Crystal Structures of the Benzo-15-crown-5 Complexes Diisothiocyanato(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin)-magnesium, -calcium–Methanol (1/1), and -calcium Hydrate

By **John D. Owen**, Molecular Structures Department, Rothamsted Experimental Station, Harpenden, Herts AL5 2JQ

The crystal structures of the three title complexes of ' benzo-15-crown-5 ' with $Mg[NCS]_2$, $Ca[NCS]_2{\cdot}MeOH$, and $Ca[NCS]_2{\cdot}H_2O$ have been determined by direct methods from diffractometer data collected with molybdenum radiation. The magnesium complex crystallises in the orthorhombic space group *Pbca* with cell dimensions $a = 16.399(3)$, $b = 25.784(5)$, $c = 9.230(3)$ Å, and $Z = 8$. The structure has been refined to R 0.064 for 1 022 observations. The co-ordination of the cation is a pentagonal bipyramid with the nitrogen atoms of the anions in axial positions. The methanol complex with calcium isothiocyanate crystallises in the triclinic space group $P\bar{1}$, with cell dimensions $a = 8.665(2)$, $b = 11.155(2)$, $c = 11.942(3)$ Å, $\alpha = 95.49(1)$, $\beta = 102.21(2)$, $\gamma = 102.47(2)°$, and $Z = 2$. The final R factor is 0.081 for 4 244 observations. The calcium ion has irregular eight-co-ordination which includes the five ether oxygens, the two isothiocyanate nitrogens, and the oxygen atom of the methanol molecule. The analogous water complex crystallises in the monoclinic space group $P2_1/c$ with cell dimensions $a = 11.248(5)$, $b = 12.929(7)$, $c = 17.100(7)$ Å, $\beta = 123.15(2)°$, and $Z = 4$. The final R factor is 0.048 for 704 observations. The co-ordination of the cation is identical with that of the methanol complex with the water oxygen replacing the methanol oxygen atom. The same conformation for the crown ether is found in both the calcium complexes, indicating that intramolecular, not intermolecular or packing, forces decide the conformation.

ALKALINE-EARTH metal cations are known to form complexes with crown ethers,[1] and the stoicheiometry depends on the radius of the cation. Thus with 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (benzo-15-crown-5) magnesium forms only a 1 : 1 complex, calcium (like sodium) forms both 1 : 1 and 2 : 1 complexes, and the larger cations form only 2 : 1 ether : metal salt complexes. Sodium[2] and calcium[3] (having similar ionic radii) show different conformations of the ether in their 1 : 1 complexes, indicating that the ether conformation may be sensitive to the charge on the cation.

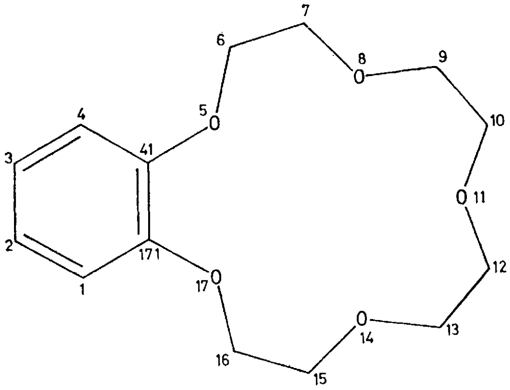

FIGURE 1 Numbering scheme for the ether atoms

This paper describes the structures of the complexes of benzo-15-crown-5 with $Mg[NCS]_2$ (1), $Ca[NCS]_2{\cdot}MeOH$ (2), and $Ca[NCS]_2{\cdot}H_2O$ (3). A preliminary report on the structures of the calcium complexes has already appeared.[3] Intensity data were collected on two four-circle diffractometers and the structures solved by direct methods and refined by the usual full-matrix least-squares techniques. Final atomic parameters are given in Tables 1—3 and bond lengths and selected bond angles in Tables 4 and 5. The atom-numbering scheme for the ether rings is shown in Figure 1. The isothiocyanate atoms are numbered 18—23 and the solvent atoms 24 and 25 where present. Hydrogen atoms are numbered according to the carbon atom to which they are bonded. Thus H(151) and H(152) are bonded to atom C(15).

