

The low packing efficiency exhibited by this structure, as well as its lack of directions of close-packing in the plane of the pentagonal polygons, indicates that strong, anisotropic local bonding is important in the stabilization of this structure. It is reasonable to anticipate the presence of similar bonding effects in  $\text{LiSn}$ , the structure of which is currently under investigation.

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## The Crystal Structure of the 1:2 Potassium Iodide–Diacetamide Complex

BY J. P. ROUX\* AND J. C. A. BOEYENS

*Chemical Physics Group of the National Physical and Chemical Research Laboratories,  
Council for Scientific and Industrial Research, Pretoria, South Africa*

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The crystal structure of the complex  $\text{KI} \cdot 2(\text{C}_4\text{H}_7\text{NO}_2)$  has been determined by three-dimensional X-ray methods and the discrepancy  $R$  for all reflexions reduced to 10.8% by least-squares refinement. A layered arrangement corresponding to the  $\text{NaBr} \cdot 2(\text{diacetamide})$  structure was found. The two structures are compared and a mechanism for the complex formation is proposed.

### Experimental

The complex was prepared as described by Gentile & Shankoff (1965) by dissolving the KI in molten diacetamide at 217°C. After cooling the saturated solution, the white complex was washed with ether to remove the excess diacetamide and then recrystallized from absolute ethanol. The cylindrically shaped crystals were triclinic and were all found to be twinned. The crystals disintegrated on exposure to the atmosphere.

Great difficulty was experienced in cutting a cubically shaped crystal suitable for mounting on the Hilger and Watts automatic diffractometer from a large twinned crystal; the layer-like nature of the crystals very easily introduced shifts in the layers relative to one another during the cutting process. The very small crystal used was hermetically sealed into a Lindemann capillary and had dimensions of approximately 0.05 mm.

Cell dimensions were measured from oscillation, Weissenberg and precession photographs and refined on the automatic diffractometer. The unit cell that was chosen for convenience of data collection and structure refinement had the following dimensions:

triclinic with

$$\begin{aligned} a &= 9.304 \pm 0.005, & b &= 7.490 \pm 0.005, \\ c &= 10.215 \pm 0.005 \text{ \AA}; & \alpha &= 91.05^\circ \pm 0.01^\circ \\ \beta &= 85.03^\circ \pm 0.01^\circ, & \gamma &= 90.89^\circ \pm 0.01^\circ. \end{aligned}$$

This, however, is not a reduced crystallographic cell. The reduced cell was related to the above unit cell by the matrix  $[100/0\bar{1}\bar{1}/010]$  and had dimensions of  $a = 9.304$ ,  $b = 12.560$ ,  $c = 7.490 \text{ \AA}$ ;  $\alpha = 125.55^\circ$ ,  $\beta = 90.89^\circ$ ,  $\gamma = 93.50^\circ$ . The measured density was  $1.79 \text{ g.cm}^{-3}$ . The calculated density for two molecules per unit cell was  $1.73 \text{ g.cm}^{-3}$ . The structure was successfully solved by use of the space group  $P\bar{1}$ .

1330 intensities were measured on the automatic diffractometer by use of an  $\omega$ - $2\theta$  scan with molybdenum radiation and Zr as  $\beta$ -filter.

Large discrepancies in background count on the two sides of the peaks were partially compensated by giving more weight to the lower background count. Since no attempt was made to refine the structure beyond the clarification of the chemical picture, this procedure was acceptable. No corrections for absorption were applied and the intensities were corrected for the Lorentz and polarization factors. A count of 10 after subtraction of the background was considered as the lowest reliable count after inspection of all the data. The 133 reflexions measured below this level were there-

\* Present address: Department of Physics, University College, Western Cape, Bellville, South Africa.

fore assigned a value of 3, that is,  $\frac{1}{3}I_{\min}$  (Hamilton, 1955).

### Determination and refinement of the structure

The coordinates of the heavy iodine atom were obtained from a three-dimensional Patterson synthesis

and used to phase a three-dimensional Fourier synthesis. The Fourier synthesis yielded all the atomic positions in the molecule together with two relatively high peaks which could not be interpreted.

