Crystal Structure of Vanadyl Phthalocyanine, Phase II

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The crystal structure of the title compound has been determined from three-dimensional X-ray diffractometer data. Crystals are triclinic, space group $P\bar{1}$, with Z = 2 in a unit cell of dimensions a = 12.027(6), b = 12.571(8), c = 8.690(5) Å, α = 96.04(5), β = 94.80(5), and γ = 68.20(5)°. The structure was solved by direct and Fourier methods and refined by least-squares techniques to R (on F) = 0.062 for 3 042 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. The compound [VO(pc)] is molecular with point-group symmetry C_1 and is non-planar with all pc atoms below the isoindole nitrogen-atom plane. Vanadium has a five-co-ordinate square-pyramidal geometry and is 0.575(1) Å above the plane. The V–O distance is 1.580(3) Å; the mean V–N distance is 2.026(7) Å. The compound is composed of sheets of approximately parallel and overlapping [VO(pc)] molecules. Intermolecular contacts occur with three nearest neighbours. The closest intermolecular approach is 3.208 Å (N···N) while the shortest centroid–centroid distance is 5.378 Å. Dimers are absent.

Vanadyl phthalocyanine, [VO(pc)], like the parent phthalocyanine and many of its metal derivatives, possesses interesting photoconductor and semiconductor properties.[1] It was shown, for example, that [VO(pc)] is a photosensitive pigment useful in both photoelectrophoretic [2] and xerographic [3] imaging. The molecular properties of the compound, however, have received far less attention than those of other transition-metal phthalocyanines, principally because of the more complex oxovanadium cation, and because of the difficulty in obtaining well characterized, single crystals of the compound.

In a recent detailed study of the polymorphism in [VO(pc)], Griffiths *et al.*[4] prepared and identified three phases of the compound. Crystals of the stable phase, II, were grown under equilibrium growth conditions by vapour sublimation. As part of our effort to understand the crystal and molecular characteristics of this compound, we have determined the three-dimensional structure of [VO(pc)]-II by X-ray techniques.

EXPERIMENTAL

Crystals were prepared as described previously.[4]

Crystal Data.—$VO(C_{32}H_{16}N_8)$, M = 579.5, Triclinic, space group $P\bar{1}$, a = 12.027(6), b = 12.571(8), c = 8.690(5) Å, α = 96.04(5), β = 94.80(5), γ = 68.20(5)°, U = 1 212 Å^3 at 23 °C, Z = 2, D_c = 1.588 g cm^{-3}, $F(000)$ = 590, λ(Mo-K_α) = 0.710 73 Å, μ(Mo-K_α) = 4.86 cm^{-1}. Cell constants were obtained by computer-centering of 25 reflections, followed by least-squares refinement of the setting angles and are identical to those reported earlier. A Delaunay reduction of the cell revealed no hidden symmetry.

X-*Ray Intensity Measurements.*—Data were collected at 23 ± 1 °C on an Enraf–Nonius CAD4 automatic diffractometer with a crystal of size 0.20 × 0.25 × 0.08 mm at the Molecular Structure Corporation. Experimental details are given in Supplementary Publication No. SUP 22838 (28 pp.).† The total number of reflections collected, using the θ—2θ scan technique, was 7 190, of which 6 970 were independent. Intensities and standard deviations on intensities were calculated as described previously.[5] Lorentz and polarization corrections were applied to the data. Extinction and absorption corrections were deemed unnecessary.

Structure Determination and Refinement.—The structure was solved by direct and Fourier methods. Hydrogen atoms were located in a difference-Fourier map. Refinement by least-squares techniques led to final agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.062$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.071$.

In the full-matrix least-squares refinement the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors were taken from Cromer and Waber.[6] Anomalous dispersion effects were included in F_c; the values of $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[7] Only the 3 042 reflections having $F_o^2 > 3\sigma(F_c^2)$ were used in the refinement.

The final positional parameters are given in the Table. The thermal parameters (U_{ij}), the positional and thermal parameters for hydrogen atoms and the distance to the attached carbon atom, the observed and calculated structure factors, and the root-mean-square displacements along the principal axes of the temperature factor ellipsoids for the non-hydrogen atoms are listed in the Supplementary Publication.

