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Thermal Stability of some Potassium Dibenzo-18-crown-6 Solid Compounds: KX(DB18C6) (X = NCS, Br, I, NO_3). Differential Scanning Calorimetry and X-ray Investigations

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Abstract

The thermal stability of the compounds KX(DB18C6) (X = NCS, Br, I, NO_3; DB18C6 = dibenzo-18-crown-6) has been determined by differential scanning calorimetry. Only the KNCS(DB18C6) complex melts congruently; the iodide and the nitrate compounds, when melting, undergo a partial dissociation into their components. The compound KI(DB18C6)-C_2H_5OH, when heated, loses the ethanol molecule without any dissociation. A KBr(DB18C6)3$CHCl_3$ compound was isolated; it dissociates into its components by evaporation of the solvate molecules.

Crystals of the compounds KNCS(DB18C6) are monoclinic, space group $P2_1/n$ with $a = 19.107(8)$, $b = 27.085(5)$, $c = 8.559(5)$ Å, $\beta = 101.96(4)^\circ$ and $Z = 8$. The structure was solved by the heavy atom method. Refinement of the atomic parameters by least-squares gave a final R factor of 0.127 (R_w = 0.116). The structure consists of independent complex molecules of KNCS(DB18C6) in which the potassium ion is coordinated by the six oxygen atoms of the crown ether and by the nitrogen atom of the thiocyanate ion.

Introduction

The crown ethers form complexes with a great variety of metals [1, 2]. The dibenzo-18-crown-6 (DB18C6) has a macrocyclic cavity suitable to give stable complexes with potassium ion both in solid and in solution [2]. Solid compounds have been isolated by using a number of synthetic procedures [3]. The thiocyanate compound KNCS(DB18C6) can be prepared from solutions involving different solvents or, in the absence of any solvent, by melting together the crown ether and the potassium salt. The phase diagram of the system KNCS/DB18C6 shows the formation of the unique 1:1 compound which melts congruently [4].

The coordinating ability of this crown ether towards alkaline metal ions in the solid phase has been investigated by X-ray analysis of the [($Rb_{0.55}$-$Na_{0.45}$)NCS(DB18C6)]$_2$(DB18C6) [5] and the NaBr(DB18C6)2H_2O [6] compounds. Furthermore, preliminary results on the crystal structure determination of the KI(DB18C6)0.5H_2O have been reported [7], as well as the principal structural details of a polymeric 1:1:1 compound KI(DB18C6)thiourea [8]. The effect of the anion on complexation in the crystal lattice and on the stoichiometry of the solid phases has been investigated for several analogous systems [9, 10].

In this paper we report the crystal and molecular structure of the KNCS(DB18C6) compound, as well as the results of a differential scanning calorimetric analysis of some compounds of the type KX(DB18C6) (X = NCS, Br, I, NO_3).

Experimental

Synthesis of the Compounds

KNCS(DB18C6)

Crystals of this compound were prepared as previously described [4].

KNO_3(DB18C6)

A boiling solution of 0.77 mmol of KNO_3 in 20 cm^3 of ethanol and 2 cm^3 of water was added to a boiling solution of 0.77 mmol of DB18C6 in 20 cm^3 of ethanol and 10 cm^3 of methylene chloride. The

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resulting solution was concentrated to 10 cm^3 and allowed to crystallize. The crystalline product was filtered, washed with cold ethanol and recrystallized from ethanol. *Anal.* Calc. for $C_{20}H_{24}O_9NK$: C, 52.05; H, 5.24; N, 3.03. Found: C, 52.2; H, 5.3; N, 3.0%.

KI(DB18C6)C_2H_5OH

1 mmol of KI in 20 cm^3 of boiling ethanol was added to a boiling solution of 1 mmol of DB18C6 in 20 cm^3 of ethanol and .10 cm^3 of methylene chloride. The resulting solution was concentrated to 10 cm^3 and allowed to cool. The product that crystallized on standing was removed by filtration, washed with ethanol and dried *in vacuo* at room temperature. *Anal.* Calc. for $C_{22}H_{30}O_7IK$: C, 46.15; H, 5.28. Found: C, 45.8; H, 5.2%.

The molecule of ethanol is released at 138 °C, as demonstrated by DSC analysis (see later Fig. 4, thermogram a). Drying of the above product for 3 h at 140 °C gave an unsolvated compound. *Anal.* Calc. for $C_{20}H_{24}O_6IK$: C, 45.63; H, 4.59. Found: C, 45.6; H, 4.6%.