Least-squares refinement of scale factor, positional coordinates and individual isotropic temperature fac-

Table 1. *Fractional coordinates and anisotropic thermal parameters, where  $T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$*

The standard deviations are given below each value.

	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
I	0.20041	0.27118	0.16929	0.01423	0.02781	0.01525	-0.00523	-0.00128	0.00513
	0.00018	0.00024	0.00018	0.00028	0.00047	0.00026	0.00025	0.00019	0.00025
K	0.42397	0.24746	0.43359	0.01093	0.01464	0.01270	-0.00188	0.00085	0.00241
	0.00051	0.00061	0.00050	0.00069	0.00103	0.00065	0.00065	0.00052	0.00063
O(1)	0.51009	0.57006	0.33499	0.01993	0.01522	0.00626	-0.00381	-0.00154	0.00102
	0.00162	0.00178	0.00139	0.00256	0.00306	0.00163	0.00216	0.00160	0.00180
O(1')	0.62999	0.25477	0.23869	0.01637	0.02112	0.01371	0.00007	0.00209	0.00115
	0.00165	0.00207	0.00163	0.00250	0.00362	0.00217	0.00234	0.00184	0.00235
N(1)	0.63476	0.52118	0.13082	0.00866	0.01709	0.01509	0.00583	0.00178	-0.00070
	0.00175	0.00235	0.00185	0.00245	0.00422	0.00261	0.00259	0.00201	0.00273
C(1)	0.55380	0.62044	0.22521	0.01493	0.00953	0.01186	-0.00615	-0.00676	0.00268
	0.00240	0.00254	0.00239	0.00354	0.00438	0.00325	0.00321	0.00275	0.00308
C(1')	0.67506	0.35238	0.14297	0.00820	0.02818	0.01455	0.00365	-0.00524	0.00572
	0.00225	0.00354	0.00242	0.00306	0.00699	0.00335	0.00371	0.00258	0.00395
Me(1)	0.53022	0.81582	0.18677	0.02530	0.01757	0.01283	0.00616	0.00502	-0.00680
	0.00291	0.00304	0.00236	0.00480	0.00549	0.00315	0.00398	0.00307	0.00328
Me(1')	0.78498	0.27742	0.03316	0.01624	0.03430	0.01127	0.00748	0.00468	-0.00339
	0.00268	0.00355	0.00232	0.00401	0.00698	0.00302	0.00422	0.00282	0.00361
O(2)	0.80032	0.76619	0.38639	0.02027	0.01726	0.01627	-0.00819	0.00791	-0.00345
	0.00191	0.00211	0.00165	0.00290	0.00354	0.00235	0.00272	0.00212	0.00226
O(2')	0.30541	0.92227	0.49973	0.01344	0.01185	0.01218	-0.00110	0.00164	0.00227
	0.00159	0.00172	0.00138	0.00223	0.00286	0.00184	0.00211	0.00168	0.00180
N(2)	0.90067	0.04351	0.36158	0.00968	0.02357	0.00909	0.00008	0.00499	0.00355
	0.00179	0.00248	0.00166	0.00248	0.00503	0.00209	0.00272	0.00188	0.00253
C(2)	0.88108	0.86197	0.33135	0.01330	0.00929	0.01650	0.00430	0.00322	-0.00989
	0.00248	0.00287	0.00241	0.00352	0.00488	0.00345	0.00328	0.00285	0.00323
C(2')	0.80696	0.13587	0.44394	0.01643	0.00960	0.01368	-0.00832	-0.00497	0.00846
	0.00272	0.00260	0.00236	0.00395	0.00453	0.00314	0.00358	0.00302	0.00319
Me(2)	0.98811	0.81209	0.21625	0.01949	0.02267	0.01981	0.00334	0.00971	0.00012
	0.00283	0.00331	0.00278	0.00434	0.00597	0.00418	0.00404	0.00353	0.00397
Me(2')	0.85160	0.33676	0.46743	0.01487	0.01534	0.01596	-0.00286	-0.00481	-0.00440
	0.00242	0.00281	0.00236	0.00352	0.00484	0.00331	0.00324	0.00269	0.00314

