By contrast for the sample with a larger composition in NG there is a tendency for the surface to become comparatively enriched in this component and this is accompanied by significant surface segregation of the stabilizer. This surface segregation may be directly confirmed by analyzing the low binding energy region of the N_{1s} levels. The main component of the N_{1s} spectrum originating from the nitrate ester groups centred at $\sim$408.3 eV unfortunately provides obscuring $K\alpha_{3,4}$ satellites in the region $\sim$400 eV appropriate to urea type nitrogen. In the case of the samples for which the DEDPU is computed to be at the 1–2% level the satellite intensity from the main component does not allow a statistically significant subtraction to be made and it is clear that the level of DEDPU in such materials is extremely low. In the 60/40 NG/NC material however the intensity of the peak at low binding energy is substantially larger than would be expected for a $K\alpha_{3,4}$ satellite and subtraction of the expected intensity, (14% of the main nitrate ester peak)[6] provides a value of 10 mol % of DEDPU in the surface regions in close agreement with the analysis based on the integrated intensities as set out above.

The e.s.c.a. data clearly adds a new dimension to current knowledge of the surface chemistry of double based propellants and the information will undoubtedly be of considerable importance in understanding many of the properties which depend on surface composition.

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A double helical model for some alkali metal ion-poly(ethylene oxide) complexes

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Introduction

The crystalline complexes of poly(ethylene oxide) (PEO) with potassium, sodium and lithium ions so far reported all have stoichiometries of 1 mol of cation to four mols of ethylene oxide (EO) unit. They are the open chain analogues of the 'crown-ether' complexes and such complexes are characterized by interactions between the cation and lone pairs of electrons from adjacent oxygen atoms brought about by a *gauche* rotation of the intervening C–C bond. Although single strand helical arrangements have been proposed[1,2], recent investigations[3,4] of the morphology and conductivity of some sodium ion and lithium ion complexes have led us to conclude that the physical properties are best described by a double strand helical arrangement of the PEO chains. In this communication we present some crystallographic data on KSCN and NaSCN complexes to support this proposal.

Experimental

X-ray fibre photographs of oriented fibres drawn from concentrated methanolic solutions were taken on a Pye-Unicam oscillation camera with the fibre stationary and using CuKα radiation[5]. Exposure times of 24 h were used but only relatively few low angle reflections were observed. Using a trial and error procedure to index the reflections the real space cell dimensions were determined to be:

For KSCN-PEO $a = 11.37$ Å $b = 8.18$ Å $c = 8.10$ Å

$\alpha = 80.3°$ $\beta = 65.7°$ $\gamma = 88.6°$

cell volume = 676 $Å^3$

For NaSCN-PEO $a = 10.25$ Å $b = 8.43$ Å $c = 7.23$ Å

$\alpha = 91.2°$ $\beta = 61.2°$ $\gamma = 103.7°$

cell volume = 529 Å.

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The densities of the complexes were determined by flotation in hydrocarbon–chloroform mixtures and using the specific gravity bottle method. The densities were found to be 1.23 g cm^{-3} for KSCN-PEO and 1.35 g cm^{-3} for NaSCN-PEO.

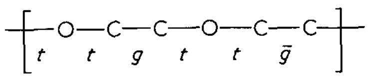
These data prescribe 1.84 and 1.67 formula units per unit cell for KSCN–PEO and NaSCN–PEO respectively. Since these quantities must be integers, we conclude that in both cases there are two formula units per unit cell.

Discussion

The unit cell composition (8 EO repeating units with 2 cations and anions) requires that either 4 chains each with 2 EO repeating units or 2 chains each with 4 EO repeating units extend across the fibre repeat distances (7.23 Å for NaSCN–PEO and 8.1 Å for KSCN–PEO). The former possibility is rejected since the fully extended (all *trans*) conformation of PEO, extends to only 7.12 Å over 2 EO units (the fibre repeat distance of the unstable, stretched form of PEO[6]) and includes none of the *gauche* conformations about C–C bonds as always observed in oligomeric EO complexes.

