The Crystal Structures of Complexes of 2,5,8,11,14,18,21,24,27,30-decaoxatricyclo[13.17.0.$0^{1,15}$]dotriacontane with Potassium Thiocyanate (1 : 1), Barium Thiocyanate (1 : 1) Dihydrate, and Ammonium Thiocyanate (1 : 2)

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Crystal structures for three complexes of the macrotricyclic polyether (I), containing a cyclohexane ring which shares opposite pairs of carbon atoms with two 15-crown-5 rings have been determined. All three compounds form 2 : 2 complexes. The cations are sandwiched between 15-crown-5 rings from two molecules, rather than between the two rings of one molecule of (I) in the hoped-for 'clam' conformation. The K^+ and Ba^{2+} ions are 10-co-ordinated in their complexes; the NH_4^+ ion forms three simple and one bifurcated N–H · · · O bonds to oxygens in (I). The anions in the K^+ complex are disordered and isolated from the complex cations. For the Ba^{2+} complex crystals, however, the two anions form infinite hydrogen-bonded chains along the crystal *c* axis with the two molecules of water. In the ammonium complex crystals, the second NH_4^+ cation and two thiocyanate anions form infnite hydrogen-bonded chains, also along the crystal *c* axis.

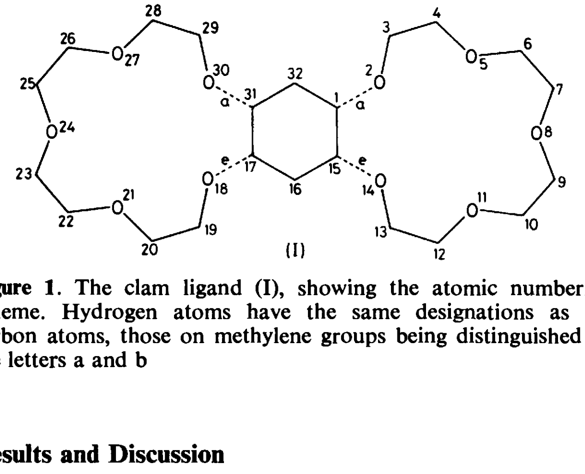
Transport of cations across biological membranes is promoted by some crown ethers.[1] Those crowns which completely enclose the cation, shielding it from interaction with solvent, enhance this transport over those crowns which either form sandwich complexes or leave the cation relatively exposed.[2] The same work [2] indicated that the introduction of lipophilic groups onto the crown imparts greater activity to it. Thus the ligand di-t-butyldibenzo-30-crown-10 gave the greatest activity, and dibenzo-30-crown-10 itself is known to wrap around K^+ and Rb^+ to the exclusion of solvent, from crystal structure determinations.[3,4]

Relatively rigid molecules have been synthesised in these laboratories which can wrap up K^+. However, they bind the cations very tightly and tend to be less soluble in non-aqueous solvents, both properties which are not desirable for good transport.[5] The cation must be fairly weakly bound so it can be released easily on demand. Part of our search for flexible molecules which can enhance transport has produced the 'clam' ligands, an example of which is (I) (Figure 1) and is the subject of this report. Model building indicated that the isomer of (I) with *cis-syn-cis* hydrogen atoms on the cyclohexane ring could form 1 : 1 complexes, if the cyclohexane ring is in the flexible, or 'twist' conformation. In this case a cavity is produced with 10 oxygens around it, and the correct size to accept a K^+ ion.

The preparation and separation of the correct isomer of (I) has been described elsewhere.[6] The energy difference of *ca.* 5.5 kcal mol^{-1} between the chair and flexible conformers ensures that cyclohexane itself exists almost entirely in the chair form at room temperature. It has been estimated [7] that one molecule in a thousand will exist in the flexible form under these conditions. Assuming a similar ratio for (I), and if a 1 : 1 complex has energy sufficiently lower than any other possible complexes, then it may be possible to crystallise such a complex from a solution.

In this paper, I report the structures of three complexes, KSCN·(I), $Ba(SCN)_2$·(I)·$2H_2O$, and $(NH_4SCN)_2$·(I). The different cations were chosen to see if any were capable of bringing about the conformational change necessary to form a 1 : 1 complex.

The final parameters are shown in Tables 1—3 for the three complexes and diagrams in Figures 2—4.



(I)

Figure 1. The clam ligand (I), showing the atomic numbering scheme. Hydrogen atoms have the same designations as the carbon atoms, those on methylene groups being distinguished by the letters a and b

Results and Discussion

These three structures are similar in two respects. Each contains two cations complexed to two clam ligands as a sandwich, and the anions are entirely separated from them. The major differences between them lie in the environments of the anions, though there are smaller differences in the conformations of the 'clam' ligands.

The Complexed Cations.—(a) K^+ *Complex.* The stereopair in Figure 2 shows this to be a 2 : 2 complex, each half related by a crystallographic centre of symmetry. The bond lengths and angles for (I) (Table 4), are as expected for these compounds except in the regions of the molecule suffering from disorder, where short bond lengths and unexpected angles are to be found. Where the disorder has been adequately described in the model, the torsion angles (Table 4c) are reasonable. Thus the two conformers with ± *gauche* angles about C(28)–C(29) are well defined, but around O(8), where the disorder is not well described, the torsions are unrealistic. The O(81) position is close enough to K^+ to be considered as bonded [3.048(14) Å], but the alternative site O(82), which is twice as populated as O(81), is 3.448(15) Å from K^+, and neither of its lone pairs point towards the cation. O(81) makes two contacts with atoms on the opposite ligand, O(81) · · · $H(22)^{I}a$ 2.797 and O(81) · · · $O(24)^{I}$ 3.114 Å, though these are not so

Table 1. Fractional co-ordinates ($\times 10^4$) for the non-hydrogen atoms of KSCN(I), and isotropic thermal parameters ($\times 10^3$ Å^2) (with estimated standard deviations in parentheses). The temperature factor is in the form: $\exp[-8\pi^2U \sin^2\theta/\lambda^2]$. For the anisotropic atoms, the equivalent isotropic parameter, U_{eq}, flagged with an asterisk, is defined as $\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j)$

