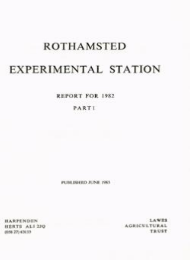
ROTHAMSTED RESEARCH

Report for 1982 - Part 1



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Molecular Structures Department

Mary R. Truter

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MOLECULAR STRUCTURES DEPARTMENT

MARY R. TRUTER

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Introduction

This year we report progress in coordination chemistry, not only in our continuing programme on selective complexing agents for alkali and alkaline earth metal cations, but also in our studies with open chain α,ω-hydroxy acid polyethers coordinated to transition metals, which yield intermediate macromolecular ligands capable of binding alkali metal ions. Production of a molecule containing cobalt II may be used as a new 'spot test' for potassium.

There has been an increase in our crystal structure solving capacity, alas only temporary, in the person of Dr C. H. L. Kennard, Reader in the University of Queensland. He has extended the range of coordination compounds to those with herbicides as ligands.

The isolation and structure determination of an ammonium complex with a bicyclic ligand has enabled us to correlate and explain some of the results we have reported earlier.

We have begun to use high resolution nuclear magnetic resonance spectroscopy for structural studies in solution and also for comparison in the solid state.

Coordination chemistry

Acyclic ligands

Polyethers. The hydroxy acid, HL, (Fig. 1) reacts with cobalt ions to form a macroligand framework $(CoL_4)^{2-}$; in this, a tetrahedral cobalt atom holds together four L^- ligands which form two hydrogen-bonded planes providing two cavities, each of ten oxygen atoms, coordinating potassium ions (*Rothamsted Report for 1981*, Part 1, 150). The potassium ions stabilize the structure, allowing the crystalline complex to be isolated. We have now found that this proposed macroligand intermediate will 'scavenge' potassium ions from potassium halide solutions in organic solvents, and the resultant blue compound is freely soluble, without dissociation, in methylene chloride. Thus, if a solution of HL in CH_2Cl_2 is treated with a pale pink solution of cobalt(II) acetate in aqueous potassium bromide, a blue colour rapidly develops in the methylene chloride layer. Only a faint colour is observed when rubidium bromide is used, and no colour is transferred at all for sodium, caesium, thallium or barium salts. This, therefore, may be used as a 'spot test' for potassium and shows the remarkable selectivity of this ligand system for potassium. The combination of transition metal and open chain ligand may also be used for transporting potassium ions across a lipid-like barrier (e.g. methylene chloride). In the absence of transition metal, transport is very slow.

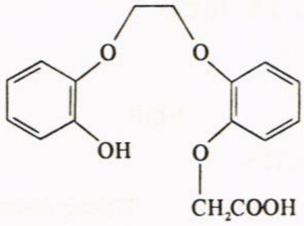


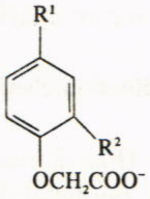
FIG. 1. An acyclic polyether, HL having a hydroxy and a carboxylic acid function.

The analogous zinc complexes $Zn(L_2M)_2$, (M = K, Rb), have also been isolated and characterized, and, apart from being colourless, are very similar to the cobalt complexes. (Wingfield)

In an attempt to change the separation of the coordinating ligands, and thereby modify the ion selectivity, a new class of macroligand has been synthesized. Reaction of HL with $Ru(CO)_3$—$(PPh_3)_2$ gave $[Ru(CO)_2(PPh_3)_2L_2]$. Infrared spectroscopy suggested that the CO groups were mutually *cis*, and that the carboxylates were monodentate and mutually *cis*. The crystal structure determination showed this to be the case, with the phosphine ligands *trans*. However, the L ligands are not held in cyclic form by hydrogen bonds but have extended conformations. The complexation of this, and similar ligands, is being studied. (Hughes and Wingfield)

Phenoxyacetic acids. Crystal structure determination has shown that potassium has eleven near neighbours [K—O, 0·2690(2)—0·3222(3); K—Cl, 0·3261(1) nm] in a complex with the herbicide, 2,4-dichlorophenoxyacetic acid, (Fig. 2(a)).

