and phenylcyclopropane to high molecular weight polymers at room temperature.

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(23) For phenylacetylene, using monomer to catalyst ratio of 100:1, polymer of average molecular weight ~10 000 was obtained in acetonitrile. Significantly, poly(phenylacetylene) thus isolated has one of the highest molecular weights recorded so far.[24]

(24) For other synthetic routes to high molecular weight poly(phenylacetylene), see (a) T. J. Katz and S. J. Lee, *J. Am. Chem. Soc.*, **102**, 422 (1980); (b) F. R. Navarro and M. F. Farona, *J. Polym. Sci., Polym. Chem.*, **14**, 2335 (1976); (c) T. Masuda, N. Sasaki, and T. Higashimura, *Macromolecules*, **8**, 717 (1975).

Planar, Pleated, and Saddle-Shaped Structures of the Phthalocyanine Dianion in Two Novel Multidentate Oxygen-Donor Complexes of Dipotassium Phthalocyanine

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The phthalocyanine macrocycle is most often found in the planar conformation and is generally presumed to be a very rigid system.[1] Although substantial nonplanar conformations of the macrocycle are known,[2] the potential flexibility of the ring is not widely appreciated despite its similarity to the flexible and isoelectronic porphyrin ring system.[3] In this paper we report on the flexibility of the phthalocyanine dianion as observed from the x-ray structural analysis of two novel, multidentate oxygen-donor complexes of dipotassium phthalocyanine, $K_2Pc(18\text{-crown-6})_2\cdot$benzene$(^3/_2)$ (**1**) and $K_2Pc(\text{diglyme})_2$ (**2**). Such species are readily prepared as a consequence of the previously unknown solubility of the dialkali metal phthalocyanines in common oxygen-donor solvents or solvents containing oxygen-donor ligands.[4,5]

Crystals of **1** were obtained from benzene containing K_2Pc[6] and excess 18-crown-6. X-ray analysis was performed on a green prism (0.25 × 0.25 × 0.30 mm) mounted in a glass capillary.[7]

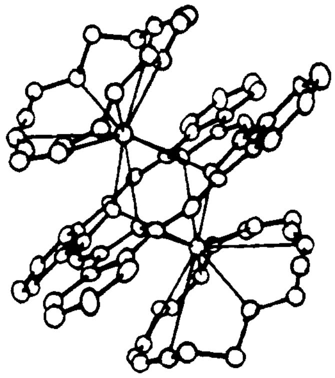

Figure 1. Perspective view of the trimacrocyclic $K_2Pc(18\text{-crown-6})_2$ complex.

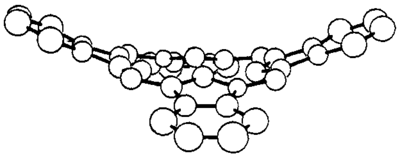

Figure 2. Saddle-shaped phthalocyanine dianion in $K_2Pc(\text{diglyme})_2$.

Table I. Phthalocyanine Interatomic Distances (Å)

bond	type	**1**, mean value	**2**, mean value
N–N	isoindole	2.782 (7)[a]	2.80 (1)
C–N	isoindole	1.362 (5)	1.36 (2)
C–N	azamethine	1.340 (1)	1.37 (2)
Cα–Cβ	pyrrole	1.473 (9)	1.46 (2)
C–C	benzene	1.414 (6)	1.41 (1)
N–K	all	2.91 (2)	2.78 (4)
O–K	all	3.39 (7)	3.03 (5)

[a] Values in parentheses are estimated variances of the mean calculated as $(\Sigma(x - \bar{x})^2/[n(n-1)])^{1/2}$.

Compound **1** crystallizes as the trimacrocyclic sandwich complex illustrated in Figure 1. The unit cell contains two crystallographically independent monomers and three molecules of benzene. Pc is flanked by two potassium ions and two molecules of crown ether.

Bond distances (Table I) and angles in the dianions are similar to those found in the coordinated ligand.[8] The conformation of the two independent centrosymmetric dianions differs, with one ion being nearly planar.[9] In the other ion (Figure 1) the relative upward and downward tilting of the isoindole rings out of the inner 4-N least-squares plane gives the dianion a pleated conformation similar to that observed in $Sn(Pc)Cl_2$.[10] The tilting of the rings takes place by rotation about the C–N azamethine bonds and leads to maximum carbon atom displacements from the 4-N least-squares plane of ±1.265 (5) Å.[11] The marked difference in conformation between the dianions shows the flexibility of the phthalocyanine system and correlates with the different packing environments of the dianions.

