Correlation between Thermal Stability and Molecular and Crystal Structure in a Series of Potassium–Dibenzo-18-Crown-6 Solid Compounds†

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The compounds [K(NO_3)L] (L = 6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*][1,4,7,10,13,16]-hexaoxacyclo-octadecin) and [K(Hpht)L] (Hpht = hydrogenphthalate) have been studied by differential scanning calorimetry and single-crystal *X*-ray analyses. Both the complexes undergo, upon melting, a partial dissociation into their components. The enthalpy of melting of [K(NO_3)L] is fairly high (14.6 kcal mol^{-1}) and equal, within experimental error, to the enthalpy of melting of the free ligand, L. The entropy of melting of the complex reflects an increased stiffening in the complexed crown ether molecule with respect to the free ligand. Crystals of [K(NO_3)L] and of [K(Hpht)L] are monoclinic, space group $P2_1/c$ with a = 15.054 4(7), b = 20.575(2), c = 14.259(1) Å, β = 97.655(5)°, Z = 8; and orthorhombic, space group $P2_12_12_1$ with a = 15.990(2), b = 17.915(1), c = 9.314(1) Å, Z = 4 respectively. Refinement of the atomic parameters by least squares gave a final R factor of 0.0544 (R' = 0.0590) and of 0.0622 (R' = 0.0735) respectively. Both the structures consist of independent complex molecules {two in an asymmetric unit for [K(NO_3)L]} in which the potassium ion is surrounded by eight oxygen donor atoms, six from L and two from the anions. The nitrate ion acts as a symmetrically bonded bidentate ligand [K $\cdots$ O 2.832(4), 2.836(4) and 2.815(4), 2.790(4) Å] while Hpht is asymmetrically bonded [K $\cdots$ O 2.729(9), 3.168(8) Å]. The potassium ions are pulled 0.631(1) and 0.465(1) Å from the least-squares plane through the six oxygen donors of L, towards the nitrate ion, and 0.592 Å toward the hydrogenphthalate ion. The comparison of these complexes with the NCS derivative shows the existence of a correlation between their thermal stability and the displacement of the potassium ion from the donor ring.

The role of the anion on complexation of alkali and alkaline-earth metal cations by dibenzo-18-crown-6 (6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin, L) has been studied for several systems.[1–3] In recent papers we have reported the results, obtained by differential scanning calorimetry (d.s.c.), on the thermal stability of a series of [KX(L)] (X = NCS, Br, I, or NO_3) solid compounds.[3,4] We have found that the most stabilizing anion is the thiocyanate, whose derivative melts congruently without any decomposition. *X*-Ray analysis of this compound showed that the thiocyanate ion is co-ordinated to the potassium, which is coplanar with the six oxygen atoms of the crown ether. The least stabilizing anion is bromide, for which [KBr(L)]·3$CHCl_3$ was isolated; it dissociates into its components by evaporation of the solvate molecules. Potassium iodide and KNO_3 with dibenzo-18-crown-6 form compounds of intermediate thermal stability which melt with partial dissociation. The behaviour of the system KNO_3–L suggested the existence of the reversible reaction KNO_3 (c) + L (l) $\rightleftharpoons$ [K(NO_3)L] (l). In fact, liquid dibenzo-18-crown-6 partially reacts with solid KNO_3 to produce the [K(NO_3)L] liquid complex.

In the same paper it was proposed that the choice of the anion occupying the apical position in the potassium–dibenzo-18-crown-6 complexes can represent a 'tuning' of the anionic stabilizing effect. Furthermore, the presence of solvate molecules is required when the stabilizing effect of the anion diminishes.

Preliminary information on the crystal structure of [KI(L)]·0.5H_2O has been reported,[5] as well as the principal structural details of a polymeric 1:1:1 compound KI–L–thiourea.[6] In both these compounds the iodide ion is co-ordinated to the complexed potassium, which lies in the plane of the six oxygen atoms of the ligand.

Because of the lack of structural information about NO_3 and Br potassium–dibenzo-18-crown-6 derivatives, a satisfactory correlation between molecular and crystal structures and the thermal stability of these compounds could not be made. For this reason we have determined, and report here, the molecular and crystal structure of the complex [K(NO_3)L]. We also report the crystal and molecular structure of the complex [K(Hpht)L] [H_2pht = phthalic acid (benzene-1,2-dicarboxylic acid)]. The thermal stability of this complex is also reported and discussed.

