# Crystal Structure of a (Tetraphenylporphine)silver–Tetraphenylporphine Molecular Solid Solution

By **M. L. Schneider,*** Department of Geological Sciences, McGill University, Montreal, Quebec, Canada

The tetragonal molecular solid solution $(AgL)_x(L)_{1-x}$ (L = tetraphenylporphine, $C_{44}H_{30}N_4$), for $x = 0{\cdot}54$, has cell dimensions $a = 13{\cdot}384$, $c = 9{\cdot}717$ Å; $Z = 2$, space-group $I4/m$. The structure was solved from diffractometer data and refined by least-squares to $R$ 0·085 for 1221 observed reflections. In $(AgL)_{0{\cdot}54}(L_{1/2}L'_{1/2})_{0{\cdot}46}$ the free base molecules are disordered in two orientations, L and L′, related to each other by a 90° rotation about an axis passing through silver atom and perpendicular to the porphine ring. This unsolvated, metastable phase has a large volume per molecule and represents <1% of the total yield of crystals, most of which are triclinic ($P\bar{1}$). The high residual, the low site-occupancy of the silver atom (0·54), and some apparently short C–H bond lengths may be produced by the effects of the positional disorder in the crystal and the molecular solid solution.

INITIAL work[1] on the $(AgL)_x(L)_{1-x}$ (L = tetraphenylporphine) molecular solid solution showed the presence of two phases: one, a complete solution series which is triclinic (space-group $P\bar{1}$) with a structure type analogous to that of the end members, which were determined by Silvers and Tulinsky;[2,3] the other, with symmetry $I4/m$, a limited solution series ($0{\cdot}08 \leqslant x \leqslant 0{\cdot}54$), with the same space-group and similar cell dimensions[4,5] as the solvated $ZnL,H_2O$. This latter phase is unlike the tetragonal phase of the free base,[6] or other unsolvated

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[1] G. Donnay and C. B. Storm, *Mol. Crystals*, 1967, **2**, 287.

[2] S. J. Silvers and A. Tulinsky, *J. Amer. Chem. Soc.*, 1967, **89**, 3331.

[3] S. J. Silvers and A. Tulinsky, personal communication.

[4] E. Fleischer, C. K. Miller, and L. E. Webb, *J. Amer. Chem. Soc.*, 1964, **86**, 2342.

[5] M. D. Glick, G. H. Cohen, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1964, **89**, 1938.

[6] M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1964, **86**, 1938.

metal tetraphenylporphine complexes,[4] with the space-group $I\bar{4}2d$. In order to obtain information about the effect that a molecular solid solution has on *X*-ray diffraction data, and to ascertain whether the crystal is solvated, the structure determination of a tetragonal crystal was undertaken.

## EXPERIMENTAL

The crystal used was one of those synthesised and described previously [1] (tetragonal sample *D*3 with starting composition $x = 0{\cdot}5335$).

*Crystal Data*.—$(AgC_{44}H_{28}N_4)_{0{\cdot}54}(C_{44}H_{30}N_4)_{0{\cdot}46}$, $M = 671{\cdot}22$, Tetragonal, $a = 13{\cdot}384$, $c = 9{\cdot}717(5)$ Å, $U = 1740{\cdot}5$ Å$^3$, $D_m = 1{\cdot}29$, $Z = 2$, $D_c = 1{\cdot}28$, $F(000) = 692{\cdot}02$. Space-group $I4/m$. Mo-$K_\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo-}K_\alpha) = 3{\cdot}63$ cm$^{-1}$. The crystal morphology is $4/m$; $\{101\}$.

Cell dimensions were obtained from 24 diffractometer measurements. A crystal of size $0{\cdot}15 \times 0{\cdot}15 \times 0{\cdot}25$ mm (along $a^*$, $b^*$, and $c^*$, respectively) was used for data collection on a Picker FACS I four-circle diffractometer with a graphite monochromator by the $\theta$—$2\theta$ scan method. Intensities for reflections $hkl$ were collected for $0° < \theta < 30°$ and $\bar{h}\bar{k}l$ for $0° < \theta < 15°$ [$(\sin\theta/\lambda)_{\max} = 0{\cdot}7132$ Å$^{-1}$]. The reflections $hkl$ and $\bar{h}\bar{k}l$ were averaged with the agreement index $\Sigma|F(hkl)_{av} - F(hkl)_{indiv}|/\Sigma|F(hkl)_{av}| = 0{\cdot}004$. 1368 Reflections were obtained of which 147 were considered unobserved ($|F| < 3\sigma$) and omitted from the refinement. Lorentz and polarization corrections were applied.

