Report for 1976 - Part 1

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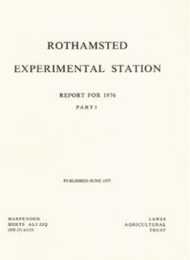

Molecular Structures Department

Mary R. Truter

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MOLECULAR STRUCTURES DEPARTMENT

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Introduction

During the year we have watched the new building going up; its topping-out ceremony was held on 11 June. Some time has been spent on planning the furniture and fitments.

Although we managed to make some measurements with our own Picker diffractometer, we continued to depend upon the use of diffractometers in other laboratories and are grateful to the Polytechnic of North London, Sheffield Polytechnic and Queen Mary College, London. The first-hand experience of using various models proved valuable when we were in the fortunate position of being able to choose a new one. Our choice, an Enraf-Nonius CAD-4, was installed at the end of September. The ease of setting a crystal and determination of accurate cell parameters is a delight and so is the efficient measurement of intensities. We look forward to being able to determine structures of more molecules with more precision and reliability.

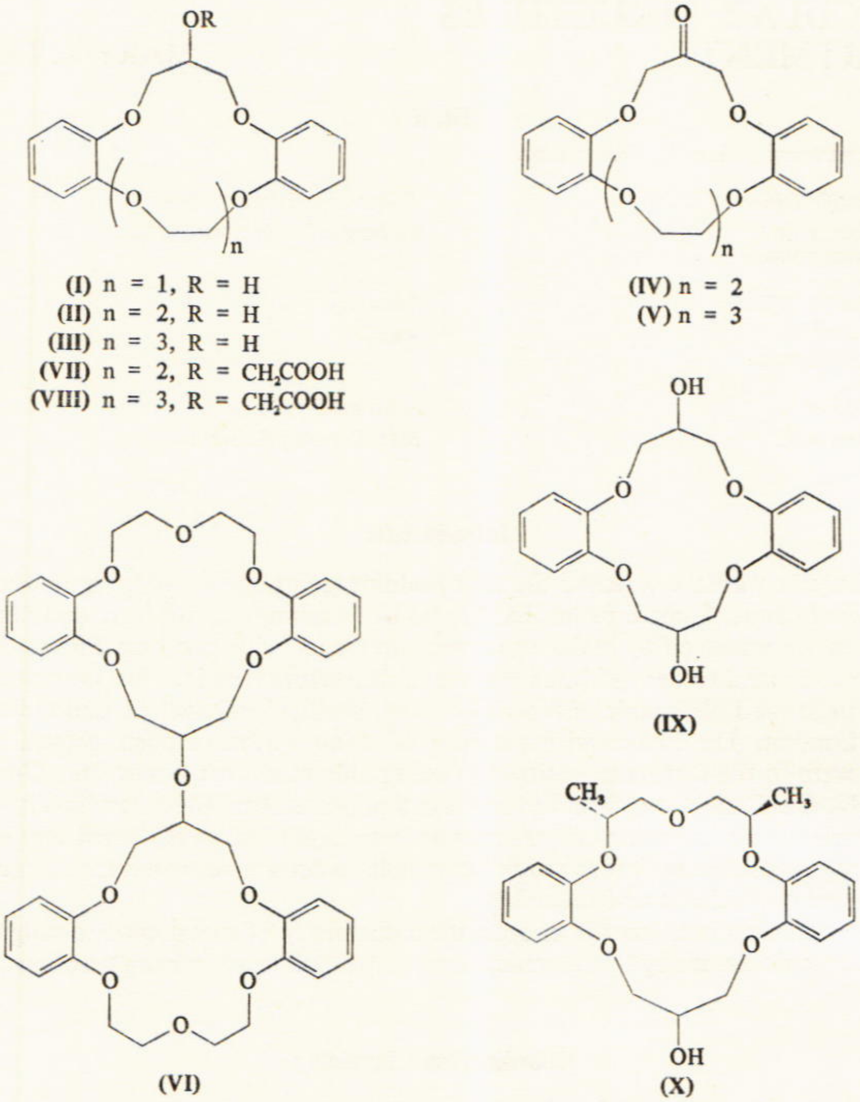
All our work has been on the coordination chemistry of metal cations ranging from synthetic organic chemistry to theoretical treatments and tests on bean seedlings.

