Inorg. Chem. **1981**, *20*, 2709–2711

Notes

Contribution from Xerox Corporation,
Webster Research Center, Webster, New York 14580

New Alkali Metal Phthalocyanine Complexes. Structure of the Quasi-Multimacrocycle $K_2Pc(DMF)_4$ and the K_2Pc Template

Ronald F. Ziolo* and Michael Extine

Received July 14, 1980

Physicochemical studies of group 1A metal phthalocyanines are virtually nonexistent, probably, in part, because of the purported insoluble or nonsublimable nature of these compounds.[1,2] Recently, however, we reported that the alkali metal phthalocyanines dissolve in common oxygen-donor solvents or in solvents containing oxygen-donor ligands to yield novel oxygen-donor metal phthalocyanine complexes.[3,4] We now report the first structural example of one such complex formed between K_2Pc and a monodentate oxygen-donor ligand, dimethylformamide (DMF).

Experimental Section

One gram of freshly prepared K_2Pc[2] was dissolved in 25 mL of hot DMF. Crystalline material formed upon cooling and was removed by filtration, washed with a heptane/DMF mixture, and dried in vacuo. Combustion analysis suggested the formulation $K_2Pc(DMF)_4$, which was confirmed by the structure analysis. Anal. Found: C, 59.19; H, 4.93; N, 18.92; K, 8.76. This complex was also obtained by dissolving phthalocyanine in strongly basic (KOH)DMF and evaporating some solvent.

A prism measuring 0.20 × 0.20 × 0.22 mm was mounted in a glass capillary for X-ray diffraction studies.[5] Cell constants were obtained by computer-centering of 25 reflections, followed by least-squares refinement. No systematic extinctions were observed and space group $P\bar{1}$ was assumed. A Delaunay reduction revealed no hidden symmetry. Cell constants (23 ± 1 °C) are $a = 7.342$ (1) Å, $b = 12.388$ (1) Å, $c = 12.768$ (1) Å, $\alpha = 97.17$ (2)°, $\beta = 99.76$ (1)°, $\gamma = 102.02$ (1)°, $V = 1104$ (2) Å^3, $D_{calcd} = 1.328$ g/cm^3, and $Z = 1$.

Data were collected at 23 ± 1 °C on an Enraf-Nonius CAD4 automatic diffractometer at Molecular Structure Corp.[6] with use of Cu Kα radiation filtered by a graphite-crystal incident-beam monochromator. Experimental details are available as supplementary material. The number of reflections collected totaled 4679 with 4341 independent. Intensities and standard deviations on intensities were calculated as described previously with the parameter p set to 0.05.[7] Lorentz–polarization and decay (<2%) corrections were applied to the data. Extinction and absorption corrections ($\mu = 23.4$ cm^{-1}) were not necessary.