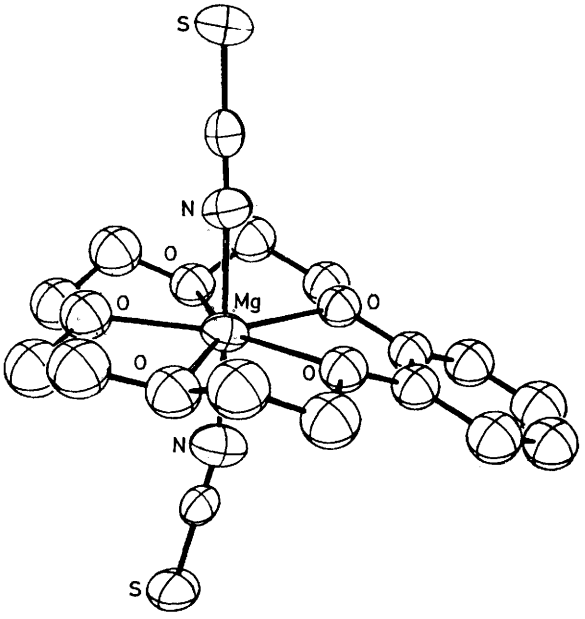

FIGURE 2 Molecule of (1) showing the 50% thermal ellipsoids

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[1] (*a*) C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017; (*b*) D. G. Parsons, M. R. Truter, and J. N. Wingfield, *Inorg. Chim. Acta*, 1975, **14**, 45; (*c*) D. G. Parsons and J. N. Wingfield, *ibid.*, 1976, **18**, 263.

[2] M. A. Bush and M. R. Truter, *J.C.S. Perkin II*, 1972, 341.

[3] J. D. Owen and J. N. Wingfield, *J.C.S. Chem. Comm.*, 1976, 318.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) for (1)

Atom	*x*	*y*	*z*
Mg	1 734(2)	1 167(1)	4 341(3)
S(18)	3 211(2)	1 407(1)	−102(3)
C(19)	2 618(6)	1 350(4)	1 319(13)
N(20)	2 220(6)	1 316(4)	2 327(11)
S(21)	526(2)	616(1)	8 868(3)
C(22)	971(6)	834(4)	7 396(13)
N(23)	1 267(5)	991(3)	6 357(10)
C(1)	790(6)	2 762(4)	3 474(12)
C(2)	179(7)	2 889(4)	2 566(13)
C(3)	−344(7)	2 550(5)	1 964(13)
C(4)	−248(6)	2 030(4)	2 264(12)
C(41)	362(6)	1 876(4)	3 174(11)
O(5)	504(4)	1 364(2)	3 582(7)
C(6)	64(6)	965(4)	2 834(12)
C(7)	330(6)	468(4)	3 517(11)
O(8)	1 194(4)	464(2)	3 451(7)
C(9)	1 546(7)	−2(4)	4 005(12)
C(10)	2 437(7)	73(5)	3 971(12)
O(11)	2 580(4)	535(2)	4 766(7)
C(12)	3 398(7)	695(5)	4 958(13)
C(13)	3 367(7)	1 161(5)	5 870(13)
O(14)	2 833(4)	1 517(3)	5 213(7)
C(15)	2 678(7)	1 978(4)	6 033(13)
C(16)	2 152(6)	2 312(4)	5 157(12)
O(17)	1 470(4)	1 997(2)	4 671(7)
C(171)	906(6)	2 223(4)	3 812(11)
H(1)	1 146	3 031	3 936
H(2)	129	3 270	2 340
H(3)	−760	2 698	1 307
H(4)	−612	1 766	1 810
H(61)	187	953	1 790
H(62)	−534	1 017	2 884
H(71)	68	164	3 057
H(72)	115	457	4 537
H(91)	1 357	−314	3 452
H(92)	1 358	−77	5 010
H(101)	2 621	100	2 938
H(102)	2 740	−229	4 346
H(121)	3 678	788	4 014
H(122)	3 763	419	5 349
H(131)	3 928	1 303	6 053
H(132)	3 191	1 049	6 857
H(151)	3 183	2 156	6 333
H(152)	2 399	1 896	6 967
H(161)	2 459	2 453	4 318
H(162)	1 958	2 623	5 677

RESULTS AND DISCUSSION

The molecules in (2) and (3) are very similar so the discussion will be limited to the former, except where significant differences occur. The magnesium cation in (1) is small enough to fit into the ring of ether oxygen atoms and is co-ordinated to seven atoms, the five ether oxygens and the two nitrogens from the anions (see Figure 2). The co-ordination polyhedron is a regular pentagonal bipyramid (see Tables 4 and 5). This is the third example of this polyhedron around magnesium.[4,5] The larger calcium cation in (2) sits to one side of the ether ring; it is co-ordinated to eight atoms, the five ether oxygens, two nitrogens from the anions, and an oxygen from the solvent (see Figure 3). The co-ordination polyhedron is very irregular.

