ROTHAMSTED RESEARCH

Report for 1978 - Part 1

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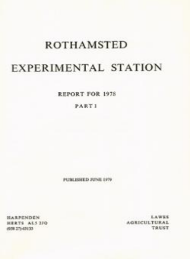

Molecular Structures Department

Mary R. Truter

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Introduction

It has been a good year. We started it having just moved all our equipment into the new building, and now have the benefit of increased working efficiency (although we can no longer claim to keep fit by running between the various locations of the Department).

Our main effort has been concentrated on the chemistry of the new bicyclic compounds, first reported last year, for complexing alkali metal and alkaline earth metal cations.

We exhibited some of our work during the Subject Days in May and at the Open Days in July. Visitors to the former from other institutes in the agricultural research service have received some of our compounds for testing. Our own work on plants has shown that the effect of a 'crown' ether on transpiration is directly related to closure of stomata.

Coordination chemistry of alkali and alkaline earth metal cations

Neutral bicyclic ligands

Synthesis. The synthesis of bridged macrocyclic polyethers has continued and a number of structural variations have been made; the structural formulae are displayed in Fig. 1.

In the [224] series (the last figure indicates the number of oxygen atoms in the bridge, I of Fig. 1 is [224]) modifications have been made to alter the solubility characteristics by substitution of alkyl groups on the aromatic ring of IIa, to give IIb, c and d.

Two examples of the [223] system IIIa, IIIb have been prepared. Measurements from molecular models suggest that the cavity is about the size of a sodium ion. In the synthesis of compound IIIa a small amount of the dimeric molecule IV was formed. Resolution of the racemate IIIb, by crystallisation of the diastereometric complexes that should be formed with sodium(-)mandelate, has not yet been achieved.

To allow for new types of bridging groups the key intermediates shown in Fig. 2 have been synthesised. (Parsons)

Structure. Compound IIIa forms crystals isomorphous with those of I. The packing of the molecules is similar; in both molecules the face including one side of the bridge has five oxygen atoms exposed, the face on the other side contains mainly hydrogen atoms. In both compounds the torsion angle about one C—O bond, marked with an

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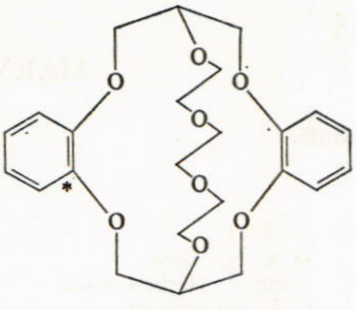
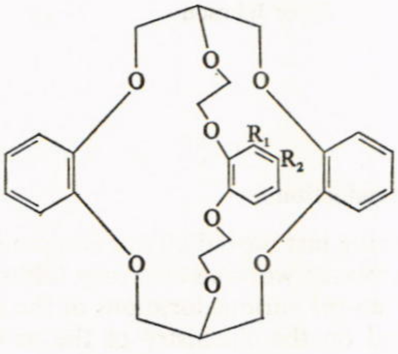
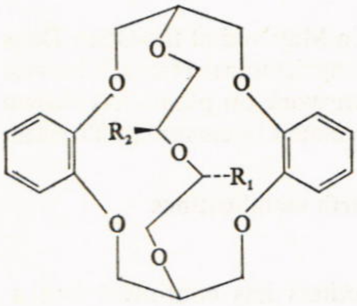


(I)



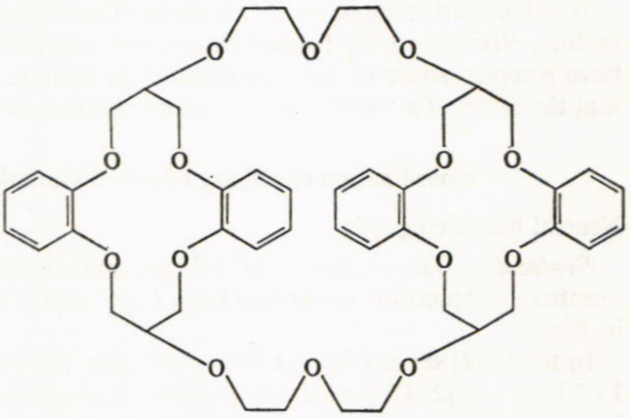
(a) $R_1 = R_2 = H$
(b) $R_1 = CH_3$ $R_2 = H$
(c) $R_1 = H$ $R_2 = CH_3$
(d) $R_1 = H$ $R_2 = C(CH_3)_3$