Experimental

Synthesis of [K(NO_3)L].—Crystals of this compound were prepared as previously described.[3]

Synthesis of [K(Hpht)L].—A boiling solution of potassium hydrogenphthalate (1 mmol) in methanol was added to dibenzo-18-crown-6 (1.2 mmol) dissolved in n-butanol and the resulting solution was refluxed for 1 h. The unreacted ligand, separated on cooling, was filtered off. The complex precipitated as white needle-like crystals by evaporation of the solution. The product obtained was filtered off, washed with ethanol, and dried *in vacuo* (Found: C, 59.5; H, 5.2; K, 6.8. Calc. for $C_{28}H_{29}KO_{10}$: C, 59.55; H, 5.15; K, 6.90%).

Differential Scanning Calorimetry.—D.s.c. analyses were carried out using a DSC-2C (Perkin-Elmer) differential

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† Dibenzo-18-crown-6 = 6,7,9,10,17,18,20,21-octahydrodibenzo-[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecin.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: cal = 4.184 J.

Table 1. Experimental data* for the crystallographic analyses

Compound		[K(NO$_3$)L]	[K(Hpht)L]
Formula		$C_{20}H_{24}KNO_9$	$C_{28}H_{29}KO_{10}$
M		461.51	564.63
Space group		$P2_1/c$	$P2_12_12_1$
a/Å		15.054 4(7)	15.990(2)
b/Å		20.575(2)	17.915(1)
c/Å		14.259(1)	9.314(1)
β/°		97.655(5)	90.0
U/Å^3		4 377.3(6)	2 668.2(4)
Z		8	4
D_c/Mg m^{-3}		1.401	1.406
D_m/Mg m^{-3}		1.41	1.41
Reflections for lattice parameters	number	23	15
	θ range/°	63.7—69.4	66.5—69.5
F(000)		1 936	1 184
Crystal size/mm		0.43 × 0.55 × 0.64	0.31 × 0.45 × 0.52
μ/cm^{-1}		25.84	22.40
θ range/°		6—70	3—70
h range		±17	0—18
k range		0—25	0—21
l range		0—18	0—11
Standard reflection		662	431
Intensity variation/%		3.6	3.9
Scan mode		ω—2θ	ω—2θ
No. of measured reflections		8 921	2 801
No. of reflections used in therefinement[$I > 2\sigma(I)$]		4 882	2 240
Min., max. height in final Δρ/e Å^{-3}		−0.32, 0.23	−0.25, 0.25
No. of refined parameters		560	262
$R = \Sigma\vert\Delta F\vert/\Sigma\vert F_o\vert$		0.0544	0.0622
$R' = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{\frac{1}{2}}$		0.0590	0.0735
$S = [\Sigma w(\Delta F)^2/(N - P)]^{\frac{1}{2}}$		0.58	1.44
k, g $\{w = k/[\sigma^2(F_o) + gF_o^2]\}$		1.0, 1.858 × 10^{-2}	1.0, 5 × 10^{-3}

* Both structures determined on a Siemens AED diffractometer using Cu-K_α radiation (λ = 1.540 51 Å) at 293 K: scan speed 3—12 min^{-1}; scan width 1.2 + 0.35 tan θ; N = no. of observations, P = no. of refined parameters.

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–drier.

Crystal-structure Determinations.—In both compounds the unit-cell parameters were determined by a least-squares method from the accurate positioning of some reflections: crystal data and structural details are reported in Table 1. The intensities were corrected for Lorentz and polarization effects and put on an absolute scale by least-squares analysis; no correction for absorption was applied.

Both structures were solved by the heavy-atom technique using Patterson and Fourier methods, the refinements were carried out isotropically, and then anisotropically. The hydrogen atoms, located from the ΔF map, were refined in the last cycle in [K(NO$_3$)L] and introduced as fixed contributors in [K(Hpht)L].

