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Oligoether Complexes of Alkaline-Earth Metal Ions. I. Structures of 2,5,8,11,14-Pentaoxapentadecane ('Tetraglyme') Complexed With Calcium, Strontium and Barium Thiocyanates

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Abstract. (1): 2,5,8,11,14-Pentaoxapentadecane–calcium thiocyanate monohydrate, $[Ca(SCN)_2(C_{10}H_{22}O_5)].H_2O$, $M_r = 396{\cdot}54$, triclinic, $P\bar{1}$, $a = 8{\cdot}860$ (6), $b = 9{\cdot}322$ (4), $c = 12{\cdot}936$ (6) Å, $\alpha = 69{\cdot}11$ (3), $\beta = 86{\cdot}10$ (3), $\gamma = 76{\cdot}58$ (3)°, $V = 970{\cdot}8$ (9) Å^3, $Z = 2$, $D_x = 1{\cdot}36$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 5{\cdot}48$ cm^{-1}, $F(000) = 420$, $T = 291$ K, $R = 0{\cdot}046$ for 2158 reflections. (2): 2,5,8,11,14-Pentaoxapentadecane–strontium thiocyanate monohydrate, $[Sr(SCN)_2(C_{10}H_{22}O_5)].H_2O$, $M_r = 444{\cdot}08$, triclinic, $P\bar{1}$, $a = 8{\cdot}989$ (3), $b = 9{\cdot}388$ (7), $c = 13{\cdot}395$ (9) Å, $\alpha = 70{\cdot}76$ (4), $\beta = 85{\cdot}47$ (4), $\gamma = 71{\cdot}48$ (4)°, $V = 1011{\cdot}5$ (11) Å^3, $Z = 2$, $D_x = 1{\cdot}46$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 30{\cdot}20$ cm^{-1}, $F(000) = 456$, $T = 291$ K, $R = 0{\cdot}058$ for 2164 reflections. (3): 2,5,8,11,14-Pentaoxapentadecane–barium thiocyanate dihydrate, $[Ba(SCN)_2(C_{10}H_{22}O_5)].2H_2O$, $M_r = 511{\cdot}82$, triclinic, $P\bar{1}$, $a = 9{\cdot}103$ (3), $b = 9{\cdot}544$ (2), $c = 14{\cdot}040$ (4) Å, $\alpha = 73{\cdot}42$ (2), $\beta = 80{\cdot}91$ (2), $\gamma = 66{\cdot}69$ (2)°, $V = 1072{\cdot}2$ (6) Å^3, $Z = 2$, $D_x = 1{\cdot}59$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 21{\cdot}31$ cm^{-1}, $F(000) = 512$, $T = 291$ K, $R = 0{\cdot}028$ for 4441 reflections. In all three complexes, the cation is coordinated equatorially to the five O atoms of the tetraglyme, and to both anions on one side and to one (or two) water molecule(s) on the other side. The conformation of the polyether chain is very similar. The sequence of torsion angles along the chain, $ag^{\pm}a$ with alternating sign, leads to a horseshoe arrangement. The size of the metal cation determines the degree of opening, increasing from Ca^{2+} to Ba^{2+}. For the Ba^{2+} complex, the O atoms of the linear polyether are located at five of the corners of a nearly regular hexagon.

