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The Crystal Structure of a Polyiodide Complex with *N*-methylacetamide – KI . KI$_3$. 6(CH$_3$CONHCH$_3$)

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The structure of KI . KI$_3$. 6(CH$_3$CONHCH$_3$) was determined. The crystals are trigonal, space group $P\bar{3}1c$, $a=12\cdot2$, $c=15\cdot2$ Å. The unit cell contains two stocichiometric units. Ions I^- and I_3^- alternate in arrays running parallel to the c axis. Cations K^+ occupy positions 000, 00¼, 00½, 00¾. NH groups of *N*-methylacetamide are linked to I^- ions, CO groups to K^+ cations. The presence of disorder in orientations of I_3^- ions is highly probable.

Introduction

The existence of complexes of polyamides with alkali polyiodides is well known (Kinoshita 1959, Arimoto 1962); their crystal structure, however, is still not very well understood. We suppose that one of the major difficulties here is the lack of information on the character of the bond between polyiodide and amide. It seemed therefore desirable to make a structure determination of a polyiodide complex with a low molecular weight amide. *N*-Methylacetamide was chosen, as here, according to Doskočilová & Schneider (1962), a greater tendency to formation of crystalline solvates with polyiodides was expected than in amides with a longer carbon chain.

Experimental

The solvate KI . KI$_3$. 6(CH$_3$CONHCH$_3$) was prepared as follows: 0·415 g potassium iodide, 0·317 g iodine and 1·1 g *N*-methylacetamide (molar ratios 1:0·5:6) were heated in a sealed glass tube at 100 °C for 8 hours. The tube containing the mixture was then slowly cooled for several hours to room temperature. In addition to a small quantity of potassium iodide, brownish-red needles of solvate crystallized from the mixture. The crystals of the complex were isolated in a dry box from the mother liquor. They are strongly hygroscopic; in moist air they disintegrate in a few minutes into a red liquid. The melting point of the brownish-red crystals is about 60 °C. The potassium and iodine contents of the crystals correspond to the formula $K_2I_4(CH_3CONHCH_3)_6$.

The same crystals together with green crystals of another solvate were obtained by a similar procedure at molar ratios $KI:I_2:CH_3CONHCH_3$ 1:1:6. The lowering of the concentration of *N*-methylacetamide in the mixture led to the crystallization of almost pure green crystals, m.p. about 100 °C. The potassium and iodine contents of the green crystals correspond approximately to the formula KI_3 . $2CH_3CONHCH_3$; this complex is probably identical with that mentioned by Doskočilová & Schneider (1962).

The green crystals are not very stable in air; within a few days they become covered with a layer of potassium iodide. They probably have orthorhombic symmetry. The green crystals are strongly pleochroic, the pleochroism indicating the planar arrangement of the I_3^- ions.

The brownish-red crystals (complex K_2I_4 . $6CH_3CONHCH_3$) crystallize in hexagonal needles having $a=12{\cdot}2$, $c=15{\cdot}2$ Å. They are also dichroic; the dichroism here indicates the linear arrangement of iodine atoms in rows parallel to the trigonal axis. In the brownish-red crystals, the ratio of heavy atoms to amide is lower than in the green crystals; for this reason the brownish-red crystals are more suitable for structure analysis, as there is a greater probability of determining the positions of the light atoms with some accuracy. Therefore the remaining part of this study is devoted solely to the latter.

As mentioned above, the crystals of K_2I_4 . $6CH_3CONHCH_3$ are extremly hygroscopic, so that all manipulations with them must be done in a dry box. For this reason we did not measure the density of the complex. The number of molecules in the unit cell was determined by comparing the observed volume of the unit cell with the calculated volume of one stoichiometric unit of the complex K_2I_4 . $6CH_3CONHCH_3$, assuming the additivity of molecular volumes of KI, I_2 and $CH_3CONHCH_3$. The observed volume of the unit cell is 1958 Å^3, and calculated volume of one stoichiometric unit is 941 Å; therefore the unit cell contains two stoichiometric units of K_2I_4 . $6CH_3CONHCH_3$.