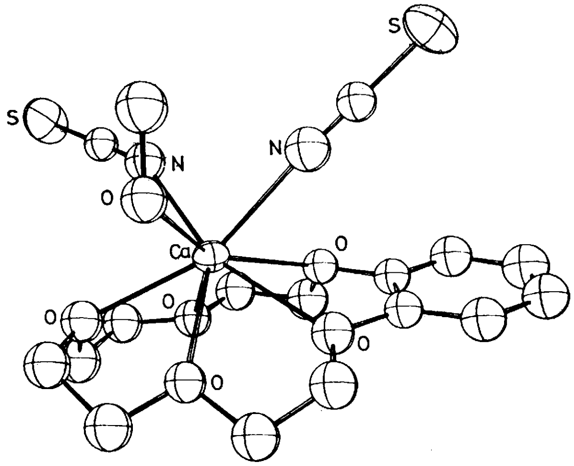

FIGURE 3 Molecule of (2) showing the 50% thermal ellipsoids

TABLE 2

Fractional atomic co-ordinates ($\times 10^4$) for (2)

Atom	*x*	*y*	*z*
Ca	−901(1)	7 113(1)	2 818(1)
S(18)	1 654(2)	3 249(1)	3 143(1)
C(19)	936(5)	4 487(4)	3 003(4)
N(20)	439(5)	5 353(4)	2 893(4)
S(21)	3 836(2)	10 558(1)	2 662(2)
C(22)	2 596(5)	9 286(4)	2 752(4)
N(23)	1 714(5)	8 364(4)	2 785(4)
O(24)	183(4)	7 287(3)	4 850(3)
C(25)	1 723(7)	7 054(5)	5 374(5)
C(1)	−3 936(6)	3 030(5)	1 518(4)
C(2)	−3 893(6)	2 161(5)	627(5)
C(3)	−3 143(7)	2 506(5)	−219(5)
C(4)	−2 365(6)	3 739(5)	−188(5)
C(41)	−2 415(5)	4 616(4)	683(4)
O(5)	−1 649(3)	5 867(3)	797(3)
C(6)	−2 155(7)	6 449(5)	−187(5)
C(7)	−1 379(7)	7 803(5)	123(5)
O(8)	−1 790(4)	8 230(3)	1 163(3)
C(9)	−1 340(7)	9 558(5)	1 445(5)
C(10)	−1 971(7)	9 879(5)	2 466(5)
O(11)	−1 316(4)	9 255(3)	3 384(3)
C(12)	−2 087(7)	9 293(5)	4 334(5)
C(13)	−3 641(7)	8 320(5)	4 098(5)
O(14)	−3 279(4)	7 166(3)	3 745(3)
C(15)	−4 682(6)	6 164(5)	3 453(5)
C(16)	−4 215(6)	5 014(5)	3 153(5)
O(17)	−3 250(4)	5 235(3)	2 327(3)
C(171)	−3 226(5)	4 264(4)	1 529(4)
H(1)	−4 452	2 778	2 121
H(2)	−4 403	1 300	610
H(3)	−3 140	1 891	−842
H(4)	−1 789	3 976	−769
H(61)	−3 320	6 315	−382
H(62)	−1 822	6 108	−840
H(71)	−1 771	8 235	−490
H(72)	−218	7 938	247
H(91)	−1 817	9 924	799
H(92)	−180	9 857	1 616
H(101)	−3 138	9 620	2 271
H(102)	−1 643	10 760	2 710
H(121)	−2 314	10 091	4 465
H(122)	−1 367	9 165	5 015
H(131)	−4 441	8 501	3 489
H(132)	−4 053	8 277	4 780
H(151)	−5 456	6 309	2 805
H(152)	−5 178	6 098	4 100
H(161)	−5 165	4 352	2 826
H(162)	−3 594	4 787	3 832
H(241)	−273	6 639	4 814
H(251)	2 020	7 376	6 193
H(252)	1 632	6 177	5 284
H(253)	2 537	7 449	5 016

Interatomic distances involving the cations are as expected from the ionic radii. The Ca–O(24) distances

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[4] M. G. B. Drew, A. H. B. Othman, S. G. McFall, and S. M. Nelson, *J.C.S. Chem. Comm.*, 1975, 818.

[5] E. Passer, J. G. White, and K. L. Cheng, *Inorg. Chim. Acta*, 1977, **24**, 13.

are significantly shorter than the Ca–O(ether) distances, indicating fairly strong co-ordination of solvent. These solvated complexes melt at the same temperature (280 °C) as the unsolvated complexes, but the crystals become opaque at *ca.* 170 °C, indicating that the solvent may be lost above this temperature.

