Report for 1979 - Part 1

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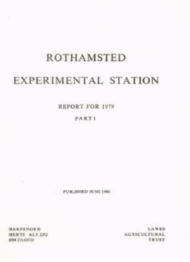

Molecular Structures Department

Mary R. Truter

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MOLECULAR STRUCTURES DEPARTMENT

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Introduction

We have concentrated on three aspects of the chemistry of compounds containing several donor oxygen atoms suitable as selective complexing agents for alkali and alkaline earth metal cations. The first is a systematic synthesis of derivatives, the second is the study of interaction with metal cations in solution and, where possible, in the solid, and the third is the study of interaction with compounds capable of forming hydrogen bonds. Interest in the last aspect derives from the need to discover whether any biological activity may be assumed to arise from interaction only with metal cations or whether, as with some naturally occurring ionophores, there are appreciable interactions with amino acids and organic amines.

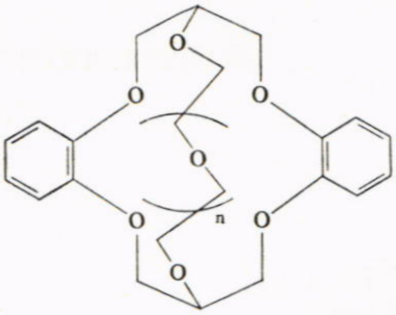
Our biological assay, direct observation of stomatal apertures on epidermal peels, shows significant differences between various test compounds and antagonism to the effect of abscisic acid.

Coordination chemistry

Synthesis and characterisation. The high pressure hydrogenation equipment has been set up and this has enabled us to reduce several aromatic crown ethers to their corresponding cyclohexane analogues. These are obtained as a mixture of isomers which have to be separated and identified; a difficult task because only small amounts of compounds are available. Considerable effort has been expended in attempts to improve the yields from the early cyclisation stages of the syntheses. Application of the technique to compound '224' (Fig. 1, I, shows the aromatic compound) has yielded two crystalline isomeric bicyclohexyl macrobicyclic molecules of melting points 102° and 136°. As an example of the control available for complex formation, the formation constants of their (1:1) complexes with potassium chloride in methanol differ by a factor of 1000. (Parsons)

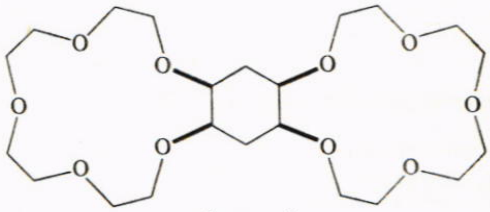
While the smaller cations form complexes with 15-membered macrocyclic rings containing five donor oxygen atoms in stoicheiometry 1:1, cations of the radius of potassium or larger form complexes with the cation sandwiched between two molecules of ligand. In an attempt to provide both rings in one molecule, a mixture of isomers which should contain the *cis*, *syn*, *cis* of the 'clam' compound (Fig. 1, II) has been obtained by reduction of the benzene derivative. For one isomer the complex with potassium thiocyanate has been isolated and found, surprisingly, to have the stoicheiometry two molecules of salt per molecule of compound. (Parsons)

A novel aromatic tricyclic compound synthesised is the dimer molecule (III of Fig. 1). This forms a crystalline complex with rubidium bromide, but like the complexes of the



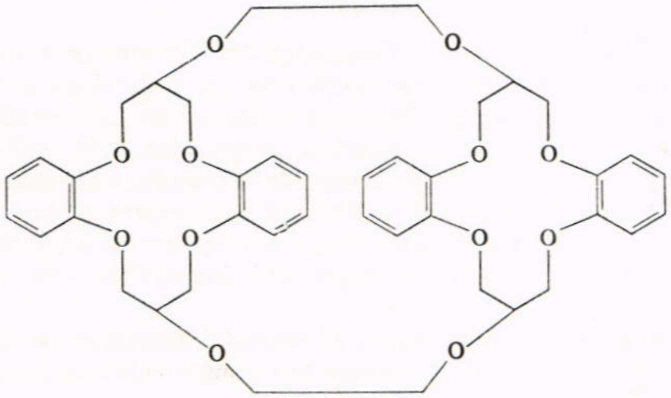
n = 1 "223"
n = 2 "224"
n = 3 "225"

