evident that the ratio of nitrate groups in each of the three perpendicular planes is 2:1:1 and some nitrates within each plane are oriented at 60° to each other. However, in $RbNO_3$ the corresponding ratio is 1:1:1 and there are two orientations at 30° to each other for nitrates in any one plane. Consequently during the transformation $TlNO_3(III) \rightarrow TlNO_3(II)$ at least four nitrate groups in three unit cells must rotate by 90° about a line in their plane and some nitrates must rotate by 30° about their plane normals. In $RbNO_3$ and $CsNO_3$ similar nitrate rotations must occur when the crystals transform to and from the high-pressure structures.

The authors would like to thank Drs E. Horn and J. Rodgers for helpful comments. Dr S. W. Kennedy proposed the undertaking of the $RbNO_3$ structure solution.

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Reaction between Dibenzo-30-crown-10* and Potassium Thiocyanate; Structures of the 1:1 Complexes, Anhydrous and Monohydrated, $[K(C_{28}H_{40}O_{10})]^+.SCN^-$ and $[K(C_{28}H_{40}O_{10})]^+.SCN^-.H_2O$

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(*Received* 17 *February* 1984; *accepted* 10 *May* 1984)

Abstract. Monohydrate: $M_r = 651{\cdot}8$, monoclinic, $P2_1/n$, $a = 13{\cdot}335$ (2), $b = 12{\cdot}386$ (1), $c = 20{\cdot}584$ (2) Å, $\beta = 102{\cdot}67$ (1)°, $U = 3317{\cdot}0$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}305$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}272$ mm^{-1}, $F(000) = 1384$, room temperature, $R = 0{\cdot}129$ for 3081 reflexions. The conditions required to obtain reproducibly the anhydrous and monohydrate forms of dibenzo-30-crown-10–potassium thiocyanate (1:1) complex have been established. The crystal structure of the anhydrous form has been re-refined and some anomalies in the published structure [Hašek, Hlavatà & Huml (1980). *Acta Cryst.* B**36**, 1782–1785] resolved by choice of a different space group, $C2/c$. The complex cation $[K(C_{28}H_{40}O_{10})]^+$ lies on a twofold axis; the ligand has the same conformation as in the corresponding potassium iodide complex, but the packing is different, the thiocyanate ions occupying (with disorder) centres of symmetry. The X-ray crystal structure of the monohydrate has been determined. The $[K(C_{28}H_{40}O_{10})]^+$ cations are without symmetry and have four torsion angles differing by more than 20° from those of the anhydrous form. There is some disorder in the aliphatic chains of the ligand, similar to that in the isomorphous rubidium complex, and the K—O distances are significantly longer than in the anhydrous complex. Thiocyanate anions and water molecules are hydrogen bonded, with some disorder of nitrogen, but not sulphur, in positions to give chains along the *b* axis.

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* Systematic name: 6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,-33-hexadecahydrodibenzo[*b*,*q*][1,4,7,10,13,16,19,22,25,28]-decaoxacyclotriacontin.

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Introduction. As part of our investigation of the solid-state NMR spectra of crown ethers and their complexes (Belton *et al.*, 1983) we sought to aid interpretation of the splittings in the ^{13}C aromatic resonances by comparing the same complex cation in the presence of differently packed anions in compounds of known crystal structure. We therefore selected the potassium iodide (Bush & Truter, 1972) and potassium thiocyanate (Hašek, Hlavatà & Huml, 1980) complexes of dibenzo-30-crown-10, but encountered two unexpected problems, one chemical, the other crystallographic.

Poonia & Truter (1973) reported the synthesis of a monohydrate of the 1:1 complex of potassium thiocyanate with dibenzo-30-crown-10 from ethanol or ethanol–methanol 1:1. The presence of water was deduced from the infrared spectrum and by elemental analysis for C, H, N and K. On heating there was a transition at 378 K and melting at 408 K. Independently, Petránek & Ryba (1974) investigated the same system; the complex was prepared by mixing the ligand in hot ethyl acetate with potassium thiocyanate in hot methanol. The complex was reported as anhydrous but only the analysis for nitrogen was given [found 2·26%, *cf.* 2·3% (Poonia & Truter, 1973) and 2·21 or 2·15% calculated for the anhydrous or hydrated forms respectively]. The melting point was 411 K and the infrared spectrum was not reported. The crystal structure of the Petránek & Ryba sample was determined by Hašek *et al.* (1980) who described the crystals as needles.

