The Crystal Structure of Potassium (Ethylenediamine)bis(oxalato)chromate(III)–Potassium Iodide–Water (1/1/2), $K[Cr\{C_2H_4(NH_2)_2\}(C_2O_4)_2]\cdot KI\cdot 2H_2O$

By **Lesley S. Dent Glasser,** Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE
James W. Lethbridge,* Department of Science, Stockport College of Technology, Wellington Road South, Stockport SK1 3UQ

The title compound is triclinic, $P\bar{1}$, $a = 9.80(2)$, $b = 10.61(2)$, $c = 7.89(2)$ Å, $\alpha = 90.0(1)$, $\beta = 108.0(1)$, $\gamma = 92.5(1)°$, $Z = 2$. Both (+)- and (−)-forms of the optically active complex anion occur in the unit cell. The anions have almost exact two fold axes parallel to *b*, and these pseudo-two fold axes are common to the structure as a whole. There is also a pseudo-*n*-glide plane, and the whole arrangement is very nearly $P2/n$. The values of α and γ reflect this pseudo-symmetry. The conformation of the ethylenediamine ligands is such that their carbon–carbon bonds are nearly perpendicular to the pseudo-threefold axes of the complex anions ($\Lambda\lambda$ and $\Delta\delta$); no evidence was found for partial adoption of the other possible conformation. The conformation appears to be determined by electrostatic interaction between the hydrogen atoms and the adjacent iodide ions.

IN conjunction with preparative and kinetic work on oxalato-amine complexes of chromium(III),[1-3] the crystal structures of compounds that seemed likely to contain interesting complex ions have been determined. In a previous structural study[4] the salt $[Cr(en)_2(ox)][Cr(en)(ox)_2]\cdot 2H_2O$ † was shown to contain extensive hydrogen bonding which accounted for its low water solubility and also controlled the relative orientation of the ethylenediamine ligands. The crystal structure of the double salt $K[Cr(en)(ox)_2]\cdot KI\cdot 2H_2O$ was determined because it contained an isolated ethylenediamine ligand potentially able to adopt either of two conformations with respect to the remainder of the complex anion; in the previous structure, this same anion had been found to adopt both conformations. The significance of the ready crystallization of the double salt from solutions containing potassium iodide was also of interest.

EXPERIMENTAL

The double salt was precipitated by addition of solid potassium iodide to a solution of the complex salt prepared *in situ*.[5] Well formed prismatic crystals were obtained by recrystallization from warm distilled water.

Crystal Data.—$K[Cr(en)(ox)_2]\cdot KI\cdot 2H_2O$, $M = 529.3$, Triclinic, $a = 9.80(2)$, $b = 10.61(2)$, $c = 7.89(2)$ Å, $\alpha = 90.0(1)$, $\beta = 106.0(1)$, $\gamma = 92.5(1)°$, $a^* = 0.106\,1(2)$, $b^* = 0.094\,1(2)$, $c^* = 0.137\,0(2)$ Å^{-1}, $\alpha^* = 89.3(1)$, $\beta^* = 74.0(1)$, $\gamma^* = 87.4(1)°$, $U = 756.5$ Å^3, $D_m = 2.16$ g cm^{-3}, $Z = 2$, $D_c = 2.32$ g cm^{-3}. Space group, $P\bar{1}$. Cu-K_α filtered radiation, $\lambda = 1.541\,8$ Å, single-crystal oscillation, rotation, Weissenberg and precession photographs about the three major axes. Mo-K_α radiation for intensity data; μ(Mo-K_α) = 32.6 cm^{-1}.

Intensity Data.—Intensities were measured using a Hilger and Watts Y-190 automatic linear diffractometer with Mo-K_α radiation and a scintillation counter. Reflections over a hemisphere of reciprocal space (layers $hk0$—$hk8$) were each measured four times; all were treated as observed, a small arbitrary value being assigned to peaks not significantly above background. Equivalent reflections on the zero layer were averaged; the intensities of a small number of low-angle reflections not accessible to the diffractometer were estimated visually from Weissenberg photographs and added to the list, but treated as unobserved. The final list contained 2 448 reflections. An empirical check showed that the effect of anisotropic absorption was small, and no correction was applied. Intensities were reduced to structure amplitudes on a relative scale in the usual way.