(II)

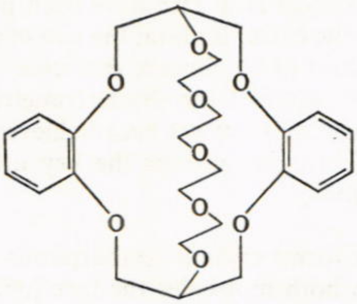


(III)

(a) $R_1 = R_2 = H$
(b) $R_1 = R_2 = CH_3$



(IV)



(V)

FIG. 1.

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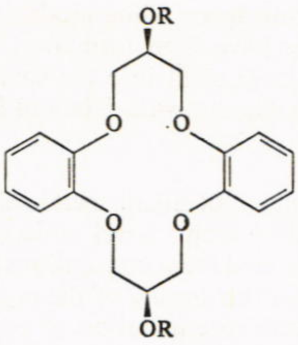


R = —CH_2CO_2Me
R = —CH_2CH_2OH

FIG. 2.

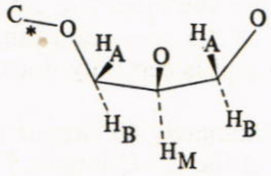


FIG. 3.

asterisk in Figs. 1 and 3, is approximately 60°, an unusual value which results in one of the hydrogen atoms of the type H_A in Fig. 3 pointing into the cavity. (Owen)

Flexible molecules can adopt several different conformations of nearly similar potential energy, and may exist in crystals in more than one low energy form. When nuclear magnetic resonance spectroscopy was used to investigate the macrobicyclic compounds in solution the observed conformations differed from those found in the crystals. Selective homonuclear ^1H decoupling was used to determine the proton resonances of Ia and IIIa. As expected, see Fig. 3, protons A and B are non-equivalent, and give rise to an AB pattern which is further coupled with proton M. All four of the H_A type protons of I are found to be equivalent in the ^1H n.m.r. even down to -50°C in $CDCl_3$. Compound IIIa has a similar ^1H n.m.r. spectrum at room temperature for protons A, B and M, but the resonances begin to broaden at -35°. Low temperature work in CD_2Cl_2 is now being carried out to see if the structure found in the crystal exists in solution at very low temperature. (Wingfield)

Complexes in solution. ^{13}C variable temperature n.m.r. of I, IIa and IIIa on complex formation with sodium bromide (1 to $\frac{1}{2}$ mol) has been measured in $CDCl_3$ and $(CD_3)_2SO$. For I and sodium bromide, both complexed and free ligand resonances are clearly seen at 0°C. These begin to broaden above 25°, and at ~50° the spectrum shows broad coalesced humps, which progressively sharpen to give the averaged spectrum at 96°C. The spectrum for IIa and NaBr seems to go through these transitions at a lower temperature suggesting a less strongly bound cation in solution. For IIIa and sodium bromide there is a sharp averaged spectrum at room temperature, which broadens as the temperature is reduced, coalescing at ~-30°, then sharpening at -50°C to give the resonances for both complexed and uncomplexed ligand. This suggests a weaker complex for IIIa with sodium than for either I or IIa in these solutions. (Wingfield)

The formation constants of complexes formed between the alkali metal bromides and the ligands in methanol at 25°C have been measured by the e.m.f. method. The results are consistent with deductions from space filling models. If there is room for the cation inside the ligand, 1:1 complexes have high formation constants, as for sodium with IIIa and V; if the cation is too large to fit into the cavity the 1:1 constant is low and a 1:2 complex is formed as for potassium with IIIa and IIIb and caesium with the [224] series. (Delve and Parsons)