Our chemical problem was that initial attempts to repeat the above preparations yielded products which often exhibited hydroxy stretching bands and split CN stretching bands of variable intensity in their infrared spectra, indicating the formation of a mixture of the anhydrous and hydrated complex. We now report methods for the reproducible syntheses for, and the characterization of, the anhydrous form and the monohydrate; for the latter we have determined the crystal structure.

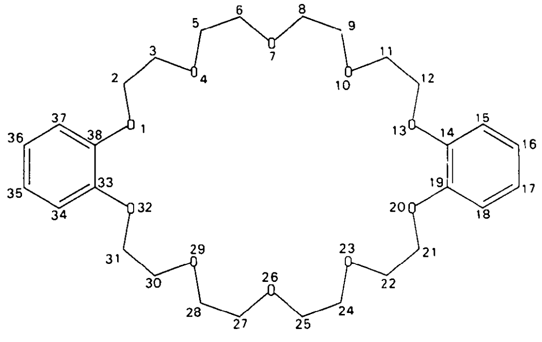

Fig. 1. The dibenzo-30-crown-10 ligand showing the numbering scheme. In space group $C2/c$, O(20) to C(38) are related to the others by a twofold axis at $(0, y, -\frac{1}{4})$ and are designated $O(1^i)$ to $C(19^i)$.

Our crystallographic problem was that the structure of the anhydrous form, as reported by Hašek *et al.* (1980), in space group *Cc* had, as they pointed out, some unsatisfactory features. We have now investigated the validity of assuming the space group to be $C2/c$. The formula of the ligand and numbering scheme are shown in Fig. 1.

Experimental. Details of the preparation and structure determination of both the monohydrate and anhydrous forms follow.

Preparation. The anhydrous form is obtained by dissolving 1:1 molar ratios of dibenzo-30-crown-10 and dried potassium thiocyanate in dry acetone, adding an equal volume of dry ethyl acetate and allowing the solution to evaporate slowly. Large chunky crystals, m.p. 411 K, are deposited. They give a sharp C≡N stretching band at 2050 cm^{-1} in the infrared spectrum.

The monohydrate is obtained by dissolving 1:1 molar ratios of dibenzo-30-crown-10 and potassium thiocyanate in hot ethyl acetate saturated with water. On cooling, crystallization occurs rapidly, producing long needles. On heating, these become opaque above 353 K, melting sharply at 411 K. They may be dehydrated by evacuation drying. In the infrared spectrum there are two hydroxy stretching bands at 3500 and 3380 cm^{-1}, the rest of the spectrum shows broader peaks than those of the anhydrous material with some changes in band position, particularly a shift in the C≡N stretch to 2060 cm^{-1}.

Anhydrous form. Hašek *et al.* (1980) reported the space group as *Cc*, with $a = 18{\cdot}749$ (3), $b = 9{\cdot}808$ (2), $c = 17{\cdot}681$ (4) Å, $\beta = 98{\cdot}64$ (3)°, $U = 3214$ Å^3, $Z = 4$. From 1625 observations, 539 parameters were refined by block-diagonal least squares, *i.e.* atomic coordinates for all atoms, individual isotropic thermal parameters for H atoms and anisotropic for other atoms. Despite superb R and R_w values, 0·029 and 0·034, there were some discrepancies the authors could not explain. There were two unrealistic bond lengths in each benzene ring and these were not improved by use of 400 additional observations with $2\sigma(I) < I < 4\sigma(I)$. They noted that the torsion angles were similar to those found for the iodide (Bush & Truter, 1972).