RESULTS AND DISCUSSION

Vanadyl phthalocyanine is illustrated in Figure 1. The molecule has point-group symmetry C_1 and is non-planar. The oxovanadium cation co-ordinates to the four isoindole nitrogens with vanadium 0.575(1) Å above the four-nitrogen plane. Interatomic angles are given in the Supplementary Publication.

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

The VO^{2+} cation lies perpendicular to the isoindole nitrogen plane with a V–O distance of 1.580(3) Å. Vanadium is five-co-ordinate in a square-pyramidal geometry. The four N–V–N base angles have a mean value of 85.4(2)°; * the two obtuse N–V–N angles are 146.8(1) and 147.2(1)°. The V–N distances do not differ significantly and have a mean of 2.026(7) Å. In the co-ordinatively similar oxovanadium(IV) porphyrin, vanadyldeoxophylloerythroetioporphyrin-1,2-dichloroethane solvate, the V–O distance is 1.62(1) Å and the vanadium lies 0.48 Å above the isoindole nitrogen plane.[8] These differences, which are marginally significant, correlate with the slightly larger co-ordination cavity of the porphyrin macrocycle.

Atomic co-ordinates with standard deviations in parentheses

Atom	*x*	*y*	*z*
V	0.217 39(7)	0.014 91(7)	−0.150 3(1)
O	0.301 8(3)	−0.051 1(3)	−0.286 9(4)
N(1)	0.074 9(3)	0.134 0(3)	−0.248 9(4)
N(2)	0.266 7(3)	0.148 6(3)	−0.064 3(4)
N(3)	0.298 1(3)	−0.058 3(3)	0.046 3(5)
N(4)	0.105 4(3)	−0.071 5(3)	−0.135 9(4)
N(5)	0.140 5(3)	0.297 2(3)	−0.227 0(5)
N(6)	0.412 3(3)	0.061 5(3)	0.138 6(5)
N(7)	0.222 5(3)	−0.213 2(3)	0.038 7(5)
N(8)	−0.054 6(3)	0.026 0(3)	−0.321 2(5)
C(1)	−0.023 4(4)	0.117 0(4)	−0.326 0(5)
C(2)	−0.094 4(4)	0.214 6(4)	−0.411 0(6)
C(3)	−0.195 8(4)	0.237 9(4)	−0.507 6(6)
C(4)	−0.240 4(5)	0.342 2(5)	−0.573 0(6)
C(5)	−0.185 6(5)	0.423 1(4)	−0.536 9(7)
C(6)	−0.084 1(5)	0.400 1(4)	−0.441 2(6)
C(7)	−0.038 1(4)	0.295 3(4)	−0.379 2(5)
C(8)	0.066 4(4)	0.243 4(4)	−0.280 9(6)
C(9)	0.230 3(4)	0.253 0(4)	−0.126 7(6)
C(10)	0.301 3(4)	0.318 0(4)	−0.050 1(6)
C(11)	0.296 5(4)	0.428 4(4)	−0.068 2(6)
C(12)	0.371 7(5)	0.468 1(4)	0.029 9(7)
C(13)	0.451 0(4)	0.399 3(4)	0.135 3(7)
C(14)	0.457 7(4)	0.288 8(4)	0.153 6(6)
C(15)	0.380 0(4)	0.249 8(4)	0.055 1(5)
C(16)	0.356 2(4)	0.143 3(4)	0.047 2(5)
C(17)	0.383 6(4)	−0.030 8(4)	0.140 6(6)
C(18)	0.442 6(4)	−0.118 3(4)	0.245 1(6)
C(19)	0.531 7(4)	−0.129 7(4)	0.360 1(6)
C(20)	0.566 3(5)	−0.223 9(5)	0.443 9(6)
C(21)	0.513 1(5)	−0.306 9(4)	0.412 5(6)
C(22)	0.422 9(4)	−0.295 9(4)	0.300 0(6)
C(23)	0.387 9(4)	0.200 4(4)	0.215 1(6)
C(24)	0.296 4(4)	−0.159 8(4)	0.094 4(6)
C(25)	0.133 4(4)	−0.169 7(4)	−0.062 0(6)
C(26)	0.047 7(4)	−0.224 6(4)	−0.115 7(6)
C(27)	0.037 4(4)	−0.325 0(4)	−0.075 1(6)
C(28)	−0.052 9(4)	−0.355 7(4)	−0.155 4(7)
C(29)	−0.130 8(4)	−0.289 4(4)	−0.261 6(7)
C(30)	−0.123 8(4)	−0.186 4(4)	−0.299 0(6)
C(31)	−0.032 2(4)	−0.155 8(4)	−0.220 3(6)
C(32)	0.004 7(4)	−0.059 0(4)	−0.233 7(6)