(I)

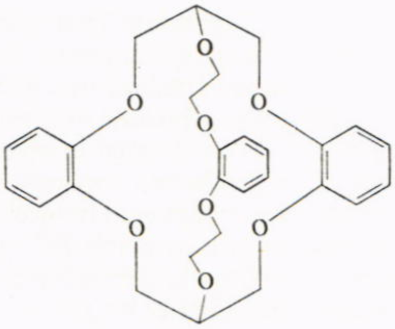


cis, syn, cis

(II)



(III)

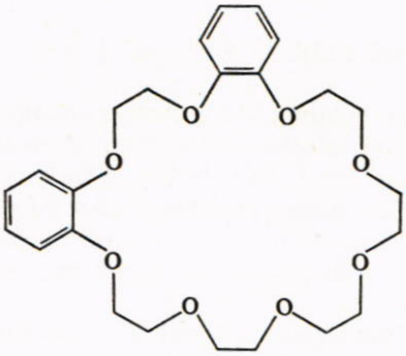


(IV)

FIG. 1. Multicyclic ligands.

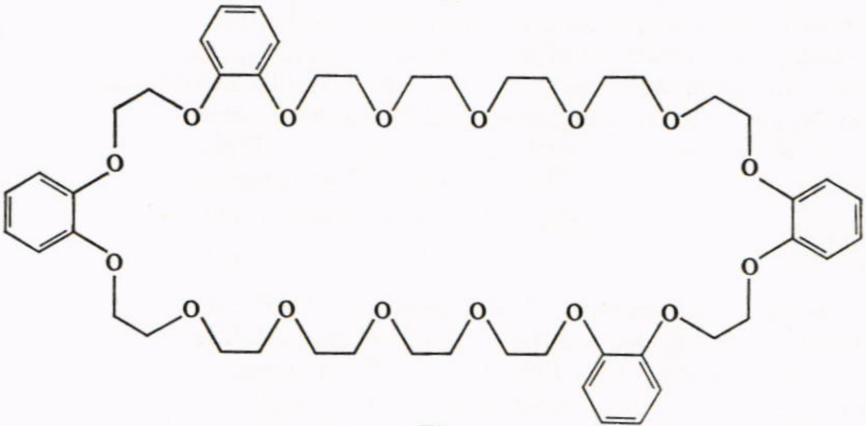
macrobicyclic ligands, it is strongly solvated. Even from methanol the rubidium bromide complex crystallises with four molecules of water and the dried sample rapidly absorbs atmospheric water on standing. (Hanson and Parsons)

Heavily solvated complexes of stoicheiometry 1:1 have been isolated from '224' and ammonium salts, and only for glycine of the amino acids investigated. Loss of solvent, accelerated by exposure to X-rays, results in degradation of the crystals, but it has been possible to establish that there are 2·5 water molecules per glycine. The infrared spectra

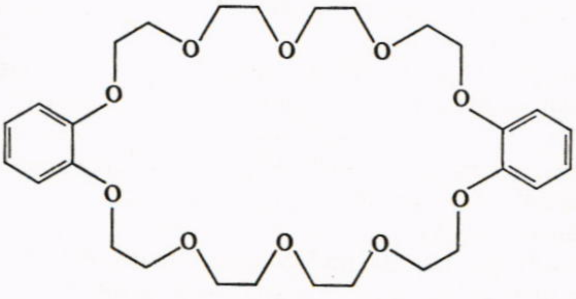


[2,6]-dibenzo-24-crown-8

(I)

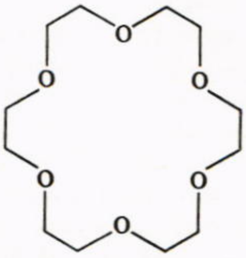


(II)