As the pairs of unusually long and unusually short carbon–carbon bond lengths would be symmetry related if the true space group were the centrosymmetric $C2/c$, it seemed possible that this was an example of refinement in a space group of unnecessarily low symmetry (Ermer & Dunitz, 1970). This postulate was tested with a computer program; the coordinates of atoms O(1)–C(19) (Fig. 1, Hašek *et al.*, 1980) were compared with those for O(20)–C(38) in equivalent positions at $x, -y, 0{\cdot}5 + z$ and the coordinates of a possible centre of symmetry relating these pairs of atoms was generated at 0·7021 (4), −0·0008 (11) and 0·4364 (5). A shift of origin to this position gave as coordinates for K −0·0007, 0·5867 and −0·2506, corresponding to location on the twofold axis at 0, *y*, $-\frac{1}{4}$, and for the C atom of the thiocyanate anion −0·2419, 0·7698, −0·0037, close to the centre of symmetry at $-\frac{1}{4}$, $\frac{3}{4}$, 0. Calculation of the bond lengths and angles from coordinates in *C*2/*c*, *i.e.* with K at 0, 0·5867, −0·25 and the atoms of the ligands at mean values obtained from application of the new origin to all atoms, and a twofold axis of symmetry to O(20)–C(38) gave reasonable values in agreement with those for the iodide, in which the complex cation is on a twofold axis. A thiocyanate anion disordered about a centre of symmetry provides an explanation for the anomalous vibration parameters found (Hašek *et al.*, 1980) in *Cc*, *viz* for the S, C and N atoms the B_{eq} values were 11·3, 6·6 and 3·8 Å^2, respectively.

A new refinement in *C*2/*c* was carried out, starting from the mean coordinates for the complex cation with mean isotropic vibration parameters derived from the pairs of B_{eq} (Hašek *et al.*, 1980). The deposited observations (Hašek *et al.*, 1980) are complete with unobserved reflections and individual e.s.d.'s. To obtain refinement comparable with theirs, only the 1620 reflections with $I > 4\sigma(I)$ were used in the full-matrix least-squares procedures in *SHELX* (Sheldrick, 1976). (The deposited data do not indicate which constitute their 1625 observations.) *R* was 0·28 with unit weights. From a difference map an electron density pattern consistent with a disordered thiocyanate ion was located; inclusion of this reduced *R* to 0·14. Refinement proceeded smoothly. All H atoms were located in a difference map, their coordinates and isotropic temperature factors were refined while the K$^+$ ion and the C and O atoms of the ligand were allowed anisotropic refinement. The thiocyanate ion electron density was best matched by fixing common anisotropic vibration parameters for all its atoms. Counting weights were introduced and the *SHELX* facility for refining the coefficient of F_o^2 gave a value of zero, so $w \propto 1/\sigma^2(F_o)$. The final *R* value for 1620 observations and 272 parameters was 0·034 and R_w was 0·038.

Refinement was also carried out on the complete data set, 2889 observations, yielding $R = 0·074$, $R_w = 0·073$ and standard deviations similar to those for the previous refinement. The weighting analysis showed that there was very poor agreement for 79 observations with $|F_o| < 1·0$. Finally, the 2327 observations having $|F_o| \geq \sigma(F_o)$ were used and refinement was concluded at $R = 0·053$, $R_w = 0·050$. Max. Δ/σ on final cycle 0·48 for ligand; higher values, for disordered thiocyanate ion; electron densities on final ΔF map within −0·23 and 0·48 e Å^{-3}. The parameters had lower standard deviations by about 0·001 Å in the bond lengths than refinements with 1620 or with 2889 observations.

Even in the centrosymmetric space group the thiocyanate ion remains unsatisfactory, the position of the C atom 0·2 Å from a centre of symmetry being nearly indeterminate. The largest peak in the final difference map, 0·5 e Å^{-3}, was 0·17 Å from the C atom, and all parameters involving this ion have high correlation coefficients. By contrast, in the complex cation, the H atoms are satisfactorily located with C—H bond lengths in the range 0·86 (4) to 1·09 (4) Å, the mean value is 0·99 Å for each of the C_{sp^2}—H and C_{sp^3}—H bonds with standard deviation 0·06 Å.

An attempt to apply the treatment of Hamilton (1965) required considerable extrapolation and indicated that the *C*2/*c* and *Cc* refinements were equally probable. However, internal consistency provides another criterion. The mean values for the aliphatic C—C bonds, aromatic C—C bonds and O—C(CH$_2$) bonds and the individual standard deviations from the spread about these mean values were calculated for four refinements (see Table 1). Even for the full-matrix refinements the standard deviations appear underestimated. Internal consistency suggests that the centrosymmetric refinement is more reliable, and further that the one based on 2327 observations is best. The corresponding revised atomic coordinates and some molecular dimensions are given in Tables 2* and 3. The conformation of the ligand molecule is nearly the same as in the potassium iodide complex (Bush & Truter, 1972) although there are some quantitative differences in torsion angles, the largest being for C(14)—C(19)—O(1′)—C(2′) which is −147 (1)° in the iodide. The geometry about the K$^+$ ions is also similar to that in the iodide. Packing in the crystal is quite different, the anions in the iodide being on twofold axes.†

