

YYW, BT, JPD and MVM thank the SPSS, Belgium, for financial support.

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Oligoether Complexes of Alkaline-Earth Metal Ions. IV. Structures of 2,5,8,11,14,17,20-Heptaoxahenicosane ('Hexaglyme') Complexed with Calcium and Strontium Thiocyanates

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(Received 3 November 1986; accepted 24 February 1987)

Abstract. (1): 2,5,8,11,14,17,20-Heptaoxahenicosane–calcium thiocyanate (1/1.5) 2.5-hydrate, $C_{14}H_{30}O_7 \cdot 1.5Ca(SCN)_2 \cdot 2.5H_2O$, $M_r = 589.78$, monoclinic, $C2/c$, $a = 21.599$ (6), $b = 12.991$ (5), $c = 21.760$ (6) Å, $\beta = 106.52$ (2)°, $V = 5854$ (3) Å³, $Z = 8$, $D_x = 1.34$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 5.44$ cm⁻¹, $F(000) = 2496$, $T = 291$ K, $R = 0.045$ for 3207 observed reflections. (2): 2,5,8,11,14,17,20-Heptaoxahenicosane–strontium thiocyanate (1/1) dihydrate, $C_{14}H_{30}O_7 \cdot Sr(SCN)_2 \cdot 2H_2O$, $M_r = 550.20$, monoclinic, $P2_1/c$, $a = 19.409$ (13), $b = 16.282$ (14), $c = 16.936$ (7) Å, $\beta = 109.81$ (5)°, $V = 5035$ (6) Å³, $Z = 8$, $D_x = 1.45$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 24.47$ cm⁻¹, $F(000) = 2288$, $T = 291$ K, $R = 0.066$ for 2491 observed reflections. Considering the doubled asymmetric unit of (1), one of the three Ca cations is coordinated by all six thiocyanate anions, whereas the other two Ca cations are symmetry equivalent and each coordinated to six of the seven ether O atoms of one hexaglyme molecule. The conformational sequence is characterized by three genuine corners. For (2) two non-equivalent complexed units (*A* and *B*) are found in the asymmetric unit; all the seven O atoms of the hexaglyme are used in both cases and in addition two thiocyanates (*A*) or two water molecules (*B*) are

coordinated. Three O–CH₂–CH₂–O units adopt a different conformation in *A* and *B*.

Introduction. The complexation of a series of oligoethylene glycol dimethyl ethers (tri-, tetra-, penta-, hexa- and heptaglyme) with alkali and alkaline-earth metal thiocyanates has been studied by ¹³C NMR spectroscopy (Dale, Krane & Thomassen, 1987). We have undertaken to study the X-ray structures of these complexes in order to compare their conformation in the solid state with that observed in solution. In preceding papers we have reported the structures of tri-, tetra- and pentaglyme complexed with calcium, strontium and barium thiocyanates (Wei, Tinant, Declercq, Van Meerssche & Dale, 1987a,b,c). We now report the structures of the complexes of 2,5,8,11,14,17,20-heptaoxahenicosane ('hexaglyme') with calcium and strontium thiocyanates.

Experimental. Crystals obtained by slow evaporation from acetone–ethyl acetate (1/1). Crystal sizes: (1) 0.30 × 0.15 × 0.20 mm, (2) 0.10 × 0.11 × 0.29 mm. Lattice parameters refined using 15 reflections in the range $5 < 2\theta < 25^\circ$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω scan,

scan width (1) 1.5° , (2) 1.3° , scan rate $1.3\text{--}30^\circ \text{ min}^{-1}$, $(\sin\theta)/\lambda_{\text{max}} = 0.561 \text{ \AA}^{-1}$. For (1) 4336 independent reflections measured ($0 \leq h \leq 19$, $0 \leq k \leq 14$, $-22 \leq l \leq 22$), 3207 observed [$I \geq 2.5\sigma(I)$]. For (2) 7438 independent reflections measured ($0 \leq h \leq 21$, $0 \leq k \leq 15$, $-17 \leq l \leq 17$), 2491 observed [$I \geq 2.5\sigma(I)$]. Standard reflection 008 for (1), 304 for (2) checked every 50 reflections: no significant deviation. Absorption correction: none for (1), numerical corrections for crystal defined by its faces for (2) using *SHELX76* (Sheldrick, 1976); max./min. transmission = 0.815 and 0.664.