Table I. Heavy-Atom Positional Parameters for $K_2Pc(DMF)_4$

atom	x	y	z
K	0.26713 (9)	−0.00117 (6)	−0.00112 (5)
O1	0.5712 (4)	0.0607 (2)	0.1808 (2)
O2	0.5564 (4)	0.1862 (2)	−0.0126 (2)
N1	0.0779 (4)	0.0995 (2)	0.1412 (2)
N2	0.0255 (4)	0.1309 (2)	−0.0734 (2)
N3	0.1221 (4)	0.2794 (2)	0.0813 (2)
N4	0.0713 (4)	−0.0386 (2)	0.2602 (2)
N5	0.6681 (4)	0.1816 (3)	0.3383 (2)
N6	0.5339 (4)	0.2905 (2)	−0.1462 (2)
C1	0.1000 (4)	0.0662 (2)	0.2389 (2)
C2	0.1637 (4)	0.1639 (2)	0.3249 (2)
C3	0.2050 (5)	0.1770 (3)	0.4363 (2)
C4	0.2623 (5)	0.2850 (3)	0.4938 (2)
C5	0.2773 (5)	0.3771 (3)	0.4422 (3)
C6	0.2380 (5)	0.3653 (3)	0.3310 (2)
C7	0.1797 (4)	0.2577 (2)	0.2730 (2)
C8	0.1242 (4)	0.2130 (2)	0.1569 (2)
C9	0.0734 (4)	0.2398 (2)	−0.0249 (2)
C10	0.0647 (4)	0.3139 (2)	−0.1054 (2)
C11	0.0966 (5)	0.4289 (2)	−0.0987 (2)
C12	0.0699 (5)	0.4719 (3)	−0.1939 (3)
C13	0.0153 (5)	0.4024 (3)	−0.2929 (2)
C14	−0.0161 (5)	0.2868 (3)	−0.3003 (2)
C15	0.0085 (4)	0.2435 (2)	−0.2051 (2)
C16	0.0148 (4)	−0.1290 (2)	0.1817 (2)
C17	0.6219 (6)	0.1564 (3)	0.2317 (3)
C18	0.7285 (6)	0.2955 (4)	0.3932 (4)
C19	0.6624 (7)	0.0926 (4)	0.4012 (3)
C20	0.5603 (6)	0.2762 (3)	−0.0438 (3)
C21	0.4919 (6)	0.1944 (4)	−0.2314 (3)
C22	0.5455 (7)	0.3992 (4)	−0.1751 (4)

[a] Values in parentheses are estimated standard deviations in the least significant digits.

The 53-atom structure was solved by direct and Fourier methods. Hydrogen atoms were located and refined isotropically after anisotropic refinement of all nonhydrogen atoms. Full-matrix least-squares refinement of the 368 variables in space group $P\bar{1}$ led to final agreement factors of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.050$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.060$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weight w defined as $4F_o^2/\sigma^2(F_o^2)$. Neutral-atom scattering factors were used,[8] and anomalous dispersion corrections were applied.[9] Only the 2733 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. Calculations were performed as described previously.[10] The esd of an observation of unit weight was 1.502, and the maximum parameter shift was 0.5 times its esd.

The final positional parameters are given in Table I. General temperature factor expressions (B_{ij}), the positional and thermal parameters for hydrogen atoms and the distance to the attached atom, the observed and calculated structure factors, and the rms displacements along the principal axes of the temperature factor ellipsoids for the nonhydrogen atoms are available as supplementary material.

Results and Discussion

Dipotassium phthalocyanine crystallizes in DMF to afford $K_2Pc(DMF)_4$ (**1**).[11] A stereoscopic unit cell view of the compound is given in Figure 1. The complex consists of infinite stacks of KPcK units along a separated by planes containing four DMF molecules normal to a. The structure mimics that of the infinite stack complex $K_2Pc(diglyme)_2$ (**2**)[4] and is similar to that of the monomeric trimacrocyclic "sandwich" complex $K_2Pc(18\text{-crown-}6)_2$ (**3**).[4]

---

(1) Lever, A. B. P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.
(2) Moser, F. H.; Thomas, A. L. *ACS Monogr.* **1963**, *No. 157*.
(3) Ziolo, R. F.; Günther, W. H. H. "Abstracts of Papers", 2nd Symposium on Macrocyclic Compounds, Provo, UT, Aug 1978; Thermochemical Institute, Brigham Young University: Provo, UT, 1978; Abstract II2. Ziolo, R. F.; Günther, W. H. H. "Abstracts of Papers", American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, HI, April 1979; American Chemical Society: Washington, D.C., 1979; INOR 62.
(4) Ziolo, R. F.; Günther, W. H. H.; Troup, J. *J. Am. Chem. Soc.* **1981**, *103*, 4629.
(5) Crystals are slightly moisture sensitive and yield H_2Pc upon protonation.
(6) Molecular Structure Corp., College Station, TX 77840.
(7) Lee, J.-S.; Titus, D. D.; Ziolo, R. F. *Inorg. Chem.* **1977**, *16*, 2487.
(8) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.
(9) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.
(10) Ziolo, R. F.; Troup, J. M. *Inorg. Chem.* **1979**, *18*, 2271.
(11) Crystals of $K_2Pc(DMF)_4$ are dichroic and are green by transmission and purple by reflection. Differential scanning calorimetry shows a loss endotherm for DMF at 157 °C.