Crystalline complexes. Complexes of alkali metal salts and the bicyclic ligands are very soluble in water and crystallise with several molecules of water of hydration. The exact number could not be determined from conventional elemental analysis or from the molecular weight determined from the density of the crystal and the volume of the unit cell. Moreover, the crystal structure determination of a typical complex KCl, IIa, xH_2O has shown that x is about 5 and cannot be determined exactly because the water molecules and chloride ions are disordered. They form hydrogen-bonded anionic columns between which are discrete $(IIaK)^+$ cations. All eight oxygen atoms of the ligand are coordinated to the potassium; the four in the bridge and two catechol oxygen atoms form a ring nearly coplanar with the cation, while the other two catechol oxygen atoms are 0·24 nm from this plane on the same side of the potassium ion. The cation has no neighbours within 0·365 nm on the other side and is certainly not coordinated by solvent or anion in the crystal.

All the torsion angles are approximately 60° about the C—C bonds (apart from 0° at the benzene rings) and 180° about the C—O bonds. The infrared spectra of complexes of this ligand with potassium bromide, potassium thiocyanate and sodium thiocyanate (all hydrated) are very similar, suggesting that the conformation of the bicyclic molecule is the same and that the water is not coordinated. (Hanson and Truter)

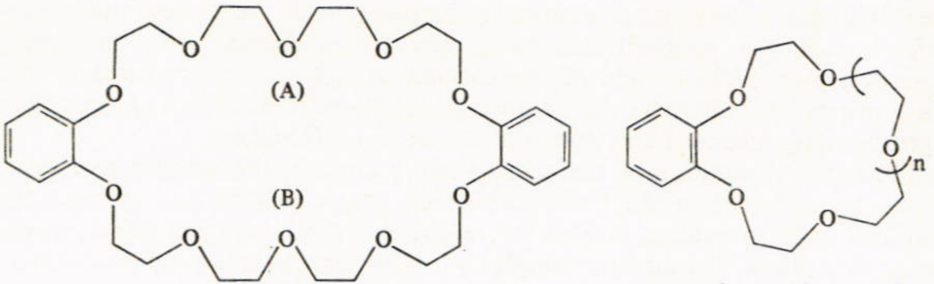
Macrocyclic 'crown', compounds

Complexes in solution. The titration apparatus attached to the batch microcalorimeter was found to be unsuitable for use with methanol which, because of its low boiling point, gave inaccuracies at the beginning of the titration. Ethylene glycol was found to be ideal for measurements with benzo-18-crown-6, and very good reproducibility was possible; the values from two separate titrations with potassium bromide are given in Table 1. (Wingfield)

TABLE 1

Titration	K_e $l mol^{-1}$	ΔH Kcal mol^{-1}	ΔG Kcal mol^{-1}	ΔS cal deg^{-1} mol^{-1}
1	$4{\cdot}17 \times 10^3$	$-8{\cdot}65$	$-5{\cdot}02$	$-11{\cdot}97$
2	$4{\cdot}08 \times 10^3$	$-8{\cdot}66$	$-5{\cdot}01$	$-12{\cdot}03$

Crystalline complexes. To obtain more reliable values for the conformations of the benzo-15-crown-5 molecule (Fig. 4) in complexes having two such molecules sandwiching one metal ion, the structure of $[K(benzo\text{-}15\text{-}crown\text{-}5)_2]^+I^-$ has been refined with the sophisticated facilities of the SHEL-X program. The previously reported (Mallinson & Truter, *Journal of the Chemical Society, Perkin II* (1972) 1818) disorder in the region of one O—CH_2—CH_2—O group has been shown to be the result of there being two conformers: A, similar to that found in the free ligand crystals, and B, a new conformation. The A:B ratio in the crystals is 3:2. In the caesium perchlorate complex with the same ligand, the cation again occupies a position with crystallographic symmetry (a two-fold axis) which relates the two benzo-15-crown-5 molecules. The Cs—O distances are in the range 0·305–0·319 nm and the cation is therefore coordinated to all ten available oxygen atoms. There are two conformers present, one similar to the B conformer of the KI