Computing.—Computations were carried out on an ICL 4/70 computer, mainly using programmes kindly supplied by Dr. F. R. Ahmed and collaborators of the National Research Council of Canada and adapted for use on this machine by Mr. J. S. Knowles of the Department of Computing, University of Aberdeen. Atomic scattering factors for neutral K, I, Cr, C, N, O, and H were taken from ref. 6.

Structure Determination.—The knowledge that the unresolved salt must contain both (+) and (−) forms of the optically active anion $[Cr(en)(ox)_2]^-$, with only two anions in the unit cell, and the near-monoclinic habit of the crystals with a very regular diffraction pattern, suggested that the structure contained a centre of symmetry. The three-dimensional Patterson function could readily be interpreted in terms of $P1$, and gave positions for the iodine, potassium, and chromium atoms. A three-dimensional electron density map was computed based on signs derived from these atomic positions; it clearly indicated positions for the chromium ligand atoms other than hydrogen. After several cycles of structure-factor least-squares calculations, further electron-density maps suggested that the iodine and chromium atoms should be given anisotropic temperature factors, and indicated positions for the water molecules. The positions of the latter seemed ill defined; the peaks on the electron-density maps were elongated and structure-factor least-squares refinement produced large isotropic temperature factors. It therefore seemed possible that the water molecules were statistically distributed over two possible positions, and a refinement based on this assumption was attempted; it was unsatisfactory and was abandoned, and the water molecules were each allotted a single set of positional parameters and anisotropic thermal parameters. At this stage

---

† In this work, en = ethylenediamine (1,2-diaminoethane), ox = oxalate (ethanedioate).

[1] M. B. Davies, J. W. Lethbridge, L.-Y. Goh, and Othman Nor, *J. Inorg. Nuclear Chem.*, 1975, **37**, 175.

[2] Othman Nor, J. W. Lethbridge, and A. G. Sykes, *J.C.S. Dalton*, 1973, 1758.

[3] M. B. Davies and J. W. Lethbridge, *J. Inorg. Nuclear Chem.*, 1975, **37**, 171.

[4] J. W. Lethbridge, L. S. Dent Glasser, and H. F. W. Taylor, *J. Chem. Soc.* (*A*), 1970, 1862.

[5] A. Werner, *Annalen*, 1914, **406**, 286.

[6] ‘ International Tables for *X*-Ray Crystallography,’ Kynoch Press, Birmingham, 1962, vol. III.

R was *ca.* 0.067 on about 1 400 reflections with $\sin^2\theta < 0.20$; reflections at higher angles showed poorer agreement, and when these were included R was >0.10.

Electron-density and difference maps computed at this stage showed small regions of relatively high electron density (1.0—3.0 e Å^{-3}) at plausible positions for the hydrogen atoms on the ethylenediamine ligand, but (not surprisingly) gave no positive indication of hydrogen atoms related to the water molecules. The inclusion of the hydrogen atoms of the ethylenediamine ligand in the refinement made little or no difference either to the positional parameters of the other atoms or to the residual: in particular there was no significant improvement in the agreement for reflections with $\sin^2\theta > 0.20$. The poorer agreements found for these higher-angle reflections is probably due to the difficulty of setting triclinic crystals accurately on the diffractometer used. After refinement of the non-hydrogen atoms was judged to be complete, structure factors were calculated with and without the inclusion of hydrogen atoms: in both cases R was *ca.* 0.095 on 1 900 reflections. Reflections for which $\Delta F/F_0 > 0.50$ were excluded from the calculations; virtually all of these lay near the limits of reciprocal space explored by the diffractometer.

TABLE 1

Final atomic co-ordinates, as fractions of cell edges, and temperature factors, with standard deviations in parentheses