TABLE 3

Fractional atomic co-ordinates (× 10^4) for (3)

Atom	*x*	*y*	*z*
Ca	988(2)	2 519(2)	4 606(2)
S(18)	−2 093(4)	4 335(4)	1 442(3)
C(19)	−911(11)	3 788(10)	2 444(9)
N(20)	−76(11)	3 396(9)	3 113(8)
S(21)	−4 381(3)	2 319(3)	3 040(3)
C(22)	−2 654(13)	2 454(11)	3 702(8)
N(23)	−1 440(11)	2 602(8)	4 197(7)
O(24)	150(8)	1 169(6)	3 460(6)
C(1)	3 681(12)	4 470(10)	3 839(8)
C(2)	3 537(13)	5 512(11)	3 584(9)
C(3)	2 857(12)	6 167(10)	3 801(9)
C(4)	2 266(12)	5 896(10)	4 296(9)
C(41)	2 396(12)	4 831(10)	4 561(8)
O(5)	1 766(7)	4 452(6)	5 010(6)
C(6)	2 463(13)	4 691(11)	5 971(10)
C(7)	1 754(14)	4 179(11)	6 362(10)
O(8)	1 633(9)	3 143(7)	6 148(6)
C(9)	1 127(13)	2 466(12)	6 593(10)
C(10)	1 540(15)	1 449(12)	6 567(11)
O(11)	1 149(8)	1 145(6)	5 677(6)
C(12)	1 915(13)	229(10)	5 684(8)
C(13)	3 316(12)	493(10)	5 867(8)
O(14)	3 604(8)	1 277(6)	5 197(5)
C(15)	4 328(13)	1 608(10)	5 276(9)
C(16)	3 996(11)	2 370(11)	4 563(8)
O(17)	3 167(7)	3 170(7)	4 659(5)
C(171)	3 094(12)	4 148(10)	4 316(8)
H(1)	4 184	4 000	3 687
H(2)	3 927	5 755	3 240
H(3)	2 802	6 876	3 610
H(4)	1 786	6 408	4 438
H(61)	2 464	5 427	6 054
H(62)	3 434	4 456	6 299
H(71)	813	4 476	6 106
H(72)	2 277	4 274	7 036
H(91)	109	2 513	6 258
H(92)	1 523	2 690	7 226
H(101)	1 090	987	6 790
H(102)	2 551	1 383	7 002
H(121)	1 376	−107	5 078
H(122)	2 039	−252	6 147
H(131)	3 784	−93	5 803
H(132)	3 934	766	6 494
H(151)	4 803	1 015	5 224
H(152)	4 954	1 907	5 891
H(161)	3 453	2 038	3 958
H(162)	4 853	2 636	4 652
H(241)	−241	1 011	3 716
H(242)	971	772	3 370

The bond lengths and angles in the ethers are similar to those found in other complexes of crown ethers. They also show the same peculiarities. For example, the CH_2–CH_2 bond lengths are shorter than usually found in aliphatic chains, and the C(2)–C(3) bond is also very short.

The isothiocyanate groups are essentially linear, but the M–N–C angles are not 180° in any of the molecules (see Table 5). The i.r. spectra of these complexes[1c] show only one ν(CN) for (1), but two for each of the other two. It therefore seems that the *cis*-disposed groups give rise to two ν(CN) absorptions in (2), but the 4° difference in the Mg–N–C angles for (1) is insufficient to give visibly different frequencies when the ligands are *trans*. The Ca–N–C angles are the major respect in which the molecules of (2) and (3) differ. In (2) this angle for the isothiocyanate group, which is above the benzene ring, is such as to bend the ligand away from the ring. In both (2) and (3) this ligand is involved in a weak interaction with the solvent oxygen atom of a neighbouring molecule.

The ether oxygen atoms in (1) form a much better plane than those of (2), and the magnesium cation is included in it (see Table 6). The calcium atom in (2) is 1.22 Å from the mean plane of the oxygen atoms, intermediate between those in the sodium[2] and potassium[6] complexes. This is as expected from the ionic radii.

The conformation of the ether in (1) is very regular, the torsion angles (Table 7) being close to the expected ±60 and 180°. However, some differences do appear, and the overall conformation is similar to that found in the sodium iodide complex.[2] The torsion angles indicate that the ether contains approximate mirror symmetry about a plane through O(11) and the centre of the benzene ring and perpendicular to it. In contrast, the conformation of the ether in (2) is very irregular, with two torsion angles in particular [about C(41)–O(5) and O(11)–C(12)] being very different from the expected values. This contrasts with the conformation of the

TABLE 4

Bond lengths (Å)

