Co-ordination of Alkali Metals by Open-chain Polyethers in Transition-metal complexes. Part 3.† The *X*-Ray Structures ‡ of 1-(*o*-Carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethane (HL) and its Acid Salt, KHL_2, a Possible Intermediate in the Formation of $Co(KL_2)_2$

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The *X*-ray crystal structures of the title compound, HL, and its acid salt, KHL_2, are reported and their hydrogen-bonding schemes compared. HL crystallises in an extended form with intermolecular hydrogen bonding linking the molecules in chains; there are no phenol to carboxyl hydrogen linkages. KHL_2 contains HL_2^- units where the two L ligands are held together by one strong hydrogen bond between the carboxyl groups across a centre of symmetry, and two weaker phenol to carbonyl interactions. The HL_2^- units then form sandwiches round potassium in pentagonal antiprism co-ordination to give a step polymer. The structure of KHL_2 is compared with those of $Co(KL_2)_2$ and $Co(RbL_2)_2$, and its role as a possible intermediate in the formation of $Co(KL_2)_2$ discussed.

The co-ordination chemistry of the alkali metals has expanded rapidly since Pedersen's [1] discovery of the cyclic polyethers. Their ability to complex alkali-metal cations and simultaneously render them lipophilic has led to considerable interest in the assisted ion transport of alkali-metal ions across lipid-like barriers by crown ethers.[2,3]

The design of new, more highly selective ligands has followed several routes, one of which has been to increase the formation constant of the complex cation by synthesis of bicyclic systems.[4,5] This approach leads to very stable complexes which, however, in some instances, require vigorous conditions to recover the cation from the complex.[5] An alternative approach has been to use a flexible molecule, such as an open-chain polyether, which can easily adopt a conformation that generates a cavity of specific size. The objective is to render the cation lipophilic, but to allow it to be released easily after, say, transport across a membrane.

During the last few years, we have been studying the co-ordination chemistry of open-chain polyethers which have various functional end groups,[6-8] and we have recently established the generation of cavities highly selective for potassium by attaching several open-chain ligands to the transition-metal ion Co^{II}.[9,10] In this paper, we report the crystal structures of the parent hydroxy acid, 1-(*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethane (HL), and its acid salt KHL_2, and discuss the reaction pathways to, and selectivities of, the cobalt species.

Experimental

Preparation of HL.—The ligand, HL, was prepared as in ref. 8, and crystals for *X*-ray determination, m.p. 124 °C, were obtained from diethyl ether–hexane (4 : 1).

Preparation of KHL_2.—This compound may be obtained in several ways, some of which are described below.

(*a*) Cobalt acetate tetrahydrate (0.125 g, 0.5 mmol) was dissolved in water (30 cm^3), and HL (0.304 g, 1.0 mmol) added. The mixture was refluxed to give an almost clear red solution, which was filtered hot. Potassium bromide (0.119 g, 1.0 mmol) in water (3 cm^3) was added, the solution refluxed for 2 h, and then allowed to stand overnight. The resulting white solid was collected on a sinter, and dried *in vacuo*. Yield 0.19 g, 59%. The product may be recrystallised from water to give *crystals* suitable for *X*-ray analysis; these undergo a transition, presumably dissociation, at 200 °C, and finally melt at 271 °C (KL melts at 270 °C) (Found: C, 59.5; H, 5.15; K, 6.1. $C_{32}H_{31}KO_{12}$ requires C, 59.45; H, 4.85; K, 6.05%).

(*b*) HL (0.6 g, 1.97 mmol) in hot ethanol (20 cm^3) was treated with potassium bromide (0.2 g, 1.68 mmol) in water (3 cm^3) and the mixture refluxed for 30 min to give a clear solution. This was filtered hot and, on standing, the filtrate deposited a crystalline solid, m.p. as above. Yield 0.36 g, 56%.

Similar reactions of potassium chloride or potassium iodide with HL also give KHL_2. Reactions of sodium bromide, rubidium bromide, or caesium bromide with HL lead only to the recovery of HL.

Preparation of $RbHL_2$.—RbL (0.13 g, 0.33 mmol) and HL (0.1 g, 0.33 mmol) were reacted together in boiling water (30 cm^3) for 15 min. The resulting solution was filtered hot, and on standing at room temperature, the filtrate deposited a crystalline solid. This was collected on a sinter and washed with a little ethanol. Yield 0.095 g, 39%. The *crystals* undergo a transition, presumably dissociation, between 175 and 185 °C, finally melting completely at 258 °C (RbL melts 256—258 °C) (Found: C, 55.10; H, 4.75. $C_{32}H_{31}O_{12}Rb$ requires C, 55.45; H, 4.50%).

