J. Am. Chem. Soc. **1994,** *116,* 7469–7470 7469

Crystal Structures of the Polymer Electrolytes Poly(ethylene oxide)$_4$:MSCN (M = NH$_4$, K)

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Received March 7, 1994

Solid polymer electrolytes consist of salts, e.g., LiClO$_4$, dissolved in coordinating high molecular weight polymers, e.g., poly(ethylene oxide) [PEO, (CH$_2$CH$_2$O)$_n$]. They can exhibit ionic conductivities approaching those of many liquid electrolytes despite possessing a *solid solvent*. The combination of a solid but flexible material with a high conductivity makes these electrolytes attractive for use in all-solid-state electrochemical devices such as lithium batteries, electrochromic displays, and smart windows. Although many physical measurements have been carried out on polymer electrolytes, progress in the field has been severely restricted by the lack of structural data on these materials.[1,2] In no small part, this is due to the difficulty encountered in determining the crystal structures of polymer:salt complexes by single crystal methods.[3,4] Recently, we have succeeded in establishing the crystal structures of poly(ethylene oxide)$_3$:NaClO$_4$ and poly(ethylene oxide)$_3$:LiCF$_3$SO$_3$ from high-resolution powder X-ray data.[5–8] In this communication we report the structure elucidation of the important complexes poly(ethylene oxide)$_4$:MSCN (M = NH$_4$ or K).[9] This represents significant progress in the field of polymer electrolytes in two ways. First, the results prove for the first time that long-held views concerning the structures of polymer electrolytes in general are seriously in error. Second, while the structures of the 3:1 complexes, e.g., PEO$_3$:NaClO$_4$, could be solved by Rietveld refinement[10] of a model based on the already known structure of PEO$_3$:NaI, this was not the case for the 4:1 complexes. These had to be solved by the still embryonic method of *ab initio* structure determination from powder diffraction data,[11–13] i.e., without any prior model for the structure. This is the first time that such methods have been used in the field of polymer electrolytes. Our results also represent the first full structure determinations of ionic polymer:salt complexes with an ether oxygen-to-cation ratio greater than 3:1.

Table 1. Refined Atomic Parameters for PEO$_4$:KSCN[a] and PEO$_4$:NH$_4$SCN[b] at 298 K[c]

atom	*x*	*y*	*z*	*U*(iso)[d]/Å^2
		PEO$_4$:KSCN		
K	0.3035(4)	0.3450(13)	0.3440(7)	0.097(4)
S	0.4157(6)	0.1729(15)	0.2838(8)	0.130(6)
C9	0.3388(11)	0.122(6)	0.230(4)	0.130(6)
N	0.2849(9)	0.082(4)	0.193(3)	0.130(6)
O1	0.3304(10)	0.103(2)	0.488(2)	0.118(5)
C1	0.3966(12)	0.048(3)	0.548(2)	0.118(5)
C2	0.4369(9)	0.211(4)	0.600(1)	0.118(5)
O2	0.4087(9)	0.351(3)	0.535(1)	0.118(5)
C3	0.4467(10)	0.499(3)	0.579(1)	0.118(5)
C4	0.4124(11)	0.641(3)	0.500(2)	0.118(5)
O3	0.0988(13)	0.085(2)	0.093(2)	0.118(5)
C5	0.1187(14)	0.233(2)	0.154(2)	0.118(5)
C6	0.1412(10)	0.171(3)	0.260(2)	0.118(5)
O4	0.2047(9)	0.104(3)	0.305(2)	0.118(5)
C7	0.2179(12)	0.025(3)	0.395(2)	0.118(5)
C8	0.2895(14)	−0.033(2)	0.467(2)	0.118(5)
		PEO$_4$:NH$_4$SCN		
N1	0.2903(8)	0.376(2)	0.3288(11)	0.071(3)
S	0.4223(4)	0.1637(10)	0.2771(5)	0.071(3)
C9	0.3441(7)	0.161(3)	0.235(2)	0.071(3)
N2	0.2933(6)	0.108(2)	0.207(2)	0.071(3)
O1	0.3260(7)	0.117(2)	0.4974(11)	0.104(5)
C1	0.3909(8)	0.073(2)	0.542(2)	0.104(5)
C2	0.4381(6)	0.217(2)	0.5892(12)	0.104(5)
O2	0.4059(6)	0.361(2)	0.5357(11)	0.104(5)
C3	0.4478(8)	0.495(2)	0.5775(10)	0.104(5)
C4	0.4172(8)	0.639(2)	0.500(1)	0.104(5)
O3	0.0948(8)	0.092(2)	0.0962(10)	0.104(5)
C5	0.1151(10)	0.240(2)	0.1545(13)	0.104(5)
C6	0.1488(7)	0.199(2)	0.2705(12)	0.104(5)
O4	0.2012(6)	0.091(2)	0.3090(11)	0.104(5)
C7	0.2160(9)	0.025(2)	0.4051(14)	0.104(5)
C8	0.2870(9)	−0.0264(13)	0.4641(15)	0.104(5)