	(1)	(2)	(3)
M–N(20)	2.059(4)	2.487(4)	2.428(12)
M–N(23)	2.063(10)	2.401(4)	2.422(10)
M–O(24)		2.382(4)	2.398(9)
M–O(5)	2.194(7)	2.547(3)	2.614(8)
M–O(8)	2.179(7)	2.508(3)	2.457(9)
M–O(11)	2.176(7)	2.542(3)	2.485(9)
M–O(14)	2.171(7)	2.546(3)	2.544(8)
M–O(17)	2.205(7)	2.509(3)	2.546(7)
S(18)–C(19)	1.639(12)	1.640(5)	1.647(13)
C(19)–N(20)	1.140(15)	1.148(6)	1.128(16)
S(21)–C(22)	1.641(12)	1.612(5)	1.637(13)
C(22)–N(23)	1.149(14)	1.150(6)	1.163(16)
O(24)–C(25)		1.438(7)	
C(1)–C(2)	1.346(16)	1.382(7)	1.398(19)
C(2)–C(3)	1.345(17)	1.355(8)	1.323(18)
C(3)–C(4)	1.377(17)	1.388(8)	1.379(17)
C(4)–C(41)	1.366(15)	1.373(7)	1.431(18)
C(41)–C(171)	1.394(14)	1.387(6)	1.389(17)
C(171)–C(1)	1.437(15)	1.379(7)	1.366(16)
C(41)–O(5)	1.392(11)	1.389(5)	1.387(14)
O(5)–C(6)	1.433(12)	1.431(7)	1.415(16)
C(6)–C(7)	1.494(15)	1.490(8)	1.451(19)
C(7)–O(8)	1.417(12)	1.429(7)	1.376(17)
O(8)–C(9)	1.426(13)	1.435(6)	1.465(17)
C(9)–C(10)	1.473(16)	1.482(8)	1.403(22)
C(10)–O(11)	1.419(13)	1.436(7)	1.390(18)
O(11)–C(12)	1.414(14)	1.435(6)	1.461(15)
C(12)–C(13)	1.468(17)	1.490(8)	1.468(17)
C(13)–O(14)	1.406(13)	1.435(6)	1.437(14)
O(14)–C(15)	1.433(13)	1.417(6)	1.419(15)
C(15)–C(16)	1.461(16)	1.462(7)	1.448(18)
C(16)–O(17)	1.453(12)	1.428(6)	1.461(15)
O(17)–C(171)	1.350(12)	1.380(5)	1.377(15)

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[6] P. R. Mallinson and M. R. Truter, *J.C.S. Perkin II*, 1972, 1818.

ether found in the 2 : 1 complex of benzo-15-crown-5 with calcium 3,5-dinitrobenzoate trihydrate.[7]

TABLE 5

Selected bond angles (°)

	(1)	(2)	(3)
C(1)–C(2)–C(3)	125.0	120.8	121.0
C(2)–C(3)–C(4)	118.4	120.4	123.8
C(3)–C(4)–C(41)	119.4	119.5	116.0
C(4)–C(41)–C(171)	122.8	119.9	119.5
C(41)–C(171)–C(1)	116.3	120.2	121.6
C(171)–C(1)–C(2)	118.0	119.1	117.9
C(4)–C(41)–O(5)	124.4	123.6	121.3
C(171)–C(41)–O(5)	112.8	116.5	119.0
C(1)–C(171)–O(17)	129.5	125.4	126.7
C(41)–C(171)–O(17)	114.2	114.4	111.6
C(41)–O(5)–C(6)	117.7	114.3	116.0
O(5)–C(6)–C(7)	105.4	107.7	109.9
C(6)–C(7)–O(8)	106.3	107.6	108.7
C(7)–O(8)–C(9)	113.3	112.7	117.0
O(8)–C(9)–C(10)	106.4	107.1	108.3
C(9)–C(10)–O(11)	105.3	108.5	112.7
C(10)–O(11)–C(12)	117.8	113.4	112.8
O(11)–C(12)–C(13)	106.1	111.7	111.9
C(12)–C(13)–O(14)	108.0	106.7	105.8
C(13)–O(14)–C(15)	115.2	112.2	112.8
O(14)–C(15)–C(16)	107.5	109.3	109.9
C(15)–C(16)–O(17)	107.3	107.3	105.9
C(16)–O(17)–C(171)	117.9	119.8	119.8
S(18)–C(19)–N(20)	178.4	179.1	177.2
S(21)–C(22)–N(23)	178.6	178.0	175.9
M–N(20)–C(19)	116.6	172.0	159.1
M–N(23)–C(22)	170.9	153.3	153.2
M–O(24)–C(25)		124.8	
N(20)–M–N(23)	177.9	85.7	81.1
N(20)–M–O(24)		79.1	74.5
N(23)–M–O(24)		85.5	85.4
N(20)–M–O(5)	91.4	71.6	74.5
N(20)–M–O(8)	88.4	130.3	131.4
N(20)–M–O(11)	93.2	157.8	154.7
N(20)–M–O(14)	86.3	121.7	122.0
N(20)–M–O(17)	91.1	76.6	78.1
N(23)–M–O(5)	89.9	99.1	101.3
N(23)–M–O(8)	90.4	81.4	85.4
N(23)–M–O(11)	84.8	80.3	82.0
N(23)–M–O(14)	93.7	140.7	142.0
N(23)–M–O(17)	90.9	156.9	155.1
O(5)–M–O(8)	72.5	63.6	62.8
O(8)–M–O(11)	72.8	64.5	65.4
O(11)–M–O(14)	73.4	64.1	64.9
O(14)–M–O(17)	73.0	62.4	62.5
O(17)–M–O(5)	68.9	61.4	59.8
E.s.d.s for angles about M^+	0.3	0.1	0.3
E.s.d.s for angles about ether atoms	0.9	0.4	0.8