Atom	x	y	z	U_{iso}/U_{eq} *
K	495(2)	−2 081(1)	−2 033(1)	49.0(5) *
C(1)	177(7)	923(5)	−2 161(5)	50(2)
O(2)	−800(5)	35(4)	−1 815(4)	56(2) *
C(3)	−2 267(11)	−109(8)	−2 355(8)	83(3)
C(4)	−2 904(11)	−1 268(8)	−2 505(8)	83(3)
O(5)	−2 226(9)	−1 884(8)	−3 158(6)	132(4) *
C(6)	−2 703(15)	−2 024(11)	−4 205(8)	116(6) *
C(7)	−1 631(16)	−2 302(10)	−4 855(10)	115(5) *
O(81)	−205(16)	−2 595(12)	−4 365(11)	68(6)
O(82)	−349(17)	−1 640(12)	−4 602(11)	119(6) *
C(9)	945(16)	−2 248(13)	−4 913(8)	131(7) *
C(10)	2 053(16)	−1 250(9)	−4 670(7)	110(5) *
O(11)	2 467(8)	−1 105(4)	−3 565(4)	79(2) *
C(12)	3 339(9)	−89(6)	−3 220(6)	63(2)
C(13)	3 541(8)	1(6)	−2 081(6)	56(2)
O(14)	2 209(5)	−47(3)	−1 650(4)	51(2) *
C(15)	1 702(7)	984(5)	−1 576(5)	47(2)
C(16)	1 776(7)	1 382(5)	−435(5)	45(1)
C(17)	1 409(8)	2 516(5)	−379(5)	50(2)
O(18)	1 637(5)	2 971(3)	672(3)	51(2) *
C(19)	2 098(9)	4 126(6)	764(6)	60(2)
C(20)	2 118(9)	4 556(6)	1 836(6)	62(2)
O(21)	614(6)	4 480(5)	2 015(5)	80(2) *
C(22)	430(10)	4 976(7)	2 974(7)	74(2)
C(23)	−1 160(11)	4 888(8)	3 044(8)	85(3)
O(24)	−1 858(7)	3 801(4)	2 934(5)	84(3) *
C(25)	−3 410(12)	3 622(9)	2 588(8)	91(3)
C(26)	−3 789(13)	3 456(9)	1 486(8)	100(3)
O(27)	−3 230(6)	2 501(5)	1 122(4)	79(2) *
C(281)	−3 576(16)	2 013(12)	47(10)	57(3)
C(291)	−2 443(16)	2 526(13)	−584(11)	59(3)
C(282)	−3 313(18)	2 788(14)	51(12)	57(3)
C(292)	−2 782(19)	1 862(15)	−476(13)	59(3)
O(30)	−1 144(5)	2 019(4)	−306(4)	61(2) *
C(31)	−164(8)	2 538(6)	−907(5)	55(2)
C(32)	−303(9)	2 060(6)	−2 023(6)	58(2)
S(1)a	5 675(15)	2 515(9)	6 639(7)	96(4) *
C(1)a	4 792(15)	3 126(9)	7 453(7)	74(13) *
N(1)a	4 171(15)	3 555(9)	8 026(7)	295(34) *
S(1)b	4 210(14)	3 457(8)	7 736(11)	103(4) *
C(1)b	5 197(14)	2 819(8)	7 019(11)	86(15) *
N(1)b	5 890(14)	2 372(8)	6 516(11)	139(19) *

short as to explain the 2 : 1 populations in favour of O(82). If O(82) is discounted, K^+ is close to ten oxygen atoms, with K–O distances in the range 2.75—3.06 Å. This is a wider range than was found in either the dibenzo-30-crown-10-complex [3] or the benzo-15-crown-5 sandwich complex [8] with K^+. The shortest contacts between neighbouring cations and anions are all of the normal van der Waals' distances, as are the contacts between the two ligands in the sandwich.

(b) Ba^{2+} *Complex*. This also forms a 2 : 2 sandwich with a crystallographic centre of symmetry relating the two halves (Figure 3). The bond length and angles in (I) are reasonable, though in the disordered part of the molecule, some unexpected angles are present (Table 4). Torsion angles are different from those in the K^+ complex, but are still reasonable, with the two possible conformers having +*gauche*, +*gauche* and −*gauche*,−*gauche* about the C(9)–C(10) and C(12)–C(13) bonds, respectively. Ba^{2+} is close to 10 oxygens, with Ba–O distances in the range 2.75—3.02 Å (Table 5). This range is similar to that found [9] for 10-co-ordinated Ba^{2+} in the barium perchlorate complex with dibenzo-24-crown-8. There are no remarkable contacts between and within the cation; contacts to the anions are discussed below.

(c) NH_4^+ *Complex*. Again a 2 : 2 sandwich is formed with a crystallographic centre of symmetry between the two halves (Figure 4). The bond lengths and angles in (I) are reasonable except in the C(22) · · · C(29) region where the disorder has not been modelled (Table 4). Here, the distances are short, the bond angles large and the torsions unreasonable, all indicative of large thermal motion, statistical disorder, or both. One NH_4^+ is co-ordinated to (I), the other to the anions in chains, which are described below. The co-ordinated N(1), is hydrogen bonded to two molecules of (I). The geometry of the hydrogen bonds is described in Table 5. Three simple N–H · · · O bonds are formed to O(5), O(14), and O(24), and one bifurcated bond, H(1)c, to O(18) and O(30). The N · · · O distances to the former are the shortest, 2.85—2.95 Å, and that to the latter of the same order as the non-bonding contacts with other oxygens of (I), 2.98—3.24 Å. The N–H · · · O geometry shows the hydrogen-bonding is comparable with that found in other hydrogen bonded complexes of crown ethers (see for example ref. 10).

Only one ammonium cation in this 1 : 2 complex is co-ordinated with the ligand (I), the other forms hydrogen-bonded chains with the anions which are described below.

Table 2. Fractional co-ordinates, *etc.* for $Ba(SCN)_2{\cdot}(I){\cdot}2H_2O$, as defined for Table 1, except that the U_{iso}/U_{eq} values have been multiplied by 10^4

