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Crown Ether Complexes of Alkaline-Earth Metal Ions. II. Structures of 1,4,7,10,13-Pentaoxacyclopentadecane (15-Crown-5) Complexed with Calcium and Magnesium Thiocyanates

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Abstract. (1): 1,4,7,10,13-Pentaoxacyclopentadecane–calcium thiocyanate monohydrate, $C_{10}H_{20}O_5.Ca(SCN)_2.H_2O$, $M_r = 394.52$, monoclinic, $P2_1/c$, $a = 15.515$ (4), $b = 8.574$ (3), $c = 14.282$ (3) Å, $\beta = 102.12$ (2)°, $V = 1857.5$ (9) Å^3, $Z = 4$, $D_x = 1.41$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 5.70$ cm^{-1}, $F(000) = 832$, $T = 291$ K, $R = 0.037$ for 2352 observed reflections. (2): 1,4,7,10,13-Pentaoxacyclopentadecane–magnesium thiocyanate, $C_{10}H_{20}O_5.Mg(SCN)_2$, $M_r = 360.74$, triclinic, $P1$, $a = 16.037$ (8), $b = 7.161$ (4), $c = 8.415$ (6) Å, $\alpha = 105.26$ (5), $\beta = 74.67$ (5), $\gamma = 103.61$ (4)°, $V = 884.8$ (8) Å^3, $Z = 2$, $D_x = 1.35$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71069$ Å, $\mu = 3.52$ cm^{-1}, $F(000) = 380$, $T = 291$ K, $R = 0.093$ for 2838 observed reflections. The two complexes are different; only the smaller Mg^{2+} cation fits into the cavity of the macrocycle. In (1) the eightfold coordination of the Ca^{2+} cation includes the five ether O atoms, two thiocyanate N and the O of the water molecule; an unusual triangular conformation of the macrocycle is observed. For the Mg^{2+} complex, the coordination polyhedron is a regular pentagonal bipyramid in both independent complex subunits. The two 15-crown-5 rings have different conformations, both flattened and difficult to classify.

Introduction. As part of a systematic analysis of the structures of crown ethers complexed with alkaline-earth thiocyanates (Wei, Tinant, Declercq, Van Meerssche & Dale, 1988*a*) we report here the structures of two new 15-crown-5 compounds: the monohydrated $C_{10}H_{20}O_5.Ca(SCN)_2$ (1) and the anhydrous $C_{10}H_{20}O_5.Mg(SCN)_2$ (2) complexes.

Experimental. Crystals obtained by slow evaporation from acetone/acetonitrile 1:1 (1), water (2). Crystal sizes: (1) 0.15 × 0.15 × 0.20, (2) 0.54 × 0.85 × 0.73 mm. Lattice parameters refined using 15 reflections in the range $5 \leq 2\theta \leq 25°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω scan, scan width 1.3 (1), 1.5° (2), scan rate 1.3–30 (1), 1.5–30° min^{-1} (2), $[(\sin\theta)/\lambda]_{max} = 0.561$ (1), 0.650 Å^{-1}(2). For (1) 2744 independent $hk\pm l$ reflections measured ($0 \leq h \leq 17$, $0 \leq k \leq 9$, $-16 \leq l \leq 15$), 2352 observed [criterion $I \geq 2.5\sigma(I)$]. For (2) 4063 $h\pm k\pm l$ measured ($0 \leq h \leq 20$,