Coordination Chemistry

Alkali and alkaline earth metal cations

Synthesis of new complexing agents. New cyclic ligands for these cations are shown in Fig. 1. They are 'crown' compounds modified by insertion of a 2-hydroxypropane-1,3 diyl group in place of the usual ethylene bridge, as in formulae I–III. The presence of the secondary hydroxyl group in the heterocyclic ring enables many structural changes to be made, so that effects on the coordination properties of the structures may be determined. Oxidation has given the keto crowns formulae IV and V, and linking two molecules together has given a 'clam' type ligand, VI. Of particular interest are the carboxymethyl derivatives VII and VIII giving water soluble salts which are to be investigated in our biological studies. The *cis* and *trans* isomers of dihydroxydibenzo-14-crown-4, IX have been separated by thin layer chromatography but not yet identified. The chiral ligand X has been synthesised and attempts are being made to effect a resolution via the brucine salt of the acid phthalate. (Parsons)

Two less symmetrical isomers of dibenzo-24-crown-8 have been synthesised, the [b,k] and [b,h] forms of Fig. 2. Complexes with sodium perchlorate have been isolated for all three; they are anhydrous with 1:1 stoicheiometry and for each the infra-red spectrum



(I) n = 1, R = H
(II) n = 2, R = H
(III) n = 3, R = H
(VII) n = 2, R = CH_2COOH
(VIII) n = 3, R = CH_2COOH

(IV) n = 2
(V) n = 3

(IX)

(VI)

(X)

FIG. 1 (I) to (X), new complexing agents.

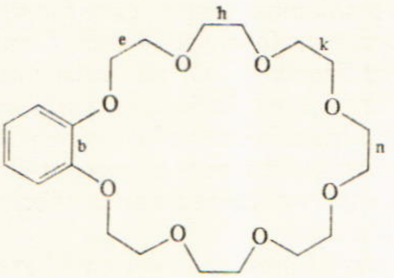


FIG. 2 Benzo-24-crown-8. Three isomers of dibenzo-24-crown-8 are designated [b, n], [b, k] and [b, h] in the text according to the bond included in the second benzene ring.

indicates that the perchlorate ion is not coordinated so the sodium ion is probably encapsulated by the ligand. (Wingfield)

The naturally occurring hydroxyacid polyether antibiotics which coordinate group IA and IIA metals are held in co-ordinating position by strong hydrogen bonds. An analogous compound, $HOC_6H_4OCH_2CH_2OCH_2CH_2OC_6H_4OCH_2COOH$, has been synthesised by a general route, and isolated as its potassium thiocyanate complex. (Wingfield)

Complexes of other cations. The use of thallium (I) as a probe for potassium in biological systems poses some subtle chemical problems (Truter, *Philosophical Transactions of the Royal Society* (1975), B272, 29–41). In complexes of thallous salts TlX(X=NCS^-, ClO_4^-, ClO_3^-, $C_6H_5COO^-$ with various crown ethers we have found the same stoicheometries as for the potassium compounds. Preliminary X-ray diffraction measurements indicate that the ion is sandwiched between two molecules of benzo-15-crown-5 (Fig. 3)

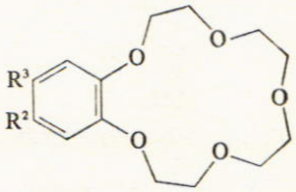


FIG. 3 Derivatives of benzo-15-crown-5 ($R^2=R^3=H$). $R^2=R^3=OCH_3$, 4,5-dimethoxybenzo-15-crown-5 $R^2=H$, $R^3=C(CH_3)_3$, 4-*tertiary*-butylbenzo-15-crown-5

and does not, as in some systems, e.g. the ascorbate (Hughes, *Journal of the Chemical Society* (*Dalton Transactions*), (1973), 2209–2215), have all ligand atoms on one side.

Transition metal ions have also been studied. Manganese, iron, cobalt and nickel halides with benzo-15-crown-5 and with 18-crown-6 give 1:1 compounds with several molecules of water of crystallisation. (Farago)

Infra-red spectra. These have proved of diagnostic value. In complexes of metal perchlorates a single band at 630 cm⁻¹ indicates that the anion is not coordinated to the metal, while splitting into two or more bands indicates that it is coordinated (see paper 6). In the various crystal structure analyses reported below, the situation found is as predicted from the i.r. spectrum.

Although it is not possible to interpret the spectra to predict the conformations of molecules such as benzo-15-crown-5, they do indicate whether the conformation is the same or different in different crystalline compounds and have been used to guide the choice of compounds for structure determination.