Atom	x	y	z	U_{iso}/U_{eq} *
Ba	6 135.0(1)	5 366.8(1)	6 873.8(2)	326(1) *
C(1)	5 334(2)	6 589(2)	5 087(3)	394(11)
O(2)	5 715(1)	6 034(1)	4 997(2)	377(10) *
C(3)	6 174(2)	6 166(3)	4 351(4)	475(12)
C(4)	6 656(2)	6 486(3)	4 878(4)	492(13)
O(5)	6 878(1)	6 010(2)	5 564(2)	450(11) *
C(6)	7 382(2)	6 213(3)	6 049(4)	595(15)
C(7)	7 282(3)	6 637(3)	6 950(4)	678(17)
O(8)	6 947(2)	6 259(2)	7 615(3)	728(16) *
C(91)	6 826(7)	6 807(7)	8 310(12)	599(53)
C(101)	6 432(6)	6 472(11)	8 988(12)	649(57)
C(92)	6 857(3)	6 481(5)	8 646(6)	637(28)
C(102)	6 285(3)	6 772(4)	8 719(8)	657(29)
O(11)	5 923(1)	6 224(2)	8 518(3)	504(12) *
C(121)	5 492(4)	6 710(6)	8 438(10)	303(37)
C(131)	5 054(5)	6 378(9)	7 826(8)	433(44)
C(122)	5 337(3)	6 373(5)	8 612(6)	624(27)
C(132)	5 108(4)	6 678(4)	7 683(5)	483(24)
O(14)	5 277(1)	6 285(2)	6 832(2)	504(12) *
C(15)	4 957(2)	6 451(2)	5 950(3)	394(11)
C(16)	4 545(2)	5 884(2)	5 725(3)	387(11)
C(17)	4 193(2)	6 081(2)	4 827(3)	373(10)
O(18)	3 797(1)	5 562(2)	4 638(3)	435(11) *
C(19)	3 240(2)	5 699(3)	4 935(4)	495(13)
C(20)	2 934(2)	6 022(3)	4 098(4)	573(14)
O(21)	2 951(2)	5 568(2)	3 277(3)	579(14) *
C(22)	2 703(3)	5 836(3)	2 384(5)	692(17)
C(23)	2 746(3)	5 338(3)	1 591(5)	684(17)
O(24)	3 303(1)	5 143(2)	1 407(3)	508(12) *
C(25)	3 607(2)	5 565(3)	735(5)	620(15)
C(26)	4 165(2)	5 312(3)	612(4)	600(15)
O(27)	4 438(2)	5 264(2)	1 565(3)	590(14) *
C(28)	4 839(2)	5 760(3)	1 754(4)	521(14)
C(29)	5 117(2)	5 579(3)	2 733(4)	484(13)
O(30)	4 745(1)	5 570(1)	3 576(2)	364(10) *
C(31)	4 541(2)	6 206(2)	3 901(3)	379(11)
C(32)	4 993(2)	6 721(2)	4 153(3)	429(12)
Wat(1)	1 416(3)	4 383(4)	2 711(5)	1 645(41) *
Wat(2)	1 085(3)	3 207(4)	4 015(6)	1 536(37) *
S(1)a	1 057(1)	6 959(1)	3 410(1)	974(9) *
C(1)a	1 268(3)	6 193(4)	3 559(5)	657(25) *
N(1)a	1 397(3)	5 661(4)	3 650(6)	1 021(31) *
S(1)b	1 851(1)	2 458(1)	698(2)	1 062(10) *
C(1)b	1 408(4)	2 411(4)	1 673(7)	899(36) *
N(1)b	1 178(3)	2 403(4)	2 310(7)	1 242(40) *

Table 3. Fractional co-ordinates, *etc.* for $(NH_4SCN)_2{\cdot}(I)$ as defined for Table 1, except that the U_{iso}/U_{eq} values have been multiplied by 10^4

Atom	x	y	z	U_{iso}/U_{eq} *
N(1)	−2 351(5)	4 096(2)	−1 582(5)	432(15)
C(1)	904(7)	4 262(3)	−1 514(6)	450(19)
O(2)	52(4)	4 687(2)	−1 671(4)	460(20) *
C(3)	−302(7)	4 978(3)	−2 805(7)	570(22)
C(4)	−929(8)	4 658(3)	−3 969(7)	618(23)
O(5)	−2 000(5)	4 429(2)	−3 899(4)	574(23) *
C(6)	−2 570(8)	4 055(3)	−4 865(8)	659(24)
C(7)	−2 028(8)	3 530(3)	−4 626(8)	685(26)
O(8)	−2 212(5)	3 307(2)	−3 577(5)	707(28) *
C(9)	−1 568(9)	2 818(4)	−3 158(9)	837(29)
C(10)	−1 745(9)	2 634(4)	−2 062(8)	811(29)
O(11)	−1 363(5)	2 979(2)	−1 031(5)	655(27) *
C(12)	−100(8)	2 957(3)	−292(8)	678(25)
C(13)	208(8)	3 403(3)	596(7)	632(24)
O(14)	119(4)	3 901(2)	−16(5)	506(22) *
C(15)	1 207(7)	4 054(3)	−211(6)	479(20)
C(16)	1 913(6)	4 447(3)	779(6)	438(19)
C(17)	3 121(7)	4 575(3)	627(6)	455(20)
O(18)	3 841(4)	4 961(2)	1 504(4)	494(21) *
C(19)	4 305(7)	4 786(3)	2 760(7)	570(22)
C(20)	5 308(7)	5 155(3)	3 486(7)	539(21)
O(21)	4 839(4)	5 657(2)	3 527(5)	578(24) *
C(22)	5 725(9)	6 066(3)	3 866(9)	770(28)
C(23)	5 190(10)	6 579(4)	3 524(9)	949(33)
O(24)	4 411(6)	6 638(3)	2 289(6)	920(33) *
C(25)	4 896(10)	6 741(4)	1 403(9)	932(32)
C(26)	4 032(9)	6 807(4)	169(9)	925(32)
O(27)	3 191(8)	6 411(3)	−319(6)	1 272(48) *
C(28)	3 174(15)	6 105(6)	−1 194(14)	1 563(55)
C(29)	2 702(10)	5 632(4)	−1 601(9)	931(32)
O(30)	2 428(5)	5 304(2)	−766(4)	525(23) *
C(31)	2 916(7)	4 788(3)	−668(7)	507(20)
C(32)	2 093(7)	4 415(3)	−1 686(7)	496(20)
N(2)	2 405(6)	2 647(2)	3 558(6)	614(19)
S(1)a	837(2)	1 363(1)	−715(2)	746(11) *
C(1)a	1 260(7)	1 646(3)	650(9)	529(38) *
N(1)a	1 552(7)	1 856(3)	1 623(7)	712(36) *
S(1)b	4 726(3)	1 726(1)	8 141(2)	911(13) *
C(1)b	3 915(8)	1 904(3)	6 711(8)	523(38) *
N(1)b	3 341(8)	2 029(3)	5 718(7)	803(39) *

Comparison of the Three Complexed Cations.—The C–C bond lengths in the methylene groups are shorter than the expected single bond length, even where no disorder is evident. This phenomena is common in crown ethers, and is retained, even when the crystal structure is determined at low temperatures.[11] The shortening of the C–C and C–O bond lengths and opening up of the angles at carbon and oxygen is probably due to the thermal motion of the atoms, though this has not yet been proved definitively.

The presence of two axial oxygen atoms on the same side of the cyclohexane ring would be expected to produce some steric effects, and this is indeed the case. If the C(1)–O(2) and C(31)–O(30) bonds were parallel, then the O(2) · · · O(30) distance would be *ca.* 2.6 Å. This distance is increased to 3.147(7), 3.154(4), and 3.043(7) Å, respectively, in these three structures. This seems to have been accomplished by two alterations in geometry. Firstly, the C(32)–C(1)–O(2) and O(30)–C(31)–C(32) angles have increased from the expected 109.7° to a mean value of 115°, and the C(1)–C(32)–C(31) angles also to 115°. Secondly, the conformation of the cyclohexane ring has also changed, the ring torsion angles about the C(17)–C(16) and C(16)–C(15) bonds are close to ±60°, larger than the ±55° mean found in cyclohexane itself.[12] This change in conformation has moved two axial hydrogen atoms closer together, so that the H(15) · · · H(17) distance is 2.38 Å, close to the van der Waals' contact distance of 2.4 Å. There are several other very close contacts between hydrogen atoms, especially to the equatorial hydrogen atom on C(32), but since the hydrogen atoms are in calculated positions on atoms which often have large thermal motion these contacts probably have no significance.