Atomic scattering factors were taken from the ref. 7, including the correction for anomalous dispersion; the final atomic co-ordinates for the non-hydrogen atoms are in Tables 2 and 3. The calculations were performed using the Cray X/MP computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, using the SHELX system of programs.[8]

The figures were drawn using ORTEP.[9]

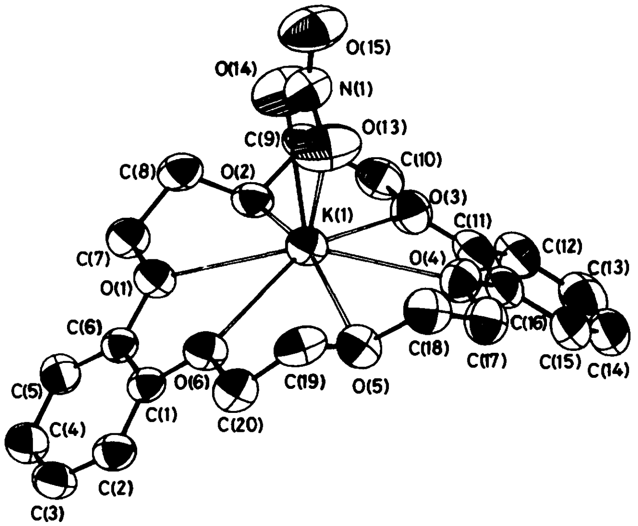

Figure 1. ORTEP[9] view of molecule (I) of [K(NO$_3$)L] with thermal motion ellipsoids drawn at 50% probability. The hydrogen atoms are omitted for clarity

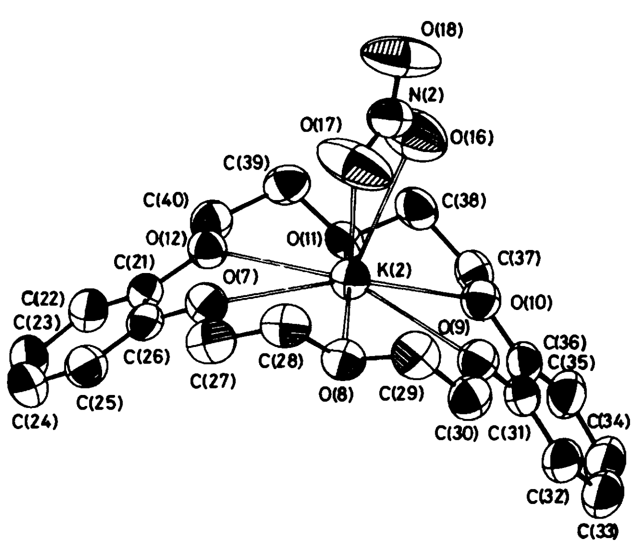

Figure 2. ORTEP[9] view of molecule (II) of [K(NO$_3$)L] with thermal motion ellipsoids drawn at 50% probability. The hydrogen atoms are omitted for clarity

Results and Discussion

Description of the Structures.—The asymmetric unit of [K(NO$_3$)L] contains two independent molecules (Figures 1 and 2), in which the potassium ion shows similar co-ordination. In both cases the metal ion is surrounded by eight oxygen atoms, six of them belonging to the crown ether and two to the nitrate ion which acts as a bidentate ligand and is symmetrically bonded.* The K···O distances (Table 4), including those concerning the nitrate ion, range from 2.766(3) to 2.868(3) Å around K(1) [molecule (I)], and from 2.711(3) to 2.835(3) Å in the K(2) environment [molecule (II)], the longest distances involving oxygen atoms adjacent to the phenyl rings. The six

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* After the submission of this manuscript a paper (R. B. Dyer, R. G. Ghirardelli, R. A. Palmer, and E. M. Holt. *Inorg. Chem.*, 1986, **25**, 3184) appeared in which the structure of the [(2*S*,6*S*)-2,6-dimethyl-1,4,7,10,13,16-hexaoxacyclo-octadecane]potassium nitrate complex was reported. The potassium ion is displaced from the mean plane of the macrocyclic ring by 0.65 Å toward the nitrate ion which is bidentat