*Solution and Refinement of the Structure*.—A set of trial co-ordinates based on the ZnL,$H_2O$ structure, excluding the water molecule, was used in the calculation of structure-factors. $F_o(hkl)$ was seen to be related to $F_c(hkl)$ rather than $F_c(hkl)$ indicating that the $x$ and $y$ co-ordinates should be interchanged. A structure-factor calculation based on the new set of parameters gave better agreement. Full-matrix least-squares refinement was then commenced (14 reflections/variable), observed hydrogen atoms (located by a difference Fourier synthesis) being refined isotropically and non-hydrogen atoms anisotropically. A population parameter was refined for silver. Weights were assigned according to the scheme $\sqrt{w} = \{1 + [(|F| - 20)/10]^2\}^{-\frac{1}{2}}$. The final $R$ was 0·085. Scattering factors were taken from ref. 7, for hydrogen atoms, and from ref. 8 for non-hydrogen atoms, with inclusion of the real and imaginary parts ($\Delta f'$ and $\Delta f''$) of the anomalous dispersion for silver. Programs used are listed in refs. 9 and 10.

Observed and calculated structure-factors are noted in Supplementary Publication No. SUP 20340 (9 pp., 1 microfiche).[*] Final atomic and thermal parameters are listed in Table 1 and bond lengths and angles in Tables 2 and 3.

TABLE 1

Final atomic and thermal parameters

| Atom | $x/a$ | $y/b$ | $z/c$ | $10^3U_{11}$ † | $10^3U_{22}$ | $10^3U_{33}$ | $10^3U_{12}$ | $10^3U_{13}$ | $10^3U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ag * | 0 | 0 | 0 | 281(4) ‡ | 281(4) | 507(9) | 0 | 0 | 0 |
| N | −0·0363(3) | 0·1498(3) | 0 | 37(2) | 39(2) | 75(3) | 1(2) | 0 | 0 |
| C(1) | −0·1312(4) | 0·1896(4) | 0 | 41(3) | 40(3) | 66(4) | 3(2) | 0 | 0 |
| C(2) | −0·1232(5) | 0·2970(4) | 0 | 45(3) | 39(3) | 86(5) | 8(2) | 0 | 0 |
| C(3) | −0·0256(5) | 0·3204(4) | 0 | 49(3) | 37(3) | 92(5) | 0(2) | 0 | 0 |
| C(4) | 0·0306(4) | 0·2284(4) | 0 | 40(3) | 37(2) | 76(4) | −3(2) | 0 | 0 |
| C(5) | 0·1344(4) | 0·2201(4) | 0 | 45(3) | 37(2) | 64(4) | −1(2) | 0 | 0 |
| C(6) | 0·1934(4) | 0·3165(4) | 0 | 41(3) | 39(3) | 75(4) | −2(2) | 0 | 0 |
| C(7) | 0·2197(4) | 0·3610(4) | −0·1228(6) | 86(4) | 59(3) | 72(3) | −18(2) | −2(3) | 5(3) |
| C(8) | 0·2739(4) | 0·4496(4) | −0·1242(7) | 84(4) | 60(3) | 97(4) | −18(3) | 6(3) | 17(3) |
| C(9) | 0·3001(6) | 0·4925(6) | 0 | 47(4) | 42(3) | 142(9) | 0(3) | 0 | 0 |
| | | | | $U_{iso}$/Å$^2$ | | | | | |
| H(2) | −0·1743(52) | 0·3361(52) | 0 | 0·08(2) | | | | | |
| H(3) | 0·0023(52) | 0·3764(53) | 0 | 0·08(2) | | | | | |
| H(7) | 0·2012(33) | 0·3320(33) | −0·2166(49) | 0·07(1) | | | | | |
| H(8) | 0·2928(38) | 0·4801(38) | −0·2260(58) | 0·09(2) | | | | | |
| H(9) | 0·3222(76) | 0·5226(72) | 0 | 0·12(5) | | | | | |

* Population 0·536(7). † In the form exp $2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)$. ‡ Ag thermal parameters × $10^4$.

TABLE 2

Principal bond lengths (Å) with standard deviations in parentheses

| | | | |
|---|---|---|---|
| Ag–N | 2·063(5) | C(6)–C(7) | 1·380(6) |
| N–C(1) | 1·377(7) | C(7)–C(8) | 1·390(7) |
| N–C(4) | 1·381(7) | C(2)–H(2) | 0·86(7) |
| C(1)–C(2) | 1·441(8) | C(8)–C(9) | 1·382(8) |
| C(2)–C(3) | 1·343(9) | C(3)–H(3) | 0·84(7) |
| C(3)–C(4) | 1·443(8) | C(7)–H(7) | 1·02(5) |
| C(4)–C(5) | 1·393(8) | C(8)–H(8) | 1·10(6) |
| C(5)–C(1) * | 1·402(8) | C(9)–H(9) | 0·50(10) |
| C(5)–C(6) | 1·512(8) | N–N * | 2·918(6) |

* Related by rotatory inversion $4^{-1}$.