For the thiocyanate ion, however, the results of structure analysis have enabled the spectra to be interpreted. In the $Ca(NCS)_2$ complexes reported last year (*Rothamsted Report for 1975*, Part 1, p. 189) there are two C–N stretching frequencies originally attributed to differences in the Ca–$\hat{N}$–C angles. In the $Mg(NCS)_2$ complex reported below, the same differences in angles are found but only one C–N stretching frequency. The difference lies in the relative position of the thiocyanate ions, *cis* in the calcium complex and *trans* in the magnesium complex. (Owen and Wingfield)

Crystal structure determinations

Macrocyclic ethers. Benzo-15-crown-5 (Fig. 3) crystallised from cyclohexane (Dr. N. S. Poonia, University of Vikram); X-ray diffraction photographs were taken of a crystal cooled to −150° and the intensities of the spots measured by the Science Research Council microdensitometer service at Chilton. The molecules are relatively loosely packed in the crystal explaining the poor diffraction at room temperature. The dimensions are more accurate than those obtained for any complexes of this molecule and show that the shortening of the carbon–carbon bond lengths in the macrocyclic ring, mean 1·493 Å, compared with 1·54 Å for the standard length, is a real effect.

For dibenzo-12-crown-4 and dimethyl dibenzo-21-crown-7, observations were collected on the Stoe 2-circle diffractometer at Sheffield Polytechnic and the phase problems were solved by direct methods; parameters are being refined. (Hughes and Owen, with Dr. I. W. Nowell, Sheffield Polytechnic)

Complexes of potassium. Two complexes of potassium with 8-hydroxyquinoline (HQ) (Fig. 4) were reported (Banerjee, Layton, Nyholm and Truter, *Journal of the Chemical Society* (*A*), (1969), 2536–2543) having formulae KHQ_2 and KH_2Q_3. They slowly give off fungicidal vapour (HQ itself) (Prof. R. L. Wain, ARC Unit of Systemic Fungicides). We have now determined the structures of both compounds with observations collected on the Picker diffractometer. In KHQ_2 the hydrogen atom of the hydroxy group was located so distinguishing the molecule HQ from the anion Q^-, an assignment confirmed by the bond angles. The crystal contains centrosymmetrical dimeric units; the Q^- anions each chelate and neutralise one K^+ cation while both the nitrogen and oxygen atoms of the neutral molecules are shared by both potassium ions of the dimer.

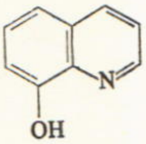


FIG. 4 8-hydroxyquinoline.

In KH_2Q_3 too the potassium ions are 6-coordinated, chelated by two parallel molecules of HQ and an anion Q^- with its plane at 78° to the HQ planes. Although the coordination numbers are the same for K^+ in both complexes, the larger cations rubidium and caesium form complexes only of the MH_2Q_3 type and are closely isostructural with the potassium complex. (Hughes)

One of the open chain compounds described in the *Rothamsted Report for 1974*, Part 1, p. 167, is 2,2′-di-*ortho*-carboxymethoxy-phenoxy diethylether, Fig. 5. It forms crystalline complexes with several alkali metal salts including potassium picrate and the crystal structure of this complex has been determined from observations collected photographically.

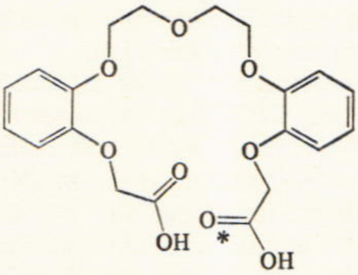


FIG. 5 2,2′-di-*ortho*-carboxymethoxyphenoxydiethylether. * marks the carbonyl oxygen atom shared between two potassium ions in the dimeric complex.

Infra-red and diffuse reflectance measurements had indicated the presence of picrate ion and complexed polyether acid, rather than free picric acid and the monopotassium salt of the polyether acid. Unequivocal location of the hydrogen atoms in the dicarboxylic acid confirmed this interpretation. The complex cation is dimeric, being held together by two bridging carbonyl groups. Each ligand spirals around one cation which contacts all five ether oxygen atoms; 8-coordination is completed by one terminal carbonyl and two bridging carbonyl oxygens. Contrary to our expectations, no intramolecular hydrogen bonding is involved in holding the acid ligand in the coordinating position. (Hughes, Mortimer, Truter and Wingfield)