	x	y	z	B (Å^2)
I	0.243 6(1)	0.110 6(1)	0.246 2(2)	*
K(1)	0.351 4(4)	0.389 0(3)	0.535 3(5)	3.39(7)
K(2)	0.149 6(4)	0.391 4(3)	0.965 4(5)	3.36(7)
Cr	0.747 7(3)	0.236 0(2)	0.249 6(4)	*
N(1)	0.846(1)	0.086(1)	0.164(2)	3.6(3)
N(2)	0.637(1)	0.091(1)	0.338(2)	3.5(3)
C(1)	0.497(2)	0.314(2)	0.023(2)	3.1(3)
C(2)	0.507(2)	0.381(1)	0.197(2)	2.7(3)
C(3)	0.992(2)	0.382(1)	0.305(2)	2.6(3)
C(4)	0.000(2)	0.318(1)	0.485(2)	2.9(3)
C(5)	0.660(2)	0.971(2)	0.249(3)	4.0(3)
C(6)	0.816(2)	0.968(2)	0.260(3)	3.9(3)
O(1)	0.602(1)	0.240(1)	0.024(2)	3.0(2)
O(2)	0.627(1)	0.365(1)	0.313(2)	3.6(2)
O(3)	0.875(1)	0.361(1)	0.183(2)	3.9(2)
O(4)	0.895(1)	0.247(1)	0.479(2)	3.0(2)
O(5)	0.397(1)	0.331(1)	0.893(2)	3.9(2)
O(6)	0.416(1)	0.449(1)	0.217(2)	3.7(2)
O(7)	0.088(1)	0.451(1)	0.283(2)	3.5(2)
O(8)	0.102(1)	0.340(1)	0.605(2)	4.6(3)
O(9)	0.912(4)	0.231(3)	0.844(4)	*
O(10)	0.610(2)	0.253(2)	0.652(3)	*

* Anisotropic temperature factors computed for the expression $f = f_0 \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)]$

	B_{11}	B_{22}	B_{33}
I	0.010 3(1)	0.007 2(1)	0.018 9(2)
Cr	0.006 5(3)	0.004 6(2)	0.018 3(6)
O(9)	0.056(8)	0.034(5)	0.037(9)
O(10)	0.026(3)	0.017(2)	0.041(7)

	B_{23}	B_{13}	B_{12}
I	−0.001 4(2)	0.006 8(2)	0.000 2(2)
Cr	−0.002 0(5)	−0.001 0(6)	−0.000 4(4)
O(9)	0.02(1)	0.02(1)	0.02(1)
O(10)	−0.004(6)	0.009(7)	0.012(4)

The final positional and thermal parameters for the non-hydrogen atoms are listed in Table 1, and tentative positions for the hydrogen atoms, together with some appropriate distances, in Table 2. More accurate location of the hydrogen atoms was not attempted, since their precise positions are relatively unimportant and would in any case be extremely difficult to establish in the presence of so many heavy atoms. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21834 (11 pp., 1 microfiche).*

TABLE 2

Hydrogen atom positions as fractions of cell edges, assigned from electron-density maps, with relevant bond lengths (Å)

	x	y	z	Bond length	
H(1)	0.812	0.075	0.031	N(1)–H(1)	1.02
H(2)	0.950	0.100	0.218	N(2)–H(2)	0.99
H(3)	0.937	0.925	0.187	C(6)–H(3)	1.54
H(4)	0.850	0.950	0.406	C(6)–H(4)	1.12
H(5)	0.625	0.950	0.094	C(5)–H(5)	1.20
H(6)	0.562	0.912	0.266	C(5)–H(6)	1.16
H(7)	0.500	0.125	0.281	N(2)–H(7)	1.36
H(8)	0.625	0.100	0.500	N(2)–H(8)	1.32

TABLE 3

Intra-ionic bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Ethylenediamine

Cr–N(1)	2.10(1)	N(1)–Cr–N(2)	83.1(6)
Cr–N(2)	2.07(1)	Cr–N(1)–C(6)	108(1)
N(1)–C(6)	1.53(2)	Cr–N(2)–C(5)	107(1)
N(2)–C(5)	1.51(2)	N(1)–C(6)–C(5)	105(1)
C(5)–C(6)	1.51(3)	N(2)–C(5)–C(6)	108(1)

