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Structure of the polymer–salt co-ordination complex $[(CH_2CH_2O)_n]$: KCF_3SO_3, obtained from powder diffraction data

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The crystal structure of the polymer–salt complex $[(CH_2CH_2O)_n]:KCF_3SO_3$ has been obtained from powder diffraction data collected on a laboratory X-ray diffractometer. Profile refinement was employed in the structure elucidation, based on a model of the previously known structure of $[(CH_2CH_2O)_n]:NaCF_3SO_3$.

Compounds involving metal salts complexed by poly(ethylene oxide) $[(CH_2CH_2O)_n]$ (usually abbreviated to PEO) can exhibit high ionic conductivity within the polymer matrix and hence show great promise for use as solid electrolytes which have the advantage over liquid-based systems of permitting the development of all solid-state electrochemical devices.[1,2] Such solid polymer electrolytes may be regarded as a class of solid-state co-ordination compounds in which the ligands (in this case PEO) are large, polymeric and link the metal centers by ether oxygen co-ordination.[3]

Despite intensive study, particularly of the ionic conductivity, and the synthesis of hundreds of polymer–salt complexes, the structural chemistry of these compounds remains largely unexplored.[3] This is particularly true for systems other than those based on lithium salts, which have received attention because of their technological use as electrolytes in lithium batteries. Single-crystal X-ray diffraction is often the method of choice for structure elucidation, however, the quality of such data obtained from polymer electrolytes is, with few exceptions, very poor and inadequate for the task of structure determination. The most successful method to date has proved to be powder X-ray diffraction which has been employed to elucidate the structures of several polymer electrolytes.[4–8] Polymer–salt complexes crystallise with well defined stoichiometries, the most common being the 3 : 1 complex (three ether oxygens per cation). However, cations larger than Na^+ do not form complexes with this composition. Potassium salts generally form complexes with a 4 : 1 composition.[3,6] The crystal structure of only one polymer–salt complex containing potassium has been solved to date, namely $PEO_4:KSCN$.[6]

In this paper we report the structure elucidation of the salt-rich complex with a 1 : 1 composition, $PEO:KCF_3SO_3$. This is the first K^+ polymer–salt complex based on a triflate salt to be structurally characterised, it is only the second K^+ complex to be investigated and only the third 1 : 1 polymer–salt complex of any type to be characterised structurally.

Table 1 Refined structural data for $PEO:KCF_3SO_3$

Atom	*x*	*y*	*z*	*U*
K1	0.527(1)	0.382(1)	0.252(3)	0.066(4)
Triflate				
S1	0.6930(9)	0.0760(8)	0.252(3)	0.20(1)
C1	0.879(1)	0.106(1)	0.277(3)	0.04(2)
F1	0.939(2)	0.016(1)	0.295(5)	0.142(8)
F2	0.910(2)	0.155(2)	0.083(3)	0.142(8)
F3	0.885(2)	0.162(2)	0.468(3)	0.142(8)
O1	0.663(2)	0.006(3)	0.431(5)	0.16(1)
O2	0.622(2)	0.169(1)	0.285(8)	0.16(1)
O3	0.675(2)	0.036(3)	0.029(4)	0.16(1)
Chain				
O4	0.351(2)	0.229(3)	0.098(5)	0.06(2)
C2	0.298(2)	0.1686(5)	0.277(9)	0.04(2)
C3	0.242(2)	0.237(3)	0.464(5)	0.04(2)
H1	0.227(3)	0.130(2)	0.22(1)	0.088 *
H2	0.366(3)	0.128(2)	0.33(1)	0.088 *
H3	0.182(3)	0.203(6)	0.559(7)	0.088 *
H4	0.202(4)	0.294(3)	0.398(7)	0.088 *

* Fixed during refinement.