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 ^{13}C NMR spectroscopy (Dale, Krane & Thomassen, 1987). For specifically deuterated glymes, all shifts could be assigned, and their upfield or downfield displacements on complexation contain information about the accompanying conformational changes. Precise crystal structures were needed as a reference and help in the interpretation, and for this purpose the structures of the crystalline alkaline-earth metal complexes have now been investigated by X-ray diffraction. In this first paper, we report the structures of the three 1:1 complexes of tetraethyleneglycol dimethyl ether ('tetraglyme') with Ca, Sr and Ba thiocyanates. The stability of linear polyether complexes with alkali- and alkaline-earth metal ions is known to be significantly influenced by the terminal groups attached to the chain (Vögtle & Weber, 1979; Hirayama, Zabel, Saenger & Vögtle, 1985). Ligands without terminal donor groups form complexes of lower stability than do, for example, ligands with terminal aromatic groups. X-ray investigations of complexes with unsubstituted oligoglymes have been reported for complexes with $HgCl_2$ (Iwamoto, 1973) and $CdCl_2$ (Iwamoto & Wakano, 1976). Only one structure determination of a complex between an alkaline-earth metal cation (Ba^{2+}) and an unsubstituted oligoglyme ('hexaglyme') has been reported (Weber, Hirayama, Saenger & Sheldrick, 1984).

Experimental. Crystals obtained by slow evaporation from (1) acetone, (2) ethyl acetate and (3) acetone–ethyl acetate 1:1. Crystal sizes: (1) 0·3 × 0·2 × 0·65 mm, (2) 0·32 × 0·22 × 0·10 mm, and (3) 0·12 × 0·26 × 0·30 mm. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, ω scan, scan width 1·3°, scan rate 1–30° min^{-1}. Lattice parameters refined using 15 reflections in the range $3 < 2\theta < 25°$. $[(\sin\theta)/\lambda]_{max} = 0{\cdot}561$ Å^{-1} for (1) and (2), 0·650 Å^{-1} for (3). Range of hkl: $h \pm k \pm l$. For (1) 2865 independent reflections measured ($0 \le h \le 9$, $-10 \le k \le 10$, $-14 \le l \le 14$), 2158 observed [criterion $I > 2{\cdot}5\sigma(I)$]. For (2) 2984 measured ($0 \le h \le 10$, $-9 \le k \le 10$, $-14 \le l \le 15$), 2164 observed. For (3), 4933 measured ($0 \le h \le 11$, $-11 \le k \le 11$, $-17 \le l \le 18$), 4441 observed. Standard reflections: one standard reflection for each measurement [$\bar{1}1\bar{3}$ for

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

$$B_{eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ca	1588 (1)	5147 (1)	2426 (1)	3·02 (1)
O(1)	1856 (5)	7280 (4)	628 (3)	6·65 (8)
O(2)	2149 (3)	4195 (4)	861 (2)	4·40 (6)
O(3)	3151 (3)	2400 (3)	2947 (2)	4·35 (5)
O(4)	2274 (3)	3848 (4)	4432 (2)	4·59 (6)
O(5)	1540 (4)	7027 (4)	3397 (3)	6·05 (7)
O(6)	4324 (3)	5172 (4)	2324 (3)	5·39 (6)
C(1)	2223 (12)	8645 (9)	364 (6)	11·78 (21)
C(2)	1386 (8)	6864 (7)	−247 (4)	6·74 (12)
C(3)	2327 (7)	5341 (7)	−207 (4)	6·23 (12)
C(4)	3235 (6)	2735 (6)	1053 (4)	6·02 (11)
C(5)	2954 (6)	1663 (6)	2186 (4)	5·81 (11)
C(6)	2990 (5)	1457 (5)	4083 (4)	5·31 (9)
C(7)	3332 (6)	2340 (7)	4756 (4)	5·70 (10)
C(8)	2588 (9)	4908 (10)	4943 (5)	8·51 (17)
C(9)	1977 (18)	6330 (11)	4479 (7)	17·01 (37)
C(10)	433 (9)	8440 (9)	3274 (8)	11·11 (22)
S(1)	−4116 (1)	8204 (2)	1899 (1)	6·43 (3)
C(11)	−2299 (6)	7396 (5)	1925 (3)	4·24 (8)
N(1)	−1009 (5)	6833 (5)	1939 (4)	6·70 (10)
S(2)	−2785 (1)	1953 (1)	3247 (1)	4·90 (2)
C(12)	−1319 (4)	2800 (5)	3076 (3)	3·34 (7)
N(2)	−295 (4)	3406 (4)	2954 (3)	4·50 (7)

(1), 322 for (2), $\bar{1}1\bar{2}$ for (3)] checked every 50 reflections: no significant deviation. Corrections for Lorentz and polarization. Absorption corrections: none for (1); numerical corrections for crystal defined by its faces for (2) and (3) using *SHELX*76 (Sheldrick, 1976). Max./min. transmission: (2) 0·778/0·319; (3) 0·799/0·537.

