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Crown ether complexes of $UO_2(NCS)_2$ and $Th(NCS)_4$: clues to solution behavior or just interesting supramolecular structures?

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Abstract

$UO_2(NCS)_2$ and $Th(NCS)_4$ were prepared in water and then reacted with 18-crown-6 in 3:1 CH_3CN:CH_3OH. The crystal structures of three salts were investigated: the mixed hydroxide/thiocyanate salt without crown ether, $[UO_2(NCS)(OH_2)_2(\mu\text{-}OH)]_2$, the second sphere complex $[UO_2(NCS)_2(OH_2)_3]\cdot1.5(\text{18-crown-6})\cdot CH_3CN$, and the outer sphere crown ether/inner sphere glycol complex, $[Th(NCS)_4(OH_2)(HOCH_2CH_2OH)_2]\cdot\text{18-crown-6}$. The outer sphere complexes provide a glimpse into possible solution states which may enhance transfer of actinide salts from a more polar to a less polar medium without direct metal/crown ether complexation. In the solid state, the supramolecular structures derived from intramolecular hydrogen bonding and S···S interactions provide additional information that may be useful in the rational design of actinide solid state complexes via crystal engineering. © 1998 Elsevier Science S.A.

Keywords: Uranyl; Thorium; Thiocyanate; 18-Crown-6; Crystal structures

1. Introduction

A fundamental understanding of the structural chemistry of the actinide elements has important implications in several areas of modern actinide research including improved intra and intergroup separations of the f-elements. Our previous work with crown ethers and polyethylene glycols (PEGs) e.g., [1,2] led to our interest in PEG-based aqueous biphasic systems which we investigate for their potential to allow liquid/liquid extraction without volatile organic compounds [3,4]. Aqueous biphasic systems (ABS) consist of two immiscible aqueous phases formed when certain water-soluble polymers (e.g., PEG) are combined with one another or with certain inorganic salts in specific concentrations [5]. Since crown ethers and small chain PEGs can act as synergists in extraction of actinide ions, and separations of metal thiocyanates in PEG–ABS are known, (these extractants can produce extractable metal complex anions [6]) we have begun to investigate complexes of $UO_2(NCS)_2$ and $Th(NCS)_4$ with hard donor crown ether ligands. One of the starting salts and two examples of second sphere complexes have been isolated and crystallographically characterized.

2. Experimental

12-Crown-4, 15-crown-5, 18-crown-6, and KSCN were purchased from Aldrich, $UO_2(ClO_4)_2$ was obtained from Alfa Products, and $Th(SO_4)_2$ from Strem Chemicals, and all were used without further purification. The uranyl thiocyanate compound was prepared by the following reaction:

$$UO_2(ClO_4)_2(aq) + 2KSCN(aq) \rightarrow 2KClO_4(s) + UO_2(NCS)_2(aq)$$

$KClO_4$ was separated from the solution, and the solution was then cooled at ice-water temperature to decrease the solubility of $KClO_4$ even further. The solution was then filtered and evaporated at 50°C with stirring until the thiocyanate salt crystallized.

The thorium thiocyanate salt was prepared by the reaction of thorium sulfate and $Ba(SCN)_2$:

$$Th(SO_4)_2(aq) + 2Ba(SCN)_2(aq) \rightarrow 2BaSO_4(s) + Th(NCS)_4(aq)$$

The $Th(NCS)_4$ solution was then evaporated at 50°C with stirring until the salt crystallized.

The complexes were prepared by the following procedure. Each salt (1 mmol) was mixed with 1 mmol of

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crown ether then dissolved in 4–5 ml of 3:1 $CH_3CN:CH_3OH$. The solutions were then slowly evaporated until crystals appeared. The crystals were placed in a P_4O_{10} desiccator overnight and then used for the crystallographic study.

The salt, $[UO_2(NCS)(OH_2)_2(\mu\text{-}OH)]_2$, and the crown complex $[UO_2(NCS)_2(OH_2)_3]\cdot1.5(18\text{-crown-}6)\cdot CH_3CN$, both crystallized from the same reaction mixture. The thorium complex, $[Th(NCS)_4(OH_2)(HOCH_2CH_2OH)_2]\cdot$ 18-crown-6, crystallized with two unexpected glycols in the formula unit. Polyethylene glycols are starting materials in the synthesis of 18-crown-6 and it is presumed that the ligands crystallized were in fact impurities in the 18-crown-6 starting material.

