

Fig. 2. Dessin de la structure vue selon [001]. Les traits les plus fins représentent les liaisons hydrogène.

Rodier, 1987), ses homologues mesurent, l'un 30,8 (3), l'autre 38,4 (3)°. En première approximation, le plan PtCl(1)C(3) [plan *P*(III)] est plan de symétrie pour le cycle et, par suite, pour le cation. En effet, N(1)N(5) et C(2)C(4) sont sensiblement perpendiculaires à *P*(III) car les angles que font les plans *P*(I), *P*(II) et C(2)C(3)C(4) avec *P*(III) valent respectivement 89,9(1), 89,9(1) et 89,4(2)°. En outre, les distances à *P*(III) des atomes qui se correspondent à travers ce plan diffèrent de moins de 0,2 Å. Il en résulte que le cation n'est pas très éloigné de la symétrie *C*_{2h}. Les liaisons C–N et C–C ont des longueurs voisines de celles de leurs homologues respectives dans le chlorure de propanediammonium-1,3 (Brisson & Brisse, 1981) ou dans le chlorure de bis(propanediamine-1,3)platine(II) déjà cité.

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Crown Ether Complexes of Alkaline-Earth Metal Ions. I. Structures of 1,4,7,10-Tetraoxacyclododecane (12-Crown-4) Complexed with Calcium, Strontium and Barium Thiocyanates

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Abstract. (1): 1,4,7,10-Tetraoxacyclododecane–calcium thiocyanate dihydrate, C₈H₁₆O₄·Ca(SCN)₂·2H₂O, *M_r* = 368.49, orthorhombic, *Pbc*2₁, *a* = 7.505 (2), *b* = 16.580 (14), *c* = 40.262 (23) Å, *V* = 5010 (5) Å³, *Z*

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Chacun des anions Cl[−] a pour voisins immédiats quatre molécules d'eau et deux cations auxquels il est uni par des liaisons hydrogène O–H...Cl et N–H...Cl. Chaque molécule d'eau participe à la réalisation de deux liaisons O–H...Cl et d'une liaison N–H...O. Les longueurs et les angles des liaisons hydrogène sont rapportées dans le Tableau 2; les liaisons hydrogène sont représentées dans le dessin de la structure vue selon [001] (Fig. 2).

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= 12, *D_x* = 1.47 g cm^{−3}, λ(Mo Kα) = 0.71069 Å, μ = 6.30 cm^{−1}, *F*(000) = 2328, *T* = 291 K, *R* = 0.064 for 2539 observed reflections. (2): 1,4,7,10-Tetraoxacyclododecane–strontium thiocyanate dihydrate,

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(2). The remaining two O and two N atoms in the coordination polyhedron belong respectively to water molecules and thiocyanate anions. The Ba²⁺ ion with coordination number ten is sandwiched between two polyether rings. Two thiocyanate anions coordinated on one side of the complex complete the coordination polyhedron. In all three complexes, the crown ether exhibits a conformation of approximate C₄ symmetry.

Introduction. The complexation of linear and cyclic polyethers ('glymes' and 'crown ethers') with alkali and alkaline-earth salts can be conveniently studied by simple titration monitored by ¹³C NMR spectroscopy. The chemical shift of each C atom is very sensitive to the conformational changes that take place going from the free ligand to the complexed ligand (Dale, 1980). To be able to interpret the shift displacement in terms of conformational changes, it is necessary to have as references accurately known crystal structures of both the free ligands and of complexes. The alkaline-earth thiocyanate complexes turned out to be particularly favourable, as they had sufficient solubility and were easy to obtain in the crystalline form (Yanagida, Takahashi & Okahara, 1978; Dale, Krane & Thomassen, 1984).

In preceding papers we have described 11 X-ray structures of the glyme complexes of Ca, Sr and Ba thiocyanates (Wei, Tinant, Declercq, Van Meerssche & Dale, 1987*a-e*) and we now report the structures of some crown ethers complexed with the same alkaline-earth metal ions. In this first communication three new complexes of 12-crown-4 are described: the dihydrated isomorphous 1:1 calcium and strontium thiocyanate complexes, (1) and (2), and the anhydrous 2:1 barium thiocyanate complex, (3).