A similar reaction between HL and KL produces KHL_2, but an acid salt is not obtained from the reaction of HL with NaL.

Reaction of KHL_2 *with Cobalt Acetate Tetrahydrate.*—KHL_2 (0.09 g, 0.14 mmol) was added to a refluxing solution of cobalt acetate tetrahydrate (0.025 g, 0.1 mmol) in ethanol (20 cm^3); a deep blue precipitate slowly formed. Reflux was continued for 30 min, and the solution allowed to stand at room temperature overnight. Blue crystals were obtained, which were found to be identical with an authentic sample of $Co(KL_2)_2$. Yield 0.06 g, 64%.

The reaction of $RbHL_2$ with cobalt acetate tetrahydrate under similar conditions does not give a blue colour or blue precipitate. Instead, a white solid is obtained which may be identified as RbL.

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† Part 2 is ref. 10.

‡ *Supplementary data available* (No. SUP 23883, 19 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Final atomic co-ordinates (fractional × 10⁴) for the refined atoms of KHL_2 *

Atom	x	y	z	Atom	x	y	z
K	5 000	5 000	5 000	C(12)	3 082(25)	6 580(13)	3 194(16)
O(1)	7 262(17)	5 742(9)	6 576(12)	C(13)	1 529(32)	6 890(17)	2 651(20)
C(2)	6 744(24)	6 081(13)	7 433(16)	C(14)	1 210(35)	6 730(18)	1 603(21)
C(3)	7 734(32)	6 010(17)	8 405(20)	C(15)	2 294(31)	6 392(16)	1 044(21)
C(4)	7 053(37)	6 333(19)	9 242(23)	C(16)	3 918(26)	6 091(14)	1 584(17)
C(5)	5 514(34)	6 688(18)	9 079(21)	C(17)	4 269(25)	6 176(13)	2 640(15)
C(6)	4 427(34)	6 750(17)	8 117(20)	O(18)	5 743(16)	5 897(8)	3 276(12)
C(7)	5 085(28)	6 410(14)	7 301(18)	C(19)	7 064(28)	5 525(16)	2 735(18)
O(8)	4 097(20)	6 376(10)	6 324(13)	C(20)	8 585(27)	5 182(14)	3 478(18)
C(9)	3 425(34)	7 180(19)	5 882(21)	O(21)	8 709(18)	5 309(10)	4 451(13)
C(10)	2 592(32)	7 044(17)	4 819(19)	O(22)	9 607(22)	4 740(14)	3 065(13)
O(11)	3 693(18)	6 667(10)	4 231(11)				

* Estimated standard deviations (e.s.d.s) are given in parentheses in Tables 1—7.

Table 2. Final atomic co-ordinates (fractional × 10⁴) for the refined atoms of HL

Atom	x	y	z	Atom	x	y	z
O(1)	3 809(3)	9 024(2)	−759.8(9)	C(14)	11 561(4)	11 673(2)	3 553(1)
C(2)	4 507(3)	7 717(2)	−1 021(1)	C(15)	9 751(5)	11 266(2)	4 105(1)
C(3)	3 376(4)	6 928(2)	−1 761(1)	C(16)	7 528(4)	9 993(2)	3 932(1)
C(4)	4 146(4)	5 631(2)	−2 022(1)	C(17)	7 111(3)	9 133(2)	3 198.7(8)
C(5)	6 019(5)	5 117(2)	−1 543(1)	O(18)	4 963(2)	7 867(1)	2 954.0(6)
C(6)	7 155(5)	5 885(2)	−797(1)	C(19)	3 097(3)	7 316(2)	3 513(1)
C(7)	6 396(3)	7 190(2)	−534.3(9)	C(20)	4 062(3)	6 338(2)	4 167.4(9)
O(8)	7 390(3)	8 058(1)	185.1(6)	O(21)	2 429(3)	5 953(2)	4 708.1(9)
C(9)	9 469(4)	7 636(2)	691(1)	O(22)	6 150(2)	5 950(1)	4 164.9(7)
C(10)	10 411(4)	8 848(2)	1 385(1)				
O(11)	8 393(2)	8 623(1)	1 925.3(6)	H(1a)	4 654(90)	9 307(43)	−244(26)
C(12)	8 955(3)	9 545(2)	2 635.4(8)	H(1b)	2 733(163)	9 438(80)	−1 163(39)
C(13)	11 184(4)	10 806(2)	2 813(1)	H(21)	2 963(77)	5 311(42)	5 116(23)