For obtaining information about the symmetry of the brown-red crystals, we recorded the equator and the first six layer lines on Weissenberg photographs with Cu $K\alpha$ radiation (rotation about the c axis). The Laue group is $\bar{3}m$; reflexions $hh\bar{2h}l$ with l odd are absent. The most prominent reflexions on the equator and on the even layer lines are those with $h-k=3n$, on odd layer lines with $h-k\neq 3n$. For this reason we selected $P\bar{3}1c$ (D_{3d}^2) as a probable space group; however, the acentric group $P31c$ (C_{3v}^4) was not excluded, so that this question remained unanswered until the structure was completely solved.

Intensities were measured on a counter diffractometer with manual setting. For making the absorption correction less important we used Mo $K\alpha$ radiation. The high hygroscopicity of the crystals prevented us from making its shape regular by grinding. We selected therefore a fragment of roughly isotropic dimensions (mean diameter 0·6 mm) and measured every reflexion six times in different equivalent orientations with subsequent averaging of intensities. It is clear that this treatment is not very accurate (linear absorption coefficient 39 cm^{-1} for Mo $K\alpha$); from the deviations of intensities of the same reflexion in different equivalent orientations it can be expected that the error of the mean intensity can in many cases reach 10%. Intensities were further corrected in the usual manner, the absorption correction was taken from tables for a spherical crystal. Most reflexions were measured with the "normal beam" arrangement on the equator and on ten layer lines (rotation about c). Reflexions lying off the reflexion sphere or having a large Lorentz factor were measured on the equator with the rotation axis in the [100] or [1$\bar{1}$0] direction. The intensity of reflexions diminished very rapidly with the diffraction angle, measurements were therefore made only in the interval $0<2\theta<45°$. Here 823 independent reflexions were examined, measurable intensity was found in 433 cases.

Determination of the approximate structure

The regular distribution of strong reflexions $hk0$ and the symmetry of the space group $P\bar{3}1c$ suggest that iodine atoms occupy special positions (f), (d) or (c) (*International Tables for X-ray Crystallography*, 1952) with x and y coordinates $\frac{1}{3}$, $\frac{2}{3}$ and $\frac{2}{3}$, $\frac{1}{3}$. For potassium atoms only positions (a), (b) or (c) remain. With these coordinates the signs of the $hk0$ reflexions were determined and the (001) projection of electron density was calculated (Fig. 1). On this projection high maxima of iodine and potassium atoms (4 atoms overlap) are dominant; beside this a number of small maxima appear. In this stage we considered them as spurious but further three-dimensional work showed that they are projections of some overlapping atoms of the organic part of the crystal.

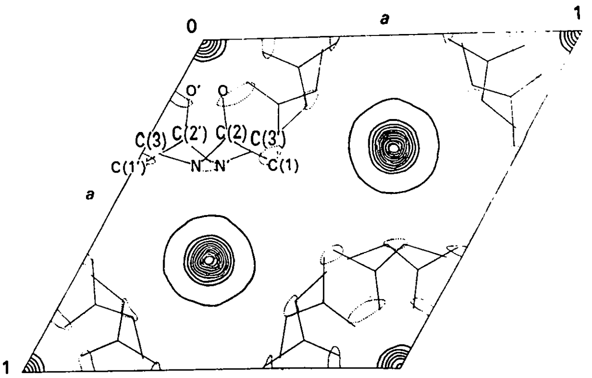


Fig. 1. Projection of electron density on (001). Contours at intervals of 20 e.Å^{-2}, broken line 10 e.Å^{-2}. Molecules are drawn with final atomic coordinates.

For the determination of the z coordinates of the iodine atoms the Patterson projection on $(1\bar{2}10)$ was calculated. From this we deduced several models of distribution of the iodine atoms all having inter-iodine vectors roughly consistent with the Patterson projection, but only the following allowed further refinement:

Atom I(1) in twofold position (*c*) $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ *etc.*
Atom I(2) in twofold position (*d*) $\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$ *etc.*
Atom I(3) in fourfold position (*f*) $\frac{1}{3}, \frac{2}{3}$, 0·06 *etc.*

