A Stable OH_3^+-Cyclic Polyether Complex Characterised by Infrared Spectroscopy

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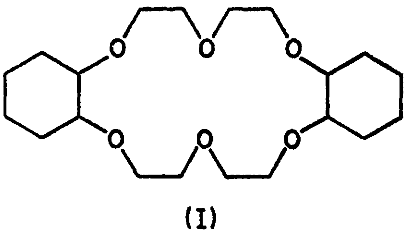
Summary A cyclic polyether complex of composition $HClO_4,H_2O,C_{20}H_{26}O_6$ has been obtained by precipitation from aqueous solution in the presence of excess of $HClO_4$ and has been shown by i.r. spectra to be the oxonium complex, $[OH_3,C_{20}H_{36}O_6^+]$ $[ClO_4^-]$.

RECENTLY cyclic polyethers and related cyclic ligands have attracted much interest because of their unusual metal-binding properties. Cyclic polyethers complex with alkali-metal cations in water and in several polar organic solvents;[1,2] they selectively complex with certain cations in preference to others depending upon cationic size, and they selectively promote ion transport through bilayer phospholipid membranes.[3] It has been shown crystallographically that cations complex with cyclic polyethers by co-ordinating in the centre of the ligand cavity; when the macrocyclic ring is large enough, the ligand folds and wraps itself around the cation.[4] Crystalline complexes of dicyclohexyl-18-crown-6 (I) (trivial name, see reference 2 for explanation of name) have been prepared with the following cations along with several protonated primary amines: Li^+, Na^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Ag^+, Cd_2^{2+}, Hg_2^{2+}, Hg^{2+}, Tl^+, Sn^{2+}, Pb^{2+}, Eu^{2+}, NH_4^+, and $(NH_2)_3C^+$. Generally 1:1 (ligand:cation) complexes are formed but 3:2 (CsI_3), 2:1 (CsSCN), and 1:2 ($LiClO_4$) are known.[2,5]

We report here the preparation of three unusual oxonium complexes with the *cis–syn–cis* isomer of (I), $[OH_3,(I)]$ $[ClO_4]$ (II), $[OD_3,(I)][ClO_4]$, (III), and $[OH_3,(I)][PF_6]$ (IV). These complexes were synthesized in good yield by adding an excess of the respective acid to an aqueous (D_2O) solution of (I). The respective m.p.s. are 143—144°, 146—147°, and 116—118°; (II) melts sharply at a temperature which is much higher than either that of the ligand (61—62°) or that of oxonium perchlorate (49—50°). Elemental analyses for C, H, and Cl as well as individual analyses for H^+, H_2O, ClO_4^-, and (I) are all consistent with the suggested formulation. Other strong acids formed oils with (I) which could not be crystallized. No complexes could be isolated using the *cis–anti–cis* isomer presumably because they were too soluble. Indeed, the *cis* isomers are readily separated by precipitating the *syn* isomer as the oxonium complex whilst the *anti* isomer remains in solution.



(I)

I.r. absorption spectra of perfluorokerosene mulls indicate that (II) contains the oxonium cation. After drying in vacuum to remove the excess of water, the OH_3^+ complex shows only five strong and distinct absorptions not found in the ligand or in the OD_3^+ complex: 2840, 2630, 2180, 1915, and 1685 cm^{-1}. These bands were readily assigned by comparison to literature values for oxonium salts; 2780—3250 (ν_1), 1048—1182 (ν_2), 2500—3100 (ν_3), 1477—1705 (ν_4), and 2050—2260 cm^{-1} ($2\nu_2$).[6] The last is a prominent overtone which has been observed in oxonium fluoride, chloride, bromide, iodide, and nitrate.[6] The absorption at 1915 cm^{-1} is unassigned. The OD_3^+ complex has only one new peak near 1935 cm^{-1} which was quite broad; the expected ν_1 and ν_3 absorptions at about 2000 and 1850 cm^{-1} were not resolved. ν_4 for OD_3^+ and ν_2 for OH_3^+ and OD_3^+ could not be seen due to strong absorptions of (I) and ClO_4^-. Between 1500 and 700 cm^{-1}, the spectra of the OH_3^+ and OD_3^+ complexes are similar but different from that of the free ligand. The breadth of the OH_3^+ absorptions indicates appreciable hydrogen bonding, probably to the ether oxygens.

The existence of the oxonium complex is not surprising considering the well-defined ammonium analogue, $[NH_4,(I)][ClO_4]$, which is known to be a stable complex. Further structural studies are under way in order to establish that the OH_3^+ is co-ordinated to the ether linkages. We believe the oxonium complex to be one of the first prepared and characterized (other than with water itself), although a variety of oxonium salts has long been known. In contrast to most oxonium salts, the complex is stable to moisture and is easy to prepare. It is stable at room temperature for over 24 months in the laboratory.

We acknowledge financial support (in part) for this work from the National Science Foundation.

(*Received, 4th September* 1972; *Com.* 1530.)

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