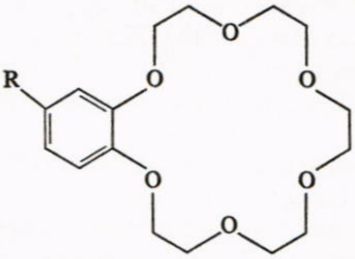
dibenzo-30-crown-10

(III)



18-crown-6

(IV)



R = H benzo-18-crown-6
R = $COCH_3$ acetylbenzo-18-crown-6
R = $C(CH_3)_3$ *tert.* butylbenzo-18-crown-6

(V)

FIG. 2. Cyclic 'crown' compounds.

show evidence of hydrogen bonding and a change in conformation of '224' on complex formation. Measurements in solution in methanol show the formation constants to be one thousand times less for NH_4^+ than for K^+ or Na^+. (Herbert, Parsons and Truter)

In the synthesis of the '2,6' isomer of dibenzo-24-crown-8 (Fig. 2, I) the dimer, II, was also obtained. Molecular weights were determined for each in solution by osmometry and II was also characterised by preliminary X-ray measurements. (Hughes and Wingfield)

Prior to a publication (Shamsipur & Popov, *Journal of the American Chemical Society* (1979), **101,** 4051–4055) claiming the existence in solution of a 3:2 complex of sodium tetraphenylborate:dibenzo-30-crown-10 (Fig. 2), we were given the first chance to determine the structure of crystals of this alleged compound isolated from acetonitrile; we were provided with a sample and the elemental analyses for C, H and B. Preliminary X-ray measurements, repetition of the reported preparation, analysis for C, H and N and the infrared spectrum were consistent with the formula $2NaBPh_4$.dibenzo-30-crown-10.$4CH_3CN$, and with its being analogous to 2NaNCS.dibenzo-30-crown-10 complex (*Rothamsted Report for 1978*, Part 1, 161, and Owen and Truter, *Journal of the Chemical Society, Dalton Transactions* (1979), 1831–1835) and containing $[2NaCH_3CN$.dibenzo-30-crown-10$]^{++}$ cations, tetraphenylborate anions and acetonitrile of solvation. (Owen and Wingfield)

Crystal structure determinations. The uncomplexed '225' molecule (Fig. 1, I) has quite a different shape and packing in the crystal from those of '223' and '224' reported previously (*Rothamsted Report for 1978*, Part 1, 157). Fourteen of the torsion angles have unusual values and result in a conformation with the aliphatic bridge bent almost on top of one of the benzene rings. It is, however, similar to that of the previous molecules in having an open face containing five oxygen atoms and in crystallising in one conformation. (Owen)

This open face persists in benzo-'224' (Fig. 1, IV) the structure of which has been determined for comparison with that of the potassium chloride complex described last year (*Rothamsted Report for 1978*, Part 1, 160) (Hanson, Parsons & Truter, *Journal of the Chemical Society, Chemical Communications* (1979), 486–488). Two different conformations are present in the crystal; both differ from the more symmetrical one in the complex which has six oxygen atoms in a fairly open face. (Hanson and Truter)

Attempts to crystallise complexes of macrobicyclic molecules free of disordered solvent have been made in two ways. The first was to provide a space-filling solvent; we used naphthalene-2,3-diol. With '223' of Fig. 1 the complex obtained was '223':H_2O:naphthalene-2,3-diol in 1:1:1 stoicheiometry. Naphthalene-2,3-diol has an internal hydrogen bond and the second hydroxy hydrogen forms a strong bond to a water molecule which is hydrogen bonded to four oxygen atoms of the '223' molecule. This produces a significant change in two torsion angles compared with an uncomplexed molecule and these were sufficient to give rise to differences in the infrared spectrum. (Herbert, Parsons and Truter)

