm l$
no. of data measd	9909	7307
R_{int} (I)		0.026
no. of data with ($I > 3\sigma(I)$)	9327	3277
abs$_{min}$/abs$_{max}$	0.82/1.31	0.79/1.24
R_1	0.031	0.026
R_2	0.057	0.054
ERRFIT	1.36	1.30

Anal. Calcd[9] for $C_{76}H_{56}N_{16}NaLu$ (**1**): C, 61.37; H, 3.77; N, 15.07. Found: C, 61.50; H, 3.69; N, 14.99. Visible spectrum (chlorobenzene) λ_{max} (log ϵ): 700 (3.46), 680 (sh), 618 (4.86), 338 (4.90) nm. ^{1}H NMR (deuteriated DMSO): 8.9 (m, 16 H), 8.2 (m, 16 H), 3.5 (s, 24 H) ppm.

Synthesis of [LuPc$_2$][NBu$_4$] (2). Tetrabutylammonium perchlorate (TBAP) (8.5 g, 25 mmol) was added to a solution (50 mL) containing dimethylformamide (DMF) (49.5 mL) and hydrazine hydrate $N_2H_4 \cdot H_2O$ (0.5 mL). To this solution was added green LuPc$_2$ (50 mg, 4.1 × 10^{-2} mmol). This mixture was stirred for 4 h. The blue-green of the starting solution rapidly became dark blue. Filtration and rapid evaporation under vacuum yielded a microcrystalline powder of composition [LuPc$_2$][NBu$_4$] (**2**).

---

(1) Laboratoire de chimie des Mētaux de Transition et de Catalyse associē au CNRS (UA 424), Institut Le Bel, Universitē Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France.

(2) Corker, G. A.; Grant, B. B.; Clecak, N. J. *J. Electrochem. Soc.* **1979**, *126*, 1339.

(3) Kasuga, K.; Tsutsui, M. *Coord. Chem. Rev.* **1980**, *32*, 67.

(4) Collin, G. C. S.; Schiffrin, D. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *139*, 335.

(5) De Cian, A.; Moussavi, M.; Fischer, J.; Weiss, R. *Inorg. Chem.* **1985**, *24*, 3162.

(6) Maitrot, M.; Guillaud, G.; Boudjema, B.; Andrē, J. J.; Streclecka, H.; Simon, J.; Even, R. *Chem. Phys. Lett.* **1987**, *133*, 59.

(7) Moskalev, P. N.; Kirin, I. S. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1972**, *46*, 1019.

(8) Diazabicyclo[5.4.0]undec-7-ene (DBU) has been used for the preparation of various metallophthalocyanines; see: Tomoda, H.; Saito, S.; Shiraushi, S. *Chem. Lett.* **1983**, 313.

(9) Centre de Microanalyse, Dēpartement de Chimie, Universitē Louis Pasteur, Strasbourg, France.

0020-1669/88/1327-1287$01.50/0

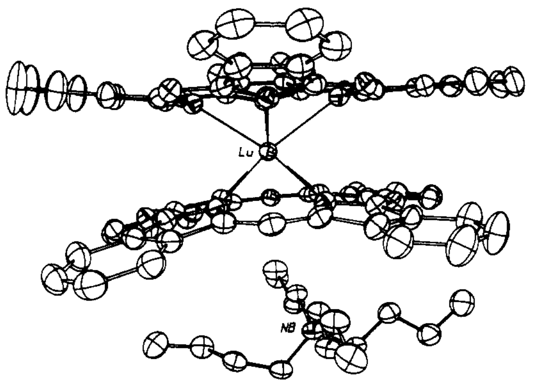

Figure 1. ORTEP plot of the [LuPc$_2$]$^-$[NBu$_4$]$^+$ ion pair as found in **2**. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

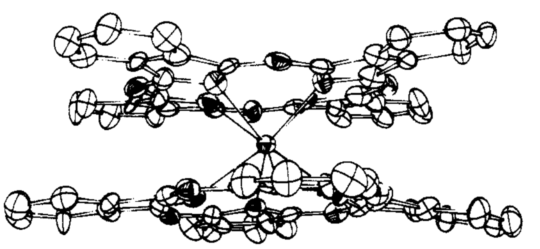

Figure 2. ORTEP plot of [LuHPc$_2$] as found in **3**. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted.

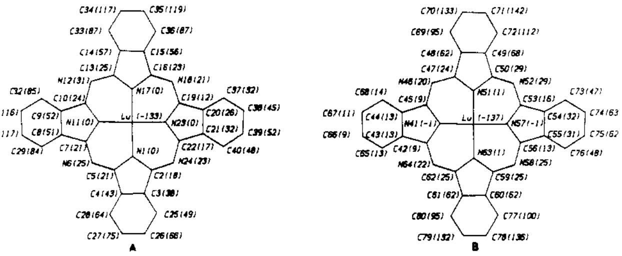

Figure 3. Stick-bond model projections of rings A and B on the 4N$_{iso}$ mean planes with the labeling scheme used for **2**. Numbers in parentheses give the deviations (in 0.01 Å units) of individual atoms with respect to the mean planes.

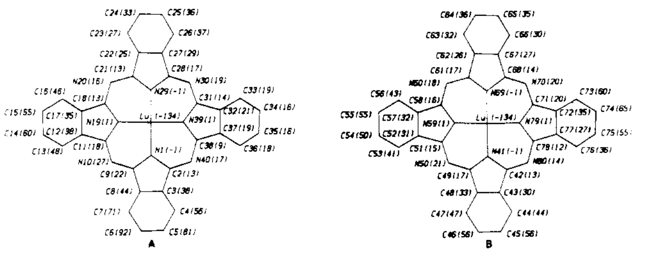

Figure 4. Stick-bond model projections of rings A and B on the 4N$_{iso}$ mean planes with the labeling scheme used for **3**. Numbers in parentheses give the deviation (in 0.01 Å units) of individual atoms with respect to the mean planes.

