

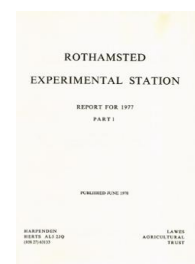
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Molecular Structures Department

Mary R. Truter

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MOLECULAR STRUCTURES DEPARTMENT

MARY R. TRUTER

Staff

Head of Department Mary R. Truter, D.Sc.

Senior Scientific Officers

D. L. Hughes, PH.D.
J. D. Owen, PH.D.
D. G. Parsons, PH.D.
J. N. Wingfield, PH.D.

Higher Scientific Officer

I. R. Hanson, B.Sc.

Personal Secretary

Joyce Johnson

Introduction

The main activity of the year was the move into our new building at the beginning of June which was accomplished with great efficiency by the Engineering and Maintenance Service Department volunteers. We arrived in time for the official opening and had not been in long enough to make the place dirty.

Unfortunately problems with the air conditioning delayed the movement of our automatic diffractometer, some X-ray equipment and the 1130 computer until mid-December. We were able to carry on using these instruments by continuing to enjoy the hospitality of our colleagues in Soil Microbiology and Computer Departments. We are very grateful to them for having housed our equipment for 3½ years.

We have been able to undertake some structural analyses for the Unit of Nitrogen Fixation and to repay some of our debts to colleagues in the Polytechnic of North London and in Sheffield City Polytechnic by collecting observations on three crystals. An unwelcome feature has been the need to divert effort to unproductive work caused by legislation on radiation safety.

The main emphasis continues to be on the coordination chemistry of alkali metals and alkaline earth metals. Now that crystal structure analysis has become more rapid, results are included with other aspects of the work under the classes of compound involved.

Coordination Chemistry

Neutral bicyclic ligands. Novel compounds which form three-dimensional cages have been synthesised. They are derived from one of the isomers of the dihydroxydibenzo-14-crown-4 compound reported last year (*Rothamsted Report for 1976*, 191) and shown in Fig. 1. Separation into *cis* and *trans* forms on a preparative scale has been achieved by selective elution from Florisil columns. It is possible to crystallise the *cis* isomer selectively as its lithium chloride complex by suitable choice of a solvent during its preparation. Reaction of the *cis* diol with the appropriate ditosyloxy compounds has produced the bicyclic compounds I, II and III of Fig. 2. These ligands require specialised isolation procedures because of their complexing properties. They form stable complexes with salts of alkali and alkaline earth metals with lead and silver salts, and also with strong acids by binding to the hydroxonium ion, H_3O^+ . (Parsons)

The crystal structure of the uncomplexed molecule (I) has been determined. The 'faces' on either side of the aliphatic chain are not equivalent, one having five oxygen atoms suitably placed to bond to one cation while the other would require change of conformation to form a bi- or tri-dentate complex. The molecule is very compact and several of the torsion angles differ from ideal values. (Owen)

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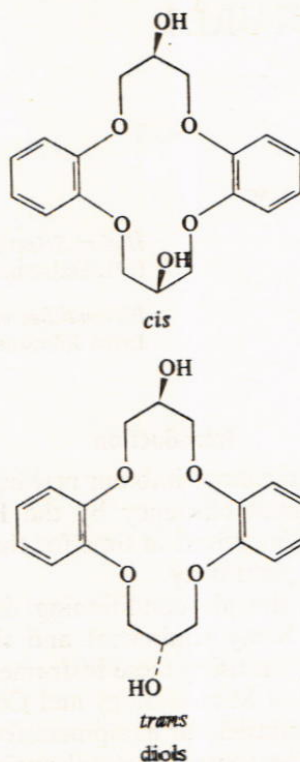


