

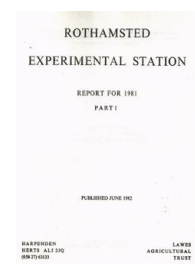
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Report for 1981 - Part 1

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Molecular Structures Department

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MOLECULAR STRUCTURES DEPARTMENT

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Introduction

There has been further progress in coordination chemistry. Two new classes of complexing agents for alkali metals have been designed and synthesised. In one class, large differences in complexing power arise from subtle differences in configurations; our explanatory hypothesis has been successful in predicting the behaviour of some members. The other class of compounds consists of transition metal complexes acting as chelating agents for alkali metals. Both classes have been investigated by crystal structure analysis.

There has been an enormous improvement in our computing facilities. The Department's own IBM 1130 computer, having given excellent service for nearly 13 years, was relinquished to be replaced by a part share of a Prime computer which was upgraded specifically to enable it to carry out our work. We have been able to transfer work not only from the 1130, but also most of that previously run on System 4. Improvement results not only from the hardware, but also from the very good cooperation of the Computer Department and the extremely good interactive programs written by Owen to make the use of the new facilities a pleasure not a struggle.

Collaboration with the Unit of Nitrogen Fixation has been resumed.

Coordination chemistry of alkali metal cations

Macrobicyclic ligands. We have shown neutral bicyclic polyethers containing two (Parsons, *Journal of the Chemical Society, Perkin Transactions I* (1978), 451–455) or three (Hanson, Parsons & Truter, *Journal of the Chemical Society, Chemical Communications* (1979), 486–488) benzene rings as substituents to be powerful complexing agents for alkali metal cations. To investigate factors which influence the selectivity we have now synthesised three isomeric macrobicyclic polyethers having one benzene and two cyclohexane rings as substituents and differing only in the relative configurations at the cyclohexane ring junctions.

Hydrogenation of the dibenzo-14-crown-4 *cis* diol (1) with a ruthenium catalyst gives a mixture from which the three possible isomers, (2a), (2b) and (2c), to be expected from *cis* hydrogenation across the ring junctions, have been isolated by fractional crystallisation. They can be distinguished by their melting points (Table 1). Each was subsequently treated with the ditosyloxy compound, X in Fig. 1, to yield the corresponding macrobicyclic polyethers, (3a), (3b) and (3c). These may be recrystallised from various solvents yielding unsolvated compounds each of which melts near to 134°C; there are significant

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differences in the 'fingerprint' region of the i.r. spectra, one characteristic band for each isomer is given in Table 1.

TABLE 1
Formation constants of the macrobicyclic polyethers

Isomer	m.p. of (2)	m.p. of (3)	Diagnostic i.r. band* of (3) cm ⁻¹	log K _f in methanol at 25° of (3)			
				NaBr	KBr	RbCl	CsCl
a	137	135	980	5.86	6.50	4.62	3.58
b	118	133	1001	7.86	8.18	7.16	5.01
c	170	133	822	4.13	4.65	2.42	1.85

* As a Nujol mull
K_f (l mol⁻¹) = [M⁺(3)]/[M⁺][(3)]

Formation constants for 1:1 complexes between (3a), (3b) and (3c) and alkali metal halides in methanol were determined by the e.m.f. method (Harris, Zaba, Truter, Parsons & Wingfield, *Archives of Biochemistry and Biophysics* (1977), **182**, 311-320). The values (Table 1) show very significant differences between isomers; all have highest values with potassium. (Parsons)

To establish the constitutions of the three isomers as shown in Fig. 1 the crystal structures of (3a), (3b) and (3c) were determined. (Bandy and Truter)