dibenzo-30-crown-10

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

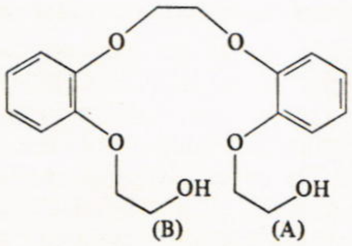
FIG. 4.

complex (see above), the other new. This, and the disorder in the anion, will be investigated further when accurate low temperature measurements can be made. (Owen)

The crystal structure of the 2:1 complex of sodium thiocyanate with dibenzo-30-crown-10 (Fig. 4) has been determined and a ligand conformation found quite different from those of the uncomplexed molecule or its 1:1 complex with potassium (Bush & Truter, *Journal of the Chemical Society, Perkin II* (1972), 345). The molecules lie on a two-fold axis through O(A) and O(B) relating the two halves of the ether which is in a 'figure of eight' shape when viewed down this axis. Each ligand complexes with two sodium cations with O(A) and O(B) shared by these ions. Each sodium is 7-coordinated in a pentagonal bipyramid, the nitrogen atom of the isothiocyanate anion forming one apex and O(A) the other. Calculations of the non-bonded interactions give similar values for this 2:1 complex and for the 1:1 complex —43·2 and —44·2 kcal mol^{-1} respectively, in contrast to the much less favourable interaction in the uncomplexed molecule —35·7 kcal mol^{-1}, the difference arising mainly from the greater number of favourable C—H interactions in the complexes. (Owen and Truter)

Open chain polyethers

Crystalline complexes. The crystal structure of Na(NCS).L, where L is the polyether diol of Fig. 5, was described in the *Rothamsted Report for 1977*, Part 1, 168. Potassium thiocyanate forms a 1:2 complex with this ligand, giving crystals of $[L_2K]_2(SCN)_2.CHCl_3$. In each of two independent cationic groups, the potassium ion is surrounded by two ligands, L and L′; five oxygen atoms of each ligand are coordinated to the potassium ion. The sixth oxygen of L, A of Fig. 5 is hydrogen bonded to the coordinated hydroxyl group (B′) of the second ligand in the same cation group and A′ is similarly bonded to B. Thus, in both this and the sodium complex, the ligands are *not* held in place by hydrogen bonds within the same ligand; this may be related to the poor ion transporting properties of L.



Open chain compound

FIG. 5.

Other hydrogen bonds link the cationic complexes with the thiocyanate anions and chloroform molecules in double-stranded, cross-linked chains. There is considerable site disorder, principally in one of the cationic complexes (where three of the four hydroxyl groups have alternate sites, allowing variations in the coordination pattern and hydrogen bonding schemes) and in one of the anions. (Hughes)

The different interactions of the thiocyanate anions in the sodium and potassium complexes are reflected in the C≡N stretching peaks in their i.r. spectra; the Na^+ complex has a sharp peak at 2095 cm^{-1}, whereas the K^+ complex has a broad peak centred at 2035 cm^{-1}. The calcium complex with this ligand (1:1, anhydrous) also shows a sharp peak at 2090 cm^{-1}. A magnesium complex, obtained from ethyl acetate/CCl_4 appears to be hydrated, $Mg(NCS)_2L_2.2H_2O$, and shows a broad structured peak at 2090 cm^{-1}. (Wingfield)

Interatomic distances. In the discrete complexes of naturally occurring and synthetic ionophores there is no ambiguity about the coordination number of the cation, but the distances from the alkali metal or alkaline earth metal cation to the donor atoms, usually oxygen or nitrogen, vary widely even within one complex.