The conformations of the macrocyclic rings are all different, being various combinations of ±*gauche* conformations in the C–C bonds, and torsions between +*gauche*, right through *anti*-conformations, to −*gauche* for the C–O bonds. Although a conformation with *m* symmetry is possible for (I), none of these structures shows it. Figures 2—4 show that the conformation of (I) in the ammonium complex is different in the relation between the macrocycles and the cyclohexane ring. These are more tilted, so that the NH_4^+ · · · NH_4^+ distance is 7.08 Å, compared with 7.44 Å for K^+ · · · K^+, and 7.56 Å for Ba^{2+} · · · Ba^{2+}. These distances are so large that it is

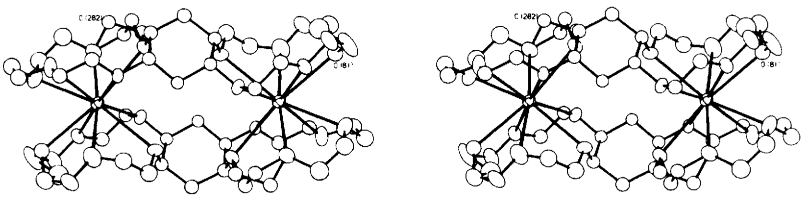


Figure 2. Stereoview of the complex cation $[K^+\cdot(I)]_2$. Atoms are represented by 30% thermal ellipsoids. K–O contacts <3.2 Å are shown

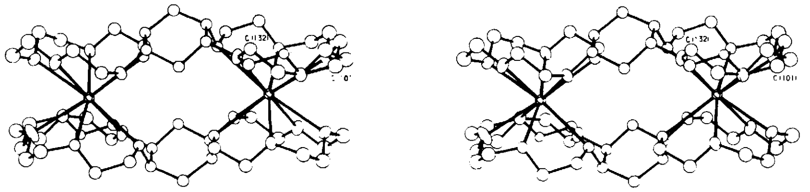


Figure 3. Stereoview of the complex cation $[Ba^{2+}\cdot(I)]_2$. Atoms are represented by 30% thermal ellipsoids

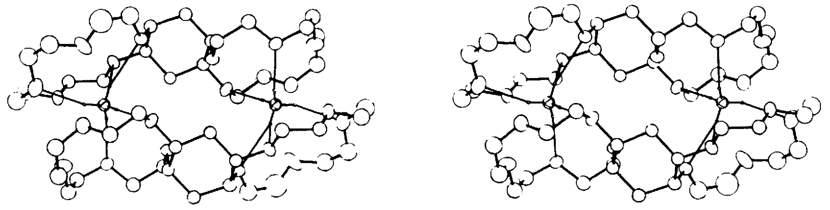


Figure 4. Stereoview of the complex cation $[NH_4^+\cdot(I)]_2$. Atoms are represented by 30% thermal ellipsoids, except the ammonium hydrogen atoms which have a radius of 0.05 Å. H ··· O contacts <2.4 Å are shown

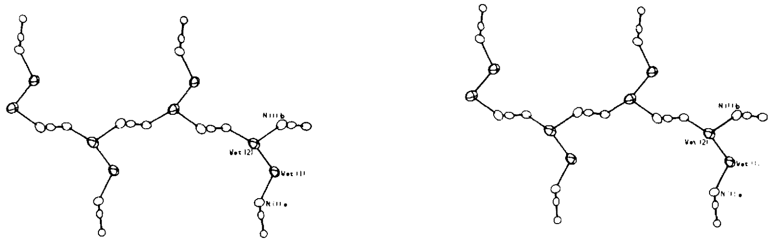


Figure 5. Stereoview of the anion-water chains in the $Ba(SCN)_2\cdot(I)\cdot 2H_2O$ crystals. Atoms are represented by 30% thermal ellipsoids. In this view, the crystallographic *c* axis lies horizontally, and the *b* axis vertically in the plane of the paper

Figure 6. Stereoview of the cation-anion chains in the $(NH_4SCN)_2\cdot(I)$ crystals. Atoms are represented by 30% thermal ellipsoids. The crystallographic *c* axis is horizontal, and the *b* axis vertical in the plane of the paper

unlikely that electrostatic repulsion is important in determining the conformation.

The arrangement of oxygen atoms around the cations is irregular. A view perpendicular to the mean plane of the oxygen atoms in each macrocycle shows that, in all cases, the oxygens are staggered, so the best description of the coordination environment is as distorted pentagonal antiprisms.

The oxygen atoms are not very coplanar, though Table 6 shows that those in the Ba^{2+} complex are the most coplanar, and those in the K^+ complex the least. The cations are equidistant from the two oxygen mean planes around them in all three structures. The shortest cation–mean plane distances are found in the Ba^{2+} complex, and the longest in the NH_4^+ complex. The former is probably due to the higher charge on the cation being more attractive to the δ^- on the oxygen atoms. The latter is probably due to the formation of the directional N–H ··· O bonds being more important than closer approach of the δ^- charges on the oxygen to the δ^+ on N(1). Overall, there are no short contacts between the ligands in the sandwich; all distances are comfortably greater than the sum of the van der Waals' radii. This implies that cross-sandwich contacts are not important in determining

Table 4. Geometry of the ligands (I)

(a) Bond lengths (Å)