*KBr(DB18C6)3*$CHCl_3$

1 mmol of KBr and 1 mmol of DB18C6 in 30 cm^3 of chloroform and 20 cm^3 of ethanol were heated under reflux until all the KBr was dissolved (24 h). The solution was evaporated to 5 cm^3 and diluted with 30 cm^3 of boiling chloroform. Crystals of the compound developed on cooling. These were filtered, washed with chloroform and dried *in vacuo* at room temperature. *Anal.* Calc. for $C_{23}H_{27}O_6Cl_9BrK$: C, 32.98; H, 3.25. Found: C, 33.1; H, 3.3%.

Differential Scanning Calorimetry

DCS analyses were carried out by using a DSC-2C (Perkin-Elmer) differential scanning calorimeter coupled with a Scanning AutoZero (Perkin-Elmer) and a 56-recorder (Perkin-Elmer). Aluminium volatile sample pans were used in all the experiments. The sample holder was purged by a flow of nitrogen (UPP grade) which had been dried with a gas filter-dryer.

Crystal Structure Determination

X-ray data collection

Crystallization from ethanol solution yielded very thin colourless needles of KNCS(DB18C6) complex. Several crystals were tested and all of them showed poor diffracting properties mainly due to the small dimensions. The crystal chosen for data collection had approximate dimensions: 0.02 × 0.02 × 0.15 mm. A Philips PW1100 automatic diffractometer was used both for determination of lattice parameters and for intensity data. The unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 carefully centered reflections. Graphite monochromatized Mo Kα radiation was used to measure the intensities of 5396 independent reflections in the range $4° < 2\vartheta < 45°$ with the ϑ–2ϑ scan technique.

705 reflections with $I > 3\sigma(I)$ were observed and used for the structure solution and refinement. The standard deviation of intensity $\sigma(I)$ was computed as: $\sigma(I) = [P + B_1 + B_2 + (0.03I)^2]^{1/2}$ where P is the total integrated count, B_1 and B_2 are the background counts, I is the peak intensity after subtraction of the background and $0.03I$ is a correction for unrealistically small standard deviations in strong reflections. Three reflections monitored periodically did not show any systematic variation in intensity during data collection. Intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure solution and refinement

Crystal data. $C_{20}H_{24}O_6KCNS$; $M = 457.58$; monoclinic, space group $P2_1/n$; $a = 19.107(8)$; $b = 27.085(5)$; $c = 3.559(5)$ Å; $\beta = 101.96(4)°$; $U = 4333.9$ Å^3; $Z = 8$; $D_c = 1.403$ g cm^{-3}; Mo Kα radiation, $\lambda = 0.7107$ Å; $\mu = 1.64$ cm^{-1}.

The large unit cell dimensions suggested the presence of eight molecules in the unit cell. This was confirmed by the Patterson map which was readily interpreted assuming two independent potassium atoms per asymmetric unit. A subsequent series of Fourier syntheses phased on their position revealed all the nonhydrogen atoms of the two complex molecules.

Refinement was performed by a blocked full matrix least-squares technique dividing the structure in two blocks each consisting of one KNCS(DB18C6) complex molecule. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = k/\sigma^2(F)$, where k is an adjustable parameter.

The benzene rings of the two DB18C6 macrocyles were refined as rigid groups (C–C distances 1.395 Å and C–C–C angles 120°). Isotropic thermal parameters were used throughout the refinement for all the atoms. A total of 198 parameters were refined against 705 observations giving an observations/parameters ratio of 3.6. With the hydrogen atoms inserted in calculated positions, the refinement converged to the final values of 0.127 and 0.116 for R and R_w factors. ($R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_c)^2]^{1/2}$). A final difference synthesis did not show any significant features above the background.