$-9 \leq k \leq 8$, $-9 \leq l \leq 10$), 2838 observed. Standard reflections $5\bar{3}\bar{2}$ (1) and 231 (2) checked every 50 reflections: no significant deviation. No correction for absorption. Structure solution: position of the Ca cation (1), Mg and S atoms (2) from an $E \times F$ Patterson map (*SHELXS*86, Sheldrick, 1985); the remaining non-H atoms from *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, Van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981) for (1), difference Fourier synthesis (*SHELX*76, Sheldrick, 1976) for (2). Attempts to refine (2) in $P\bar{1}$ were unsuccessful: the Mg^{2+} and thiocyanate ions and even the O atoms of the crowns are perfectly related by an inversion centre. On the other hand, during the centrosymmetric trials two distinct positions appeared for the atoms C(3) and C(10) and high temperature factors were observed for the other C atoms. This could be due to a positional disorder, in which case the same duplication should appear in $P1$. In fact, in this space group only one position was detected for C(3) and C(10) in the two independent molecules and for this reason $P1$ was definitely selected as the correct space group. Anisotropic least-squares refinement (*SHELX*76) using F. (1): all H atoms located from a difference Fourier synthesis, refined with common isotropic temperature factor; (2): all H atoms included in the refinement in idealized positions (C—H = 1·08 Å, H—C—H = 109·4°). 275 (1) and 397 (2) LS parameters. Weighting scheme $w = [\sigma^2(F) + gF^2]^{-1}$; $g = 0.00026$ (1) and 0·00068 (2). (1) $R = 0.037$, $wR = 0.043$, $S = 3.68$ for 2352 observed reflections. (2) $R = 0.093$, $wR = 0.117$, $S = 3.97$ for 2838 observed reflections. $(\Delta/\sigma)_{max}$ in final refinement cycle: (1) 0·08 [x of atom C(10)], (2) 1·06 [x of atom C(6B)]. Max. and min. heights in final Fourier synthesis 0·63, −0·29 (1), 0·96, −0·36 e Å^{-3} (2). The high value of the R index in (2) is due to the poor quality of crystals. 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 while bond and torsion angles in the macrocycles are listed in Table 4.

As can be seen from the stereoscopic views of each compound (Figs. 1 and 2) the geometry of the two complexes is very different. This is not surprising since it can be expected that only the smaller Mg^{2+} ion (effective ionic radii of Ca^{2+} 1·12 Å, of Mg^{2+} 0·72 Å)

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

$$B_{eq} = \tfrac{4}{3}\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq}
Ca	2267 (1)	1723 (1)	865 (1)	2·65 (1)
S(1)	288 (1)	5002 (1)	−1842 (1)	4·37 (2)
S(2)	3795 (1)	6925 (1)	660 (1)	5·48 (2)
O(1)	3315 (1)	1181 (2)	2494 (1)	4·30 (4)
O(2)	3861 (1)	1095 (3)	817 (2)	4·34 (4)
O(3)	2600 (2)	1203 (3)	−762 (1)	4·65 (4)
O(4)	1273 (1)	−263 (2)	−108 (1)	4·11 (4)
O(5)	2008 (1)	−765 (2)	1721 (1)	3·83 (4)
O(6)	1159 (2)	2247 (3)	1715 (2)	4·42 (5)
C(1)	4184 (2)	643 (5)	2467 (3)	5·68 (8)
C(2)	4476 (2)	1482 (5)	1676 (4)	6·11 (8)
C(3)	4070 (3)	1618 (5)	−71 (4)	6·36 (9)
C(4)	3460 (3)	809 (5)	−853 (3)	5·84 (8)
C(5)	1891 (3)	340 (5)	−1397 (2)	5·98 (8)
C(6)	1584 (3)	−972 (5)	−878 (3)	5·68 (8)
C(7)	871 (3)	−1381 (5)	451 (3)	6·16 (8)
C(8)	1519 (2)	−2027 (4)	1224 (3)	4·84 (7)
C(9)	2532 (3)	−1210 (4)	2620 (3)	5·16 (7)
C(10)	2907 (3)	247 (5)	3117 (3)	5·42 (8)
C(11)	832 (2)	4115 (3)	−880 (2)	3·31 (5)
C(12)	3333 (2)	5346 (3)	954 (2)	3·73 (5)
N(2)	3004 (2)	4237 (3)	1165 (2)	5·70 (6)
N(1)	1224 (2)	3454 (3)	−228 (2)	4·94 (6)

(Shannon, 1976) can fit into the cavity of 15-crown-5 of approximate diameter 1·7–1·8 Å (Hilgenfeld & Saenger, 1982).