	K^+	Ba^{2+}	NH_4^+
C(1)-O(2)	1.442(8)	1.451(5)	1.435(8)
C(1)-C(15)	1.507(9)	1.494(6)	1.495(9)
C(1)-C(32)	1.552(10)	1.516(6)	1.539(10)
O(2)-C(3)	1.430(10)	1.429(5)	1.414(8)
C(3)-C(4)	1.460(13)	1.503(7)	1.500(10)
C(4)-O(5)	1.383(11)	1.428(6)	1.421(9)
O(5)-C(6)	1.379(12)	1.437(6)	1.422(9)
C(6)-C(7)	1.449(18)	1.492(8)	1.452(10)
C(7)-O(8)		1.420(7)	1.412(9)
C(7)-O(81)	1.499(19)		
C(7)-O(82)	1.327(18)		
O(8)-C(9)			1.440(10)
O(8)-C(91)		1.469(10)	
O(8)-C(92)		1.462(7)	
O(81)-C(9)	1.381(19)		
O(82)-C(9)	1.590(20)		
C(9)-C(10)	1.472(18)		1.422(12)
C(91)-C(101)		1.475(11)	
C(92)-C(102)		1.501(9)	
C(10)-O(11)	1.442(11)		1.402(9)
C(101)-O(11)		1.467(9)	
C(102)-O(11)		1.433(7)	
O(11)-C(12)	1.406(9)		1.421(10)
O(11)-C(121)		1.431(8)	
O(11)-C(122)		1.451(7)	
C(12)-C(13)	1.474(10)		1.470(10)
C(121)-C(131)		1.492(11)	
C(122)-C(132)		1.487(9)	
C(13)-O(14)	1.409(9)		1.426(9)
C(131)-O(14)		1.443(9)	
C(132)-O(14)		1.441(7)	
O(14)-C(15)	1.432(7)	1.445(5)	1.436(8)
C(15)-C(16)	1.534(9)	1.541(6)	1.508(9)
C(16)-C(17)	1.499(9)	1.519(6)	1.535(10)
C(17)-O(18)	1.434(8)	1.437(5)	1.434(8)
C(17)-C(31)	1.535(10)	1.515(6)	1.509(9)
O(18)-C(19)	1.425(8)	1.429(6)	1.408(8)
C(19)-C(20)	1.469(10)	1.489(7)	1.497(10)
C(20)-O(21)	1.427(9)	1.426(6)	1.393(8)
O(21)-C(22)	1.407(10)	1.439(7)	1.420(10)
C(22)-C(23)	1.470(13)	1.459(8)	1.430(12)
C(23)-O(24)	1.394(11)	1.422(7)	1.382(10)
O(24)-C(25)	1.429(12)	1.435(7)	1.360(11)
C(25)-C(26)	1.436(14)	1.448(8)	1.416(12)
C(26)-O(27)	1.445(11)	1.435(7)	1.377(11)
O(27)-C(28)		1.413(6)	1.258(14)
O(27)-C(281)	1.476(15)		
O(27)-C(282)	1.461(16)		
C(28)-C(29)		1.511(7)	1.328(15)
C(281)-C(291)	1.499(21)		
C(282)-C(292)	1.485(24)		
C(29)-O(30)		1.439(6)	1.388(10)
C(291)-O(30)	1.456(15)		
C(292)-O(30)	1.483(17)		
O(30)-C(31)	1.379(9)	1.436(5)	1.413(8)
C(31)-C(32)	1.528(10)	1.539(6)	1.537(10)

(b) Bond angles (°) (mean e.s.d. 0.7°)

	K^+	Ba^{2+}	NH_4^+
O(2)-C(1)-C(15)	109.0	107.9	106.8
O(2)-C(1)-C(32)	114.7	114.2	115.4
C(15)-C(1)-C(32)	108.3	109.5	108.6
C(1)-O(2)-C(3)	112.9	113.5	117.5
O(2)-C(3)-C(4)	110.5	113.5	114.7
C(3)-C(4)-O(5)	114.8	107.7	109.2
C(4)-O(5)-C(6)	121.0	114.6	113.8
O(5)-C(6)-C(7)	116.0	112.8	114.2
C(6)-C(7)-O(8)		106.9	109.2
C(6)-C(7)-O(81)	119.4		
C(6)-C(7)-O(82)	110.6		
C(7)-O(8)-C(9)			113.5
C(7)-O(81)-C(9)	111.5		
C(7)-O(82)-C(9)	109.2		
C(7)-O(8)-C(91)		96.1	
C(7)-O(8)-C(92)		120.5	
O(8)-C(9)-C(10)			110.1
O(81)-C(9)-C(10)	126.6		
O(82)-C(9)-C(10)	92.4		
O(8)-C(91)-C(101)		100.0	
O(8)-C(92)-C(102)		108.5	
C(9)-C(10)-O(11)	108.5		115.6
C(91)-C(101)-O(11)		115.7	
C(92)-C(102)-O(11)		104.5	
C(10)-O(11)-C(12)	113.8		114.8
C(101)-O(11)-C(121)		114.1	
C(102)-O(11)-C(122)		114.9	
O(11)-C(12)-C(13)	108.2		108.7
O(11)-C(121)-C(131)		104.5	
O(11)-C(122)-C(132)		112.0	
C(12)-C(13)-O(14)	113.9		112.4
C(121)-C(131)-O(14)		107.2	
C(122)-C(132)-O(14)		109.0	
C(13)-O(14)-C(15)	113.4		113.9
C(131)-O(14)-C(15)		121.2	
C(132)-O(14)-C(15)		111.4	
C(1)-C(15)-O(14)	111.5	110.1	110.4
C(1)-C(15)-C(16)	112.2	112.4	112.4
O(14)-C(15)-C(16)	109.7	109.5	110.0
C(15)-C(16)-C(17)	108.6	108.8	109.6
C(16)-C(17)-O(18)	110.5	108.7	113.7
C(16)-C(17)-C(31)	111.4	112.0	111.4
O(18)-C(17)-C(31)	112.1	110.3	106.5
C(17)-O(18)-C(19)	112.8	115.9	114.2
O(18)-C(19)-C(20)	109.9	110.2	107.7
C(19)-C(20)-O(21)	106.8	106.3	109.9
C(20)-O(21)-C(22)	114.0	112.5	114.2
O(21)-C(22)-C(23)	108.8	108.2	112.1
C(22)-C(23)-O(24)	111.5	112.5	116.0
C(23)-O(24)-C(25)	116.0	115.4	118.5
O(24)-C(25)-C(26)	114.4	109.8	114.8
C(25)-C(26)-O(27)	108.8	110.6	117.9
C(26)-O(27)-C(28)		115.2	124.5
C(26)-O(27)-C(281)	123.3		
C(26)-O(27)-C(282)	94.4		
O(27)-C(28)-C(29)		106.7	135.4
O(27)-C(281)-C(291)	109.6		
O(27)-C(282)-C(292)	102.7		
C(28)-C(29)-O(30)		113.6	118.0
C(281)-C(291)-O(30)	105.2		
C(282)-C(292)-O(30)	110.1		
C(29)-O(30)-C(31)		115.9	114.4
C(291)-O(30)-C(31)	101.4		
C(292)-O(30)-C(31)	128.2		
C(17)-C(31)-O(30)	107.9	106.8	108.7
C(17)-C(31)-C(32)	108.7	109.0	110.7
O(30)-C(31)-C(32)	115.9	115.0	112.3
C(1)-C(32)-C(31)	115.2	116.6	114.3

(c) Torsion angles (°) (mean e.s.d. 1°)

	K^+	Ba^{2+}	NH_4^+
C(15)-C(1)-O(2)-C(3)	−178	−167	175
O(14)-C(15)-C(1)-O(2)	54	52	56
C(32)-C(1)-C(15)-C(16)	55	54	58
C(31)-C(32)-C(1)-C(15)	−52	−50	−53
C(1)-O(2)-C(3)-C(4)	144	88	61
O(2)-C(3)-C(4)-O(5)	−67	67	60
C(3)-C(4)-O(5)-C(6)	−90	173	−171
C(4)-O(5)-C(6)-C(7)	157	84	81
O(5)-C(6)-C(7)-O(8)		58	66

Table 4 (*continued*)