Structure resolution: (1) *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and *DIRDIF*81 (Beurskens, Bosman, Doesburg, Gould, Van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981); (2) *SHELX*84 (Sheldrick, 1984) and *DIRDIF*81 (Beurskens *et al.*, 1981); (3) Ba^{2+} position from an $E{\times}F$ Patterson map, positions of remaining non-H atoms from a subsequent difference Fourier synthesis. Anisotropic least-squares refinement with *SHELX*76 (Sheldrick, 1976) on F. H atoms from difference Fourier synthesis, 12 for (1), 0 for (2), 25 for (3). Other H atoms included in idealized positions (C—H = 1·08 Å, H—C—H = 109·4°). H isotropic with common refined temperature factors. 251 (1), 209 (2) and 290 (3) LS parameters. Weights $w = [\sigma^2(F) + gF^2]^{-1}$ [g for: (1) 0·00069, (2) 0·00766, (3) 0·0048]. Atomic scattering factors from *International Tables for X-ray Crystallography*, 1974). (1) $R = 0{\cdot}046$, $wR = 0{\cdot}052$ for 2158 reflections. (2) $R = 0{\cdot}058$, $wR = 0{\cdot}062$ for 2164 reflections. (3) $R = 0{\cdot}028$, $wR = 0{\cdot}031$ for 4441 reflections. $(\Delta/\sigma)_{max}$ in final refinement cycle: (1) 0·12 [x of atom C(9)], (2) 0·08 [z of atom C(7)], (3) 0·05 [z of atom O(4)]. S = (1) 1·69, (2) 0·81, (3) 0·58. Max. and min. heights in final Fourier synthesis (1) 0·47, −0·51, (2) 1·56, −1·08, (3) 0·33, −1·22 e Å^{-3}. Largest peak close to the cation in all three structures.

Discussion. Final atomic parameters for the three structures are given in Tables 1, 2 and 3.* Although the unit-cell dimensions of the three complexes are comparable, only (2) and (3) present some similarity in the

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

$$B_{eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Sr	1738 (1)	2729 (1)	2712 (1)	3·07 (1)
O(1)	2643 (8)	242 (8)	4417 (5)	6·05 (14)
O(2)	1868 (7)	3285 (8)	4511 (5)	5·10 (13)
O(3)	1745 (7)	5589 (7)	2606 (5)	5·11 (13)
O(4)	1750 (7)	4770 (9)	830 (4)	5·71 (13)
O(5)	3157 (9)	1599 (10)	1195 (6)	6·84 (17)
O(6)	4634 (6)	2668 (8)	2699 (5)	5·04 (12)
C(1)	2466 (16)	−1254 (15)	4531 (12)	9·58 (32)
C(2)	2505 (14)	500 (17)	5398 (8)	8·00 (26)
C(3)	2897 (13)	1971 (21)	5293 (9)	7·97 (29)
C(4)	2081 (14)	4798 (19)	4412 (10)	7·42 (31)
C(5)	1181 (15)	5996 (15)	3518 (11)	7·19 (29)
C(6)	1044 (14)	6762 (12)	1651 (11)	7·51 (25)
C(7)	1878 (15)	6250 (16)	771 (10)	8·30 (29)
C(8)	2622 (17)	4204 (21)	42 (9)	8·92 (32)
C(9)	2504 (17)	2614 (27)	178 (11)	10·67 (44)
C(10)	3520 (20)	−39 (20)	1299 (15)	11·32 (46)
S(1)	−2400 (3)	450 (3)	1649 (2)	5·02 (5)
C(11)	−960 (9)	825 (9)	2066 (6)	3·57 (14)
N(1)	82 (10)	1065 (11)	2359 (6)	5·84 (18)
S(2)	−4401 (3)	5679 (3)	2811 (3)	6·30 (6)
C(12)	−2521 (10)	4860 (10)	2850 (6)	4·06 (16)
N(2)	−1158 (9)	4299 (10)	2888 (7)	6·04 (19)

