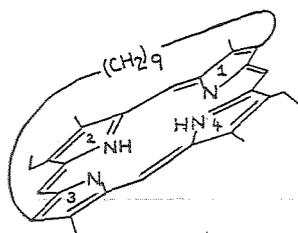


09.2-34 THE LOW TEMPERATURE (-100°C) STRUCTURE OF A "STRAPPED" PORPHYRIN. F.W.B. Einstein and T. Jones, Department of Chemistry, Simon Fraser University, Burnaby, B.C., Canada, V5A 1S6, and D. Dolphin, Department of Chemistry, The University of British Columbia, Vancouver, B.C., Canada, V6T 1W5.

The strapped porphyrin 7,17-diethyl-2,8,12,18-tetramethyl-3,13-nonamethylene porphyrin was prepared by "2 + 2 synthesis" of the appropriate dipyrromethane. It was expected the nine-carbon "strap" would cause non-planarity of the porphyrin core, thus providing a model to examine the importance of doming in the metalloporphyrin oxygenation process.



The crystals belong to space group $P2_1/c$ with $Z = 4$. The cell dimensions at -100°C are: $a = 14.774(3)$, $b = 13.828(3)$, $c = 17.634(2)$ Å, $\beta = 103.31(1)^{\circ}$. Intensities were measured, at -100°C , for 3712 independent reflections of which 2349 were classed observed [$I \geq 2.3\sigma(I)$] and used in refinement. The structure was solved using MULTAN. Hydrogen atoms were easily

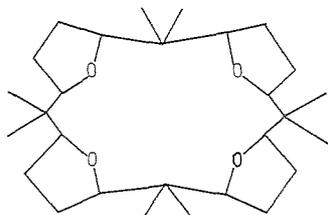
located and behaved well when coordinates and isotropic temperature factors were refined. All non-hydrogen atoms were refined anisotropically yielding a final R-value of 0.036. The porphyrin core was indeed distorted; the angle between the planes of rings 1 and 3 being 112° compared to 14° between 2 and 4. The two pyrrole hydrogens are found to be attached to the "unstrapped" pyrrole rings (2 and 4). Bond distances and angles have errors $< 0.005\text{Å}$ and $< 0.4^{\circ}$, respectively.

09.2-35 STRUCTURE OF THE CROWN ETHER 5,5,10,10,15,15,20,20-OCTAMETHYL-1,4:6,9:11,14:16,19-TETRAEPOXYCYCLOEICOSANE. By G.S.D. King and J. Aerts, Lab. voor Kristallografie, K.U.Leuven, Celestijnenlaan 200 C, B-3030 Leuven, Belgium.

Two isomers of $\text{C}_{28}\text{H}_{48}\text{O}_4$ are obtained by hydrogenation of the product of the reaction of furane and acetone with LiClO_4 in acid medium. One of them forms a complex with two Li^+ ions in solution while the other does not. We have determined the crystal structure of the former.

Crystal data: $\text{C}_{28}\text{H}_{48}\text{O}_4$ from ethylbenzene, $M = 448.7$, $a = 10.996(5)$, $b = 13.366(6)$, $c = 10.958(4)$ Å. $\alpha = 98.54(3)$, $\beta = 112.84(3)$, $\gamma = 110.74(4)^{\circ}$, $U = 1306(2)$ Å³. Space group $P\bar{1}$, $D_c(Z=2) = 1.14$ g/cm³. Intensities were measured on a Syntex P21 diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation. 2480 of the 4504 reflexions measured had $I > 1.5\sigma(I)$ and were accepted as observed. The structure was solved using MULTAN80 and refined by full-matrix methods to $R = 0.066$.

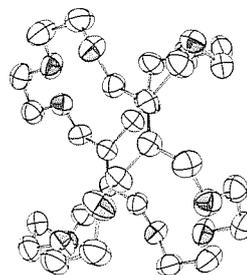
The molecule has a non-crystallographic twofold axis through one pair of opposing dimethylmethylene groups. The tetrahydrofurane groups have the envelope conformation with O as the flap and are all cis-substituted. The free electron pairs of the O atoms of opposing tetrahydrofurane rings are on the same side of the molecule and could be expected to chelate to a Li^+ ion.