	K^+	Ba^{2+}	NH_4^+
O(5)–C(6)–C(7)–O(81)	10		
O(5)–C(6)–C(7)–O(82)	−48		
C(6)–C(7)–O(8)–C(9)			−172
C(6)–C(7)–O(81)–C(9)	−146		
C(6)–C(7)–O(82)–C(9)	154		
C(6)–C(7)–O(8)–C(91)		−170	
C(6)–C(7)–O(8)–C(92)		169	
C(7)–O(8)–C(9)–C(10)			177
C(7)–O(81)–C(9)–C(10)	99		
C(7)–O(82)–C(9)–C(10)	172		
C(7)–O(8)–C(91)–C(101)		175	
C(7)–O(8)–C(92)–C(102)		104	
O(8)–C(9)–C(10)–O(11)			−59
O(81)–C(9)–C(10)–O(11)	40		
O(82)–C(9)–C(10)–O(11)	79		
O(8)–C(91)–C(101)–O(11)		−61	
O(8)–C(92)–C(102)–O(11)		64	
C(9)–C(10)–O(11)–C(12)	−170		−83
C(91)–C(101)–O(11)–C(121)		−86	
C(92)–C(102)–O(11)–C(122)		176	
C(10)–O(11)–C(12)–C(13)	174		170
C(101)–O(11)–C(121)–C(131)		173	
C(102)–O(11)–C(122)–C(132)		84	
O(11)–C(12)–C(13)–O(14)	−61		−68
O(11)–C(121)–C(131)–O(14)		−67	
O(11)–C(122)–C(132)–O(14)		49	
C(12)–C(13)–O(14)–C(15)	−84		−87
C(121)–C(131)–O(14)–C(15)		−134	
C(122)–C(132)–O(14)–C(15)		165	
C(13)–O(14)–C(15)–C(1)	122		135
C(131)–O(14)–C(15)–C(1)		156	
C(132)–O(14)–C(15)–C(1)		129	
C(1)–C(15)–C(16)–C(17)	−62	−60	−61
C(15)–C(16)–C(17)–C(31)	62	60	58
C(31)–C(17)–O(18)–C(19)	−87	−132	−169
C(16)–C(17)–C(31)–C(32)	−57	−54	−53
O(30)–C(31)–C(17)–O(18)	−55	−51	−53
C(17)–O(18)–C(19)–C(20)	173	90	163
O(18)–C(19)–C(20)–O(21)	−71	59	66
C(19)–C(20)–O(21)–C(22)	−173	−176	−163
C(20)–O(21)–C(22)–C(23)	177	180	162
O(21)–C(22)–C(23)–O(24)	58	−57	−52
C(22)–C(23)–O(24)–C(25)	−156	−85	−83
C(23)–O(24)–C(25)–C(26)	91	−180	−179
O(24)–C(25)–C(26)–O(27)	61	−57	−54
C(25)–C(26)–O(27)–C(28)		−105	−110
C(25)–C(26)–O(27)–C(281)	172		
C(25)–C(26)–O(27)–C(282)	−161		
C(26)–O(27)–C(28)–C(29)		−174	159
C(26)–O(27)–C(281)–C(291)	90		
C(26)–O(27)–C(282)–C(292)	−179		
O(27)–C(28)–C(29)–O(30)		−62	−22
O(27)–C(281)–C(291)–O(30)	77		
O(27)–C(282)–C(292)–O(30)	−80		
C(28)–C(29)–O(30)–C(31)		−70	−129
C(281)–C(291)–O(30)–C(31)	−179		
C(282)–C(292)–O(30)–C(31)	−91		
C(29)–O(30)–C(31)–C(17)		−176	152
C(291)–O(30)–C(31)–C(17)	155		
C(292)–O(30)–C(31)–C(17)	178		
C(17)–C(31)–C(32)–C(1)	52	50	51

Table 5

(a) Cation–oxygen distances (Å)

	K	Ba	N(1)
O(2)	3.064(5)	3.015(3)	3.243(7)
O(5)	2.805(8)	2.818(3)	2.950(7)
O(8)		2.833(4)	3.079(8)
O(81)	3.048(14)		
O(82)	3.448(15)		
O(11)	3.047(6)	2.835(4)	3.030(7)
O(14)	2.749(4)	2.776(4)	2.854(7)
O(18)$^{\text{I}}$	2.946(5)	2.752(4)	2.981(7)
O(21)$^{\text{I}}$	2.998(6)	2.904(4)	3.031(7)
O(24)$^{\text{I}}$	2.907(6)	2.853(4)	2.929(9)
O(27)$^{\text{I}}$	2.795(6)	2.803(4)	2.989(9)
O(30)$^{\text{I}}$	3.039(5)	2.901(3)	3.113(7)
symmetry operator, $^{\text{I}}$	$-x$, $-y$, $-z$	$1 - x$, $1 - y$, $1 - z$	$-x$, $1 - y$, $-z$

(b) Hydrogen bonding geometry for complexed cation in $(NH_4SCN)_2\cdot$(I)

A–B · · · C	A–B (Å)	B · · · C (Å)	A–B–C angle (°)
N(1) H(1)a O(24)$^{\text{I}}$	0.86(2)	2.12(6)	158
N(1) H(1)b O(5)	0.85(2)	2.14(6)	159
N(1) H(1)c O(18)$^{\text{I}}$	0.86(2)	2.30(7)	136
N(1) H(1)c O(30)$^{\text{I}}$		2.34(7)	150
N(1) H(1)d O(14)	0.85(2)	2.01(4)	170

Table 6. Deviations (Å) from the mean planes through the oxygen atoms of (I)

	M = K	Ba	N(1)
Plane A			
O(2)	−0.306(7)	0.048(4)	−0.214(7)
O(5)	0.145(7)	0.062(4)	0.305(7)
O(8)		−0.138(4)	−0.289(7)
O(81)	0.068(7)		
O(11)	0.266(7)	0.167(4)	0.140(7)
O(14)	0.359(7)	0.140(4)	0.058(7)
M	1.716(3)	1.614(2)	1.858(6)
Plane B			
O(18)	−0.342(7)	−0.186(4)	0.171(7)
O(21)	0.446(7)	0.206(4)	−0.064(7)
O(24)	−0.307(7)	−0.140(5)	−0.063(7)
O(27)	0.076(7)	0.030(4)	0.146(7)
O(30)	0.127(7)	0.090(5)	−0.189(7)
M	−1.728(3)	−1.614(2)	−1.838(6)
Interplanar angles (°)	8.40(11)	5.92(7)	16.24(11)

the conformations of the ligands. Closer contacts exist to other molecules and the anions, and it is probable that these, along with interactions to the cations, and within the ligands, are determining the conformations.

It is clear that none of these cations can induce the clam conformation for (I) to form a 1 : 1 complex in the solid state. In solution, the available evidence[6] is as yet insufficient to distinguish between the existence of 1 : 1 and 2 : 2 species Further spectroscopic investigations currently planned here may clarify this.

The Environment of the Anions.—(a) K^+ *Complex.* The anions here are disordered in two positions related by 180°. Contacts to molecules of (I) are all of a reasonable length, the sulphur atoms being surrounded by hydrogen atoms at or near the van der Waals' contact distance.