[a] Space group *C*2/*c*, a = 25.512(3) Å, b = 8.0813(8) Å, c = 16.097(1) Å, β = 125.98(1)°. [b] Space group *C*2/*c*, a = 25.663(2) Å, b = 8.2318(7) Å, c = 15.801(1) Å, β = 125.26(1)°. [c] Hydrogen atoms included in refinement but not in table. [d] Values constrained according to atom type.

All attempts to solve these structures by using the known 3:1 complexes as starting models were unsuccessful. The structure of the NH$_4$SCN complex was therefore solved in an *ab initio* manner, by first locating the S atom of the thiocyanate *via* direct methods. This was followed by difference Fourier techniques applied to the whole powder diffraction profile to locate the remainder of the structure.[14] Having established the basic crystal structure by this method, we obtained the precise bond lengths and angles by Rietveld profile refinement. The KSCN complex was determined by Rietveld refinement using the refined NH$_4$-

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(9) The samples were prepared by mixing appropriate molar ratios of dry PEO (Aldrich, MW = 5 × 10^6) and thiocyanate (Aldrich ACS reagent) in an argon-filled glovebox. The mixture was removed from the glovebox and ground at liquid nitrogen temperature for about 20 min. After the mixture was returned to room temperature, it was transferred to the glovebox and sealed in a 0.5-mm glass capillary. This was heated at 150 °C for 4 days to promote dissolution of the salt in the polymer, followed by a further annealing at 50 °C for 4 days.

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(14) X-ray data were collected on a Stoe STADI/P powder diffractometer operating in transmission mode, using Cu Kα_1 radiation and a small, linear, position-sensitive detector. Samples were mounted in 0.5-mm-diameter Lindemann tubes, and data were collected over the range 5° $< 2\theta <$ 65° at 298 K. The powder X-ray patterns were first indexed on the basis of Hibma's initial suggestion for the KSCN complex.[15] Due to the similarity between the KSCN and NH$_4$SCN patterns, it was found that unit cell parameters for the NH$_4$SCN complex could be determined by a straightforward adjustment and refinement of those for the KSCN complex. Results for the two compounds, space group C2/*c*, were as follow. NH$_4$SCN: a = 25.663(2) Å, b = 8.2318(7) Å, c = 15.801(1) Å, β = 125.26(1)°. KSCN: a = 25.512(3) Å, b = 8.0813(7) Å, c = 16.097(1) Å, β = 125.99(1)°. *Ab initio* structure solution by direct methods requires extraction of individual intensities from the powder pattern. This was carried out by the LeBail method[16] using the GSAS program.[17] This generated 172 reflections for the NH$_4$SCN data set, which were used as input to the direct methods program SIR88.[18] The top peak in the best Fourier map was assigned as S, and the model developed from that point *via* successive cycles of difference Fourier and refinement. All calculations were performed using GSAS. Bond lengths were constrained as C–C = 1.57(1) Å, C–O = 1.43(1) Å, angles as 109°. Dihedral angles were not constrained. Temperature factors were constrained according to atom type. Hydrogen atoms were included in calculated positions and refined with constraints. The final model consisted of 120 (110) variables refined against 2750 (2750) profile points and 409 (465) reflections for NH$_4$SCN (KSCN), respectively. Final agreement factors were R_{wp} = 4.90 (4.98), χ^2 = 1.52 (1.26).