In complex (1), the Ca^{2+} cation has an irregular eight coordination which includes the five ether O atoms, two N of the thiocyanate anions and the O of the water molecule. The ether O atoms are located at the corners of a nearly regular skew pentagon; O···O distances range from 2·657 (2) to 2·738 (2) Å and the deviations from the mean plane through the five O atoms from 0·118 to 0·437 Å. The cation lies 1·189 Å out of this plane. This geometry is very similar to that observed for the complex of benzo-15-crown-5 with $Ca(SCN)_2.H_2O$ (Owen, 1978). Also the coordination distances are similar in both complexes, the average Ca···O values being 2·540 (2) Å as compared to 2·529 (9) Å in the benzo-15-crown-5 complex. However, the conformation of the macrocycle observed here is uncommon. The sequence of torsion angles $ag^{\mp}a$ $ag^{\mp}a$ $g^{\mp}g^{\mp}a$ $g^{\mp}g^{\mp}a$ $ag^{\pm}g^{\pm}$* indicates a triangular [348] conformation with C(5), C(7) and C(10) as corner atoms. To our knowledge, only quinquangular [33333] or [23343] conformations, the former with five $ag^{\pm}g^{\pm}$ units, as observed for the sandwich-type complex with $BaBr_2$ (Feneau-Dupont, Arte, Declercq, Germain & Van Meerssche, 1979), and a uniangular conformation, as observed for the $NaSCN.\frac{1}{2}H_2O$ complex (Groth, 1981), have been reported for 15-crown-5. In the complex of 15-crown-5 with $CuCl_2$ a uniangular conformation was also observed for the macrocycle, but the ether O atoms are not here directly coordinated to the cation (Arte,

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* $g^+ = 0$ to $120°$, $g^- = 0$ to $-120°$, $a = \pm 120$ to $\pm 180°$.

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

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

	Molecule A				Molecule B			
	x	y	z	B_{eq}	x	y	z	B_{eq}
Mg	0	0	0	3·75 (3)	5021 (2)	9890 (3)	10094 (3)	3·50 (3)
S(1)	−1560 (2)	−4930 (4)	−3856 (3)	6·70 (3)	3379 (2)	4963 (4)	6359 (3)	6·33 (3)
S(2)	1653 (2)	4889 (4)	3750 (3)	5·94 (3)	6593 (2)	14844 (4)	13966 (3)	5·57 (3)
N(1)	−639 (5)	−2342 (8)	−1502 (7)	6·12 (3)	4384 (4)	7532 (7)	8567 (7)	4·99 (3)
N(2)	659 (4)	2331 (7)	1593 (7)	4·80 (3)	5666 (4)	12255 (7)	11704 (7)	4·59 (3)
C(11)	−1067 (4)	−3482 (7)	−2487 (7)	3·44 (3)	3947 (4)	6444 (7)	7655 (7)	3·00 (3)
C(12)	1029 (5)	3371 (8)	2512 (8)	5·10 (3)	6010 (5)	13279 (8)	12647 (7)	4·58 (3)
O(1)	1040 (4)	−1629 (7)	−191 (7)	6·68 (3)	3976 (4)	11439 (7)	10306 (6)	5·27 (3)
O(2)	−396 (4)	−1572 (7)	2063 (7)	5·75 (3)	5437 (4)	11421 (7)	8030 (6)	6·19 (3)
O(3)	−1271 (4)	660 (7)	1448 (7)	6·27 (3)	6354 (4)	9395 (7)	8704 (7)	6·28 (3)
O(4)	−338 (5)	2207 (8)	−1070 (7)	7·15 (3)	5349 (4)	7731 (6)	11126 (6)	5·62 (3)
O(5)	987 (5)	521 (8)	−2193 (7)	7·79 (3)	4032 (5)	9548 (7)	12426 (7)	7·10 (3)
C(1)	850 (6)	−2930 (9)	837 (8)	7·30 (3)	4081 (6)	12644 (9)	9237 (9)	7·98 (3)
C(2)	239 (6)	−2267 (9)	2434 (8)	7·24 (3)	4893 (6)	12602 (9)	7922 (8)	6·48 (3)
C(3)	−1042 (6)	−773 (9)	3351 (9)	8·19 (3)	6281 (6)	11650 (9)	7167 (8)	6·33 (3)
C(4)	−1608 (7)	159 (9)	2967 (8)	7·79 (3)	6666 (6)	9955 (9)	7166 (8)	7·07 (3)
C(5)	−1516 (6)	2367 (9)	1425 (8)	6·90 (3)	6620 (6)	7849 (9)	9059 (9)	7·60 (3)
C(6)	−1199 (6)	2464 (9)	−412 (8)	6·73 (3)	6258 (6)	7590 (9)	10792 (8)	7·40 (3)
C(7)	156 (6)	2317 (9)	−2669 (8)	7·20 (3)	5039 (6)	7851 (9)	12859 (8)	6·90 (3)
C(8)	1050 (6)	2055 (9)	−2937 (8)	6·58 (3)	4112 (6)	8253 (9)	13287 (9)	7·89 (3)
C(9)	1776 (6)	−117 (9)	−2581 (8)	7·37 (3)	3280 (6)	10288 (9)	12660 (9)	8·35 (3)
C(10)	1798 (7)	−1272 (9)	−1367 (9)	9·44 (3)	3493 (6)	12002 (9)	11937 (8)	6·82 (3)

