# Crystal structure of poly(ethylene oxide)–sodium iodide complex

**Yozo Chatani and Sigeru Okamura**
*Department of Material Systems Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan*
*(Received 10 April 1987; accepted 27 April 1987)*

The crystal structure of poly(ethylene oxide)–sodium iodide (PEO–NaI) complex, a highly ionic conductor, was determined by the X-ray diffraction method. The crystals belong to the monoclinic system of space group $P2_1/a$. The cell constants are $a = 18.15$ Å, $b = 8.41$ Å, $c$ (chain axis) $= 7.98$ Å and $\gamma = 122.3°$ (first setting). The molar ratio (EO:NaI) is 3:1, and there are 12 monomer units (two chains) and four NaI ion pairs in the unit cell. The crystal structure is characterized as follows: (1) The polymer chain, in which the asymmetric unit consists of three monomer units, takes a 2/1 helix of conformation $(TTGTTGTT\bar{G})_2$($T$, *trans*; $G$ and $\bar{G}$, plus and minus *gauche*, respectively). (2) $Na^+$ and $I^-$ ions are linked alternately to form a zigzag chain. (3) The NaI chain is coiled round by the helical polymer chain in such a way that a couple of NaI ion pairs makes the same repeat period to that of the polymer helix. (4) Each $Na^+$ ion is coordinated by three polymer oxygen atoms and two $I^-$ ions.

**(Keywords: complex; poly(ethylene oxide); sodium iodide; ionic conductor; crystal structure; X-ray diffraction)**

## INTRODUCTION

Crystalline complexes of poly(ethylene oxide) (PEO) with inorganic and organic compounds are widely known like those of crown ethers. Among them, however, only two crystal structures of PEO–$HgCl_2$ complexes having molar ratio (EO:$HgCl_2$) of 4:1 and 1:1 are known[1,2]. Crystalline complexes of PEO with alkali-metal salts such as NaI, NaSCN and KSCN were found by Wright *et al.*[3] in 1973. These systems exhibit ionic conductivity of the order of $10^{-4}$–$10^{-3}$ S cm$^{-1}$ at 100°C[4,10]. After this finding, these crystalline complexes together with amorphous complexes with $NaBF_4$, RbSCN, RbI, etc., have been paid much attention as high ionic conductors or solid electrolytes. Elucidation of the structures and properties of these complexes has been attempted by a variety of methods[4–29].

Armand[10] postulated that a helical PEO chain surrounds cations so as to provide a specific pathway for cation transport, while anions are separated from the cations by the polymer chain. A more detailed structure model of the complexes was reported by Papke and coworkers[11,13]. Their proposal from infra-red and Raman spectroscopic studies on the Na and K salt complexes is such that PEO chains have a helical conformation comprising *trans* ($T$) C–O bonds and alternating *gauche* ($G$) and minus *gauche* ($\bar{G}$) C–C bonds, and that each cation placed inside the helix is coordinated by four polymer oxygen atoms. Wright *et al.*[7] reported for the KSCN and NaSCN complexes that PEO chains assume not the single helix but a double-stranded helix, and that cations are again placed in the cavity. Hibma[16] reported the two-dimensional structure viewed along the chain axis for the PEO–KSCN complex. According to his structure, which is not always conclusive, both cations and anions are outside deformed helices. No detailed structure, however, is known for any PEO–alkali-metal salt complex.

In this paper the crystal structure analysis of the PEO–NaI complex will be reported. The result is rather different from the previous proposals.

## EXPERIMENTAL

The stoichiometric molar ratio of crystalline PEO–Na and K salt complexes (EO:salt) has been estimated[6,11] to be probably 4:1. Hibma[16] proposed a unit cell of the PEO–NaI complex in which the molar ratio was supposed to be 3:1 rather than 4:1. Therefore we prepared samples of PEO–NaI with several molar ratios and tested them to determine the stoichiometry in the PEO–NaI crystals.

### *Preparation of complex*

High-molecular-weight PEO (*MW* 5 000 000, Dow Chemical Co.) and reagent-grade anhydrous NaI were used. Because of the sensitivity of both PEO and NaI to atmospheric moisture, they were dried and stored in a desiccator. PEO was dissolved in NaI methanol solutions with appropriate molar ratios. Film specimens for X-ray and d.s.c. measurements were obtained by casting the solutions in an oven at 50°C. Hereafter the sample with molar ratio $N$:1 is named the $N$:1 sample.