FIG. 1. Isomers of dihydroxydibenzo-14-crown-4

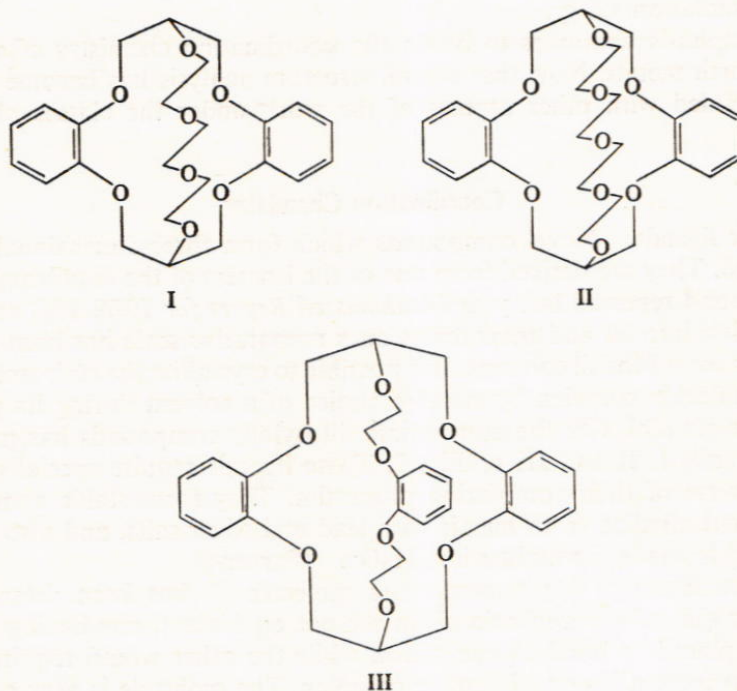


FIG. 2. New bicyclic complex agents

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The high formation constants have made it necessary to improve the accuracy of measurements of e.m.f. in methanol. A constant ionic strength is maintained with tetrabutylammonium bromide and the solution is buffered to keep the hydrogen ion concentration low compared with that of the cation. In water there are problems because the alkali metal halide complexes are much more soluble than the ligands. The method adopted is to measure the free cation concentration present in a saturated solution of the ligand. The values obtained for the formation constants are given in Table 1; these show a 100-fold discrimination against rubidium compared with sodium and potassium for ligand I, and a smaller discrimination against sodium for ligand II. The actual values are among the highest recorded for aqueous solutions of the alkali metal cations and are unique for compounds devoid of pH sensitive nitrogen atoms. (Parsons and Delve)

TABLE 1

Formation constants ($l \text{ mol}^{-1}$) where $K_e = [M^{n+}L]/[M^{n+}][L]$ in water at 25°C

Ligand, L	$M^{n+} = \text{Na}^+$	K^+	Rb^+
I	3×10^5	5×10^5	5×10^3
II	3×10^3	2×10^4	2×10^4

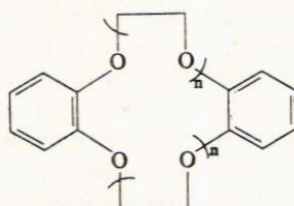
Neutral macrocyclic molecules. Complexes are known of the molecules with two benzene rings shown in Fig. 3 where $n = 2, 3$ and 4 , but not of that with $n = 1$. Dibenzo-12-crown-4 (Fig. 3) crystallises with the centre of the molecule on the centre of symmetry. The two rigid catechol groups are related by a deep step so that the parallel planes of the benzene rings are 2.09 \AA apart. The torsion angles in the ring indicate some conformational strain. Space-filling models suggest that the molecule is unlikely to be able to change its conformation to one with all oxygen atoms suitably disposed to complex a cation. (Hughes, with Dr I. W. Nowell, Sheffield Polytechnic)

As reported (*Rothamsted Report for 1974*, Part 1, 167 and for 1975, Part 1, 184) derivatives of dibenzo-18-crown-6 having two or four methyl groups in the macrocyclic ring form complexes. The unsymmetrical potential ligand, dimethyldibenzo-21-crown-7 (Fig. 3) has been subjected to crystal structure analysis. One oxygen atom faces out of the ring and a methyl group faces in, and several torsion angles are not of the ideal values at 180 or $\pm 60^\circ$. (Owen, with Dr. I. W. Nowell, Sheffield Polytechnic)

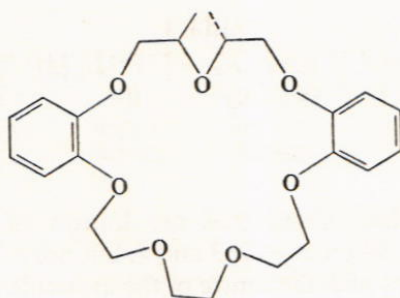
Complexes with alkali and alkaline earth metal cations. Sodium tetraphenylborate reacts with benzo-15-crown-5 (Fig. 3) to form 1:1 solvated complexes and a 1:2 complex (Parsons, Truter and Wingfield, *Inorganica Chimica Acta* (1975), **14**, 45–48). Crystal structure analysis of the 1:2 complex has shown that the sodium ions are sandwiched between two molecules of benzo-15-crown-5 which are not related to one another. The arrangement is quite different from that in the analogous sodium perchlorate complex (*Rothamsted Report for 1976*, Part 1, 145). Thus the change of anion has completely altered the shape of the cationic complex. The two molecules of benzo-15-crown-5 have the same conformation as those in the free molecule. The sodium ion is within 2.7 \AA of five oxygen atoms with the sixth at 2.9 \AA and calculation of the bond valences shows that four more contacts up to 3.3 \AA are still significant. (Owen)