We have had some success in fitting the observations to an empirical scheme which derives from Pauling's concept of 'electrostatic valence' (*Journal of the American Chemical Society* (1929), **51**, 1010) and retains the idea that the sum of the fractional 'bond valences' reaching an ion should be equal to its formal oxidation state. We use 'bond' instead of 'electrostatic' because we do not imply a specific type of bonding.

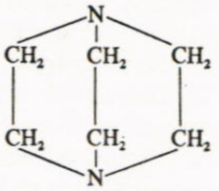
While the need for a new postulate arose from consideration of discrete complexes, it applies to all compounds in which a cation is surrounded by ligand molecules having donor atoms, X, which are themselves attached to carbon or to two hydrogen atoms, e.g. monatomic anions are excluded. The postulate is that for each coordination number n there is a standard M—X distance R_n (corresponding to equidistant X atoms) and that for each observed distance R the bond valence S is given by $S = (1/n)(R/R_n)^{-Y}$. The relation $R_n = R_6(n/6)^{1/8}$ between radius and coordination number is used to derive values of R_n from R_6 which, like Y, is a parameter. The parameters have been derived by minimisation of the difference between ΣS and 1·0 for alkali metal cations or 2·0 for alkaline earth metal cations. A total of 282 environments for sodium, potassium, rubidium and caesium yielded Y values for the cations and R_6 for M—O, M—N and M—S; a total of 98 environments for magnesium, calcium, strontium and barium yielded Y and R_6 for M—O. After refinement of the parameters 90% of the sums of bond valences are within the ranges 0·9–1·1 or 1·9 and 2·1 for the alkali metal and alkaline earth metal cations respectively.

For sodium and magnesium the R_6 values for M—O are larger than the sums of the ionic radii of the cations and oxygen; this is consistent with some covalent character in the bonding. (Truter and Welbank)

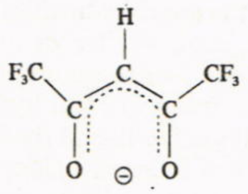
Chelated complexes with other cations

Malonates. Malonic acid and its derivatives in aqueous solution have been investigated by ^1H and ^{13}C n.m.r. In D_2O the free acids $RCH(COOH)_2$ [malonic acid (R=H), ethylmalonic acid ($R=CH_3CH_2$) and benzylmalonic acid ($R=C_6H_5CH_2$)] show slow exchange of the CH proton with the deuterium of D_2O but no exchange occurs on neutralisation with sodium carbonate. The cobalt (III) and aluminium complexes have also been studied. In neutral D_2O the complex $[Co(NH_2CH_2CH_2NH_2)_2(COO^-)_2]^+$ has ^{13}C and ^1H n.m.r. spectra consistent with a chelating malonate group, but in basic solution, a fast ring opening equilibrium occurs, together with exchange of the CH protons. (Wingfield, with Dr. M. E. Farago, Bedford College, London)

Copper β-diketonates. In reactions between a bidentate, but non-chelating, nitrogen ligand, ted, and the chelated copper complex $(hfac)_2Cu$ (Fig. 6) products were obtained with the stoicheiometries 1:1, 2:1 and 1:2 and the crystal structure of the 1:1 complex reported (Belford, Fenton & Truter, *Journal of the Chemical Society, Dalton Transactions* (1972), 2208–2213). Use of the CAD4 diffractometer has allowed complete refinement of the crystal structure of the 2:1 complex $[(hfac)_2Cu]_2ted$. Each of the Cu-atoms is 5-coordinate, chelated by two hfac groups (Cu—O 0·192–0·197 nm) in the basal plane from which it is displaced towards a N-atom of the ted molecule at the apex of a square pyramid (Cu—N 0·223–0·227 nm); thus, the ted molecules connect pairs of $Cu(hfac)_2$ planes. This is one of the few complexes having Cu—N larger than Cu—O distances; in particular if Cu—N is part of a chelate group it will be shorter than the Cu—O distance.



ted, 1,4-diazabicyclo[222]octane



hfac, (1,1,1,5,5,5-hexafluoropentane-2,4-dionato) anion

FIG. 6.