Monohydrate form. Colourless needles, crystal size 0·33 × 0·43 × 0·79 mm. Cell dimensions calculated from positions of 20 reflexions $10 < \theta < 14°$. Data collected within $1·5 < \theta < 20°$, CAD-4 diffractometer, index range *h* ±12, *k* 0/11, *l* 0/19. Intensities of two standard reflexions changed by <5% during data collection, data corrected for this; no absorption correction, but weak intensities corrected using Bayesian statistics (French & Wilson, 1978). 3459 planes measured, equivalent planes averaged ($R_{int} = 0·018$), systematic absences removed, 3081 remained. Multisolution direct methods used to solve structure, H atoms in calculated positions; K, O and thiocyanate atoms refined with anisotropic temperature factors, C atoms of ligand isotropically; phenyl H atoms given a

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths and angles for both structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39479 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† *Note added in proof:* Dr J. Hašek confirms that his unpublished refinement in *C*2/*c* gave results consistent with those of Table 2. The different habits for the anhydrous form prepared in subtly different ways in the two laboratories are also confirmed.

Table 1. *Mean bond lengths* (Å) *with* σ_x *from the expression* $\sigma_x^2 = [\sum_n (x-\bar{x})^2]/(n-1)$ *for refinements of the anhydrous form*

(*a*) In *Cc* with 1625 observations (Hašek *et al.*, 1980);
(*b*) in *C*2/*c* with 1620 observations (see text);
(*c*) in *C*2/*c* with 2889 observations (see text);
(*d*) in *C*2/*c* with 2327 observations (see text).

	(*a*)	(*b*)	(*c*)	(*d*)
O–C(CH_2)	1·428 (53)	1·422 (13)	1·423 (11)	1·423 (13)
C–C(benzo)	1·378 (79)	1·379 (18)	1·379 (15)	1·379 (17)
C–C	1·470 (90)	1·481 (14)	1·486 (16)	1·481 (13)
Ranges of e.s.d. for bond lengths in the ligand from full-matrix least-squares refinements (*SHELX*)		0·003–0·006	0·003–0·007	0·003–0·006
From block-diagonal least squares (Hašek *et al.*, 1980)	0·005–0·011			

common $U_{\rm iso}$ [refined value 0·118 (11) Å^2] and remaining H's treated similarly [refined $U_{\rm iso} = 0\cdot175$ (8) Å^2]; water H atoms could not be located and were omitted. There is evidence in the large temperature factors for statistical as well as thermal disorder in the positions of some of the C atoms in the ligand. There is also considerable disorder in the positions of the thiocyanate and O(*w*) atoms, but separate sites could not be found on ΔF maps. For all 3081 planes used to refine the structure, with 250 parameters, $R = 0\cdot129$ and $R_w = 0\cdot127$; high R values probably due to disorder; $w \propto 1/\sigma^2(F_o)$. (With the 2504 observations having $|F| > \sigma F$, R was reduced to 0·113, R_w 0·119, but the standard deviations were 10% larger and internal consistency in bond lengths was the same as with the full set. We consider this indicated that the use of Bayesian statistics had provided realistic values for the weak reflexions.) Max. Δ/σ in final cycle 0·042, electron densities (e.d.) on final ΔF map $-0\cdot57 < \text{e.d.} < 0\cdot61$ e Å^{-3}, except for one peak 0·93 e Å^{-3} close to C(21), C(22), O(23), probably due to inadequate description of disorder in this part of molecule. Scattering factors calculated from published analytical coefficients (*International Tables for X-ray Crystallography* 1974). Structure solution and refinement (on *F*) carried out using *SHELX* (Sheldrick, 1976). Data reduction and geometry with local programs on a Prime 550 computer.

Discussion. The coordinates for the non-hydrogen atoms of the monohydrate are given in Table 4.* It is isomorphous with the rubidium complex, $C_{28}H_{40}O_{10}$.RbNCS.H_2O reported by Hašek, Huml & Hlavatà (1979). The $P2_1/c$ equivalent of our cell is 13·335 × 12·386 × 21·928 Å, $\beta = 113\cdot79°$, compared with 13·596 (3) × 12·411 (3) × 21·869 (7) Å, $\beta = 114\cdot36$ (2)° for the rubidium compound.

