

Oligoether Complexes of Alkaline-Earth Metal Ions. III. Structures of 2,5,8,11,14,17-Hexaoxaoctadecane ('Pentaglyme') Complexed with Calcium, Strontium and Barium Thiocyanates

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(Received 23 September 1986; accepted 23 February 1987)

Abstract. (1): 2,5,8,11,14,17-Hexaoxaoctadecane–calcium thiocyanate (1/1), $C_{12}H_{26}O_6 \cdot Ca(SCN)_2$, $M_r = 422.58$, monoclinic, $C2/c$, $a = 13.785$ (5), $b = 10.074$ (4), $c = 15.556$ (4) Å, $\beta = 103.03$ (2)°, $V = 2104$ (1) Å³, $Z = 4$, $D_x = 1.33$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 5.07$ cm⁻¹, $F(000) = 896$, $T = 291$ K, $R = 0.042$ for 3207 observed reflections. (2): 2,5,8,11,14,17-Hexaoxaoctadecane–strontium thiocyanate (1/1) monohydrate, $C_{12}H_{26}O_6 \cdot Sr(SCN)_2 \cdot H_2O$, $M_r = 488.13$, monoclinic, $P2_1$, $a = 8.646$ (7), $b = 17.374$ (13), $c = 7.878$ (7) Å, $\beta = 111.27$ (7)°, $V = 1103$ (2) Å³, $Z = 2$, $D_x = 1.47$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 27.78$ cm⁻¹, $F(000) = 504$, $T = 291$ K, $R = 0.045$ for 1199 observed reflections. (3): 2,5,8,11,14,17-Hexaoxaoctadecane–barium thiocyanate (1/1) monohydrate, $C_{12}H_{26}O_6 \cdot Ba(SCN)_2 \cdot H_2O$, $M_r = 537.85$, triclinic, $P\bar{1}$, $a = 34.908$ (19), $b = 8.900$ (5), $c = 7.894$ (2) Å, $\alpha = 68.92$ (3), $\beta = 89.17$ (4), $\gamma = 88.88$ (5)°, $V = 2288$ (2) Å³, $Z = 4$, $D_x = 1.56$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 19.94$ cm⁻¹, $F(000) = 1080$, $T = 291$ K, $R = 0.059$ for 5253 observed reflections. The coordination geometry of the anhydrous Ca^{2+} complex (1) is very different from that of the monohydrated Sr^{2+} and Ba^{2+} complexes (2) and (3). In (1) a roughly equatorial arrangement of the ether O atoms and a perpendicular *trans* arrangement of the anions is observed. For (2) and (3), both anions are on the same side with the water molecule coordinated on the opposite side. The polyether chain adopts the conformational sequence $ag^+a ag^-a ag^+a ag^+a ag^+a$ in the Ca^{2+} complex (1) instead of a sequence of units with alternating sign, as is observed for the Sr^{2+} (2) and Ba^{2+} (3) complexes.

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). An X-ray

analysis of the alkaline-earth complexes has been undertaken in order to compare the conformations of the glymes in the solid state with that observed in solution. In two preceding papers, we have reported the structures of tri- and tetraglyme complexed with Ca, Sr and Ba thiocyanates (Wei, Tinant, Declercq, Van Meerssche & Dale, 1987*a,b*). Here we report and compare the structures of the complexes of 2,5,8,11,14,17-hexaoxaoctadecane (pentaglyme) with the same alkaline-earth thiocyanates.