The compound, μ-aqua-di-μ[2-chlorophenoxyacetato-(O,O′)]-bis[2-chlorophenoxyacetato]-bis(pyridine)nickel(II)hydrate (Fig. 2(b)) has two octahedral nickel(II) atoms [Ni–Ni, 0·360(1) nm], bridged by two carboxylate groups and an oxygen of a water molecule [Ni–O(H_2O)–Ni, 110(1)°].



(a) $R^1 = R^2 = Cl$
(b) $R^1 = H \quad R^2 = Cl$
(c) $R^1 = COOH \quad R^2 = H$

FIG. 2. Phenoxyacetic acids.

Two transition-metal complexes of *p*-carboxyphenoxyacetic acid (Fig. 2(c)) were prepared and their structures shown to be significantly different. Tetraaquabis(*p*-carboxyphenoxyacetato)manganese(II) is polymeric with the ligand linking different distorted octahedral manganese atoms through the terminal acid groups. The coordination around the metal atom is made up of four water molecules and the two different ends of the ligand *cis* to one another. In the corresponding nickel(II) complex, the metal atom is octahedral and at a centre of symmetry. The ligand is bonded through the phenoxy acid oxygen, with the *p*-carboxy acid end hydrogen bonded to another symmetry related carboxy group. (Kennard)

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Monocyclic ligands

Investigation of the crystal structures of the three isomeric diols (Fig. 3) (*Rothamsted Report for 1981*, Part 1, 150) by X-ray diffraction has been completed with the determination of isomer C, m.p. 170°C. The hydroxy groups each take part in hydrogen bonding which holds the molecules in double chains with links of 0·269 and 0·285 nm. Neutron diffraction measurements of isomer B, m.p. 118°C, have allowed us to determine the hydrogen atom coordinates with more confidence, confirming that only one hydroxy hydrogen atom takes part in O—H . . . O bonding; this holds the molecules in single chains with links of 0·293 nm.

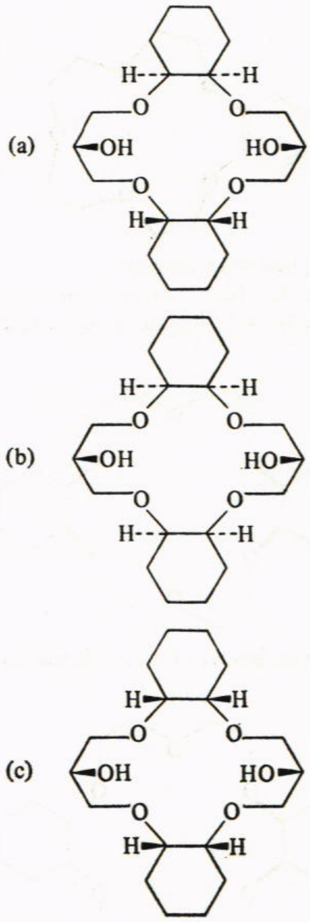


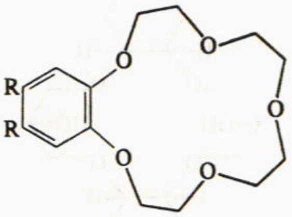
FIG. 3. Three isomeric dicyclohexano-14-crown-4 diols.

Comparison with the bicyclic molecules formed by treating each diol with o-di(TsOCH$_2$CH$_2$O)C$_6$H$_4$ (*Rothamsted Report for 1981*, Part 1, 150) shows that isomers A and C require an inversion of one cyclohexano ring, while for isomer B only, changes in some macrocyclic torsion angles are necessary. (Kennard, Owen, Parsons and Truter)

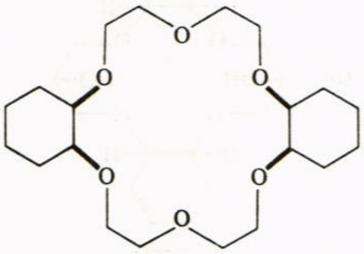
In collaboration with the Food Research Institute in Norwich, we have begun an investigation of the cyclic polyethers and their complexes with solid state nuclear magnetic resonance on the 300 MHz Brucker spectrometer. Benzo-15-crown-5 (Fig. 4(a)), and a series of its complexes with sodium and potassium were chosen for study, since the crystal structures of many of them had previously been determined. Good resolution