0002-7863/94/1516-7469$04.50/0

Table 2. Selected Bond Distances (Å)

PEO_4:KSCN		PEO_4:NH_4SCN	
K1–O1	2.79(2)	N1–O1	3.11(2)
K1–O2	2.63(2)	N1–O2	2.88(2)
K1–O3	2.83(3)	N1–O3	3.04(2)
K1–O4	2.96(2)	N1–O4	3.16(2)
K1–O4′	3.09(2)	N1–O4′	2.91(2)
K1–N	3.05(4)	N1–N2	2.96(2)
K1–N′	2.74(2)	N1–N2′	2.68(2)

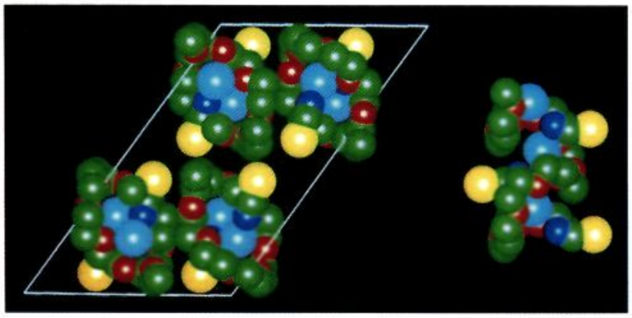

Figure 1. (Left) View of the structure of the PEO_4:NH_4SCN or PEO_4:KSCN complex down the fiber axis (*b*). Light blue spheres, potassium; dark blue, nitrogen; yellow, sulfur; green, carbon; red, oxygen. (Right) A portion of the PEO_4:NH_4SCN or PEO_4:KSCN structure showing a single PEO chain with associated ions.

SCN complex as an initial structural model. The use of soft chemical constraints to stabilize the refinements was critical to the success of the method.

The two complexes are essentially isostructural, with only minor differences being caused by the differing sizes of the two cations. Final refined atomic coordinates for the two complexes are given in Table 1, and selected bond distances and angles are given in Table 2. Figure 1 shows views of (left) the unit cell down the fiber axis and (right) a single PEO chain with associated ions. As in the previously determined 3:1 complexes of Li^+ and Na^+,[5-8] the PEO chain adopts a helical arrangement which encloses the cation. However, there are important differences between the previously known structures and the present examples which may be ascribed to the larger nature of the cations in the present case. The PEO chain itself is forced to adopt a novel conformation in this case, *viz.* ttgttgttḡttḡ, i.e., *all* C–O bonds *trans*, but C–C bonds adopting the *gauche* or *gauche minus* conformation as shown. This contrasts with the conformation ttgttgttḡ adopted by all the previously known 3:1 complexes of the Li^+ and Na^+ cations. This rearrangment causes an effectively "fatter" PEO helix, which has two important consequences: firstly, the PEO repeat distance along the axis of the helix is greatly shortened, leading to eight EO units within a shorter fiber axis compared to the six in the 3:1 complexes, and secondly, a higher coordination number around the cation is obtained due to the availability of five coordinating ether oxygens as opposed to three in the $LiCF_3SO_3$ complex[6] or 3(+1) in the $NaClO_4$[5] and NaSCN complexes.[4]

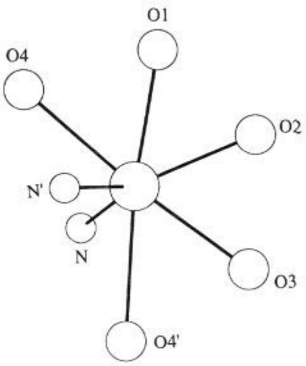

Figure 2. Local coordination around the cation, showing five ether oxygens and two nitrogens from neighboring anions.

A seven-coordinate environment around the cation is completed by two nitrogens from the SCN^- ions (Figure 2). Two of the five ether oxygens coordinate two cations simultaneously, and the nitrogen of each thiocyanate bridges two neighboring cations along the chain. As in the previously known structures, there are, again, no direct *inter*chain links; the cations and anions being associated with one PEO chain only.

A previous study[15] of the KSCN complex using two-dimensional diffraction data from a fiber sample suggested that the K^+ ions were external to the PEO helix. The present study clearly shows that this is not the case and that instead cations larger than Na^+ are accommodated within the helix, in complete contrast to the established views in the field. Hibma's model is radically different from the one presented here in that it requires eight separate polymer chains of four units each per unit cell rather than four chains each of eight units, as here. The data which Hibma had available were considerably inferior to those studied here. Hibma suggested that "quite different conformations of the polymer chain give only slightly larger discrepancy factors" than the one proposed to be correct. We can conclude that Hibma's models were in error because the possibility of only four separate chain segments per unit cell had not been considered. In the present case, all atoms were found by crystallographic means, commencing with *ab initio* (and hence model-independent) methods, i.e., using the intensity data directly; hence, assumptions made using "model-building" methods were avoided. There is no ambiguity in our model. This work will lay the foundation for a major reappraisal and re-interpretation of other work in the field which has relied on this previous study.

Acknowledgment. P.G.B. is indebted to the Royal Society for the award of a Pickering Research Fellowship and to SERC for financial support.

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