Signs determined from this model together with measured structure factors $h0\bar{h}l$ led to the electron density projection on $(1\bar{2}10)$ (Fig. 2). Here, beside the iodine atoms we observe also the potassium atoms [positions (*a*) and (*b*)] with coordinates 000, $00\frac{1}{2}$ and $00\frac{1}{4}$, $00\frac{3}{4}$ and unresolved projections of molecules of *N*-methylacetamide in odd eighths of *c*. More accurate coordinates of atoms in the organic part of the crystals were obtained from the three-dimensional electron density, calculated with signs of structure factors as determined by iodine and potassium contributions. For survey we present here the bounded projection of electron density on (001) with $z_1=0\cdot30$, $z_2=0\cdot46$ (Fig. 3). Here the molecule of *N*-methylacetamide is clearly resolved; as the signs of the structure factors were in no way affected by any hypothesis about the organic part of the crystal this is a good proof of the correctness of our model of the distribution of the iodine atoms.

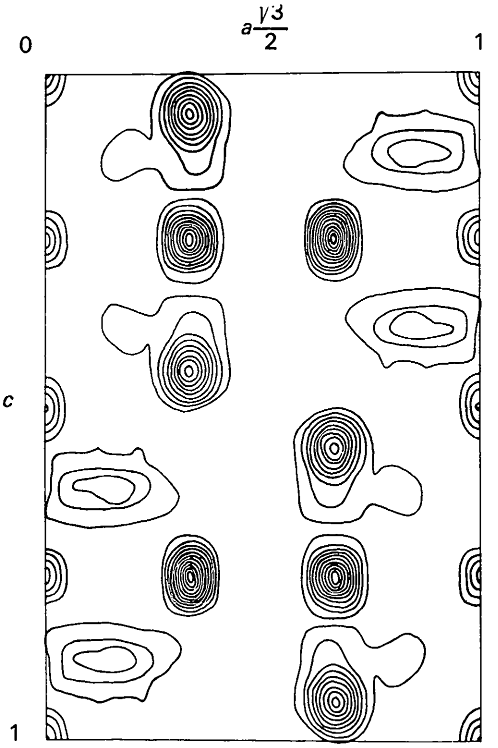


Fig. 2. Projection of electron density on $(1\bar{2}10)$. Contours at intervals of 10 e.Å^{-2}.

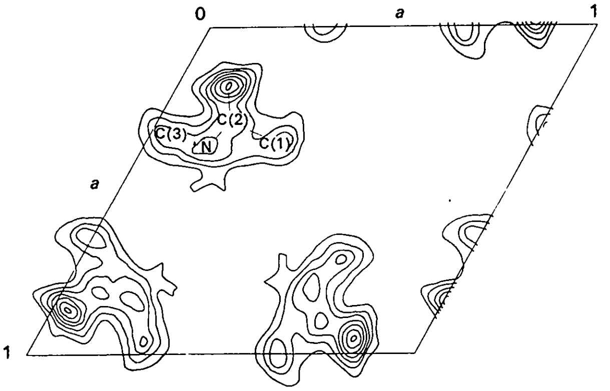


Fig. 3. Bounded projection of unit-cell content between $z_1=0\cdot30$ and $z_2=0\cdot46$ on (001). Contours at intervals of 1 e.Å^{-2}.

Refinement

The input coordinates of all atoms are given in Table 1. The over-all temperature factor was determined by Wilson's statistical method. In the expression $\exp(-B \sin^2\theta/\lambda^2)$ we found B equal to 7·6 Å^2 (for reflexions $hk0$).

Table 1. *Input coordinates for refinements*

Atom	x	y	z	Atom	x	y	z
I(1)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	C(1)	0·365	0·340	0·350
I(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	C(2)	0·305	0·203	0·375
I(3)	$\frac{1}{3}$	$\frac{2}{3}$	0·06	C(3)	0·330	0·025	0·405
K(1)	0	0	0	N	0·380	0·163	0·390
K(2)	0	0	$\frac{1}{4}$	O	0·185	0·135	0·375

The coordinates and thermal parameters were not refined by simple cycles of least-squares calculations as is usual. The reason for this was that in such cases as this, where heavy atoms are together with light molecules, the coordinates of light atoms do not usually converge smoothly to refined values.