The co-ordination cavity of the phthalocyaninato-ligand is square. There are no significant differences between the four adjacent N–N distances which have a mean value of 2.748(2) Å. The four N–N–N angles are 90°.

The structure of vanadyl phthalocyanine is nearly identical to that of tin(II) phthalocyanine.[9] The size difference between the V^{4+} and Sn^{2+} ions is countered by incorporation of the vanadium into the VO^{2+} ion whose interatomic mid-point lies 1.16 Å above the four-nitrogen plane. The Sn^{2+} ion in tin phthalocyanine is 1.11 Å above the four-nitrogen plane.[9] Vanadyl phthalocyanine is reported to be isomorphous with its titanium analogue, [TiO(pc)],[10] which also displays photosensitivity.[2]

A table of 11 weighted least-squares planes, interplanar dihedral angles, atom distances and estimated standard deviations is given in the Supplementary Publication. With the exception of vanadium and oxygen, all of the atoms in the molecule lie below the isoindole nitrogen atom plane (plane 1). The closest non-hydrogen atom to the plane is N(7) at 0.028(4) Å, and the farthest is C(13) at −0.762(5) Å. The dihedral angle between the four-nitrogen plane and the all-atom (exclusive of V and O) least-squares plane is 2°. The distances of the atoms from the four-nitrogen plane increase from the centre to the periphery of the macrocycle. The phenyl ring C(26)—(31) is closest to the plane at an average atom distance of −0.12 Å. The average distance from the plane of ring C(18)—(23) is −0.29 Å, ring C(2)—(7) is −0.37 Å, and ring C(10)—(15) is −0.53 Å. The dihedral angles of the phenyl rings with plane 1 show a similar pattern being 1.3, 5.9, 6.1, and 11.0° for the four rings, respectively. The phenyl ring C(10)—(15) has the largest average displacement from the plane and bends toward a hole, away from the isoindole of an adjoining molecule. The isoindole rings (planes 8—11) are planar and show the same trend as do the phenyl groups. The dihedral angles between plane 1 and the four respective isoindole planes are 2.0, 5.4, 6.5, and 9.4°. These observations suggest that packing effects contribute significantly to the non-planarity of the macrocyclic ligand.

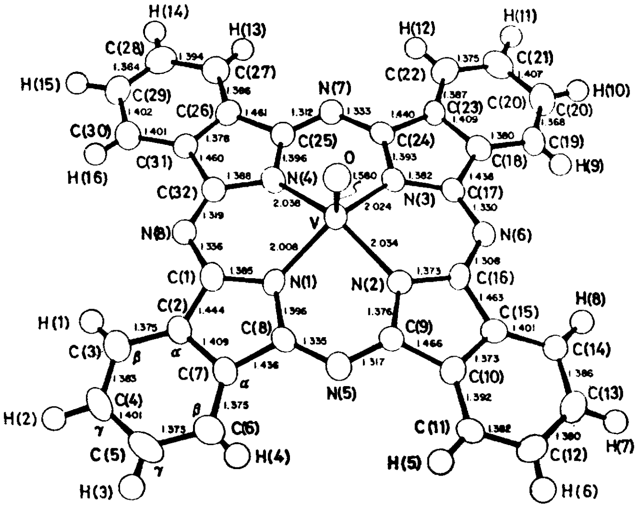

FIGURE 1 Perspective view of vanadyl phthalocyanine with interatomic distances. The estimated standard deviations are 0.003 for V–O and V–N, 0.005 for N–C, and 0.006 Å for C–C distances. Bond angles and C–H distances are given in SUP 22838

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* The value in parentheses of chemically equivalent distances and angles is the estimated variance of the mean calculated as $[\Sigma(x - \bar{x})^2/n(n - 1)]^{\frac{1}{2}}$.