Each of the two independent molecules in the crystal contains two-fold symmetry; in one, the diad axis passes through the two Cu-atoms and the N-atoms of the (disordered) ted group; the second molecule is arranged perpendicularly to the first, with its two-fold axis normal to the Cu . . . Cu line and passing through a C—C bond of the ted group. (Hughes)

Collaboration with the Unit of Nitrogen Fixation. The structure of the complex $[M(NNH_2)(PMe_2Ph)_3(8\text{-quin})]^+X^-$ (where M = molybdenum and X^- is bromide and 8-quin is shown in Fig. 7), has been determined and can be compared with those for M = Mo or W and X^- = iodide reported in the *Rothamsted Report for 1977*, Part 1, 168.

In these three structures, the metals are surrounded by six atoms in almost identical, approximately octahedral arrangements. The analyses confirm that the hydrazido(2-) group is *trans* to the O-atom of the 8-quinolinolato ligand with which the N_2H_2 group

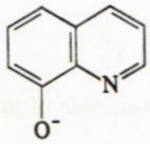


FIG. 7.

is roughly coplanar. The dimensions of the linear M—N—N systems are very similar and indicate considerable multiple bonding and delocalisation of electrons. In each complex the environment of the β-N atom suggests tetrahedral hybridisation, the two N—H— —X^- hydrogen bonds and the N—N bond forming a shallow pyramid.

The hydrogen bonds connect molecules in chains along glide planes in the complex with MX = MoBr, whereas in both iodide complexes they form dimeric molecules containing an element of symmetry, *viz.* a centre of inversion when MX = MoI and a two-fold axis when MX = WI. The three molecules differ in the orientations of the phosphine ligands and may be described as 'distortional isomers'. They exhibit several features common in oligophosphine complexes, resulting from overcrowding of bulky ligand groups. The differences in overall shape and in the extended hydrogen bonding schemes result in completely different overall packing. (Hughes)

A product of the reaction of $WCl_4(PMe_2Ph)_2$ with $PhNHNHSiMe_3$ formed fine green crystals, containing, it was hoped, the novel hydrazido(1-) ligand. X-ray analysis showed, however, a phenylhydrazido(2-) ligand, similar in dimensions to other hydrazido(2-) complexes. The hydrogen atom of the β-nitrogen atom has not yet been located, but the presence in the crystal of a chloro group in ideal hydrogen bonding position indicates the hydrazido(2-) rather than the diazenido ligand (both have linear M—N—N systems).

In this crystal, there are two almost identical independent molecules of $[WCl_3(PMe_2Ph)_2(NNHPh)]^\circ$ arranged as a dimer about a pseudo centre of symmetry and connected by the pair of proposed hydrogen bonds. The two phosphine ligands in each molecule are mutually *trans*, and the three chloro groups and the hydrazido ligand lie in the equatorial plane of this octahedrally coordinated complex of tungsten. (Hughes)

Effect of ionophores on transpiration

We have started to investigate the effect of synthetic ionophores on plants. The first compound used is the water soluble benzo-18-crown-6 (Fig. 4) which has a high formation constant with potassium ions. The presence of 5 mM-benzo-18-crown-6 in standard Letcombe solutions* as a bathing medium for the roots of young tomato plants reduced the rate of transpiration with respect to that of controls (measured by weight loss) by about 20% during the first day. Further experiments on whole bean plants, excised tomato leaves and freshly cut oat shoots all showed a general reduction in transpiration rates, measured either by weight loss or by porometer. Porometer measurements were also made on bean plants whose leaves had previously been sprayed with

TABLE 2

Inhibition of stomatal opening by benzo-18-crown-6

Treatment time	Crown concentration in mmol litre^{-1}	Stomatal opening in μm*
1 h	0	9·1
	1	7·7
	5	4·1
	10	1·8
2 h	0	12·6
	1	10·7
	5	6·1
	10	1·8

* Average of 30 readings, 10 on each of three strips

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* 1·5 mM-$Ca(NO_3)_2.4H_2O$, 5 mM-KNO_3, 1 mM-KH_2PO_4, 1·5 mM-$MgSO_4.7H_2O$, 2·0 mM-$NaNO_3$

benzo-18-crown-6 solutions but, in this case, no significant differences in relative humidity were detected between test and control plants.