Experimental. Crystals obtained by slow evaporation from water/ethanol for (1) and (2), water for (3). Crystal sizes: (1) 0.15 × 0.15 × 0.20, (2) 0.197 × 0.148 × 0.234, (3) 0.272 × 0.240 × 0.240 mm. Lattice parameters refined using 15 (1), 24 (2) and 15 (3) reflections in the range 5 ≤ 2θ ≤ 30°. For (1) and (3) Syntex P2₁ diffractometer, graphite-monochromatized Mo Kα radiation, ω scan, scan width 1.3°, scan rate 1.3–30° min⁻¹, [(sinθ)/λ]_{max} = 0.561 Å⁻¹. For (2) Huber four-circle diffractometer, graphite-monochromatized Cu Kα radiation, θ/2θ scan, scan width 2.2° + 0.4° tanθ, scan rate 2–20° min⁻¹, [(sinθ)/λ]_{max} = 0.60 Å⁻¹. For (1) 3779 independent *hkl* reflections measured (0 ≤ *h* ≤ 8, 0 ≤ *k* ≤ 18, 0 ≤ *l* ≤ 44), 2539 observed [criterion *I* ≥ 2.5σ(*I*)]. For (2) 4747 *hkl* measured (0 ≤ *h* ≤ 9, 0 ≤ *k* ≤ 19, 0 ≤ *l* ≤ 48), 4078 observed. For (3) 1872 *hk+l* measured (0 ≤ *h* ≤ 12, 0 ≤ *k* ≤ 16, -16 ≤ *l* ≤ 16), 1732 observed. Standard reflections 329 (1), 213 (2) and 441 (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: 0.456, 0.336 (2); 0.696, 0.658 (3). The structures of (1) and (3) were solved first by locating the cation [and S atom in (1)] from an *E* × *F* Patterson map and then applying direct methods on the unknown part of the structure using *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, Van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981); structure of (2) is isomorphous with that of (1). Anisotropic [block cascade for (1) and (2)] least-squares refinement with *SHELX76* (Sheldrick, 1976) on *F*. For (1) and (2) one of the three independent crown ethers (labelled *A*) was disordered; O and C atoms of this ring were refined isotropically with constrained O–C and C–C distances. Only for complex (2) was the disorder solved: two positions for O and C atoms with occupation factors 0.5 were refined. Six H atoms belonging to water molecules of (1) were located on a difference Fourier synthesis; all H atoms of the crown ether rings were calculated with C–H = 1.08 Å, H–C–H = 109.5°. 588 (1), 558 (2) and 283 (3) LS parameters. Weights *w* = [σ²(*F*) + *gF*²]⁻¹; *g* = 0.00035 (1), 0.01155 (2) and 0.0019 (3). (1) *R* = 0.064, *wR* = 0.058, *S* = 3.71 for 2539 observed reflections. (2) *R* = 0.054, *wR* = 0.062, *S* = 0.71 for 4078 observed reflections. (3) *R* = 0.030, *wR* = 0.034, *S* = 1.02 for 1732 observed reflections. (*Δ*/σ)_{max} in final refinement cycle: (1) 0.39 [*z* of atom C(6*B*)], (2) 1.15 [*U*₁₃ of atom C(6*C*)], (3) 0.62 [*x* of atom C(5*B*)]. Max. and min. heights in final Fourier synthesis 0.63, -0.29 (1), 1.64, -1.46 (2), 0.61, -0.39 e Å⁻³ (3) (largest peak close to the cation). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters for the three structures are given in Tables 1–3.* Stereoscopic views of each complex depicting the atom-numbering scheme are presented in Figs. 1–3 (program *PLUTO*, Motherwell & Clegg, 1978). The structures of (1) and (2) are isomorphous and each have three independent complex subunits, labelled *A*, *B* and *C*, in the asymmetric part of the unit cell. In both cases one of the crown ethers (*A*) was disordered, but only for (2) was it possible to distinguish its two positions. As a consequence, the geometrical parameters of the polyether rings are poorly determined and a relatively large dispersion of individual bond lengths and angles is observed. The weighted average values in each ring for