The larger rings dibenzo-24-crown-8 and dibenzo-30-crown-10 may form complexes with the ratio cation:ligand 1:1 or 2:1. Further investigation of the factors affecting this has led to the isolation and characterisation of 1:1 complexes. With $L =$ dibenzo-24-crown-8, calcium picrate gives a tetrahydrate, and barium picrate a dihydrate. With $L =$ dibenzo-30-crown-10 anhydrous compounds were obtained with calcium tetraphenylborate, barium picrate and potassium picrate. (Wingfield)

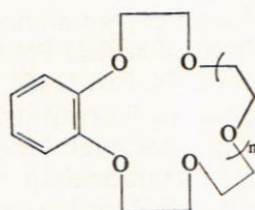
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- n = 1 dibenzo-12-crown-4
- n = 2 dibenzo-18-crown-6
- n = 3 dibenzo-24-crown-8
- n = 4 dibenzo-30-crown-10



dl-7,9-dimethyldibenzo-21-crown-7



- n = 1 benzo-15-crown-5
- n = 2 benzo-18-crown-6

FIG. 3. Some macrocyclic compounds

Crystals of the complex between rubidium thiocyanate and dibenzo-30-crown-10 have been shown to be hydrated and identical with those originally reported (J. Hašek, K. Huml and D. Hlavatá, personal communication) to be anhydrous and to have the same conformation of the ligand as in the potassium iodide complex (Bush and Truter, *Journal of the Chemical Society, Perkin Transactions (1972) II*, 345). (Owen and Wingfield)

The crystal structure of barium picrate dibenzo-24-crown-8 dihydrate has been determined by the heavy atom method (see Paper 6). The results show the first known example of a hydrated cation where both the barium ion and its water of hydration are jointly co-ordinated by the polyether. The dibenzo-24-crown-8 molecule, in a conformation unlike any of the four found previously, has a pseudo centre of symmetry in the ring. The barium cation lies away from this and is coordinated to five ring oxygen atoms and to the oxygen atom of a solvent water molecule which occupies the pseudo-symmetrically related site. This water molecule is hydrogen bonded to two of the remaining oxygen atoms. Ten-fold coordination to the barium is completed by interaction with

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a second water molecule and with the two picrate ions, one of which coordinates through one phenolate oxygen, and the other chelates through the phenolate oxygen atom and one on an *o*-nitro group. Hydrogen bonding involving the two water molecules connects the complexes in chains parallel to the crystal *a* axis. There is site disorder in one of the O-CH₂-CH₂-O sections of the polyether ring. (Hughes)

Complexes with other cations. Work started last year (*Rothamsted Report for 1976*, Part 1, 193) on complexes of thallium compounds has been published (M. E. Farago, *Inorganica Chimica Acta* (1977), **23**, 211-213) as has that on transition metal ions (M. E. Farago, *Inorganica Chimica Acta* (1977), **25**, 71-76).

Effects on plants. Experiments have been carried out to determine the effect of crowns on the uptake and release of potassium and sodium ions from field beans. Root bathing solutions containing varying concentrations of benzo-18-crown-6 (Fig. 3) have been studied, and results indicate that the crown is taken up by the plant, and at 5 mM and above, blackening of roots, shoots and leaves takes place. Ion release into the bathing solution, and ion content of roots and shoots of treated plants are similar to those obtained from treatment with Triton X at similar concentrations (i.e. above the critical micelle concentration), and may be explained by non-selective damage to the root membranes, causing a general leakage of root material into the bathing solution. (Bradbury, Parsons and Wingfield)

Open chain compounds. Investigation of open chain compounds as complexing agents, last reported in *Rothamsted Report for 1974*, Part 1, 167, has continued with the hydroxy acids, hydroxy esters and diols shown in Fig. 4. Reactions with the metal thiocyanates were tested. Only one fully characterised complex of a hydroxy acid has been obtained, i.e. $n = 2$, $R = H$ gives a 1:1 complex with potassium thiocyanate and one methanol of crystallisation. The corresponding ester, i.e. $n = 2$, $R = C_2H_5$ forms complexes more readily and the potassium and calcium thiocyanate complexes have been characterised. In the diols the larger one with $n = 2$ gives complexes with potassium and calcium thiocyanates while sodium, rubidium and magnesium thiocyanates appear not to react.

