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Has Monopotassium Phthalocyanine, KPc, Been Synthesized?

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A recent publication described the synthesis and characterization of monopotassium phthalocyanine, KPc. A reevaluation of the original EPR, magnetic susceptibility, and X-ray diffraction data, along with a comparison to the powder diffraction pattern of an authentic sample of Na_2Pc, indicates that the material was actually Na_2Pc.

This investigation was prompted by a recent report[1] of the synthesis of monopotassium phthalocyanine, KPc, by the reaction of copper phthalocyanine and elemental potassium in the vapor phase (eq 1).

$$\mathrm{CuPc} + \mathrm{K}^0 \rightarrow \mathrm{KPc} + \mathrm{Cu}^0 \qquad (1)$$

KPc is an oxidized species in which the oxidation state of the phthalocyanine ring system is 1− rather than the oxidation state of 2− that occurs in the vast majority of phthalocyanine and porphyrin complexes. The syntheses of other oxidized phthalocyanines and porphyrins, such as monolithium phthalocyanine (LiPc)[2−4] and monolithium tetraphenylporphyrin (LiTPP),[5] begin with a phthalocyanine or porphyrin in its normal oxidation state (Li_2Pc and Li_2TPP, respectively). The complex is then oxidized by one electron, either electrochemically or with a chemical oxidizing agent. The preparation of KPc by the reaction of a normal-valent phthalocyanine complex with a strong *reducing* agent was therefore quite surprising.

The reported magnetic susceptibility and EPR spectrum of KPc are more consistent with a diamagnetic closed-shell species such as K_2Pc rather than the radical KPc. The compound had a magnetic susceptibility that was estimated to correspond to 0.07 spin-$^1/_2$ centers per molecule. From variable-temperature EPR measurements, a spin density of 5×10^{-4} per molecule was determined. Both are consistent with a diamagnetic material with traces of a paramagnetic impurity. Materials that consist entirely of open-shell molecules are not usually diamagnetic.

The solid-state structure of the material, determined by synchrotron X-ray powder diffraction,[1] is shown in Figure 1. Full occupation of the metal atom sites corresponds to a stoichiometry of K_2Pc. However, the occupancy of the potassium sites was allowed to vary, and the optimal agreement with the diffraction data occurred with an occupancy of 0.54, corresponding to 1.08 potassium atoms per Pc ring. On that basis, it was proposed that the compound was KPc and that the structure was the one shown with random 0.5 occupancy of the potassium sites.

A close examination of the metal−nitrogen bond lengths in the compound leads to a possible alternative formulation. The three symmetry-inequivalent M−N bond lengths are 2.44(1), 2.44(1), and 2.45(1) Å. They can be compared to K−N and Na−N distances in previously reported potassium and sodium phthalocyanines and porphyrins, given in Table 1. The K−N distances range from 2.74 to 2.91 Å, while the Na−N distances range from 2.41 to 2.51 Å. Thus, it seems highly likely that the metal present in the compound in question is sodium rather than potassium.

Formulation of the compound as Na_2Pc is fully consistent with all of the reported data. The synthesis (eq 2), which somehow incorporated sodium rather than potassium metal, yields a compound that is in a reasonable oxidation state (if there is not an excess of alkali metal present). A product

$$\mathrm{CuPc} + 2\mathrm{Na}^0 \rightarrow \mathrm{Na_2Pc} + \mathrm{Cu}^0 \qquad (2)$$

consisting of diamagnetic Na_2Pc and traces of paramagnetic CuPc or Na_3Pc would have the small magnetic susceptibility and weak EPR signal that were observed. The crystal structure is consistent with the metal atom sites being fully occupied by sodium. Modeling those sites as potassium with partial occupancy would lead to an occupancy of just over 0.5, as was observed. Finally, as mentioned above, the M−N distances are consistent with sodium and inconsistent with potassium.

We attempted the reactions of CuPc with both sodium and potassium under the conditions described in the original report,[1] but we had some difficulty in obtaining pure

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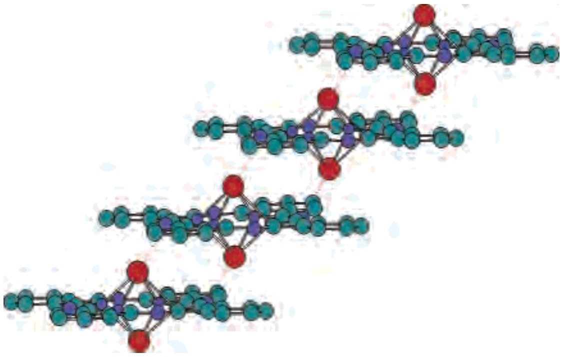

Figure 1. Schematic view of the structure of "KPc" determined by synchrotron X-ray powder diffraction.[1] Hydrogen atoms are not shown.