^{13}C spectra were obtained by spinning the sample at the magic angle and applying cross polarization techniques. Further pulse techniques eliminated the resultant side bands, and our preliminary results show significant resonance inequivalence in the solid state in comparison with solution spectra. This is attributed to the molecular packing in the crystal. (Payne and Wingfield)

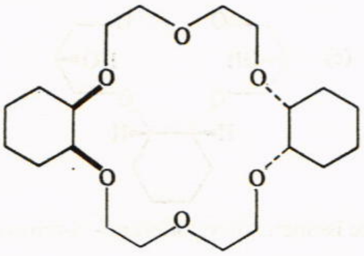
A detailed analysis of the electrical conductivities of sodium bromide complexes of a series of substituted benzo-15-crown-5 complexes (Fig. 4(a), (b) and (c)) in methanol demonstrated that the extent of ion pairing in *solution* was independent of substituent R, and thus bore little relation to complex stability, and the adoption or not of ion pairing in the solid state crystal structure. The results are thus supportive of a purely ion-dipole metal-ligand interaction. (Payne)



(a) R = H, benzo-15-crown-5
(b) R = Br, 4,5-dibromobenzo-15-crown-5
(c) R = OCH_3, 4,5-dimethoxybenzo-15-crown-5



(d) *cis syn cis* isomer of dicyclohexano-18-crown-6



(e) *cis anti cis* isomer of dicyclohexano-18-crown-6

FIG. 4. Crown ethers.

Of the isomeric compounds, dicyclohexano-18-crown-6, (Fig. 4), the *cis-syn-cis* isomer, has been found consistently to give higher stability constants in its complexes in solution. To compare the isomeric ligands with the same complexed entity, we determined the crystal structures of complexes formed by dimethylthallium picrate with each isomer. In each there are complex cations, $[Me_2T1.crown]^+$ consisting of linear Me_2T1

entities normal to the plane through the six O-atoms of the crown ligands, and picrate anions.

In the complex with the *cis-syn-cis* isomer there is an approximate plane of symmetry through the Me_2Tl group and the O-atoms of the $-CH_2-O-CH_2-$ groups. This differs by inversion of one cyclohexane ring from the conformation found in complexes with other metals.

In the complex, with the *cis-anti-cis* isomer, the thallium atoms lie on, and the picrate anions are disordered about, centres of symmetry. The conformation of the crown ligand, with $\bar{1}$-symmetry, is the same as that in the sodium complex of this isomer (Mercer & Truter, *Journal of the Chemical Society, Dalton Transactions* (1973), 2215–2220).

In both isomers, one O-atom is axially, and the other equatorially, substituted on each cyclohexane ring. The Tl . . . O_{axial} distances are significantly longer than the Tl . . . $O_{equatorial}$ lengths. This difference can be seen, but has not previously been noted, in several similar complexes; we postulate that it results from steric hindrance between hydrogen atoms on the cyclohexane and the polyether macrocyclic rings. (Hughes and Truter)

Bicyclic ligands

The kinetics and thermodynamics of complexation for the macrobicyclic ligand in Fig. 5(a) with alkali metal salts in dimethyl formamide have been investigated. Activation free energies of decomplexation were determined by variable temperature ^{13}C NMR, while free energies of complex formation were calculated from stability constants ob-