Experimental. Crystals obtained by slow evaporation from (1) hexane–ethyl acetate (1/1), (2) hexane–acetone (1/1) and (3) acetone. Crystal sizes: (1) 0.30 × 0.15 × 0.20 mm, (2) 0.288 × 0.256 × 0.096 mm, (3) 0.356 × 0.193 × 0.177 mm. Lattice parameters refined using 15 reflections in the range $3 \leq 2\theta \leq 25^\circ$. Syntex $P2_1$ diffractometer, graphite-monochromatized $Mo K\alpha$ radiation, ω scan, scan width 1.3° , scan rate $1.3\text{--}30^\circ \text{ min}^{-1}$. For (1) $(\sin\theta)/\lambda_{\max} = 0.596 \text{ \AA}^{-1}$, 1851 independent reflections measured ($0 \leq h \leq 16$, $0 \leq k \leq 11$, $-18 \leq l \leq 18$), 1125 observed [$I \geq 2.5\sigma(I)$]. For (2) $(\sin\theta)/\lambda_{\max} = 0.561 \text{ \AA}^{-1}$, 1689 reflections measured ($0 \leq h \leq 9$, $0 \leq k \leq 19$, $-7 \leq l \leq 7$), 1199 observed [$I \geq 2.5\sigma(I)$]. For (3) $(\sin\theta)/\lambda_{\max} = 0.561 \text{ \AA}^{-1}$, 6760 reflections measured ($0 \leq h \leq 39$, $-8 \leq k \leq 9$, $-8 \leq l \leq 8$), 5253 observed [$I \geq 2.5\sigma(I)$]. Standard reflections: $\bar{1}16$ (1), 200 (2) and 222 (3) checked every 50 reflections: no significant deviation. Absorption corrections: none for (1), numerical corrections for crystal defined by its faces for (2) and (3) using *SHELX76* (Sheldrick, 1976). Max./min. transmission: (2) 0.747/0.540; (3) 0.763/0.724. The three structures were solved by first locating the cation [and S atom in (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 (3)]. H atoms from a difference Fourier synthesis for (1), included in the refinement in idealized positions (C–H = 1.08 Å, H–C–H = 109.5°) for (2) and (3), water H atoms were not considered. 156 (1), 235 (2) and 472 (3) LS parameters. Weighting scheme $w = 1/[\sigma^2(F) + gF^2]$, $g = 0.00138$ for (1), 0.00067 for (2) and 0.00011 for (3). (1) $R = 0.042$, $wR = 0.046$ for 1125 reflections. (2) $R = 0.045$, $wR = 0.044$ for 1199 reflections. (3) $R = 0.059$, $wR = 0.061$ for 5253 reflections. $(\Delta/\sigma)_{\max}$ in final refinement cycle: (1) 0.15 [x of atom C(1)], (2) 0.014 [z of atom C(12)], (3) 0.19 [x of atom Ba(1B)]. $S = 1.03$ for (1), 1.28 for (2), 3.2 for (3). Max. and min. heights in final Fourier synthesis (1) 0.25, –0.21; (2) 0.39, –0.44; (3) [near Ba(1B) atom] 1.14, –1.12 e Å^{–3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters for the three structures are given in Tables 1, 2 and 3.* A comparison of bond lengths and coordination distances is presented in Table 4. Bond angles and torsion angles for the pentaglyme chain are listed in Table 5. Figs. 1, 2 and 3, depicting the numbering scheme, give top views of each complex, and Figs. 4, 5 and 6 give the corresponding side views (*PLUTO*; Motherwell & Clegg, 1978). In complex (1) a twofold axis passes through the Ca²⁺ cation and the midpoint of the pentaglyme chain, so that the asymmetric unit contains only half of the complex. Complex (3) exists as two independent molecules (*A* and *B*) in the asymmetric unit. The sequence of torsion angles (Table 5) is very similar for the two, so that molecules *A* and *B* have essentially the same conformation. In Tables 4 and 5 only the mean values of the bond distances and bond angles are reported for this complex because the individual values are affected by large standard deviations. Furthermore, the atoms at both ends of the pentaglyme chain, especially in (3), are affected by relatively high temperature factors (*cf.* B_{eq} in Table 3). This would imply that the numerical values for the torsion angles involving these atoms (Table 5) are less accurately determined.

The coordination geometry is very different for the anhydrous Ca²⁺ complex (1) on the one hand, and the monohydrated Sr²⁺ and Ba²⁺ complexes (2) and (3) on the other hand. In the former case, the coordination number is eight, and the salient feature is the roughly equatorial arrangement of the ether O atoms and the perpendicular *trans* arrangement of the thiocyanate anions, one above and one below (Fig. 4). In the latter

Table 1. *Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å²) for (1)*

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

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Ca	10000	–92 (1)	2500	3.45 (2)
S(1)	6606 (1)	–256 (1)	269 (1)	6.07 (3)
N(1)	8482 (2)	–504 (4)	1377 (2)	4.95 (7)
O(1)	11015 (2)	2017 (3)	2565 (2)	5.89 (7)
O(2)	10851 (2)	221 (3)	1287 (2)	5.97 (7)
O(3)	10478 (2)	–2182 (3)	1830 (2)	4.84 (6)
C(1)	11234 (6)	2819 (7)	3343 (5)	8.1 (2)
C(2)	11849 (5)	1873 (7)	2160 (4)	7.5 (1)
C(3)	11472 (5)	1365 (8)	1259 (4)	8.3 (2)
C(4)	11074 (4)	–896 (6)	808 (4)	6.6 (1)
C(5)	10413 (4)	–2006 (6)	906 (3)	5.9 (1)
C(6)	9970 (5)	–3336 (5)	2016 (3)	6.0 (1)
C(13)	7705 (3)	–402 (4)	921 (3)	3.73 (7)