Table 2. *Atomic coordinates* (×10^4) *and* U_{eq} ($\text{Å}^2 \times 10^3$) *for the anhydrous form after refinement in C*2/*c with 2327 observations*

$$U_{\rm eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
K(1)	0	5859·6 (8)	−2500	53·7 (3)
S(*t*)	−2913 (3)	6246 (4)	77 (2)	104 (1)
C(*t*)	−2478 (6)	7640 (16)	−49 (10)	104 (1)
N(*t*)	−2075 (10)	8486 (13)	−179 (9)	104 (1)
O(1)	913·1 (9)	3436 (2)	−2384 (1)	62·8 (6)
C(2)	1139 (2)	2876 (4)	−1640 (2)	78 (1)
C(3)	558 (2)	3119 (3)	−1165 (2)	78 (1)
O(4)	401·2 (9)	4515 (2)	−1066 (1)	68·8 (7)
C(5)	924 (2)	5216 (5)	−549 (2)	95 (2)
C(6)	669 (3)	6619 (4)	−449 (2)	95 (2)
O(7)	671 (1)	7344 (2)	−1142 (1)	75·4 (8)
C(8)	408 (2)	8693 (4)	−1130 (3)	96 (2)
C(9)	−395 (2)	8755 (5)	−1215 (3)	99 (2)
O(10)	−668 (1)	8188 (2)	−1934 (1)	78·6 (8)
C(11)	−1442 (2)	8009 (4)	−2074 (3)	92 (2)
C(12)	−1703 (2)	6817 (3)	−1698 (2)	82 (1)
O(13)	−1435·3 (9)	5631 (2)	−2039 (1)	65·3 (7)
C(14)	−1664 (1)	4406 (3)	−1797 (1)	59·1 (9)
C(15)	−2142 (1)	4223 (5)	−1268 (2)	78 (1)
C(16)	−2327 (2)	2915 (5)	−1072 (2)	93 (2)
C(17)	−2053 (2)	1802 (5)	−1375 (2)	105 (2)
C(18)	−1584 (2)	1976 (4)	−1898 (2)	86 (1)
C(19)	−1398 (1)	3252 (3)	−2112 (1)	59·5 (9)

Table 3. *Selected molecular dimensions for the anhydrous form*

(*a*) Environment of the potassium ion

Bond lengths (Å)

K–O(1)	2·919 (2)	K–O(10)	2·857 (2)
K–O(4)	2·858 (2)	K–O(13)	2·935 (2)
K–O(7)	2·926 (2)		

Bond angles (°) in the form O_a–K–O_b, all e.s.d.'s 0·05°

O_a	(1)	(4)	(7)	(10)	(13)
O_b					
(4)	59·2				
(7)	99·9	58·5			
(10)	155·5	97·4	58·1		
(13)	118·1	81·3	96·3	59·7	
(1^i)	70·9				
(4^i)	76·1	125·0			
(7^i)	129·7	169·0	120·3		
(10^i)	113·1	127·5	74·5	73·8	
(13^i)	53·5	94·6	88·1	128·8	171·2

(*b*) Torsion angles in the macrocyclic ring. e.s.d.'s 0·2–0·4°

C(19^i)–O(1)–C(2)–C(3)	−178·6
O(1)–C(2)–C(3)–O(4)	−60·6
C(2)–C(3)–O(4)–C(5)	−74·6
C(3)–O(4)–C(5)–C(6)	−175·3
O(4)–C(5)–C(6)–O(7)	−68·6
C(5)–C(6)–O(7)–C(8)	177·6
C(6)–O(7)–C(8)–C(9)	−77·4
O(7)–C(8)–C(9)–O(10)	−61·7
C(8)–C(9)–O(10)–C(11)	172·6
C(9)–O(10)–C(11)–C(12)	−78·3
O(10)–C(11)–C(12)–O(13)	−65·7
C(11)–C(12)–O(13)–C(14)	−175·7
C(12)–O(13)–C(14)–C(19)	−178·8
O(13)–C(14)–C(19)–O(1^i)	2·1
C(14)–C(19)–O(1^i)–C(2^i)	−121·1

Symmetry code: (i) 0, *y*, $-\frac{1}{4}$.

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* See deposition footnote.

