

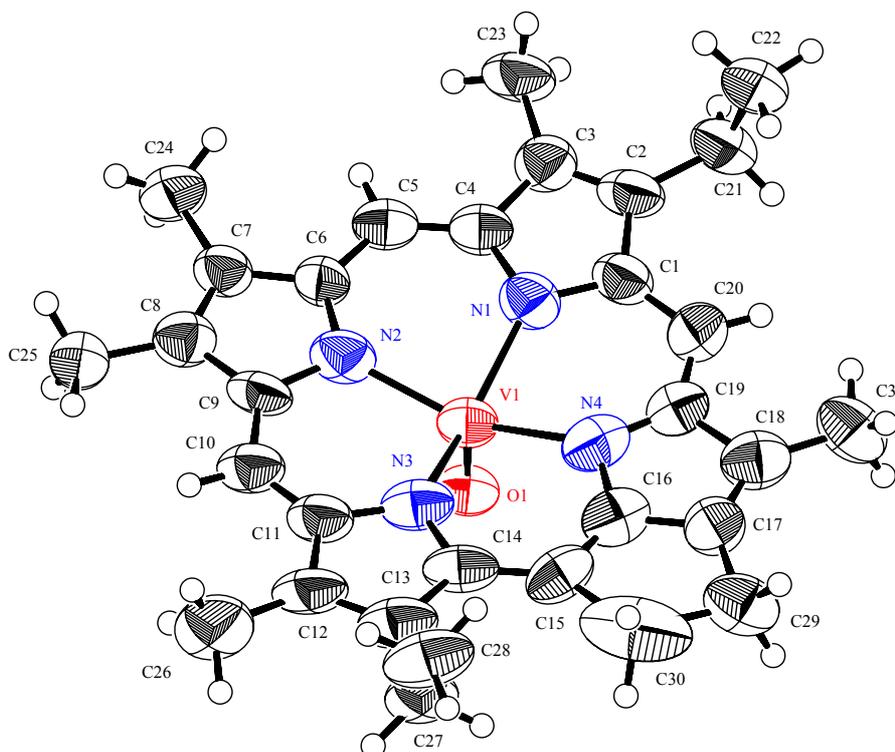
Supplementary material (X-ray crystallography data)

The molecular structures of six isolated porphyrins (including five compounds analyzed isotopically) were determined by X-ray crystallography. Crystals were prepared from 100–800 μg of each isolated compound. Dark-red colored crystals of isolated individual vanadyl porphyrins were grown by vapor diffusion (methanol into CHCl_3 solution). Single crystals of various dimensions (as small as $0.1 \times 0.1 \times 0.02$ mm) were subjected to X-ray diffraction analyses. Measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Cu–K α radiation.

We obtained conclusive crystallographic information for compounds **1a**, **1b**, **1c**, **1d**, and **1e**, which were determined to be deoxophylloerythroetioporphyrin (DPEP), 3-methyl-DPEP, 3-nor-DPEP, 8-nor-DPEP, and 17-nor-DPEP, respectively. Given that the structural information for DPEP (**1a**) and 8-nor-DPEP (**1d**) is reported in Kashiya et al. (in press) and Kashiya et al. (2007b), respectively, we provide the crystallographic information for the other three compounds below.