Table 3. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2) *for* (3)

$$B_{eq} = \tfrac{8}{3}\pi^2\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ba	2237 (1)	2324 (1)	2694 (1)	2·48 (1)
O(1)	2673 (4)	120 (3)	4597 (2)	4·26 (5)
O(2)	1991 (3)	3266 (3)	4518 (2)	3·67 (4)
O(3)	1966 (3)	5413 (3)	2700 (2)	3·68 (4)
O(4)	1961 (4)	4724 (3)	875 (2)	4·78 (5)
O(5)	2909 (4)	1645 (4)	749 (2)	4·74 (5)
O(6)	5016 (3)	−369 (3)	2611 (2)	4·50 (5)
O(7)	5028 (3)	2830 (3)	2567 (3)	6·06 (6)
C(1)	2486 (7)	−1343 (6)	4790 (4)	5·80 (9)
C(2)	2413 (5)	666 (5)	5478 (3)	4·53 (6)
C(3)	2907 (5)	2027 (5)	5271 (3)	4·61 (7)
C(4)	2203 (6)	4687 (5)	4432 (3)	4·87 (8)
C(5)	1290 (5)	5895 (4)	3588 (3)	4·79 (7)
C(6)	1296 (6)	6610 (4)	1833 (4)	5·42 (8)
C(7)	2202 (7)	6078 (6)	932 (4)	6·03 (9)
C(8)	2748 (8)	4224 (7)	−15 (3)	7·15 (11)
C(9)	2310 (7)	2931 (6)	−79 (3)	6·43 (10)
C(10)	2913 (6)	205 (7)	621 (4)	5·96 (10)
S(1)	−4342 (1)	5888 (1)	2830 (1)	5·22 (2)
N(1)	−1024 (4)	4282 (5)	2834 (3)	5·91 (8)
C(11)	−2393 (4)	4945 (4)	2841 (3)	3·64 (5)
S(2)	−1829 (1)	624 (1)	1489 (1)	4·57 (2)
N(2)	443 (5)	527 (5)	2657 (3)	5·15 (7)
C(12)	−524 (4)	588 (4)	2181 (2)	3·49 (5)

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters, more complete lists of bond lengths and angles, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43742 (61 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atomic coordinates. A comparison of bond lengths and coordination distances is presented in Table 4. Bond and torsion angles of the ligands are listed in Table 5. Figs. 1, 2 and 3, depicting the numbering scheme, give for each complex a view drawn by *PLUTO* (Motherwell & Clegg, 1978). In all the structures, shortened C—C bonds and widened C—O—C bond angles are observed; these are common features of polyethers (Maverick, Seiler, Schweizer & Dunitz, 1980). For (1) and, to a lesser extent, for (2), the atoms at both ends of the glyme chain are affected by high temperature factors. This explains the abnormally short distances in these parts of the molecules.