(b) Ba^{2+} *Complex.* Although the water hydrogen atoms could not be located, the interatomic distances (Table 7) clearly show that the anions and water molecules form infinite hydrogen-bonded chains parallel to the crystal *c* axis (Figure 5). Four chains pass through each unit cell, and within the

Table 7. Geometry of the anions, and associated hydrogen-bonding
(a) Ba(SCN)$_2$·(I)·2H$_2$O

A	B	C	A–B distance (Å)	A–B–C angle (°)
S(1)a	C(1)a	N(1)a	1.634(8)	177.8(7)
C(1)a	N(1)a	Wat(1)	1.120(9)	144.6(6)
N(1)a	Wat(1)	Wat(2)	2.856(11)	116.4(3)
S(1)b	C(1)b	N(1)b	1.686(10)	173.3(11)
C(1)b	N(1)b	Wat(2)	1.015(10)	135.6(8)
Wat(2)	S(1)b^{II}	C(1)b^{II}	3.200(8)	98.7(3)
Wat(1)	Wat(2)	S(1)b^{II}	3.041(11)	125.0(3)
N(1)b	Wat(2)	S(1)b^{II}	2.797(12)	106.4(3)
N(1)b	Wat(2)	Wat(1)		87.9(3)

symmetry operation: II = x, $1/2 - y$, $1/2 + z$

(b) (NH$_4$SCN)$_2$·(I)

A	B	C	A–B distance (Å)	A–B–C angle (°)
N(2)	H(2)a	N(1)a	0.85(2)	166(6)
N(2)	H(2)b	S(1)b^{III}	0.86(2)	176(6)
N(2)	H(2)c	N(1)b	0.87(2)	172(6)
N(2)	H(2)d	S(1)a^{II}	0.86(2)	167(6)
H(2)a	N(1)a	C(1)a	2.04(5)	162.7(16)
N(1)a	C(1)a	S(1)a	1.165(9)	178.9(8)
C(1)a	S(1)a	H(2)d^{III}	1.620(10)	86.7(16)
S(1)a	H(2)d^{III}		2.54(6)	
H(2)c	N(1)b	C(1)b	1.93(5)	158.0(19)
N(1)b	C(1)b	S(1)b	1.134(9)	179.5(8)
C(1)b	S(1)b	H(2)b^{II}	1.626(9)	77.7(17)
S(1)b	H(2)b^{II}		2.49(6)	

symmetry operation: III = x, $1/2 - y$, $z - 1/2$.

cell, the two halves of each chain are related by a *c*-glide plane. All the atoms in the chains are undergoing large anisotropic thermal motion, and this probably explains the short interatomic distances and the deviations from linearity within the anions.

Contacts to atoms in the chains are all at or near expected values, in particular S(1)a, which does not take part in hydrogen-bonding, and forms several contacts to hydrogens on various ligands at 2.9—3.1 Å. Although there are some C–H · · · Wat contacts, their geometry does not indicate hydrogen-bonding, and so the anion–water chains are essentially isolated from each other and from the complex cations.

(c) NH$_4^+$ *Complex*. In this case, the second ammonium cation forms infinite hydrogen bonded chains with the anions, extending through the crystals, again parallel to the *c* axis (Figure 6). There are two chains passing through each unit cell, the two halves of each again being related by a *c* glide plane. Although the atoms of the cations were not freely refined, their geometry indicates strong hydrogen-bonding to both nitrogen and sulphur atoms of the anions (Table 7). The anions themselves are linear as expected, and undergo much less thermal motion than those in the Ba^{2+} complex. Contacts to the anions are all at expected values, so again the chains are isolated from each other and from the complex cations.

The structure of ammonium thiocyanate itself[13] shows strong N–H · · · N bonding, but only weak N–H · · · S interactions in a three-dimensional network in the crystals. Also the thiocyanate nitrogen atom bridges two cations, so the structure is entirely different from that shown in the complex with (I). However, it is probable that similar solid-state reactions can occur since crystals of both compounds turn yellow on ageing.

Experimental

Procedures common to all three crystals are described first, followed by those for the individual analyses. Approximate unit cell dimensions were obtained from preliminary photographs. One crystal of each compound was mounted on a CAD4 diffractometer, and unit cell dimensions obtained from accurately centred reflections with high 2θ values. Mo-K_α Radiation with a graphite monochromator was used, $\lambda = 0.7107$ Å (1 Å ≡ 10^{-10} m). Intensities were collected using the ω—2θ scan procedure and reduced to structure amplitudes.[14] Structure solution and refinement were carried out using the SHELX suite,[15] and the diagrams drawn using ORTEP.[16] These, and other local programs, were run on a PRIME 550 computer.

Scattering factors were calculated using the analytical approximation in Table 2.2B of ref. 17, and real and imaginary parts of the anomalous dispersion correction were from Table 2.3.1 of the same reference. Observed and calculated structure factors and anisotropic temperature factors have been deposited in Supplementary Publication No SUP 23521 (70 pp.).*

Potassium Thiocyanate Complex KSCN·(I).—*Crystal data* C$_{23}$H$_{40}$NO$_{10}$SK, $M = 561.7$. Triclinic, $a = 9.238(1)$, $b = 12.415(1)$, $c = 13.076(1)$ Å, $\alpha = 93.23(1)$, $\beta = 97.04(1)$, $\gamma = 98.91(1)$°, $U = 1466.1(2)$ Å^3, D_m (flotation) = 1.28, $Z = 2$, $D_c = 1.272$ g cm^{-3}, $F(000) = 598$, space group $P\bar{1}$ (C_i, No. 2) from structure analysis. No molecular symmetry is required, $\mu = 0.294$ mm^{-1}, no absorption correction was applied. A crystal 0.43 × 0.23 × 0.23 mm was used to collect data for 4 920 planes with $h \geqslant 0$, and $1.5 < \theta < 24$°. The data were corrected for a fall of 9% in the intensity of two standard reflections measured throughout the data collection. A total of 4 596 unique planes were obtained, of which 3 611 had $F_o \geqslant 4\sigma(F_o)$ and were classed as observed.

The intensity distribution was centric, indicating the space group $P\bar{1}$, but attempts to solve the structure using SHELX in this space group failed. However, a solution was obtained using direct methods in $P1$ and the origin shifted to the centre of symmetry relating the two molecules. Refinement in $P\bar{1}$, however, gave disordered positions for several atoms. A return to $P1$ with one of the K$^+$ atoms fixed at the origin, failed to resolve the disorder, so all later refinements were carried out in $P\bar{1}$.

The disordered anions were represented as two rigid linear groups with S–C 1.64 and C–N 1.15 Å, with occupation factors 0.5, and related by 180° rotation. The atoms were given anisotropic temperature factors, though no significance should be placed on their values. The parameters of the anions were highly correlated in the least squares refinement. Two sites could be distinguished for atom O(8), but not for atoms C(6), C(7), C(9), and C(10), which were given anisotropic thermal parameters to compensate. The occupational factor, q, for O(81) refined to 0.38(2), and that of O(82) was set to $(1 - q)$. No significance should be placed on the geometry of this part of the molecule.