Table 3. *Bond lengths and coordination distances* (Å)

	(1) $M=\text{Ca}^{2+}$	(2) $M=\text{Mg}^{2+}$	
		Molecule A	Molecule B
C(1)—O(1)	1·433 (4)	1·363 (9)	1·357 (10)
C(10)—O(1)	1·439 (4)	1·369 (10)	1·393 (8)
C(2)—O(2)	1·427 (5)	1·368 (12)	1·382 (11)
C(3)—O(2)	1·444 (5)	1·391 (9)	1·352 (10)
C(4)—O(3)	1·409 (4)	1·356 (9)	1·387 (9)
C(5)—O(3)	1·470 (5)	1·375 (10)	1·400 (11)
C(6)—O(4)	1·426 (4)	1·382 (11)	1·432 (11)
C(7)—O(4)	1·468 (4)	1·381 (9)	1·397 (8)
C(8)—O(5)	1·424 (4)	1·373 (10)	1·364 (11)
C(9)—O(5)	1·420 (4)	1·376 (12)	1·377 (12)
C(2)—C(1)	1·487 (6)	1·476 (10)	1·470 (11)
C(4)—C(3)	1·476 (6)	1·388 (15)	1·485 (12)
C(6)—C(5)	1·480 (6)	1·509 (10)	1·464 (10)
C(8)—C(7)	1·438 (5)	1·441 (13)	1·512 (14)
C(10)—C(9)	1·494 (6)	1·485 (12)	1·442 (10)
N(1)—C(11)	1·149 (4)	1·227 (9)	1·183 (8)
N(2)—C(12)	1·148 (4)	1·113 (9)	1·099 (8)
C(11)—S(1)	1·641 (5)	1·579 (6)	1·614 (6)
C(12)—S(2)	1·628 (3)	1·646 (7)	1·663 (7)
O(1)···M	2·585 (2)	2·200 (7)	2·165 (7)
O(2)···M	2·546 (2)	2·189 (6)	2·170 (6)
O(3)···M	2·524 (2)	2·168 (6)	2·208 (7)
O(4)···M	2·512 (2)	2·239 (7)	2·179 (7)
O(5)···M	2·532 (2)	2·142 (6)	2·202 (4)
O(6)w···M	2·347 (2)	—	—
N(1)···M	2·490 (3)	2·054 (6)	2·071 (6)
N(2)···M	2·435 (3)	2·107 (5)	2·117 (6)