Experimental

The complex was prepared by grinding together appropriate amounts of PEO (dried under vacuum at 55 °C for 72 h) and potassium triflate powder (dried under vacuum at 120 °C for 72 h) using the cryogrinding technique.[9,10] The mixture was then sealed under argon in a 0.7 mm diameter Lindemann (glass) tube before melting at 240 °C for 4 h at which temperature the salt dissolves in the polymer, followed by annealing at 70 °C for 7 d to promote crystallisation. The powder diffraction pattern, Fig. 1, was collected on a STOE STADI/P powder diffractometer in transmission mode with Cu-Kα_1 radiation. The peaks in the diffraction pattern were then indexed using the TREOR program[11] which yielded a monoclinic unit cell with $a = 9.981(1)$, $b = 13.436(2)$, $c = 5.933(1)$ Å and $\beta = 89.28(1)°$. The space group was unambiguously determined to be $P2_1/c$ through the use of systematic absences. These data are consistent with the previously solved $PEO:NaCF_3SO_3$,[12] which has an identical space group and similar but slightly smaller unit cell, $a = 9.8491(4)$, $b = 12.7862(5)$, $c = 5.7750(3)$ Å and $\beta = 90.638(5)°$. This may be expected given the greater ionic radius of potassium, 1.38 Å, when compared with sodium, 1.02 Å.[13] Given the same space group, similar unit cell dimensions and similar powder diffraction pattern, structure elucidation was undertaken using the Rietveld method[14] applied to a starting model based upon that of the sodium analogue and using the same soft constraints of bond angles and bond lengths used previously in the refinement stage of the structure elucidation of $PEO_3:LiCF_3SO_3$.[4] This produced a final refinement structure, Fig. 2, which yielded a good fit to the powder diffraction pattern (see Fig. 1) having $\chi^2 = 1.94$. The coordinates of atoms and selected interatomic distances and angles are listed in Tables 1 and 2, respectively.

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See http://www.rsc.org/suppdata/dt/1998/1073/ for crystallographic files in .cif format.

Results and Discussion

The structure exhibits a number of features in common with the only other 1 : 1 complexes solved so far, $PEO:NaSCN$[15] and $PEO:NaCF_3SO_3$,[12] the most notable being that the PEO chain adopts a stretched 'zig-zag' conformation with all C–C bonds *gauche* (g) or anti-*gauche* ($\bar{g}$) and the C–O bonds either the