All calculations were performed with the SHELX76 set of programs [11], with coefficients for analytical approximation to the scattering factors and anomalous dispersion corrections from the International Tables [12]. Final atomic coordinates and

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^4$) for KNCS(DB18C6)

Atom	*x*	*y*	*z*	*U*
K1	1741(7)	1028(6)	2062(19)	422(54)
O1	587(22)	525(18)	2802(57)	511(164)
O2	1422(22)	123(15)	1067(50)	455(148)
O3	2579(25)	520(17)	220(57)	571(171)
O4	2848(23)	1500(19)	1069(55)	674(171)
O5	1794(20)	2021(14)	2481(46)	326(138)
O6	857(18)	1573(15)	3605(42)	177(119)
C1	835(28)	82(22)	3174(65)	53(180)
C2	927(37)	-240(27)	1607(83)	727(275)
C3	1613(25)	-84(19)	-370(43)	510(253)
C4	1273(25)	-447(19)	-1416(43)	634(265)
C5	1556(25)	-585(19)	-2728(43)	454(233)
C6	2178(25)	-361(19)	-2995(43)	720(284)
C7	2518(25)	1(19)	-1949(43)	864(308)
C8	2235(25)	139(19)	-636(43)	415(231)
C9	3191(32)	757(24)	98(81)	434(231)
C10	3440(30)	1196(22)	1141(72)	267(202)
C11	2921(26)	1960(20)	1966(64)	44(171)
C12	2345(30)	2339(24)	1947(77)	465(232)
C13	1255(18)	2333(17)	2738(47)	431(229)
C14	1185(18)	2845(17)	2588(47)	210(196)
C15	589(18)	3080(17)	2953(47)	687(267)
C16	63(18)	2804(17)	3467(47)	185(186)
C17	133(18)	2293(17)	3617(47)	320(210)
C18	729(18)	2057(17)	3252(47)	246(204)
C19	270(31)	1305(22)	3904(73)	265(205)
C20	550(32)	808(24)	4183(77)	373(222)
C21	3272(33)	950(20)	5622(68)	154(183)
N1	2644(26)	867(18)	5041(57)	316(177)
S1	4047(11)	919(8)	6517(28)	828(89)
K2	1478(7)	3178(6)	6582(18)	406(52)
O7	2671(19)	2763(16)	5690(46)	285(132)
O8	1809(23)	2219(17)	7432(52)	546(154)
O9	763(19)	2561(15)	8401(44)	197(121)
O10	261(20)	3634(17)	7367(51)	374(142)
O11	1031(26)	4073(18)	5541(61)	915(189)
O12	2192(22)	3747(16)	4676(54)	525(156)
C22	2941(31)	2398(23)	6872(78)	404(226)
C23	2428(30)	1983(22)	6950(69)	259(208)
C24	1344(18)	1894(17)	7854(41)	153(176)
C25	1426(18)	1383(17)	7787(41)	129(193)
C26	926(18)	1071(17)	8254(41)	553(239)
C27	344(18)	1269(17)	8788(41)	646(273)
C28	262(18)	1780(17)	8855(41)	318(204)
C29	762(18)	2092(17)	8389(41)	284(211)
C30	80(31)	2792(23)	8558(74)	365(215)
C31	246(29)	3263(23)	8786(70)	263(202)
C32	438(33)	4089(25)	7670(79)	476(240)
C33	464(34)	4403(26)	6006(80)	630(264)
C34	1245(27)	4288(17)	4097(45)	251(195)
C35	839(27)	4644(17)	3133(45)	674(274)
C36	1076(27)	4835(17)	1820(45)	1344(403)
C37	1718(27)	4671(17)	1472(45)	415(231)
C38	2124(27)	4315(17)	2436(45)	195(190)
C39	1887(27)	4124(17)	3748(45)	987(329)
C40	2862(33)	3551(24)	4571(84)	575(253)
C41	3173(31)	3133(24)	5853(73)	415(222)
C42	2810(28)	3399(20)	9977(68)	48(169)
N2	2263(30)	3392(21)	9490(69)	688(216)
S2	3727(11)	3373(8)	11073(26)	764(83)

thermal parameters with estimated standard deviations obtained from least-squares calculations are reported in Table I.

Results and Discussion

Description of the Structure

The asymmetric unit consists of two independent ion pairs KNCS(DB18C6) in which the ligand macrocycle shows the same conformation with small differences appearing only in some minor structural details. Figure 1 shows the asymmetric unit contents (excluding hydrogen atoms) together with the arbitrary numbering scheme adopted in this work. A stereoview of the unit cell is depicted in Fig. 2.

In the complex molecule the potassium ion is coordinated by the six oxygen atoms of the crown ether and by the nitrogen atom of the thiocyanate ion and sits at the center of the base of an orthogonal hexagonal pyramid with the nitrogen atom at the apex. Averaged K–O and K–N distances are the same within experimental error, being 2.76(5) and 2.74(5) Å, respectively.

