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Oligoether Complexes of Alkaline-Earth Metal Ions. V. Structure of 2,5,8,11,14,17,20,23-Octaoxatetraicosane ('Heptaglyme') Complexed with Barium Thiocyanate

By Yun Yi Wei, Bernard Tinant, Jean-Paul Declercq and Maurice Van Meerssche

Laboratoire de Chimie physique et de Cristallographie, Université de Louvain, place Louis Pasteur, 1, 1348 *Louvain-la-Neuve, Belgium*

and Johannes Dale

Kjemisk Institutt, Universitetet i Oslo, Oslo 3, *Norway*

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Abstract. 2,5,8,11,14,17,20,23-Octaoxatetraicosane–barium thiocyanate (1/1), $C_{16}H_{34}O_8.Ba(SCN)_2$, $M_r = 607{\cdot}94$, monoclinic, $P2_1/n$, $a = 9{\cdot}321\,(4)$, $b = 23{\cdot}552\,(17)$, $c = 12{\cdot}467\,(9)$ Å, $\beta = 95{\cdot}08\,(5)°$, $V = 2726\,(3)$ Å^3, $Z = 4$, $D_x = 1{\cdot}48$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 16{\cdot}87$ cm^{-1}, $F(000) = 1232$, $T = 291$ K, final $R = 0{\cdot}051$ for 2840 observed reflections. The coordination number of Ba is ten, all eight O atoms of the glyme and two thiocynates being coordinated. The anions are in a perpendicular *trans* arrangement. The conformation of the polyether chain is characterized by having only $ag^{\pm}a$ units with CC *gauche* bonds of alternating sign and normal torsion-angle values.

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). 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. The structures of tri-, tetra-, penta- and hexaglyme complexed with Ca, Sr and Ba thiocyanates have already been reported (Wei, Tinant, Declercq, Van Meerssche & Dale, 1987*a,b,c,d*). In continuation of this work we report here the structure of the anhydrous complex of 2,5,8,11,14,17,20,23-octaoxatetraicosane ('heptaglyme') with barium thiocyanate.

Experimental. Crystal of dimensions $0{\cdot}352 \times 0{\cdot}160 \times 0{\cdot}144$ mm grown from acetone/ethyl acetate. Lattice parameters refined using 15 reflections in the range $5 < 2\theta < 15°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω scan, scan width 1·3°, scan rate 1·3–30° min^{-1}. 4784 independent reflections collected up to $(\sin\theta)/\lambda = 0{\cdot}595$ Å^{-1}; $0 \leq h \leq 11$, $0 \leq k \leq 27$, $-14 \leq l \leq 14$. No significant decline in intensity of a standard reflection (221). Numerical absorption corrections for crystal defined by its faces using *SHELX*76 (Sheldrick, 1976); max./min. transmission: 0·821 and 0·784. 2840 reflections with $I \geq 2{\cdot}5\sigma(I)$. Structure solved first by location of the Ba^{2+} position from a Patterson map and then direct methods [*SHELX*84 (Sheldrick, 1984) and *DIRDIF*81 (Beurskens *et al.*, 1981)]. Anisotropic least-squares refinement with *SHELX*76 (Sheldrick, 1976) on *F*. H atoms included in idealized positions (C—H = 1·08 Å, H—C—H = 109·5°). 283 LS parameters. $R = 0{\cdot}051$, $wR = 0{\cdot}056$, $w^{-1} = \sigma^2(F) + 0{\cdot}00237F^2$, $S = 1{\cdot}15$. Max. $\Delta/\sigma = 0{\cdot}23$ [*z* of atom C(7)], largest peak 0·98 e Å^{-3} (close to Ba^{2+}), largest hole 1·25 e Å^{-3} in final map. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are given in Table 1.* Bond lengths and coordination distances are presented in Table 2, and bond and torsion angles in the polyether are listed in Table 3. Figs. 1 and 2 are top and side views respectively of the complex depicting the numbering scheme.