09.2-36 THE CRYSTAL AND MOLECULAR STRUCTURES OF A NOVEL TRICYCLIC CYLINDRICAL POLYETHER IN UNCOMPLEXED AND COMPLEXED FORMS. By R.C. Haltiwanger, D.M. Walba, and R.M. Richards, Department of Chemistry, University of Colorado, Boulder, Colorado 80309, U.S.A.

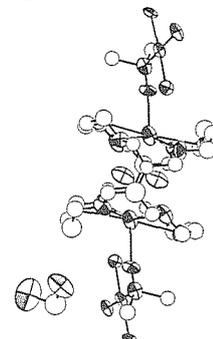
In the initial phase of a project directed towards the synthesis of cylindrical organic hosts possessing hydrophobic interiors, the tricyclic polyether I, containing the novel tetrahydroxymethylethylene (THYME) unit, has been synthesized. The THYME unit was envisioned as ideal for incorporation into such hosts because of its rigidity and lack of stereochemistry. Indeed host I is shown to form the novel and provocative complex II, containing a tightly bound water molecule within a cavity composed of two K^+ ions and twelve encircling oxygens. The neutral guest is bound by ion-dipole interactions with the K^+ ions and H-bonding to the ether oxygens.

The uncomplexed host I, $\text{C}_{28}\text{H}_{48}\text{O}_{12}$, crystallizes in space group $P\bar{1}$, $a = 8.451(4)$, $b = 10.722(7)$, $c = 10.054(6)$ Å, $\alpha = 93.05(5)$, $\beta = 102.59(4)$, $\gamma = 95.33(4)$ deg, $U = 882.7(8)$ Å³, $\text{FW} = 668.8$ amu, $Z = 1$, $D_c = 1.26$ g/cc, $D_o = 1.29$ g/cc. The structure, solved by direct methods, was refined using full-matrix least-squares procedures with the disordered solvent treated as a rigid group. For 1091 observed structure amplitudes measured with $\text{MoK}\alpha$ radiation using θ - 2θ scans to 40.0 deg, the final residuals were $R = 0.056$ and $wR = 0.070$.



The uncomplexed ligand and the toluene solvate are both located about inversion centers. While this posed no difficulty for the uncomplexed ligand it required that the toluene be disordered. The compound crystallizes with four of the twelve oxygens oriented such that they are within the cage, four outside and four between the inside and outside. Examination of models suggested flexibility for the compound and it appeared that it could coordinate to a metal through the ether oxygen atoms or possibly through the double bonds.

$[\text{K}_2\text{C}_{28}\text{H}_{48}\text{O}_{12} \cdot 2\text{H}_2\text{O}][\text{PtCl}_3(\text{CH}_3)_2\text{SO}]_2 \cdot 2\text{C}_2\text{H}_5\text{Cl}_2$, the complexed ligand II, crystallizes in space group $P2_1/c$, $a = 10.297(6)$, $b = 25.36(2)$, $c = 12.050(4)$ Å, $\beta = 113.99(4)$, $U = 2874(3)$ Å³, $\text{FW} = 1601.8$ amu, $Z = 2$, $D_c = 1.85$ g/cc and $D_o = 1.9$ g/cc. The structure, solved by a combination of heavy atom techniques and direct methods, was refined as above. For 1293 observed structure amplitudes measured as above, the final residuals were $R = 0.087$ and $wR = 0.099$.



The complexed ligand is located about an inversion center with the K^+ ions coordinated to the planar ether oxygens in the ligand. Inside the cage between the two K^+ ions, which are separated by 4.91 Å, is a water molecule disordered about the inversion center. 2.84 Å above the K^+ is the oxygen of the dimethyl sulfoxide which in turn is coordinated to the platinum atom.

Details of the structural results and comparisons between the complexed and uncomplexed ligand will be presented.