In both molecules the six oxygen atoms of the ligand are coplanar with a maximum deviation of 0.17 Å from the least-squares plane through them (Table II). The potassium ion lies in this plane (0.18 and 0.07 Å are its deviations in the two molecules). The same behaviour has been observed in the analogous KI(DB18C6)$0.5H_2O$ compound [7], whereas in the rubidium complex of DB18C6 [5] the larger rubidium ion is out of the mean oxygen plane by 0.94 Å.

In the two structures referred to above and in the compound investigated here the distances of the six oxygen atoms from the center of the complexed ligand ring fall within the range 2.73–2.79 Å, showing that the potassium ion fits perfectly into the DB18C6 central cavity. Table III reports bond lengths and angles for the two independent complex molecules.

The limited accuracy of the present data do not allow a detailed discussion and comparison of bond lengths and angles. However, (apart from some unreasonably short and some unreasonably long C–O and C–C bond distances) we observe the same trend reported for the DB18C6 ligand in the rubidium complex [5] in the chemically equivalent

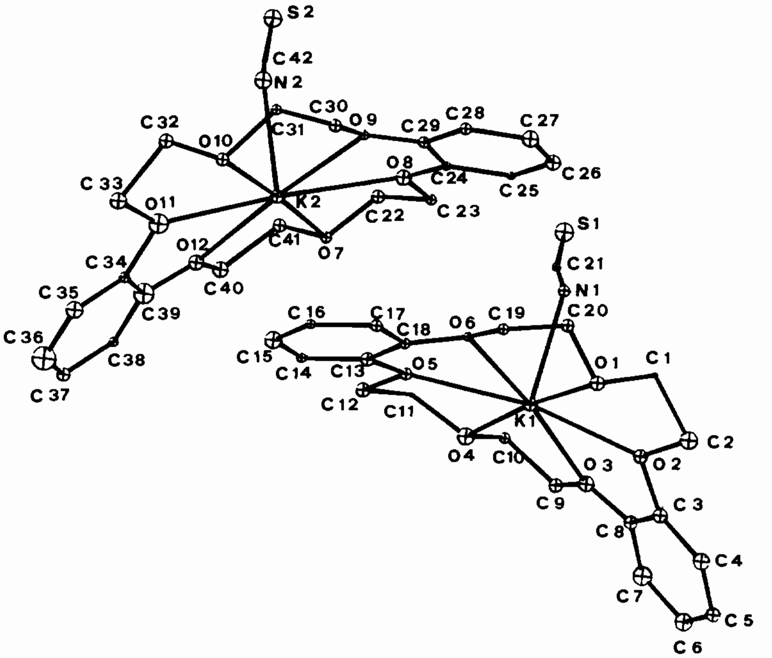

Fig. 1. Ortep [14] drawing of the asymmetric unit contents and numbering scheme. Thermal ellipsoids are drawn at 30% probability.

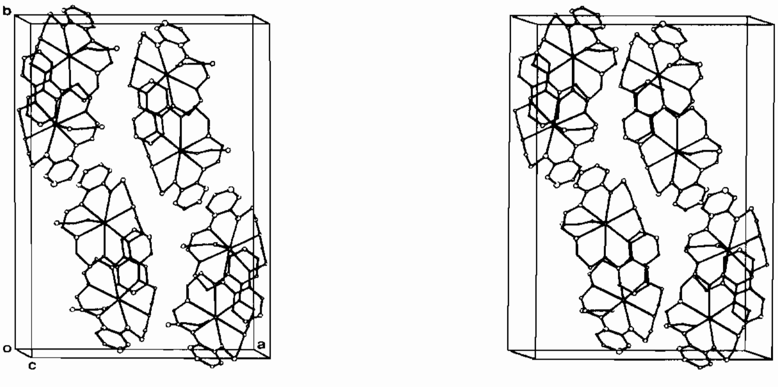

Fig. 2. Stereoview of the unit cell contents.

$C_{aliphatic}$–O and $C_{aromatic}$–O bond distances, which averaged 1.44(8) and 1.38(8) Å, respectively.

