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Crystal Structure of an Open Chain Polyether Dicarboxylic Acid Complexed with Potassium Picrate

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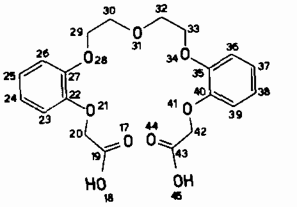

Figure 1. 2,2′ di-*o*-carboxymethoxyphenoxydiethyl ether, I, showing the crystallographic numbering of the atoms.

The study of several naturally occurring antibiotics has shown that they are able to coordinate Group IA and IIA metal ions strongly, being held in suitable coordinating conformations by strong intramolecular hydrogen bonds [1]. Intramolecular hydrogen bonds may also hold ligands in coordinating positions, as in potassium *o*, *o*′-catecholdiacetate [2]. Synthetic open chain ethers such as pentaglyme, however, which cannot form hydrogen bonds, have very much lower stability constants than the corresponding cyclic ethers of similar molecular weight [3]. We have therefore synthesised 2,2′ di-*o*-carboxymethoxyphenoxydiethyl ether, I, and a number of related compounds where hydrogen bonding of the carboxyl groups may hold the ligand in a cyclic conformation suitable for complexation. From methanol, I (Fig. 1) forms crystalline complexes with several alkali metal salts including KCl, KBr, KI, NaBr, RbNCS, sodium picrate, and in this communication we describe the crystal structure of its potassium picrate complex, II.

Attempted preparation of the complex sodium *o*-nitrophenolate·I resulted in liberation of *o*-nitrophenol and the isolation of the monosodium salt of I. Infrared and diffuse reflectance measurements on II, however, suggested the presence of picrate ion. The dimensions in the picrate anion and unequivocal location of the hydrogen atoms in the dicarboxylic acid showed that the latter acts as a neutral ligand.

The complex cation (Fig. 2) is dimeric with a centre of symmetry. Each ligand is held in coordinating position by potassium–oxygen bonds, and the two monomers are joined by bridging carbonyl oxygen atoms (O(17) and O(17′)) to give a K···K′ distance of 4.74 Å. Contrary to expectation, there are no intramolecular hydrogen bonds holding the ligand in a conformation for complexing, making this open chain polyether–potassium complex unique. Each potassium ion has irregular eight-fold coordination, the ligand spiralling around the cation. The cation is close to the poorly defined plane of the five ether oxygen atoms, with K···$O_{catechol}$ bond lengths in the range 2.84–2.94 Å and K···O(31) shorter (2.75 Å). K···O bridging carbonyl distances (2.82, 2.77 Å) are shorter than the K···O terminal carbonyl distance (2.88 Å). Although the ligand is not constrained to be cyclic, the C–O torsion angles round O(31) (152°, 75°) differ significantly from the normal 180° or 60°.

The acidic hydrogen atoms of the ligand form hydrogen bonds, that on O(18) to the O^- of a picrate

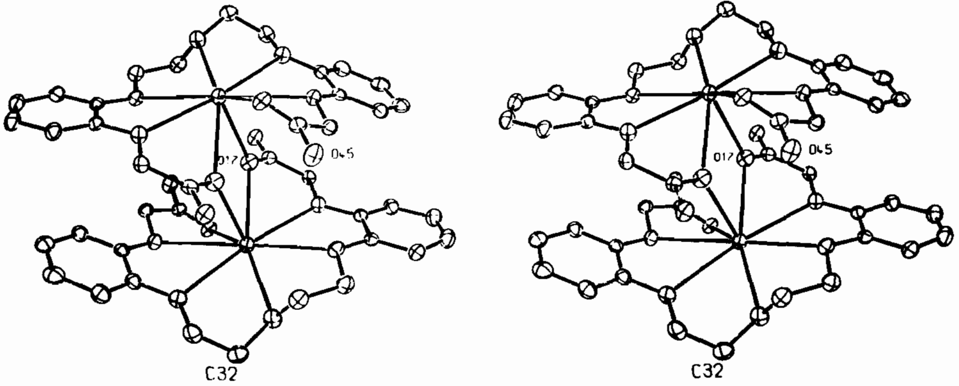

Figure 2. Stereo-pair showing the potassium ion coordination from the X-ray structure of (potassium picrate·I)$_2$.

anion (not shown) (O···O = 2.55 Å) and that on O(45) to a centrosymmetrically related acid group (O(45)···O(44″) = 2.74 Å). The picrate ion makes contact through the hydrogen bond to one complex cation and is parallel and close to a benzene ring of another dimeric complex cation.

Experimental

I was synthesised by heating *o*-hydroxyphenoxy acetic acid (16.8g) and sodium hydroxide (8.0g) in water (30ml) and dimethylsulphoxide (100ml) at 100 ℃ with 2,2-dichlorodiethyl ether (7.2g) to give the hydrated product (9.5g, mp. 100 ℃). Dehydration with boiling toluene gave anhydrous I, mp. 143 ℃.

II was obtained as small orange needles, mp. 148–9 ℃ with dec., from a 1:1 molar solution of I and potassium picrate in methanol.

Crystals of II, $C_{26}H_{24}KN_3O_{16}$, are triclinic, space group $P\bar{1}$, $a = 9.35$, $b = 11.32$, $c = 15.16$ Å, $\alpha = 95.2$, $\beta = 99.3$, $\gamma = 108.1°$, Z = 2, D_m(flotation) = 1.54, D_c = 1.54. Intensities were measured by the SRC microdensitometer service from Weissenberg films taken with CuK_α radiation. The structure was solved by direct methods. Hydrogen atom parameters, either from a difference Fourier map or calculated geometrically, were included in the final refinement, which gave R of 6.55% for the 2210 observed planes.

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