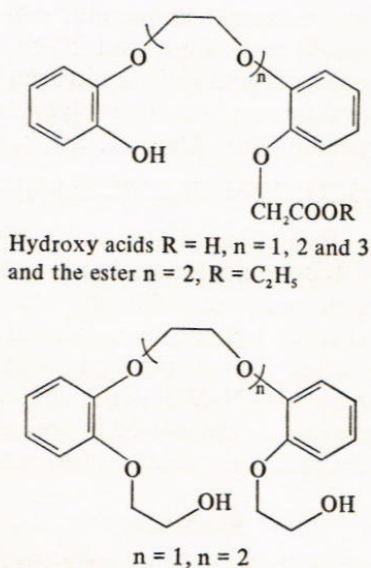


FIG. 4. Open chain compounds

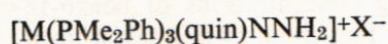
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The smaller compound $n = 1$ forms solvated complexes with sodium, potassium or calcium thiocyanates. (Wingfield)

The crystal structure of the sodium thiocyanate complex of the $n = 1$ diol has been determined; there are two independent NaNCS , L entities in the asymmetric unit. Each sodium ion is coordinated in approximately a pentagonal bipyramid. Five of the oxygen atoms from one ligand constitute the equatorial plane, one apex is formed by the nitrogen of a thiocyanate ion and the other by a terminal OH group from a second ligand molecule. Chains of molecules are thus connected through the crystal. There are two almost identical chains, one from each crystallographically independent entity, suggesting that the arrangement in the ligand molecule represents a stable conformation. (Hughes)

Collaboration with the Unit of Nitrogen Fixation

Some intermediates in the reduction of molecular nitrogen having the general formula:



where $M =$ molybdenum or tungsten, $X =$ chlorine, bromine or iodine, and quin = 8-quinolinolato anion shown in Fig. 5, have been received from Dr R. L. Richards.

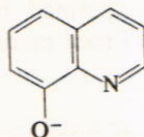


FIG. 5. 8-Quinolinolato ligand, the anion of 8-hydroxyquinoline

Structures of the compounds with $M = \text{Mo}$ or W and $X = \text{I}$ have been determined. In both, the coordination about the metal is octahedral with the metal in the plane formed by the three phosphorus atoms and with the oxygen atom of the chelating 8-quinolinolato anion *trans* to the NNH_2 ligand. Refinement of the structure of the tungsten compound is complete and the crystals have been found to contain disordered solvent molecules of 8-hydroxyquinoline. This has reduced the precision obtainable in the bond lengths of particular interest, $\text{W-N} = 1.76 \pm 0.04$ and $\text{N-N} = 1.36 \pm 0.02$ Å. Greater accuracy has been attained with the molybdenum compound, which crystallises in a different form, without any solvent, $\text{Mo-N} = 1.743(4)$ and $\text{N-N} = 1.347(7)$ Å which is intermediate between the values for single and double nitrogen-nitrogen bonds. (Hanson)

In nitrogenase, one enzyme fraction contains molybdenum and sulphur so there is particular interest in the compound, from Dr G. J. Leigh, of formula:



The structure confirms the formation of the novel NNCOOEt ligand. The molybdenum atom has pentagonal bipyramidal coordination, two dimethyldithiocarbamate ions lie in the equatorial plane, each coordinating the molybdenum through both sulphur atoms and the third chelates at the fifth equatorial and one apical position. The dinitrogen ligand is in the other apical position with $\text{Mo-N} = 1.732 \pm 0.005$ Å, $\text{N-N} = 1.274 \pm 0.007$ Å and the Mo-N-N entity is linear. Unfortunately the dichloromethane solvent molecule appears to be disordered in several orientations and, at present, cannot be properly resolved. Further compounds in this series are in hand. (Hughes)

Equipment

A low temperature device for the CAD-4 diffractometer has been installed and tested and was used to obtain accurate unit cell dimensions for benzo-15-crown-5. (Hanson)