Table 2. *Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å²) for (2)*

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

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Sr	1370 (1)	4308	–5376 (1)	3.43 (2)
C(1)	–2028 (22)	3263 (9)	–4702 (25)	7.6 (4)
C(2)	–1424 (19)	4457 (13)	–2907 (21)	5.9 (4)
C(3)	–424 (31)	5043 (13)	–2341 (36)	12.2 (8)
C(4)	1762 (28)	5853 (12)	–2080 (26)	5.6 (4)
C(5)	1978 (23)	6299 (10)	–3539 (26)	6.4 (4)
C(6)	2922 (25)	6164 (11)	–6130 (33)	6.2 (5)
C(7)	3979 (23)	5678 (12)	–6723 (26)	6.9 (4)
C(8)	4207 (23)	4480 (13)	–7794 (25)	6.5 (5)
C(9)	3457 (30)	3690 (14)	–8196 (27)	9.2 (6)
C(10)	2760 (34)	2590 (14)	–6632 (40)	9.9 (7)
C(11)	2838 (25)	2345 (11)	–4750 (30)	7.3 (4)
C(12)	1833 (30)	2616 (12)	–2481 (31)	6.7 (5)
C(13)	–1705 (25)	3257 (10)	–9108 (22)	4.4 (3)
C(14)	–2026 (21)	5533 (9)	–8675 (26)	4.2 (3)
N(1)	–593 (18)	3596 (9)	–8209 (20)	6.2 (3)
N(2)	–914 (18)	5324 (8)	–7412 (19)	5.5 (3)
O(1)	–1040 (13)	3944 (6)	–4171 (13)	5.5 (2)
O(2)	759 (13)	5198 (6)	–2815 (14)	6.4 (2)
O(3)	2708 (12)	5807 (6)	–4539 (12)	4.3 (2)
O(4)	3224 (14)	4940 (7)	–7214 (15)	5.4 (3)
O(5)	3301 (15)	3372 (7)	–6525 (17)	6.0 (3)
O(6)	1815 (14)	2834 (6)	–4212 (18)	5.5 (3)
O(7)	4194 (9)	4275 (9)	–2620 (10)	5.1 (2)
S(1)	–3376 (7)	2772 (3)	–10440 (7)	5.6 (1)
S(2)	–3556 (6)	5816 (4)	–10480 (7)	5.3 (1)

cases, the coordination number is nine, and both anions are on the same side, with the water molecule coordinated on the opposite side (Figs. 5 and 6).

Of particular interest is the detailed folding geometry of the pentaglyme chain. We have shown (Wei *et al.*, 1987*a,b*) that the tetraglyme chain already has difficulties in folding to a 'horseshoe' in the familiar alternating $ag^{\pm}a$ pattern around the smallest of these cations (Ca²⁺) due to steric interaction between the terminal methoxy groups. With the present pentaglyme chain the steric conflict would be intolerable in the analogous conformation. In the Ca²⁺ complex (1) of C_2 symmetry the chain has chosen the conformational sequence $ag^{\pm}a$