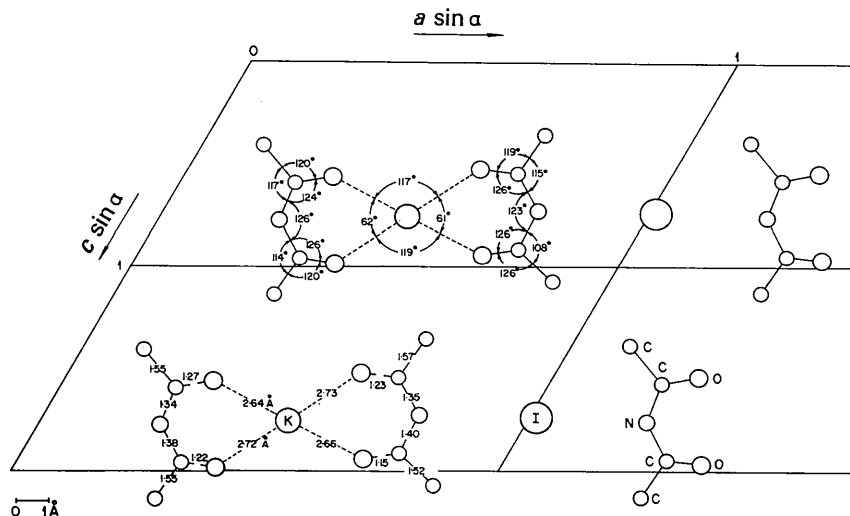


Fig. 1. A typical layer of the structure shown in projection along [010]. All atoms are represented by circles with diameters roughly proportional to atomic numbers.

tors showed these extra peaks to be spurious. A featureless difference Fourier synthesis calculated at this stage confirmed the structure.

The coordinates were refined with the full-matrix least-squares programs ORFLS of Busing, Martin & Levy (1962) on an I.B.M. 360/40 computer. The quan-

tity minimized is  $\sum \omega(F_o - kF_c)^2$ . Unitary weights were used for all reflexions. The residual, defined as

$$R = \frac{\sum |hkl| F_o - F_c}{\sum F_o}$$

was 17% after initial refinement and decreased to

Table 2. Observed and calculated structure factors on an absolute scale

Table with 20 columns of structure factors (F\_o, F\_c) for various hkl reflections. The table lists observed and calculated values for reflections such as h=0 k=0 l=0, h=1 k=1 l=0, etc., up to h=5 k=5 l=5. The values are numerical, often with signs, representing the intensity of the reflections.

10.8% after refinement of anisotropic thermal parameters.

The final atomic coordinates are given in Table 1, the observed and calculated structure factors on an absolute scale,  $F(000)=360$ , in Table 2 and the interatomic distances in Table 3. All the bond parameters which involve Me(1) indicate that its position is wrong, probably because of some systematic error. The computer programs and atomic scattering factors used in this analysis were as described before (Roux & Boeyens, 1969).

### Description of the structure

To be able to compare the structure of KI.2DA with that of NaBr.2DA (DA  $\equiv$  diacetamide) (Roux & Boeyens, 1969), the unit cell chosen initially was transformed to the new body-centered unit cell having dimensions of  $a=15.204$ ,  $b=14.401$ ,  $c=7.490$  Å;  $\alpha=88.69^\circ$ ,  $\beta=119.7^\circ$ ,  $\gamma=95.3^\circ$  by use of the matrix  $[11\bar{1}/101/0\bar{1}0]$ .

All figures and subsequent discussion will refer to this transformed unit cell.