The coordination number of the Ba^{2+} cation is ten; in addition to the eightfold coordination of the cation to all the ether O atoms, two thiocyanates are coordinated in a perpendicular *trans* arrangement, one above and one below the polyether. The mean distances $Ba^{2+}\cdots O = 2{\cdot}904\,(8)$ and $Ba^{2+}\cdots N = 2{\cdot}794\,(9)$ Å are similar to those observed for the complex of hexaglyme with $Ba(SCN)_2$ (Weber, Hirayama, Saenger & Sheldrick, 1984), but the coordination geometry is different. In this latter complex the two anions are on the same side with regard to the chain.

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* 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 43867 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Glyme ligands containing more than six O atoms are for steric reasons too long to fold in a planar circular or horseshoe arrangement around Ba (Wei *et al.*, 1987*c*,*d*). Thus, only the first six ether O atoms of the hexaglyme chain are roughly coplanar with Ba, the end of the chain forming a helical structure initiated by one 'genuine corner' in the fifth unit: ag^+a ag^-a ag^+a ag^-a ag^+g^+ ag^+a (Weber *et al.*, 1984; Dale, 1980). Surprisingly, the structure of the present heptaglyme–$Ba(SCN)_2$ complex reveals the conformational sequence ag^+a ag^-a ag^+a ag^-a ag^+a ag^-a ag^+a (Table 3) with the regular sign alternation expected ideally to produce an 18-crown-6 ring structure and then repeat itself in the last unit. The same sequence of torsion angles was also observed for one of the two complexed molecules present in the asymmetric unit of the hexaglyme–$Sr(SCN)_2$ complex. In both cases the steric

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic temperature factors* (Å²)

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

	x	*y*	*z*	B_{eq}
Ba	379 (1)	1279 (1)	2422 (1)	4·23 (1)
O(1)	3133 (9)	1280 (3)	3750 (7)	7·7 (2)
O(2)	3080 (9)	1240 (3)	1478 (7)	7·4 (2)
O(3)	590 (11)	1111 (3)	127 (6)	7·8 (2)
O(4)	−1586 (9)	561 (3)	1049 (6)	6·8 (2)
O(5)	−1935 (8)	651 (3)	3244 (7)	6·5 (2)
O(6)	−357 (10)	1378 (4)	4606 (6)	7·8 (2)
O(7)	759 (10)	2317 (3)	3635 (7)	7·9 (2)
O(8)	1012 (9)	2393 (3)	1490 (7)	7·4 (2)
C(1)	3276 (15)	970 (6)	4723 (10)	9·0 (4)
C(2)	4422 (13)	1261 (6)	3182 (12)	8·5 (3)
C(3)	4144 (14)	1537 (6)	2061 (12)	8·6 (4)
C(4)	3003 (16)	1359 (6)	342 (11)	8·8 (4)
C(5)	1929 (15)	994 (6)	−239 (11)	8·9 (4)
C(6)	−533 (16)	810 (6)	−503 (10)	9·1 (4)
C(7)	−1869 (16)	822 (6)	41 (10)	10·0 (4)
C(8)	−2864 (13)	392 (6)	1538 (11)	8·0 (3)
C(9)	−2428 (14)	181 (5)	2643 (11)	8·0 (3)
C(10)	−1607 (15)	518 (6)	4362 (11)	8·8 (4)
C(11)	−1435 (15)	1043 (6)	4960 (10)	8·8 (4)
C(12)	−367 (16)	1924 (7)	5103 (12)	10·8 (5)
C(13)	753 (18)	2275 (6)	4734 (10)	10·6 (5)
C(14)	1528 (19)	2752 (6)	3203 (13)	10·9 (5)
C(15)	1061 (19)	2873 (5)	2107 (13)	11·5 (5)
C(16)	254 (18)	2542 (6)	471 (12)	10·1 (5)
S(1)	3777 (4)	−538 (1)	2775 (3)	7·5 (1)
S(2)	−3422 (5)	2844 (2)	2793 (4)	10·7 (1)
C(17)	2366 (12)	−126 (4)	2757 (8)	5·3 (2)
C(18)	−2667 (12)	2285 (5)	2325 (9)	6·1 (3)
N(1)	1363 (11)	162 (4)	2739 (9)	7·3 (2)
N(2)	−2137 (10)	1907 (4)	1980 (8)	7·0 (2)

Table 2. *Bond and coordination distances* (Å)