Both structures were solved by first locating the cation [and S atoms for (1)] from an $E \times F$ Patterson map and then applying direct methods on the unknown part of the structure using *SHELX84* (Sheldrick, 1984) and *DIRDIF81* (Beurskens *et al.*, 1981). Structures were refined by anisotropic least squares on F [by block cascade for (2)]. H atoms from a difference Fourier synthesis for (1), included in the refinement in idealized positions (C–H = 1.08 \AA , H–C–H = 109.5°) for (2). 397 (1) and 524 (2) LS parameters. Weighting scheme $w = 1/[\sigma^2(F) + gF^2]$, $g = 0.0008$ for (1) and 0.0007 for (2). (1) $R = 0.045$, $wR = 0.049$ for 3207 reflections. (2) $R = 0.066$, $wR = 0.049$ for 2491 reflections. $(\Delta/\sigma)_{\text{max}}$ in final refinement cycle: (1) 0.12 [x of atom Ca(1)]; (2) 0.50 [U_{22} of atom Sr(1)]. $S = (1) 1.45$; (2) 1.89 . Max. and min. heights in final Fourier synthesis (1) 0.47 , -0.14 ; (2) 0.64 , -0.47 e \AA^{-3} . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters for the two structures are given in Tables 1 and 2.* A comparison of bond lengths and coordination distances is presented in Table 3. Bond and torsion angles for the hexaglyme chains are listed in Table 4. Figs. 1 and 2 give top views of each complex and the atomic numbering schemes. Figs. 3 and 4 are side views showing the folding of the polyether chain around the cation for the Ca^{2+} and Sr^{2+} complexes (molecules *A* and *B*) (*PLUTO*; Motherwell & Clegg, 1978).

The coordination of each complex is unexpected and remarkable. Two different entities are present in the asymmetric unit of (1). Considering the doubled asymmetric unit ($\frac{1}{2}$ of the cell), one of the three Ca cations is coordinated by all six thiocyanate anions in an octahedral arrangement, whereas the other two Ca cations are equivalent and each coordinated to one hexaglyme molecule. The coordination number is eight;

* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles, least-squares-planes data and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43866 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) for (1)

$$B_{\text{eq}} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Ca(1)	8252 (1)	−30 (1)	11087 (1)	2.84 (1)
O(1)	8423 (1)	−1336 (2)	11926 (1)	4.31 (5)
O(2)	8203 (1)	−1805 (2)	10690 (1)	4.54 (5)
O(3)	8683 (1)	−184 (2)	10155 (1)	4.11 (5)
O(4)	8733 (1)	1540 (2)	10810 (1)	4.41 (5)
O(5)	8073 (2)	1429 (2)	11690 (2)	5.46 (6)
O(6)	7196 (1)	−47 (2)	11399 (1)	4.35 (5)
O(7)	6266 (1)	−441 (2)	10199 (1)	4.99 (6)
O(8)	7401 (1)	387 (3)	10161 (1)	5.29 (6)
O(9)	9367 (1)	−45 (2)	11661 (2)	5.64 (6)
O(10)	10000	−1646 (3)	12500	7.84 (13)
C(1)	8340 (4)	−1120 (5)	12542 (3)	6.99 (13)
C(2)	8363 (3)	−2394 (3)	11758 (2)	5.21 (9)
C(3)	8570 (3)	−2516 (3)	11162 (2)	5.10 (9)
C(4)	8328 (3)	−1893 (4)	10075 (2)	5.90 (11)
C(5)	8860 (3)	−1200 (4)	10027 (2)	5.67 (10)
C(6)	9115 (3)	606 (4)	10073 (3)	5.72 (11)
C(7)	8837 (3)	1603 (4)	10192 (3)	6.02 (11)
C(8)	8551 (3)	2484 (3)	11048 (2)	5.55 (10)
C(9)	8510 (3)	2275 (4)	11709 (2)	5.76 (11)
C(10)	7492 (3)	1642 (5)	11745 (4)	11.01 (20)
C(11)	7071 (3)	804 (4)	11759 (3)	6.12 (11)
C(12)	6712 (2)	−850 (4)	11292 (2)	5.38 (10)
C(13)	6108 (2)	−575 (5)	10785 (2)	5.46 (10)
C(14)	5729 (3)	−93 (5)	9688 (3)	6.59 (12)
Ca(2)	5000	201 (1)	7500	3.16 (2)
S(1)	5595 (1)	3496 (1)	6523 (1)	6.42 (3)
S(2)	5487 (1)	−2518 (1)	5983 (1)	7.67 (3)
S(3)	7471 (1)	44 (1)	8677 (1)	5.04 (2)
C(1')	5359 (2)	2369 (3)	6696 (2)	4.42 (8)
C(2')	5336 (2)	−1724 (3)	6478 (2)	4.16 (7)
C(3')	6698 (2)	79 (2)	8328 (2)	3.51 (7)
N(1)	5199 (2)	1572 (3)	6826 (2)	5.84 (8)
N(2)	5232 (2)	−1157 (3)	6836 (2)	6.72 (8)
N(3)	6146 (2)	110 (2)	8077 (2)	4.89 (7)