### *D.s.c. measurements*

A Rigaku Denki differential scanning calorimeter was employed. Samples were run from room temperature to 200°C at a heating rate of 10°C min$^{-1}$. After the first run, the sample was cooled to room temperature at a rate of 10°C min$^{-1}$ and the second run was then taken in the same way.

### *X-ray measurements*

Uniaxially oriented specimens were prepared by hot-drawing the cast films to about 30 times their original

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length. Drawn specimens about 0.3 mm thick and wide were fixed on a metal holder under tension and stored in a desiccator. X-ray fibre photographs of the samples were taken in a dry nitrogen stream. Nickel-filtered copper K$\alpha$ radiation was used throughout this study. Spacings were measured with a cylindrical camera of 100 mm diameter and were corrected to those of NaCl powder. As mentioned later, the X-ray fibre photographs were varied depending on the molar ratios. *Figure 1* shows the X-ray fibre photograph of the PEO–NaI complex free from PEO and NaI crystals. Reflection intensities were obtained using the same camera by the multiple-film method, and were estimated visually with a standard intensity scale. The Lorentz polarization factor was corrected for the observed intensities. Since the absorption of X-rays by the sample could not be ignored, the intensities were also corrected for the absorption by assuming a rod-shaped sample. Meriodional reflections ($00l$) were also measured by using a Weissenberg camera.

### *Density measurements*

The densities of the samples were determined by a flotation method with densities of the liquid media measured with a pycnometer. Tetrachloromethane for light and chlorobromomethane or bromoform for heavy were used for the liquid media.

## STRUCTURE ANALYSIS

### *Molar ratio of PEO–NaI complex*

The d.s.c. traces of several samples are shown in *Figure 2*. Two endothermic peaks in the vicinity of 60°C and 180°C correspond to the melting of PEO crystals and of the complex crystals, respectively. The peak of uncomplexed PEO crystals was observed in 5:1 and 4:1 samples but was unobserved in 3:1 and 2.5:1 samples. This peak in 5:1 and 4:1 samples became smaller in the second run, and especially disappeared in the 4:1 sample.

The X-ray photograph of the 5:1 sample was composed of the diffraction patterns of PEO crystals and of the complex crystals, while the 4:1 sample gave the diffraction pattern of the complex alone. Besides the 2.5:1 sample, the 3:1 sample seldom gave not only the diffraction pattern of the complex but of excess NaI crystals. These facts indicated that the molar ratio of the crystalline complex might be either 3:1 or 4:1, but did not give the final answer. The final molar ratio of 3:1 was decided by the following structure analysis.