Table 2. Fractional atomic co-ordinates (× 10^4) for [K(NO_3)L], with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
K(1)	3 577(1)	6 490(1)	8 533(1)	C(24)	3 908(4)	4 681(3)	4 098(4)
C(1)	1 575(3)	5 640(2)	7 158(3)	C(25)	3 892(3)	4 248(2)	4 853(4)
C(2)	844(3)	5 240(2)	7 034(3)	C(26)	3 163(3)	3 859(2)	4 894(3)
C(3)	678(3)	4 858(2)	6 236(4)	O(7)	3 070(2)	3 440(1)	5 629(2)
C(4)	1 243(3)	4 859(2)	5 566(4)	C(27)	3 749(3)	3 481(2)	6 443(4)
C(5)	2 012(3)	5 260(2)	5 688(3)	C(28)	3 469(3)	3 089(2)	7 214(4)
C(6)	2 172(3)	5 653(2)	6 484(3)	O(8)	2 700(2)	3 381(1)	7 519(2)
O(1)	2 881(2)	6 065(1)	6 663(2)	C(29)	2 446(4)	3 084(3)	8 337(4)
C(7)	3 495(3)	6 080(2)	5 976(3)	C(30)	1 693(4)	3 454(3)	8 641(3)
C(8)	4 262(3)	6 512(2)	6 374(3)	O(9)	926(2)	3 387(2)	7 944(2)
O(2)	4 702(2)	6 208(1)	7 193(2)	C(31)	187(3)	3 745(2)	8 087(3)
C(9)	5 498(3)	6 535(2)	7 585(4)	C(32)	122(4)	4 118(2)	8 883(4)
C(10)	5 925(3)	6 161(2)	8 428(4)	C(33)	−651(5)	4 491(3)	8 929(4)
O(3)	5 365(2)	6 206(2)	9 161(2)	C(34)	−1 357(4)	4 469(3)	8 219(4)
C(11)	5 620(3)	5 865(2)	9 971(4)	C(35)	−1 315(4)	4 076(3)	7 422(4)
C(12)	6 425(3)	5 518(3)	10 149(4)	C(36)	−540(3)	3 726(2)	7 352(3)
C(13)	6 617(5)	5 186(3)	10 996(5)	O(10)	−411(2)	3 361(1)	6 572(2)
C(14)	6 049(5)	5 196(3)	11 650(5)	C(37)	−1 088(2)	3 413(2)	5 778(3)
C(15)	5 243(4)	5 549(3)	11 500(4)	C(38)	−774(2)	3 053(2)	4 980(3)
C(16)	5 045(4)	5 881(2)	10 653(4)	O(11)	−52(2)	3 395(1)	4 661(2)
O(4)	4 269(2)	6 232(2)	10 412(2)	C(39)	240(3)	3 104(2)	3 854(3)
C(17)	3 630(4)	6 230(3)	11 088(4)	C(40)	970(3)	3 510(2)	3 546(3)
C(18)	2 818(4)	6 586(2)	10 650(4)	O(12)	1 736(2)	3 470(1)	4 266(2)
O(5)	2 423(2)	6 225(1)	9 839(2)	N(1)	3 665(2)	8 070(2)	8 568(2)
C(19)	1 599(3)	6 490(2)	9 408(3)	O(13)	3 185(3)	7 775(2)	9 058(3)
C(20)	1 210(3)	6 043(2)	8 636(3)	O(14)	4 089(3)	7 753(2)	8 016(3)
O(6)	1 796(2)	6 049(1)	7 922(2)	O(15)	3 768(3)	8 656(2)	8 613(3)
K(2)	1 337(1)	3 175(1)	6 106(1)	N(2)	1 404(3)	1 604(2)	6 102(2)
C(21)	2 444(3)	3 876(2)	4 164(3)	O(16)	690(2)	1 892(2)	5 904(3)
C(22)	2 456(3)	4 302(2)	3 410(3)	O(17)	2 053(2)	1 925(2)	6 337(4)
C(23)	3 208(4)	4 715(3)	3 400(4)	O(18)	1 471(3)	1 014(2)	6 065(3)