(*b*) Oxalate ligands

(i)		(ii)	
Cr–O(1)	1.95(1)	Cr–O(3)	1.95(1)
Cr–O(2)	1.99(1)	Cr–O(4)	1.98(1)
O(1)–C(1)	1.32(2)	O(3)–C(3)	1.29(2)
O(2)–C(2)	1.30(2)	O(4)–C(4)	1.26(2)
C(1)–C(2)	1.52(2)	C(3)–C(4)	1.49(2)
C(1)–O(5)	1.23(2)	C(3)–O(7)	1.22(2)
C(2)–O(6)	1.22(2)	C(4)–O(8)	1.23(2)
O(1)–Cr–O(2)	81.6(5)	O(3)–Cr–O(4)	82.7(5)
Cr–O(1)–C(1)	114(1)	Cr–O(3)–C(3)	113(1)
Cr–O(2)–C(2)	115(1)	Cr–O(4)–C(4)	113(1)
O(1)–C(1)–C(2)	115(1)	O(3)–C(3)–C(4)	116(1)
O(2)–C(2)–C(1)	112(1)	O(4)–C(4)–C(3)	116(1)
O(5)–C(1)–C(2)	121(1)	O(7)–C(3)–C(4)	123(1)
O(6)–C(2)–C(1)	123(1)	O(8)–C(4)–C(3)	121(1)
O(1)–C(1)–O(5)	124(1)	O(3)–C(3)–O(7)	122(1)
O(2)–C(2)–O(6)	125(1)	O(4)–C(4)–O(8)	123(1)

(*c*) Other angles about chromium

N(1)–Cr–O(1)	92.1(5)	N(2)–Cr–O(4)	91.5(5)
N(1)–Cr–O(3)	91.7(6)	O(1)–Cr–O(3)	94.5(5)
N(1)–Cr–O(4)	91.8(5)	O(2)–Cr–O(3)	94.0(5)
N(2)–Cr–O(1)	91.7(5)	O(2)–Cr–O(4)	94.7(5)
N(2)–Cr–O(2)	91.8(5)		

DISCUSSION

Description of the Structure.—The overall structure (Figure 1) can be regarded as a body-centred arrangement of complex chromium anions, with the other ions fitting in between them. The complex anion is roughly ellipsoidal, with its short axis, the pseudo-threefold axis, orientated along the short *c*-axis of the crystal. Alternate complex anions have opposite optical configurations. The complex anions also have almost exact twofold axes parallel to *b*, and these pseudo-twofold axes at $\frac{1}{4},y,\frac{1}{4}$ are common to the whole structure,

---

* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

which also has a pseudo-n-glide plane at $y = \frac{1}{2}$. The whole arrangement is very nearly $P2/n$.

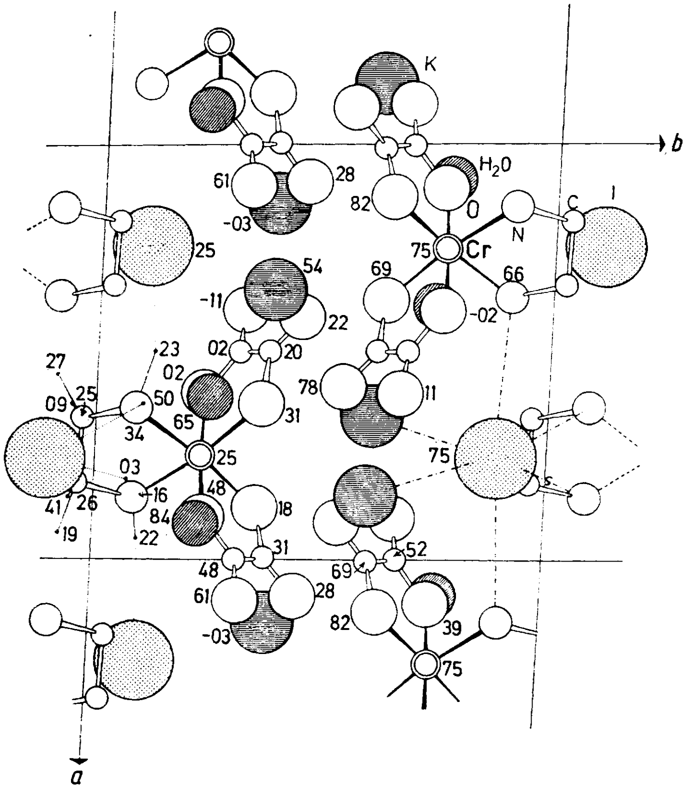

FIGURE 1 General view of just over one unit cell of the structure, viewed along c: the directions labelled 'a' and 'b' are strictly the traces of theses axes on a plane perpendicular to c. Labels at the top right of the drawing show how the different atom types are represented. Solid tapered lines show the co-ordination about the Cr atoms. Dotted lines at the lower left show the I$^-$–H contacts: dot–dash lines at lower right show the co-ordination about the iodide ion. Heights are in c/100

Each complex anion is in contact with four iodide and eight potassium ions. The iodide ions form an 'open cage' around the ethylenediamine ligand and the potassium ions form an 'open cage' around the two co-ordinated oxalate groups (Figure 2). Bond distances and angles within the complex anion are listed in Table 3.