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Electrically operated shutters for our X-ray tubes have been designed and one has been installed and used satisfactorily. The shutters are interlocked to the camera position and cannot be opened unless the camera is in front of the X-ray port. Complete enclosures for our X-ray tables, similarly interlocked, are at present under construction in the E. and M.S. Workshop. We hope that these measures will bring our equipment into compliance with the legislation on Radiation Safety expected in July 1978. (Hanson)

An L.K.B. batch microcalorimeter fitted with a dual injection system has been used to carry out an 'entropy titration', where ΔG , ΔH and ΔS values may be obtained from one experiment. Data so far obtained in water give, for benzo-18-crown-6, K_e values (see Table 1 for definition) in very good agreement with those previously obtained using ion selective electrodes for alkali metals, and this method may now be extended to investigate calcium and magnesium ion complexation. (Wingfield)

Computing

4-70 programs. A new and more powerful version of a program MULTAN 76 (Dr P. Main and Dr M. M. Woolfson, University of York) has been implemented. Although it is expensive in computer time it can solve structures which are otherwise intractable. It was used to solve the structure of sodium tetraphenylborate (benzo-15-crown-5)₂, described above, in which 64 non-hydrogen atoms had to be located all with similar scattering power. (Owen)

Updating, improvement and maintenance of the program SHEL-X have continued. The program PEAKS reads a list of peak positions on a Fourier synthesis and interactively assigns atom names suitable for input to SHEL-X. Simple geometry from a list of atomic coordinates or peaks on a Fourier synthesis to give distances and angles is computed by BONDS. Improved and more convenient weighting schemes for refinement of parameters (WET) and, finally, a print out of these and their standard deviations in a form suitable for publication (ATPAR) results from subsidiary programs. (Hanson and Owen)

1130 programs. Improvements have been made in several existing programs. The plotting program (INIAX) will now draw 1000 atoms, needs a less complicated input and runs faster than previously. Torsion angles (TORSN) can be calculated about every bond between 1.2 and 1.6 Å, thus removing the need to punch tedious input. (Owen)

The symbolic addition program for solving structures by direct methods has been made more flexible. (Hughes)

PDP8 computer. The CAD-4 diffractometer is controlled by this dedicated computer. Programs are supplied in FORTRAN and can be modified and expanded. CELSQ has been written; from a list of measured θ values of reflections it refines the unit cell dimensions of a crystal with constraints imposed by the lattice symmetry. (Owen)

Visits and visitors

We enjoyed lectures from two overseas visitors, Dr W. L. Duax of the Medical Foundation of Buffalo, and Dr D. Eatough of Brigham Young University, Provo.

Mary R. Truter visited the United States in August, primarily to give an invited lecture at the 1st Symposium on Macrocyclic Compounds held at Brigham Young University, Provo, and also to lecture at Michigan State University.

Catherine L. Mortimer was awarded the degree of Ph.D. of the University of London and left in June for a permanent appointment. Mr M. Bradbury and Mr R. K. G. Delve, both of North-East London Polytechnic, worked in the Department.

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Publications

THESIS

- 1 MORTIMER, C. L. (1977), Crystal structures of complexes of d° cations. Ph.D. Thesis, University of London.

GENERAL PAPERS

- 2 HUGHES, D. L. & OWEN, J. D. (1977) Natural products and related compounds. *Chemical Society: Specialist Periodical Report. Molecular Structure by Diffraction Methods* **5**, Ch. 3, pp. 147-217.
- 3 TRUTER, M. R. (1977) Effects of cations on groups IA and IIA on crown ethers. In: *Metal-ligand interactions in organic chemistry and biochemistry*. Eds. B. Pullman & N. Goldblum, Dordrecht-Holland: D. Reidel Publishing Co., Part 1, 317-335.

RESEARCH PAPERS

- 4 HARRIS, E. J., ZABA, B., TRUTER, M. R., PARSONS, D. G. & WINGFIELD, J. N. (1977) Specificities of cation permeabilities induced by some crown ethers in mitochondria. *Archives of Biochemistry and Biophysics* **182**, 311-320.
- 5 HUGHES, D. L., MORTIMER, C. L., PARSONS, D. G., TRUTER, M. R. & WINGFIELD, J. N. (1977) Crystal structure of an open chain polyether dicarboxylic acid complexed with potassium picrate. *Inorganica Chimica Acta* **21**, L23-L24.
- 6 HUGHES, D. L. & WINGFIELD, J. N. (1977) Crystal structure of a simultaneous water-barium ion coordination to 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 (Chemical Communications)*, 804.