* 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 43865 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) for (3)
$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Molecule A	x	y	z	B_{eq}
Ba	1290 (1)	1399 (1)	463 (1)	3.59 (1)
C(1)	761 (4)	-1676 (25)	-652 (27)	14.1 (7)
C(2)	1358 (4)	-1213 (18)	-2197 (20)	13.5 (5)
C(3)	1675 (5)	-105 (23)	-3046 (27)	11.9 (6)
C(4)	2092 (4)	1718 (16)	-2794 (17)	6.7 (3)
C(5)	2295 (3)	1939 (16)	-1273 (17)	6.5 (3)
C(6)	2215 (3)	3013 (18)	1105 (17)	6.9 (3)
C(7)	1961 (4)	4106 (19)	1572 (19)	8.0 (4)
C(8)	1354 (5)	4436 (18)	2750 (22)	9.8 (5)
C(9)	978 (4)	3598 (22)	3249 (21)	9.0 (4)
C(10)	505 (7)	2926 (34)	2187 (27)	16.9 (9)
C(11)	286 (4)	3153 (23)	231 (35)	15.8 (7)
C(12)	342 (5)	1856 (30)	-2092 (23)	16.4 (7)
C(13)	721 (3)	-1857 (20)	4134 (18)	7.8 (3)
C(14)	1884 (3)	-2123 (14)	3905 (16)	4.7 (2)
N(1)	882 (4)	-743 (20)	3244 (20)	13.8 (4)
N(2)	1781 (3)	-964 (14)	2676 (15)	7.3 (3)
O(1)	1070 (3)	-669 (15)	-1288 (18)	11.4 (4)
O(2)	1785 (2)	679 (11)	-2046 (11)	7.0 (2)
O(3)	2039 (2)	2702 (8)	-402 (9)	4.6 (1)
O(4)	1608 (2)	3396 (9)	2240 (10)	5.3 (2)
O(5)	839 (3)	3407 (15)	1812 (17)	4.7 (2)
O(6)	490 (3)	2046 (15)	-609 (15)	10.0 (3)
O(7)	1257 (2)	4317 (9)	-2453 (10)	6.2 (2)
S(1)	499 (1)	-3419 (4)	5502 (5)	6.63 (7)
S(2)	2026 (1)	-3665 (4)	5591 (4)	5.32 (6)

Molecule B	x	y	z	B_{eq}
Ba	3781 (1)	8566 (1)	9516 (1)	3.64 (1)
C(1)	3304 (4)	11812 (19)	10682 (23)	10.4 (5)
C(2)	3890 (3)	11224 (15)	12219 (19)	6.5 (3)
C(3)	4180 (4)	9951 (21)	13018 (21)	9.2 (4)
C(4)	4613 (3)	8090 (15)	12558 (17)	6.2 (3)
C(5)	4799 (3)	7877 (15)	10974 (19)	6.8 (3)
C(6)	4683 (4)	6908 (16)	8573 (16)	6.8 (3)
C(7)	4432 (4)	5808 (19)	8102 (20)	8.2 (4)
C(8)	3787 (6)	5701 (23)	7143 (24)	11.0 (6)
C(9)	3417 (6)	6398 (24)	6798 (22)	11.1 (6)
C(10)	2911 (5)	7311 (25)	8094 (29)	11.6 (6)
C(11)	2751 (4)	7183 (21)	9979 (30)	11.4 (5)
C(12)	2878 (4)	8123 (21)	12399 (20)	10.2 (4)
C(13)	4378 (3)	11974 (13)	6042 (15)	4.3 (2)
C(14)	3210 (3)	11847 (15)	5809 (15)	5.0 (2)
N(1)	4281 (3)	10879 (14)	7271 (16)	7.9 (3)
N(2)	3371 (4)	10721 (18)	6654 (18)	11.8 (4)
O(1)	3619 (2)	10716 (12)	11299 (12)	7.3 (2)
O(2)	4312 (2)	9200 (10)	11883 (11)	6.6 (2)
O(3)	4532 (2)	7099 (9)	10167 (10)	5.2 (2)
O(4)	4065 (3)	6572 (11)	7633 (10)	7.0 (2)
O(5)	3271 (3)	6703 (13)	8345 (15)	9.3 (3)
O(6)	2989 (2)	8164 (11)	10696 (13)	7.6 (2)
O(7)	3751 (2)	5638 (9)	12418 (10)	6.2 (2)
S(1)	4523 (1)	13533 (4)	4378 (4)	4.96 (6)
S(2)	2989 (1)	13492 (4)	4498 (5)	6.38 (7)

ag^+a ag^+a ag^+a ag^+a^* instead of a sequence of units with alternating sign. The folding can thus be described as part of a 'crown' or 'horseshoe', considering only the three middle units, and as parts of a polymer helix, considering two terminal units starting at one or the other end. This is also illustrated by the fact that the four central O atoms lie in one plane including the Ca^{2+} cation, whereas the two terminal O atoms are lifted by 1.1 Å out of this plane in opposite directions. The final adjustment of their positions is largely determined by the exact value of the C(2)—C(3)—O(2)—C(4) torsion angle which, although classifiable as *anti* (120–180°),

* $g^+ = 0$ to 120°, $g^- = 0$ to -120°, $a = \pm 120$ to $\pm 180^\circ$ (Dale, 1980).