Table 4. *Bond angles* (°) *and torsion angles* (°) [$\sigma = 1°$ *for* (1) *and* 3° *for* (2)] *in* 15-crown-5

	(1)	(2)	
		Molecule A	Molecule B
C(10)—O(1)—C(1)	112·1 (3)	126·9 (8)	116·6 (6)
C(3)—O(2)—C(2)	116·8 (3)	120·2 (6)	119·2 (6)
C(5)—O(3)—C(4)	115·0 (3)	111·1 (6)	122·4 (6)
C(7)—O(4)—C(6)	113·1 (3)	127·9 (8)	105·6 (7)
C(9)—O(5)—C(8)	113·0 (2)	111·2 (6)	124·3 (6)
C(2)—C(1)—O(1)	107·6 (3)	111·2 (6)	113·9 (8)
C(1)—C(2)—O(2)	106·6 (3)	108·0 (7)	114·9 (6)
C(4)—C(3)—O(2)	107·0 (3)	119·3 (7)	108·8 (6)
C(3)—C(4)—O(3)	106·7 (3)	110·8 (7)	110·4 (6)
C(6)—C(5)—O(3)	110·6 (3)	102·0 (5)	113·5 (6)
C(5)—C(6)—O(4)	105·0 (3)	113·8 (8)	105·4 (8)
C(8)—C(7)—O(4)	111·1 (3)	114·1 (8)	106·8 (7)
C(7)—C(8)—O(5)	107·7 (3)	104·5 (6)	111·9 (6)
C(10)—C(9)—O(5)	107·2 (3)	110·9 (6)	109·3 (7)
C(9)—C(10)—O(1)	110·4 (3)	116·6 (9)	105·7 (5)
C(10)—O(1)—C(1)—C(2)	170	151	151
O(1)—C(1)—C(2)—O(2)	−60	43	−3
C(1)—C(2)—O(2)—C(3)	−172	−177	−164
C(2)—O(2)—C(3)—C(4)	168	172	−167
O(2)—C(3)—C(4)—O(3)	58	−19	−38
C(3)—C(4)—O(3)—C(5)	−172	−147	−179
C(4)—O(3)—C(5)—C(6)	99	−172	176
O(3)—C(5)—C(6)—O(4)	60	−50	45
C(5)—C(6)—O(4)—C(7)	175	−176	−169
C(6)—O(4)—C(7)—C(8)	89	178	173
O(4)—C(7)—C(8)—O(5)	50	43	−40
C(7)—C(8)—O(5)—C(9)	167	170	−175
C(8)—O(5)—C(9)—C(10)	−172	161	163
O(5)—C(9)—C(10)—O(1)	−50	5	50
C(9)—C(10)—O(1)—C(1)	−81	167	165

Feneau-Dupont, Declercq, Germain & Van Meerssche, 1979). As will be discussed below, the conformations of the two independent 15-crown-5 molecules of the Mg(SCN)_2 complex are also very different from that of the Ca(SCN)_2 complex.

The structure of the Mg(SCN)_2 complex (2) offers the opportunity to compare the two independent complex subunits. At first sight they do not appear to differ very much. In both subunits the coordination polyhedron is a regular pentagonal bipyramid with the N atoms of the anions in axial positions (Table 3). The O···O ether oxygen distances range from 2·531 (9) to 2·596 (8) Å with an average value of 2·574 (7) Å for

molecule A and from 2·538 (8) to 2·609 (8) Å with an average of 2·575 (8) Å for B.