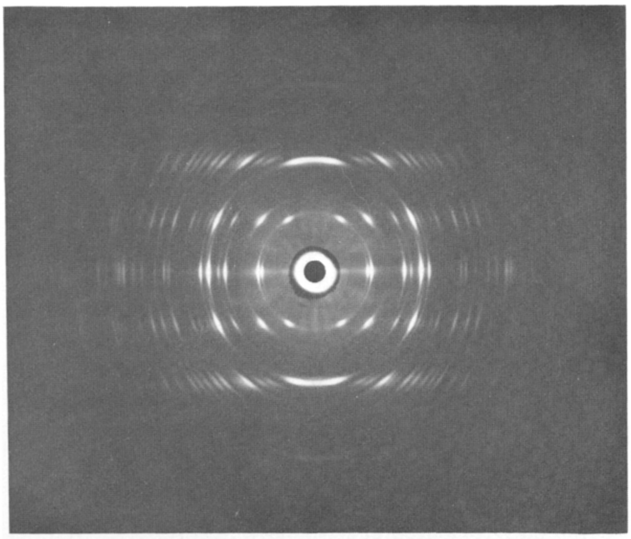

**Figure 1** X-ray fibre photograph of PEO–NaI complex

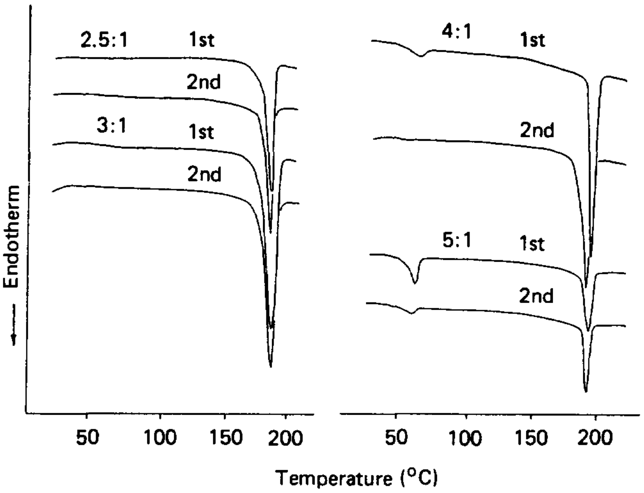

**Figure 2** D.s.c. traces of PEO–NaI system with the indicated molar ratios (EO:NaI)

### *Unit cell and space group*

The PEO–NaI complex crystals were found to belong to the monoclinic system. The cell constants are $a=18.15$ Å, $b=8.41$ Å, $c$ (chain axis) $=7.98$ Å and $\gamma=122.3°$ (first setting). Hibma[16] proposed a monoclinic unit cell with cell constants of $a=17.01$ Å, $b$ (chain axis) $=8.00$ Å, $c=16.88$ Å and $\beta=115.1°$ (second setting). Except that the volume of his unit cell is twice as large as ours, both cells are essentially identical, i.e. both cells are transformed into each other as follows: $\boldsymbol{a}_0=\boldsymbol{a}_{\mathrm{H}}+\boldsymbol{c}_{\mathrm{H}}$, $\boldsymbol{b}_0=-\boldsymbol{c}_{\mathrm{H}}/2$ and $\boldsymbol{c}_0=\boldsymbol{b}_{\mathrm{H}}$, where subscripts H and 0 denote Hibma and our, respectively. Although Hibma did not describe the space group, all reflections were well explained in terms of our small cell. Systematic absences of reflections ($hk0$ when $h=2n+1$, $h00$ when $h=2n+1$ and $00l$ when $l=2n+1$) indicated that the space group is $P2_1/a$. Space group $P2_1/a$ has four general equivalent points. Referring to the unit-cell volume, it was again reasonably assumed that four NaI ion pairs are in the unit cell. *Table 1* shows observed and calculated densities for several samples with different molar ratios, where the calculated densities were evaluated in such a way that there are four NaI ion pairs and a certain number of EO units satisfying the indicated molar ratio in the unit cell. The best fitting between observed and calculated densities was for 3:1. Therefore the structure analysis was started on the basis of the molar ratio of 3:1. In practice, in the crystal structure analysis it became clear that the unit cell has too small an open space to accommodate PEO chains with a molar ratio of 4:1.

### *Positions of $Na^+$ and $I^-$ ions*

The position of $I^-$ ion was easily determined because of the large X-ray scattering power of $I^-$ ion. At this stage the discrepancy factor $R$ was 0.25. The position of $Na^+$ ion was then determined by a trial-and-error procedure. The $R$ factor dropped to 0.21, still ignoring the contribution of PEO chains. The structure of NaI in the complex thus obtained is quite different from the previous

**Table 1** Observed and calculated densities

| Number in unit cell | | Molar ratio | Observed density | Calculated density[a] |
|---|---|---|---|---|
| EO | NaI | (EO:NaI) | ($g\,cm^{-3}$) | ($g\,cm^{-3}$) |
| 10 | 4 | 2.5:1 | 1.85 | 1.68 |
| 12 | 4 | 3:1 | 1.80 | 1.82 |
| 16 | 4 | 4:1 | 1.74 | 2.10 |
| 20 | 4 | 5:1 | 1.64 | 2.39 |