TABLE 6

Deviations (Å) from the means planes through (*a*) the ether oxygen atoms and (*b*) the benzene carbon atoms

(*a*)	O(5)	O(8)	O(11)	O(14)	O(17)	M^+
(1)	−0.025	0.093	−0.125	0.109	−0.053	0.003
(2)	−0.314	0.477	−0.387	0.183	0.041	−1.224
(3)	−0.284	0.465	−0.392	0.204	0.006	−1.229
(*b*)	C(1)	C(2)	C(3)	C(4)	C(41)	C(171)
(1)	−0.004	0.005	−0.005	0.003	−0.001	0.002
(2)	−0.013	−0.003	0.015	−0.012	−0.004	0.017
(3)	−0.005	−0.003	0.008	−0.005	−0.003	0.008

Interplanar angle (°):	(1)	(2)	(3)
	22	6	7

The crystal structure of (1) consists of discrete molecules of the complex, with no obvious intermolecular interactions (Figure 4). This is remarkable in view of the high melting point (>350 °C) of these crystals. The crystals of (2) and (3) (see Figures 5 and 6) consist of different packings of very similar molecules. The molecules in (2) form dimers joined by a weak interaction O(24)–H · · · S(18) of 3.18 Å (Figure 5). The two halves of the dimer are related by a centre of symmetry at 0, $\frac{1}{2}$, $\frac{1}{2}$. The molecules of (3) form polymeric chains along the crystallographic *b* axis, joined by another weak

TABLE 7

Torsion angles (°)

	(1)	(2)	(3)
C(171)–C(41)–O(5)–C(6)	−171	−124	−107
C(41)–O(5)–C(6)–C(7)	−179	173	175
O(5)–C(6)–C(7)–O(8)	−53	−54	−53
C(6)–C(7)–O(8)–C(9)	−177	−170	−172
C(7)–O(8)–C(9)–C(10)	−175	175	172
O(8)–C(9)–C(10)–O(11)	55	57	52
C(9)–C(10)–O(11)–C(12)	178	−168	−163
C(10)–O(11)–C(12)–C(13)	−177	82	83
O(11)–C(12)–C(13)–O(14)	−54	51	53
C(12)–C(13)–O(14)–C(15)	175	−178	179
C(13)–O(14)–C(15)–C(16)	177	−178	−178
O(14)–C(15)–C(16)–O(17)	51	−50	−54
C(15)–C(16)–O(17)–C(171)	−179	−152	−158
C(16)–O(17)–C(171)–C(41)	168	172	173
O(17)–C(171)–C(41)–O(5)	1	4	6

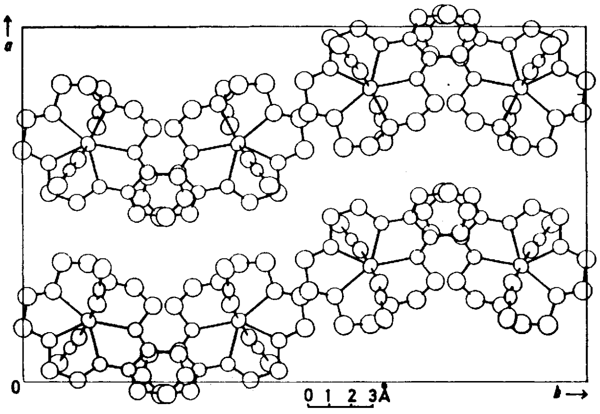

FIGURE 4 Unit cell of (1) viewed down the crystallographic *c* axis, negative *z* towards the reader

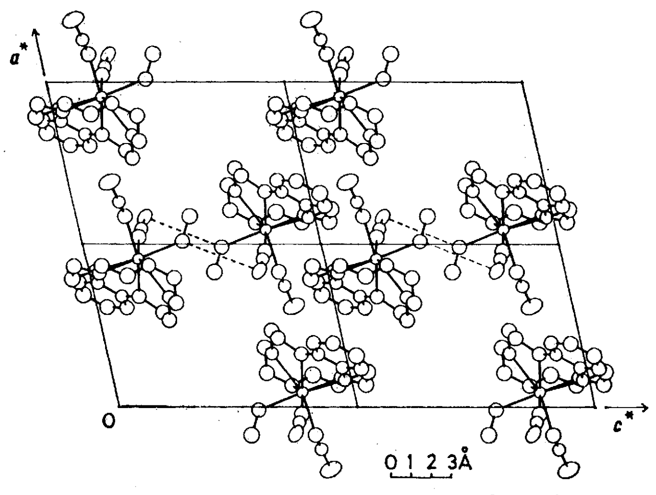

FIGURE 5 Four unit cells of (2) viewed down the crystallographic *b* axis, positive *y* towards the reader