in addition to six of the seven O atoms of the ether ligand, two water molecules are coordinated in a perpendicular *trans* arrangement. One of these [O(9)] is hydrogen bonded to a third water molecule [O(10)], which lies on a twofold axis. The second cation-coordinated water molecule [O(8)] is hydrogen bonded to the O atom of the hexaglyme [O(7)] that is not used for coordination to calcium [O(8)⋯O(7) = 2.701 \AA].

For (2) two non-equivalent complexed units, molecules *A* and *B*, are found in the asymmetric unit. For each, the coordination number of the Sr cation is nine. All the seven O atoms of the hexaglyme are used in both cases, and in addition either two thiocyanate anions (molecule *A*) or two water molecules (molecule *B*). The anions in molecule *A*, as well as the water molecules in *B*, are in a perpendicular *trans* arrangement, one above and one below the glyme chain (Figs. 3 and 4). It should be noted that both arrangements found here for the Sr^{2+} complex differ, not only from each other and from that found for the Ca^{2+} complex, but also from that reported for the hexaglyme complex with Ba^{2+} (Weber, Hirayama, Saenger & Sheldrick, 1984). This latter complex resembles molecule *A* of (2) by having all seven O atoms of the ligand and two

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) for (2)
$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Molecule A	x	y	z	B_{eq}
Sr	6435 (1)	3103 (1)	5819 (1)	3.24 (3)
C(1)	7138 (9)	1404 (9)	4805 (9)	6.8 (2)
C(2)	7691 (10)	1481 (11)	6314 (12)	11.2 (3)
C(3)	8097 (9)	2081 (12)	6793 (13)	10.6 (3)
C(4)	8202 (8)	3389 (11)	7415 (11)	7.5 (3)
C(5)	7755 (9)	4093 (10)	7476 (11)	7.3 (3)
C(6)	6983 (8)	5120 (9)	6557 (11)	6.5 (2)
C(7)	6664 (9)	5260 (9)	5630 (11)	5.7 (2)
C(8)	5813 (9)	4754 (10)	4392 (10)	6.3 (2)
C(9)	5187 (9)	4188 (10)	4091 (11)	6.5 (2)
C(10)	4825 (8)	2791 (10)	3992 (9)	6.3 (2)
C(11)	5073 (8)	1960 (10)	4347 (9)	5.6 (2)
C(12)	5431 (9)	1264 (9)	5662 (10)	6.4 (2)
C(13)	5568 (9)	1424 (10)	6551 (11)	7.2 (2)
C(14)	6437 (8)	2005 (11)	7742 (9)	8.1 (2)
C(15)	5584 (7)	4080 (9)	7227 (10)	3.9 (2)
C(16)	7751 (9)	3322 (9)	4682 (9)	4.7 (2)
N(1)	5658 (7)	3706 (7)	6672 (8)	5.5 (2)
N(2)	7286 (7)	3470 (7)	4912 (7)	4.9 (2)
O(1)	7118 (5)	1704 (5)	5592 (7)	5.5 (2)
O(2)	7733 (5)	2753 (7)	6974 (6)	5.5 (2)
O(3)	7276 (5)	4302 (6)	6664 (7)	5.8 (2)
O(4)	6110 (5)	4684 (5)	5286 (6)	4.3 (2)
O(5)	5407 (5)	3372 (6)	4322 (5)	4.6 (2)
O(6)	5330 (5)	2043 (6)	5234 (6)	5.5 (2)
O(7)	6239 (5)	1881 (6)	6871 (6)	5.1 (2)
S(1)	5519 (3)	4641 (3)	7983 (3)	6.9 (1)
S(2)	8437 (2)	3124 (3)	4356 (3)	8.5 (1)