0020-1669/81/1320-2709$01.25/0

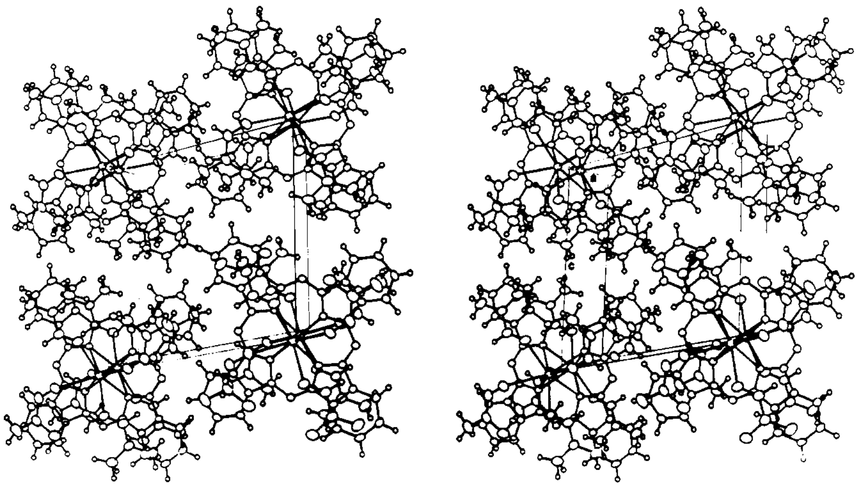

Figure 1. Stereoscopic unit cell view of $K_2Pc(DMF)_4$.

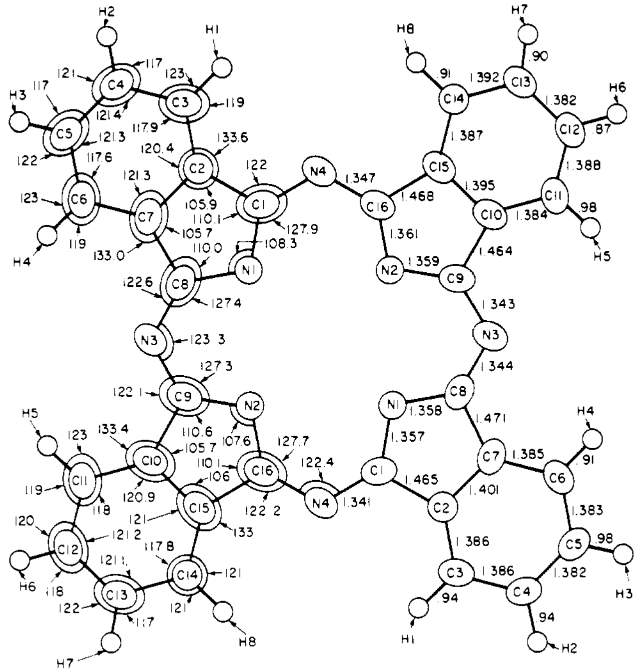

Figure 2. Atom labeling scheme, distances (Å), and angles (deg) in the phthalocyanine dianion. The estimated standard deviations are 0.003–0.005 Å for distances and 0.1–0.3° for angles. N–K distances are 2.777 (2), 2.781 (2), 2.782 (2), and 2.792 (2) Å.