TABLE 4

Inter-ionic contacts (Å) with estimated standard deviations in parentheses *

(*a*) About I	
I–K(1)	3.667(4)
I–K(2)	3.708(4)
I–N(1)	3.76(2)
I–N(2)	3.74(1)
I–N(1′)	3.73(2)
I–N(2′)	3.85(1)
(*b*) About K(1)	
K(1)–O(2′)	2.85(1)
K(1)–O(5)	2.81(1)
K(1)–O(6)	2.82(1)
K(1)–O(8)	2.68(1)
K(1)–O(10)	2.90(2)
K(1)–O(6′)	3.02(1)
K(1)–O(7)	2.89(1)
K(1)–O(2)	3.63(1)
(*c*) About K(2)	
K(2)–O(3′)	2.87(1)
K(2)–O(5′)	2.74(1)
K(2)–O(7)	2.81(1)
K(2)–O(8)	2.80(2)
K(2)–O(9)	2.76(4)
K(2)–O(6)	2.85(1)
K(2)–O(7′)	3.14(1)
K(2)–O(3)	3.57(1)

* Atoms marked with a prime are on sites transformed through the centre of symmetry from the positions given in Table 1.

Interionic contacts are listed in Table 4. Six non-hydrogen atoms (four nitrogen atoms of different complex anions and two potassium ions) lie at *ca.* 3.7 Å from the iodide ions in a distorted octahedron (Figure 1, lower right). The positions assigned to the hydrogen atoms lie approximately along the nitrogen–iodide ion contacts (Figure 1, lower left).

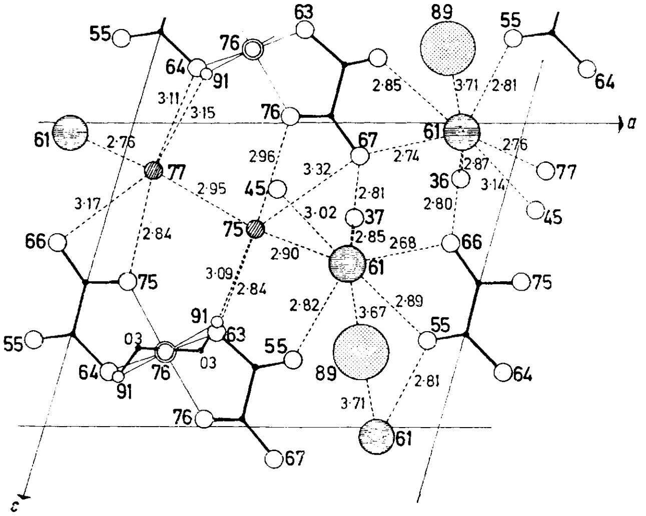

FIGURE 2 The structure viewed along b, showing the co-ordination of the potassium ions and the water molecules. For simplicity, atoms between $y = 0$ and $y = \frac{1}{2}$ are in general omitted. Heights are in b/100, and distances in Å

The co-ordination of the potassium ions and the water molecules is most easily seen from Figure 2, in which the structure is viewed along the pseudo-twofold axis, only slightly more than half the atoms being shown. Each potassium ion is surrounded by a ring, roughly in the plane of the diagram, of five oxygen atoms at *ca.* 2.7—2.9 Å, one of which is a water molecule. Its co-ordination sphere is completed by contact with an iodide ion, above the plane of the ring, at *ca.* 3.7 Å and with two oxygen atoms, below the plane of the ring, one at *ca.* 2.85 Å and the other at >3 Å. Of these latter, the nearer is also bonded to chromium but the more distant one is not. The co-ordination of the water molecules is rather peculiar. Each is associated with one potassium ion, with the other water molecule, with an ethylenediamine nitrogen, with two oxalate oxygens bound to chromium, and with another, unbound, oxalate oxygen that is rather more distant. The exact co-ordination of these molecules, and in particular the use and orientation of the hydrogen atoms in hydrogen bonding, is thus not clear, and their situation within the structure may account for the difficulties encountered in locating them on the electron-density map. It is at least apparent that the binding of the water molecules is not, in this instance, a critical factor in determining the crystal structure.