The ether O atoms are coplanar in each macrocycle and the Mg^{2+} cation lies only 0·02 Å out of the mean planes (Roberts & Sheldrick, 1975). The coordination distances [average value 2·188 (6) Å for A, 2·185 (6) Å for B] are as expected from the ionic radii. This complex bears a striking resemblance to that of
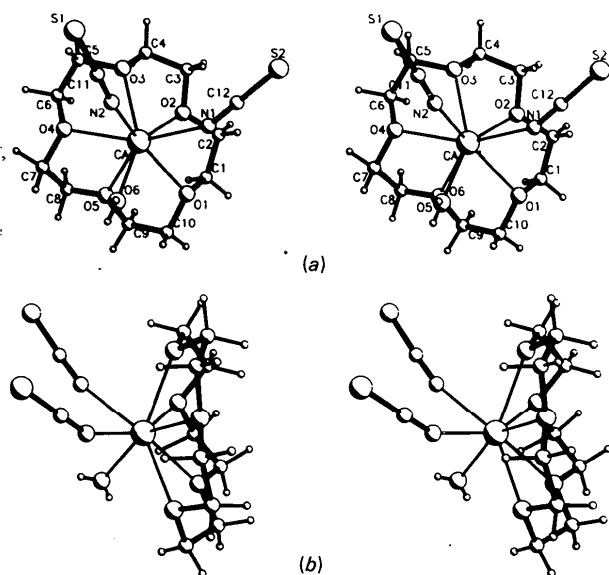

Fig. 1. Stereoscopic views of (1): (a) top view and atom numbering, (b) side view (*PLUTO*, Motherwell & Clegg, 1978).

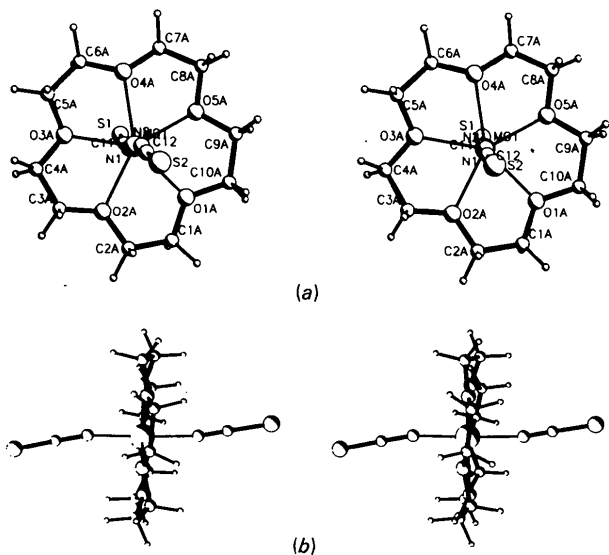
Fig. 2. Stereoscopic views of (2) (molecule A): (a) top view and atom numbering, (b) side view (*PLUTO*, Motherwell & Clegg, 1978).

benzo-15-crown-5 with $Mg(SCN)_2$ (Owen, 1978). It is noteworthy that only 15-crown-5 is able to complex the Mg^{2+} cation directly, presumably because its diameter matches the cavity size. In the 12-crown-4.$MgCl_2$ (Neuman, Steiner, van Remoortere & Boer, 1975) and 18-crown-6.$Mg(SCN)_2$ (Wei, Tinant, Declercq, Van Meerssche & Dale, 1988b) complexes the Mg^{2+} cation forms a hydrate which is held in the lattice by hydrogen bonds to the crown ether.

What is different between the two subunits A and B is the conformation of the macrocycle as expressed by the exact positions of the CH_2 C atoms. For both rings the torsion-angle sequence is characterized by only $ag^\pm a$ units, i.e. without any corner.

If all bonds had been kept close to staggered (± 60 or 180°), such a sequence would not be expected for topological reasons to close a ring structure with an odd number of ring atoms unless one of the *anti* bonds were changed into *gauche* to produce a corner, resulting then in a uniangular conformation (Dale, 1976). Actually, in subunit B one bond [C(1)–C(2)] is practically eclipsed (−3°), and this conformation can be viewed as a transition state in the interconversion between two uniangular conformations having their single corner at C(1) and C(2) respectively (Dale, 1976). The remaining four *gauche* bonds have the expected sign alternation. In benzo-15-crown-5 the eclipsed position is of course imposed by the aromatic unit, and this will then be the stable conformation not only in its Mg^{2+} complex, as observed by Owen (1978), but also in the free ligand. In subunit A the situation is further complicated by the presence of two nearly eclipsed bonds [C(9)–C(10) and C(3)–C(4)], and in the longer chain between them the two *gauche* bonds show the expected sign alternation.