Table 3. Fractional atomic co-ordinates (× 10^4) for [K(Hpht)L], with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
K	3 617(1)	2 939(1)	−329(1)	C(10)	1 672(5)	2 921(5)	1 811(8)
O(1)	3 637(3)	1 450(2)	−1 277(5)	C(11)	1 700(4)	4 072(4)	479(6)
O(2)	2 468(3)	1 958(3)	797(4)	C(12)	838(4)	4 163(4)	551(7)
O(3)	2 135(3)	3 496(3)	1 066(5)	C(13)	453(4)	4 769(4)	−156(10)
O(4)	3 018(3)	4 442(2)	−349(5)	C(14)	927(5)	5 268(4)	−869(9)
O(5)	4 292(2)	3 937(2)	−2 192(5)	C(15)	1 785(4)	5 200(4)	−973(8)
O(6)	4 535(3)	2 401(2)	−2 702(4)	C(16)	2 173(4)	4 596(3)	−300(7)
O(7)	4 726(6)	2 361(6)	1 600(10)	C(17)	3 504(4)	4 929(3)	−1 218(7)
O(8)	5 228(5)	3 502(5)	1 329(8)	C(18)	4 366(4)	4 593(4)	−1 364(8)
O(9)	6 082(5)	4 314(3)	2 829(9)	C(19)	5 087(4)	3 628(4)	−2 565(8)
O(10)	6 620(4)	4 139(3)	5 011(8)	C(20)	4 944(4)	2 982(4)	−3 508(7)
C(1)	4 308(4)	1 760(4)	−3 400(7)	C(21)	6 039(4)	2 608(4)	2 678(6)
C(2)	4 525(4)	1 609(4)	−4 862(7)	C(22)	6 545(4)	3 087(3)	3 523(6)
C(3)	4 268(6)	944(5)	−5 478(8)	C(23)	7 233(4)	2 779(4)	4 171(6)
C(4)	3 790(5)	464(4)	−4 735(11)	C(24)	7 454(4)	2 042(4)	4 069(6)
C(5)	3 563(4)	586(4)	−3 282(8)	C(25)	6 950(6)	1 572(4)	3 306(8)
C(6)	3 832(4)	1 250(3)	−2 641(7)	C(26)	6 246(5)	1 849(5)	2 622(8)
C(7)	3 082(4)	964(3)	−494(8)	C(27)	5 262(7)	2 858(8)	1 813(9)
C(8)	2 947(5)	1 295(4)	981(8)	C(28)	6 396(5)	3 898(4)	3 834(8)
C(9)	2 234(5)	2 307(5)	2 121(7)				

oxygen atoms of the crown ether ligand are roughly coplanar, with a maximum deviation from the mean plane of 0.166(4) for (**I**) and 0.080(4) Å for (**II**). The potassium ions K(1) and K(2) are 0.631(1) and 0.465(1) Å, respectively, out of this plane and towards each nitrate ion, which are each planar and quite orthogonal with respect to the mean plane of the crown ether [78.4(2) for (**I**) and 91.6(2)° for (**II**)].

Figure 3 shows the perspective view of [K(Hpht)L], in which the potassium ion is surrounded by the six oxygen atoms of the macrocyclic ligand at distances ranging from 2.715(4) to 2.881(5) Å, and by two carboxylic oxygens of the phthalate ion at 2.729(9) and 3.168(8) Å (Table 5), in an arrangement similar to that found in the nitrate complex. The six oxygen atoms of the crown ether are coplanar with a maximum deviation from the mean plane of 0.091(4) Å, the potassium ion being displaced 0.592(1) Å out of this plane towards the phthalate ion. It is interesting that the displacement of K with respect to the mean plane of the oxygen atoms of the macrocyclic ligand is comparable with that found in the nitrate complex, while in [K(NCS)L][3] the potassium lies in the mean plane of the oxygen atoms of the crown. This behaviour is found in other potassium complexes, *e.g.* dibenzo-18-crown-6–potassium–ethyl aceto-

Table 4. Bond distances (Å) and angles (°) in the co-ordination polyhedra for $[K(NO_3)L]$