The wrapping mode of linear polyether ligands around cations is known to depend on their lengths (Vögtle & Weber, 1979; Dale, 1980). Ligands with five heteroatoms fold in an equatorial plane around the cation, while a helical arrangement is observed with longer polyethers. The structures of all three complexes under study have indeed the expected horseshoe arrangement. The five O atoms of the glyme are coplanar within ±0·3 Å in (1) and (2), and ±0·2 Å in (3). The metal cations are only slightly out of these planes: Ca^{2+} and Sr^{2+} ~0·5 Å; Ba^{2+} ~0·2 Å.* The

Table 4. *Bond lengths and coordination distances* (Å)

	(1) M = Ca^{2+}	(2) M = Sr^{2+}	(3) M = Ba^{2+}
O(1)—C(1)	1·307 (10)	1·420 (17)	1·418 (7)
C(2)—O(1)	1·433 (8)	1·402 (15)	1·426 (5)
C(3)—C(2)	1·455 (9)	1·492 (26)	1·477 (8)
O(2)—C(3)	1·439 (5)	1·432 (12)	1·413 (4)
C(4)—O(2)	1·422 (6)	1·455 (20)	1·414 (7)
C(5)—C(4)	1·493 (7)	1·428 (16)	1·483 (5)
O(3)—C(5)	1·426 (7)	1·409 (17)	1·416 (5)
C(6)—O(3)	1·436 (5)	1·416 (12)	1·432 (5)
C(7)—C(6)	1·479 (9)	1·479 (20)	1·498 (7)
O(4)—C(7)	1·433 (6)	1·406 (18)	1·420 (7)
C(8)—O(4)	1·452 (10)	1·410 (16)	1·445 (6)
C(9)—C(8)	1·247 (12)	1·481 (33)	1·467 (11)
O(5)—C(9)	1·355 (9)	1·422 (15)	1·418 (5)
C(10)—O(5)	1·412 (8)	1·428 (21)	1·434 (8)
C(11)—S(1)	1·608 (5)	1·626 (10)	1·642 (3)
N(1)—C(11)	1·140 (6)	1·154 (14)	1·152 (4)
C(12)—S(2)	1·635 (5)	1·616 (9)	1·634 (4)
N(2)—C(12)	1·150 (6)	1·168 (11)	1·161 (5)
M···O(1)	2·503 (3)	2·627 (5)	2·862 (2)
M···O(2)	2·465 (3)	2·647 (7)	2·896 (3)
M···O(3)	2·486 (3)	2·643 (7)	2·861 (3)
M···O(4)	2·490 (3)	2·617 (6)	2·871 (2)
M···O(5)	2·487 (4)	2·652 (9)	2·901 (3)
M···N(1)	2·444 (4)	2·638 (11)	2·824 (3)
M···N(2)	2·488 (4)	2·588 (8)	2·812 (5)
M···O(6)	2·424 (3)	2·584 (6)	2·820 (2)
M···O(7)	—	—	2·739 (3)

Table 5. *Bond angles* (°) *and torsion angles* (°) ($\sigma = 2°$) *for the glyme chain in the three complexes*

	(1)	(2)	(3)
C(2)—O(1)—C(1)	117·9 (5)	110·3 (10)	111·9 (3)
C(3)—C(2)—O(1)	109·8 (4)	109·7 (9)	109·3 (3)
O(2)—C(3)—C(2)	108·4 (4)	109·2 (11)	110·3 (4)
C(4)—O(2)—C(3)	112·4 (4)	113·8 (10)	111·9 (4)
C(5)—C(4)—O(2)	107·3 (4)	109·3 (13)	108·6 (4)
O(3)—C(5)—C(4)	107·6 (4)	108·2 (10)	108·4 (3)
C(6)—O(3)—C(5)	113·6 (4)	113·8 (8)	112·1 (3)
C(7)—C(6)—O(3)	106·5 (4)	107·3 (8)	108·5 (3)
O(4)—C(7)—C(6)	108·7 (4)	110·2 (10)	109·5 (4)
C(8)—O(4)—C(7)	114·4 (4)	111·4 (11)	111·2 (4)
C(9)—C(8)—O(4)	115·8 (8)	108·8 (12)	108·2 (5)
O(5)—C(9)—C(8)	125·3 (9)	107·4 (16)	108·6 (5)
C(10)—O(5)—C(9)	108·1 (7)	112·2 (15)	112·4 (4)
N(1)—C(11)—S(1)	179·5 (4)	178·7 (8)	179·0 (4)
N(2)—C(12)—S(2)	179·5 (3)	178·2 (11)	177·7 (3)
C(1)—O(1)—C(2)—C(3)	126	173	170
O(1)—C(2)—C(3)—O(2)	58	58	61
C(2)—C(3)—O(2)—C(4)	−169	176	169
C(3)—O(2)—C(4)—C(5)	179	172	176
O(2)—C(4)—C(5)—O(3)	−59	−62	−64
C(4)—C(5)—O(3)—C(6)	−177	−174	−172
C(5)—O(3)—C(6)—C(7)	176	174	174
O(3)—C(6)—C(7)—O(4)	58	60	65
C(6)—C(7)—O(4)—C(8)	−174	−176	177
C(7)—O(4)—C(8)—C(9)	162	177	−174
O(4)—C(8)—C(9)—O(5)	−24	−61	−63
C(8)—C(9)—O(5)—C(10)	159	−163	−165