Molecule B	x	y	z	B_{eq}
Sr	8259 (1)	7082 (1)	4331 (1)	3.21 (3)
C(1)	9796 (8)	6927 (10)	3527 (10)	6.9 (2)
C(2)	8869 (9)	6014 (10)	2859 (10)	6.4 (2)
C(3)	8324 (10)	5431 (10)	2984 (10)	7.1 (2)
C(4)	7109 (9)	5502 (9)	3125 (9)	5.5 (2)
C(5)	6575 (8)	6137 (9)	3150 (9)	5.1 (2)
C(6)	6380 (7)	7162 (10)	4088 (9)	5.1 (2)
C(7)	6502 (8)	7986 (10)	3779 (10)	6.3 (2)
C(8)	7418 (8)	9020 (9)	4095 (10)	5.5 (2)
C(9)	8153 (9)	9213 (10)	4697 (10)	6.2 (2)
C(10)	9404 (9)	8804 (10)	4969 (11)	8.1 (3)
C(11)	9705 (10)	8269 (11)	5684 (11)	8.8 (3)
C(12)	9883 (8)	6882 (11)	6068 (9)	5.9 (2)
C(13)	9759 (8)	6030 (10)	5760 (10)	6.2 (2)
C(14)	8752 (9)	5092 (8)	5405 (9)	6.9 (2)
C(15)	6853 (8)	8560 (11)	6075 (9)	4.9 (2)
C(16)	9276 (11)	5811 (9)	7674 (10)	6.0 (2)
N(1)	7020 (7)	7903 (8)	6317 (7)	6.3 (2)
N(2)	8782 (8)	6188 (8)	7355 (9)	6.7 (2)
O(1)	9217 (6)	6434 (6)	3604 (6)	5.7 (2)
O(2)	7807 (6)	5880 (6)	3254 (6)	4.5 (2)
O(3)	6851 (5)	6552 (6)	3935 (6)	4.3 (2)
O(4)	7242 (5)	8190 (6)	4261 (5)	4.1 (2)
O(5)	8659 (6)	8645 (6)	4536 (6)	5.4 (2)
O(6)	9584 (5)	7440 (7)	5382 (6)	5.4 (2)
O(7)	8986 (5)	5903 (7)	5340 (6)	6.0 (2)
S(1)	6610 (3)	9490 (3)	5751 (3)	7.6 (1)
S(2)	46 (4)	5351 (5)	8157 (4)	15.0 (2)
O(8)	7886 (5)	7749 (5)	2859 (5)	3.8 (2)
O(9)	8058 (5)	7093 (6)	5766 (5)	5.1 (2)

Table 3. Bond lengths and coordination distances (\AA)