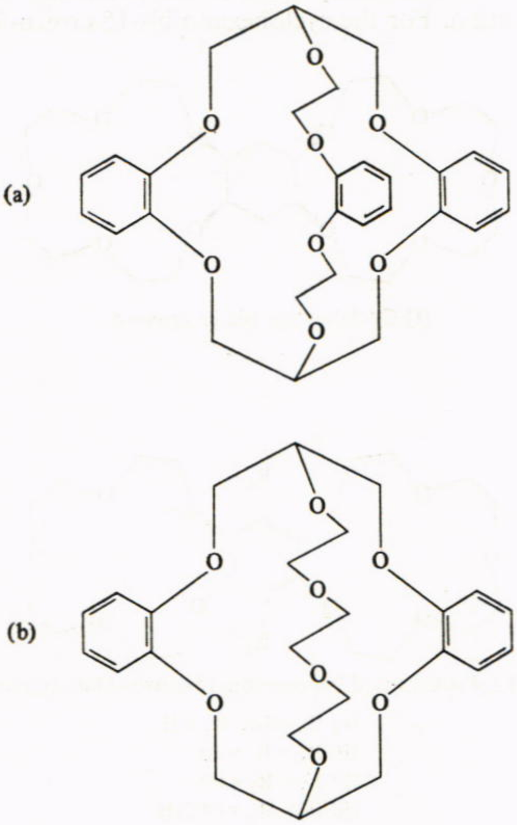
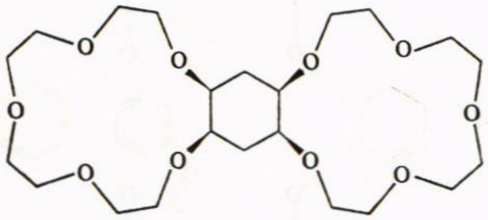


FIG. 5. Two macrocyclic polyethers.

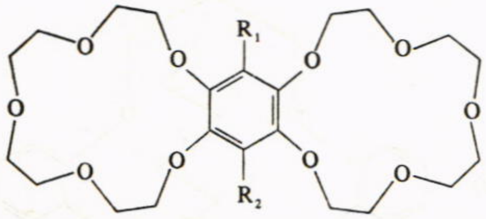
tained by potentiometric titrations using ion-selective glass electrodes. Remarkably, the sodium complex, which has a lower free energy of formation than the potassium one, has a higher free energy of activation for decomplexation, i.e. it is more difficult to decompose than the potassium complex. A high resolution ^{1}H NMR study, using a Varian XL 200 spectrometer at University College London, of the solution structure of the ligand and complexes is currently being undertaken to explain this feature. (Payne and Wingfield)

With the ammonium salts studied previously, the complexes with ligand in Fig. 5(b) crystallize with labile water. However, the ammonium iodide complex has been found to be sufficiently stable for crystal structure determination. Its empirical formula is $NH_4I, C_{24}H_{30}O_8, nH_2O$. Two centrosymmetrically related ammonium ions are entrapped between two ligand molecules forming dimeric complex cations. In packing, these form channels which are occupied by iodide ions and water molecules, the latter being disordered over several sites to give $n \sim 1{\cdot}5$. In the complex cations, each ammonium nitrogen atom is nearly coplanar with, and equidistant (0·272 – 0·284 nm) from, six oxygen atoms of one ligand; on one side are the remaining two oxygen atoms on a benzene ring at $>0{\cdot}30$ nm and, on the other, the nitrogen atom is hydrogen bonded (N . . . O 0·298 nm) to one of the aliphatic oxygen atoms of the other ligand in the dimer. This is a new form of coordination for the ammonium ion. Changes in conformation of the ligand from the uncomplexed form (Owen, *Journal of the Chemical Society, Perkin Transactions II* (1981), 12–18) result in higher symmetry. (Kennard, Parsons and Truter)

A number of complexes of the potential 'clam' type of bis-crown ethers (*Rothamsted Report for 1980*, Part 1, 145) with metal and ammonium salts have been prepared and characterized. With 1:1 stoichiometry there is the possibility of both polyether rings coordinating a single cation. For the cyclohexano bis-15-crown-5 compound, (Fig. 6) I,



(I) Cyclohexano bis-15-crown-5



(II) 1,4 substituted benzene(bis-15-crown-5) derivatives

IIa R_1 = Br, R_2 = H
IIb R_1 = R_2 = Br
IIc R_1 = R_2 = CN
IId R_1 = R_2 = $CONH_2$

Fig. 6. (I) Cyclohexano bis-15-crown-5. (II) 1,4 substituted benzene(bis-15-crown-5) derivatives.