Every step of the refinement consisted therefore of two or three cycles of least-squares calculations in which the scale factor, anisotropic temperature factors of iodine atoms, anisotropic temperature factors of potassium atoms, the over-all anisotropic temperature factor of the organic molecule (here the isotropy of vibrations perpendicular to the c axis was assumed) and the z coordinate of I(3) were varied and the coordinates of light atoms held constant. The calculation was of the full-matrix scheme. The second part of the same step was the three-dimensional F_o-F_c synthesis. This included the bounded projection between $0\cdot30<z<0\cdot45$ and the calculation of one-dimensional functions through assumed atomic centres in a direction parallel to the c axis. According to these F_o-F_c functions we corrected coordinates and introduced small individual contributions to the temperature coefficients of light atoms and repeated the step.

The least-squares calculations were performed in three modes differing in assumptions about the vibrations of iodine atoms.

Mode 1. All eight iodine atoms vibrate with the same mean amplitude.

Mode 2. Iodines I(1) and I(2) vibrate with the same, the I(3) with a different mean amplitude.

Mode 3. Iodines I(1), I(2) and I(3) all vibrate with different mean amplitudes.

In all modes the equality of vibrations for both crystallographically non-equivalent positions of potassium atoms were assumed. The calculation was performed with constant weights and included 485 reflexions. From this about 50 had intensity below the threshold value. These were inserted in a refinement with $\frac{1}{2}F_{\text{th}}$ as is usual. This group of non-observed reflexions includes cases where the low value of the structure factor is caused by a large compensation of appreciable contributions from individual atoms.

The initial disagreement factor $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was rather high (0·259), the progress of refinement is shown in Table 2.

Table 2. *Progress of refinement* *

	Step 1	Step 2	Step 3
Mode 1	0·223	—	—
Mode 2	0·160	0·155	—
Mode 3	—	0·134	0·126

* The list of observed and calculated structure factors will be sent on request.

As seen from Table 2, the final agreement is strongly dependent on the assumption made about vibrations of iodine atoms. It seems therefore certain that the differences in mean amplitudes of vibrations of all three crystallographically independent atoms are significant. Final parameters together with their standard deviations are summarized in Table 3.

The accuracy of the coordinates of atoms in the organic part of the crystal is probably not very great, as the major part of intensity of most reflexions is determined by the contributions of iodine and potassium atoms. We suppose that the error in coordinates can in extreme cases be as high as 0·005. The interatomic distances involving light atoms are therefore only indicative. For this reason we did not compute the complete list of interatomic distances. Some selected distances are in Table 4.

Table 4. *Selected interatomic distances*

I(3)–I(3′)	5·89 Å	O–C(2)	1·25 Å
I(1)–I(3)	2·945	C(1)–C(2)	1·54
I(2)–I(3)	4·64	C(2)–N	1·27
I(2)–N	3·74	C(3)–N	1·39
I(3)–N	4·01	C(3)–C(1′)	3·91
K–O	2·74	O–N′	4·54

All calculations (crystal setting, Fourier functions, least squares) were executed on Ferranti–Sirius with programming in Autocode. For Fourier calculations we used a matrix scheme, in a similar way to that described by Jaggi (1961). The simplicity of introducing matrix subroutines in programs in Autocode make this possibility very attractive. The speed of calculation is acceptable. For a centric projection (input matrices F_{obs} 16 × 16, output function with mesh 0·02), 20 minutes of machine time is needed.

Discussion of the structure

In the crystals of $K_2I_4 . 6(CH_3CONHCH_3)$ iodine atoms are arranged in linear systems parallel to the trigonal axis. These consist of triiodide ions alternating with I^- ions. The over-all length *D* of the triiodide ion is here 5·89 Å. The distance between triiodide ions and I^- ions is 4·64 Å, thus larger than corresponds to the van der Waals contact. Individual I_3 ions are isolated; this explains the red colour of the crystals.