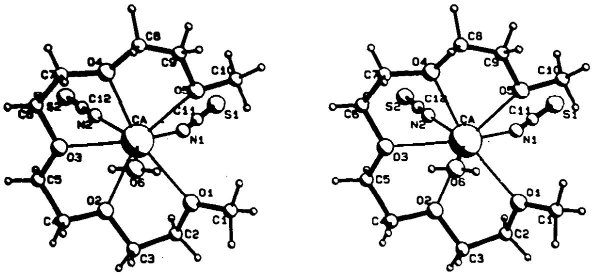

Fig. 1. View of the complex (1) with atom numbering.

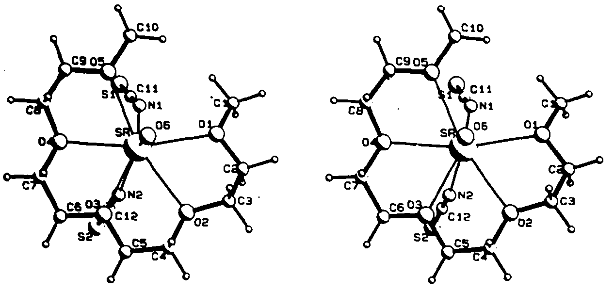

Fig. 2. View of the complex (2) with atom numbering.

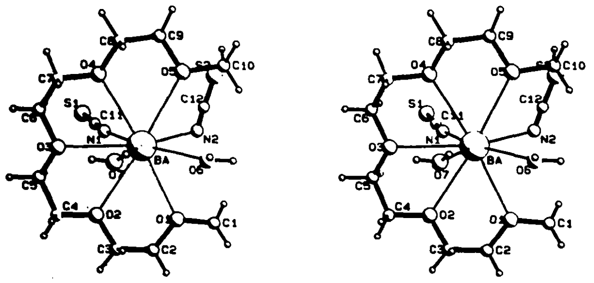

Fig. 3. View of the complex (3) with atom numbering.

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* See deposition footnote.

torsion angles in the polyether chain indicate the same sequence $ag^{+}a\ ag^{-}a\ ag^{+}a\ ag^{-}a$ in the three complexes. Moreover, with the exception of the torsion angles in the O(1)—C(2) and C(8)—C(9) bonds of (1), resulting probably from the high thermal agitation in these parts of the molecule, the numerical values are very similar in all three complexes. The sequence $ag^{\pm}a$ with alternating signs observed here is also typical of the familiar conformation of 18-crown-6 when 'equatorially' coordinated to a central cation (Dale, 1980). It is also observed in the complex of tetraethyleneglycol dimethyl ether with $HgCl_2$ (Iwamoto, 1973) and in part in 2,5,8,11,14,17,20-heptaoxahenicosane–barium thiocyanate (Weber, Hirayama, Saenger & Sheldrick, 1984).