Thermal Stability

KNCS/DB18C6

In a previous paper [4] we have reported the thermogram of a 1:1 mixture of KNCS and DB18C6. It shows a small endothermic peak at 142 °C, due to the transition between the crystalline modifications I and II of KNCS; it also shows peaks corresponding to the melting of DB18C6 and consequent formation and crystallization of the 1:1 complex which melts congruently at 245 °C. In the same paper reversibility of the melting process of this complex was demonstrated. The same complex was obtained from different solvents (organic and aqueous–organic solutions) and was always found to be free from any solvate molecules.

KNO_3/DB18C6

A compound of formula KNO_3(DB18C6) was prepared and thermally analyzed as described in 'Experimental'. The thermogram in Fig. 3a revealed a unique peak at 188 °C. Successive examinations of the cooled sample (Fig. 3a) showed a small exothermic effect between 114 °C and 130 °C, then a small endothermic peak at 131 °C, followed by two pronounced endothermic peaks at 160 °C and 185 °C. This means that the complex melts with a partial dissociation into the components: presum-

TABLE II. Least Squares Planes through Various Groups of Atoms

Equations of planes in direct space

Plane (1): $8.19050x - 6.80017y + 6.50660z = 1.88657$
Plane (2): $-8.77897x + 18.24771y - 4.03135z = -1.38845$
Plane (3): $5.31135x + 3.67966y + 7.46922z = 3.62500$
Plane (4): $7.96342x + 9.81573y + 6.24100z = 8.33431$
Plane (5): $5.67302x + 0.67414y + 7.46628z = 6.81025$
Plane (6): $7.40242x + 19.18944y + 4.25195z = 10.87145$

Acute angles between planes (deg)

Plane (1)–Plane (2)	29.7	Plane (1)–Plane (3)	24.4
Plane (2)–Plane (3)	54.1	Plane (4)–Plane (5)	21.8
Plane (4)–Plane (6)	24.5	Plane (5)–Plane (6)	45.9

Deviations from planes (Å)

(a) Atoms included in calculations

Plane (1)		Plane (2)		Plane (3)		Plane (4)		Plane (5)		Plane (6)	
O(1)	0.061	C(5)	0.054	C(15)	0.027	O(7)	0.056	C(26)	−0.050	C(36)	−0.022
O(2)	−0.111	C(6)	0.024	C(16)	0.030	O(8)	−0.076	C(27)	0.032	C(37)	−0.010
O(3)	0.015	C(7)	−0.034	C(17)	−0.009	O(9)	0.031	C(28)	0.070	C(38)	0.017
O(4)	0.121	C(8)	−0.063	C(18)	−0.052	O(10)	0.038	C(29)	0.026	C(39)	0.032
O(5)	−0.177	C(9)	−0.071	C(19)	−0.085	O(11)	−0.057	C(30)	−0.187	C(40)	0.005
O(6)	0.091	C(10)	0.091	C(20)	0.089	O(12)	0.008	C(31)	0.109	C(41)	−0.022

(b) Additional atoms

K(1)	0.182					K(2)	0.070				

TABLE III. Bond Lengths (Å) and Angles (deg) for KNCS(DB18C6)

Bond lengths

K(1)–O(1)	2.77(5)	K(1)–O(2)	2.62(4)	K(1)–O(3)	2.83(5)
K(1)–O(4)	2.75(5)	K(1)–O(5)	2.71(4)	K(1)–O(6)	2.77(4)
K(1)–N(1)	2.80(5)	O(1)–C(1)	1.30(7)	O(1)–C(20)	1.42(8)
O(2)–C(2)	1.50(9)	O(2)–C(3)	1.47(6)	O(3)–C(8)	1.35(6)
O(3)–C(9)	1.36(8)	O(4)–C(10)	1.39(7)	O(4)–C(11)	1.45(7)
O(5)–C(12)	1.50(8)	O(5)–C(13)	1.39(6)	O(6)–C(18)	1.36(6)
O(6)–C(19)	1.40(7)	C(1)–C(2)	1.64(9)	C(9)–C(10)	1.50(9)
C(11)–C(12)	1.50(8)	C(19)–C(20)	1.45(9)	S(1)–C(21)	1.53(6)
N(1)–C(21)	1.22(7)	K(2)–O(7)	2.79(4)	K(2)–O(8)	2.73(5)
K(2)–O(9)	2.82(4)	K(2)–O(10)	2.83(4)	K(2)–O(11)	2.66(5)
K(2)–O(12)	2.80(5)	K(2)–N(2)	2.69(5)	O(7)–C(22)	1.43(7)
O(7)–C(41)	1.37(7)	O(8)–C(23)	1.48(8)	O(8)–C(24)	1.35(6)
O(9)–C(29)	1.27(6)	O(9)–C(30)	1.48(7)	O(10)–C(31)	1.58(8)
O(10)–C(32)	1.29(8)	O(11)–C(33)	1.52(9)	O(11)–C(34)	1.50(7)
O(12)–C(39)	1.35(6)	O(12)–C(40)	1.40(8)	C(22)–C(23)	1.50(9)
C(30)–C(31)	1.32(9)	C(32)–C(33)	1.67(9)	C(40)–C(41)	1.60(9)
S(2)–C(42)	1.81(5)	N(2)–C(42)	1.04(7)		