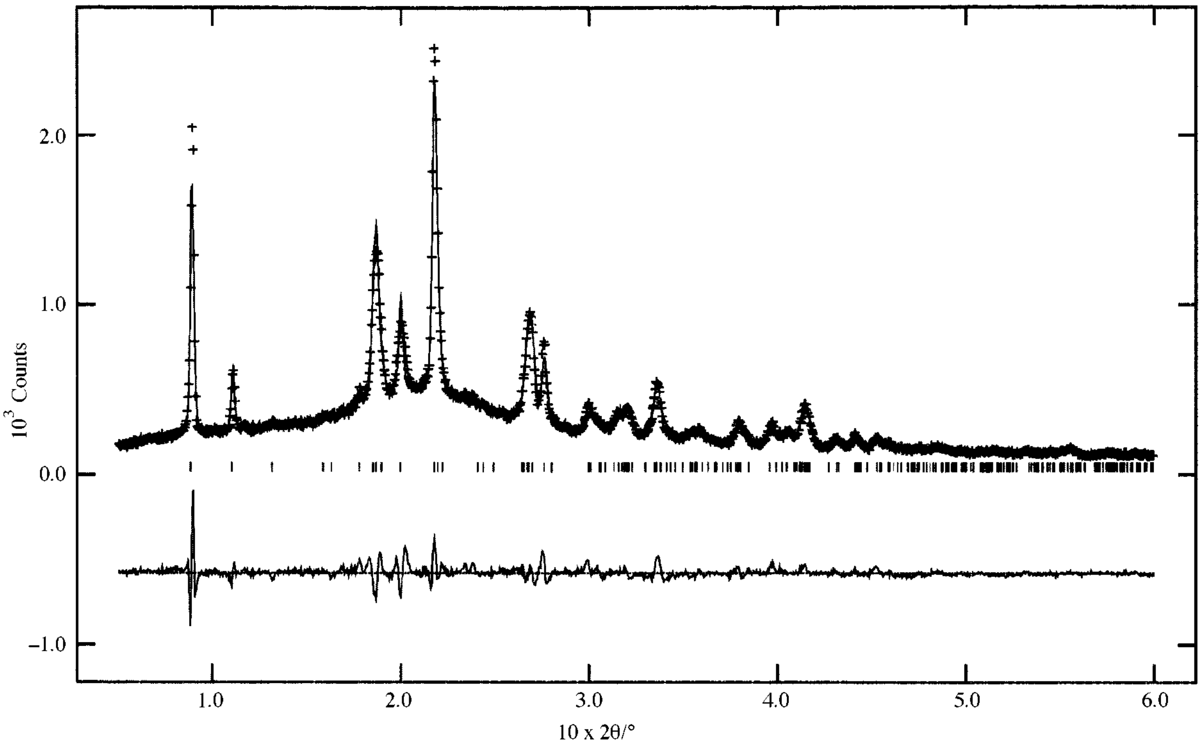

Fig. 1 Diffraction patterns of PEO : KCF_3SO_3, + observed, — calculated. Solid lines oscillating around $y = 0$ represent the difference profile. Vertical solid lines indicate positions of reflections

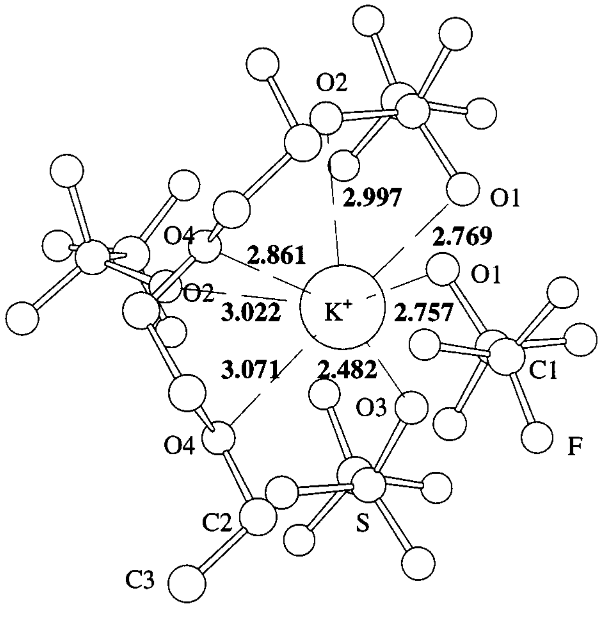

Fig. 2 Co-ordination around the potassium ion in the final structural model of PEO : KCF_3SO_3. Hydrogen atoms are not shown. Numbers indicate distances in Å between the potassium ion and its nearest neighbours

Table 2 Selected bond distances (Å), angles (°) and torsion angles (°) in PEO : KCF_3SO_3*

S1–C1	1.909(8)	Triflate oxygens	
S1–O1	1.444(9)	K–O1	2.76(3)
S1–O2	1.450(9)	K–O1	2.77(4)
S1–O3	1.442(9)	K–O2	3.00(5)
C1–F1	1.361(8)	K–O2	3.012(2)
C1–F2	1.353(8)	K–O3	2.49(4)
C1–F3	1.357(8)		
C2–H1	0.95(1)	Chain oxygens	
C2–H2	0.94(1)	K–O4	2.86(3)
C3–H3	0.94(1)	K–O4	3.07(3)
C3–H4	0.95(1)	O4–C2	1.429(7)
C2–C3	1.538(7)	O4–C3	1.430(5)
C1–S1–O1	106.1(7)	O4–C2–C3	109.0(6)
C1–S1–O2	106.1(7)	O4–C3′–C2′	109.0(6)
C1–S1–O3	106.5(7)	C3′–O4–C2	108.6(6)
O1–S1–O2	111.1(8)	O4–C2–H1	107.4(13)
O1–S1–O3	114.0(8)	O4–C2–H2	108.6(13)
O2–S1–O3	112.4(9)	O4–C3′–H3′	107.5(13)
S1–C1–F1	104.1(7)	O4–C3′–H4′	111.3(13)
S1–C1–F2	104.4(7)	C2–C1–H1	109.7(13)
S1–C1–F3	103.9(7)	C2–C1–H2	111.1(13)
F1–C1–F2	113.3(9)	C1–C2–H3	111.3(13)
F1–C1–F3	113.5(9)	C1–C2–H4	109.5(13)
F2–C1–F3	115.9(9)	H1–C2–H2	111.0(15)
		H3–C3–H4	111.4(15)
O4–C2–C3–O4′	−80.24	$\bar{g}$	
C2–C3–O4′–C2′	−177.72	*t*	
C3–O4′–C2′–C3′	79.44	*g*	
O4′–C2′–C3′–O4″	80.24	*g*	
C2′–C3′–O4″–C2″	177.72	*t*	
C3′–O4″–C2″–C3″	−79.44	$\bar{g}$	