Single crystal XRD data for all three compounds were obtained using a Siemens CCD area detector-equipped platform diffractometer. A brief summary of data collection parameters is given in Table 1 and crystallographic coordinates, hydrogen atom positions, and bond distances and angles have been deposited with the Cambridge Crystallographic Database.

In $[UO_2(NCS)_2(OH_2)_3]\cdot1.5(18\text{-crown-}6)\cdot CH_3CN$, disorder was observed for the crown ether which has hydrogen-bonding contacts on only one side of the molecule. This less tightly held ether exhibits 50/50 conformational disorder for O(6) and the ethylene linkages C(7)-C(8), C(9)-C(10). Elongated ellipsoids were also observed for O(4) and O(5) which are bonded to these ethylene groups, however, alternate positions could not be resolved due to their proximity to one another.

$[Th(NCS)_4(OH_2)(HOCH_2CH_2OH)_2]\cdot$18-crown-6 suffers from disorder and high-thermal motion, most likely the result of the weak nature of the hydrogen bonding holding the large crown ether molecules in the lattice. In the Th moiety, S(1) has elongated thermal ellipsoids and C(3) is disordered 50/50 with C(3′). (The latter produces a +gauche/−gauche disorder in the O-C-C-O torsion angle.) Reducing the symmetry to *Cc* did not help. The S positions corresponding to S(2) still had high thermal motion, the C(3) positions were still disordered, and there was high correlation between atoms related by the two-fold axis in *C*2/*c*.

The hydrogen-bonded crown ether molecules also suffered from these effects. One crown ether resides around a center of inversion and has essentially D_{3d} symmetry. The observed thermal motion is high, but disorder was not resolved. A second unique crown ether also resides around a center of inversion, however, a disorder model could be resolved for this ether. One oxygen atom [O(7)] and one carbon atom [C(11)] are common to both conformations

Table 1
Summary of crystal data and structure refinement

Compound	$[UO_2(NCS)(OH_2)_2(\mu\text{-}OH)]_2$	$[UO_2(NCS)_2(OH_2)_3]\cdot$ 1.5(18-crown-6) $\cdot CH_3CN$	$[Th(NCS)_4(OH_2)(HOCH_2CH_2OH)_2]\cdot$ 18-crown-6
Color/shape	Yellow/parallelepiped	Yellow/plate	Colorless/fragment
Empirical formula	$C_2H_{10}N_2O_{10}S_2U_2$	$C_{22}H_{45}N_3O_{14}S_2U$	$C_{32}H_{62}N_4O_{17}S_4Th$
Formula weight	762.30	877.76	1135.14
Temperature, K	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$C2/c$
Unit cell dimensions			
a, Å	6.2496(2)	41.5557(5)	24.4504(3)
b, Å	16.1411(2)	9.1181(2)	12.7813(1)
c, Å	15.2238(4)	18.3312(4)	18.7919(1)
α, deg	90	90	90
β, deg	99.802(1)	101.123(1)	124.488(1)
γ, deg	90	90	90
Volume, $Å^3$	1513.29(7)	6815.4(2)	4840.47(8)
Z	4	8	4
ρ_{calc}, g cm^{-3}	3.346	1.711	1.558
μ, mm^{-1}	21.690	4.949	3.319
Radiation/λ, Å	Mo Kα/0.71073	Mo Kα/0.71073	Mo Kα/0.71073
Measured/Independ./ Observed reflections	9537/3510/2603 ($R_{int}=0.0512$)	20657/7798/5495 ($R_{int}=0.0806$)	15176/5612/4639 ($R_{int}=0.0579$)
Relative transmission factors	0.94/0.55	0.97/0.65	0.93/0.68
Data/parameters	3506/164	7364/416	5605/336
GOF	1.010	0.990	1.063
Weight parameters	0.0287, 0.0000	0.1189, 0.0000	0.0863, 17.6608
Final *R* indices [$I>2\sigma(I)$] Data	$R1=0.0368$ $wR2=0.0656$	$R1=0.0711$ $wR2=0.1767$	$R1=0.0608$ $wR2=0.1485$
R indices (all data)	0.0652, 0.0761	0.1001, 0.1952	0.0766, 0.1618
Extinction coefficient	0.00026(6)	0.00022(6)	0.0

and are included at full occupancy. Each of the remaining unique atoms [O(8), O(9), C(12)–C(16)] were resolved into two positions at 50% occupancy each. The disorder was still evident when investigating the *Cc* space group.