A two-chain unit cell is therefore the only reasonable possibility for the alkali metal ion-PEO complexes. This arrangement in which 4 EO units extend over 7.23 Å in the fibre direction readily accounts for the observed[3] extended chain lamellar thickness of 400–450 Å for NaSCN and NaI complexes with PEO 10000. Three possibilities for the mutual disposition of the 2 chains must be considered: (i) They may enclose the cations in 2 separate, side-by-side single helical units similar to the model proposed by other workers[1,2]; (ii) the cations may be equally coordinated by two chains which complex the cations on either side (compared with the $HgCl_2$ complexes); (iii) the two chains are mutually intertwined in a double helix which encloses both cations along its axis.

The proposed double helical structure is shown in *Figure 1* and the component strands are readily constructed by minor modifications of the pure PEO (7/2) helix. The conformational sequence over a fibre repeat may be represented as



$$\left[\begin{array}{l}-\mathrm{O}-\mathrm{C}-\mathrm{C}-\mathrm{O}-\mathrm{C}-\mathrm{C}-\\ \quad t\qquad t\qquad g\qquad t\qquad t\qquad \bar{g}\end{array}\right]$$

where t, g and $\bar{g}$ indicate *trans*,, *gauche* and *gauche* minus conformations respectively. Two cations are accommodated over the observed fibre repeat distances and these distances and the effective cage size may be readily adjusted, within limits, by adjustment of the bond rotation angles. Using cation–oxygen distances in crown-ether complexes as criteria for cage size, calculations show that lithium and sodium ions may be readily accommodated within the cavities but that potassium ions are barely accommodated and require that two of the C–C bonds adopt rotation angles within the *trans* domain.

Space filling models show that a single or double helix sufficiently contorted to coordinate a $Li^+/Na^+/K^+$ ion and to repeat after 7–8 Å would have a diameter of approximately 8 Å. In projection down the c-axis the dimensions of the unit cells are 8.9 × 8.4 Å^2 with an interaxial angle of 104.6° for the NaSCN complex and 10.4 × 8.1 Å^2 with an interaxial angle of 92.8° for the KSCN complex. Within such dimensions, two separate helices per unit cell (as in (i) above) would require considerable intercalation of the chains particularly in the case of the NaSCN complex. Further, the a axes for both complexes are at angles far from 90° with respect to the c-axis (61.2° for NaSCN and 65.7° for KSCN). Successive chains along the a-axis are therefore displaced by $a \cos \beta$ measured along the chain repeat (c-axis), i.e. 4.9 Å for the NaSCN complex and 4.7 Å for the KSCN complex which is approximately $\frac{1}{2}$ the chain repeat. This makes the intercalation of a second chain in the middle of the unit cell particularly difficult since the helices across the diagonal are essentially out of phase. If such intercalation did occur it would also involve the outer hydrogen atoms of the second chain coming very close to the potassium ions in the first helix.

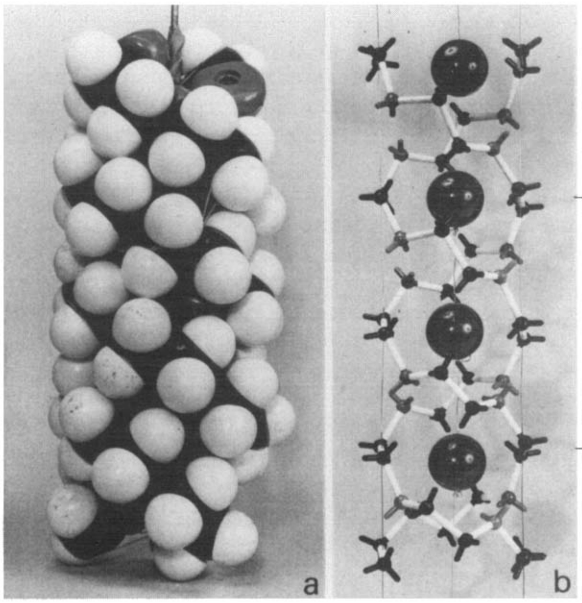


Figure 1 **(a) Space filling and (b) ball-and-stick models of proposed double helical structure for alkali metal PEO complexes**

A chain in the centre of the unit cell might be expected to cause systematically absent or, at least, systematically weak reflections of the type $h+k=$ odd on the zero layer. An examination of the intensity data for both complexes shows this is not the case.