The second method was to provide a large anion, the picrate, $C_6H_3N_3O_7^-$. With '225', (Fig. 1) potassium picrate and rubidium picrate formed crystalline complexes, shown to be isomorphous. The crystal structure of the rubidium compound was determined and shown to contain the following entities, [Rb '225']$^+$, picrate$^-$, water [(picrate Rb '225')-$^{O}_{2}$ water]. The first rubidium ion is coordinated by the nine oxygen atoms of the '225' molecule giving a complex cation. The second rubidium ion is coordinated again by nine oxygen atoms from '225' and also by a nitro oxygen atom from a picrate ion; two such complex ion pairs are related by symmetry and share a water molecule so that the rubidium cation has 11 oxygen atom neighbours. (Hanson, Parsons and Truter)

The compound 18-crown-6 (Fig. 2, IV), forms complexes with a variety of molecules which act as hydrogen bond donors; ammonium bromide, for example, forms three such bonds (Nagano, Kobayashi & Sasaki, *Bulletin of the Chemical Society of Japan* (1978), **51,** 790–793) in a 1:1 complex. Calorimetric determinations in methanol suggested that two such bonds were formed with the guanidinium ion $[C(NH_2)_3]^+$, as donor (Izatt, Izatt, Lamb, Rossiter & Christensen, *Journal of the American Chemical Society* (in the press)). We synthesised the crystalline complex between guanidinium nitrate and 18-crown-6, and found the product to have 2:1 stoicheiometry. In the crystal the crown molecule is centrosymmetric with one guanidinium ion singly hydrogen bonded on either side; the conformation of the crown differs from those found in the uncomplexed molecule or in other complexes. (Herbert, Truter and Wingfield)

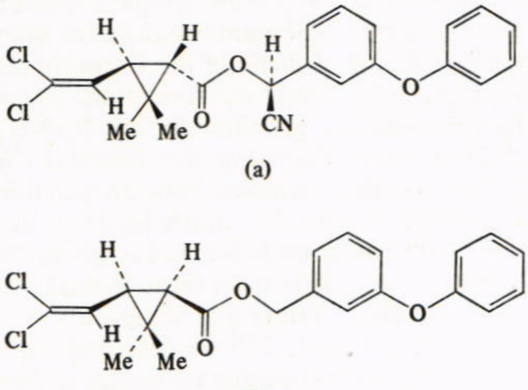
In *Rothamsted Report for 1973*, Part 1, 212 we described one form of coordinative saturation by anionic and neutral rigid chelating molecules as exemplified in the crystal structures of the sodium and the rubidium complexes, found to contain discrete molecules of M^+(o-nitrophenolate)$^-$(1,10-phenanthroline)$_2$ (Hughes, *Journal of the Chemical Society, Dalton Transactions* (1973), 2347–2354). As part of that project an ammonium compound, NH_4^+(picrate)$^-$(1,10-phenanthroline) was synthesised. Its crystal structure determination is now complete. One hydrogen of the ammonium ion is chelated as a metallic cation by the two nitrogen atoms of a 1,10-phenanthroline molecule, but the remaining hydrogen atoms take part in five further hydrogen bonds with three picrate ions so that the structure is polymeric. (Hughes, with Dr. G. H. W. Milburn and Dr. L. Sawyer, Napier College, Edinburgh)

Effect of ionophores on stomata

The inhibition to opening of stomata in epidermal peels of *Commelina communis* by the action of benzo-18-crown-6 (*Rothamsted Report for 1978*, Part 1, 164) is fully reversible at 5 mM crown concentration if the peels are transferred to a crown-free solution after 3 hours. Benzo-18-crown-6 (Fig. 2) has an antagonistic effect on abscisic acid (ABA). In a typical experiment the measured aperture of stomata in peels treated with 10^{-7} M-ABA was 3·7 μm, whereas the aperture in solution containing 10^{-7} M-ABA plus 4×10^{-3} M-benzo-18-crown-6 was 7·7 μm. Results obtained with 18-crown-6 and acetylbenzo-18-crown-6 indicate similar but lesser effects, even though the formation constant of 18-crown-6 with potassium is greater than that of benzo-18-crown-6. This indicates that solubility of the crown in the lipid membranes may be important. *t*-Butyl-benzo-18-crown-6 was synthesised because of its large lipid-like R group. Preliminary indications suggest that this molecule is one hundred times more effective than its parent compound. (Georgiou, Richardson, Truter and Wingfield)