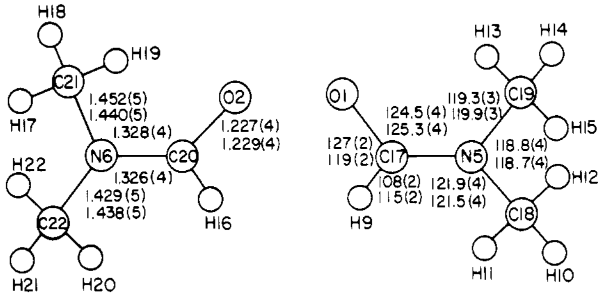

Figure 3. Atom labeling scheme, distances (Å), and angles (deg) in the DMF molecules. The upper entries refer to the labeled molecule while the lower entries refer to the equivalent portion of the adjacent molecule. O–K distances are 2.838 (2), 2.838 (2), 2.842 (2), and 2.868 (3) Å.

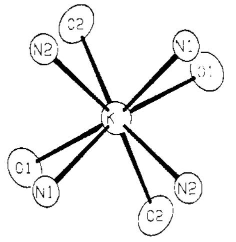

Figure 4. Potassium ion coordination in $K_2Pc(DMF)_4$. N1–N2 = 2.789 (4) Å; N2–N1′ = 2.780 (4) Å; O1–O2 = 3.076 (4) Å; O2–O1′ = 3.366 (4) Å.

The phthalocyanine ligand exists as the dianion with bond distances and angles (Figure 2) similar to those found in the coordinated ligand. In addition, the central cavity of the phthalocyanine is square and has a typical isoindole N–N distance of 2.785 (3) Å. Identical distances have been observed in several transition-metal phthalocyanine complexes.[12] The K–Pc (4-N isoindole plane[13]) distance, however, is 1.967 Å and exceeds typical transition-metal M–Pc distances, which range from 0 to 1.5 Å.[14] The N–K distances (Figure 2; mean value 2.783 (5) Å[15]) suggest coordination of the potassium by the anion and are slightly shorter than the N–K distances in the multicyclic complex $K[C_{18}H_{36}N_2O_6]I$.[16] Similar observations were made for **2** and **3**. The equivalence of the N–N and N–K distances in **1**, however, leads to a regular K_2N_4 octahedron with N–K–N angles of approximately 60 and 90°.

The dianion in **1** is nearly planar[13] in contrast to the saddle-shaped ion in **2**. The largest deviation from planarity is the bending of the C10 and C10′ benzene rings above and below the 4-N plane with the two outermost carbon atoms 0.315 Å from the plane. All other atoms in the macrocycle are less than 0.1 Å from the 4-N plane. A similar conformation for the anion is observed in the monomer, **3**, and appears to be the result of crystal packing effects.[4] The benzene rings have a distorted hexagonal geometry as observed previously in, for example, VOPc.[17]

Bond distances and angles in the DMF molecules are given in Figure 3 and appear normal.[18] With the exception of the

---

(12) See, for example: Bennett, W. E.; Broberg, D. E.; Baenziger, N. C. *Inorg. Chem.* **1973**, *12*, 930 and references therein.

(13) Weighted least-squares planes, dihedral angles, and atom distances from the planes are given as supplementary material.

(14) See, for instance: Boucher, L. J. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter 7.

(15) Estimated variances of the mean values of chemically equivalent distances or angles were calculated as $[\sum(x - \bar{x})^2/(n(n-1))]^{1/2}$.

(16) Moras, D.; Metz, B.; Weiss, R. *Acta Crystallogr., Sect. B* **1973**, *B29*, 383.

(17) Ziolo, R. F.; Griffiths, C. H.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2300.

methyl hydrogen atoms, all of the atoms of the two DMF molecules and two symmetry-related molecules lie in a plane.[13] The largest atom deviation from the four-molecule plane is –0.009 Å for N5 in one DMF and 0.011 Å for C20 in the other. The four DMF molecules have a radial distribution in the plane (Figure 1) and form a quasi-macrocyclic oxygen-donor ligand. The four oxygen atoms form a rectangle with its sides (3.076 (4) and 3.366 (4) Å) relating to the head-to-head and tail-to-tail distribution of the DMF molecules. The dihedral angle between the 4-O DMF and 4-N isoindole planes is –1.4°.