the best fit would be expected for potassium and barium, the divalent cation having the advantage that stronger interactions may encourage the 'clam' formation. The ammonium ion was found to give a 2:1 cation:ligand stoichiometry. Complexes of each of these cations gave suitable crystals for structure analysis, see below. The results indicated that if these bis-crowns are to take up a 'clam' conformation, the cyclohexano ring must be forced into the energetically less favourable 'boat' conformation. In an endeavour to achieve this by forming a bridge between the two unsubstituted carbon atoms, we have started by making a substituted aromatic precursor, II. Stepwise bromination has yielded first the monobromo compound, (Fig. 6), IIa, then the dibromo compound, IIb. This has then been converted to the dinitrile, IIc, which has, in turn, been hydrolyzed (hydrated) to the diamide, IId. (Parsons)

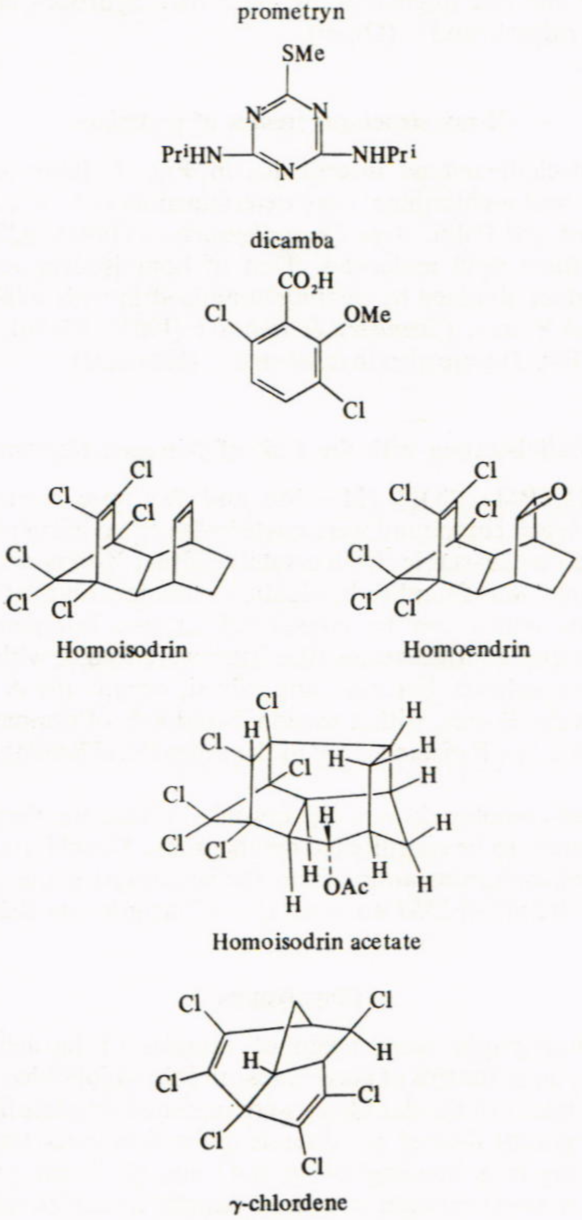


FIG. 7. Pesticides.

Crystal structure determinations of KSCN(I), $Ba(SCN)_2$(I) $2H_2O$ and $(NH_4SCN)_2$(I) have shown all three to contain dimeric complex cations consisting of two cations and two ligands (I) related by a crystallographic centre of symmetry. (The second ammonium ion is not coordinated to the ligand but forms hydrogen bonds N—H . . . N and N—H . . . S to the two anions). The cyclohexane rings are in the 'chair' conformation with the polyether rings of one ligand nearly coplanar; the cations are sandwiched between two 15-crown-5 rings from different ligands. The ligands exhibit different conformations in each of the three complexes and also different patterns of disorder. Each potassium ion is coordinated to ten oxygen atoms; the K–O distances are between 0·275 and 0·306 nm, a wider range than in monocyclic complexes. The ten barium–oxygen distances range from 0·275 to 0·302 nm. The ammonium ion forms simple hydrogen bonds to two oxygen atoms of one ligand and one single and one bifurcated hydrogen bond to involve three oxygen atoms of the other ligand. (Owen)