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles and mean-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44394 (64 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)
$$B_{eq} = \frac{1}{3} \pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B_{eq}
Ba	0	515 (1)	0	3.0 (1)
S(1)	-179 (5)	3642 (4)	2051 (3)	5.8 (1)
S(2)	230 (5)	3616 (4)	-2042 (3)	5.8 (1)
N(1)	-559 (11)	2029 (9)	1069 (9)	6.9 (1)
N(2)	628 (10)	2010 (7)	-1041 (7)	4.6 (1)
O(1A)	-1015 (8)	185 (7)	-1757 (7)	6.7 (1)
O(2A)	-1009 (7)	-1277 (6)	-606 (5)	5.4 (1)
O(3A)	-2194 (8)	-243 (6)	644 (6)	7.1 (1)
O(4A)	-2346 (7)	1207 (7)	-623 (6)	6.3 (1)
C(1A)	-867 (9)	-816 (7)	-1947 (8)	6.4 (1)
C(2A)	-1515 (9)	-1480 (7)	-1431 (6)	6.0 (1)
C(3A)	-1713 (8)	-1690 (7)	69 (7)	5.6 (1)
C(4A)	-2706 (9)	-1083 (7)	267 (8)	7.0 (1)
C(5A)	-3053 (8)	526 (6)	568 (6)	4.9 (1)
C(6A)	-3384 (8)	793 (9)	-334 (6)	6.2 (1)
C(7A)	-2338 (7)	1389 (6)	-1561 (5)	4.8 (1)
C(8A)	-2155 (9)	517 (7)	-2018 (7)	6.1 (1)
C(9)	-447 (10)	2686 (6)	1505 (8)	4.2 (1)
C(10)	410 (10)	2695 (7)	-1414 (7)	4.1 (1)
O(1B)	1202 (7)	387 (5)	1700 (6)	4.9 (1)
O(2B)	2404 (8)	1085 (7)	429 (5)	5.8 (1)
O(3B)	2058 (7)	-466 (6)	-571 (6)	6.1 (1)
O(4B)	898 (10)	-1221 (8)	773 (8)	8.6 (1)
C(1B)	2085 (10)	1132 (11)	1857 (10)	9.7 (1)
C(2B)	3034 (9)	1046 (9)	1260 (8)	6.8 (1)
C(3B)	3184 (12)	805 (9)	-270 (12)	9.0 (1)
C(4B)	3198 (12)	-195 (10)	-492 (11)	10.1 (1)
C(5B)	2019 (14)	-1526 (10)	-387 (7)	10.9 (1)
C(6B)	1931 (12)	-1609 (9)	558 (7)	8.1 (1)
C(7B)	795 (13)	-1174 (10)	1755 (8)	9.6 (1)
C(8B)	1567 (11)	-443 (6)	2136 (7)	6.4 (1)

C—C [1.471 (22), 1.481 (13), 1.470 (3) Å] and C—O [1.441 (9), 1.424 (10), 1.448 (14) Å] distances and for C—C—O [109.6 (8), 110.7 (8), 108.3 (12)°] and C—O—C [114.4 (9), 113.1 (6), 111.6 (9)°] bond angles compare quite well with those reported for other 12-crown-4 metal-ion complexes (North, Steiner, van Remoortere & Boer, 1976).

The complexes of Ca^{2+} (1) and Sr^{2+} (2) are very similar and have a structure that is completely different from that observed for the Ba^{2+} complex (3). Only one crown is coordinated to the cation in (1) and (2), while a sandwich-type 2:1 complex is observed for (3).

In each of the three independent complex subunits of (1) and (2), the cation is eightfold coordinated in an approximate square antiprismatic geometry. The four coplanar ether O atoms form a square with average O...O distances of 2.71 (2) Å in (1) and 2.75 (1) Å in (2). Two O atoms belonging to the water molecules and the two N atoms of the thiocyanate anions are located approximately on the apices of the second square with side 3.00 (2) and 3.20 (2) Å respectively for (1) and (2). The cation is located ~ 1.6 Å (Ca^{2+}) or 1.8 Å (Sr^{2+}) above the mean plane of the ether O atoms. The coordination distances are compared in Table 4. The mean values of the distances between the cation and the O atoms of the polyether are respectively 2.526 (12) Å for (1) and 2.641 (8) Å for (2). These values are those expected when the effective ionic radii (1.12 Å for Ca^{2+} , 1.26 Å for Sr^{2+}) are considered (Shannon, 1976). The average Ca...O distance is similar to that observed for the 12-crown-4.CaCl₂,

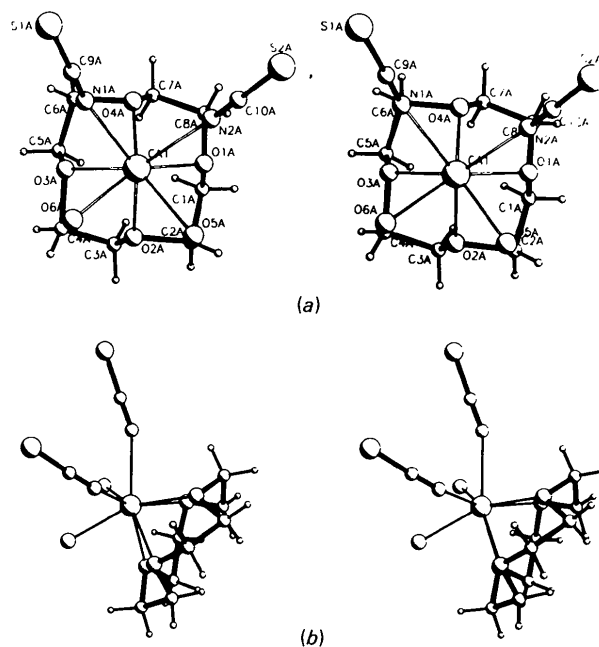


Fig. 1. Stereoscopic views of complex (1) (molecule A): (a) top view and atom numbering, (b) side view.