Isomer (3c) is sparingly soluble in methanol from which it deposits crystals having 1:1 stoichiometry of CH₃OH to (3c); these have an i.r. spectrum which differs from that of the pure compound in showing sharp bands at 3555 cm⁻¹, the hydroxy stretching frequency, and an additional band at 1028 cm⁻¹. The crystal structure was determined at 22° and, to obtain more accurate measurements, at -150°C. The hydroxy hydrogen atom forms a bifurcated hydrogen bond with the two oxygen atoms on the aromatic ring, the H...O distance being 2.37 and 2.28 Å ± 0.07 Å at 22°; 2.43 and 2.32 ± 0.04 Å at -150°. This is a particularly interesting example of the phenomenon of 'molecular recognition'; methanol acts as guest only with (3c), not (3a) or (3b). Isomer (3c) as host forms the 1:1 complex only with methanol, and not with other alcohols. (Bandy, Hughes, Parsons and Truter)

The crystal structure of the complex of (3b) with potassium perchlorate has been determined and the potassium ion found to be coordinated to seven oxygen atoms of the ligand with K...O distances in the range 2.670-2.853 Å; the distance to the eighth oxygen atom is 3.145 Å. The potassium ion is not completely enclosed by the ligand, making a contact of 2.922 Å to an oxygen atom of a perchlorate ion so that the complex entity is [(3b)KClO₄]⁰. This contrasts with complete enclosure by the macrobicyclic ligand having three benzene ring substituents (Hanson, Parsons & Truter, *Journal of the Chemical Society, Chemical Communications* (1979), 486-488) and is consistent with the slightly lower formation constant shown by (3b). (Bandy, Parsons and Truter)

The large differences in the complex formation constants of the isomers, e.g. for potassium the constant is 3400 times higher for (3b) than for (3c), may be explained by the postulate that approach and binding of a cation induces a significant electropositive charge on those hydrogen atoms attached to the carbon atoms which are joined to the ether oxygen atoms, and particularly so at the ring junctions where there is only one hydrogen atom. Because of the relative rigidity of the molecules, isomer C is less able than is isomer B to adopt a conformation with the ring junction hydrogen atoms out of the cavity which is consequently less electronegative than that of B. To test this hypothesis, the three isomers of (5) were obtained both by hydrogenation of the dibenzo compound having an aliphatic bridge and also by synthesis, from the diols using the ditosyloxy compound (TsOCH₂CH₂OCH₂CH₂OCH₂CH₂OTs). The formation constants of the