Table 4. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for the monohydrate*

U_{eq} is defined as in Table 2.

	x	y	z	U_{iso}/U_{eq}
K	2104 (1)	2321 (1)	−1057·2 (9)	67·6 (8)*
O(1)	3103 (4)	747 (5)	−99 (3)	83 (3)*
C(2)	2456 (7)	241 (8)	312 (5)	92 (3)
C(3)	1641 (9)	−277 (10)	−123 (6)	119 (4)
O(4)	1031 (5)	474 (6)	−537 (3)	108 (3)*
C(5)	311 (11)	−35 (12)	−1023 (8)	167 (5)
C(6)	−185 (10)	575 (12)	−1524 (6)	148 (5)
O(7)	548 (5)	982 (5)	−1923 (3)	98 (3)*
C(8)	48 (8)	1549 (9)	−2494 (5)	110 (3)
C(9)	−426 (7)	2590 (8)	−2332 (5)	94 (3)
O(10)	402 (4)	3243 (5)	−1983 (3)	77 (2)*
C(11)	67 (7)	4202 (8)	−1711 (4)	79 (3)
C(12)	−285 (7)	3999 (7)	−1083 (4)	77 (3)
O(13)	556 (4)	3581 (4)	−601 (3)	74 (2)*
C(14)	424 (6)	3348 (7)	20 (4)	71 (2)
C(15)	−546 (7)	3342 (8)	185 (5)	92 (3)
C(16)	−575 (8)	3082 (8)	841 (5)	100 (3)
C(17)	261 (9)	2854 (9)	1292 (6)	120 (4)
C(18)	1239 (8)	2855 (8)	1152 (5)	96 (3)
C(19)	1261 (7)	3098 (7)	486 (4)	80 (3)
O(20)	2200 (5)	3067 (5)	307 (3)	87 (3)*
C(21)	2825 (10)	3936 (11)	576 (6)	137 (4)
C(22)	3594 (12)	4130 (14)	325 (8)	184 (6)
O(23)	3557 (6)	4140 (7)	−365 (4)	130 (4)*
C(24)	3399 (11)	5076 (12)	−708 (7)	158 (5)
C(25)	3502 (9)	4928 (10)	−1380 (6)	132 (4)
O(26)	2763 (6)	4203 (6)	−1718 (4)	129 (4)*
C(27)	2794 (12)	3988 (14)	−2342 (8)	172 (6)
C(28)	3355 (11)	3174 (12)	−2488 (7)	157 (5)
O(29)	3128 (5)	2110 (7)	−2203 (3)	121 (4)*
C(30)	4051 (8)	1449 (9)	−2041 (5)	103 (3)
C(31)	4695 (7)	1709 (8)	−1380 (4)	89 (3)
O(32)	4134 (4)	1443 (5)	−895 (3)	84 (3)*
C(33)	4600 (7)	1468 (7)	−225 (5)	77 (3)
C(34)	5605 (8)	1867 (9)	6 (5)	102 (3)
C(35)	5963 (8)	1842 (9)	714 (5)	106 (3)
C(36)	5378 (8)	1454 (9)	1100 (6)	112 (4)
C(37)	4409 (8)	1077 (8)	875 (5)	98 (3)
C(38)	4028 (8)	1093 (8)	196 (5)	80 (3)
S(*t*)	−3426 (3)	3849 (4)	−1834 (3)	188 (3)*
C(*t*)	−2997 (11)	2756 (11)	−1667 (14)	222 (14)*
N(*t*)	−2720 (11)	1954 (16)	−1568 (13)	304 (14)*
O(*w*)	−2868 (8)	−270 (11)	−2023 (5)	234 (7)*

* U_{eq}.

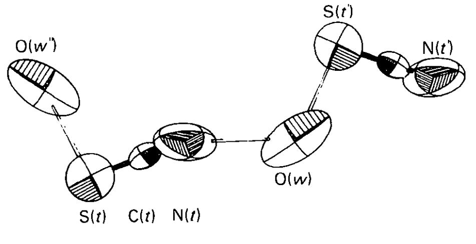

Fig. 2. The suggested hydrogen-bonding pattern of the monohydrate. Roman numeral superscripts refer to the equivalent positions relative to the coordinates in Table 4. (i) $-\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$. Distances are O(*w*)···N(*t*) 2·90 (2) Å, O(*w*)···S(t^{I}) 3·39 (1) Å; angles are N(*t*)···O(*w*)···S(t^{I}) 121·4 (5)°, C(*t*)—S(*t*)···O(w^{II}) 103·1 (9)° and C(*t*)—N(*t*)—O(*w*) 146 (2)°.