(1) $M = Ca^{2+}$		(2) $M = Sr^{2+}$	
		Mol. A	Mol. B
O(1)—C(1)	1.430 (7)	1.43 (2)	1.42 (2)
C(2)—O(1)	1.418 (5)	1.39 (2)	1.39 (2)
C(3)—C(2)	1.496 (8)	1.34 (2)	1.49 (3)
O(2)—C(3)	1.439 (5)	1.39 (2)	1.44 (2)
C(4)—O(2)	1.444 (6)	1.41 (2)	1.43 (2)
C(5)—C(4)	1.486 (8)	1.46 (2)	1.48 (2)
O(3)—O(5)	1.423 (6)	1.42 (2)	1.42 (2)
C(6)—O(3)	1.433 (6)	1.43 (2)	1.43 (2)
C(7)—C(6)	1.483 (8)	1.50 (2)	1.49 (2)
O(4)—C(7)	1.425 (7)	1.40 (2)	1.43 (1)
C(8)—O(4)	1.430 (5)	1.43 (2)	1.44 (2)
C(9)—C(8)	1.492 (8)	1.47 (2)	1.48 (2)
O(5)—C(9)	1.442 (6)	1.41 (2)	1.44 (2)
C(10)—O(5)	1.323 (8)	1.43 (2)	1.41 (2)
C(11)—C(10)	1.423 (9)	1.49 (2)	1.44 (2)
O(6)—C(11)	1.423 (7)	1.42 (2)	1.43 (2)
C(12)—O(6)	1.448 (5)	1.44 (2)	1.43 (2)
C(13)—C(12)	1.493 (6)	1.46 (2)	1.47 (2)
O(7)—C(13)	1.420 (6)	1.44 (2)	1.44 (2)
C(14)—O(7)	1.433 (6)	1.41 (2)	1.41 (2)
C(1')—S(1)	1.630 (4)	S(1)—C(15)	1.61 (2)
C(2')—S(2)	1.591 (4)	S(2)—C(16)	1.64 (2)
C(3')—S(3)	1.626 (4)	—	—
N(1)—C(1')	1.152 (6)	N(1)—C(15)	1.17 (2)
N(2)—C(2')	1.140 (6)	N(2)—C(16)	1.12 (2)
N(3)—C(3')	1.162 (5)	—	—
Ca(2)...N(1)	2.422 (4)	Sr...N(1)	2.608 (15)
Ca(2)...N(2)	2.421 (4)	Sr...N(2)	2.676 (14)
Ca(2)...N(3)	2.440 (3)	—	—
Ca(1)...O(1)	2.443 (2)	Sr...O(1)	2.728 (10)
Ca(1)...O(2)	2.454 (3)	Sr...O(2)	2.676 (9)
Ca(1)...O(3)	2.467 (3)	Sr...O(3)	2.635 (10)
Ca(1)...O(4)	2.439 (3)	Sr...O(4)	2.729 (9)
Ca(1)...O(5)	2.399 (3)	Sr...O(5)	2.678 (8)
Ca(1)...O(6)	2.559 (3)	Sr...O(6)	2.668 (9)
Ca(1)...O(7)	—	Sr...O(7)	2.782 (11)
Ca(1)...O(8)	2.372 (3)	Sr...O(8)	—
Ca(1)...O(9)	2.377 (3)	Sr...O(9)	—

from the cation to the O of the glyme chain are: $Ca \cdots O = 2.460$ (3) and $Sr \cdots O = 2.684$ (9) \AA .

A focal point of this study is the detailed folding geometry of the hexaglyme chain. It has already been noted that the wrapping mode of linear polyether ligands around cations depends on their lengths (Vögtle & Weber, 1979; Dale, 1980). Ligands with five heteroatoms generally fold in an equatorial plane around the cation; longer ligands adopt a pseudo helical arrangement. We have shown (Wei *et al.*, 1987*b,c*) that already the tetraglyme and *a fortiori* the pentaglyme chains have difficulties in folding to a horseshoe around the small Ca^{2+} cation, while this conformation is preferred, although with some deformation, for the Sr^{2+} and Ba^{2+} pentaglyme complexes. In the present study we observe the conformational sequence $ag^-a g^-g^-a ag^+a ag^-g^- ag^-a g^+g^+a$ for the Ca^{2+} hexaglyme complex. This unusual arrangement brings four adjacent O atoms [O(2), O(3), O(4), O(5)] into a common plane (maximum deviation 0.11 \AA) with the cation only 0.04 \AA out of the same plane. These atoms may be considered as equatorial donors. The two remaining coordinated O atoms of the hexaglyme, O(1) and O(6),

thiocyanate anions coordinated to the cation, except that the anions are now on the same side (*cis*).