Anal. Calcd for $C_{80}H_{68}N_{17}Lu$ (**2**): C, 66.62; H, 4.71; N, 16.51. Found: C, 66.06; H, 4.60; N, 16.17. Visible spectrum (chlorobenzene) λ_{max} (log ϵ): 695 (3.42), 616 (4.80), 328 (4.90) nm. ^{1}H NMR (deuteriated DMSO): 8.3 (m, 16 H), 9 (m, 16 H); signals due to NBu$_4$$^+$ were not well resolved. Slow evaporation in air of the blue DMF solution led to blue crystals containing two DMF molecules of solvation, [LuPc$_2$]-[NBu$_4$]·2DMF (vide infra).

Synthesis of [LuHPc$_2$] (3). A solution of [LuPc$_2$][Na$\subset$18c.6] was prepared as indicated above using only 20 mg (7.5 × 10^{-2} mmol) of 18-crown-6 and 100 mg (20 mmol) of sodium hydride (dispersion in oil) for 80 mg (6.7 × 10^{-2} mmol) of green [LuPc$_2$]. After filtration, 10 mL of methyl alcohol was added to 50 mL of the solution. Concentration under vacuum and subsequent addition of pentane led to blue crystals of composition [LuHPc$_2$] (**3**).

Anal. Calcd for $C_{64}H_{33}N_{16}Lu$ (**3**): C, 64.00; H, 2.75; N, 18.67. Found: C, 63.84; H, 2.73; N, 18.64. Visible spectrum (chlorobenzene) λ_{max} (log ϵ): 694 (3.95), 614 (4.82) 324 (4.85) nm. ^{1}H NMR (deuteriated DMSO): 7.4 (m, 16 H), 8.1 (m, 16 H), 9.0 (s, 1 H). The signal located at 9 ppm does however not disappear by addition of a base such as triethylamine. Thus, the assignment of this signal to the acidic hydrogen is uncertain. Mass spectrum (field ion desorption mode) run directly after that of [LuPc$_2$]: M_r(obsd) for **3**, 1200; M_r(obsd) for [^{175}LuHPc$_2$], 1201; M_r(obsd) for [LuPc$_2$], 1999, M_r(calcd) for [^{175}LuPc$_2$], 1200.

X-ray Crystallography. For both compounds, the diffraction data were collected at −100 °C on a Philips PW1100/16 automatic diffractometer equipped with a locally built low-temperature device. Both parallelepipedic crystals were cut out from a cluster of crystals, glued at the end of a glass wire, and mounted on a goniometer head without any rotation arc. Data collection parameters and crystal data are displayed in Table I. Orientation matrices and unit cell parameters were obtained from 25 machine-centered reflections. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. No equivalent reflections were recorded for **2**. The data collection sets were transferred to a PDP11/60 computer, and for all computations the Enraf-Nonius SPD/PDP[10] package was used, with the exception of a local data-reduction program.

Three standard reflections measured every hour revealed no decay over the duration of the data collections. The raw step-scan data were converted to intensities by using the Lehmann-Larsen method[11] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the empirical method of Walker and Stuart[12] since face indexation was not possible under the cold gas stream.

The structure of **2** was solved by Patterson techniques in space group $P\bar{1}$ assumed on the basis of an Nz cumulative test on $|F_o|$. **3** is isomorphous with the green form of GdPc$_2$;[13] therefore, the coordinates of this structure were used as a starting point. After refinements of the heavy atoms, difference Fourier maps revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. Hydrogen atoms were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such that $B(H) = 1 + B_{eq}(C)$ Å^2. No hydrogen atom parameter was allowed to vary during full-matrix least-squares refinements minimizing $\sum w(|F_o| - |F_c|)^2$. The absolute structure was determined for **3**: the two enantiomers differ by 0.014 and 0.018 on $R_1(F)$ and $R_2(F)$ respectively. The unit weight observation given in Table I is for $p = 0.08$ in $\sigma^2(F^2) = \sigma^2(\text{counts}) + (pI)^2$. The final difference map revealed no significative maxima. The scattering factors and anomalous dispersion coefficients were taken respectively from ref 14 and 15.

Results and Discussion

The mass spectrum of **3** run directly after that of [LuPc$_2$] in which one phthalocyanine ring is present as a radical cation shows a difference in mass of one unit with respect to that of [LuPc$_2$] (see Experimental Section). Moreover, (**3**) is EPR inactive and diamagnetic as are **1** and **2**. Furthermore, whereas **1** and **2** are clearly ionic species, containing in the solid state [Na$\subset$18c.6]$^+$ (for **1**) and [NBu$_4$]$^+$ (for **2**), respectively, no cation could be found in the solid-state structure of **3**. Indeed the acidic hydrogen could not be located by X-rays (vide infra). Therefore, whereas **3**

---

(10) Frenz, B. A. In *Computing in Crystallography*; Schenk, M., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, C. G., Eds.; Delft University Press: Delft, The Netherlands, **1978**; p 64.

(11) Lehman, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A.: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

(12) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 159.

