Molecular Solid Solution of Tetraphenyl-porphin and Silver Tetraphenylporphin

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Molecular solid solutions have received surprisingly little attention in the past, yet we must study them before we can hope to understand why their natural occurrence appears to be so much more limited than that of their inorganic counterparts. Examples might conceivably have escaped attention because single-crystal X-ray work has not been carried out on "impure" molecular crystals. Porphyrins are well suited for solid solution study. Because of their biological importance, their molecular structure is known in detail from numerous refined crystal structures that have appeared in recent years.[1] Methods of porphyrin synthesis have been perfected over many years in the laboratory of Professor A. H. Corwin at The Johns Hopkins University.

The triclinic modifications of tetraphenylporphyrin (TPP) and silver tetraphenylporphyrin (AgTPP) are isostructural, in space group P$\bar{1}$, and with one molecule per cell. Refined structure determinations[2] showed them to be similar enough for complete solid solution to be expected.

The end members as well as five intermediate compositions were synthesized as follows. The TPP was synthesized from pyrrole and benzaldehyde by a slight modification[3] of the method of Ball, Dorough, and Calvin.[4] As to AgTPP, it was prepared by heating TPP with an excess of $AgNO_3$ in pyridine on a steam bath for about

30 minutes.[5] The pyridine is removed on a rotary evaporator; the AgTPP is dissolved in chloroform, passed over a short column of alumina, and crystallized from chloroform-methanol. The solubilities of the end members in ethylene dichloride were measured. AgTPP is about 1.5 times as soluble as TPP, 6.59 against 4.39 mM/l.

The solid solutions are obtained in this way: Portions of TPP and AgTPP are weighed on a micro balance and placed in a test-tube. Ethylene dichloride (Fisher "Certified Reagent") is added in sufficient quantity to dissolve all the porphyrin mixture. This solution (∼ 15 ml) is filtered through Whatman No. 1 filter paper into a 28×100 mm test-tube, which is then placed in a glass-stoppered jar with ∼ 50 ml of methanol. The jar is put in a dark place at room temperature. The methanol slowly distills into the ethylene dichloride solution, and the porphyrin mixture crystallizes. No attempt was made to exclude air or moisture.

For any composition the crystals coming from a first batch are indistinguishable from those of later batches of crystallization as evidenced by the constancy of X-ray intensities on Weissenberg photographs (see below). This is, of course, to be expected for the pure end members. For intermediate compositions it is surprising.

Absorption spectra of samples of the solution were taken on a Beckman DK-2 recording spectrometer. The spectra of TPP and AgTPP differ sufficiently to be readily told apart; in the spectra of intermediate compositions the peaks of the two distinct molecular species are not resolved (for reasons not yet understood), and an intermediate type of pattern is obtained. In the course of crystallization the AgTPP/TPP ratio in the mother liquor increases. All crystals when redissolved in dichloroethylene give spectra similar to those of the original mother liquor.

The triclinic phase only is obtained for compositions of 0, 74.88, 85.85, and 100 mole- % AgTPP. A few small tetragonal dipyramids (101) appear, in addition to the triclinic crystals, when compositions of 8.84, 35.12, and 53.35 mole- % AgTPP are crystallized. Since their cell dimensions change slightly with composition (Table 1), they must contain either the two kinds of molecules

(TPP and AgTPP) or varying amounts of solvent (chloroform, methanol, or water). Conceivably both effects may be present. Their Laue group is $4/m$; the lattice is body centered, so $I4/m$, $I\bar{4}$, and $I4$ are possible space groups. A test for piezoelectricity kindly performed for us by Dr. D. Appleman of the U.S. Geological Survey was negative. The morphology indicates $I4/m$, compatible with the test. The molecular volume, obtained from the triclinic crystals (Table 2), leads to two molecules in the tetragonal cell. The required molecular symmetry is therefore $4/m$. Fleischer,

TABLE 1   Tetragonal Crystal Data

Sample description	D2	D1	D3	$ZnTPP \cdot 2H_2O$[a]
Mole-% AgTPP	8.84	35.12	53.35	——
a, Å	13.37	13.37	13.42	13.44
c, Å	9.73	9.70	9.72	9.715
c/a	0.727_7	0.725_5	0.724_3	0.722_8
Dx (anhydrous)	1.19	1.25	1.27	
Dx (monohydrate)	1.23	1.28	1.31	
Dm	——	——	1.29	

Lengths known to $\pm 0.3\%$.

[a] Fleischer, E. B., Miller, C. K., and Webb, L. E., *J. Am. Chem. Soc.* 86, 2342 (1964).

Miller, and Webb[6] describe crystals of $ZnTPP \cdot 2H_2O$, which are almost identical with ours (Table 1). Their space group is $I4/m$; their structure is known but has not yet been described in detail. We know, however, that the phenyl rings make an angle of $90°$ with the plane of the porphyrin ring, whereas in the triclinic phase the same angle is about $62°$. Thus two very different looking molecules crystallize from one and the same solution.