X-Ray Analysis of KHL_2.—*Crystal data.* $C_{32}H_{31}KO_{12}$, M = 646.7, monoclinic, space group $P2_1/a$, a = 7.920(3), b = 14.993(5), c = 13.133(6) Å, β = 100.77(4)°, U = 1 532(1) Å³, Z = 2, D_c = 1.402 g cm⁻³, $F(000)$ = 676, μ(Mo-$K_{\bar{\alpha}}$) = 2.3 cm⁻¹, λ(Mo-$K_{\bar{\alpha}}$) = 0.710 69 Å.

Crystals of KHL_2, grown from aqueous solution, were prisms of diamond-shaped cross-section and most samples selected for X-ray analysis were found to be twinned. A few, small, single crystals were found and we have determined the structure from one with dimensions 0.06 × 0.08 × 0.08 mm.

The crystals diffract poorly and the diffraction beams are diffuse. Intensities were measured twice, slowly, on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation and after correction for Lorentz and polarisation effects (corrections for absorption and deterioration were not necessary), the two data sets were merged to give, for the θ range 1.4—20°, 1 421 independent reflections of which only 621 had $I > 2\sigma(I)$.

A Patterson map confirmed that the potassium ion lies on a centre of symmetry ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$); the carbon and oxygen atoms of the single independent L ligand were located in electron density maps. Hydrogen atoms, except those involved in hydrogen bonds, were placed in idealised positions; the phenolic and acidic hydrogen atoms were not positively located and hence not included in this analysis.

Refinement of the structure, by full-matrix least-squares methods using the SHELX program,[11] was terminated at R = 0.185 for 936 reflections with $I > \sigma(I)$; reflections were weighted $w = [\sigma(F)^2 + 0.0065\ F^2]^{-1}$ for the refinement. Scattering factors were from ref. 12. The final difference map showed no further atom peaks.

Calculations on the final atomic parameters (Table 1) showed that for the 621 reflections with $I > 2\sigma(I)$, the agreement index R was 0.13.

Considering that the accurately measurable data used in this analysis were limited to low θ values, and that most of the data were of weakly diffracting reflections (by most criteria considered ' unobserved '), we are not too concerned by the high R factors quoted above. We are confident that the model is correct (the refinement proceeded smoothly, and the final difference map did not show any peaks of significance) and we are concerned now only that the molecular dimensions should be interpreted with caution.

The dimensions in the potassium co-ordination sphere are given in Table 3. Molecular dimensions of the ligand are recorded, with those of the acid HL (see below), in Tables 4 (bond lengths), 5 (valence angles), 6 (selected torsion angles), and 7 (hydrogen bond dimensions).

X-Ray Analysis of HL.—*Crystal data.* $C_{16}H_{16}O_6$, M = 304.3, triclinic, space group $P\bar{1}$ (no. 2), a = 5.229(1), b = 8.759(1), c = 16.436(2) Å, α = 90.78(1), β = 96.33(1), γ = 105.06(1)°, U = 721.8(1) Å³, Z = 2, D_c = 1.400 g cm⁻³, $F(000)$ = 320, μ(Mo-$K_{\bar{\alpha}}$) = 1.0 cm⁻¹, λ(Mo-$K_{\bar{\alpha}}$) = 0.710 69 Å.

Large, well formed, clear, colourless, prismatic crystals were obtained by recrystallisation from diethyl ether–hexane. The single crystal selected for X-ray analysis was 0.48 mm long, with diagonals of its parallelepiped section measuring 0.24 × 0.40 mm. Preliminary photographs showed strong, clear diffraction.