K(1)–O(1)	2.868(3)	K(1)–O(5)	2.766(3)	K(2)–O(7)	2.835(3)	K(2)–O(11)	2.770(3)
K(1)–O(2)	2.778(3)	K(1)–O(6)	2.854(3)	K(2)–O(8)	2.711(3)	K(2)–O(12)	2.834(6)
K(1)–O(3)	2.783(3)	K(1)–O(13)	2.832(4)	K(2)–O(9)	2.807(3)	K(2)–O(16)	2.815(4)
K(1)–O(4)	2.794(3)	K(1)–O(14)	2.836(4)	K(2)–O(10)	2.825(3)	K(2)–O(17)	2.790(4)
O(13)–K(1)–O(14)	44.5(1)	O(3)–K(1)–O(4)	55.3(1)	O(16)–K(2)–O(17)	43.2(1)	O(9)–K(2)–O(10)	55.3(1)
O(6)–K(1)–O(14)	119.3(6)	O(2)–K(1)–O(14)	78.5(1)	O(12)–K(2)–O(17)	100.4(1)	O(8)–K(2)–O(17)	79.3(1)
O(6)–K(1)–O(13)	99.0(1)	O(2)–K(1)–O(13)	123.0(1)	O(12)–K(2)–O(16)	102.7(1)	O(8)–K(2)–O(16)	116.1(1)
O(5)–K(1)–O(14)	125.0(1)	O(2)–K(1)–O(6)	111.0(1)	O(11)–K(2)–O(17)	118.7(1)	O(8)–K(2)–O(12)	115.0(1)
O(5)–K(1)–O(13)	80.5(1)	O(2)–K(1)–O(5)	156.6(1)	O(11)–K(2)–O(16)	82.0(1)	O(8)–K(2)–O(11)	161.6(1)
O(5)–K(1)–O(6)	59.6(1)	O(2)–K(1)–O(4)	115.9(1)	O(11)–K(2)–O(12)	60.6(1)	O(8)–K(2)–O(10)	116.1(1)
O(4)–K(1)–O(14)	110.1(1)	O(2)–K(1)–O(3)	61.7(1)	O(10)–K(2)–O(17)	110.0(1)	O(8)–K(2)–O(9)	61.4(1)
O(4)–K(1)–O(13)	89.3(1)	O(1)–K(1)–O(14)	96.7(1)	O(10)–K(2)–O(16)	80.2(1)	O(7)–K(2)–O(17)	81.5(1)
O(4)–K(1)–O(6)	116.6(1)	O(1)–K(1)–O(13)	117.9(1)	O(10)–K(2)–O(12)	120.5(1)	O(7)–K(2)–O(16)	118.2(1)
O(4)–K(1)–O(5)	60.2(1)	O(1)–K(1)–O(6)	53.7(1)	O(10)–K(2)–O(11)	61.2(1)	O(7)–K(2)–O(12)	54.7(1)
O(3)–K(1)–O(14)	89.5(1)	O(1)–K(1)–O(5)	112.4(1)	O(9)–K(2)–O(17)	99.4(1)	O(7)–K(2)–O(11)	114.7(1)
O(3)–K(1)–O(13)	109.7(1)	O(1)–K(1)–O(4)	151.3(1)	O(9)–K(2)–O(16)	97.1(1)	O(7)–K(2)–O(10)	161.1(1)
O(3)–K(1)–O(6)	149.3(1)	O(1)–K(1)–O(3)	117.0(1)	O(9)–K(2)–O(12)	159.0(1)	O(7)–K(2)–O(9)	121.2(1)
O(3)–K(1)–O(5)	114.2(1)	O(1)–K(1)–O(2)	58.5(1)	O(9)–K(2)–O(11)	115.5(1)	O(7)–K(2)–O(8)	61.2(1)

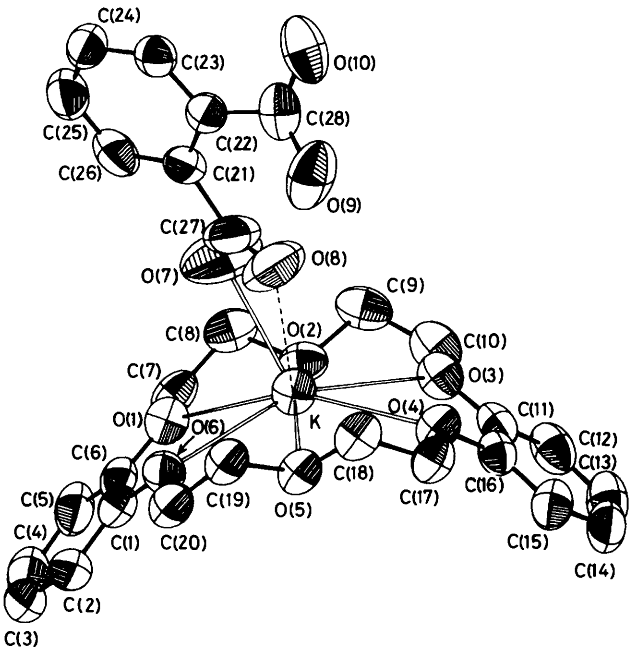

Figure 3. ORTEP[9] view of [K(Hpht)L] with thermal motion ellipsoids drawn at 50% probability. The hydrogen atoms are omitted for clarity

acetate enolate,[10] where the anion is strongly bidentate (K ··· O 2.651, 2.733 Å) and potassium is displaced 0.9 Å out of the macrocyclic oxygen plane, while in the corresponding thiocyanate complex[11] the cation is coplanar with the crown ether oxygens. The benzene rings form a dihedral angle of 84.7(2)°.