Table 1. M−N Bond Distances in Previously Reported Sodium and Potassium Phthalocyanines and Porphyrins[a]

compound	M−N distances (Å)
$Na_2Pc(OPPh_3)_2$[6]	2.409(2), 2.438(2)
$Na_2OEP(THF)_4$[7]	2.452(2), 2.469(2), 2.508(2), 2.479(2)
K_2Pc(18-crown-6)$_2$[8]	2.91(2)
K_2Pc(diglyme)$_2$[8]	2.78(4)
$K_2Pc(DMF)_4$[9]	2.777(2), 2.781(2), 2.782(2), 2.792(2)
K_2OEP(pyridine)$_4$[7]	2.740(7), 2,757(7), 2.794(6), 2.790(8)

[a] OEP = octaethylporphyrin; Ph = phenyl.

materials by that method. Therefore, we instead synthesized Na_2Pc and K_2Pc by the Linstead procedure.[10] We expected the synthesis to produce mainly unsolvated Na_2Pc and K_2Pc. The reaction of 1,2-dicyanobenzene with the alkali metal pentoxide in refluxing *n*-pentanol yields a precipitate of the alkali metal phthalocyanine, which was filtered, washed with ether, and held under vacuum for 1 h. ^{1}H NMR and elemental analysis indicated the presence of about 0.5 equiv of pentanol per Na_2Pc.[11] It is most likely that the pentanol is present as occluded or surface solvent that was incompletely removed in the washing or that there is both amorphous Na_2Pc(pentanol)$_x$ and crystalline, unsolvated Na_2Pc present in the product (as indicated by X-ray diffraction below).

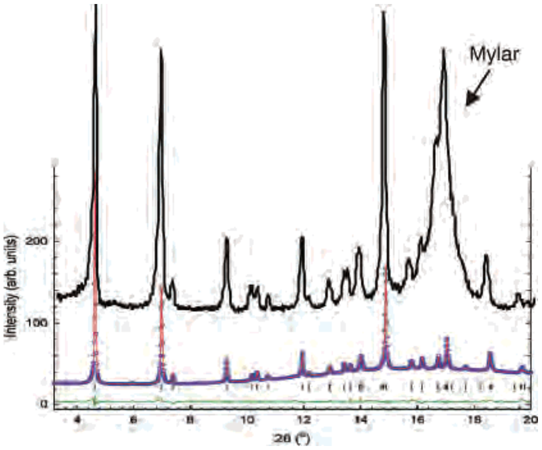

Figure 2. X-ray powder diffraction patterns of Na_2Pc (top) and "KPc" (bottom). The broad peak at $2\theta = 16.8°$ is due to a protective Mylar film.

The X-ray powder diffraction patterns of Na_2Pc and K_2Pc prepared by the Linstead method have not been published. We found that both materials diffracted well and their powder diffraction patterns were significantly different, indicating that they are most likely not isomorphous (see the Supporting Information for the powder diffraction pattern of K_2Pc). The diffraction pattern of Na_2Pc (adjusted to correspond to the X-ray wavelength of 1.0008 Å of the previous report) is shown in Figure 2, along with the diffraction pattern reported for "KPc". The diffraction patterns match well, and it seems clear that the previously reported material is, in fact, Na_2Pc.

There are several examples in the literature of X-ray crystal structure solutions wherein the identity of one or more atoms was misassigned and the structure solution and refinement were, nevertheless, often well-behaved.[12] While ref 12 is mainly concerned with the purported phenomenon of bond-stretch isomerism, it also reviews examples of X-ray structure solutions that were later found to contain misidentified atoms.

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Supporting Information Available: Powder diffraction patterns of Na_2Pc and K_2Pc. This material is available free of charge via the Internet at http://pub.acs.org.

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(11) ^{1}H NMR (DMSO-d_6): δ 9.26 (dd, 8H), 8.02 (dd, 8H), and pentanol resonances. Anal. Found (calcd) for $Na_2Pc\cdot0.5$pentanol$\cdot0.5H_2O$ ($C_{34.5}H_{23}N_8Na_2O$): C, 67.45 (67.75); H, 3.38 (3.79); N, 17.99 (18.32); Na, 8.00 (7.52).

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