[a] See text

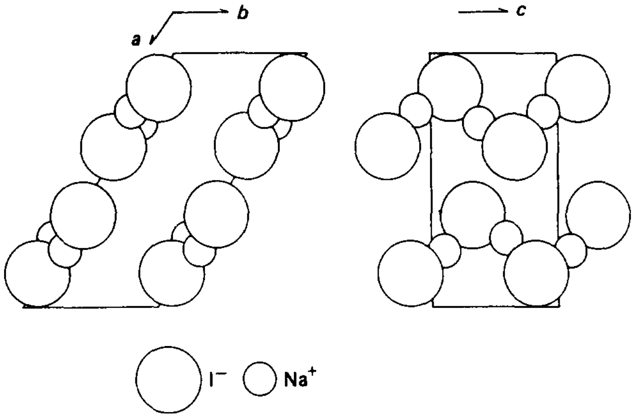

**Figure 3** Arrangement of NaI ions in the complex

proposal that only cations are placed in PEO helices. As shown in *Figure 3*, $Na^+$ and $I^-$ ions are linked alternately to form a zigzag chain along the *c* axis (chain axis) with 2/1 helix symmetry.

*Structure of PEO in the complex*

The observed fibre period of 7.98 Å has to comprise at least three EO units: two EO units have a shorter repeat period of 7.12 Å even in the fully extended form[30]. Twelve EO units in the unit cell could thus be divided into two, three or four chains passing through the unit cell. But it seemed inadequate that the monoclinic cell involves three chains, which must be non-equivalent crystallographically. Therefore there must be two or four chains in the unit cell; the fibre period comprises six EO units in the former case, and three EO units in the latter case. The arrangement of NaI chains in the unit cell (*Figure 3*) is able to provide appropriate open space to accommodate the two chains when each polymer chain coils round each NaI chain. However, in the case of four chains per unit cell, there is no appropriate open space. The open space is also too small to accommodate a polymer chain that makes up the fibre period of eight EO units with a molar ratio of 4:1. Since the NaI chain has a two-fold screw axis parallel to the *c* axis, the PEO chain which wraps the NaI chain again has to possess the same symmetry, three successive EO units being the asymmetric unit.

The model was refined under the following conditions: (1) six EO units make up the observed fibre period with 2/1 helix symmetry; (2) comparably large discrepancies between observed and calculated structure factors for several reflections when only $I^-$ and $Na^+$ ions were taken into account must vanish by introduction of the PEO chains; (3) the C–O bonds assume preferably *trans* form; and (4) no abnormal interchain distances are allowable. Finally all atomic coordinates were refined by the diagonal least-squares method. The final atomic coordinates are listed in *Table 2*. Observed and calculated structure factors are compared in *Table 3*. The final *R* factor is 0.14 for all observed reflections. The crystal structures projected onto the *ab* and *ac* planes are shown in *Figure 4*.

## RESULTS AND DISCUSSION

### *Structure of the complex*

The characteristics of the crystal structure of the PEO–NaI complex are summarized as follows.

(1) The molar ratio (EO:NaI) is 3:1, as Hibma[16] supposed.

(2) $Na^+$ and $I^-$ ions are linked alternately to form a zigzag chain (2/1 helix). That is, with respect to the $Na^+\cdots I^-$ coordination, the coordination number is 2. The $Na^+\cdots I^-$ distances are alternately 3.20 Å and 2.91 Å. These values are intermediate between 3.24 Å in an NaI crystal and 2.71 Å in an NaI gas molecule. The six-fold coordination in NaI crystal brings about the rather long distance due to the repulsion between $I^-$ ions. Therefore the $Na^+\cdots I^-$ distances found in the complex seem to be normal.

(3) The NaI chain is coiled round by the helical PEO chain that makes a fibre period of 7.98 Å with six EO units (*Figure 4*). The polymer chains assume a 2/1 helix, three EO units being the symmetric unit. The conformation of the asymmetric unit is expressed as

$$\begin{array}{ccccccccccccccccccc} -\mathrm{O} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{C} & - & \mathrm{C} & - \\ & T & & T & & G & & T & & T & & G & & T & & T & & \bar{G} \end{array}$$

Although it would not be expected that the accuracy in atomic positions found for NaI ions would also be found for carbon and oxygen atoms, the final internal coordinates of the PEO chain are shown in *Table 4*. The formation of the 2/1 helix in the complex is ascribed to the coordination of oxygen atoms to $Na^+$ ions as shown below.