X-ray structural studies of pesticides

The structures of cyclodiene-type insecticides in Fig. 7, homoisodrin, homoendrin, homoisodrin acetate and γ-chlordene, were determined as part of a long-term investigation (Smith, Kennard and Palm, *Acta Crystallographica* (1981), B37, 2237–2239) of the mode of action of these rigid molecules. That of homoisodrin acetate confirmed the structure of this product obtained by treating homoisodrin with sulphuric acid in boiling acetic acid (Bird and Yeung, *Chemistry & Industry* (1981), 95–96). Herbicides, prometryne and dicamba (Fig. 7) were also investigated. (Kennard)

Collaboration with the Unit of Nitrogen Fixation

Samples of $[MCl_2H_2(PMe_2Ph)_4]$, (M = Mo and W) were received from Dr R. L. Richards. Crystals of each compound were coated with epoxy resin although the tungsten complex was found to be air-stable. Both crystals diffract X-rays well.

The tungsten complex was found to be eight-coordinate with the ligands arranged in a dodecahedral pattern which can be considered as two interpenetrating tetrahedra, A and B. The chloro and hydrido atoms (the latter were found, with W—H *ca.* 0·16 nm in difference Fourier syntheses, but were not refined) occupy the A sites, and the phosphorous atoms lie at the B sites, with a pseudo 2-fold axis of symmetry passing through the shorter A—A links. W—P distances are in the range 0·2457–0·2551 nm and W—Cl are 0·253 nm.

Analysis of the Mo-complex showed the crystals to have the formula $[MoCl_2(PMe_2Ph)_4]$ and the metal atom to be coordinated octahedrally. The chloro groups are mutually *trans*, and the four phosphorous atoms form the equatorial plane about the Mo-atom. Mo—P distances are 0·2519–0·2554 nm and Mo—Cl lengths are 0·2449 and 0·2438 nm. (Hughes)

Biopolymers

Laue-type X-ray photographs were taken of samples of hordein protein fractions, (a) coated (and dried) on to the tips of glass fibres, and (b) as solidified drops on cellophane sheeting (1 × 1 mm squares of the flat plates were mounted on glass fibres).

None of the photographs showed any discrete diffraction spots, but all showed rings of intensity corresponding to a 'spacing' of *ca.* 0·43 nm, [N.B. the pitch of an α-helix is *ca.* 0·45 nm and the distance between strands of parallel or anti-parallel β-sheet structure would also be about this value]. (Hughes with Shrewry, Biochemistry)

Powder diffraction

Indexed powder patterns of seven herbicides and insecticides were provided for the Powder Data File. (Kennard)

Computing

A VDU for general online work has been connected to the Prime 550. This is well used and has relieved the pressure on the Tektronix 4051 with associated hard copy device, which are essential for online graphics and analysis of NMR spectra.

An investigation of the use of a BBC Micro Model B as a colour graphics terminal attached to the Prime has confirmed how useful colour can be in representing different aspects of molecules and their surfaces. The Micro performed well and may be suitable for other graphics use, but the resolution of the screen was inadequate for our needs. This investigation has shown that the minimum resolution which can adequately represent atoms as circles is 1024 × 760 pixels, and eight to 16 different colours are sufficient (Owen)

Two programs have been written for our suite of Prime crystallographic programs. BLOKLS allows up to 200 anisotropic atoms to be refined using block-diagonal least squares techniques. CONTUR allows us to print contour maps of electron density sections using the graphics capabilities of the Printronix printer. This is much faster than SURFACE II which we have used until now, though the contours produced are more angular. The maps are therefore quite suitable as working drawings, but not for publication. The actual routines for contouring were obtained from Mr D. Sutcliffe of the Rutherford Laboratories and made available to us by K. E. Bicknell, RES Computer Unit. (Owen)