The four phenyl rings are planar. The largest atom deviation from a plane is 0.021(5) Å for C(26). The mean values of the 24 C–C distances and C–C–C angles are 1.387(3) Å and 120.0(5)° respectively. The C–C–C angles range from 115.6 to 122.8°. The mean value of the 16 C–H distances is 0.93(2) Å. Despite the normal C–C and C–C–C values, the phenyl rings are not hexagonal. The rings show a distortion as illustrated for the phenyl ring C(2)—(7) where the carbon atoms are labelled α, β, and γ. For all rings, the α–β–γ angle is less than 120° causing elongation along the β–β axis. The β–β C–C distance in each ring is 0.10 Å greater than the α–γ distances. Similar distortions have been noted in other phthalocyanines [9,11] and have not been explained.

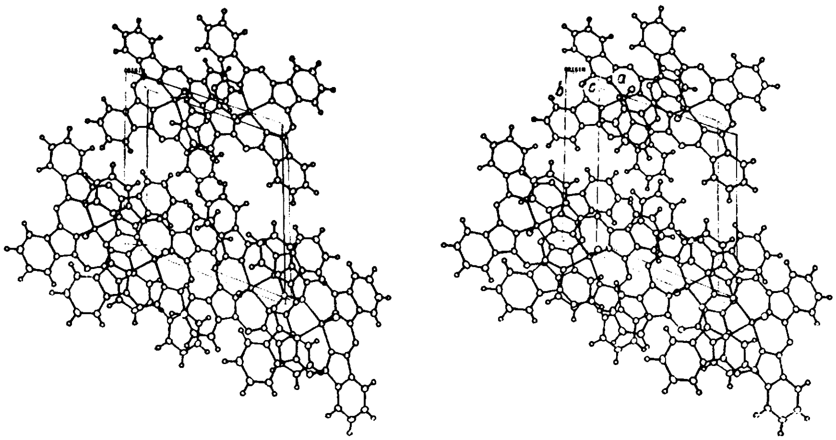

FIGURE 2 Stereoscopic packing diagram and unit cell of [VO(pc)]-II

The carbon–nitrogen distances in the macrocycle fall into two groups. The C–N distances of the isoindole rings have a mean value of 1.386(3) Å and range from 1.373(5) to 1.396(5) Å. Those involving the azomethine N range from 1.308(5) to 1.336(5) Å and have a mean value of 1.324(4) Å. These distances are similar to those observed in other pc structures such as [Sn(pc)],[9] [Cu(pc)],[12] and $[Mg(pc)]\cdot H_2O\cdot 2C_5H_5N$.[13]

Packing of the [VO(pc)] molecules differs from that of phthalocyanine itself [14] and is illustrated in Figure 2. The structure is composed of sheets of approximately parallel and overlapping [VO(pc)] molecules. The non-hydrogen intermolecular contacts less than 3.4 Å are listed in the Supplementary Publication and indicate interactions with three nearest neighbours. Maximum overlap occurs between molecules stacked back to back along *a*. These molecules have the shortest centroid–centroid distance (5.378 Å) with contacts ranging from 3.212 to 3.376 Å. The shortest contact [N(6)(···6'); 3.208 Å] occurs between molecules stacked head to head along *a*. Other contacts between these molecules, however, range from 3.390 to 3.398 Å. Intermolecular contacts ranging from 3.361 to 3.381 Å occur between molecules stacked head to head along *c*. The overlap in this case is intermediate. Intermolecular hydrogen–non-hydrogen contacts less than 2.7 Å are O(1)···H(1''') at 2.61(5) Å and O(1)···H(8') at 2.68(4) Å. The present structural results confirm the absence of a discrete dimer pair in solid [VO(pc)]-II. The assumption of such a pair was shown to be inadequate in the interpretation of the solid-state optical absorption spectrum of [VO(pc)]-II.[4,*]

[9/2014 *Received*, 21*st December*, 1979]

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[*] *Note added at proof:* The domed stereochemistry found in [VO(pc)]-II is also observed in [Pb(pc)] (K. Ukei, *Acta C yst.* 1973, **B29**, 2290).