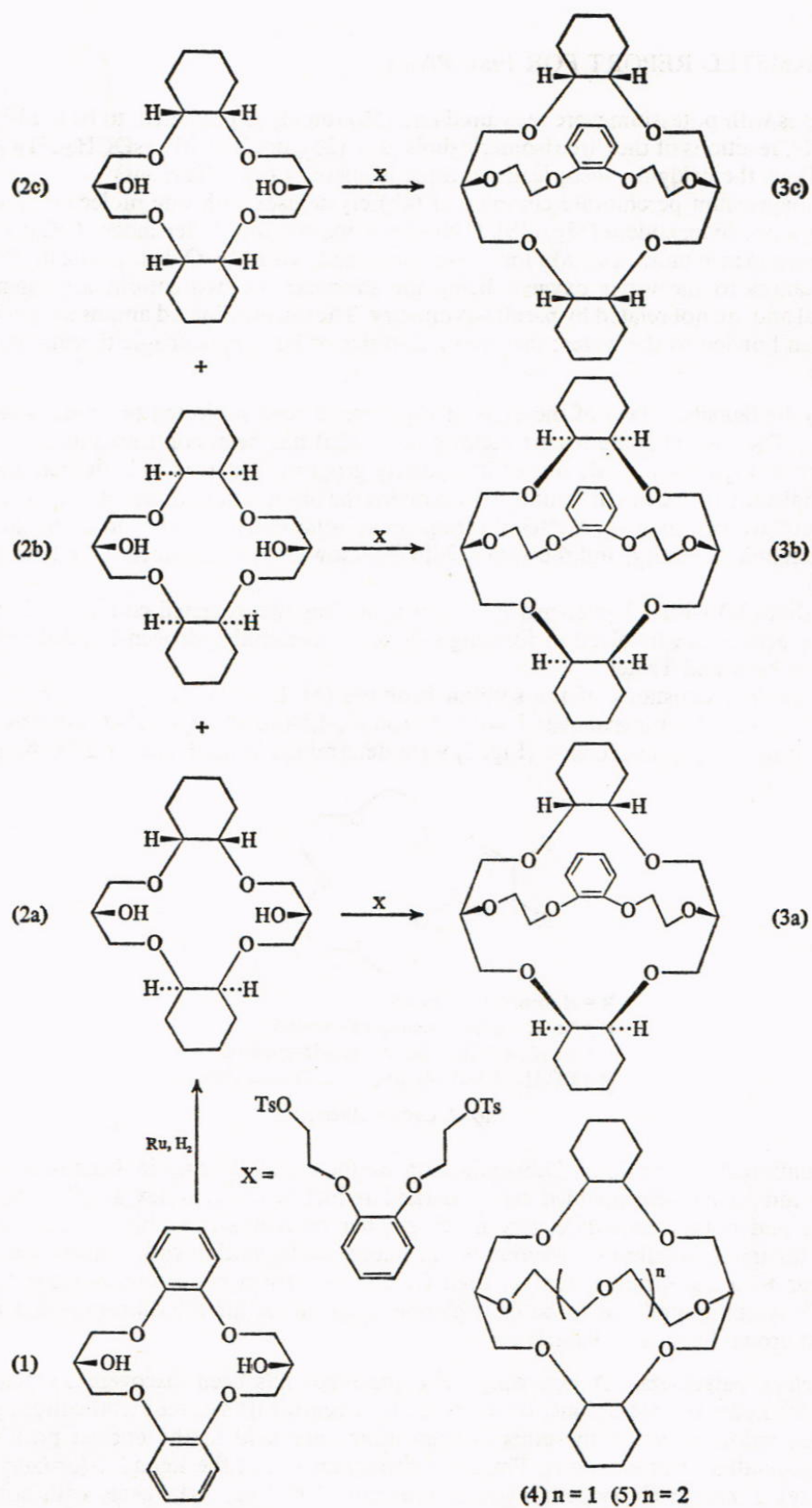


FIG. 1. Isomeric macrobicyclic ligands. The reaction scheme shows the synthesis of three isomers containing a benzene ring (3a, b and c). If other reagents are used at X, macrobicyclic compounds with aliphatic bridges can be obtained, each of (4) and (5) having three isomers.

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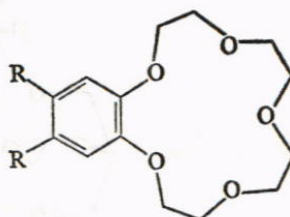
complexes with potassium were measured and (5b) found, as predicted, to be the highest. Similarly, reactions of the three isomeric diols (2a), (2b), or (2c) with $\text{TsOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OTs}$ as the bridging agent leads to three isomers of (4). (Parsons)

The magnesium perchlorate complex of (4b) crystallises with one molecule of water. There are two independent $[\text{Mg}, (4b), \text{H}_2\text{O}]^{2+}$ cations and four independent ClO_4^- anions in the asymmetric unit. Each Mg ion is 8-coordinated, with Mg-O distances 2.05–2.57 Å, the distances to the water oxygens being the shortest; the two cations are essentially identical and are not related by pseudo-symmetry. The uncoordinated anions are probably hydrogen bonded to the water; they show disorder or large anisotropic thermal motion. (Owen)

Monocyclic ligands. Two of the diols of Fig. 1 have been subjected to crystal structure analysis. The one with the lowest melting point (2b) has been confirmed as having the expected configuration. Only one of its hydroxy groups is involved in hydrogen bonding which links the molecules in chains. This explains the observation in the infrared spectrum that there are two hydroxy stretching frequencies, one sharp corresponding to the non-hydrogen bonded entity, and the other shifted to lower wave numbers and broadened. (Owen)

The diol (2a) with a higher melting point again has the expected configuration; both hydroxy groups are involved in forming a three-dimensional hydrogen-bonded network. (Bandy, Owen and Truter)