Pyrethroids

Cypermethrin ('NRDC 149') is a mixture of four diastereomeric pair of enantiomers, two *cis* and two *trans* about the cyclopropane ring. The non-insecticidal *trans* pair had been purified by crystallisation from hexane by workers in the Department of Insecticides and Fungicides. The crystals are triclinic with a centrosymmetrical space group and contain equal numbers of molecules of αS, 1S and αR, 1R configuration (Fig. 3a shows the former). The molecular conformation in the crystal is similar for some bonds, but strikingly different for others, compared with those found for 'NRDC 161' (Owen, *Journal of the Chemical Society, Perkin I* (1975), 1865–1868) and 'NRDC 157' (*ibid.* (1975), 1231–1235). Crystallisation of this racemic pair contrasts with the spontaneous resolution shown by a racemic solution of 'NRDC 157' (Fig. 3b), and its optical antipode; this deposits crystals which consist either of the 1R isomer, 'NRDC 157' or of the 1S isomer.



(a)

(b)

FIG. 3

Collaboration with the Unit of Nitrogen Fixation

A complex of tantalum, $[Ta(CO)Cl_2(\eta^5\text{-}C_5H_5)(PMe_2Ph)_2].C_4H_8O$ (Fig. 4), was prepared as a possible analogue of a N_2-complex in which the dinitrogen might be reduced. The deep red needle crystals obtained by repeated recrystallisation from tetrahydrofuran/hexane were analysed by X-ray diffraction methods to establish the stereochemical arrangement of the ligands about the metal atom. Crystals, which are slightly air-sensitive, were mounted on glass fibres and coated with epoxy resin under a dry dinitrogen atmosphere. The crystal structure was determined by the heavy atom method from diffractometer intensity data. The complex molecule has a distorted octahedral arrangement of ligands:

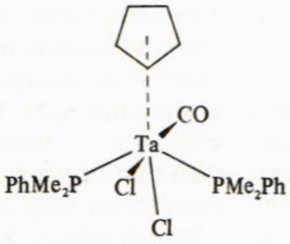
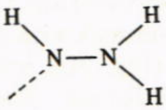


FIG. 4

In the crystal there also appear to be molecules of tetrahydrofuran disordered over several orientations and not satisfactorily resolved. Coordination dimensions reflect considerable steric crowding. Distortion of the cyclopentadienyl ring from a regular pentagon results from very short inter-ligand contacts. (Hughes)

Very small, fine, pink needles (in mixture with brown plate crystals of the tungsten complex $[WBr_2(NNH_2)(PMe_2Ph)_3]$ were thought to contain the elusive hydrazido(1-), ligand. Being quite air-sensitive these crystals were mounted as for the tantalum com-



pound. From rather weak photographs, cell dimensions and space group symmetry were determined, but intensity measurements could not be made satisfactorily by either diffractometry or photography. Takashi, Mizobe, Sato, Uchida & Hidai (*Journal of the American Chemical Society*, **101,** 3405–3406 (1979) have published results of the crystal structure analysis of a complex whose molecular geometry strongly suggests a hydrazido(2-)-hydrido complex, $[WClBrH(NNH_2)(NNH_2)(PMe_2Ph)_3]Br$. Cell dimensions of this crystal were similar to those of our sample, and the space group was the same, indicating that the samples are isomorphous; the formula of our compound would then be $[WBr_2H(NNH_2)(PMe_2Ph)_3]Br$. (Hughes)

Computing

The program MULTAN 78 from the University of York has been implemented on the System 4 to allow us to use two new and powerful programs for structure determination—the random phase set YZARC78 and the Magic integer generation program MAGIC78. The plotting program ORTEP has been amended to use GHOST routines which allow our diagrams to be drawn on the new Benson plotter. (Owen)

DLRED, the Delaunay Reduction program for the IBM 1130 computer, has been improved, and also adapted for interactive use on the PDP8 computer. (Hughes)

Staff and Visitors

The resignation of I. R. Hanson at the end of September left a vacancy which we await permission to fill.