(4) Each $Na^+$ ion is coordinated by three polymer oxygen atoms and two $I^-$ ions. The scheme of the coordination including the atomic distances is shown in *Figure 5*. $Na^+\cdots O$ distances found so far for many low-molecular-weight compounds range between 2.22 and 2.75 Å depending on the coordination number[31]. The distances found in the complex (2.28, 2.48 and 2.70 Å) are never unusual.

### *Comment on ionic conduction*

As for crystalline PEO–alkali-metal salt complexes

**Table 2** Fractional atomic coordinates and thermal parameters

| | *x* | *y* | *z* | *B* (Å²) |
|---|---|---|---|---|
| I | 0.135 | 0.038 | 0.169 | 14 |
| Na | 0.278 | 0.045 | 0.409 | 17 |
| O1 | 0.297 | 0.364 | 0.533 | 15 |
| C1 | 0.264 | 0.385 | 0.691 | 16 |
| C2 | 0.166 | 0.231 | 0.703 | 15 |
| O2 | 0.155 | 0.055 | 0.696 | 15 |
| C3 | 0.064 | −0.088 | 0.707 | 15 |
| C4 | 0.058 | −0.281 | 0.697 | 16 |
| O3 | 0.088 | −0.305 | 0.853 | 16 |
| C5 | 0.079 | −0.492 | 0.846 | 15 |
| C6 | 0.114 | −0.511 | 0.021 | 14 |

**Table 3** Observed and calculated structure factors

| *hkl* | $F_0$ | $F_c$ |
|---|---|---|
| 200, −210 | 105 | 75 |
| 010 | 218 | 179 |
| −410 | 186 | 186 |
| 210, −220 | 82 | 77 |
| 400, −420 | 252 | 227 |
| 020 | 156 | 154 |
| 410, −430 | 80 | 88 |
| 220, −230 | 98 | 103 |
| 600, −630 | 73 | 68 |
| 030 | 88 | 94 |
| −820 | 89 | 96 |
| −810, −830 | 119 | 130 |
| 420, −440 | 82 | 91 |
| −640 | 55 | 58 |
| 230, −240 | 69 | 76 |
| 800, −840 | 100 | 85 |
| −(10)10, −(10)40, 620, −650 | 38 | 50 |
| 430, −450, 810, −850 | 59 | 57 |
| 240, −250 | 35 | 34 |
| 630, 820, −660, −860, −(12)10, −(12)50 | 50 | 52 |
| 250, (12)00, −260, −(12)60 | 41 | 32 |
| 101 | 79 | 95 |
| 201, −211 | 108 | 101 |
| 011 | 36 | 46 |
| −311 | 16 | 23 |
| 111 | 30 | 42 |
| 301 | 90 | 96 |
| −411 | 49 | 38 |
| 211, −221, −321 | 205 | 199 |
| −121 | 72 | 88 |
| 401, −421 | 53 | 51 |
| −511, 021 | 62 | 60 |
| −521, 311 | 83 | 69 |
| 121, 501 | 31 | 24 |
| −611, −621 | 119 | 114 |
| 411, −331, −431 | 29 | 40 |
| 221, −231, −531 | 104 | 94 |
| −721, 601, −131, −631 | 106 | 118 |
| 511, 321, 031 | 79 | 65 |
| 701, 131, −811, −831 | 26 | 27 |
| 421, −541, −441 | 77 | 64 |
| 611, −641, −341 | 86 | 79 |
| −921, −741, 231, −241, −931 | 45 | 54 |
| 801, −841, −911, −141 | 36 | 38 |
| 331, −941, −(10)21, −(10)31 | 71 | 70 |
| 901, −(10)11, −(10)41, 621, −651, −551 | 58 | 57 |
| 431, −451, −(11)31, 811, −851 | 50 | 52 |
| 721, (10)01, −(11)11, −(10)51, 531 | 45 | 40 |
| 441, −(13)21, (10)11, −461 | 33 | 21 |
| −(13)31, −861, −(12)11, (11)01, −(12)51 | 35 | 21 |
| 102 | 88 | 97 |
| −112 | 54 | 44 |
| 012 | 61 | 94 |
| −312 | 120 | 145 |
| 112 | 52 | 92 |
| 302 | 58 | 57 |
| −412 | 110 | 126 |
| 212, −222, −322 | 102 | 126 |
| 402, −422 | 86 | 87 |
| −512, 022 | 85 | 80 |
| −522, 312 | 99 | 105 |
| 122 | 66 | 66 |
| 502 | 80 | 87 |
| 412, −332, −432 | 95 | 101 |
| 222, −232, −532 | 53 | 57 |
| −722, 602, −132, −632 | 37 | 53 |
| −712 | 29 | 31 |
| 512, 322, 032, −732 | 85 | 87 |
| 702, 132, −812, −832 | 71 | 67 |
| 422, −542, −442 | 39 | 43 |
| 612, −642, −342 | 49 | 62 |
| −922, −742 | 42 | 45 |
| −242, −932 | 35 | 30 |
| 522 | 37 | 34 |
| −652, −552, −752, 142, 342 | 49 | 42 |
| −(11)22, −352 | 42 | 36 |
| 722, (10)02, −(11)12, −(10)5·2, 532, −(12)32 | 48 | 28 |
| −(11)52, 342 | 35 | 20 |
| 632, 822, −762, −662, −(13)32, −862, −(12)12, (11)02, −(12)52 | 36 | 27 |
| −113, 203, −213 | 45 | 61 |
| −313 | 48 | 65 |
| 303 | 43 | 55 |
| −323, −123 | 65 | 71 |
| −513, 023 | 38 | 36 |
| −523, 313 | 70 | 75 |
| 123, 513 | 43 | 43 |
| 223, −233, −533 | 68 | 62 |
| 7723, 603, −133, −633 | 52 | 57 |
| −713 | 46 | 50 |
| 513, 323, 033, −733 | 62 | 59 |
| 703, 133 | 37 | 35 |
| 423, −543, −443 | 38 | 35 |
| −923, −743 | 30 | 20 |
| 233, −243, −933 | 30 | 28 |
| −843, −913, −143, 523 | 42 | 37 |
| 713, 333, −943, −(10)23, −(10)33 | 52 | 49 |
| −(10)13, −(10)43, 623, −653, −553, −753, 143 | 32 | 22 |