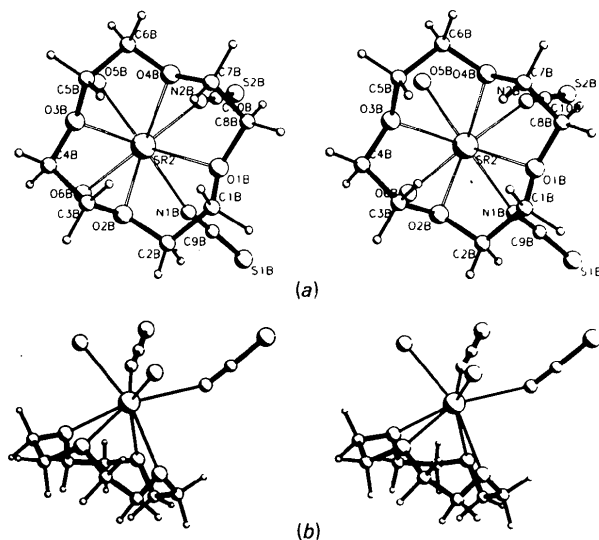


Fig. 2. Stereoscopic views of complex (2) (molecule B): (a) top view and atom numbering, (b) side view.

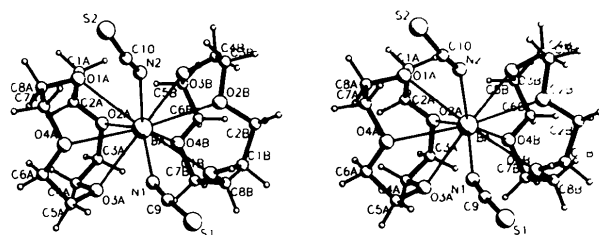


Fig. 3. Stereoscopic view of complex (3) and atom numbering.

Table 4. Coordination distances (Å)

	(1) M = Ca			(2) M = Sr				(3) M = Ba	
	A	B	C	A	A'	B	C		
M ²⁺ ...N(1)	2.512 (11)	2.505 (11)	2.481 (11)	2.621 (10)	—	2.630 (10)	2.618 (8)	2.823 (11)	
M ²⁺ ...N(2)	2.509 (10)	2.470 (11)	2.483 (10)	2.639 (8)	—	2.632 (8)	2.629 (9)	2.798 (8)	
M ²⁺ ...O(1)	2.526 (12)	2.551 (7)	2.552 (9)	2.668 (13)	2.593 (12)	2.670 (5)	2.677 (7)	2.931 (9)	2.899 (8)
M ²⁺ ...O(2)	2.469 (15)	2.502 (8)	2.529 (9)	2.583 (11)	2.620 (11)	2.603 (6)	2.647 (7)	2.935 (8)	2.892 (9)
M ²⁺ ...O(3)	2.495 (15)	2.581 (8)	2.528 (10)	2.673 (13)	2.669 (12)	2.659 (6)	2.615 (7)	2.954 (9)	2.916 (8)
M ²⁺ ...O(4)	2.434 (13)	2.530 (8)	2.490 (9)	2.632 (12)	2.656 (13)	2.649 (6)	2.608 (7)	2.952 (8)	2.910 (10)
M ²⁺ ...O(5)(w)	2.417 (8)	2.374 (9)	2.408 (9)	2.522 (6)	—	2.551 (8)	2.547 (8)	—	—
M ²⁺ ...O(6)(w)	2.373 (9)	2.410 (8)	2.420 (9)	2.501 (6)	—	2.535 (6)	2.571 (6)	—	—

Table 5. Torsion angles (°) in the polyether ring ($\sigma = 3^\circ$)