As potassium influx to the guard cells of stomata had been shown to occur during stomatal opening (Fisher, *Plant Physiology* (1968), **43**, 1947–1952), it seemed possible that the ionophore was affecting the stomata and a specific test has been made using the plant *Commelina communis*, as described by Ogunkanmi, Tucker and Mansfield (*New Phytology* (1971), **72**, 277–282). Leaf epidermal peels are floated in solutions containing various concentrations of crown compound in 50 mM-KCl solution buffered at pH 6·15 over a light box and stomatal openings of 10 stomata on each of three replicate strips are measured at hourly intervals for each treatment, and then averaged. The results in Table 2 show a clear inhibition of stomatal opening. Neutral red treatment of the peels after treatment showed that all cells were living. (Richardson and Wingfield)

Equipment

Work has continued to bring our X-ray equipment to conform to forseeable safety standards; we now have complete enclosures for all our X-ray tables and various shutter interlocks. (Hanson)

Computing

4-70 programs. Two programs for processing the data from microcalorimeter measurements (Christensen, Izatt, Harrison & Partridge, *Journal of Physical Chemistry* (1966), **70**, 2003–2010) received from Brigham Young University have been implemented. (Owen)

PDP8 program. A small program has been written to scan through a file of intensity data collected by the CAD4 diffractometer, pick out the intensity control planes and plot their relative changes on the terminal. It is then possible by eye to estimate when the intensities change significantly, so enabling correction for crystal deterioration to be easily applied. (Owen)

Visits and Visitors

We were joined by Judith Herbert who is supported by a grant from the Joint Committee for Powder Diffraction Standards.

Margaret E. Welbank worked in the Department as a vacation student.

Mary R. Truter was re-appointed Visiting Professor in University College, London, and is a member of the Council of the Dalton Division of the Chemical Society.

Professor G. A. Jeffrey, University of Pittsburgh and Professor J. S. Bradshaw of Brigham Young University, Provo, both visited the Department. Professor Bradshaw gave a lecture on 'Preparation and Complexation Properties of Macrocyclic Polyether diester Compounds'.

J. D. Owen attended an International Summer School on Crystallographic Computing at Twente in Holland.

Publications

GENERAL PAPERS

1 Truter, M. R. (1978) Conformational changes in medium sized organic molecules induced by cations. In: *Ions in macromolecular and biological systems.* Ed. D. H. Everett & B. Vincent), *Proceedings of the 29th Symposium of the Colston Research Society, University of Bristol, April* 1977, pp. 108–120.

Research Papers

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3 (Butler, G., Chatt, J.), Hughes, D. L., (Hussain, W. & Leigh, G. J.) (1978) Carbethoxydiazenido-complexes of molybdenum and tungsten and the lengths of molybdenum nitrogen multiple bonds. *Inorganica Chimica Acta* **30,** L287–L288

4 Hanson, I. R. (1978) The structure of benzo-15-crown-5(6, 7, 9, 10, 12, 13, 15, 16-octahydrobenzo[1, 4, 7, 10, 13]pentaoxacyclopentadecin) at −150°C. *Acta Crystallographica* B **34,** 1026–1028.

5 Hughes, D. L. (1978) Crystal structure of 2,8-bis (bromomethyl)-1,7-dioxaspiro [5,5]undecane, an intermediate in the synthesis of analogues of A23187. *Tetrahedron Letters* No. 41, 3959–3960.

6 Hughes, D. L. (1978) The crystal structure of (–) -Avenaciolide. *Acta Crystallographica* B **34,** 3674–3678.

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