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[7] P. D. Cradwick and N. S. Poonia, *Acta Cryst.*, 1977, **B33**, 197.

interaction O(24)-H $\cdots$ S(18) of 3.17 Å (Figure 6) to a molecule at $-x, y - \frac{1}{2}, \frac{1}{2} - z$. The benzene rings of molecules at x, y, z and $1 - x, 1 - y, 1 - z$ are partially stacked, but this is the only case in these three crystals where such an interaction occurs.

The presence of the same conformer in the two crystal structures of (2) and (3) where the packing is entirely different indicates that steric effects from neighbouring molecules are not deciding the conformation. The conformation of the complexed ether in the 3,5-dinitrobenzoate complex[7] is similar to that found in the crystals of uncomplexed benzo-15-crown-5 itself,[8] and contains crystallographic mirror symmetry. Two factors may explain the different conformation found in the 3,5-dinitrobenzoate complex. (*i*) The cation co-ordination number is nine (five ether oxygens and four oxygen atoms from the two anions), and thus the electron density on the cation will be different. (*ii*) One of the 3,5-dinitrobenzoate anions is stacked above the benzene ring of the ether (parallel to and 3.4 Å from it) and the two ether oxygen atoms, O(5) and O(17), are 2.78 Å from the cation. This indicates a steric interaction between the anion and ether which weakens the bonding to two of the ether oxygen atoms. It is therefore perhaps not so surprising to find a different conformation where strong interactions occur within the complex molecules.

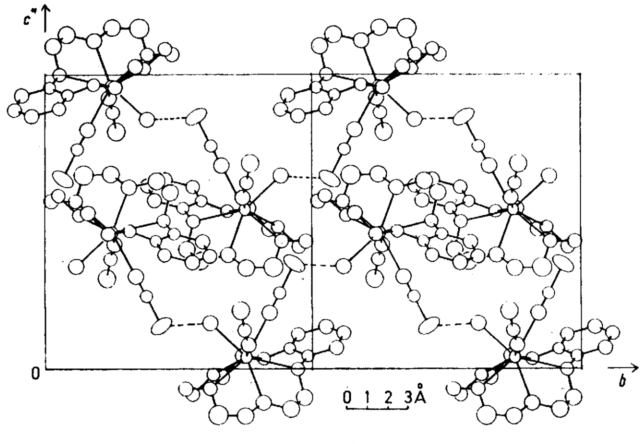

FIGURE 6 Two unit cells of (3) viewed down the crystallographic a axis, positive x towards the reader

The evidence so far available indicates that the conformation of benzo-15-crown-5 in its complexes with metals of Groups 1A and 2A depends to a major extent on the nature of the cation and the stoicheiometry, and very little on so-called ' packing forces ' in the crystalline state.

EXPERIMENTAL

Crystal Data.—(1), $C_{16}H_{20}MgN_2O_5S_2$, $M = 408.79$, Orthorhombic, colourless needles, $a = 16.399(3)$, $b = 25.784(5)$, $c = 9.230(3)$ Å, $U = 3\,903$ Å^3, $D_m = 1.39$ g cm^{-3} (flotation), $Z = 8$, $D_c = 1.39$ g cm^{-3}, $F(000) = 1\,712$, space group $Pbca$ (D_{2h}^{15}, no. 61), no molecular symmetry required, Mo-$K_{\bar{\alpha}}$ radiation, graphite monochromator, $\lambda = 0.710\,7$ Å, $\mu = 3.19$ cm^{-1}, no absorption correction applied.

(2) $C_{17}H_{24}CaN_2O_6S_2$, $M = 456.60$, Triclinic, colourless needles, $a = 8.665(2)$, $b = 11.155(2)$, $c = 11.942(3)$ Å, $\alpha = 95.49(1)$, $\beta = 102.21(2)$, $\gamma = 102.47(2)°$, $U = 1\,089$ Å^3, $D_m = 1.39$ g cm^{-3} (flotation), $Z = 2$, $D_c = 1.39$ g cm^{-3}, $F(000) = 480$, space group $P\bar{1}$ (C_i, no. 2), no molecular symmetry required, Mo-$K_{\bar{\alpha}}$ radiation, graphite monochromator, $\lambda = 0.710\,7$ Å, $\mu = 4.64$ cm^{-1}, no absorption correction applied.