As a crown ether complex, **1** is atypical in that potassium is external to the 18-crown-6 cavity.[12] The location of the K^+ ions (1.6 Å from the mean O plane) clearly indicates competitive coordination between the ligands with the N–K and O–K distances (Table I) suggesting a high degree of structural integrity for the K_2Pc core. Significant changes in conformation from that of the

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(1) See, for instance: Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Oxford University Press: London, 1962; Chapter 25. See also ref 8.

(2) See, for example, ref 10, 17, and 18. See also: Gieren, A.; Hoppe, W. *J. Chem. Soc., Chem. Commun.* **1971**, 413. Ukei, K. *Acta Crystollogr., Sect. B* **1973**, *B29*, 2290.

(3) See, for instance: Fleischer, E. B. *Acc. Chem. Res.* **1970**, *3*, 105. Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 1938. Silvers, S.; Tulinsky, A. *Ibid.* **1964**, *86*, 927. Also see ref 15.

(4) 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.

(5) Ziolo, R. F.; Günther, W. H. H. "Abstracts of Papers", American Chemical Society/Chemical of Japan Chemical Congress, Honolulu, HI, April 1979; American Chemical Society: Washington, DC, 1979; INOR 62.

(6) Moser, F. H.; Thomas, A. L. *ACS Monogr.* **1963**, *No. 157*, 112.

(7) Space group $P\bar{1}$; $a = 11.878$ (5), $b = 20.915$ (8), $c = 13.056$ (4) Å; $\alpha = 90.93$ (3), $\beta = 97.36$ (3), $\gamma = 90.64$ (3)°; $Z = 2$ (23 °C). A total of 7736 reflections were measured (CAD 4) for $\theta < 45°$, of which 3109 were considered to be observed. Full matrix least-squares refinement (559 variables) produced agreement factors of $R = 0.117$ and $R_w = 0.142$. The crown ether rings were found to be disordered and were approximated, therefore, by placing the atoms at the locations of highest electron density from a ΔF map. This approximation gave rise to a featureless final ΔF map.

(8) Boucher, L. J. in "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed., Plenum Press: New York, 1979, Chapter 7.

(9) Distances of the Pc atoms from the linear 4-N least-squares plane reach ±0.232 Å, while the dihedral angle between neighboring isoindole least-squares planes is 3.1°. Dihedral angles between the 4-N plane and the isoindole rings are 1.6 and 2.1°.

(10) Rogers, D.; Osborn, R. S. *J. Chem. Soc., Chem. Commun.* **1971**, 840.

(11) Dihedral angles between isoindole rings and the 4-N plane are 5.2 and 15.9°; between isoindole neighbors, 12.6°. A slight sideways tilt (ruffle) occurs in the 5.2° ring.

(12) Dalley, N. K. In "Synthetic Multidentate Macrocyclic Compounds"; Izatt, R. M. and Christensen, J. J., Eds.; Academic Press: New York, 1978; Chapter 4.

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highly symmetrical cyclic polyether compound are observed for both independent ethers as a result of the ligand competition.

Crystals of **2** were obtained by cooling a hot solution of K_2Pc[6] in diglyme (DG). Crystal structure analysis was performed on a green prism (0.25 × 0.25 × 0.35 mm) mounted in a glass capillary.[13]

The structure of **2** mimics that of **1** with two DG molecules forming a quasi-macrocyclic oxygen-donor ligand and taking the place of one crown ether molecule. In contrast to **1**, however, **2** consists of infinite stacks of $KPcK(DG)_2$ units with the DG_2 quasi-macrocycles flanked by two potassium ions approximately 1.8 Å from the mean oxygen plane. While the distance between the mean nitrogen and oxygen planes is the same in **1** and **2**, the shorter N–K and O–K distances in **2** reflect less competition for coordination by the DG_2 ligand and its better adaptability to the K_2Pc template.

