A New Class of Macrocyclic Ether–Ester Ligands

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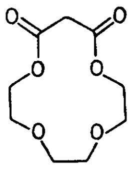
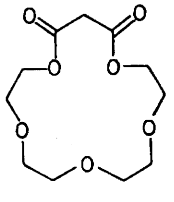
Summary Three new crown ether–esters have been prepared, 2,4-diketo(13-crown-4) (I), 2,4-diketo(16-crown-5) (II), and 2,4-diketo(19-crown-6) (III); (II) and (III) complex with alkaline-earth-metal ions.

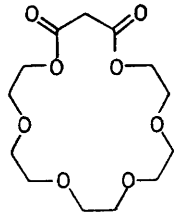
Crown ethers have been used extensively as complexing agents to dissolve inorganic salts in organic media so that ionic reactions may be carried out in solvents with low dielectric constants.[1] We now describe a new class of macrocyclic ether–ester compounds which are easy to prepare and have somewhat different metal binding properties than crown ethers. Compounds (I)—(III) have been prepared and a qualitative study of their complexation with alkaline-earth-metal ions carried out. These compounds have two possible binding sites for metal ions, the 1,3-dicarbonyl group and the ether oxygens. Models show that (II) and (III) definitely have a cavity in the centre of the ring, the size of (III) being large enough to accommodate K^+. Space filling models also show that both carbonyl groups cannot be directed into the cavity.

2,4-Diketo(19-crown-6) (III) was prepared by slowly adding 15·0 g (0·063 mol) of pentaethylene glycol in 200 cm^3 of benzene and 8·88 g (0·063 mol) of malonyl dichloride in 200 cm^3 of benzene through separate dropping funnels to 600 cm^3 of stirred benzene at 60—70 °C. After the benzene was removed under vacuum, the residue was dissolved in one part of chloroform (about 20—25 cm^3) and then nine parts of hexane were added. A brown gummy material separated from the milky solvent layer. The solvent was decanted into a beaker and allowed to slowly evaporate. White needles formed and were isolated before the solution was completely evaporated yielding 7·41 g (III), (38%); m.p. 68—69 °C; ^1H n.m.r., δ 3·40 (2H, s, $COCH_2CO$), 3·65 (16H, m, OCH_2CH_2O), 4·27 (4H, m, $COOCH_2$); i.r. 1725 cm^{-1}. Compounds (I) (m.p. 51·5—52·5 °C) and (II) (m.p. 66·5—68 °C) were prepared in the same manner to give comparable yields.†

Compound (I) does not complex with any of the alkaline-earth cations shown by the lack of any temperature rise due to reaction during thermometric titrations of solutions of (I). Compound (II) complexes with magnesium, calcium, strontium, and barium ions in aqueous solution. Evidence of formation of complexes was obtained from thermometric titration curves. This is the first instance of complex formation between the magnesium ion and a crown compound. However, the magnesium ion may not be bound inside the cavity but instead to the externally directed 1,3-dicarbonyl group. Pentan-2,4-dione which is known to complex magnesium ion sets a precedent for this.[2] On the other hand, the copper(II) ion which complexes to 1,3-dicarbonyl groups more strongly than the magnesium ion[3] was not complexed by (II). This indicates that the weakly enolizable 1,3-dicarbonyl group in (II) is not a good ligand and probably is not the magnesium ion binding site. We believe the magnesium ion to be bound in the cavity.


(I)


(II)


(III)

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† Satisfactory elemental analyses and molecular weight determinations were obtained on these products.

Compound (III) also forms complexes with calcium, strontium, and probably with barium ions in aqueous solution.

Work is now in progress to determine the exact ion binding properties of these compounds and their selectivities. Other crown ether–esters containing sulphur and nitrogen groups are also being prepared.

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[1] J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351; C. L. Liotta and H. P. Harris, *J. Amer. Chem. Soc.* 1974, **96**, 2250; D. J. Sam and H. E. Simmons, *ibid.*, p. 2252.

[2] L. G. Sillen and A. E. Martell, 'Stability Constants of Metal Ion Complexes,' *Chem. Soc. Special Publ.*, *No.* 17, 1964, p. 445.

[3] Ref. 2, pp. 444, 483, 540.