**Table 4** Bond lengths, bond angles and internal rotation angles of PEO chain

| | Bond length (Å) |
|---|---|
| O1–C1 | 1.44 |
| C1–C2 | 1.55 |
| C2–O2 | 1.39 |
| O2–C3 | 1.44 |
| C3–C4 | 1.57 |
| C4–O3 | 1.41 |
| O3–C5 | 1.49 |
| C5–C6 | 1.58 |
| C6–O1′ | 1.43 |
| | Bond angle (deg) |
| O1–C1–C2 | 109 |
| C1–C2–O2 | 110 |
| C2–O2–C3 | 109 |
| O2–C3–C4 | 106 |
| C3–C4–O3 | 106 |
| C4–O3–C5 | 106 |
| O3–C5–C6 | 105 |
| C5–C6–O1′ | 108 |
| C6–O1′–C1′ | 108 |
| | Internal rotation angle (deg) |
| O1–C1–C2–O2 | 60 |
| C1–C2–O2–C3 | 179 |
| C2–O2–C3–C4 | 180 |
| O2–C3–C4–O3 | 73 |
| C3–C4–O3–C5 | 178 |
| C4–O3–C5–C6 | 180 |
| O3–C5–C6–O1′ | −62 |
| C5–C6–O1′–C1′ | 178 |
| C6–O1′–C1′–C2′ | 177 |

which exhibit the Arrhenius temperature dependence in a conductivity plot (log $\sigma$ vs. $1/T$), one of previous proposals is that cations move in the cavity of a PEO helix, and that the conductivity is due mainly to cation transport. However, as long as the NaI complex is concerned, such a model for ionic conduction is not always probable. In the NaI complex crystal, as shown in *Figure 4*, $Na^+$ and $I^-$ ions are linked alternately. Although we are not sure what type of defect, in a wide sense, is generated to enable ions to move in the crystal,