For all structures, geometrically constrained hydrogen atoms were placed in calculated positions and allowed to ride on the bonded atoms with $B=1.2{*}U\mathrm{eqv}(\mathrm{C})$. It was possible to locate the aquo and alcoholic hydrogen atoms for the Th complex from a difference Fourier map and these were included and allowed to ride on the bonded O atoms with $B=1.2{*}U\mathrm{eqv}(\mathrm{O})$. Aquo and hydroxide hydrogen atoms for the two uranyl structures could not be located and were not included in the final refinements. Refinement of nonhydrogen atoms was carried out with anisotropic temperature factors for all three complexes.

3. Results

The uranyl thiocyanate salt, $[\mathrm{UO_2(NCS)(OH_2)_2(\mu\text{-}OH)}]_2$, is a hydroxide bridged dimer (Fig. 1). Each unique uranium atom is 7-coordinate, pentagonal bipyramidal with the uranyl oxygen atoms [U-O = 1.767(5) Å] in axial positions and the remaining ligands in the equatorial plane. The thiocyanate anions are N-bound [U-N = 2.448(9) Å] and on opposite sides of the dimer. The U-OH bridging distances average 2.37(2) Å and all four U-$\mathrm{OH_2}$ distances average 2.44(2) Å. Interestingly, the water molecules coordinated trans to the U···U axis are further away [U-O(4), O(10) average 2.460(6) Å] than the remaining two water molecules [U-O(3), O(9) = 2.423(7) Å]. The pentagonal planes are twisted slightly ($\delta=6.5°$) resulting in a closer O(1)···O(7) contact (3.763(7) Å) than observed for O(2)···O(8) [4.163(7) Å].

All available hydrogen-bond donors contribute to a hydrogen-bonding network which joins the dimers. The hydrogen-bond acceptors include both unique sulphur atoms and all four unique uranyl oxygen atoms. In addition to the hydrogen bonding, an additional weak attractive intermolecular force is responsible for the observed crystal structure. A weak attractive S···S interaction between symmetry-related S(1) positions [S···S = 3.730(3) Å] connects the hydrogen-bonded networks. (The crystallographic evidence for attractive interactions of this type along with the range in contact separations, all less than van der Waals distances, and directionality of the contacts are discussed in Ref. [7]). Although the distance observed is close to the van der Waals contact separation, the directionality of the interaction [C(1)-S(1)···S(1′) = 114.0(3)°] argues for the presence of an interaction when compared with the existing crystallographic evidence.

The S···S interactions, which join the dimers into chains along *b*, are depicted in Fig. 1 along with a portion of the hydrogen bonding. Only the S(1) atoms participate in this interaction; the S(2) atoms are only involved in hydrogen bonding and this is reflected in the number of hydrogen-bonding interactions. S(1) has three hydrogen bonds plus the S···S interaction, while S(2) accepts four hydrogen bonds. S(2) deviates significantly more from the U(2) pentagonal plane (0.86 Å) than S(1) does from the U(1) pentagonal plane (0.23 Å) which may be a consequence of the different intermolecular interactions each