TABLE 3

Principal angles (°)

| | | | |
|---|---|---|---|
| C(1)–N–C(4) | 107·7(4) | N–C(1)–C(5) * | 125·4(5) |
| N–C(1)–C(2) | 108·5(5) | N–C(4)–C(5) | 125·9(5) |
| C(1)–C(2)–C(3) | 107·7(5) | C(1) *–C(5) C(4) | 126·4(5) |
| C(2)–C(3)–C(4) | 108·0(5) | C(1) *–C(5)–C(6) * | 116·7(5) |
| C(3)–C(4)–N | 108·1(5) | C(4)–C(5)–C(6) | 116·9(5) |

* Related by rotatory inversion $4^{-1}$.

There were no significant peaks appearing on the final difference Fourier map, thus proving the crystal to be

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[*] For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[7] R. F. Stewart, personal communication.

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] J. M. Stewart, '*X*-Ray '63' System of Programs, Report TR 64 6, University of Maryland, 1970 version.

[10] P. Bird, personal communication (data reduction program).

unsolvated. Isotropic refinement in the space-groups $I4$ and $I\bar{4}$ was tried, but did not significantly decrease the residual, nor did a model in which the silver atom was displaced along $z$, out of the plane of the macrocyclic ring.

## RESULTS AND DISCUSSION

Because the averaged molecule is centred on a four-fold axis and lies on a mirror plane (Figure 1), its point symmetry must be $4/m$. From the atomic co-ordination in the refined structure, however, the molecular symmetry is $4/mmm$. The lowering of the point symmetry in the crystal is caused by a 13° rotation of the molecule about $z$, which maximizes the intermolecular contacts between the phenyl groups.

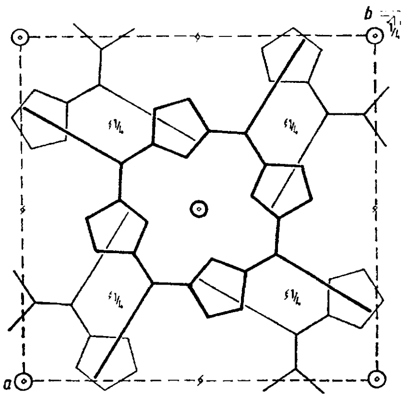

FIGURE 1 Projection of the cell contents on (001). Origin is in upper left-hand corner

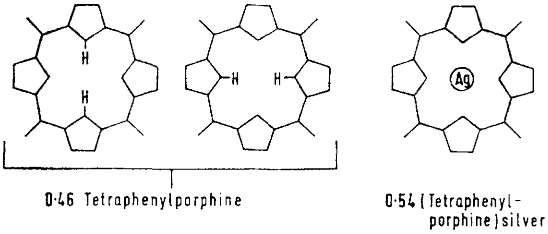

FIGURE 2 Components of $(AgL)_{0\cdot54}(L_{1/2}L'_{1/2})_{0\cdot46}$

$(AgL)_{0\cdot54}(L)_{0\cdot46}$ can be described as a substitution solid solution of the free base and the metal complex. If a four-fold symmetry axis is to operate rigorously, then the free base must have orientational disorder, since only two hydrogen atoms are bonded to the nitrogen atoms in the macrocyclic ring (Figure 2). As these hydrogen atoms were not observed on the difference Fourier map, and their effect on the symmetry of the weighted reciprocal space is small, this hypothesis cannot be proved experimentally by X-ray diffraction. The tetragonal crystal structure [6] of the pure base shows ' half-hydrogen atoms ', and is taken as a model for the disorder hypothesis. The solid solution now becomes: $(AgL)_{0\cdot54}(L_{1/2}L'_{1/2})_{0\cdot46}$, where L and L′ refer to the two orientations of the free base (Figure 2).

A comparison of the molecular volumes for different refined tetraphenylporphine and metal–tetraphenylporphine structures (Table 4) indicates that the $U/Z$ value of the present tetragonal phase is abnormally large for an unsolvated species, although it is similar to that of a solvated structure. Crystals of this phase are not always found in repeated preparations of the solid solution,[11] even under similar experimental conditions. When the tetragonal phase is present, its yield is <1% of the crystalline product. These experimental observations lead to the conclusion that this is a metastable phase. Inefficient packing of the molecules, with large molecular volumes, is a feature expected in such a case; the voids in this structure are located along the $z$ axis, where the solvent molecule has been observed in solvated structures.