Bond angles

O(1)–K(1)–O(2)	58(1)	O(2)–K(1)–O(3)	59(1)
O(3)–K(1)–O(4)	60(1)	O(4)–K(1)–O(5)	65(1)
O(5)–K(1)–O(6)	55(1)	N(1)–K(1)–O(1)	95(1)
N(1)–K(1)–O(2)	102(1)	N(1)–K(1)–O(3)	97(1)
N(1)–K(1)–O(4)	89(1)	Ni(1)–K(1)–O(5)	92(1)
N(1)–K(1)–O(6)	88(1)	K(1)–O(1)–C(1)	104(3)
K(1)–O(2)–C(2)	129(4)	K(1)–O(2)–C(3)	123(3)
K(1)–O(3)–C(8)	114(3)	K(1)–O(3)–C(9)	114(4)

(continued)

TABLE III *(continued)*

K(1)–O(4)–C(10)	112(4)	K(1)–O(4)–C(11)	103(3)
K(1)–O(5)–C(12)	122(3)	K(1)–O(5)–C(13)	128(3)
K(1)–O(6)–C(18)	120(3)	K(1)–O(6)–C(19)	114(3)
C(1)–O(1)–C(20)	112(5)	C(2)–O(2)–C(3)	107(4)
C(8)–O(3)–C(9)	130(5)	C(10)–O(4)–C(11)	120(4)
C(12)–O(5)–C(13)	107(4)	C(18)–O(6)–C(19)	115(4)
O(1)–C(1)–C(2)	113(5)	O(2)–C(2)–C(1)	95(5)
O(2)–C(3)–C(4)	130(4)	O(2)–C(3)–C(8)	110(4)
O(3)–C(8)–C(3)	125(4)	O(3)–C(8)–C(7)	115(5)
O(3)–C(9)–C(10)	120(6)	O(4)–C(10)–C(9)	107(4)
O(4)–C(11)–C(12)	126(4)	O(5)–C(12)–C(11)	99(5)
O(5)–C(13)–C(14)	131(4)	O(5)–C(13)–C(18)	109(4)
O(6)–C(18)–C(13)	119(4)	O(6)–C(18)–C(17)	121(4)
O(6)–C(19)–C(20)	103(5)	O(1)–C(20)–C(19)	116(5)
S(1)–C(21)–N(1)	165(5)	K(1)–N(1)–C(21)	135(4)
O(7)–K(2)–O(8)	62(1)	O(8)–K(2)–O(9)	53(1)
O(9)–K(2)–O(10)	67(1)	O(10)–K(2)–O(11)	57(1)
O(7)–K(2)–O(12)	62(1)	O(11)–K(2)–O(12)	58(1)
N(2)–K(2)–O(7)	91(1)	N(2)–K(2)–O(8)	85(1)
N(2)–K(2)–O(9)	82(1)	N(2)–K(2)–O(10)	91(2)
N(2)–K(2)–O(11)	101(2)	N(2)–K(2)–O(12)	100(2)
K(2)–O(7)–C(22)	106(3)	K(2)–O(7)–C(41)	106(3)
K(2)–O(8)–C(23)	119(3)	K(2)–O(8)–C(24)	124(3)
K(2)–O(9)–C(29)	126(3)	K(2)–O(9)–C(30)	110(3)
K(2)–O(10)–C(31)	93(3)	K(2)–O(10)–C(32)	106(4)
K(2)–O(11)–C(33)	130(4)	K(2)–O(11)–C(34)	120(3)
K(2)–O(12)–C(39)	124(3)	K(2)–O(12)–C(40)	113(4)
C(22)–O(7)–C(41)	107(4)	C(23)–O(8)–C(24)	114(4)
C(29)–O(9)–C(30)	115(4)	C(31)–O(10)–C(32)	120(5)
C(33)–O(11)–C(34)	109(4)	C(39)–O(12)–C(40)	122(5)
O(7)–C(22)–C(23)	114(4)	O(8)–C(23)–C(22)	105(5)
O(8)–C(24)–C(25)	123(4)	O(8)–C(24)–C(29)	117(4)
O(9)–C(29)–C(24)	113(4)	O(9)–C(29)–C(28)	127(4)
O(9)–C(30)–C(31)	103(5)	O(10)–C(31)–C(30)	123(5)
O(10)–C(32)–C(33)	112(5)	O(11)–C(33)–C(32)	94(5)
O(11)–C(34)–C(35)	123(4)	O(11)–C(34)–C(39)	117(4)
O(12)–C(39)–C(34)	114(4)	O(12)–C(39)–C(38)	126(5)
O(12)–C(40)–C(41)	116(6)	O(7)–C(41)–C(40)	107(4)
S(2)–C(42)–N(2)	172(6)	K(2)–N(2)–C(42)	134(6)