The stability constants of the sodium bromide (M:L, 1:1) and potassium bromide (M:L, 1:1 + 1:2) complexes with L = 4,5-dibromo-, 4,5-dimethoxy-, 4,5-di-*n*-butoxy- and unsubstituted benzo-15-crown-5 (Fig. 2) were determined in methanol at 25°C by means



- R = H, benzo-15-crown-5
- R = Br, 4,5-dibromobenzo-15-crown-5
- R = OCH₃, 4,5-dimethoxybenzo-15-crown-5
- R = OC₄H₉, 4,5-di-*n*-butoxybenzo-15-crown-5

FIG. 2. Crown ethers.

of potentiometric titrations. Dibromination of the aromatic ring in benzo-15-crown-5 was found to be accompanied by a marked reduction in complex stability for both sodium and potassium, while very much smaller decreases in stability were generally found for the 4,5-dialkoxy compounds; 1:2 complex formation with sodium was found to occur to a significant extent at high (*c.* 25 mM) crown concentrations for the 4,5-dimethoxy compound but to be of negligible importance for the dibromo- and unsubstituted crown ligands. (Payne)

Open chain polyethers. A new range of compounds has been discovered. Open chain polyether hydroxy acid anions, coordinated to a central transition metal cation, yield a complex anion in which the ether oxygen atoms are held in the correct positions to coordinate alkali metal cations. Thus, the potassium salt of the ligand 1-(*ortho*hydroxyphenoxy) 2-(*ortho*carboxymethoxyphenoxy)ethane LH (Fig. 3a), reacts with cobaltous chloride in acetonitrile to give a blue complex. Although most crystals of this product

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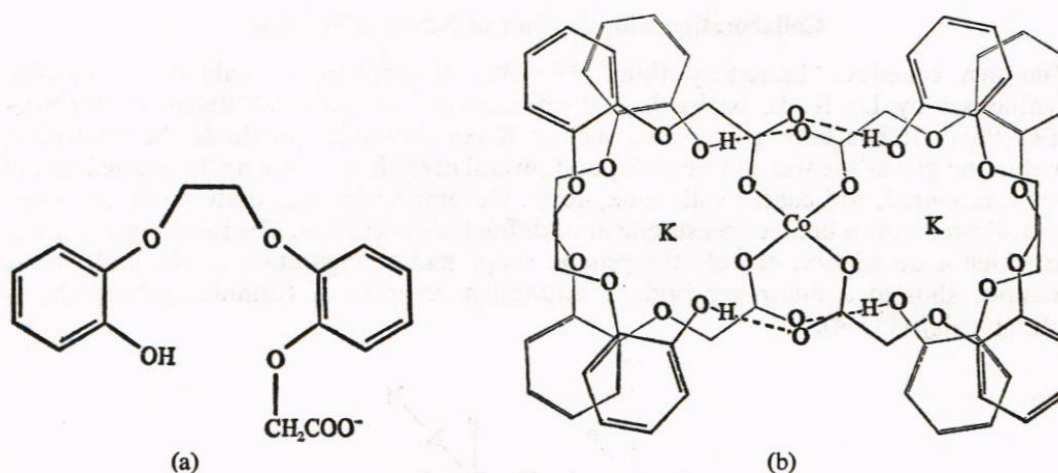


FIG. 3. (a) An open chain polyether anion, L^- . (b) The complex $[Co(L_2K)_2]$.

are twinned and split, a single one was found and its structure determined by X-ray analysis. This showed four ligands, L^- , each bound through a carboxylic O-atom to a central Co-atom, in a rather flattened tetrahedral arrangement. A pair of ligands, lying almost parallel, above and below the level of the Co-atom, enclose a potassium ion; a two-fold symmetry axis through the Co-atom (and normal to the ligand planes) repeats the arrangement in the other pair of ligands. The neutral, molecular unit thus has the formula $[Co(L_2K)_2]$, (Fig. 3b). Each potassium ion interacts with ten O-atoms, five from each surrounding ligand, in an approximately pentagonal anti-prismatic arrangement. There is formation of hydrogen-bonds between each phenolic group and the carboxyl group of the symmetry-related ligand forming two large, cyclic, roughly planar, dimeric units, one above and one below the Co-atom.