Two sites were obtained for each of C(28) and C(29), and reasonable geometry ensued from refinement with independent fractional co-ordinates. The occupation factor, p, for C(281) and C(291) refined to 0.530(9) and those of C(282) and C(292) were set to $(1 - p)$. C(281) and C(282) were given a common isotropic temperature factor, which refined to $U_{iso} = 0.057(3)$ Å^2. C(291) and C(292) were treated in a similar way, and U_{iso} refined to 0.059(3) Å^2.

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* For details of Supplementary Publications see Notice to Authors in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

All remaining carbon atoms were given isotropic temperature factors, and the oxygens and potassium atoms anisotropic temperature factors. Hydrogen atoms on C(6), C(7), C(9), and C(10) were excluded, but all the others were included in positions calculated from the geometry of the rest of the molecule, with C–H fixed at 0.98 Å. A common isotropic temperature factor was given to the hydrogens, and this refined to U_{iso} 0.082(5) Å^2.

Full matrix refinement of this model gave a final $R = 0.118$ and $R' = 0.132$, using weights w calculated from the expression $w = 7.41/[\sigma^2(F_o) + 0.0012\ F_o^2]$, and the maximum shift/e.s.d. on the final cycle was 0.86. Four planes 010, 001, 011, 002, with $F_o \ll F_c$ were considered to be suffering from extinction, and were omitted, leaving 3 607 observations.

The high R factor is due to the poor description of the disorder in atoms C(6), C(7), O(8), C(9), and C(10), the exclusion of eight hydrogen atoms, and further possible disorder in other parts of the molecule. Evidence for the last comes from the final ΔF map, the major features of which are peaks 1.0—0.7 eÅ^{-3} close to O(5) and O(11).

An analysis of the weighting scheme showed the worst agreement between F_o and F_c occurred for the lowest Bragg angle reflections, again probably due to the disorder.

The final atomic parameters are given in Table 1.

Barium Thiocyanate Complex, Ba(SCN)$_2$·(I)·2H$_2$O.—*Crystal data*. $C_{24}H_{44}N_2O_{12}S_2Ba$, $M = 754.1$. Orthorhombic, $a = 24.144(3)$, $b = 20.093(3)$, $c = 13.333(2)$ Å, $U = 6468.2(14)$ Å^3, D_m (flotation) = 1.54, $Z = 8$, $D_c = 1.55$ g cm^{-3}, $F(000) = 3\,072$, space group $Pbca$ (D_{2h}^{15}, No. 61), uniquely defined. No molecular symmetry is required; $\mu = 1.407$ mm^{-1}, an absorption correction was applied.

Intensities were collected for 5 678 planes in the hkl octant with $1.5° < \theta < 25°$, from a crystal 0.46 × 0.38 × 0.30 mm. The intensities of two reflections were monitored every 50 normal reflections, and showed a mean fall of *ca.* 3% over the data collection. The data were corrected for this. Nine reflections and their symmetry equivalents were collected in the ψ scan mode, and these data used to apply a semi-empirical absorption correction.[18] 4 400 planes had $F_o \geqslant 4\sigma(F_o)$, and were classed as observed.

The structure was determined from Patterson and electron density difference maps. All non-hydrogen atoms, except the carbons of the polyether, were given anisotropic temperature factors. The hydrogen atoms of the water molecules could not be located, but the remaining hydrogens were placed in positions calculated from the geometry of the rest of the molecule, with a C–H distance of 0.98 Å. They were given a common isotropic temperature factor which refined to $U_{iso} = 0.065(3)$ Å^2.

Two positions were found for each of C(9), C(10), C(12), and C(13). The occupation factor for C(91), *etc.*, p, was refined to 0.333(11) and that of C(92), *etc.* set to $1 - p$. Reasonable geometry was obtained with each atom having an independent isotropic temperature factor, the C–C distances tied to one common value and the C–O distances tied to another. These target values refined to 1.489(8) and 1.450(5) Å, respectively.

Full matrix refinement of this model gave a final $R = 0.041$ and $R' = 0.044$, using weights calculated from the counting statistics. The maximum shift/e.s.d. on the final cycle was 0.37. Two planes, 020 and 040, were excluded because of extinction, leaving 4 438 observations.

The final difference Fourier map showed one peak, *ca.* 1.0 eA^{-3}, near the centre of the C(9)–C(10) bonds, the remaining peaks were all <0.5 eA^{-3}. Final atomic parameters are given in Table 2.

Ammonium Thiocyanate Complex (NH$_4$SCN)$_2$·(I).—*Crystal data*. $C_{24}H_{48}N_4O_{10}S_2$, $M = 616.8$. Monoclinic, $a = 11.820(2)$, $b = 25.253(5)$, $c = 11.437(2)$ Å, $\beta = 111.50(1)°$, $U = 3176.4(9)$ Å^3, D_m (flotation) = 1.29, $Z = 4$, $D_c = 1.29$ g cm^{-3}, $F(000) = 1\,168$, space group $P2_1/c$ (C_{2h}^5, No. 14), uniquely defined. No molecular symmetry is required; $\mu = 0.142$ mm, no absorption correction was applied.

A crystal 0.46 × 0.30 × 0.15 mm was used to collect 4 652 planes in the hkl and $hk\bar{l}$ octants. Two reflections were measured throughout the data collection, and their nett intensities fell by *ca.* 3%. The data were corrected for this, and after reduction, 4 411 unique planes remained, 2 727 of which had $F_o \geqslant 4\sigma(F_o)$ and were classed as observed.

Multisolution direct methods were used to determine the phases, and the resulting E map showed all the non-hydrogen atoms. The thiocyanate atoms and the oxygens were given anisotropic thermal parameters, the rest isotropic. Hydrogens on the ligand were included in calculated positions and given a common isotropic temperature factor which refined to 0.086(4) Å^2. Although the ammonium hydrogen atoms could be located on a difference Fourier map, unrestrained refinement gave unacceptable geometry. The geometry was therefore restrained to be close to tetrahedral, and the target N–H distance refined to 0.858(19) Å. The hydrogens on each cation were given a common isotropic temperature factor, which refined to 0.125(20) Å^2 for those on N(1), and 0.113(18) Å^2 for those on N(2).

Full matrix refinement then gave $R = 0.090$ and $R' = 0.093$ using weights calculated from the counting statistics. The maximum shift/esd on the final cycle was 0.32. The final difference Fourier map showed several peaks <0.85 eA^{-3} close to the C(22) · · · C(29) atoms. Investigation of this disorder did not give discrete alternative positions, so the retention of isotropic single atoms in this part of the molecule explains the rather high R factor, and the poor agreement for the low θ planes found in the weighting analysis. Final atomic parameters are given in Table 3.

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