The coordination distances are those expected when one considers the values of the effective ionic radii (Shannon, 1976). The mean values of the distances

Table 4. Bond angles ($^{\circ}$) and torsion angles ($^{\circ}$) [(1) $\sigma = 2^{\circ}$, (2) $\sigma = 5^{\circ}$] for the hexaglyme chain in the two complexes

	(1) $M = \text{Ca}^{2+}$	(2) $M = \text{Sr}^{2+}$	
		Mol. A	Mol. B
C(2)–O(1)–C(1)	113.9 (4)	118 (1)	110 (1)
C(3)–C(2)–O(1)	107.3 (4)	118 (1)	110 (1)
O(2)–C(3)–C(2)	108.1 (4)	118 (1)	109 (1)
C(4)–O(2)–C(3)	113.6 (4)	114 (1)	117 (1)
C(5)–C(4)–O(2)	111.7 (4)	109 (1)	109 (1)
O(3)–C(5)–C(4)	107.0 (5)	109 (1)	108 (1)
C(6)–O(3)–C(5)	114.8 (4)	117 (1)	116 (1)
C(7)–C(6)–O(3)	107.0 (5)	106 (1)	112 (1)
O(4)–C(7)–C(6)	107.2 (4)	109 (1)	105 (1)
C(8)–O(4)–C(7)	115.1 (3)	111 (1)	111 (1)
C(9)–C(8)–O(4)	106.9 (3)	108 (1)	107 (1)
O(5)–C(9)–C(8)	109.2 (4)	111 (1)	107 (1)
C(10)–O(5)–C(9)	118.0 (4)	113 (1)	115 (1)
C(11)–C(10)–O(5)	118.0 (5)	110 (1)	112 (1)
O(6)–C(11)–C(10)	111.1 (6)	107 (1)	107 (1)
C(12)–O(6)–C(11)	114.0 (4)	113 (1)	109 (1)
C(13)–C(12)–O(6)	112.7 (4)	108 (1)	110 (1)
O(7)–C(13)–C(12)	108.1 (4)	108 (1)	109 (1)
C(14)–O(7)–C(13)	112.8 (4)	111 (1)	114 (1)
C(1)–O(1)–C(2)–C(3)	–171	121	174
O(1)–C(2)–C(3)–O(2)	–54	45	58
C(2)–C(3)–O(2)–C(4)	–176	–174	159
C(3)–O(2)–C(4)–C(5)	–91	173	–160
O(2)–C(4)–C(5)–O(3)	–56	–53	–57
C(4)–C(5)–O(3)–C(6)	–175	–159	–177
C(5)–O(3)–C(6)–C(7)	177	166	–89
O(3)–C(6)–C(7)–O(4)	55	61	–63
C(6)–C(7)–O(4)–C(8)	171	–176	–174
C(7)–O(4)–C(8)–C(9)	–176	–174	173
O(4)–C(8)–C(9)–O(5)	–55	–59	62
C(8)–C(9)–O(5)–C(10)	–105	–176	172
C(9)–O(5)–C(10)–C(11)	–177	–173	102
O(5)–C(10)–C(11)–O(6)	–30	55	57
C(10)–C(11)–O(6)–C(12)	–169	167	179
C(11)–O(6)–C(12)–C(13)	76	–170	180
O(6)–C(12)–C(13)–O(7)	62	–63	–57
C(12)–C(13)–O(7)–C(14)	–175	–176	–149