However, a double helix would give effectively a cylindrical structure with the anions occupying spaces between cylinders. Thus the NaSCN complex gives, in projection ⊥ (perpendicular) to c, dimensions which are close to those which might be expected for close packing of cylinders of diameter approximately 8 Å. Although the KCNS complex has chains in a much more nearly square arrangement, the difference may be accounted for simply by varying the anion arrangement. This possibility may not be surprising bearing in mind the more open double helix required for the K^+ ion (c axis 10% larger) which would allow greater anion-cation interaction. A repeat distance of ~8 Å perpendicular to the chain is common to both complexes and this might be expected to correspond to the helical diameter. With the anions disposed outside the helical 'tubes' the effective encapsulation of the cations should reduce specific ion interactions and with cations of optimum size the unit should be mechanically inflexible even with a proportion of the cages vacated by migrating cations.

An initial examination of the Patterson function calculated using the zero layer intensity data for KSCN–PEO has suggested a structural model with two potassium atoms superimposed along the z axis at 0,0 with the two thiocyanates at $(\frac{1}{2},0)$ and $(0,\frac{1}{2})$ in the x,y planes. This model gives an R-factor of 34% for the observed reflections, and adds further evidence for the proposed model. Refinement of the model is continuing although hampered by the lack of reflections.

A structure conforming to case (ii) above may be constructed using molecular models. However, we consider the following three observations are most easily accounted for by a molecular unit consisting of a double helix of PEO chains:

(i) The thermal stabilities of high molecular weight PEO–$LiBF_4$ complexes apparently depend on the degree of entanglement encountered by the polyether chains at the stage of their association with the cations in competition with the solvent, prior to deposition of the complex adduct on the crystal lattice[4]. Thus deposition of $LiBF_4$–PEO 5×10^6 from chloroform–acetone gives a high melting material (433K) whereas deposition from cation-solvating methanol gives almost complete melting at a lower endotherm (~340K) which may be observed in various proportions with the higher melting one in DTA traces of all sodium and lithium ion PEO complexes. The latter material gives the same X-ray reflections as the high melting material but with rather less long range order. Pure uncomplexed PEO is not detected by X-ray analysis. Recrystallization from melts effects no change in the thermal behaviour of the respective samples. However, no such solvent effect is observed with PEO chains below the critical entanglement limit for undiluted systems. PEO 4000–$LiBF_4$ is deposited from methanol to give a high melting complex (413K).

Any single strand arrangement would render the chains no more conformationally constrained by entanglements than any other semicrystalline linear synthetic polymer system which, to the authors knowledge, display no such specific solvent dependence on bulk state thermal stabilities.

We therefore propose that the higher endotherm is the melting of discrete molecular units composed of long uninterrupted double helical sequences in the same helical sense (phase I), whereas the discrete lower endotherm, particularly prominent in lithium ion complexes deposited from methanol denotes the disintegration of imperfect double helical sequences which may include frequent reversals of helical sense (phase II).

(ii) The molecular units of NaI and NaSCN complexes are inflexible over the temperature range between ~340K and the melting point despite considerable ion migration (as revealed by high ionic conductivities) and the high flexibility of single strand PEO chains[3]. The breakdown of intermolecular interactions over this range gives rise to behaviour characteristic of a mesophase. Furthermore, morphological studies and thermal analysis reveal that NaSCN–PEO molecular units, at least, remain intact and extended in the melt.

(iii) The melting temperatures of NaSCN, NaI and $LiCF_3SO_3$ complexes (443–467K with PEO 4000 or greater) are independent of the nature of the complexing ions depending only on PEO molecular weight and morphology[3]. The slightly reduced high temperature endotherm observed so far in $LiBF_4$–PEO (~433K) may have a morphological explanation or may relate to the lower melting temperature of the pure salt (115°C). However, we assume that this complex is isomorphous with the others.

Finally, we note that the only other proposal for a double helix in synthetic polymers is that of Tadokoro and coworkers[7] for isotactic poly(methylmethacrylate). This proposal has recently been contested by Lovell and Windle[8] on the grounds that X-ray diffraction does not reveal the presence of double stranded units in the glassy state. We point out that our proposal for disintegration of imperfect double helical sequences at the lower endotherm (phase II) also implies an amorphous melt of single stranded chains.

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