Only one carboxylate group of the phthalate ion is involved in the co-ordination. The different behaviour of the two carboxylate groups can be considered responsible for their orientation with respect to the phenyl ring [28.4(3) and 33.8(8)° for co-ordinated and unco-ordinated carboxylate groups respectively]. The corresponding dihedral angles in potassium hydrogenphthalate were 31.7 and 75.4°,[12] and the carboxylate groups are coplanar with the phenyl ring in LiHpht.[13] An intermolecular contact between the two carboxylate groups is present, O(8) ··· O(9) 2.44(1) Å, which can be considered as a hydrogen bond. Unfortunately, the hydrogen atom is not localized because of the thermal agitation of the carboxylate groups.

Table 5. Bond distances (Å) and angles (°) in the co-ordination polyhedron for [K(Hpht)L], with e.s.d.s in parentheses

K–O(1)	2.810(4)	K–O(5)	2.715(4)
K–O(2)	2.750(5)	K–O(6)	2.823(4)
K–O(3)	2.881(5)	K–O(7)	2.729(9)
K–O(4)	2.858(4)	K–O(8)	3.168(8)
O(1)–K–O(2)	61.4(2)	O(3)–K–O(5)	112.8(1)
O(1)–K–O(3)	118.7(2)	O(3)–K–O(6)	154.0(1)
O(1)–K–O(4)	153.7(1)	O(3)–K–O(7)	111.7(2)
O(1)–K–O(5)	114.8(1)	O(3)–K–O(8)	109.8(2)
O(1)–K–O(6)	54.8(1)	O(4)–K–O(5)	60.6(1)
O(1)–K–O(7)	80.8(2)	O(4)–K–O(6)	119.4(1)
O(1)–K–O(8)	116.5(2)	O(4)–K–O(7)	125.4(2)
O(2)–K–O(3)	60.0(1)	O(4)–K–O(8)	88.6(2)
O(2)–K–O(4)	112.4(2)	O(5)–K–O(6)	61.2(1)
O(2)–K–O(5)	158.4(1)	O(5)–K–O(7)	114.4(2)
O(2)–K–O(6)	115.3(1)	O(5)–K–O(8)	77.2(2)
O(2)–K–O(7)	86.6(2)	O(6)–K–O(7)	92.8(2)
O(2)–K–O(8)	124.1(2)	O(6)–K–O(8)	93.9(2)
O(3)–K–O(4)	53.2(1)	O(7)–K–O(8)	43.2(3)

The conformations of the ligands, described by using the torsion angles (see Supplementary data), are the same in the nitrate and phthalate complexes. The torsion angles around the C–C bonds range from 64.7 to 68.2° and from 66.6 to 70.0° for nitrate complexes (**I**) and (**II**) respectively and from 66.6 to 68.8° for the phthalate complex, corresponding to a *gauche* configuration. Torsion angles around the C–O bonds are *ca.* 180° as found in other dibenzo-18-crown-6 complexes.[14]

Bond lengths and angles in the macrocyclic ligands are comparable for both structures and are in accord with those found in the rubidium–dibenzo-18-crown-6 complex.[15]

Thermal Stability.—The complex [K(Hpht)L] was analyzed by differential scanning calorimetry using the apparatus described in the Experimental section. This compound is thermally stable up to its melting point, 188 °C, and undergoes a partial dissociation into its components during the melting process. In fact, a thermogram obtained from a sample cooled at room temperature after melting reveals two endothermic peaks at 152 and 185 °C respectively, the first attributed to the melting of the free dibenzo-18-crown-6 produced by the dissociation of the complex, and the second to the melting of the undissociated complex. The melting points of both the free ligand and of the complex occur a few degrees lower than those found for the pure

Table 6. Thermal data determined by differential scanning calorimetry

	L	$[K(NO_3)L]$	$[K(NCS)L]$
Melting point (°C)	161^a	188^b	245^a
ΔH_m/kcal mol^{-1}	$14.5(2)^{a,c}$	14.6(2)	$14.3(2)^a$
ΔS_m/cal K^{-1} mol^{-1}	33.4^a	31.7	27.6^a

[a] From ref. 4. [b] From ref. 3. [c] Values in parentheses are standard deviations in the last significant figure.

ligand (161 °C) and [K(Hpht)L] (188 °C). This is probably due to partial miscibility between the two compounds in the solid phase. Under these conditions we cannot evaluate the fraction of dissociated complex by determining the quantity of released ligand, L. However, repeated heating–cooling cycles reveal that this fraction rapidly reaches a maximum and then remains almost constant.