A subroutine, ALTRIX, has been added to the program DELRED, our Delaunay Reduction routine which is used to produce the conventional Bravais cell for any crystal lattice. For a triclinic cell, the 'best cell', i.e. that with the most orthogonal set of axes is now calculated; all possibilities of primitive and centred cells are considered. (Hughes)

A BASIC computer program for the simulation and analysis of nuclear magnetic resonance spectra has been written, and implemented on the Tektronix 4051 Graphics System as an aid to coupling constant analysis. (Payne)

Safety of Equipment

Safety features on some of our older X-ray cameras have been brought into line with current safety regulation proposals. Shutters on all X-ray windows are now remote-controlled, and the radiation protection screens are interlocked with shutter-closing devices.

Our three prototype Weissenberg cameras have been overhauled, with the help of the Engineering Workshop. (Hughes)

Staff

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

Mary R. Truter and D. G. Parsons presented a poster at a Symposium on Macrocyclic Compounds in Strasbourg.

J. N. Wingfield presented posters at the XXII International Conference on Coordination Chemistry in Budapest and at the Second International Symposium on Clathrate Compounds and Molecular Inclusion Phenomena in Parma, Italy.

A. Sharp completed his sandwich course training period.

Dr C. H. L. Kennard of the Department of Chemistry, University of Queensland, Australia, spent five months in the department as a Visiting Scientist with support, for which we are grateful, from the Joint Committee for Powder Diffraction Standards. Dr G. De Paoli spent one week working in the department; this was supported by a grant from NATO.

Publications

General Papers

1 Truter, M. R. (1982) Li, Na, K, Rb, Cs, Fr; Be, Mg, Ca, Sr, Ba, Ra. *Annual Reports A 1981 of the Royal Society of Chemistry* **78,** (Inorganic Chemistry), 3-18.

Research Papers

2 (Anderson, S. N., Richards, R. L.) & Hughes, D. L. (1982) Preparation and crystal structure of $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$. *Journal of the Chemical Society—Chemical Communications* 1291–1292.

3 Bandy, J. A., Hughes, D. L. & Truter, M. R. (1982) The structures of the isomer C of the macrobicyclic polyether (21*S*,26*R*,29*S*,34*R*)-21,22,23,24,25,26,29,30,31,32,33,34-dodecahydro-1,4,7,14,17,20,28,35–octaoxa[2^{3,29}*anti*.2^{18,34}*anti*][7.7] orthocyclophane at 295 K and of its methanol complex at 295 and 123 K. *Acta Crystallographica* **B38,** 2648–2657.

4 Bandy, J. A. & Truter, M. R. (1982). Structures of two isomeric macrobicyclic polyethers, $C_{28}H_{42}O_8$, and the potassium perchlorate complex of one. *Acta Crystallographica* **B38,** 2639–2648.

5 Hanson, I. R., Parsons, D. G. & Truter, M. R. (1982). Crystal structures of complexes between alkali-metal salts and cyclic polyethers. 12. The complex between sodium bromide and 2,3-dimethoxybenzo-15-crown-5 {bromo(2,3-dimethoxy-6,7,9,10,12,13,15,16-octahydrobenzo[1,4,7,10,13]pentaoxacyclopentadecene) sodium}. *Acta Crystallographica* **B38,** 448–451.

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9 Hughes, D. L. & Truter, M. R. (1982) The crystal structures of complexes between dimethylthallium picrate and two isomers of dicyclohexano-18-crown-6. *Journal of the Chemical Society—Chemical Communications* 727–729.

10 Hughes, D. L. & Wingfield, J. N. (1982) Co-ordination of alkali metals by open-chain polyethers in transition-metal complexes. Part 1. X-Ray crystal and molecular structure of tetrakis-[1-*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethanato-(1-)]-dipotassiumcobalt(II), a trinuclear potassium-cobalt-potassium complex. *Journal of the Chemical Society—Dalton Transactions* 1239–1245.

11 Parsons, D. G., Truter, M. R., (Brookes, P. W. & Hall, K.) (1982) Field desorption and chemical ionization mass spectra of 'crown' and macrobicyclic polyether complexes of potassium. *Inorganica Chimica Acta* **59,** 15–18.