ably the liquid DB18C6 and the solid KNO_3. In fact, the peaks at 131 °C and 160 °C correspond, respectively, to the transition form I → form **II** of the solid KNO_3 and to the melting of the DB18C6.

Similar and reproducible thermograms were obtained on a 1:1 mixture of KNO_3 and DB18C6 maintained at 200 °C for several hours. This behaviour suggested the existence of a reversible reaction: $KNO_{3(c)} + DB18C6_{(l)} = KNO_3(DB18C6)_{(l)}$. An excess of KNO_3 produced a diminution of the peak of melting of DB18C6 and an increase in that of the complex (Fig. 3c).

KI/DB18C6

This system behaved similarly to that described for KNO_3/DB18C6 and has been previously studied by a DTA analysis [13]. The complex KI(DB18C6) melts at 234 °C (Fig. 4b) with a partial dissociation. In fact, thermograms (Fig. 4c) recorded from samples cooled just after the melting point revealed a peak due to the melting of the free DB18C6 and a new peak at 211 °C probably due to a compound with a stoichiometry different from that of the 1:1 composition. This peak had also been observed in the DTA analysis made on KI/DB18C6 containing a large excess of KI; the peak was attributed to a supposed $(DB18C6)KI_2$ compound.

KBr/DB18C6

Thermograms of KBr/DB18C6 mixtures (Fig. 5c) revealed only the melting of the free DB18C6 without the formation of any complex. The thermal analysis of the solvate compound $KBr(DB18C6)3CHCl_3$, obtained as described in 'Experimental', revealed (Fig. 5a) a sharp peak at 77 °C due to a loss of two molecules of chloroform followed by a large peak

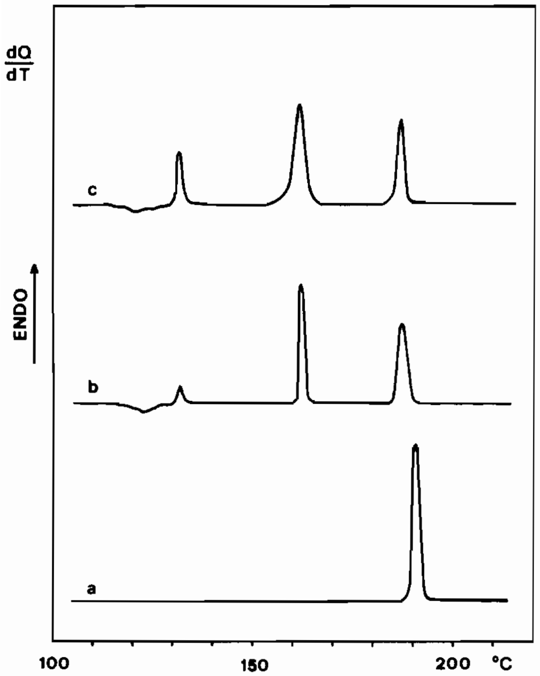

Fig. 3. KNO_3/DB18C6. Thermogram a: KNO_3(DB18C6) compound. Thermogram b: KNO_3(DB18C6) compound after melting and cooling at room temperature. Thermogram c: 2:1 KNO_3:DB18C6 mixture.