(13) GdPc$_2$ (single crystals prepared by electrocrystallization): $C_{64}H_{32}N_{16}Gd$, orthorhombic, space group, $P2_12_12_1$, a = 10.556 (3) Å, b = 50.724 (9) Å, c = 8.875 (3) Å, V = 4752.1 Å^3, D_{calcd} = 1.652, R_1 = 0.047, R_2 = 0.065. Moussavi, M.; De Cian, A.; Fischer, J.; Weiss, R., unpublished results.

(14) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2b.

(15) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table II. Positional Parameters and Their Estimated Standard Deviations for **2**

atom	*x*	*y*	*z*	*B*,[a] Å^2	atom	*x*	*y*	*z*	*B*,[a] Å^2
Lu	0.25596 (1)	0.31465 (1)	0.16735 (1)	1.841 (4)	C54	0.2833 (2)	0.5956 (2)	0.1265 (3)	3.01 (8)
N1	0.3268 (1)	0.2219 (2)	0.2236 (2)	2.47 (6)	C55	0.2229 (2)	0.5967 (2)	0.1492 (3)	2.99 (8)
C2	0.3145 (2)	0.1295 (2)	0.2040 (3)	2.70 (7)	C56	0.2022 (2)	0.5038 (2)	0.1329 (3)	2.31 (7)
C3	0.3700 (2)	0.0818 (2)	0.1830 (3)	2.86 (8)	N57	0.2478 (1)	0.4463 (2)	0.1049 (2)	2.22 (6)
C4	0.4164 (2)	0.1486 (2)	0.2004 (3)	2.80 (8)	N58	0.1442 (1)	0.4788 (2)	0.1320 (2)	2.52 (6)
C5	0.3880 (2)	0.2372 (2)	0.2275 (3)	2.62 (7)	C59	0.1227 (2)	0.3904 (2)	0.1011 (3)	2.27 (7)
N6	0.4195 (1)	0.3178 (2)	0.2553 (3)	2.76 (6)	C60	0.0583 (2)	0.3629 (2)	0.0790 (3)	2.64 (7)
C7	0.3958 (2)	0.3980 (2)	0.2940 (3)	2.52 (7)	C61	0.0531 (2)	0.2673 (2)	0.0405 (3)	2.69 (7)
C8	0.4332 (2)	0.4847 (2)	0.3453 (3)	2.76 (7)	C62	0.1141 (2)	0.2384 (2)	0.0399 (3)	2.39 (7)
C9	0.3940 (2)	0.5523 (2)	0.3882 (3)	2.72 (7)	N63	0.1546 (1)	0.3138 (2)	0.0793 (2)	2.27 (6)
C10	0.3340 (2)	0.5055 (2)	0.3629 (3)	2.53 (7)	N64	0.1250 (1)	0.1490 (2)	0.0003 (2)	2.39 (6)
N11	0.3361 (1)	0.4131 (2)	0.3011 (2)	2.51 (6)	C65	0.1534 (2)	−0.0560 (3)	−0.0886 (3)	3.44 (9)
N12	0.2863 (1)	0.5500 (2)	0.4051 (3)	2.67 (6)	C66	0.1807 (2)	−0.1401 (3)	−0.1305 (4)	4.0 (1)
C13	0.2325 (2)	0.5057 (2)	0.3990 (3)	2.62 (7)	C67	0.2386 (2)	−0.1433 (3)	−0.1539 (4)	4.1 (1)
C14	0.1843 (2)	0.5544 (2)	0.4647 (3)	2.57 (7)	C68	0.2759 (2)	−0.0631 (3)	−0.1355 (4)	3.78 (9)
C15	0.1387 (2)	0.4859 (2)	0.4496 (3)	2.64 (7)	C69	0.4484 (2)	0.2019 (3)	−0.1558 (3)	3.36 (8)
C16	0.1598 (2)	0.3984 (2)	0.3755 (3)	2.39 (7)	C70	0.4951 (2)	0.2485 (3)	−0.1860 (4)	3.58 (9)
N17	0.2156 (1)	0.4140 (2)	0.3432 (2)	2.43 (6)	C71	0.4985 (2)	0.3443 (3)	−0.1545 (3)	3.39 (8)
N18	0.1277 (1)	0.3186 (2)	0.3507 (2)	2.39 (6)	C72	0.4559 (2)	0.3966 (2)	−0.0906 (3)	3.03 (8)
C19	0.1500 (2)	0.2379 (2)	0.3005 (3)	2.47 (7)	C73	0.3176 (2)	0.6748 (3)	0.1350 (5)	4.6 (1)
C20	0.1171 (2)	0.1499 (2)	0.2862 (3)	2.51 (7)	C74	0.2898 (2)	0.7559 (3)	0.1650 (7)	7.6 (2)
C21	0.1580 (2)	0.0826 (2)	0.2493 (3)	2.50 (7)	C75	0.2297 (2)	0.7589 (3)	0.1877 (7)	7.4 (2)
C22	0.2138 (2)	0.1298 (2)	0.2374 (3)	2.24 (7)	C76	0.1949 (2)	0.6791 (3)	0.1784 (5)	4.7 (1)
N23	0.2062 (1)	0.2219 (2)	0.2633 (2)	2.34 (6)	C77	0.0082 (2)	0.4122 (3)	0.0842 (4)	3.47 (9)
N24	0.2621 (1)	0.0864 (2)	0.2075 (2)	2.50 (6)	C78	−0.0475 (2)	0.3629 (3)	0.0505 (4)	4.2 (1)
C25	0.3805 (2)	−0.0113 (3)	0.1489 (4)	4.3 (1)	C79	−0.0530 (2)	0.2672 (3)	0.0153 (4)	3.8 (1)