Similar behaviour was found for the $[K(NO_3)L]$ complex.[3] In this case no miscibility was observed between the released crown ether and the complex [see ref. 3, Figure 3(*b*)]. So, by means of the enthalpy of melting of dibenzo-18-crown-6 previously determined, and the area of the relative peak, we can evaluate the quantity of ligand released during the melting of the complex and, by difference, the quantity of undissociated complex (48.7%). By integrating the area of the peak of melting of the undissociated complex the relative enthalpy change (ΔH_m = 14.6 kcal mol^{-1}) was obtained. The complex $[K(NO_3)L]$ presents a fairly high enthalpy of melting and, rather surprisingly, it is equal, within experimental error, to that found for the free ligand, L and the complex [K(NCS)L] (Table 6). On the other hand, as we can see from Table 6, the complexes have entropies of melting smaller than that of the ligand. Flexible molecules exhibit a rapid rise in entropy of melting with molecular weight,[16] but the presence of the cation in the complex causes a stiffening of the ligand molecule leading to a smaller entropic gain. This effect is presumably more perceptible in the [K(NCS)L] complex, where the potassium ion is coplanar with the six oxygen atoms of the crown ether, than in $[K(NO_3)L]$ in which the potassium is 0.631—0.465 Å out of the least-squares plane through the six oxygen donor atoms of L.

The relative dimensions of the crown ether cavity and of the metal ion, as well as the charge of the cation, primarily control the co-ordination behaviour of crown ethers towards the alkali-metal ion, both in solution and in the solid.[2,17] The diameter of the hole formed by the disposition of dibenzo-18-crown-6 (2.6—3.2 Å)[18] fits very well the dimensions of potassium (ion diameter 2.66 Å). So, the potassium can drop suitably into the hole of the macrocyclic ligand in an hexagonal arrangement of oxygen-donor atoms, with the apical positions available for further co-ordination by the counter anion or solvate molecules. The contribution of the charge density of the cation towards its complexation with the crown ether is mainly due to its ability to polarize the donor atoms and to organize the resulting ion–dipole interactions. The formation of cation–anion couples reduces the charge density of the cation and consequently its ligating ability. In other words, the ion pairing increases the size of the cation, reducing the crown:metal dimensions ratio. The bigger the ligating tendency of the anion, the smaller is the co-ordination ability of the cation towards the polyether. Among the halide and pseudo-halide ions considered in this paper, the most strongly pairing with the potassium ion is thiocyanate, followed by iodide and bromide, while chelating anions are still more pairing. This tendency is reflected in the crystal properties of these complexes. In fact, in the thiocyanate and iodide derivatives of the $[KL]^+$ ion the K^+ is positioned in the plane of the six oxygen donors while in the $[K(NO_3)L]$ complex, where the NO_3 is strongly co-ordinated as a bidentate ligand, the potassium ion is pulled 0.631 and 0.465 Å from the donor ring toward the anion. Also, in the [K(Hpht)L] complex the chelating carboxylate group, though asymmetrically bonded (K ··· O distances are respectively 2.729 and 3.168 Å), pulls the potassium ion 0.592 Å from the plane of the donor atoms.

The pairing ability of the anions considered here results in a 'doming' effect which not only affects the structural properties of the relevant $[KL]^+$ complexes, but can represent a key to understanding the thermal behaviour of the same compounds.

The chelating anions partially 'extract' the potassium ion from the donor ring even in the solid phase, so that it is not surprising that in the liquid phase a partial dissociation of these complexes into the free ligand and the corresponding potassium salt takes place. On the contrary, the thiocyanate derivative, in which the cation is placed into the donor ring, shows a wide thermal stability and can be heated without any dissociation until its ligand decomposition occurs. It is worth noting that the lattice energy of K(NCS) is the lowest among the potassium salts considered here and this is not a favourable contribution to the dissociation of the complex by separation of solid K(NCS). Also, the KI derivative shows a partial dissociation upon melting, but the formation of ill defined species[3] does not allow us to present meaningful discussions about a correlation between its thermal stability and the pairing ability of the iodide ion.

Acknowledgements

The authors are indebted to Professor Alessandro Mangia (University of Parma), for the preparation of crystals of [K(Hpht)L] suitable for *X*-ray analyses, and Dr. Stefano Costantini Seniori (University of Florence) for microanalyses. Financial support from Progetto Chimica Fine e Secondaria of the Italian Research Council (CNR) and from the University of Parma is gratefully acknowledged.

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Received 29*th August* 1986; *Paper* 6/1748