This compound, $Co(L_2K)_2$ and the rubidium analogue may be synthesised from cobaltous acetate and LH plus ML ($M=K, Rb$), but no such product is isolated when $M=Na, NH_4$.

The blue-mauve crystalline rubidium complex is not isomorphous with the potassium compound, although results of the X-ray analysis show the molecular units of the K and Rb complexes to be very similar.

This new class of complexes may allow the alkali metal to be held or released by changing (i) pH, (ii) transition metal oxidation state, (iii) transition metal coordination. These aspects are now being investigated. (Hughes and Wingfield)

Effect of ionophores on stomata

Epidermal peels of *Commelina communis* have been treated in the presence of potassium ions with three series of cyclic crown polyethers based respectively on substituted 15-crown-5, 18-crown-6 and 30-crown-10 ligands. The concentration of the crown compounds required just to inhibit stomatal opening under the test conditions correlates well with their lipophilicities measured by partition from aqueous potassium chloride solution into 1-octanol, and also with bonding stoichiometries for potassium as observed in organic solvents and in isolated crystalline complexes. Similar results are obtained when the cation is changed from potassium to sodium. Increasing the potassium (or sodium) ion concentration from 50 mM whilst keeping the crown concentration constant induces the stomata to open, until at 150 mM metal ion concentration the stomatal apertures are comparable with those of control stomata. (Simmons, Sharp, Truter and Wingfield)

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Collaboration with the Unit of Nitrogen Fixation

Tungsten complex. Extremely thin, plate-like, air-sensitive crystals of a complex synthesised by Dr R. L. Richards had an empirical formula calculated as 'W(N₂)₂-(PEt₂Ph)₃'. It has been partly analysed by X-ray diffraction methods. Manipulation within the glove-box was not possible, and several crystals were hurriedly selected in the open, mounted, and coated with epoxy-resin. Decomposition was quite rapid, however, and allowed only a limited measurement of diffraction intensities. The resulting structure, in which a description of only the general shape and configuration of the molecule is feasible, showed a dinitrogen-bridged ditungsten complex of formula [μ -N₂{W(N₂)₂-(PEt₂Ph)₃}₂], (Fig. 4).

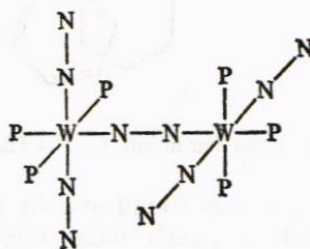


FIG. 4. A complex of tungsten with dinitrogen, P represents the phosphine ligand, PEt₂Ph.

A model structure was refined with constraints on the geometries of many parts of the molecule. No molecular dimensions are therefore available, but it is shown that (i) each tungsten atom is octahedrally coordinated, (ii) on each W-atom, the pair of terminal N₂ ligands are mutually *trans*, and (iii) the coordination octahedra of the W-atoms are rotated by *c.* 90° about the W-N-N-W line. (Hughes)

Rhenium complex. Dr R. L. Richards found the reaction of [*trans*-(ReCl(N₂)(Ph₂PCH₂-CH₂PPh₂)₂)] with CO₂ in toluene to yield large golden-brown crystalline chunks in which it seemed possible that the N₂ ligand had been replaced by a CO₂ group. X-ray analysis shows, however, that the N₂ ligands have been removed to leave a five-coordinate complex, [ReCl(Ph₂PCH₂CH₂PPh₂)₂] (Fig. 5) with a rare trigonal bipyramidal arrange-

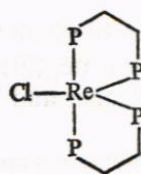


FIG. 5. A complex of rhenium, the two phenyl groups on each phosphorus atom have been omitted.

ment of ligands. The chloro group is equatorially situated (Re-Cl, 2.403 Å) and each of the diphosphine ligands has one axial and one equatorial phosphorus atom with Re-P distances of 2.37 and 2.26 Å respectively.