C26	0.4397 (2)	−0.0331 (3)	0.1348 (5)	5.1 (1)	C80	−0.0032 (2)	0.2180 (3)	0.0099 (3)	3.21 (8)
C27	0.4856 (2)	0.0348 (3)	0.1571 (5)	5.0 (1)	NB	0.1745 (1)	0.2521 (2)	−0.3215 (3)	3.01 (7)
C28	0.4747 (2)	0.1274 (3)	0.1905 (4)	3.96 (9)	CB1	0.1165 (2)	0.2796 (3)	−0.3752 (3)	2.95 (8)
C29	0.4949 (2)	0.5053 (3)	0.3629 (3)	3.25 (8)	CB2	0.0637 (2)	0.2858 (3)	−0.2995 (3)	3.53 (9)
C30	0.5160 (2)	0.5963 (3)	0.4239 (4)	4.06 (9)	CB3	0.0114 (2)	0.3231 (3)	−0.3562 (4)	4.1 (1)
C31	0.4764 (2)	0.6658 (3)	0.4663 (4)	3.58 (9)	CB4	−0.0450 (2)	0.3210 (3)	−0.2934 (4)	4.5 (1)
C32	0.4158 (2)	0.6445 (3)	0.4498 (4)	3.51 (9)	CB5	0.1633 (2)	0.1629 (3)	−0.2968 (3)	3.24 (8)
C33	0.1794 (2)	0.6448 (3)	0.5317 (3)	3.10 (8)	CB6	0.1324 (2)	0.0822 (3)	−0.4023 (3)	3.68 (9)
C34	0.1269 (2)	0.6676 (3)	0.5859 (4)	3.60 (9)	CB7	0.1284 (2)	−0.0038 (3)	−0.3657 (4)	4.3 (1)
C35	0.0810 (2)	0.6000 (3)	0.5741 (4)	3.55 (9)	CB8	0.0984 (3)	−0.0865 (3)	−0.4684 (5)	6.2 (1)
C36	0.0860 (2)	0.5075 (3)	0.5047 (3)	3.04 (8)	CB9	0.2189 (2)	0.2401 (3)	−0.4174 (3)	3.02 (8)
C37	0.0583 (2)	0.1259 (3)	0.3013 (3)	3.00 (8)	CB10	0.2834 (2)	0.2311 (3)	−0.3738 (3)	3.42 (9)
C38	0.0419 (2)	0.0342 (3)	0.2792 (4)	3.67 (9)	CB11	0.3208 (2)	0.2176 (3)	−0.4806 (4)	3.93 (9)
C39	0.0827 (2)	−0.0322 (3)	0.2435 (4)	3.68 (9)	CB12	0.3849 (2)	0.1998 (3)	−0.4509 (4)	4.5 (1)
C40	0.1411 (2)	−0.0095 (2)	0.2298 (3)	3.07 (8)	CB13	0.1995 (2)	0.3269 (3)	−0.2003 (3)	3.22 (8)
N41	0.2317 (1)	0.1753 (2)	−0.0050 (2)	2.35 (6)	CB14	0.2185 (2)	0.4208 (3)	−0.2076 (3)	3.40 (9)
C42	0.1795 (2)	0.1218 (2)	−0.0182 (3)	2.40 (7)	CB15	0.1725 (2)	0.4926 (3)	−0.1806 (4)	3.79 (9)
C43	0.1902 (2)	0.0233 (2)	−0.0675 (3)	2.61 (7)	CB16	0.1991 (2)	0.5864 (3)	−0.1749 (4)	4.6 (1)
C44	0.2505 (2)	0.0208 (2)	−0.0899 (3)	2.65 (7)	OS1	0.3745 (2)	0.7719 (3)	0.7435 (4)	6.8 (1)
C45	0.2750 (2)	0.1167 (2)	−0.0545 (3)	2.46 (7)	C1S1	0.3580 (2)	0.6907 (4)	0.7186 (4)	5.0 (1)
N46	0.3294 (1)	0.1409 (2)	−0.0729 (3)	2.59 (6)	NS1	0.3789 (2)	0.6371 (3)	0.7771 (3)	4.88 (9)
C47	0.3506 (2)	0.2286 (2)	−0.0464 (3)	2.48 (7)	C2S1	0.4257 (3)	0.6741 (5)	0.8815 (5)	7.9 (2)
C48	0.4055 (2)	0.2534 (2)	−0.0894 (3)	2.69 (7)	C3S1	0.3559 (3)	0.5420 (4)	0.7429 (7)	8.5 (2)
C49	0.4100 (2)	0.3495 (2)	−0.0556 (3)	2.67 (7)	OS2	0.2486 (2)	−0.0037 (3)	0.4708 (4)	8.4 (1)
C50	0.3585 (2)	0.3813 (2)	0.0108 (3)	2.38 (7)	C1S2	0.2978 (3)	−0.0244 (4)	0.4417 (5)	6.5 (1)
N51	0.3245 (1)	0.3074 (2)	0.0169 (2)	2.40 (6)	NS2	0.3326 (3)	−0.0746 (4)	0.4818 (5)	10.2 (2)
N52	0.3485 (1)	0.4696 (2)	0.0522 (2)	2.41 (6)	C2S2	0.3914 (4)	−0.0952 (7)	0.4432 (8)	12.5 (3)
C53	0.2971 (2)	0.4988 (2)	0.0949 (3)	2.65 (7)	C3S2	0.2930 (4)	−0.1660 (7)	0.5000 (8)	12.4 (3)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) $[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

corresponds to the reduced protonated form, [LuHPc$_2$], of the one-electron ligand-oxidized species [LuPc$_2$], **2** and **3** are salts containing the reduced form [LuPc$_2$]$^-$ of the same species, [LuPc$_2$].