A focal point of this study is the influence of the metal ion on the structure of the tetraglyme complexes. Ca^{2+} and Sr^{2+} cations are eightfold, Ba^{2+} ninefold coordinated; in addition to the five equatorial O atoms of the tetraglyme chain, two thiocyanate anions are coordinated through the N atom on one side of the cation, and one water molecule [two for complex (3)] on the opposite side. The coordination distances are those expected when the values of the effective ionic radii (1·12 for Ca^{2+}, 1·26 for Sr^{2+}, 1·47 Å for Ba^{2+}) are considered (Shannon, 1976). As the distances from the cation to the oxygen atoms of the glyme chain are very similar within each complex, a mean value has been calculated: for (1) Ca$^{2+}\cdots$O = 2·486 (3), for (2) Sr$^{2+}\cdots$O = 2·637 (6) and for (3) Ba$^{2+}\cdots$O = 2·878 (3) Å. For this latter complex, the observed Ba$^{2+}\cdots$O distances are longer than observed for hexaglyme barium thiocyanate while the Ba$^{2+}\cdots$N distances are similar (Weber *et al.*, 1984). The ideal conformation of the tetraglyme chain places the O atoms on five of the corners of a regular hexagon, the remaining corner being empty and the metal cation being located at the centre of the hexagon. The degree of opening or closing of this horseshoe depends on the size of the cation. For the Ca^{2+} complex, the O$\cdots$O distances range from 2·698 (8) to 2·734 (8) Å with O(1)$\cdots$O(5) = 3·502 (8) Å. The O$\cdots$O distances are longer in the Sr^{2+} complex (2) ranging from 2·729 (10) to 2·761 (10) Å with O(1)$\cdots$O(5) = 4·111 (10) Å as a result of the longer Sr$^{2+}\cdots$O distances. In these two structures, the coordination distances are too short to allow the glyme chain in the above depicted ideal conformation: the chain folds more tightly, and the tightest folding is observed for (1). Actually, in the case of Ca^{2+}, the terminal methyl groups come so close that both terminal monomer units have to adopt unusual, but different, torsion angles (Table 5), whereby the ligand loses the approximate symmetry plane observed with Sr^{2+} and Ba^{2+} (Table 5). For the Ba^{2+} complex, (3), the O$\cdots$O distances range from 2·766 (5) to 2·823 (5) Å with O(1)$\cdots$O(5) = 5·172 (6) Å. As the Ba$^{2+}\cdots$O distances are only slightly greater than the O$\cdots$O distances, the oxygen atoms of the glyme now almost coincide with the corners of a regular hexagon, which of course requires equal distances for $M\cdots$O and O$\cdots$O. Fig. 4 shows the mean O$\cdots$O distance observed in the three complexes as a function of the mean coordination distance. It can be seen that a perfect hexagon can be expected for a coordination distance of 2·78 Å. For those complexes that lie under the 'perfect hexagon' line, the coordination distance is too short to allow the positioning of a sixth oxygen atom. As a consequence it can be predicted that pentaglyme or 18-crown-6 Ca^{2+} and Sr^{2+} complexes will not adopt a circular conformation with the cation at the centre, whereas this possibility exists for Ba^{2+} complexed with 18-crown-6.

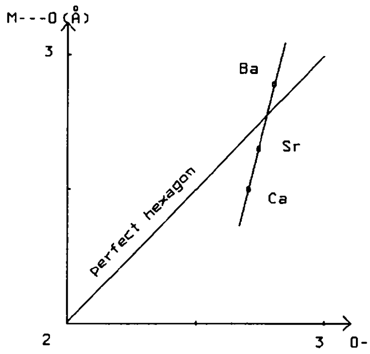

Fig. 4. O$\cdots$O and coordination distances in the three complexes.

There are no obvious linkages between the complex units in any of the three structures.