The habit of the triclinic crystals varies from acicular to short prismatic along a but is not a function of the composition. The large faces, in order of decreasing importance, are designated (010), $(0\bar{k}1)$, (001), and the small terminal face (100). This indexing,

which was used by Tulinsky [7] for the silver end member, leads to cells (Table 2) in which $(0\bar{k}1)$ becomes $(0\bar{1}1)$. They can be transformed to the Bravais reduced cells by means of the matrix $\bar{1}\bar{1}0/00\bar{1}/100$.) Our choice of axes has the advantage that a single mounting of the crystal can be used to take the Weissenberg and precession photographs that are needed for the cell determination.

TABLE 2   Triclinic Crystal Data[a]

Sample description	TPP	D2	D1	D3	D4	D5	AgTPP
Mole-% AgTPP	0	8.84	35.12	53.35	74.88	85.85	100
a, Å	6.45	6.45	6.45	6.45	6.40	6.39	6.37
b, Å	11.19	11.19	11.20	11.22	11.22	11.23	11.23
c, Å	12.43	12.43	12.43	12.43	12.45	12.47	12.47
α	100°50′	101°12′	101°15′	101°0′	100°55′	100°55′	100°50′
β	80°48′	80°55′	81°10′	81°30′	81°50′	82°0′	82°23′
γ	113°15′	113°15′	113°10′	113°10′	113°0′	113°1′	113°1′
V, Å³	806 ± 6	805 ± 6	806 ± 6	809 ± 6	804 ± 6	807 ± 6	805 ± 6
Dx	1.27	1.29	1.34	1.38	1.43	1.45	1.49
Dm	1.27	1.29	1.36	1.36	1.43	1.46	1.48
I(004)	7	7	6	6	2	0	3
I(005)	4	3	6	7	6	7	8
I(006)	6	5	0	1	0	5	6

[a] Lengths to ± 0.3%, angles to ± 10′. Measured densities to ± 0.01. Intensities are visual estimates on a-axis, zero-layer Weissenberg films taken with CuKα radiation. They are based on a scale of 10 (0 = unobserved, 10 = maximum blackening observable).

For a-axis Weissenberg data (see intensities, Table 2), the main zone is adjusted in prism position on the two-circle goniometer. (The α^* angle can be measured between (010) and (001).) For precession work (100) is centered in polar position, involving a change of about 24° from the previous setting.

The changes in cell dimensions (Table 2) across the complete solid solution are insignificant except for a 1°35′ increment of the β angle. The cell volume remains constant at 806 ± 6 Å³, so that the calculated density is proportional to the molecular weight.

Densities were very difficult to obtain experimentally because the crystals resist wetting. However, after many unsuccessful trials, the following procedure gave results. A solution of 80 vol.-% ethanol–20% water is saturated with LiBr and filtered. The crystals are covered with about 2 cc of this solution in a tapered centrifuge tube which is degassed to remove air bubbles from the crystals. A nearly saturated aqueous solution of LiBr ($Dm \sim 1.58$ g/cc) is then added dropwise to the centrifuge tube and stirred. The tube is then centrifuged and one observes whether the crystals sink, rise, or float. When the density of the solution is the same as that of the crystals, a 2 cc sample of it is weighed in a volumetric flask. The reproducibility of the measurement is of the order of ± 0.002 g/cc.

Even though there is complete solid solution between TPP and AgTPP, its existence would go undetected if only powder patterns were taken. The crystals are so soft that it is difficult to obtain a good powder, and the powder pattern shows broad diffuse halos. Even the patterns of the end members were indistinguishable. The intensities of reflections on single-crystal patterns, on the other hand, change so drastically with composition that it is possible to estimate the composition from selected intensities to about $\pm 3\%$. The silver atoms, which are located at cell origins, always add their maximum positive contribution to the structure factors.

The question now arises: Is there any ordering in the replacement of one type of molecule by the other? Determination of short-range order coefficients by diffuse X-ray studies would be very difficult, so another approach was tried. J. A. Leone of the Chemistry Department at The Johns Hopkins University studied the electron spin resonance spectra of our crystals. Even the one of lowest silver concentration, 8.84 mole-% AgTPP, showed such pronounced broadening of the hyperfine lines (owing to the silver–silver interactions in the crystal structure) that the data could not be used in quantitative calculations. Leone grew a crystal composed of 0.73 mole-% AgTPP and 99.27 mole-% TPP, which was $0.1 \times 0.5 \times 2$ mm in size. Its spectrum shows no line broadening. Crystals with compositions ranging between 1 and 8 mole-%

AgTPP should give interpretable results, leading to information on the random nature of substitution of the paramagnetic AgTPP molecules.

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