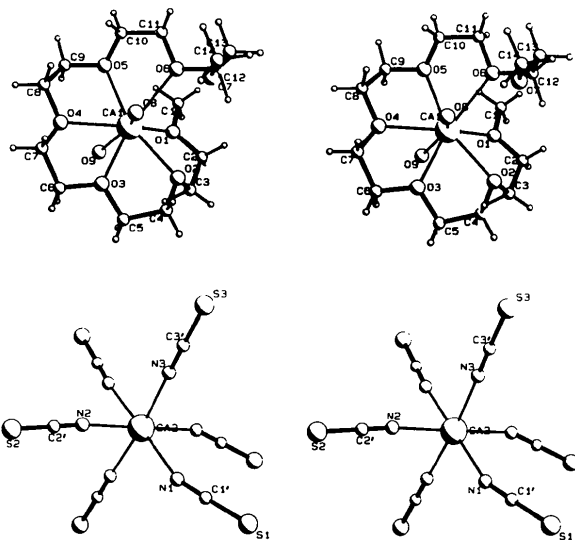


Fig. 1. Stereoscopic views of complex (1) with atom numbering [the water molecule O(10) is not represented].

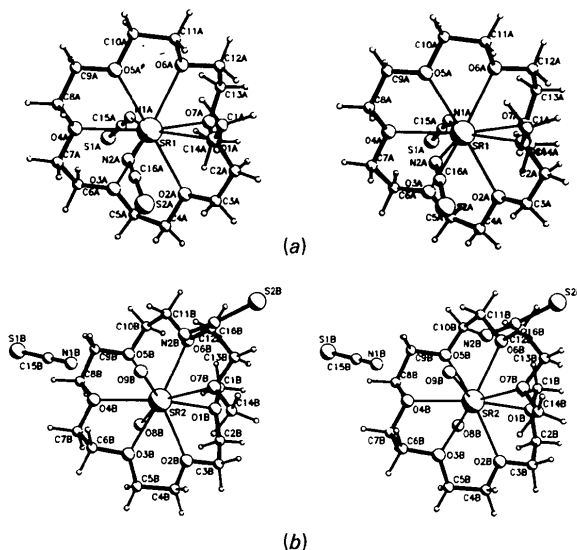


Fig. 2. Stereoscopic top view of complex (2) with atom numbering: (a) molecule A, (b) molecule B.

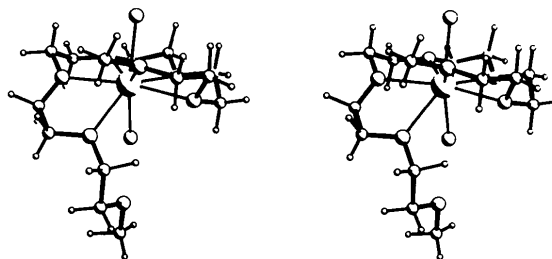


Fig. 3. Side view of the folding of the hexaglyme chain around the Ca^{2+} cation in complex (1).

are located symmetrically ~ 1.4 Å above and below the plane so as to avoid the steric hindrance between the ends of the chain, but an extra unit is present on one side with O(7) out of the coordination sphere. The sequence of torsion angles is characterized by three genuine corners $g^{\pm}g^{\pm}$ (Dale, 1980). These are unsymmetrically placed in every second unit of the hexaglyme chain. One can only speculate as to the reason for this incomplete and asymmetric use of the polyether chain and for the astonishing crowding of six anions around a single cation, leaving two cations without anion contact.

In the two Sr^{2+} complexes the rough outline of the folded hexaglyme chain looks quite similar and symmetrical, with the central part roughly equatorial, and the terminal O atoms competing with the anions for the apical positions in molecule A and with the water molecules in molecule B. Nevertheless, the conformational details reveal that the hexaglyme conformation is very different in A and B, and quite unsymmetric in