As in the case of NaBr.2DA the structure of KI.2DA consists of layers of molecules and ions. In

Table 3. Interatomic distances and standard deviations in Å

K—I	3.557 ± 0.006
N(1)—I	3.668 ± 0.018
N(2)—I	3.684 ± 0.015
O(1)—K	2.717 ± 0.015
O(1')—K	2.642 ± 0.016
O(2)—K	2.661 ± 0.017
O(2')—K	2.730 ± 0.015
C(1)—N(1)	1.384 ± 0.028
C(1')—N(1)	1.335 ± 0.028
C(2)—N(2)	1.402 ± 0.026
C(2')—N(2)	1.348 ± 0.029
C(1)—O(1)	1.224 ± 0.024
C(1')—O(1')	1.270 ± 0.026
C(2)—O(2)	1.149 ± 0.025
C(2')—O(2')	1.227 ± 0.024
C(1)—Me(1)	1.546 ± 0.031
C(1')—Me(1')	1.554 ± 0.032
C(2)—Me(2)	1.519 ± 0.031
C(2')—Me(2')	1.575 ± 0.029

All angles given in Fig. 1 have standard deviations of  $2^\circ$  except those involving the potassium ion where the standard deviations are  $0.5^\circ$ .

any layer the cation is chelated by the four oxygen atoms of the two DA molecules which are approxi-

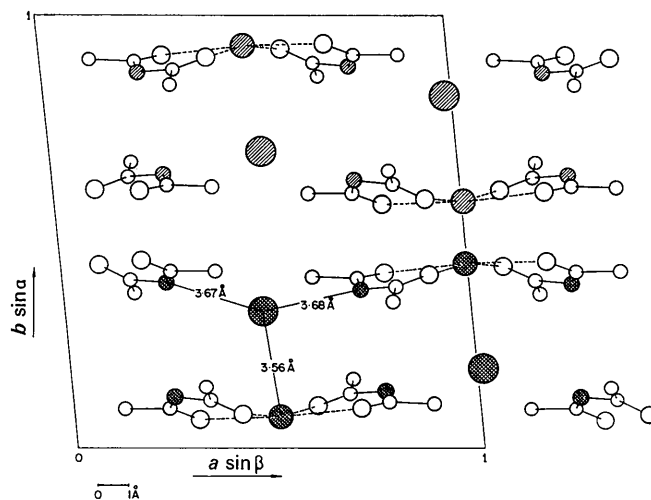


Fig. 2. Projection of the structure along [001]. Atoms and ions similarly hatched lie in approximately the same plane.

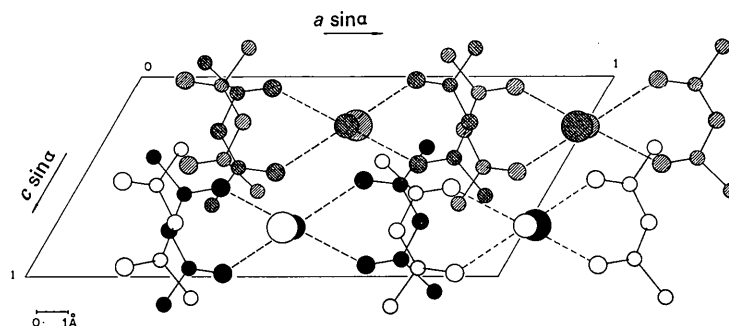


Fig. 3. The superposition of four neighbouring layers related by a centre at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  shown in projection along [010]. Atoms lying in the four different (010) planes are open, black, striped and crossed circles respectively.

ately in the same plane. The anion lies slightly out of this plane with the four methyl groups of two DA molecules surrounding it (Fig. 1).