There is also a molecule of solvent, toluene, in the crystal; it lies quite close to the chloro group. (Hughes)

Protein crystallography

We have reported the X-ray analysis of the complex formed between a trifluoroacetylated dipeptide anilide inhibitor, CF₃CO-Lys-Ala-NH-C₆H₄-*p*-CF₃ and the serine protease, porcine pancreatic elastase (*Rothamsted Report for 1980, Part 1, 145*).

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Examination of the binding mode of the inhibitor molecule has shown that the CF_3CO group is in the S_1 subsite at the active centre of elastase, and that the dipeptide anilide residues lie close to the S_1' - S_3' subsites; the dipeptide portion is associated in a parallel β -sheet fashion with the protein chain. This arrangement contrasts sharply with the binding of N-acetylated short peptide inhibitors with elastase, but is in agreement with kinetic and NMR spectroscopic observations on a series of trifluoroacetylated oligo-peptide inhibitor molecules.

At the active centre of the elastase molecule, the hydrogen-bonding arrangements connecting the His-57 ring with both the Asp-102 and Ser-195 residues (which comprise the proposed charge-relay-system) appear to be intact and in good orientation for activation of the peptide hydrolysis reaction. However, the tight binding of the CF_3CO group, coupled with the multiple hydrogen-bonding interactions in the parallel-pleated sheet formation, prevent the reaction and block the site to binding by other substrate molecules. (Hughes)

Powder diffraction

Indexed patterns of plant growth hormones and some of the polyethers and their complexes have been measured as standards for the Powder Data File. The technique has been used to establish that crystals used for structure analysis are typical of the bulk sample. (Bandy)

Computing

Almost all of our work has been transferred to the enhanced Prime 550 computer in the Computer Department. This provided an opportunity to convert our programs to interact with the user where possible, and to improve and extend them in some cases. Eleven programs have been converted, the geometry program has been rewritten, and four other new programs written to make setting up and running of larger programs easier.

Instructions for using the Prime, and its peripherals, and documentation for our programs have also been written. The aim is to enable the newcomer to get started, and the expert to refer to lesser-used options. Because the revised programs are more interactive, the user normally needs to be shown only once how to run each, and the programs are now more forgiving of typographical errors.

The transfer went relatively smoothly, mainly due to the help and documentation supplied by members of the Computer Department, to whom we are very grateful.

A Tektronix 4611 hard-copy device producing cheap, quick, paper copies of the graphics terminal screen has been installed. This enables us to produce working drawings from Cambridge and Edinburgh, as well as from local drawing programs. The Tektronix 4051 itself is now running at higher speeds on the Prime and System 4 computers, making drawing much quicker. A package of statistical software in BASIC is running on the Tektronix 4051. This is mostly used to carry out simple regressions on experimental data. A simple graphics package in BASIC has also been written for the Tektronix 4051. This allows production of scatter plots, bar charts and histograms. Also it will plot any user-defined mathematical function and add experimental points to see how well they fit. This package is interactive and designed to be used by the non-specialist. (Owen)

Staff

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

Mary R. Truter and J. D. Owen presented papers at the 12th Congress of the International Union of Crystallography in Ottawa.

Judith A. Bandy left in mid-August for a post in the Royal Society of Chemistry. She

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has been awarded the degree of Doctor of Philosophy of the Council of National Academic Awards.

K. L. Simmons completed his sandwich course training period and A. Sharp started his.

Financial support from the Joint Committee for Powder Diffraction Standards is gratefully acknowledged.

Publications

RESEARCH PAPERS

- 1 BANDY, J. A., PARSONS, D. G. & TRUTER, M. R. (1981) Synthesis and X-ray crystal structures of three isomeric macrobicyclic polyethers having similar melting points and different complexing power for alkali-metal cations. *Journal of the Chemical Society—Chemical Communications* 729–731.
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- 9 HANSON, I. R., OWEN, J. D. & TRUTER, M. R. (1981) The crystal structure of 1,5,12,16,23,26,29,32,35-nonaoxa[13³,14][5.5]orthocyclophane and its complex with rubidium picrate. *Journal of the Chemical Society—Perkin Transactions II* 1606–1615.
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