C(1)—O(1)	1·41 (1)	C(9)—C(8)	1·49 (2)
C(2)—O(1)	1·45 (2)	C(11)—C(10)	1·44 (1)
C(3)—O(2)	1·37 (1)	C(13)—C(12)	1·44 (1)
C(4)—O(2)	1·44 (1)	C(15)—C(14)	1·42 (1)
C(5)—O(3)	1·39 (1)	C(17)—S(1)	1·63 (1)
C(6)—O(3)	1·44 (1)	C(18)—S(2)	1·62 (1)
C(7)—O(4)	1·40 (1)	N(1)—C(17)	1·15 (1)
C(8)—O(4)	1·44 (1)	N(2)—C(18)	1·12 (1)
C(9)—O(5)	1·39 (1)		
C(10)—O(5)	1·44 (1)	N(1)···Ba	2·803 (8)
C(11)—O(6)	1·38 (1)	N(2)···Ba	2·785 (9)
C(12)—O(6)	1·43 (2)	O(1)···Ba	2·929 (7)
C(13)—O(7)	1·37 (1)	O(2)···Ba	2·873 (8)
C(14)—O(7)	1·39 (2)	O(3)···Ba	2·912 (8)
C(15)—O(8)	1·37 (1)	O(4)···Ba	2·930 (7)
C(16)—O(8)	1·44 (1)	O(5)···Ba	2·878 (7)
C(3)—C(2)	1·54 (2)	O(6)···Ba	2·876 (8)
C(5)—C(4)	1·46 (1)	O(7)···Ba	2·880 (7)
C(7)—C(6)	1·47 (1)	O(8)···Ba	2·951 (7)

Table 3. *Bond angles* (°) *and torsion angles* (°) ($\sigma \simeq 3°$) *in the polyether chain*

C(1)—O(1)—C(2)	113 (1)	C(1)—O(1)—C(2)—C(3)	173
O(1)—C(2)—C(3)	110 (1)	O(1)—C(2)—C(3)—O(2)	−61
C(2)—C(3)—O(2)	109 (1)	C(4)—O(2)—C(3)—C(2)	−164
C(3)—O(2)—C(4)	113 (1)	C(3)—O(2)—C(4)—C(5)	175
O(2)—C(4)—C(5)	110 (1)	O(2)—C(4)—C(5)—O(3)	62
C(4)—C(5)—O(3)	108 (1)	C(6)—O(3)—C(5)—C(4)	173
C(5)—O(3)—C(6)	111 (1)	C(5)—O(3)—C(6)—C(7)	166
O(3)—C(6)—C(7)	110 (1)	O(3)—C(6)—C(7)—O(4)	−60
C(6)—C(7)—O(4)	108 (1)	C(8)—O(4)—C(7)—C(6)	−163
C(7)—O(4)—C(8)	114 (1)	C(7)—O(4)—C(8)—C(9)	−174
O(4)—C(8)—C(9)	108 (1)	O(4)—C(8)—C(9)—O(5)	69
N(1)—C(17)—S(1)	179 (1)	C(10)—O(5)—C(9)—C(8)	174
C(8)—C(9)—O(5)	106 (1)	C(9)—O(5)—C(10)—C(11)	−167
C(9)—O(5)—C(10)	112 (1)	O(5)—C(10)—C(11)—O(6)	−59
O(5)—C(10)—C(11)	108 (1)	C(12)—O(6)—C(11)—C(10)	171
C(10)—C(11)—O(6)	112 (1)	C(11)—O(6)—C(12)—C(13)	180
C(11)—O(6)—C(12)	110 (1)	O(6)—C(12)—C(13)—O(7)	52
O(6)—C(12)—C(13)	110 (1)	C(14)—O(7)—C(13)—C(12)	163
C(12)—C(13)—O(7)	115 (1)	C(13)—O(7)—C(14)—C(15)	−159
C(13)—O(7)—C(14)	119 (1)	O(7)—C(14)—C(15)—O(8)	−52
O(7)—C(14)—C(15)	113 (1)	C(16)—O(8)—C(15)—C(14)	168
C(14)—C(15)—O(8)	111 (1)		
C(15)—O(8)—C(16)	107 (1)		
N(2)—C(18)—S(2)	178 (1)		