The high co-ordination numbers displayed by the ions and the environments of the individual nitrogen and oxygen atoms of the co-ordinating ligands clearly indicate a highly ionic structure. The iodide and potassium ions give a near close-packed structure with each other and with the oxygens of the complex anions. We consider that this near close-packing gives the structure a relatively high lattice energy and low water solubility compared with that for the simple salt $K[Cr(en)(ox)_2]$.

The low symmetry of this ionic structure, even when additional elements of pseudo-symmetry are present, is probably the result of the maximization of attractive ionic forces within a structure containing a large non-spherical ion which also has an anisotropic charge distribution. Thus the fact that the angle β is considerably larger than 90° means that all the nitrogen–iodine contacts and several of the oxygen–potassium contacts are shorter than they would be for an equivalent orthogonal structure (*viz.*: $\beta = 90°$ in Figure 2). Although the deviation of the angle γ from 90° is small (Figure 1), it is reasonable to assume that similar factors cause the adoption of the triclinic rather than the monoclinic habit.

Ethylenediamine Conformation.—For bis- and tris-chelated complex ions such as $[Cr(en)_2Cl_2]^+$ and $[Cr(en)(ox)_2]^-$, the complex ions can be regarded as left-handed (Λ) or right-handed (Δ) propellors.[7] Ethylenediamine can adopt one of two conformations within these ions: the carbon–carbon bond can lie either across the pseudo-threefold axis of the propellor ($\Lambda\lambda$ or $\Delta\delta$) or have an orientation almost parallel with this axis ($\Lambda\delta$ or $\Delta\lambda$). Intramolecular forces are expected to favour the latter parallel conformation but either conformation may be found if intermolecular forces are important. Thus in $[Cr(en)_2(ox)][Cr(en)(ox)_2]\cdot 2H_2O$ the dominant intermolecular hydrogen bonding forces result in the $\Lambda\lambda\lambda$ conformation rather than $\Lambda\delta\delta$ in the cations, whilst in the anions both $\Lambda\delta$ and $\Lambda\lambda$ conformations are found.

In the present structure the carbon–carbon bond of the ethylenediamine is nearly perpendicular to the pseudo-threefold axis of the complex anion ($\Lambda\lambda$ and $\Delta\delta$). There was no evidence from Fourier maps for partial occurrence of ethylenediamine ligands with the opposite conformation. Since there can be very little intramolecular constraint on the conformation of a single ethylenediamine ligand it is probable that it is determined by the bonding of the complex anion within the rest of the structure. In particular, since the amine nitrogen atoms are the atoms closest to the iodide ions (other than hydrogen), it is this interaction which appears to determine the ethylenediamine conformation. If the projected positions for the amine hydrogens are accepted the interaction could involve what can almost be described as ' hydrogen bonding ' to the iodide ion. The four nitrogen–iodide ion contact distances (3.76, 3.74, 3.73, and 3.85 Å) are little more than the sums of the relevant covalent and ionic radii (3.65 Å). However since the hydrogen atoms attached to nitrogen provide the most positively charged regions around the complex ion, the ethylenediamine conformation can again be regarded more simply as a means of maximizing the electrostatic interaction.

Conclusion.—The structure of $K[Cr(en)(ox)_2]\cdot KI\cdot 2H_2O$ is very largely determined by electrostatic forces. The lower solubility and ready crystallization of $K[Cr(en)(ox)_2]$ as the double salt with potassium iodide is due to the incorporation of a second, relatively large, anion into the crystal structure which, together with the potassium cations, is able to pack favourably around the polar complex anion. The conformation of the ethylenediamine ligand in this complex is determined largely by electrostatic forces in contrast to other structures where it is determined by more covalent hydrogen bonding forces or by intramolecular steric interaction.

[6/354 *Received*, 19*th February*, 1976]

---

[7] I.U.P.A.C., *Inorg. Chem.*, 1970, **9**, 1; K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 842.