Structures of [LuPc$_2$][NBu$_4$]·2DMF (2) and [LuHPc$_2$] (3). The crystals corresponding to these compounds contain in their asymmetric units one formula unit of **2** and **3**, respectively. Figure 1 shows an [LuPc$_2$]$^-$[NBu$_4$]$^+$ ion pair present in **2**. Figure 2 displays the geometry of [LuHPc$_2$] without the acidic hydrogen, which could not be located. Parts A and B of Figure 3 show the stick-bond model projections of the two phthalocyanine rings A and B present in the [LuPc$_2$]$^-$ ion of **2** on their 4N$_{iso}$ mean planes. Parts A and B of Figure 4 show these projections for the two rings A and B present in [LuHPc$_2$] (**3**). Tables II and III list the coordinates of the non-hydrogen atoms of **2** and **3** respectively. Selected bond distances and angles found in **2** and **3** are given in Table IV.

Both compounds contain lutetium diphthalocyanine sandwich units, and the structures of these units are very similar. The metal is eightfold coordinated in both units by the isoindole nitrogens of the two phthalocyanine rings forming the sandwich. One ring is rotated by 43° (**2**) and 41° (**3**) with respect to the other. Thus, the coordination polyhedron of the metal is, as in [LuPc$_2$], a slightly distorted square antiprism. The four isoindole nitrogens of the phthalocyanine rings are almost coplanar in both compounds. The corresponding mean planes are almost parallel in both sandwiches, their dihedral angles being 0.4° in [LuPc$_2$]$^-$ and 0.2° in [LuHPc$_2$]. In [LuPc$_2$]$^-$ (**2**), the lutetium atom lies 1.334 Å away from the 4N$_{iso}$ mean plane of ring A (Figure 3A) and 1.367 Å out of the 4N$_{iso}$ mean plane of ring B (Figure 3B). Thus, a slight dissymmetry is present in the sandwich structure of the [LuPc$_2$]$^-$ ion of **2**, the distance between ring A and ring B being 2.701 Å. This dissymmetry is also reflected by the Lu–N$_{iso}$ bond

Table III. Positional Parameters and Their Estimated Standard Deviations for **3**