In the hydrates, the complex cations are isostructural, even down to the kind of disorder in the ligands, but our interpretation of the disorder in the thiocyanate–water system differs from that of Hašek *et al.* (1979). As shown in Fig. 2 the disorder appears to be based on relatively fixed S atoms with cooperative disorder in the C and N atoms and the water molecules. In contrast, Hašek *et al.* (1979) treated the ion as having 3:2 occupation of sites SCN or NCS leading to S—C and C—N bond lengths of 1·39 and 1·03 Å, respectively, with an angle of 148·7°. Our scheme gives 1·48 (2) and 1·07 (2) Å respectively, with angle 177 (3)°.

Hašek *et al.* (1979) obtained a better *R* factor, 0·046, partly because of the presence of a heavy atom and partly because they used 390 parameters compared with our 250. [With the 2053 corresponding observations, $|F| \geq 4\sigma(F)$, our *R* is improved to 0·099, R_w 0·111, and the standard deviations are 20% larger.] Their internal consistency is better than ours by a factor of two.

The evidence for disorder in the ligand follows a remarkably similar pattern for the K and Rb complexes. We have found that most of the aliphatic C—C bonds probably represent statistical averages, the worst is C(21)—C(22) with an apparent length 1·268 (16) Å and an O—C—C—O torsion angle of 44 (2)°. The range of these bonds is great, the longest being 1·504 Å for C(8)—C(9); the mean, excluding C(21)—C(22), is 1·42 Å with e.s.d. from the spread 0·07 Å (compared with a mean of 1·38 Å and e.s.d. 0·04 Å for the aromatic C—C bonds), which, as shown in Table 1, is normal.

The torsion angles of the ligand in the hydrate are in Table 5; none differs by more than 15° from the corresponding one in the rubidium complex (Hašek *et al.*, 1979). For the anhydrous form the conformation is similar to that in the iodide (Bush & Truter, 1972). Stereoviews of the two published structures on a strictly comparable basis can be seen in Dobler's (1981) book and are not reproduced here. The torsion angles in Tables 3 and 5 show that the anhydrous form has approximately the pattern from O(1) to O(13) of *t*, −*g*, −*g*; *t*, −*g*, *t*; −*g*, −*g*, *t*; −*g*, −*g*, *t*, while, in the hydrate, O(1) to O(13) runs *t*, +*g*, *t*; *t*, −*g*, *t*; −*g*, −*g*, *t*; −*g*, −*g*, *t*, whereas O(20) to O(32) runs *t*, −*g*, −*g*; *t*, −*g*, *t*; −*g*, −*g*, *t*; −*g*, −*g*, *t*. The different sign of the *gauche* angle at C(2)—C(3), gives a difference of 124°, change of kind at C(3)—O(4) a difference of 97°, while C(28)—O(29) at 148° is 32° from truly *trans*; the fourth angle which differs by more than 30° between the two forms is C(33)—C(38)—O(1)—C(2) [or C(14^{I})—C(19^{I})—O(1)—C(21)] at 54°. The effect of the last is that O(1) and C(2) in the hydrate are within 0·1 Å of the plane of the benzene ring, whereas in the anhydrous form, as at O(20) and C(21) for the hydrate, the C atom is 1·1 Å out of the plane of the benzene ring. In the anhydrous

Table 5. *Selected molecular dimensions for the monohydrate*

(*a*) Environment of the potassium ion

Bond lengths (Å)

K–O(1)	2·883 (6)	K–O(20)	2·933 (6)
K–O(4)	3·017 (7)	K–O(23)	3·106 (7)
K–O(7)	2·933 (7)	K–O(26)	2·930 (8)
K–O(10)	2·861 (6)	K–O(29)	2·984 (7)
K–O(13)	2·904 (5)	K–O(32)	2·868 (6)