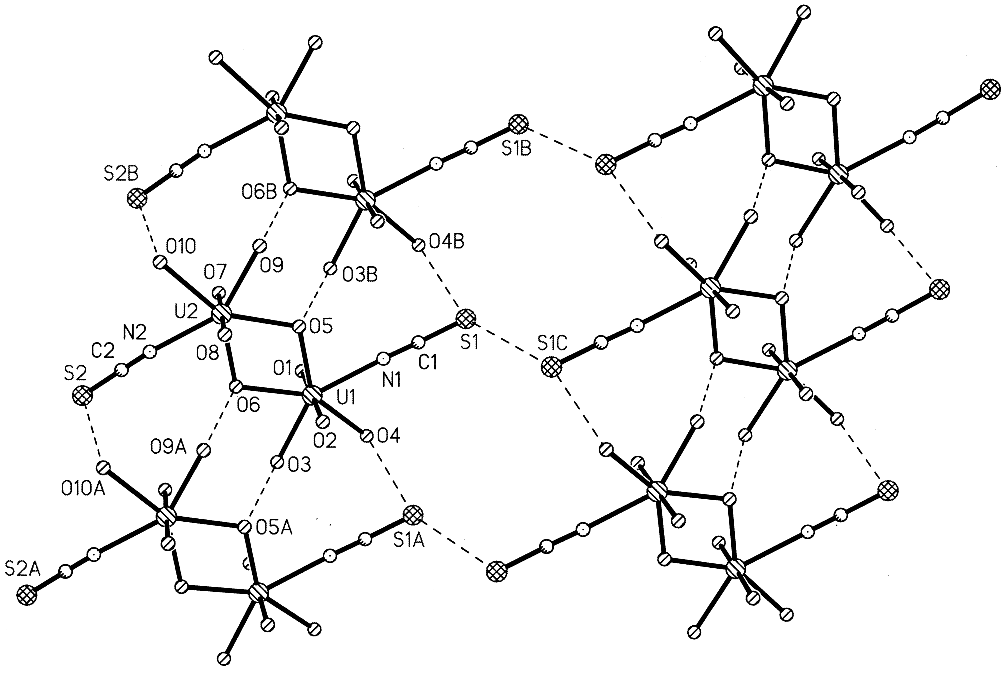

Fig. 1. The S(1)···S(1′) contacts of 3.730(3) Å [C(1)-S(1)···S(1′) = 114.0(3)°] associate the dimeric $[\mathrm{UO_2(NCS)(OH_2)_2(\mu\text{-}OH)}]_2$ units along *b*. Only a portion of the hydrogen-bonded network is depicted.

participates in. There is also a significant difference in the U-N-C angles, 177.2(8)° for N(1) and 161.3(9)° for N(2).

The unique uranium atom in the second sphere crown complex, $[UO_2(NCS)_2(OH_2)_3]\cdot1.5(18\text{-crown-6})\cdot CH_3CN$ is coordinated in a pentagonal bipyramidal geometry to two uranyl oxygen atoms [U-O = 1.764(3) Å], three water molecules [U-O = 2.46(3) Å], and through the nitrogen atoms to two thiocyanate anions [both U-N = 2.428(9) Å]. One anion is nearly linear [U-N(1)-C(19) = 173.8(8)°] and one is severely bent [U-N(2)-C(20) = 142.6(8)°].

The 18-crown-6 molecules are coordinated to the second coordination sphere via the coordinated water molecules. Interestingly, solvent acetonitrile interacts with one side of one of the two unique crown molecules terminating what would otherwise be a hydrogen-bonded polymer into a hydrogen-bonded dimer (Fig. 2). The dimers are stacked along *a* and separated by a solvent region. Interestingly there are no S···S contacts less than 4.890(3) Å.

One crown ether is bridging, resides around a center of inversion, and accepts three hydrogen bonds on each side, two from O(12) and one from O(13). All six ether oxygens thus accept hydrogen bonds and this ether adopts the commonly observed D_{3d} conformation. The second unique ether is terminal and accepts two hydrogen bonds from O(14) and one bifurcated hydrogen bond from O(13). The two oxygen atoms not involved in the O-H···O hydrogen bonds [O(1), O(5)], interact weakly via C-H acidic hydrogen bonds with an acetonitrile solvent molecule. This ether deviates strongly from the more symmetric D_{3d} conformation, to accommodate the different weak interactions.

The thorium complex, $[Th(NCS)_4(OH_2)(HOCH_2\text{-}CH_2OH)_2]\cdot18\text{-crown-6}$, combines aspects of both previous structures, second sphere hydrogen-bond coordination of 18-crown-6 and attractive S···S contacts. The unique thorium atom resides on a crystallographic two fold axis and is 9-coordinate, tricapped trigonal prismatic with the two alcoholic O(2) positions and the water molecule [O(3)] in capping positions [Th-O(2) = 2.499(5), Th-O(3) = 2.524(8) Å]. The remaining alcoholic atoms [Th-O(1) = 2.478(6) Å] and anions [Th-N = 2.48(1) Å, average] occupy the prismatic sites. This is only the second example of a crystallographically characterized Th/glycol structure, the other being coordination by pentaethylene glycol [8].