Complexes of sodium. Sodium perchlorate with benzo-15-crown-5 forms complexes of (1:1) and (1:2) stoicheiometry, see paper 6. In the 1:1 compound the ether shows the same conformation as in the hydrated complex with sodium iodide (Bush & Truter, *Journal of the Chemical Society* (*Perkin Transactions II*) (1972), 341–344). Two oxygen atoms of the perchlorate anion complete 7-coordination about the cation. The 1:2 complex appears isomorphous with the potassium iodide complex, KI $(\text{benzo-15-crown-5})_2$ (Mallinson and Truter, *Journal of the Chemical Society* (*Perkin Transactions II*) (1972), 1818–1823); refinement is incomplete because one perchlorate ion is disordered. (Owen)

Sodium bromide 4,5-dimethoxybenzo-15-crown-5. This complex with the ligand shown in Fig. 3 consists of Na^+Br^- ion pairs with the sodium irregularly coordinated by the 5 oxygen atoms of the macrocyclic ring while the oxygen atoms of the methoxy groups take no part in the coordination. (Hanson)

Complexes of alkaline earth metal cations. In $Mg(SCN)_2$ benzo-15-crown-5 the cation is in the (good) plane of the 5 oxygen atoms, with the N atoms of the anions above and below, giving 7-coordination. The new conformation of the ether is the most regular yet found, the torsion angles being close to the expected 60° and 180°. (Owen)

Strontium perchlorate benzo-18-crown-6 trihydrate consists of complex cations $[(H_2O)_3 \cdot \text{Sr benzo-18-crown-6}]^{2+}$ with the Sr^{2+}9-coordinated by 6 ether oxygens (mean Sr–O, 2·68 Å) and 3 water molecules (mean Sr–O, 2·57 Å), the latter being hydrogen bonded to the anions. The observations were collected on the CAD-4 diffractometer in Dr. M. B. Hursthouse's laboratory, Queen Mary College, London. (Mortimer and Truter)

Barium perchlorate [b,n]dibenzo-24-crown-8 provided a difficult technical problem. There are two independent neutral entities in the asymmetric unit related to each other by a non-crystallographic centre of symmetry. Each entity consists of a barium ion 10-coordinated by the 8 oxygen atoms of a ligand and one oxygen from each of two perchlorate anions. (Hughes, Mortimer and Truter)

Theoretical treatments

Adaptation of a formula relating cation-oxygen distances to coordination number (Brown and Shannon, *Acta Crystallographica*, 1973, A29, 266) indicates that the assumption of purely electrostatic interaction may be valid for our complexes with sodium but not for those of potassium. (Truter)

The conformational energy of a molecule should reflect the strain imposed by its shape, or conformation, and is computed at the sum of the repulsions between pairs of atoms which are close but not bonded. For the six conformations of benzo-15-crown-5 found in eight crystalline compounds, the conformational energy is greatest the more nearly coplanar are the oxygen atoms, so it is largest for the $Mg(NCS)_2$ complex and least for the sodium bromide complex of 4,5-dimethoxybenzo-15-crown-5. The differences are small and sensitive to the accuracy of the atomic positions. (Owen)

Investigations on solutions

Formation constants. The availability of the MINIQUAD program (Sabatini, Vacca & Gans, *Talanta* (1974), 21, 53–77) allowing the simultaneous calculation of stability constants for co-existing complexes of different stoicheiometries has confirmed the predominance of the 1:2 sandwich formed by two substituted 15-crown-5 rings with potassium ions in methanol solution, over a simple 1:1 combination. Evidence of similar sandwich formation between the substituted 18-membered rings and caesium ions has been found, again paralleling the type of complexation found on crystallisation of the complexes. (Parsons and Wingfield)

Transport of ions through organic phases. We have extended this work by developing a method for measuring the partition coefficient of metal ions between water and a solution of crown in chlorobenzene/butanol. The results so determined are in good agreement with those obtained for ion transport across a stirred organic phase of crown in chlorobenzene/butanol, and these in turn are in accord with stability constants determined in methanol by EMF measurements. (Bradbury, Parsons and Wingfield)

^{13}C nuclear magnetic resonance (nmr) spectra. A catalogue of the ^{13}C nmr resonances of the known crowns and their relevant open chain precursors has been compiled. Assignment of individual peaks has been achieved either by analogy with known compounds or by (1) off-resonance de-coupling, which indicates the number of protons attached to a particular carbon; (2) selective proton de-coupling, which indicates the type of proton attached, or (3) T_1 relaxation studies which indicate the rate at which a carbon nucleus decays from its excited state and is often inversely proportional to the number of protons attached to the carbon atom.