The anion associated with any particular cation appears in a layer a quarter of a cell translation above the

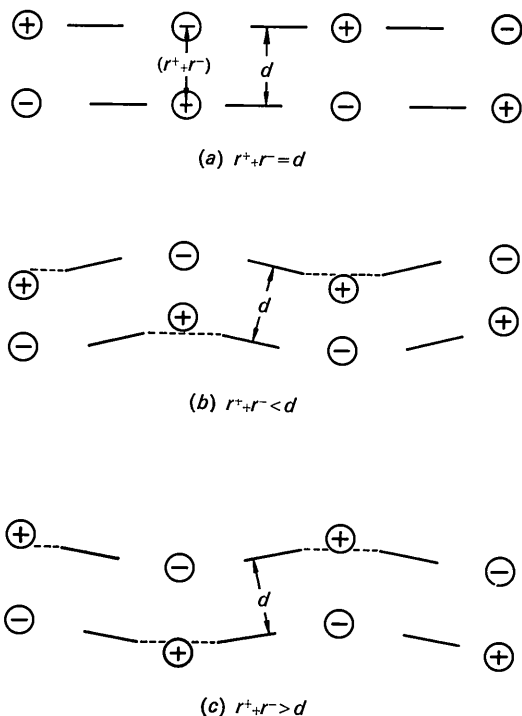


Fig. 4. Schematic diagram of the linear chains of cations, anions and diacetamide molecules. (a)  $r^+ + r^- = d$ ; (b)  $r^+ + r^- < d$ ; (c)  $r^+ + r^- > d$ .

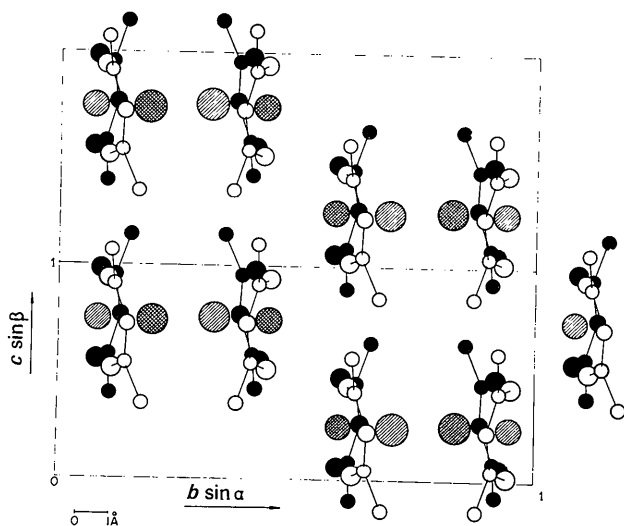


Fig. 5. Projection of the structure along [100] showing its layerlike nature. Anions and cations similarly hatched lie approximately in the same (100) plane. The black atoms lie below the atoms indicated by open circles.

cation. This identical layer therefore appears to be shifted through half a cell translation with respect to the first layer (Fig. 2).

The basic unit, consisting of the ion pair and two DA molecules, is inverted through the centre of symmetry at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  to fit into the third and fourth layers which are identical with the first two layers described.

As seen from Fig. 2, planes parallel to (100) which contain only anions and cations, alternate with parallel planes containing only DA molecules.

In the case of the NaBr·2DA structure, which has basically the same arrangement within the layers, the planes containing the ions and molecules, respectively, are merged into each other in such a way that the cation-anion pairs are separated by pairs of diacetamide molecules along the [100] direction. In the case of the KI complex, this packing is not possible mainly because of the size of the anion.

In the KI·2DA structure the closest neighbours of the potassium ion are the four chelating oxygen atoms around it at distances of 2.64, 2.66, 2.72 and 2.73 Å. The best plane through these four oxygen atoms as calculated by a method of least squares, is given by  $0.0752U - 0.9971V - 0.0081W = 0$  where  $U, V, W$  are orthogonal coordinates (in Å) related to the fractional coordinates  $x, y, z$  of the atoms in the triclinic axial system of the unit cell by the equations

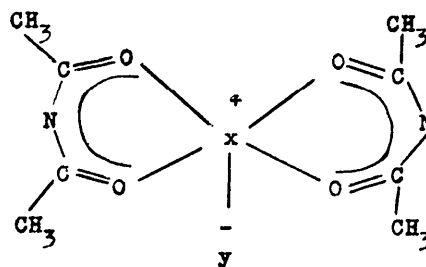
$$\begin{aligned} U &= xa + yb \cos \gamma + zc \cos \beta \\ V &= yb \sin \gamma - zc \sin \beta \cos \alpha^* \\ W &= zc \sin \beta \sin \alpha^* \end{aligned}$$

The distance of the potassium ion from this plane is 0.18 Å.