(3) $C_{16}H_{22}CaN_2O_6S_2$, $M = 442.57$, Monoclinic, colourless needles, $a = 11.248(5)$, $b = 12.929(7)$, $c = 17.100(7)$ Å, $\beta = 123.15(2)°$, $U = 2\,082$ Å^3, $D_m = 1.41$ g cm^{-3}, $Z = 4$, $D_c = 1.41$ g cm^{-3}, $F(000) = 928$, space group $P2_1/c$ (C_{2h}^5, no. 14), no molecular symmetry required, Mo-$K_{\bar{\alpha}}$ radiation, Zr filter, $\lambda = 0.710\,7$ Å, $\mu = 5.17$ cm^{-1}, no absorption correction applied.

Data Collection.—Crystals of (1) were obtained by methods which have been described [1c] and recrystallised from acetone. A crystal of dimensions 0.10 × 0.12 × 0.33 mm was mounted on a Philips four-circle diffractometer. Accurate cell dimensions were obtained from the settings of 22 reflections. Intensity data were collected by symmetric ω—2θ scans of 1°, at 0.05° s^{-1}, and background measurements of 10 s taken after the scan. Three standard reflections were measured every 100 reflections and showed no systematic variation of intensity throughout the data collection. Intensities were collected for all the planes with both h and $l \geqslant 0$ up to a maximum 2θ of 50°. Equivalent reflections were averaged to give 2 044 planes of which 1 022 had $I \geqslant 2\sigma(I)$ and were classed as observed.

A crystal of (2) of dimensions 0.48 × 0.21 × 0.21 mm was mounted on the Philips diffractometer and accurate cell dimensions obtained from the settings of 25 reflections. The ω—2θ scan width was 1.3°, again at 0.05° s^{-1}, and each background was measured for 13 s. Three standard reflections were measured every 200 normal reflections and showed no systematic variation in intensity throughout the data collection. Intensities were collected for all the planes with positive l index up to a maximum 2θ of 64°. The data were processed as described for (I) to give 4 245 observed reflections. The structure solution and initial refinement were carried out using the 1 990 observed planes with $(\sin \theta)/\lambda \leqslant 0.5$.

A Picker diffractometer was used for data collection in the case of (3). The crystal size was 0.07 × 0.12 × 0.38 mm and the cell refined from 15 accurately centred reflections. Intensity data were collected by ω—2θ scans at 0.5° min^{-1}, from $2\theta_{\text{calc.}}$ (K_{α_1}) $-0.6°$ to $2\theta_{\text{calc.}}$ (K_{α_2}) $+ 0.6°$. Stationary crystal–stationary counter background measurements were taken for 25s. The intensities of all the reflections to a maximum 2θ of 33° were measured. A reference reflection measured every 25 normal reflections showed no systematic change in intensity over the data collection. The data were processed as described for (1) to give 1 118 independent planes, of which 704 were classed as observed.

Structure Determination.—All the three structures were solved and refined in a similar way. A multisolution direct-methods program [9] was used. In each case, all but two or three atoms were located on the E maps, and the rest on subsequent Fourier maps. Full-matrix refinement using weights calculated from the counting statistics was

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[8] I. R. Hanson, *Acta Cryst.*, 1978, **B34**, 1026

[9] G. M. Sheldrick, SHEL-X, Programs for Crystal Structure Determination, University Chemical Laboratory, Cambridge.

carried out[10] and the final conventional R indices were:

Complex	No. of observations	R	R'
(1)	1 022	0.064	0.058
(2)	4 244	0.081	0.095
(3)	704	0.048	0.043

Weighting analyses showed no obvious trends against ranges of $(\sin\theta)/\lambda$ or $|F_o|$. The hydrogen atoms were located on difference maps but could not be refined. They were therefore included in positions calculated[10] from the geometry of the rest of the molecule where possible, with a C–H bond length of 0.96 Å, and with fixed isotropic temperature factors of $U_{\text{iso.}} = 0.051$. Hydrogen atoms of the solvent molecules in (2) and (3) were located from the difference maps and were included with fixed temperature factors also of $U_{\text{iso}} = 0.051$. Scattering factors were calculated using the analytical approximation coefficients given in Table 2.2B of ref. 11.

Geometry calculations were carried out on an IBM 1130 computer[10] and the Figures drawn using ORTEP.[12] Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22318 (43 pp.).*

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[7/2199 *Received, 16th December, 1977*]

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* For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[10] '*X*-RAY ARC' Library of Programs for the IBM 1130 Computer, *J. Appl. Cryst.*, 1973, **6**, 309.

[11] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 99.

[12] ORTEP, Report No. ORNL-3794, C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.