Table 4. Bond lengths and coordination distances (Å)

	(1) $M = Ca$	(2) $M = Sr$	(3) $M = Ba^\dagger$
O(1)—C(1)	1.429 (6)	1.43 (2)	1.41 (1)
O(1)—C(2)	1.437 (7)	1.46 (2)	1.39 (1)
C(2)—C(3)	1.471 (8)	1.31 (2)	1.47 (1)
C(2)—C(3)	1.441 (7)	1.24 (2)	1.34 (2)
O(2)—C(4)	1.421 (6)	1.42 (2)	1.40 (1)
C(4)—C(5)	1.472 (8)	1.45 (2)	1.47 (1)
O(3)—C(5)	1.430 (5)	1.45 (2)	1.44 (1)
O(3)—C(6)	1.420 (6)	1.47 (2)	1.44 (1)
C(6)—C(7)	1.489 (10)‡	1.44 (3)	1.46 (2)
O(4)—C(7)	—	1.43 (2)	1.41 (1)
O(4)—C(8)	—	1.36 (2)	1.41 (2)
C(8)—C(9)	—	1.50 (3)	1.46 (2)
O(5)—C(9)	—	1.48 (2)	1.36 (2)
O(5)—C(10)	—	1.43 (3)	1.31 (2)
C(10)—C(11)	—	1.52 (3)	1.61 (2)
O(6)—C(11)	—	1.40 (2)	1.50 (2)
O(6)—C(12)	—	1.41 (2)	1.37 (1)
S(1)—C(13)	1.628 (4)	1.67 (2)	1.62 (1)
N(1)—C(13)	1.148 (4)	1.13 (2)	1.15 (1)
S(2)—C(14)	—	1.63 (2)	1.62 (1)
N(2)—C(14)	—	1.16 (2)	1.16 (1)
M...O(1)	2.534 (3)	2.660 (10)	2.797 (10)
M...O(2)	2.457 (3)	2.741 (9)	2.848 (7)
M...O(3)	2.503 (3)	2.829 (10)	2.861 (5)
M...O(4)	—	2.749 (11)	2.865 (7)
M...O(5)	—	2.711 (11)	2.833 (10)
M...O(6)	—	2.700 (11)	2.903 (6)
M...O(7)(H ₂ O)	—	2.614 (7)	2.785 (5)
M...N(1)	2.440 (3)	2.578 (15)	2.777 (8)
M...N(2)	—	2.700 (14)	2.777 (8)

† Mean value for molecules A/B.

‡ C(7) corresponding to C(6*).

Table 5. Bond angles (°) and torsion angles (°) [$\sigma \approx 1^\circ$ (1) and 3° (2) and (3)] in the polyether chain

	(1) $M = Ca$	(2) $M = Sr$	(3) $M = Ba^\dagger$
C(1)—O(1)—C(2)	113.1 (4)	116 (1)	114.5 (10)
O(1)—C(2)—C(3)	107.8 (5)	115 (1)	113.5 (10)
C(2)—C(3)—O(2)	109.6 (4)	126 (2)	113.7 (10)
C(3)—O(2)—C(4)	114.7 (4)	120 (1)	114.8 (8)
O(2)—C(4)—C(5)	109.6 (4)	110 (1)	106.8 (7)
C(4)—C(5)—O(3)	107.4 (4)	109 (1)	108.5 (6)
C(5)—O(3)—C(6)	112.6 (4)	115 (1)	112.7 (6)
O(3)—C(6)—C(7)	106.8 (4)‡	109 (2)	107.4 (7)
C(6)—C(7)—O(4)	—	109 (1)	110.0 (9)
C(7)—O(4)—C(8)	—	110 (1)	114.4 (8)
O(4)—C(8)—C(9)	—	109 (1)	110.9 (11)
C(8)—C(9)—O(5)	—	109 (1)	109.4 (10)
C(9)—O(5)—C(10)	—	116 (2)	109.9 (11)
O(5)—C(10)—C(11)	—	108 (2)	107.3 (11)
C(10)—C(11)—O(6)	—	108 (2)	108.3 (10)
C(11)—O(6)—C(12)	—	110 (2)	116.3 (9)
S(1)—C(13)—N(1)	179.7 (2)	179 (2)	177.3 (10)
S(2)—C(14)—N(2)	—	178 (2)	178.0 (9)