	(1)			(2)				(3)	
	A	B	C	A	A'	B	C	A	B
C(8)—O(1)—C(1)—C(2)	-169	162	-158	-75	-163	162	-154	-70	84
O(1)—C(1)—C(2) O(2)	64	-56	46	-61	60	-55	46	-62	57
C(1)—C(2)—O(2)—C(3)	88	-84	89	169	80	-82	89	166	-168
C(2)—O(2)—C(3)—C(4)	-170	175	-168	-80	-158	170	-160	-84	90
O(2)—C(3)—C(4)—O(3)	57	-58	55	-60	48	-59	47	-66	47
C(3)—C(4)—O(3)—C(5)	86	-81	92	164	92	-83	95	159	-154
C(4)—O(3)—C(5)—C(6)	-169	160	-161	-87	-172	161	-155	-64	89
O(3)—C(5)—C(6) O(4)	62	-55	49	-49	66	-52	44	-69	64
C(5)—C(6)—O(4)—C(7)	84	-82	87	165	77	-86	93	169	-174
C(6)—O(4)—C(7)—C(8)	-165	171	-163	-83	-166	169	-162	-76	73
O(4)—C(7)—C(8)—O(1)	55	-56	46	-65	51	-58	42	-65	57
C(7)—C(8)—O(1)—C(1)	81	-85	97	169	84	-82	99	162	-166

complex (2.525 Å) (North *et al.*, 1976) and the average Sr...O distance is comparable to that observed in the triglyme.Sr(SCN)₂ complex [2.660 (8) Å] (Wei *et al.*, 1987*b*), these two complexes also having a square antiprismatic geometry. As can be seen from the torsion-angle values listed in Table 5, the 12-crown-4 ring adopts a conformation of approximate C₄ symmetry (torsion-angle sequence $ag^\pm g^\pm ag^\pm g^\pm ag^\pm g^\pm ag^\pm g^\pm$) in all three independent subunits of both complexes. This quadrangular [3333] conformation is also the most stable one for cyclododecane itself (Anet, Cheng & Wagner, 1972), and it is the most common one for 12-crown-4 metal-ion complexes, having been observed for complexes with NaCl, NaOH, LiSCN and CaCl₂ (van Remoortere & Boer, 1974; Boer, Neuman, van Remoortere & Steiner, 1974; Groth, 1981; North *et al.*, 1976).

In the case of the anhydrous Ba(SCN)₂ complex (3), the Ba²⁺ cation is tenfold coordinated. The cation is sandwiched between two 12-crown-4 rings which are not parallel. The tilt allows the two anions to be attached from the same side, thus completing the coordination polyhedron. The four ether O atoms within each ring are coplanar, the maximum deviation from the mean plane through O(1)O(2)O(3)O(4) being 0.054 Å in crown A and 0.028 Å in crown B. The cation is located at an equal distance (2.17 Å) from each plane. In this configuration the SCN and the ether O atoms of each crown are related by a twofold axis passing through the Ba²⁺ and oriented along **b**. However, the C atoms do not respect this symmetry element as the two quadrangular ring conformations have opposite chirality, all eight *gauche* angles being positive in one ring and negative in the other (Table 5); space group C₂/c is thereby excluded. The mean planes through the ether O atoms of A and B form a dihedral

angle of 43° (Roberts & Sheldrick, 1975) so that the distance O(2A)...O(4B) is very short [2.95 (1) Å]. The Ba...O coordination distances [mean value 2.924 (8) Å] are slightly longer than usual, as shown by comparison with the value 2.904 (8) Å observed in the heptaglyme complex with the same coordination number for Ba (Wei *et al.*, 1987*e*); this indicates a less tight folding for the sandwich structure described here.

It is remarkable that the 12-crown-4 conformation stays practically unchanged in the nine independent molecules reported here, although they interact with cations of three different sizes (Table 5). The averaged values for the torsion angles of the 'monomer' unit are: in the Ca²⁺ complex (1) $\mp 166, \pm 55, \pm 86^\circ$; in the Sr²⁺ complex (2) $\mp 164, \pm 54, \pm 85^\circ$; and in the Ba²⁺ complex (3) $\mp 165, \pm 61, \pm 79$. As always, the COCC *gauche* angle is much wider than the adjacent OCCO *gauche* angle.

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

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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, $C_{10}H_{20}O_5 \cdot Ca(SCN)_2 \cdot H_2O$, $M_r = 394.52$, 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) Å³, $Z = 4$, $D_x = 1.41$ 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, $C_{10}H_{20}O_5 \cdot Mg(SCN)_2$, $M_r = 360.74$, 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) Å³, $Z = 2$, $D_x = 1.35$ 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, 1988a) we report here the structures of two new 15-crown-5 compounds: the monohydrated $C_{10}H_{20}O_5 \cdot Ca(SCN)_2$ (1) and the anhydrous $C_{10}H_{20}O_5 \cdot Mg(SCN)_2$ (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 $5 \leq 2\theta \leq 25^\circ$. 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 ($0 \leq h \leq 20$,