The O–K distances (Figure 3) have a mean value of 2.847 (7) Å and suggest coordination by the DMF. The potassium ions, therefore, are in an eight-coordinate environment and are 1.704 Å from the 4-O DMF plane. The coordination around the potassium ion is distorted cubic and is illustrated in Figure 4. The coordinated O and N atoms are in slightly staggered positions when viewed along the potassium ion chain. The O–K–O angles (68, 72, and 106°) differ from the N–K–N angles and reflect the distortion in the coordination geometry. No unusually close intermolecular DMF contacts are observed.

Structural results for **1**, **2**, and **3** suggest a strong coordination template effect for K_2Pc with both monodentate and sterically more restrictive multidentate oxygen donor ligands. In solution, the coordination template effect is known to enhance ring-closure reactions.[19] Similar enhancement may be possible using the alkali metal phthalocyanines.

In DMF, K_2Pc is a nonelectrolyte (10^{-3} M) and exhibits the single MPc-like Q band (667 nm) associated with a D_{4h} symmetry of the phthalocyanine ring. These observations suggest the presence of the K_2Pc moiety in solution where a species similar to **1** is expected. A similar model for H_2Pc in solution was suggested by Martin and Stillman.[20]

Replacement of the $(DMF)_4$ quasi-macrocycle in **1** with a phthalocyanine dianion is sterically feasible and suggests a possible stacked structural model for the M_2Pc (M = Na, K) compounds, namely, $nM^+(MPc^-)_n$. The structures of these compounds are unkown.

Registry No. $K_2Pc(DMF)_4$, 76081-82-8; K_2Pc, 25047-77-2.

Supplementary Material Available: Tables of the observed and calculated structure factors, the general temperature factor expressions (B_{ij}), the rms amplitudes of thermal vibration, the positional and thermal parameters for the hydrogen atoms and the distance to the attached atom, and weighted least-squares planes (23 pages). Ordering information is given on any current masthead page.

---

(18) For comparative values see, for example: Broomhead, J. A.; Evans, J.; Grumley, W. D.; Sterns, M. *J. Chem. Soc., Dalton Trans.* **1977**, 173. Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Warmald, J. *Inorg. Chem.* **1972**, *11*, 1818.

(19) Greene, R. N. *Tetrahedron Lett.* **1972**, 1793.

(20) Martin, K. A.; Stillman, M. J. *Inorg. Chem.* **1980**, *19*, 2473–2475.

Contribution from the Chemistry Department,
MLK College, Balrampur 271201, Uttar Pradesh, India

Organobimetallic Tetrathiocyanates and Their Complexes

Pashupati P. Singh,* Subir Kumar, and M. P. Reddy

Received April 23, 1980

Simple salts of transition and main group elements have been used as Lewis acids frequently. Similarly simple organometallic compounds like $(C_6H_5)_2SnCl_2$ and $(C_6H_5)_3SnCl$ have also been used as Lewis acids. Recently a new class of mixed-metal, bimetallic compounds of general formula $MM'(NCS)_4$ (M = Co, Ni; M′ = Zn, Cd, Hg) have been used as Lewis acids, and a review[1] has recently appeared on this class of bimetallic Lewis acids. We now wish to report the preparation of some organobimetallic, mixed-metal compounds of the type $(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$ and $(EtOH)_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$. These organobimetallic compounds act as Lewis acids, and the products containing various Lewis bases are reported also.

Experimental Section

Materials and Manipulations. Phenylmercury thiocyanate was prepared by stirring an ethanolic solution of phenylmercury acetate (BDH) with an ethanolic solution of KNCS (BDH) in 1:1 molar ratio. Phenylmercury thiocyanate precipitated immediately, and the solid was isolated by filtration, washed with solvent, recrystallized from acetone, and dried under vacuum. The purity of the compound was determined by elemental analysis, melting point, and infrared spectra.[2] Cobalt and nickel thiocyanates were prepared by reacting their respective nitrates with potassium thiocyanate in ethanol. $Co(NCS)_2{\cdot}2py$ and $Ni(NCS)_2{\cdot}4L$ (L = pyridine, nicotinamide, aniline) were prepared by the method described elsewhere.[3] Dimethyl sulfoxide (Me_2SO), 1,10-phenanthroline (phen), 2,2′-bipyridyl (bpy), tetrahydrofuran (THF), pyridine (py), nicotinamide (Nia), aminopyridine (Amp), dioxane (DIOX), methanol (MeOH), ethanol (EtOH), and acetone were used after purification by known methods.[4] All solvents were purified and dried before use.