(3) $M = Ba$

	(1) $M = Ca$	(2) $M = Sr$	Mol. A	Mol. B
C(1)—O(1)—C(2)—C(3)	-165	175	174	173
O(1)—C(2)—C(3)—O(2)	-50	2	40	45
C(2)—C(3)—O(2)—C(4)	-131	180	179	174
C(3)—O(2)—C(4)—C(5)	178	-132	-155	-160
O(2)—C(4)—C(5)—O(3)	-52	-57	-63	-66
C(4)—C(5)—O(3)—C(6)	-172	177	-179	177
C(5)—O(3)—C(6)—C(7)	-176‡	167	167	168
O(3)—C(6)—C(7)—O(4)	63‡	60	65	65
C(6)—C(7)—O(4)—C(8)	—	180	179	180
C(7)—O(4)—C(8)—C(9)	—	176	174	176
O(4)—C(8)—C(9)—O(5)	—	-59	-63	-58
C(8)—C(9)—O(5)—C(10)	—	-174	-171	-177
C(9)—O(5)—C(10)—C(11)	—	175	165	166
O(5)—C(10)—C(11)—O(6)	—	59	64	62
C(10)—C(11)—O(6)—C(12)	—	179	172	-179

† Mean value for molecules A/B.

‡ C(7) corresponding to C(6*).

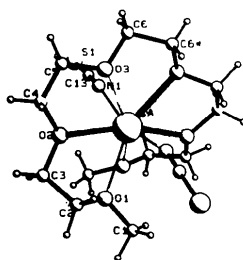


Fig. 1. Stereoscopic view of complex (1) with atom numbering.

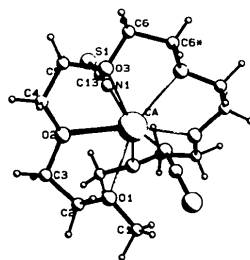


Fig. 2. Stereoscopic view of complex (2) with atom numbering.

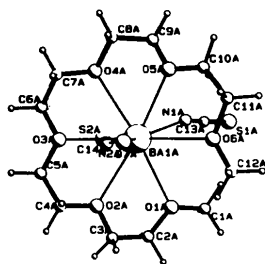


Fig. 3. Stereoscopic view of complex (3) with atom numbering - molecule A.

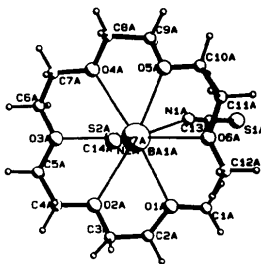


Fig. 4. Side view of complex (1).

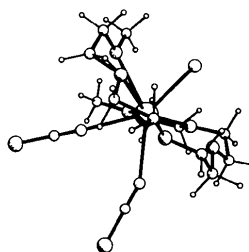


Fig. 5. Side view of complex (2).

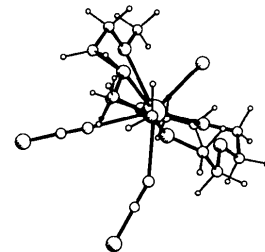


Fig. 6. Side view of complex (3).

assumes the highly irregular value of 131° (Table 5). The Ba^{2+} complex (3) on the other hand surprisingly reveals the conformational sequence $ag^+a\ ag^+a\ ag^+a\ ag^-a\ ag^+a$ with sign alternation typical for a 'crown' or 'horseshoe' folding. The expected steric conflict between the ends is nevertheless well avoided (Fig. 6) although it is not possible to trace it back to one or a few abnormal torsion angle values (Table 5). Figs. 3 and 6 show clearly that the chain folding is very unsymmetric, and this is best illustrated by the fact that the first four ether O atoms [O(1), O(2), O(3) and O(4)] lie in one plane, with the Ba^{2+} cation only about $0.1\ \text{\AA}$ out of it, while the last two ether O atoms [O(5) and O(6)] are 1.3 and $1.9\ \text{\AA}$ respectively out of this plane on the same side as the coordinated water molecule.

Finally, in the Sr^{2+} complex (2) the conformational sequence is the same as for (3), but two of the torsion angles have abnormal values: 2° for C(2)—C(3) and -132° for the O(2)—C(4) (Table 5). These angles are however not decisive for the overall shape, since they belong to that part of the glyme chain where four O atoms [O(1), O(2), O(3), O(4)] lie in a plane, and are possibly not very significant since the bond lengths are also abnormal in this region (Table 4). The Sr^{2+} cation is now well out of this plane ($0.36\ \text{\AA}$) on the same side as the water molecule and O(5) and O(6) of the non-coplanar end of the pentaglyme chain.

All coordination distances are reasonable for the three complexes. As was found for the triglyme and tetraglyme complexes, there are no linkages between the complex units in any of the three pentaglyme complexes.

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,