In the presence of metal ions the relaxation times are considerably shortened, indicating binding in solution, but no good assessment of binding strength has so far been made. (Wingfield)

Field bean cultures. Work on the growing of field bean seedlings in nutrient cultures dosed with crown has recently started. We are determining the potassium uptake and stomatal resistance on varying both crown and potassium concentrations. (Bradbury, Parsons and Wingfield)

Biophysical experiments. Uptake of potassium, rubidium and caesium by rat liver mitochondria is greatest in the presence of a macrocyclic ether large enough to enclose the cation completely. Less effective compounds are those such as tertiary butyl benzo-15-crown-5 (Fig. 3), two molecules of which enclose the cation in a 'sandwich' while compounds which allow the cation to contact solvent or anion are completely ineffective. Within a series of sandwich-forming compounds the rank order of effectiveness with mitochondria does not follow that of the equilibrium stability constants; all compounds of Fig. 3 have similar stability constants with potassium in methanol, but only the tertiary butyl derivative is effective with mitochondria. (Parsons, Wingfield and Truter, with Drs. E. J. Harris and B. Zaba, University College, London)

Crystallographic technique

A routine has been developed for the calculation of all unit cell parameters from single crystal photographs taken on a Weissenberg camera. Photographs may routinely be made with the crystal held at a controlled temperature between room temperature and −150°C.

MOLECULAR STRUCTURES DEPARTMENT

A new automatic diffractometer, the Enraf-Nonius CAD-4 with Kappa geometry, has been installed and its facilities tested. (Hanson and Hughes)

Computing

4-70 Programs. An updated version of the program SHEL-X was implemented and a routine written to allow the use of up to a four degree polynominal weighting scheme with it. (Hanson and Owen)

MINIQUAD, a program from Dr. P. Gans of Leeds University, has been implemented. This program is used to calculate the equilibrium formation constants of complexes with metal cations, as described in the *Rothamsted Computer Newsletter*, June 1976. Major amendments needed for our problems were for non-ideal electrode response and for the addition of solid instead of titration of solutions. (Owen)

CAD-4 a program from Dr. M. Hursthouse's group at Queen Mary College adapted to process the data tapes produced by the CAD-4 diffractometer. (Owen)

IBM 1130 Programs. SFACT calculates atomic scattering factors for copper or for molybdenum $K_{\bar{\alpha}}$ radiations from the analytical coefficients in *International Tables for X-ray Crystallography*, (1974) **IV**, 99–101. This is faster and more accurate than the previous curve interpolation program. (Hanson)

Staff and visiting workers

Mary R. Truter received the Chemical Society award for Structural Chemistry, she read an invited paper at the 9th Jerusalem Symposium on Quantum Chemistry and Biochemistry and lectured at the Universities of Padua and Ferrara.

Dr. Margaret E. Farago, Bedford College, London and two sandwich students, P. Andreas and M. Bradbury worked in the Department.

Publications

GENERAL PAPERS

1 TRUTER, M. R. (1976) Chemistry of the calcium ionophores. In: Calcium in Biological Systems. *Symposium of the Society for Experimental Biology* No. 30, pp. 19–40.

RESEARCH PAPERS

2 HANSON, I. R., HUGHES, D. L. & TRUTER, M. R. (1976) Crystal and molecular structure of 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosin (Dibenzo-24-crown-8). *Journal of the Chemical Society* (*Perkin Transactions II*), 972–976.

3 HUGHES, D. L. (1976) Crystal structures of the dihydro- and 2α-hydroxydihydro-derivatives of phytuberin. *Journal of the Chemical Society* (*Perkin Transactions I*), 1338–1345.

4 OWEN, J. D. & WINGFIELD, J. N. (1976) A new conformation of the cyclic polyether benzo-15-crown-5 in its solvated complexes with calcium isothiocyanate: X-ray crystal structure analysis. *Journal of the Chemical Society* (*Chemical Communications 1976*), 318–319.

5 Owen, J. D. X-ray crystal structures of two pyrethroid insecticides: cis-3-phenoxybenzyl 3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate and the 3-(2,2-dichlorovinyl) analogue. *Journal of the Chemical Society* (*Perkin Transactions I*), 1231–1235.

6 Parsons, D. G. & Wingfield, J. N. (1976) Perchlorate anion to metal coordination in some alkali metal-cyclic polyether complexes. *Inorganica Chimica Acta* **17**, L25–L26.

7 Parsons, D. G. & Wingfield, J. N. (1976) Alkaline earth metal complexes with some macrocyclic 'crown' polyethers. *Inorganica Chimica Acta* **18**, 263–267.