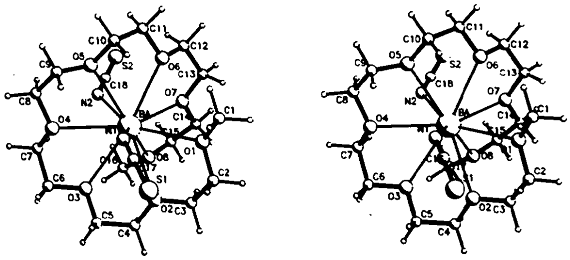

Fig. 1. Stereoscopic view of the complex with atom numbering (*PLUTO*, Motherwell & Clegg, 1978).

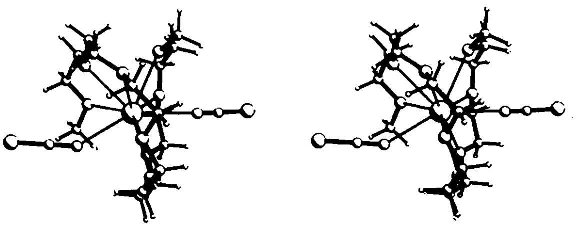

Fig. 2. Side view of the complex (*PLUTO*, Motherwell & Clegg, 1978).

conflict between the ends of the chain is nevertheless well avoided by deviations from the ideal torsion angles 60 and 180° in every unit. In the complex described here, the four central O atoms [O(3), O(4), O(5), O(6)] are coplanar within 0·06 Å, the Ba cation lying only 0·10 Å out of the same plane. The two O atoms at one end of the chain [O(1) and O(2)] are above this plane by 1·97 and 1·53 Å; those at the other end [O(7) and O(8)] are below the plane by 1·26 and 1·71 Å. In this arrangement the distance between O(1) and O(7) is 3·29 Å, and between O(8) and O(2) 3·33 Å. As a consequence of this wrapping mode for both ends of the chain, the thiocyanate anions are no longer perfectly *trans* in apical positions.

The approximate twofold symmetry axis of the heptaglyme ligand, the *trans* arrangement of the anions, and the absence of coordinated water molecules, is reminiscent of the pentaglyme–$Ca(SCN)_2$ complex (Wei *et al.*, 1987*c*). Also in the pentaglyme complex the four O atoms that are coplanar with the cation are symmetrically located, implying an $ag^{\pm}a$ conformation with sign alternation in the three central units. Because of the need to fold more sharply onto the smaller Ca cation, both outer units deviate from this scheme both in torsion-angle sign and their numerical values.

There are no obvious linkages between the complex units.

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Platinum(II) Halide Complexes with Thiocarbamic Esters. Structure of *trans*-Bis[*O*-ethyl (*N*-ethyl)thiocarbamate]diiodoplatinum(II), $[Pt(ETC)_2I_2]$

BY R. BARDI* AND A. M. PIAZZESI

Biopolymer Research Centre, CNR, University of Padua, Via Marzolo 1, 35100 *Padua, Italy*

A. DEL PRA

Istituto Chimico Farmaceutico, University of Milan, Viale Abruzzi 42, 20131 *Milan, Italy*

AND L. TRINCIA†

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, University of Padua, Via Loredan 4,
35100 *Padua, Italy*

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Abstract. $[PtI_2(C_5H_{11}NOS)_2]$, $M_r = 715{\cdot}3$, monoclinic, $C2/c$, $a = 11{\cdot}232\,(3)$, $b = 14{\cdot}987\,(3)$, $c = 11{\cdot}306\,(3)$ Å, $\beta = 93{\cdot}3\,(1)°$, $V = 1900\,(8)$ Å^3, $Z = 4$, $D_m = 2{\cdot}50$, $D_x = 2{\cdot}501$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 108{\cdot}9$ cm^{-1}, $F(000) = 1312$, $T = 297$ K, final $R = 0{\cdot}0346$ ($wR = 0{\cdot}0341$), 1593 unique reflections. The complex exhibits square-planar geometry about the metal atom. The thiocarbamic group is planar and is tilted 80·3 (3)° to the coordination plane. The Pt—S distance [2·314 (4) Å] is significantly shorter than the sum

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* To whom correspondence should be addressed.

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