The hydrogen bonding between coordinated glycol and water molecules to the two unique crown ethers produces an interesting polymeric structure (Fig. 3). The O(4)-O(6) crown ether resides around a center of inversion and accepts only one hydrogen bond [from O(2)] on each side. As a result, this crown ether adopts the more elliptical conformation of uncomplexed 18-crown-6, rather than the symmetric D_{3d} conformation of complexed 18-crown-6. Hydrogen bonding to this crown molecule results in zigzag polymeric chains which propagate along *a*.

The second unique ether molecule hydrogen bonds in a terminal fashion through four hydrogen bonds. Both alcoholic O(1) positions and the water molecule donate hydrogen bonds to this ether. This produces a very distorted conformation necessary to bring four oxygen atoms to the same side for hydrogen-bond formation and in fact this crown molecule is severely disordered.

The polymeric hydrogen-bonded chains are joined in the *b* direction by attractive S(2)···S(2′) contacts of 3.501(3) Å [C(2)-S(2)···S(2′) = 146.3(4)°; Fig. 4]. The S(2) anion is coordinated in a linear fashion [Th-N(2)-C(2) = 177.3(7)°] while the second unique anion is slightly bent

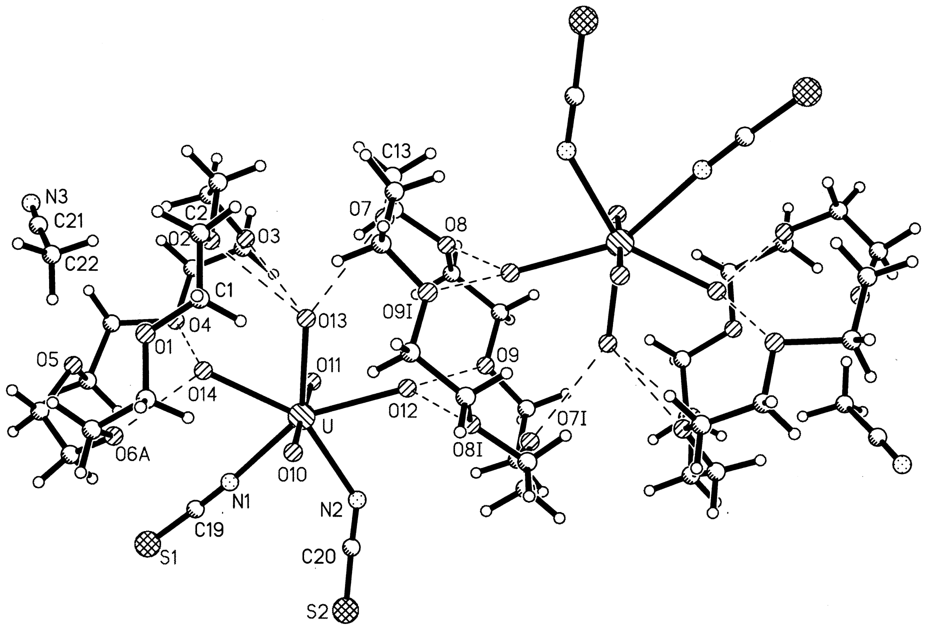

Fig. 2. The hydrogen-bonded dimer in $[UO_2(NCS)_2(OH_2)_3]\cdot1.5(18\text{-crown-6})\cdot CH_3CN$.

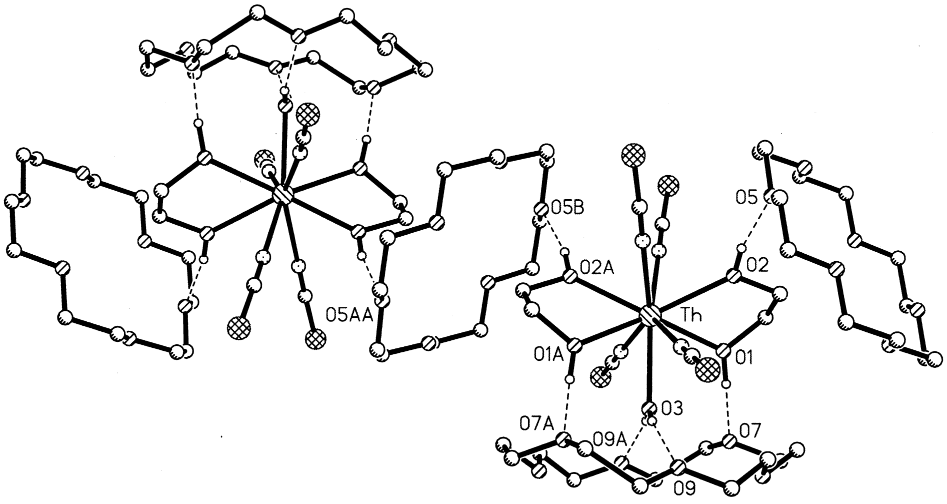

Fig. 3. A portion of the hydrogen-bonded polymer in $[Th(NCS)_4(OH_2)(HOCH_2CH_2OH)_2]\cdot$18-crown-6.