* Weighted *R* profile = 0.079, *R* profile = 0.060. Number of structural parameters varied in least squares 60. Number of variables in refinement 66. Number of reflections 250. No. of soft constraints 39.

trans, *gauche* or anti-*gauche*, *i.e.* *tggt*$\bar{g}\bar{g}$. This contrasts with the helical PEO chain found in more dilute 3 : 1 and 4 : 1 PEO : salt systems.[4–6,16] In these more dilute complexes, the cations are located within each turn of the PEO helix and co-ordination by ether oxygens from only one chain. Two anions co-ordinate each cation and these each co-ordinate one further neighbouring cation along the same chain. Therefore each PEO chain is associated with a dedicated set of cations and anions, forming a discrete, infinitely long, one-dimensional co-ordination complex. There is no appreciable interaction between neighbouring chains and as a result the melting temperature of these more dilute complexes is low. The structures of the 1 : 1 complexes are quite different. Each K^+ ion is co-ordinated by two ether oxygens and five oxygens from the SO_3 moieties of four $CF_3SO_3^-$ ions. Three of the triflate anions each donate one oxygen to the co-ordination sphere of the K^+ ion with the remaining triflate donating two oxygens. The total co-ordination number of seven contrasts with PEO : $NaCF_3SO_3$ in which the total co-ordination number is six. The difference arises from a rotation of one triflate ion such that two oxygens from one SO_3 moiety are brought into the co-ordination sphere of the K^+ ion instead of only one in the case of PEO : $NaCF_3SO_3$.[12] The co-ordination number of seven is identical to that found in PEO_4 : KSCN although the differences in the proportion of salt in the 1 : 1 and 4 : 1 complexes result in an inversion in the number of anions and ether oxygens in the primary co-ordination sphere. Each ether oxygen is simultaneously co-ordinated to 2 K^+ ions associated with the same PEO chain. Each triflate co-ordinates four cations, three of which are associated with the same PEO chain and the fourth is associated with a different chain thus acting as an ionic bridge between neighbouring chains. Hence the 1 : 1 complex, in contrast to the 3 : 1 or 4 : 1 complexes, exhibits strong ionic cross-linking of chains and as a result the melting point of the PEO : KCF_3SO_3 complex is high at 257 °C[17] compared to 95 °C for PEO_4 : KSCN. It should be noted that it has not proved possible to prepare a crystalline complex with the composition PEO_4 : KCF_3SO_3. The 1 : 1 complexes are truly three-dimensional solid-state co-ordination compounds as opposed to the one-dimensional structures of the more dilute systems. The elongated unit cell in the *b* direction in the case of PEO : KCF_3SO_3 when compared with the sodium analogue leads to a slightly greater chain separation, 6.64 Å between the point of closest approach against 6.46 Å in the case of PEO : $NaCF_3SO_3$.

Conclusion

Our understanding of the structural details of polymer–salt complexes is still in its infancy compared to many other areas of co-ordination chemistry. By solving the structures of compounds such as PEO : KCF_3SO_3 and understanding how their structure, particularly the local co-ordination, compares with other related systems, we shall develop an understanding of the general principles governing why certain co-ordinating complexes form but not others as well as why the systems adopt the structures that they do.

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