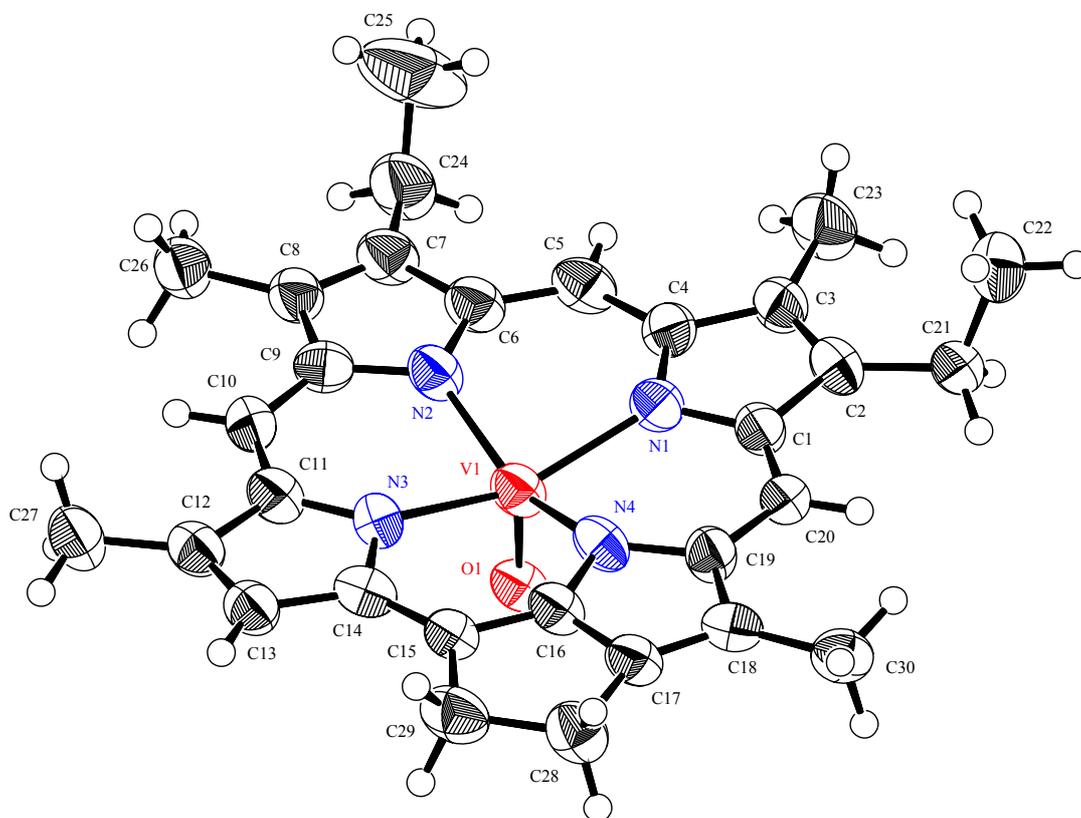
Compound 1b

$C_{31}H_{32}N_4OV$, fw 527.56, crystal dimensions 0.20 x 0.10 x 0.03 mm, triclinic, space group P-1 (#2), $a = 8.6340(4)$ Å, $b = 12.6127(5)$ Å, $c = 12.9031(5)$ Å, $\alpha = 70.4199(17)^\circ$, $\beta = 84.429(2)^\circ$, $\gamma = 74.715(2)^\circ$, $V = 1276.97(9)$ Å³, $Z = 2$, CuK α radiation ($\lambda = 1.54187$ Å), $D_{\text{calc}} = 1.372$ g cm⁻³, $\mu(\text{CuK}\alpha) = 34.974$ cm⁻¹, 12807 measured reflections, 4488 unique reflections [$R_{\text{int}} = 0.072$], 4488 reflections included in the refinement, $R1 = 0.1183$ [$I > 2.00 \sigma(I)$], $wR2 = 0.3838$ (all reflections). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 668113). This information can be obtained free of charge from www.ccdc.cam.ac.uk.



Compound 1e

$C_{30}H_{30}N_4OV$, fw 513.53, crystal dimensions 0.10 x 0.10 x 0.04 mm, triclinic, space group P-1 (#2), $a = 9.6551(3)$ Å, $b = 10.9130(3)$ Å, $c = 12.2787(3)$ Å, $\alpha = 81.7071(17)^\circ$, $\beta = 74.0418(15)^\circ$, $\gamma = 82.7403(18)^\circ$, $V = 1225.77(6)$ Å³, $Z = 2$, CuK α radiation ($\lambda = 1.54187$ Å), $D_{\text{calc}} = 1.391$ g cm⁻³, $\mu(\text{CuK}\alpha) = 36.287$ cm⁻¹, 13897 measured reflections, 4387 unique reflections [$R_{\text{int}} = 0.062$], 4387 reflections included in the refinement, $R1 = 0.0664$ [$I > 2.00 \sigma(I)$], $wR2 = 0.1934$ (all reflections). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 668111). This information can be obtained free of charge from www.ccdc.cam.ac.uk.



Compound 2

We obtained preliminary crystallographic information for Compounds **2**, which suggests that the crystal consists of a one-to-one pair of diastereomers of C_{33} bicycloalkanoporphyrin (biCAP). Namely, the two structures illustrated below are suggested to be present in the analyzed crystal with equal probability. The analysis also indicates that carbon atoms at C-13 and C-13A, as well as those at C-15 or C-15A, are present with equal probability, and that each diastereomer has only one of each pair (C-13 or C-13A, and C-15 or C-15A) in its structure. Considering the subcultures of naturally occurring tetrapyrroles, we concluded the chemical structure of Compounds **2** to be that shown in the Appendix figures.