The most striking feature of **2** is the remarkable conformation of the dianion in which nearly planar isoindole rings tilt alternately up and down to give rise to the saddle-shaped phthalocyanine illustrated in Figure 2. The opposite isoindole rings make angles of 135.5 and 151.6° with respect to each other, while the dihedral angles between neighboring rings range from 25.3 to 27.1°. As in **1**, the nonplanar conformation is achieved by rotation of the isoindole rings about the C–N(aza) bonds. The maximum carbon atom displacements from the 4-N plane are ±1.68 Å while the four C–N(aza)C–N(iso) torsion angles (0° in planar systems) are −14.9, −15.0, 12.6, and 17.4°. As a result, the inner core geometry of the saddle configured dianion is a flattened disphenoid having isoindole N–N distances equal to those in **1**. The dianion in $K_2Pc(DG)_2$ exhibits the greatest distortion from planarity found in any phthalocyanine system.

Although the saddle-shaped conformation is known in other macrocyclic systems,[14] the present conformation bears a remarkable resemblance to the saddle-shaped core of the porphyrin diacids studied by Stone and Fleischer.[15] In those systems, however, steric and repulsive forces are the predominant influencing factors. Since steric factors are absent in **2**, the saddle-shaped conformation of the dianion is attributed predominantly to crystal packing effects. Inner core repulsive forces, if present, are weak as evidenced by the existence of the planar dianion in **1** and $K_2Pc(DMF)_4$.[16]

The variation in conformation of the dianion from nearly planar in **1** and $K_2Pc(DMF)_4$,[16] through the pleated to saddle-shaped conformation in **2**, demonstrates the heretofore unknown flexibility of the Pc system. While the degree of flexibility is novel, the mode is not, since the substantial nonplanar conformation of the metallophthalocyanines (SnPc,[17] VOPc,[18] and others) also occur principally through rotations about the C–N(aza) bonds. In these cases, however, metal coordination properties usually dominate the ring conformation. An important inference regarding the metallophthalocyanines is that the planarity of the MPc systems is not due to any inherent planar rigidity of the Pc macrocycle. This conclusion amplifies the criticality of "hole size" in determining the difference in degree of distortion from planarity between the metallophthalocyanines and their porphyrin analogues.

Complexes in this new series of compounds provide much needed sources of soluble phthalocyanine[4,5,16] and offer potential for use as starting materials in the synthesis of new and known derivatives.

The solution absorption spectra of **1** and **2** exhibit the single MPc-like Q band associated with a D_{4h} symmetry of the phthalocyanine ring and suggest that species similar to **1** and **2** exist in solution. The spectra resemble those of basic solutions of H_2Pc,[19] $(NH_4)_2Pc$ and Li_2Pc in Me_2SO[20] and *N*,*N*-dimethylacetamide,[21] respectively, and K_2Pc in DMF.[16]

Supplementary Material Available: Positional and thermal parameters and observed and calculated structure factors for **1** and **2** (22 pages). Ordering information is given on any current masthead page.

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(13) Space group $C2/c$; a = 24.734 (8), b = 7.579 (5), c = 22.165 (5) Å; β = 112.15 (2)°, Z = 4 (23 °C). A total of 2603 reflections were measured for θ < 45°, of which 664 were considered to be observed. The final agreement factors are R = 0.085 and R_w = 0.092. The positions of the diglyme molecules are approximate due to disorder. Attempts to refine various disorder models were unsuccessful because of the limited number of observed data.

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

Wavelength and Solvent Effects on Ionic Photodissociation of Charge-Transfer Complexes. The Hexamethyl(Dewar benzene) System

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Photoisomerization reactions driven by irradiation of charge-transfer complexes have been only recently reported.[1] Our study of the rearrangement of hexamethyl(Dewar benzene) (HMDB) exciplexes[2] has been extended to the investigation of photochemistry of ground-state (CT) complexes of HMDB. We have observed again the unusual adiabatic photoisomerization[2,3] of HMDB in nonpolar solvents. For rearrangement in more polar media we have obtained another novel result, a dependence of photoisomerization quantum yield on excitation wavelength. A recent review[4] shows that such wavelength effects remain relatively rare in solution photochemistry. In the present case we ascribe the quantum yield dependence to photoionization from upper vibrational levels of the first excited CT state.[5]

Red-shifted absorption bands were obtained on combination of HMDB or hexamethylbenzene (HMB) with electron acceptors, fumaronitrile (FUM) and diethyl-1,2-dicyanofumarate (DDF),[6] as shown in Figure 1. The new structureless bands (λ_{max}, Table I) were assigned to CT transitions[8] involving complexes of the HMDB and HMB electron donors.[9,11] Irradiation of the complex

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(9) Oxidation potentials for HMDB and HMB are 1.58 and 1.62 V vs. SCE, respectively.[10]

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