atom	*x*	*y*	*z*	*B*,[a] Å^2
Lu	0.92670 (4)	0.87582 (1)	0.79375 (5)	2.006 (7)
N1	1.1446 (7)	0.8641 (1)	0.782 (1)	2.3 (1)
C2	1.1853 (8)	0.8384 (2)	0.790 (1)	2.4 (2)
C3	1.3015 (9)	0.8351 (2)	0.708 (1)	2.5 (2)
C4	1.3771 (9)	0.8129 (2)	0.682 (1)	3.3 (2)
C5	1.485 (1)	0.8170 (2)	0.600 (1)	3.4 (2)
C6	1.519 (1)	0.8411 (2)	0.550 (1)	4.5 (2)
C7	1.442 (1)	0.8637 (2)	0.571 (1)	4.3 (3)
C8	1.3343 (9)	0.8595 (2)	0.651 (1)	3.0 (2)
C9	1.2334 (9)	0.8776 (2)	0.703 (1)	2.5 (2)
N10	1.2364 (7)	0.9036 (1)	0.6737 (8)	2.3 (1)
C11	1.1514 (9)	0.9200 (2)	0.729 (1)	2.6 (2)
C12	1.1639 (9)	0.9487 (2)	0.710 (1)	2.6 (2)
C13	1.244 (1)	0.9640 (2)	0.621 (1)	3.4 (2)
C14	1.224 (1)	0.9911 (2)	0.625 (2)	4.1 (2)
C15	1.128 (1)	1.0025 (2)	0.706 (2)	4.2 (2)
C16	1.049 (1)	0.9872 (2)	0.798 (1)	3.3 (2)
C17	1.0677 (9)	0.9602 (2)	0.795 (1)	2.6 (2)
C18	0.9976 (9)	0.9383 (2)	0.865 (1)	2.3 (2)
N19	1.0482 (7)	0.9146 (1)	0.8186 (8)	2.3 (1)
N20	0.9045 (7)	0.9424 (1)	0.9638 (9)	2.4 (1)
C21	0.8526 (9)	0.9227 (2)	1.040 (1)	2.6 (2)
C22	0.756 (1)	0.9270 (2)	1.157 (1)	3.0 (2)
C23	0.6904 (9)	0.9491 (2)	1.201 (1)	2.8 (2)
C24	0.5996 (9)	0.9458 (2)	1.312 (1)	3.0 (2)
C25	0.574 (1)	0.9211 (2)	1.377 (1)	4.0 (2)
C26	0.643 (1)	0.8992 (2)	1.331 (1)	3.4 (2)
C27	0.7314 (9)	0.9021 (2)	1.221 (1)	2.6 (2)
C28	0.8110 (9)	0.8836 (2)	1.140 (1)	2.4 (2)
N29	0.8778 (7)	0.8959 (1)	1.0278 (8)	2.2 (1)
N30	0.8124 (7)	0.8576 (1)	1.176 (1)	2.9 (2)
C31	0.8877 (8)	0.8405 (2)	1.108 (1)	2.9 (2)
C32	0.8932 (9)	0.8127 (2)	1.150 (1)	3.0 (2)
C33	0.817 (1)	0.7978 (2)	1.247 (1)	3.3 (2)
C34	0.842 (1)	0.7708 (2)	1.250 (1)	3.6 (2)
C35	0.937 (1)	0.7598 (2)	1.162 (1)	4.0 (2)
C36	1.011 (1)	0.7748 (2)	1.067 (1)	3.3 (2)
C37	0.9871 (9)	0.8013 (2)	1.060 (1)	2.3 (2)
C38	1.0366 (8)	0.8223 (2)	0.964 (1)	2.4 (2)
N39	0.9713 (7)	0.8456 (1)	0.9897 (9)	2.3 (1)
N40	1.1337 (7)	0.8187 (1)	0.8763 (9)	2.5 (1)
N41	0.7685 (7)	0.9067 (1)	0.717 (1)	2.6 (1)
C42	0.7972 (9)	0.9288 (2)	0.639 (1)	2.6 (2)
C43	0.7081 (9)	0.9499 (2)	0.682 (1)	2.6 (2)
C44	0.699 (1)	0.9765 (2)	0.637 (1)	3.3 (2)
C45	0.603 (1)	0.9910 (2)	0.704 (2)	4.0 (2)
C46	0.520 (1)	0.9802 (2)	0.807 (1)	3.8 (2)
C47	0.527 (1)	0.9540 (2)	0.847 (1)	3.4 (2)
C48	0.6243 (9)	0.9391 (2)	0.782 (1)	2.9 (2)
C49	0.6626 (9)	0.9112 (2)	0.802 (1)	2.8 (2)
N50	0.5972 (7)	0.8949 (1)	0.8853 (9)	2.7 (2)
C51	0.6255 (9)	0.8691 (2)	0.897 (1)	2.6 (2)
C52	0.5490 (9)	0.8502 (2)	0.980 (1)	2.9 (2)
C53	0.444 (1)	0.8535 (2)	1.073 (2)	4.4 (3)
C54	0.394 (1)	0.8308 (2)	1.141 (2)	4.6 (3)
C55	0.446 (1)	0.8055 (2)	1.111 (2)	4.3 (2)
C56	0.552 (1)	0.8026 (2)	1.018 (1)	3.6 (2)
C57	0.5998 (9)	0.8253 (2)	0.954 (1)	2.9 (2)
C58	0.7095 (8)	0.8295 (2)	0.856 (1)	2.5 (2)
N59	0.7246 (7)	0.8565 (1)	0.8313 (8)	2.2 (1)
N60	0.7770 (7)	0.8098 (1)	0.8038 (9)	2.4 (1)
C61	0.8692 (9)	0.8134 (2)	0.701 (1)	2.7 (2)
C62	0.9408 (9)	0.7913 (2)	0.638 (1)	2.7 (2)
C63	0.938 (1)	0.7643 (2)	0.667 (1)	3.5 (2)
C64	1.023 (1)	0.7489 (2)	0.587 (1)	3.9 (2)
C65	1.107 (1)	0.7595 (2)	0.484 (1)	3.6 (2)
C66	1.110 (1)	0.7863 (2)	0.456 (1)	3.3 (2)
C67	1.0245 (9)	0.8027 (2)	0.532 (1)	2.8 (2)
C68	1.0040 (9)	0.8309 (2)	0.539 (1)	2.7 (2)
N69	0.9158 (7)	0.8370 (1)	0.6465 (8)	2.2 (1)
N70	1.0620 (8)	0.8476 (1)	0.4448 (9)	2.8 (2)
C71	1.0377 (8)	0.8730 (2)	0.439 (1)	2.5 (2)
C72	1.0947 (9)	0.8913 (2)	0.331 (1)	2.6 (2)
C73	1.177 (1)	0.8868 (2)	0.211 (1)	3.4 (2)
C74	1.217 (1)	0.9088 (2)	0.131 (1)	3.7 (2)
C75	1.172 (1)	0.9338 (2)	0.164 (1)	3.3 (2)
C76	1.0856 (9)	0.9380 (2)	0.280 (1)	2.9 (2)
C77	1.0482 (9)	0.9162 (2)	0.363 (1)	2.7 (2)
C78	0.9580 (9)	0.9129 (2)	0.488 (1)	2.6 (2)
N79	0.9615 (7)	0.8873 (1)	0.5365 (9)	2.6 (2)
N80	0.8871 (7)	0.9324 (1)	0.5371 (9)	2.6 (2)

[a] See footnote *a* in Table II.

Table IV. Selected Bond Distances (Å), Bond Angles (deg), and Averages with Their Estimated Standard Deviations

[LuPc$_2$][NBu$_4$]·2DMF (**2**)		LuHPc$_2$ (**3**)	
Lu–N1	2.366 (3)	Lu–N1	2.380 (7)
Lu–N11	2.366 (3)	Lu–N19	2.359 (7)
Lu–N17	2.388 (3)	Lu–N29	2.364 (7)
Lu–N23	2.376 (3)	Lu–N39	2.362 (7)
Lu–N41	2.394 (3)	Lu–N41	2.389 (7)
Lu–N51	2.407 (3)	Lu–N59	2.373 (7)
Lu–N57	2.372 (3)	Lu–N69	2.364 (7)
Lu–N63	2.398 (3)	Lu–N79	2.378 (8)
⟨Lu–N_{iso}⟩	2.384 (1)	⟨Lu–N_{iso}⟩	2.371 (2)
	Isoindoles: Mean Values[a]		
N_{iso}–C_α	1.370 (1)	N_{iso}–C_α	1.373 (3)
C_α–C_β	1.459 (1)	C_α–C_β	1.463 (3)
C_β–C_β	1.391 (2)	C_β–C_β	1.390 (5)
N_m–C_α	1.328 (1)	N_m–C_α	1.329 (3)
C_{Ph}–C_{Ph}	1.386 (1)	C_{Ph}–C_{Ph}	1.386 (2)
C_α–N_{iso}–C_α	107.3 (1)	C_α–N_{iso}–C_α	107.5 (2)
N_p–C_α–C_β	110.0 (1)	N_p–C_α–C_β	109.7 (2)
C_α–C_β–C_β	106.2 (1)	C_α–C_β–C_β	106.3 (2)
C_α–N_m–C_α	122.8 (1)	C_α–N_m–C_α	122.4 (3)
	NBu_4^+: Mean Values		
N–C	1.522 (2)		
C–C	1.514 (1)		
	DMF: Mean Values		
N–C	1.293 (4)		
N–CH_3	1.513 (4)		
C=O	1.212 (4)		