[Th-N(1)-C(1) = 169.5(9)°]. The hydrogen-bonded polymers pack along *a* and are linked in the *b* direction via the sulphur interactions.

4. Conclusions

Crown ethers are typically unable to directly coordinate thorium(IV) and the uranyl ion in the presence of water. This makes applying the concepts of molecular recognition to explain extraction or synergistic enhancement of actinide partitioning using crown ethers difficult to justify. Crystal structural results may provide clues to the solution behavior. Given the nature of the second sphere coordination of crown ethers to actinides through bound water hydrogen bonding, it may be possible to explain any partitioning enhancement in terms of production of a large extractable complex which shields the hydrophilic metal inner coordination sphere yet does not require complete dehydration. A satisfactory answer to this puzzle is still waiting for detailed solution studies to confirm the presence of similar hydrogen-bonded species in solution.

Short chain polyethylene glycols and thiocyanate anions can coordinate the metal ions and may also assist in extraction of actinides. The use of these species as extractants in aqueous biphasic systems are currently under active investigation in our laboratories.

Although the distances and angles associated with the

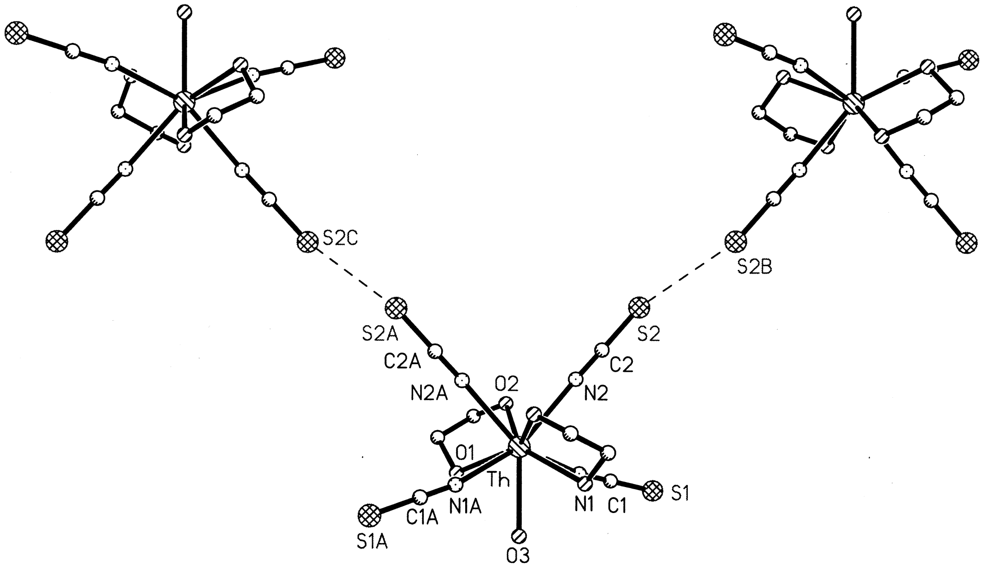

Fig. 4. The attractive S···S interactions in $[Th(NCS)_4(OH_2)(HOCH_2CH_2OH)_2]\cdot$18-crown-6 [S(2)···S(2′) = 3.501(3)Å C(2)-S(2)···S(2′) = 160.1(3)°] are directional and significantly less than van der Waals contact distance. These interactions link the hydrogen-bonded polymeric chains into corrugated sheets along *c*.

directly coordinated ligands are normal for structures of this type, the supramolecular structures obtained by combination of a variety of weak interactions (e.g., hydrogen bonding, S···S interactions, etc.) are interesting from the standpoint of understanding these interactions and using them to design and construct specific solid state architectures. This field (Crystal Engineering) may have important future implications in the immobilization of actinides by providing information that can be used to optimize specific solid-state structures.

Acknowledgements

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