09.2-37 SYNTHESIS AND CRYSTAL STRUCTURES OF THREE ISOMERIC MACROCYCLIC POLYETHERS HAVING THE SAME MELTING POINT AND DIFFERENT COMPLEXING POWER FOR ALKALI METAL CATIONS. By Judith A. Bandy, D. G. Parsons and Mary R. Truter, Molecular Structure Department, Rothamsted Experimental Station, Harpenden, Herts.

Three isomers of I have the same melting point, 133°, and diagnostically different, but not interpretable, infrared spectra. Stability constants for formation of complexes with potassium bromide in methanol are 1.5 x 10^7, 3.2 x 10^6 and 4.5 x 10^5 mol^-1. The third isomer also yields from methanol crystals of a 1:1 solvate with an infrared spectrum indicating no hydrogen bonding by the OH group. The configuration of each of the three isomers has been determined by X-ray diffraction. Intensities were measured on a CAD4 diffractometer with Mo-Kα radiation; the phase problem was solved by direct methods and final parameters obtained by full matrix refinement.

Hydrogen atoms were located unequivocally. There is a cis substitution at the cyclohexane bridges, at each of which the hydrogen atoms may be on the same or the opposite side as the OCH₃CH₂OCH₂CH₂O link. The configurations provide a basis for understanding their behaviour as ligands.

Ia Monoclinic, a = 15.615(2), b = 21.492(4), c = 8.021(1) Å, β = 96.99°, Z = 4 in P2₁/a.

R = 0.078 for 2163 reflections.

Ib Triclinic, a = 8.842(2), b = 16.702(6), c = 10.650(3), α = 114.10(3), β = 98.97(2), γ = 91.21(2)°, Z = 2 in P1. R = 0.066 for 2071 observed reflections.

Ic, CH₃OH Monoclinic, a = 14.520(2), b = 15.391(3), c = 12.754(2), β = 95.02(2)°, Z = 4 in P2₁/n.

R = 0.062 for 2071 observed reflections. The shortest (hydroxy) H...O (ligand) distances are 2.37 and 2.33(10) Å.

Crystals of complexes with alkali metal salts are being investigated.