There are no obvious linkages between the complex units in either of the two compounds.

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Crown Ether Complexes of Alkaline-Earth Metal Ions. III. Structures of 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-Crown-6) Complexed with Magnesium and Barium Thiocyanates

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Abstract. (1): 1,4,7,10,13,16-Hexaoxacyclooctadecane–magnesium thiocyanate tetrahydrate, $C_{12}H_{24}O_6.Mg(SCN)_2.4H_2O$, $M_r = 476.85$, orthorhombic, $Pna2_1$, $a = 9.225$ (2), $b = 19.256$ (7), $c = 13.267$ (4) Å, $V = 2357$ (1) Å^3, $Z = 4$, $D_x = 1.34$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 2.99$ cm^{-1}, $F(000) = 1016$, $T = 291$ K, $R = 0.041$ for 1279 observed reflections. (2): 1,4,7,10,13,16-Hexaoxacyclooctadecane–barium thiocyanate monohydrate, $C_{12}H_{24}O_6.Ba(SCN)_2.H_2O$, $M_r = 535.84$, monoclinic, $P2_1$, $a = 8.030$ (3), $b = 17.304$ (11), $c = 8.551$ (7) Å, $\beta = 110.78$ (5)°, $V = 1111$ (1) Å^3, $Z = 2$, $D_x = 1.60$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 20.55$ cm^{-1}, $F(000) = 536$, $T = 291$ K, $R = 0.021$ for 1582 observed reflections. The Mg^{2+} ion is not bonded directly to the ether O atoms, but complex (1) involves Mg(SCN)$_2$.4H$_2$O units that are hydrogen-bonded through the water molecules to the O atoms of the crown ether. The Ba^{2+} ion is coordinated to the six O atoms of the crown ether, to the two N atoms of the anions on one side and to the O of the water molecule on the opposite side. The cation is displaced 0.59 Å from the mean plane of the hexaether. In both molecular (1) and ionic (2) complexes the 18-crown-6 possesses approximate D_{3d} symmetry.

Introduction. As part of a systematic analysis of the structures of crown ethers complexed with alkaline-earth thiocyanates (Wei, Tinant, Declercq, Van

Meerssche & Dale, 1988), we report here the structures of two new 18-crown-6 compounds: the tetrahydrated $C_{12}H_{24}O_6.Mg(SCN)_2$ (1) and the monohydrated $C_{12}H_{24}O_6.Ba(SCN)_2$ complexes.

Experimental. Both crystals obtained by slow evaporation from water. Crystal sizes: (1) 0.30 × 0.15 × 0.20, (2) 0.288 × 0.160 × 0.144 mm. Lattice parameters refined using 15 reflections in the range $5 \le 2\theta \le 25°$. Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω scan width 1.3°, scan rate 1.3–30° min^{-1}, $[(\sin\theta)/\lambda]_{max} = 0.561$ Å^{-1}. For (1) 1648 independent hkl reflections measured ($0 \le h \le 10$, $0 \le k \le 21$, $0 \le l \le 14$), 1279 observed [criterion $I \ge 2.5\sigma(I)$]. For (2) 1700 $hk\pm l$ measured ($0 \le h \le 9$, $0 \le k \le 19$, $-9 \le l \le 8$), 1582 observed. Standard reflections 062 (1) and 24$\bar{3}$ (2) checked every 50 reflections: no significant deviation. Absorption corrections: none for (1), numerical corrections for crystal defined by its faces for (2) using *SHELX*76 (Sheldrick, 1976); max./min. transmission 0.817, 0.704. Structure solution: position of Mg and S atoms (1), Ba (2) from an $E \times F$ Patterson map (*SHELXS*86, Sheldrick, 1985); the remaining non-H atoms from *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, Van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). Anisotropic least-squares refinement (*SHELX*76, Sheldrick, 1976) using *F*. H atoms of three water molecules in (1) and of the crown ether except