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Oligoether Complexes of Alkaline-Earth Metal Ions. II. Structures of 2,5,8,11-Tetraoxadodecane ('Triglyme') Complexed With Calcium and Strontium Thiocyanates

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Abstract. (1) 2,5,8,11-Tetraoxadodecane–calcium thiocyanate monohydrate, $[Ca(SCN)_2(C_8H_{18}O_4)].H_2O$, $M_r = 352{\cdot}49$, monoclinic, $P2_1/n$, $a = 14{\cdot}672\,(10)$, $b = 16{\cdot}306\,(8)$, $c = 7{\cdot}286\,(2)$ Å, $\beta = 92{\cdot}89\,(4)°$, $V = 1741\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}35$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 5{\cdot}97$ cm^{-1}, $F(000) = 744$, $T = 291$ K, $R = 0{\cdot}048$ for 1474 reflections. (2) 2,5,8,11-Tetraoxadodecane–strontium thiocyanate dihydrate, $[Sr(SCN)_2(C_8H_{18}O_4)].2H_2O$, $M_r = 418{\cdot}04$, monoclinic, $P2_1/c$, $a = 7{\cdot}608\,(6)$, $b = 13{\cdot}612\,(14)$, $c = 17{\cdot}393\,(39)$ Å, $\beta = 93{\cdot}46\,(14)°$, $V = 1798\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}54$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 33{\cdot}79$ cm^{-1}, $F(000) = 856$, $T = 291$ K, $R = 0{\cdot}058$ for 1339 reflections. The two triglyme complexes are very different. In the Ca^{2+} complex, the triglyme chain is equatorially coordinated in the familiar, loosely coiled conformation characterized by $ag^{\pm}a$ units with CC *gauche* bonds of alternating sign. In the Sr^{2+} complex, the chain is tightly folded so as to coordinate entirely from one side. The conformation of the triglyme chain contains two $ag^{\pm}g^{\pm}$ units, and all *gauche* bonds are of the same sign.

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 ^{13}C 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 the first paper we reported the structures of 2,5,8,11,14-pentaoxapentadecane ('tetraglyme') complexed with Ca, Sr and Ba thiocyanates (Wei, Tinant, Declercq, Van Meerssche & Dale, 1987*a*). Here we report the structures of the complexes of triglyme with calcium thiocyanate monohydrate (1) and strontium thiocyanate dihydrate (2).

Experimental. Crystals obtained by slow evaporation from (1) acetone, (2) ethyl acetate–acetone 1:1. Crystal sizes: (1) 0·15 × 0·15 × 0·20 mm, (2) 0·06 × 0·08 × 0·20 mm. Lattice parameters refined using 15 reflections in the range $5 \leq 2\theta \leq 20°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, ω scan, scan width 1·3°, scan rate 1·3–30° min^{-1} $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}561$ Å^{-1}. For (1) 2570 $h\ k\ \pm l$ independent reflections measured ($0 \leq h \leq 16$, $0 \leq k \leq 18$, $-8 \leq l \leq 8$), 1474 observed [criterion $I \geq 2{\cdot}5\sigma(I)$]. For (2) 2671 $h\ k\ \pm l$ measured ($0 \leq h \leq 8$, $0 \leq k \leq 15$, $-18 \leq l \leq 18$), 1339 observed. Standard reflections: one standard reflection [202 for (1), $21\bar{2}$ for (2)] checked every 50 reflections for each measurement: no significant deviation. Absorption correction: none for (1), numerical corrections for crystal defined by its faces for (2) using *SHELX*76 (Sheldrick, 1976). Max./min. transmission: 0·829 and 0·757.

Structure solution: in both structures the position of the cation was found from an $E \times F$ Patterson map (*SHELX*84; Sheldrick, 1984) and the positions of the remaining non-H atoms from subsequent difference Fourier synthesis. Anisotropic least-squares refinement with *SHELX*76 (Sheldrick, 1976) on *F*. Hydrogen atoms [except H of the water molecule in (1) located

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