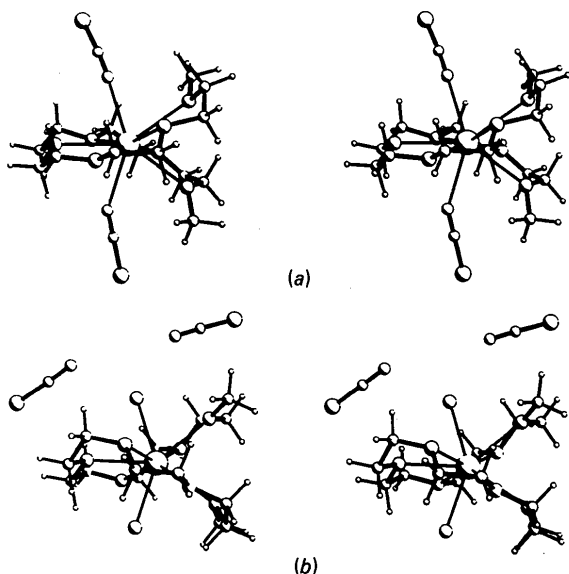


Fig. 4. Side views of complex (2): (a) molecule A, (b) molecule B.

both cases. The sequence of torsion angles in molecule A is $ag^+a ag^-a ag^+a ag^-a ag^+a ag^-a$, i.e. the familiar ag^+a pattern with alternating signs, but a group of four adjacent O atoms [O(2), O(3), O(4), O(5)] that are coplanar (within 0.03 Å), the cation being 0.44 Å out of this plane, is not centrally located. All the torsion angles have rather normal values, except for one terminal torsion angle C(1)—O(1)—C(2)—C(3) which is 121° , just between *gauche* and *anti*, as a result of steric hindrance. The steric conflict between the ends of the polyether chain is nevertheless well avoided because O(1) is 0.72 Å below, whereas O(6) and O(7) are respectively 1.60 and 2.39 Å above the equatorial plane. In molecule B the torsion angle sequence is $ag^+a ag^-a g^-g^-a ag^+a g^+g^+a ag^-a$, where three of the units now adopt a different conformation, and two of these contain genuine corners. Furthermore, the best mean plane through four adjacent O atoms is now the plane through O(4), O(5), O(6), O(7), that is, as unsymmetrically located as possible. The deviations of these atoms from the plane (max. 0.18 Å) are larger as compared with the situation in A, and the cation is as much as 0.85 Å out of the same plane. It is not easy to understand how the simple replacement of two thiocyanate anions with two water molecules as ligands should provoke such drastic changes in the conformational details of the hexaglyme chain; the resulting coordination geometry is after all practically identical.

Genuine corners ($g^\pm g^\pm$), as observed in two of the complexes described here [(1) and (2B)], are relatively rare in open-chain ligands, especially if located in the middle part of the chain. In the $Ba(SCN)_2$ -hexaglyme complex there is only one corner at the end of the polyether chain (Weber *et al.*, 1984). In the $Sr(SCN)_2$

complex with heptaethylene glycol, there is an additional sequence of two $ag^\pm g^\pm$ units of the same sign at the other end (Ohmoto, Kai, Yasuoka, Kasai, Yanagida & Okahara, 1979). Also the conformation of the triglyme chain complexed with $Sr(SCN)_2$ has two genuine corners in adjacent units with all *gauche* bonds of the same sign (Wei *et al.*, 1987a). This tight folding brings all four O atoms into a planar square for one-sided coordination to Sr^{2+} similar to that observed for 12-crown-4 sandwich complexes (Dale, 1980).

As already observed in all these complexes containing genuine corners, the *gauche* CO bond has a larger value of the torsion angle than the adjacent *gauche* CC bond of the same unit.

In contrast with the shorter ligand chains (tri-, tetra- and pentaglymes) complexed with Ca, Sr or $Ba(SCN)_2$ (Wei *et al.*, 1987a,b,c) linkages are observed between the complex units in (1): a water molecule O(10) lying on a twofold axis is hydrogen bonded to the complexed water molecules O(9). The distance O(10)···O(9) is 2.848 Å [O(9): x, y, z and $2-x, y, 2.5-z$]. For (2), the N atoms N(1B) and N(2B) of the free SCN anions are hydrogen bonded to the complexed water molecules. These atoms are located at distances of 2.818 and 2.971 Å from O(9B)(x, y, z) and at 2.793 and 2.785 Å from O(8B)[N(1B), N(2B): $x, 1.5-y, z-0.5$].

YYW, BT, JPD and MVM thank the SPPS, Belgium, for financial support.

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