Mr. S. N. Kilényi worked in the Department as a vacation student.

Mary R. Truter was re-appointed Visiting Professor in University College, London.

J. N. Wingfield attended a Summer School on Bioenergetics and Thermodynamics: Model Systems at Tabiano, Italy. D. G. Parsons attended two conferences in the USA: (1) Third Symposium on Macrocyclic Compounds, Brigham Young University, Provo, Utah; (2) Seventh International Congress of Heterocyclic Chemistry, University of South Florida, Tampa, Florida. Mary R. Truter read a paper at the Fifth European Crystallographic Meeting in Copenhagen.

Publications

GENERAL PAPERS

1 (SUTTON, L. E.) & TRUTER, M. R. (Eds.) (1979) *Specialist periodical report—molecular structure by diffraction methods*, Volume 6. The Chemical Society.

2 TRUTER, M. R. (1979) Chemists' guide to discovering information about molecular structures in crystalline solids. In: *Specialist periodical report—molecular structure by diffraction methods*, Volume 6. Ed. L. E. Sutton & M. R. Truter. The Chemical Society, pp. 93–116.

RESEARCH PAPERS

3 (AMIRHAERI, S., FARAGO, M. E., GLUCK, J. A. P.) & WINGFIELD, J. N. (1979) ^1H and ^{13}C N.M.R. studies on malonic and ethylmalonic acids and their cobalt (III) complexes. *Inorganica Chimica Acta* **33,** 57–61.

4 (CHATT, J., FAKLEY, M. E., HITCHCOCK, P. B., RICHARDS, R. L., TUYET LUONG-THI, N.) & HUGHES, D. L. (1979) Hydrazido(2-) (or isodiazene) complexes of tungsten. *Journal of Organometallic Chemistry* **172,** C55–68.

5 (Chatt, J., Fakley, M. E., Richards, R. L.), Hanson, I. R. & Hughes, D. L. (1979) The influence of ligand environment of the protonation reactions of hydrazido(2-) complexes of molybdenum and tungsten: X-ray structures of [M(8-quin) (NNH_2) ($PMe_2Ph)_3$]I (M = Mo or W; 8-quin = quinolin-8-olate). *Journal of Organometallic Chemistry* **170,** C6–C8.

6 Hanson, I. R., Parsons, D. G. & Truter, M. R. (1979) Complexes of alkali metal salts with bridged macrocyclic polyethers: X-ray crystal structure of (1,4,7,14,17,20,28,35-octaoxa[$2^{3,29}.2^{18,34}$][7.7]-ortho-cyclophane)potassium chloride multihydrate. *Journal of the Chemical Society, Chemical Communications* 486–488.

7 Hughes, D. L. & Truter, M. R. (1979) Alkali-metal complexes. Part 8. Crystal structures of potassium quinolin-8-olate-quinolin-8-ol (1/1) and -quinolin-8-ol (1/2). *Journal of the Chemical Society. Dalton Transactions* 520–527.

8 Owen, J. D. & Truter, M. R. (1979) Crystal structures of complexes between alkali-metal salts and cyclic polyethers. Part 10. Complex formed between 6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo[*b*, *q*] [1,4,7,10,13,16,19,22,25,28] decaoxacyclotriacontin(dibenzo-30-crown-10) and two molecules of sodium isothiocyanate. *Journal of the Chemical Society, Dalton Transactions* 1831–1835.

9 Richardson, C. H., Truter, M. R., Wingfield, J. N., (Travis, A. J., Mansfield, T. A. & Jarvis, R. G.) (1979) The effect of benzo-18-crown-6, a synthetic ionophore, on stomatal opening, and its interaction with abscisic acid. *Plant, Cell and Environment* **2,** 325–327.