Bond angles (°) in the form O_a–K–O_b, all e.s.d.'s 0·2°

O_a / O_b	(1)	(4)	(7)	(10)	(13)	(20)	(23)	(26)	(29)
(4)	55·1								
(7)	101·1	57·3							
(10)	154·8	99·8	57·9						
(13)	113·4	82·3	92·4	58·9					
(20)	69·0	79·8	129·5	111·9	53·5				
(23)	91·6	133·2	167·2	109·9	83·0	56·0			
(26)	135·7	169·2	114·3	69·4	91·7	103·8	54·2		
(29)	105·0	123·3	81·7	86·7	141·6	148·5	94·5	57·8	
(32)	51·8	100·4	112·3	145·0	152·4	99·6	75·2	89·1	58·3

(*b*) Torsion angles in the macrocyclic ring, e.s.d.'s 0·7–2·1°

C(38)–O(1)–C(2)–C(3)	166
O(1)–C(2)–C(3)–O(4)	63
C(2)–C(3)–O(4)–C(5)	−172
C(3)–O(4)–C(5)–C(6)	167
O(4)–C(5)–C(6)–O(7)	−66
C(5)–C(6)–O(7)–C(8)	−175
C(6)–O(7)–C(8)–C(9)	−67
O(7)–C(8)–C(9)–O(10)	−62
C(8)–C(9)–O(10)–C(11)	172
C(9)–O(10)–C(11)–C(12)	−79
O(10)–C(11)–C(12)–O(13)	−61
C(11)–C(12)–O(13)–C(14)	−179
C(12)–O(13)–C(14)–C(19)	171
O(13)–C(14)–C(19)–O(20)	1
C(14)–C(19)–O(20)–C(21)	−109
C(19)–O(20)–C(21)–C(22)	164
O(20)–C(21)–C(22)–O(23)	−44
C(21)–C(22)–O(23)–C(24)	−94
C(22)–O(23)–C(24)–C(25)	−174
O(23)–C(24)–C(25)–O(26)	−62
C(24)–C(25)–O(26)–C(27)	179
C(25)–O(26)–C(27)–C(28)	−90
O(26)–C(27)–C(28)–O(29)	−54
C(27)–C(28)–O(29)–C(30)	148
C(28)–O(29)–C(30)–C(31)	−84
O(29)–C(30)–C(31)–O(32)	−65
C(30)–C(31)–O(32)–C(33)	−171
C(31)–O(32)–C(33)–C(38)	174
O(32)–C(33)–C(38)–O(1)	1
C(33)–C(38)–O(1)–C(2)	−175

These angles are for a molecule related to that defined in Table 4 by inversion.

form the rings are nearly parallel [angle between the normals 0·7 (2)°], whereas in the monohydrate the angle between the normals is 28·1 (3)°.

The two forms show a different pattern of K–O distances; in the anhydous form, Table 3, the range is 2·857 (2) to 2·935 (2) Å [*cf.* 2·850 (6) to 2·931 (6) Å in the iodide] with the mean distance to the aromatic O atoms longer than that to the aliphatic ones, while, for the hydrate, Table 5, the range is 2·861 (6) to 3·106 (7) Å with the mean distances to the aromatic O atoms shorter than that to the aliphatic ones. The pattern is the same as that for the rubidium compound for which individual Rb–O values are from 0·069 to 0·152 Å longer than the corresponding K–O ones. The bond valence approach of Brown & Wu (1976), which is most useful in comparing irregularly coordinated with regularly coordinated cation environments in ionic structures, leads here to a higher bond valence, 1·11, around potassium in the anhydrous than in the hydrated form, 1·02.

The two compounds show a large difference in conformation brought about by subtle differences in the crystal packing. The monohydrate crystal transforms on heating to the anhydrous form (m.p. 411 K compared with 380 K for uncomplexed dibenzo-30-crown-10) so it is reasonable to suggest that the hydrogen bonding causes crystallization before the ligand has adopted the 'best' conformation.

From the difference in the volumes between hydrate and anhydrous forms, that occupied by the water molecule is 25·7 Å^3; this value is in fair agreement with 24·5 Å^3 obtained (Leclaire & Monier, 1982) from a survey of crystalline hydrates and anhydrous crystals and does not suggest that the complex cation in the former occupies a significantly larger volume than in the latter.

While the hydroxy stretching region of the infrared spectrum is consistent with a hydrogen-bonded water molecule, the higher C≡N stretching frequency in the hydrate form is unexpected because the hydrogen bonding should lead to a lower value. Unfortunately, the disorder associated with the thiocyanate anions in both structures precludes an explanation in terms of dimensions.

We thank Rothamsted Experimental Station Computing Unit for facilities and the Royal Society for some equipment.

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