[a] N_{iso}, C_α, C_β, N_m, C_{Ph} stand respectively for the iso nitrogen, α and β carbon, meso nitrogen, and phenyl carbon atoms.

Table V. Dihedral Angles in **2** and **3**

	[LuPc$_2$][NBu$_4$]· 2DMF (**2**)	[LuHPc$_2$] (**3**)		[LuPc$_2$][NBu$_4$]· 2DMF (**2**)	[LuHPc$_2$] (**3**)
		Dihedral Angles (deg) between the 4N_{iso} Mean Plane and Py*i* and Ph*i*[a]			
		Molecule A			
Py1	10.0	10.6	Py1	7.9	11.6
Py2	13.3	9.4	Py2	16.0	5.1
Py3	14.3	6.4	Py3	15.0	2.6
Py4	7.3	5.1	Py4	5.7	1.2
		Molecule B			
Py5	3.0	7.8	Py5	0.7	5.9
Py6	16.8	8.0	Py6	17.9	5.1
Py7	8.1	6.1	Py7	7.6	2.2
Py8	15.9	8.1	Py8	17.7	8.3
		Dihedral Angles between Py*i* and Ph*i*[a]			
		Molecule A			
Py1/Ph1	3.5	1.2	Py3/Ph3	0.9	4.6
Ph2/Ph2	2.8	4.3	Py4/Ph4	2.8	6.1
		Molecule B			
Py5/Ph5	3.6	1.9	Py7/Ph7	1.0	3.8
Py6/Ph6	1.9	3.0	Py8/Ph8	2.0	2.1

[a] Py*i*, *i* = 1–8, denote the pyrrole rings N1, N11, N17, N23, N41, N51, N57, and N63 in **2** and the pyrrole rings N1, N19, N29, N39, N41, N59, N69, and N79 in 3. Ph*i* denotes the phenyl rings belonging to the same isoindole moiety as Py*i*.

lengths, which range from 2.366 (3) to 2.388 (3) Å (mean value 2.374 (2) Å)[16] with the isoindole nitrogens of ring A and from

---

(16) Hamilton, W. C. Lecture presented at the NATO Advanced Study Institute on Experimental Aspects of X-Ray and Neutron Single Crystal Diffraction Methods, Aarhus University, Denmark, 1972.

Table VI. Average Bond Lengths (Å) Found in Several Lutetium Diphthalocyanine Complexes and in the Phthalocyanine Ligands of Typical Metallophthalocyanines, $Si(Pc)(OSi(CH_3)_3)_2$, and H_2Pc

	$[LuPc_2]^-$ ($\mathbf{2}^-$)	$[LuHPc_2]$ (**3**)	$[LuPc_2]^c$	mean $M(Pc)^d$	$Si(Pc)(OSiMe_3)_2{}^d$	H_2Pc^e
Lu–Np (A)[a]	2.374 (2)	2.366 (4)	2.387 (4)			
Lu–Np (B)	2.392 (2)	2.376 (4)	2.372 (3)			
⟨Lu–Np⟩	2.383 (1)	2.371 (3)	2.380 (2)			
$Lu\cdots 4N_{iso}(A)^a$	1.334	1.337	1.350			
$Lu\cdots 4N_{iso}(B)$	1.367	1.339	1.341			
$4N_{iso}(A)\cdots 4N_{iso}(B)$	2.701	2.676	2.691			
$N_{iso}-C_\alpha{}^b$	1.370 (1)	1.373 (3)	1.376 (3)	1.377 (10)	1.375 (4)	1.37
$C_\alpha-C_\beta{}^b$	1.459 (1)	1.463 (3)	1.456 (2)	1.453 (3)	1.449 (3)	1.47
$C_\beta-C_\beta$	1.391 (2)	1.390 (5)	1.390 (4)	1.394 (4)	1.386 (5)	1.41
$N_m-C_\alpha{}^b$	1.328 (1)	1.329 (3)	1.327 (2)	1.326 (7)	1.321 (4)	1.30
$C_{Ph}-C_{Ph}{}^b$	1.386 (1)	1.386 (2)	1.389 (3)	1.390 (4)	1.383 (8)	1.40

[a] N_p denotes the centroid of the four isoindole nitrogens. [b] See Table IV for definition of N_{iso}, C_α, C_β, N_m, and C_{Ph}. [c] Data of ref 5. [d] Data of ref 17. [e] Data of ref 18.