The iodide ion is 3.56 Å above the potassium ion and below it are two oxygen atoms belonging to different DA molecules at distances of 2.82 Å and 2.97 Å. The nearest neighbours of the iodide ion are the potassium ion at 3.56 Å in the layer below the iodine, the two DA nitrogen atoms at 3.68 Å and 3.67 Å, respectively, in nearly the same plane as the iodine, and the two methyl groups which are 3.99 Å and 3.96 Å away in the layer above the iodide ion (Fig. 2).

#### Discussion

Since the DA complexes of the present type are formed only with alkali halides with sufficient covalent character to exist as binary units in a diacetamide solution, it is reasonable to assume that the structures are built



up around these binary units. The cation becomes chelated by the oxygen atoms of two DA molecules in a process which presumably involves delocalization of electrons and therefore lies in their common plane, giving the arrangement shown above (compare Fig. 3).

The anion protrudes at right angles to the molecular planes. These structural units which probably exist in solutions of moderately polar solvents, now come together with polarity alternately reversed so that each anion lies centrally between two nitrogen atoms.

This leads to the formation of a linear double-layer structure. Each layer consists of a chain of cations and anions bonded to dissimilar ions in the other chain and bridged within the chain by polar ligand molecules. This situation, which is illustrated schematically in Fig. 4(a), can occur only if the interionic distance is fortuitously equal to the average van der Waals separation between superposed ligands. Because of the interplay of several factors the way in which this arrangement will change in the general case where the condition ( $d=r^++r^-$ ) does not hold, cannot be foreseen. Even in the actual structures the observed molecular tilts are not directly reducible to differences in van der Waals and ionic separations. The main problem comes from the fact that the mode of superposition of the ligands in neighbouring layers depends on the ionic sizes. Since the ligands are not planar, but have protruding methyl groups, the separation between the average planes through the superposed ligand molecules must depend on the relative positions of these methyl groups, which in turn depend on the mode of superposition. In this way the separations between the average planes of superposed DA molecules in the NaBr (Roux & Boeyens, 1969) and the KI complexes are 3.58 and 3.71 Å respectively. In both these complexes the DA molecules are tilted in such a way as to align themselves between the cations and anions which do not occur in a straight chain. If the best plane through a DA molecule is calculated the Na<sup>+</sup> and K<sup>+</sup> ions are both at an average of 0.4 Å outside of this plane, while Br<sup>-</sup> and I<sup>-</sup> lie at distances of 0.8 and 0.05 Å respectively from the plane.

In the two cases, however, the tilts are of opposite sense although in each case  $r^++r^-$  (2.78 for NaBr and 3.56 Å for KI) is less than the separation between the mean planes through the superposed DA molecules. It is, however, reasonable to assume that the closest atomic contacts between DA molecules are the same in the two cases. Since the positions of hydrogen atoms have not been determined this distance cannot be determined from our results. According to Sutor (1963) it should be about 3.4 Å. Since this value lies between the values of interionic distance for NaBr and KI, the closest atomic approach rather than the distance between mean planes could well be the decisive factor ( $d$ ) which determines the sense of the molecular tilts as shown schematically in Fig. 4 (b) and (c). The most obvious difference between the two cases can be described in terms of the plane through the four oxygen atoms surrounding a cation. In the first case the cation and its associated anion are on the same side of this plane (NaBr.2DA) and in the second case they are on different sides (KI.2DA). The cations are respectively 0.623 and 0.176 Å from such planes.

In both structures the chains come together in such a way that the methyl groups complete approximately planar hexagons and octagons of atoms around cations and anions respectively (Fig. 1). This arrangement now constitutes a double layer as shown in Figs. 3 and 5. There exists a remarkable similarity between these double layers in the DA complexes of NaBr and KI. The structural differences are largely a result of the different ways in which these double layers are stacked to allow for molecular tilts and ionic protrusions.

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