TABLE 4

Space-groups and molecular volumes of related molecules (L = tetraphenylporphine)

| Molecule | Space-group | $Z$ | $U/Z$ |
|---|---|---|---|
| CuL [a] | $I\bar{4}2d$ | 4 | 788·3 Å$^3$ |
| PdL [a] | $I\bar{4}2d$ | 4 | 796·0 |
| L [b] | $I\bar{4}2d$ | 4 | 796·7 |
| L [c] | $P\bar{1}$ | 1 | 801·9 |
| AgL [d] | $P\bar{1}$ | 1 | 805·0 |
| $AgL_{0\cdot54}L_{0\cdot46}$ [e] | $I4/m$ | 2 | 870·2 |
| MgL,$H_2O$ * [f] | $I4/m$ | 2 | 876·9 |
| ZnL,$H_2O$ * [a,g] | $I4/m$ | 2 | 877·4 |
| ClFeL * [a,h] | $I4/m$ | 2 | 899·4 |

* Disordered Cl or $H_2O$.

[a] Ref. 4. [b] Ref. 6. [c] Ref. 2. [d] Refs. 1 and 3. [e] Present work. [f] R. Timkovich and A. Tulinsky, *J. Amer. Chem. Soc.*, 1969, **91**, 4430. [g] Ref. 5. [h] J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, 1967, **89**, 1992.

Had earlier work not shown that this phase is a solid solution, it would have been impossible to ascertain it from preliminary $X$-ray diffraction data or physical properties. The films show no diffuse reflections, and the agreement between symmetry-related reflections is good. An initial indication of the molecular solid solution is found in the low site-occupancy of the silver atom, a feature that could be missed if the molecule did not contain a heavy atom. The Fourier and difference Fourier maps give sharp peaks, showing only the expected anisotropic motion of the atoms. In the later stages of refinement, additional abnormalities appear: some C–H bond lengths (Table 2) are shorter than the normal value of 1·08 Å, and the final $R$, is much larger than would be expected from the quality of the data which showed an agreement index between symmetry-related reflections of 0·004.

The molecular geometry (Figure 3) is consistent with that of related structures, although this is the first example of the free base with the phenyl rings perpendicular to a planar macrocyclic ring. This configuration again demonstrates the flexibility of the geometry of the porphine molecule in different environments. In both forms of the free base the porphine ring is slightly puckered and the phenyl rings are tilted to the

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[11] C. B. Storm, personal communication.

mean plane of the macrocyclic system: 62° in the triclinic form, and 81·5° in the tetragonal form.

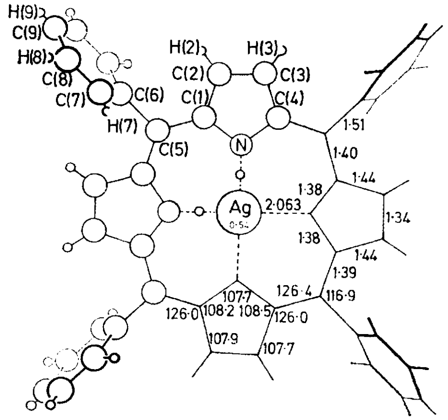

FIGURE 3 View of averaged molecule showing selected bond lengths, angles, and atomic site-occupancy; two hydrogen atoms are not shown.

In the preparation of the crystals,[1] the two components were dissolved together, but they crystallized in a molecular solid solution of the same composition as in the solvent. Although fractional crystallization is a standard method for the separation of compounds, the possibility of a molecular solid solution should be considered whenever the molecules have similar structures and solubilities. Failure to include this possibility in the analysis of $X$-ray diffraction data could remain unnoticed in a structural determination. In the case of spectral studies, the spectra, assumed to be due to a single compound, would contain bands of both molecules, and thus cause an incorrect interpretation. Elemental analysis and physical properties should indicate the purity of the compound, an approximately stoicheiometric solid solution could be erroneously interpreted as being a different molecule; in the present case this could be the chemically unreasonable $Ag(L)_2$.

I thank Professor Gabrielle Donnay for suggesting and discussing this problem, Professor J. D. H. Donnay for discussions of the symmetry problems and for a critical reading of this paper, Dr. C. B. Storm for providing the crystal employed in the study, Dr. P. Bird, for the use of his diffractometer, and the National Research Council of Canada for financial support.

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