2.372 (3) to 2.407 (3) Å (mean value 2.392 (2) Å)[16] with the isoindole nitrogens of ring B. In contrast, no such dissymmetry appears in the structure of $[LuHPc_2]$, where the lutetium atom lies 1.337 Å away from ring A and 1.339 Å out of ring B, the total separation between rings A and B being only 2.676 Å. Table V gives the dihedral angles between the mean planes of the pyrrole rings and phenyl rings with the corresponding $4N_{iso}$ mean planes of the phthalocyanine ligands. These ligands are severely distorted, but as usual the average bond distances and bond angles are not significantly different from those found in typical metallophthalocyanine[5,17] and H_2Pc[18] (Table VI).

The acidic hydrogen could not be located in the structure of $[LuHPc_2]$. The mean value of the $Lu-N_{iso}$ bond distances of 2.371 (3) Å is smaller than those found in $[LuPc_2]^-$ (2.383 (1) Å) and $[LuPc_2]$ (2.380 (2) Å). Thus, most probably the protonation does not take place at an isoindole nitrogen but at a methine nitrogen. In addition, the bond distances and angles found within the phthalocyanine ligands, which are not significantly different from those present in $[LuPc_2]^-$, $[LuPc_2]$,[5] typical metallophthalocyanine,[5,17] and $[H_2Pc]$[18] (Table VI), indicate that the protonated molecule must be completely disordered in the crystal. The slight dissymmetry which is present in the structure of the $[LuPc_2]^-$ ion in **2** and absent in $[LuHPc_2]$ (**3**) is most probably due to the cation–anion packing. The $[NBu_4]^+$ cations lie approximately over the phthalocyanine ring B. The electrostatic interactions between these groups lead to longer $Lu-N_{iso}(B)$ bond distances with respect to the $Lu-N_{iso}(A)$ bond lengths and to a slightly larger separation between the $4N_{iso}$ mean planes in $[LuPc_2]^-$ with respect to $[LuHPc_2]$ where the acidic hydrogen is completely delocalized over both phthalocyanine rings A and B. The bond distances and bond angles found in the cation $[NBu_4]^+$ and DMF molecules of solvation present in **2** show their usual values (Table IV).

Acknowledgment. We thank Professor J. S. Buchler, Institut für Anorganische Chemie, Technische Hochschule, Darmstadt, West Germany, for helpful discussions and Priv. Doz. Dr. M. Veith and M. Fischer (Technische Hochschule, Darmstadt, West Germany) for the mass spectrum.

Registry No. **1**, 112816-38-3; **2**, 112816-39-4; **2**·2DMF, 112839-63-1; **3**, 12369-74-3; $[LuPc_2]$, 79079-35-9; $[GdPc_2]$, 82800-45-1.

Supplementary Material Available: Tables SM-1 and SM-2 (anisotropic thermal parameters for all non-hydrogen atoms for **2** and **3**), Tables SM-3 and SM-4 (hydrogen atom parameters for **2** and **3**), Tables SM-5 and SM-6 (complete set of bond lengths for **2** and **3**), and Tables SM-7 and SM-8 (complete set of bond angles for **2** and **3**) (24 pages); Tables SM-9 and SM-10 (observed and calculated structure factors for all observed reflections (×10) for **2** and **3**) (53 pages). Ordering information is given on any current masthead page.

---

(17) Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, E.; Fragala, I.; Herbstein, F. H.; Ratner, M. A.; Marks, T. I. *J. Am. Chem. Soc.* **1984**, *106*, 7748.

(18) Hoskins, B. F.; Mason, S. A. White, J. B. C. *J. Chem. Soc., Chem. Commum.* **1969**, 554.

Notes

Contribution from the Laboratoire de Chimie des Solides,
UA CNRS No. 279, Université de Nantes,
2, rue de la Houssinière, 44072 Nantes Cedex 03, France

General Trends Observed in the Substituted Thiophosphate Family. Synthesis and Structure of $AgScP_2S_6$ and $CdFeP_2S_6$

Stephen Lee,[1] Pierre Colombet,* Guy Ouvrard,
and Raymond Brec

Received September 23, 1987

The systematic study of a specific family of crystalline compounds can often reveal exciting trends in crystal structure chemistry. We report in this paper the synthesis and structure of $AgScP_2S_6$ and $CdFeP_2S_6$. The interest in these compounds is that they illustrate three points of general chemical interest: that metal superstructure is dependent on the oxidation state of the metals, that Ag(I) undergoes a distortion of its octahedral environment due to a suggested second-order Jahn–Teller effect, and that extended Hückel calculations together with a steric effect argument may help to explain the way in which metals order.

Experimental Section

Materials. Both $AgScP_2S_6$ and $CdFeP_2S_6$ were prepared in sealed quartz tubes from a stoichiometric mixture of the elements held at 600 °C for a 2-week period. In the case of $AgScP_2S_6$ the mixture was first left at a lower temperature (450 °C) to avoid any reaction with the quartz tube. The solid solution $Cd_xFe_{1-x}PS_3$ (x = 0.20, 0.40, 0.60, 0.80) was also synthesized. The single crystals used for the X-ray analysis were selected from the sample mass.

X-ray Crystallographic Procedure. X-ray powder patterns were obtained from an Enraf-Nonius Guinier camera using Cu $K\alpha_1$ radiation. The photographs were calibrated with silicium (a = 5.430 88 Å) and the unit cell dimensions refined by least-squares fits of the data. The diffraction patterns indicate that $AgScP_2S_6$ and $Fe_xCd_{1-x}P_2S_6$ are isotypic to $AgInP_2S_6$[2] and $FePS_3$[3] (or $CdPS_3$), respectively. The powder data of

---

* To whom correspondence should be addressed.

(1) NATO postdoctoral fellow. Current address: Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.

0020-1669/88/1327-1291$01.50/0