Preparation of $(py)_2(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$. A 3.32-g sample of $Co(NCS)_2{\cdot}2py$ (1 mmol) was dissolved in 50 mL of ethanol. To this solution was added a suspension of 6.7 g of C_6H_5HgSCN (2 mmol) in 50 mL of ethanol, and the mixture was stirred for 72 h. A pink solid was formed which was filtered, washed with solvent, and dried under vacuum. The compound was recrystallized from Me_2SO.

Preparation of the Lewis acid $(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$. This compound was prepared by heating $(py)_2(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$ under vacuum at 50–60 °C for about 0.5 h, until the pink color changed to blue; mp 192 °C.

Preparation of $L_2(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$ and $[Co(L\text{-}L)_3][C_6HHg(SCN)_2]_2$ (L = py, Nia, Amp, Me_2SO, THF, DIOX; L-L = phen and bpy). All of these complexes were prepared by stirring a suspension of the Lewis acid in ethanol with a solution of the ligand in the some same solvent for 24 h in stoichiometric ratios. The THF, DIOX, and Me_2SO complexes were prepared by stirring the Lewis acid in these solvents. The complexes of bpy and phen were recrystallized from a mixture of ethanol and Me_2SO. The pyridine and nicotinamide complexes melted at 192 and 125 °C, respectively, and rest of the complexes decomposed in the range 170–250 °C.

Preparation of $L_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ (L = MeOH, EtOH, THF, Me_2SO, DIOX). A solution of 1.75 g of $Ni(NCS)_2$ (1 mmol) in 50 mL of methanol was mixed with a solution of 6.7 g (2 mmol) of phenylmercury thiocyanate in 50 mL of acetone, and the mixture was refluxed for 10 h. The methanol complex appeared as a green precipitate, which was filtered and washed with methanol. The compound was recrystallized from Me_2SO and hexane mixture. The remainder of the complexes were prepared similarly by substituting another solvent for methanol. In each case a green solid appeared, which was recrystallized from Me_2SO and hexane mixture. These complexes decomposed in the range 220–260 °C.

Preparation of $L_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ (L = py, Nia, 4-Amp, Ani). $Ni(NCS)_2{\cdot}4L$ (1 mmol) was dissolved in 50 mL of acetone and mixed with a solution of C_6H_5HgSCN (2 mmol) in 50 mL of the same solvent. The reaction mixture was stirred for 2 h, and thereafter 5 mL of methanol was added and stirring continued for 48 h. Violet or bluish green precipitates appeared in each case which were filtered, washed with solvent, recrystallized from a mixture of Me_2SO and hexane, and dried under vacuum. These complexes decomposed in the range 160–230 °C.

Alternatively these complexes were also prepared by refluxing an ethanolic solution of 1 mmol of $(MeOH)_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ with a solution of 2 mmol of the ligands in the same solvent for 15 h.

---

(1) Singh, P. P. *Coord. Chem. Rev.* **1980**, *32*, 33–65.

(2) Dehnick, Kurt. *J. Organomet. Chem.* **1967**, *9(1)*, 11–17.

(3) Koshits, Porai. *Kristallografiya* **1959**, *4*, 259 and references therein.

(4) Vogel, A. I. "A Textbook of Practical Organic Chemistry", 3rd ed.; ELBS and Longman Group Ltd.: New York, 1973.

0020-1669/81/1320-2711$01.25/0