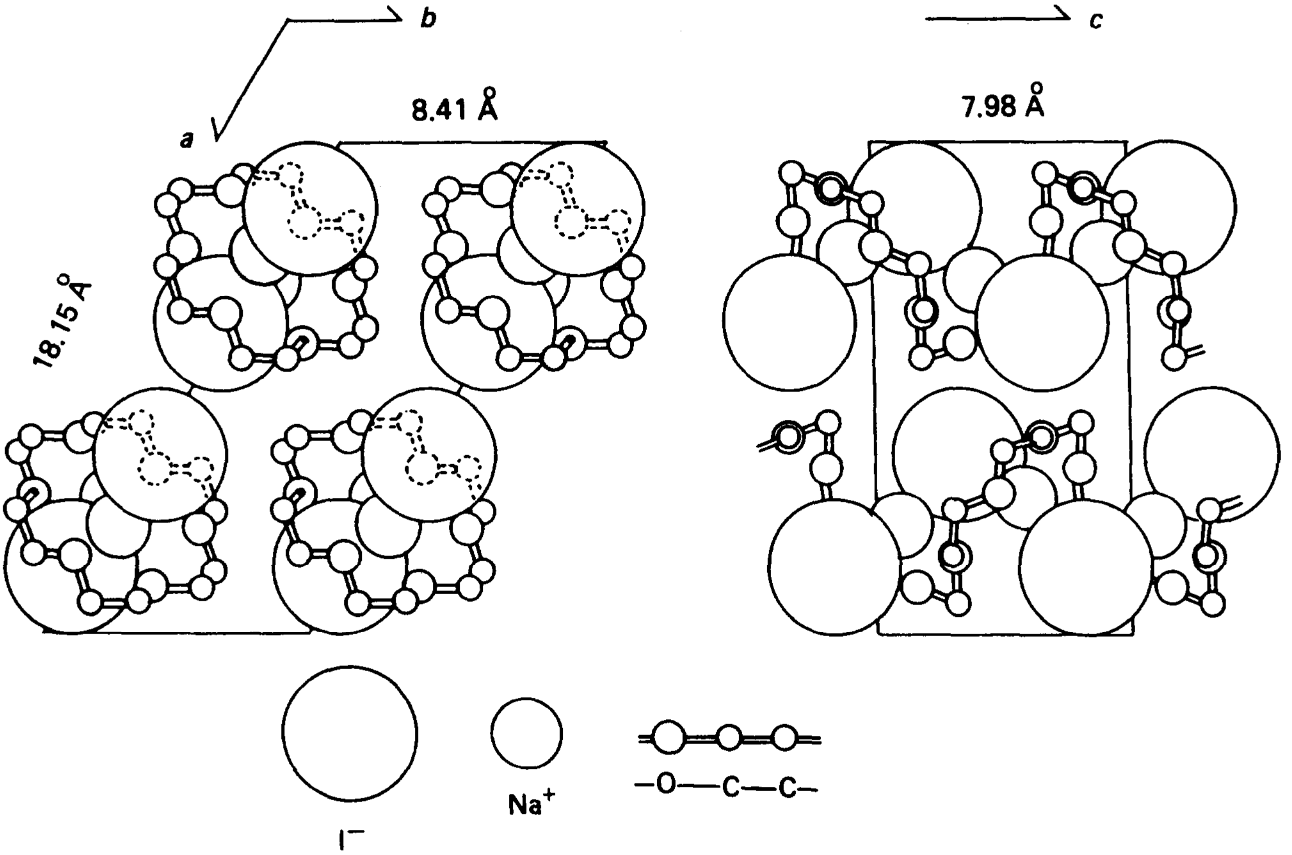

**Figure 4** Crystal structure of the complex

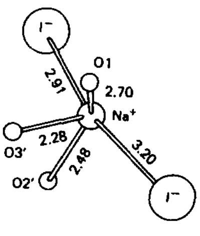

**Figure 5** Scheme of coordination and interatomic distances (Å) in the complex

transport of both cations and anions in the lateral direction also cannot be ruled out. Unfortunately, we are not aware of any data on anisotropy of conductivity or on the transference number for the NaI complex.

An alternative proposal which is now accepted is that the amorphous part does play the major role in conductivity[28]. Wright *et al.*[6] reported that the conductivity of the NaI complex depends on the morphology of the system. The crystalline part, crystal boundaries and the amorphous part must exhibit distinguishable behaviours in ionic conduction. Information on structures of many complexes is indispensable to clarify the relation between structure and conductivity of the PEO–alkali-metal salt systems.

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