The trigonal symmetry of the positions (*c*) and (*f*) requires a linear character of the triiodide ion; centrosymmetry requires equal distances between end atoms I(3) and the central I(1). Based on coefficients B_{11} and B_{33} for iodine atoms (Table 3) we suppose that the high symmetry of the triiodide ions as found by us is not an intrinsic property of the triiodide ions in our red crystals but merely a consequence of a statistical distribution of essentially asymmetric triiodide ions. The opposite was found by Havinga & Wiebenga (1958)

Table 3. *Coordinates* (*fractional*) *and thermal parameters* (Å²)

Atom	*x*	*y*	z	B_{11}	B_{33}	Atom	*x*	*y*	*z*	B_{11}	B_{33}
I(1)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	6·4 0·3	11·0 0·75	C(1)	0·360	0·345	0·352	6·7*	11·8†
I(2)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{3}{4}$	4·2 0·35	7·6 0·70	C(2)	0·295	0·203	0·376	6·4*	
I(3)	$\frac{1}{3}$	$\frac{2}{3}$	0·0559 0·0004	10·4 0·25	10·5 0·45	C(3)	0·329	0·035	0·403	7·6*	
K(1)	0	0	0	4·3	5·1	N	0·373	0·163	0·388	7·6*	
K(2)	0	0	$\frac{1}{4}$	0·35	0·85	O	0·176	0·137	0·377	5·4*	

* Standard deviation about 1·2 Å².
† Standard deviation about 1·0 Å².

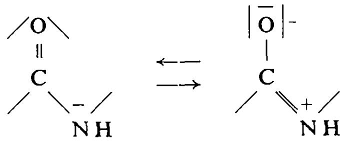
for crystals of $N(C_2H_5)_4I_7$. The arguments favouring our assumption are the following. The coefficient B of the over-all temperature factor found by us using Wilson's method for $hk0$ reflexions is 7·6 Å^2. This high value (independent of any specific assumption about symmetry) indicates a considerable disorder in the structure. The least-squares calculation showed that this disorder is mostly concentrated on atoms I(1) and I(3) (constituting triiodide ions). Therefore we suppose that this is a consequence of random rotations about the trigonal axis and orientation disorder of triiodide ions, which are in most cases non-linear and asymmetric (Tasman & Boswijk 1955). The origin of this disorder we can seek in the nonpolar arrangement of the other components in the crystal $K_2I_4 . 6(CH_3CONHCH_3)$, so that on both ends of the triiodide ion the same grouping of molecules and ions exists. Nothing indicates a preference therefore for one or the other orientation of the triiodide ion.

K^+ cations are also arranged in linear arrays parallel to the c axis. Their mutual distance in an array is 3·80 Å.

The planar molecules of N-methylacetamide are arranged approximately in planes (001) (with inclination about 5° around the C–O bond). Every plane contains three molecules. They are arranged in such a manner that to one I^- ion six NH groups and to one K^+ cation six carbonyl oxygen atoms are coordinated, NH groups and oxygen atoms from equilateral triangles lying in odd eighths of the period c. Thus the NH triangles are situated above and below the I^- ions (with respect to the c axis), and the triangles of oxygen atoms exactly mid-way between neighbouring K^+ cations. Every two K^+ cations thus share the same oxygen triangle. On the other hand, the triangles of NH groups are substantially nearer to the I^- ions (distance 3·74 Å) than to end atoms of triiodide ions (distance 4·01 Å). Therefore we do not believe in the existence of any appreciable interaction between triiodide ions and NH groups in the complex $K_2I_4 . 6(CH_3CONHCH_3)$.

The molecules of N-methylacetamide in the structure of the complex $K_2I_4 . 6(CH_3CONHCH_3)$ are thus oriented with their polar groups to the I^- ions and K^+ cations. On the other hand, the CH_3 groups surround the triiodide ions laterally.

During the preparation of the manuscript of this paper, the paper by Reddy, Knox & Robin (1964) on the structure of the $HI_3 . 2C_6H_5CONH_2$ complex appeared. According to these authors, molecules of benzamide in this complex are bound in pairs by hydrogen bonds in the same manner as is the case in pure benzamide crystals. The organic molecules from here only a rigid framework for incorporating the triiodide ions. In the case of our complex $K_2I_4 . 6(CH_3CONHCH_3)$ the situation is completely different. On the ground of our results we cannot expect any interaction to exist between individual molecules of N-methylacetamide (the distance between NH groups and CO in neighbouring molecules is 4·54 Å) similar to that in pure crystalline N-methylacetamide (Katz & Post 1960). The crystal structure of $K_2I_4 . 6(CH_3CONHCH_3)$ presumably owes its stability to the interaction of the I^- and K^+ ions with the dipolar group of N-methylacetamide



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