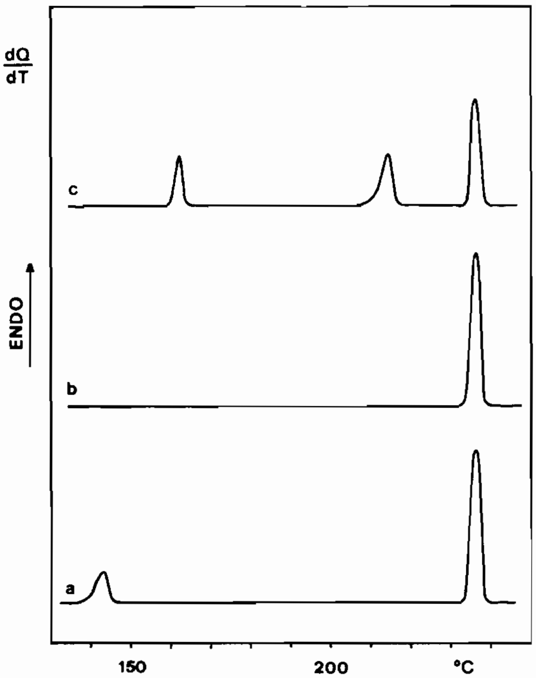

Fig. 4. KI/DB18C6. Thermogram a: KI(DB18C6)C_2H_5OH compound. Thermogram b: KI(DB18C6) compound. Thermogram c: KI(DB18C6) compound after melting and cooling at room temperature.

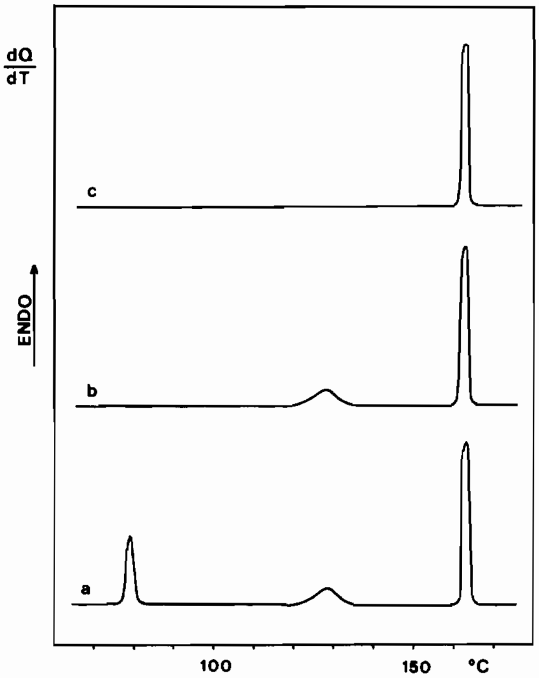

Fig. 5. KBr/DB18C6. Thermogram a: KBr(DB18C6)$3CHCl_3$ compound. Thermogram b: the same compound after drying at 100 °C. Thermogram c: the same compound dried at 140 °C.

between 117 °C and 136 °C due to the loss of the third molecule of chloroform. After that, only the melting of the DB18C6 is observed. This leads to the conclusion that an unsolvated complex with KBr is not formed in our experiments. Attempts to prepare such a complex from solutions were unsuccessful.

In conclusion, the effect of the anion on the thermal stability of the potassium dibenzo-18-crown-6 complexes is demonstrated. It is shown that the less stabilizing anion is bromide, whilst iodide and nitrate have an intermediate capacity. The most stabilizing anion is the thiocyanate which, as shown by the results of the X-ray analysis reported here, is strongly coordinated to the potassium. Structural determinations on NO_3 and Br compounds do not exist in the literature. The structure of the iodide compound KI(DB18C6)$0.5H_2O$ consists of two different complex molecules, one having the iodide and one having a molecule of water in the apical position of the hexagonal coordination pyramid [7]. In the KI(DB18C6)thiourea compound the iodide is coordinated to the potassium and the structure is stabilized by hydrogen bonds [8]. Thus, the occupation of the apical position seems to contribute to the stabilization of these compounds. Furthermore, the presence of solvate molecules is required when the stabilizing effect of the anion diminishes.

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