Intensity data for 2 543 independent reflections in the θ range 1.3—25° were measured on the diffractometer and processed as for KHL_2; 2 079 reflections had $I > 2\sigma(I)$ and 2 300 had $I > 0.5\sigma(I)$. The positions of all 22 non-hydrogen atoms were clear from the two ' best ' E maps produced by the automatic direct-methods routine EEES in the program suite SHELX.[11] Refinement to convergence was straightforward and rapid. In the final cycles of full-matrix refinement, all the non-hydrogen atoms were allowed anisotropic thermal parameters; most hydrogen atoms were included in idealised positions with variable $U_{\text{iso.}}$ parameters, but the acidic and phenolic H atoms, located in difference maps, were refined independently. The phenolic H atoms are disordered (assumed equally) over two possible sites. Finally, R was 0.043 and R' 0.051 for 2 300 reflections weighted according to $w = [\sigma(F)^2 - 0.0015 F^2]^{-1}$.

The refined atomic co-ordinates are in Table 2, and molecular dimensions are in Tables 4—7.

Computing.—All computations were executed on our Prime 550 computer. In addition to the SHELX suite,[11] programs used in these analyses include a CAD4 processor program,[13] the ORTEP plotting program,[14] and Dr. J. D. Owen's suite [15] of molecular geometry routines written or adapted for the Prime computer.

Results

Description of the Structure of KHL_2.—The crystal structure confirms that KHL_2 is the acid salt. The HL_2^- anion is shown in Figure 1, with the two L ligands related by a centre of symmetry $(1, \frac{1}{2}, \frac{1}{2})$. The O(21) · · · O(21$^{\text{I}}$) distance across this centre is 2.45(3) Å, and with the bonding orbitals of the O(21) atoms pointing towards each other, we suggest that this is a strong symmetric bond of Type A, as described by Speakman.[16] There are two other hydrogen bonds in the HL_2^- unit, each made up of the interaction between the phenolic oxygen, O(1), of one L ligand and carbonyl oxygen, O(22), of the other L ligand [O(1) · · · O(22$^{\text{I}}$) 2.54 Å]. The HL_2^- unit is therefore held reasonably planar by three hydrogen bonds.

Potassium ions are now sandwiched by the planar units in the following manner. Each HL_2^- unit has a potassium ion K, above one L ligand, and another potassium ion, K$^{\text{I}}$, below the other L ligand, Figures 1 and 2. Another HL_2^- unit lies parallel to the first, with one L ligand, II, above the first potassium ion, K, completing the sandwich. The other L ligand, IV, of this HL_2^- unit is not directly over the first HL_2^-, but points away. Another parallel HL_2^- unit lies below K$^{\text{I}}$, with the L ligand, III, co-ordinating the potassium ion. This arrangement is continued to form a step polymer (Figure 2).

Each potassium ion is thus irregularly co-ordinated in a sandwich by eight close oxygen atoms, four from each of two L ligands in different HL_2^- units. The K–O distances range from 2.71 to 2.87 Å. Two further oxygen atoms, O(21) and O(21$^{\text{II}}$), one from each of the sandwiching HL_2^- units, are 3.19 Å from K. The C(20)–O(21)–K angle is 107.6(12)° which is favourable for lone-pair interaction, and the five oxygen atoms O(1), O(8), O(11), O(18), and O(21) of L, although not making a very good plane (deviation about mean, −0.18 to −0.15 Å), are much more regularly distributed in space round the potassium ion than when the four close oxygen atoms are considered alone. Only the angle O(21)–K–O(1), 66.9(4)°, is significantly larger than the other O–K–O angles (53—58°), and therefore the co-ordination around potassium should be considered as ten or, at least, ' eight-plus-two '. In the cobalt complexes, $Co(ML_2)_2$, the M–O(21) distances, for M = K

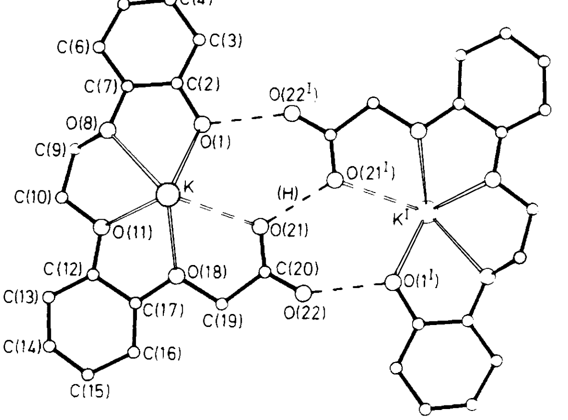

Figure 1. The HL_2^- anion with its co-ordinated K^+ ions in KHL_2. The atom-numbering and hydrogen-bonding schemes are shown

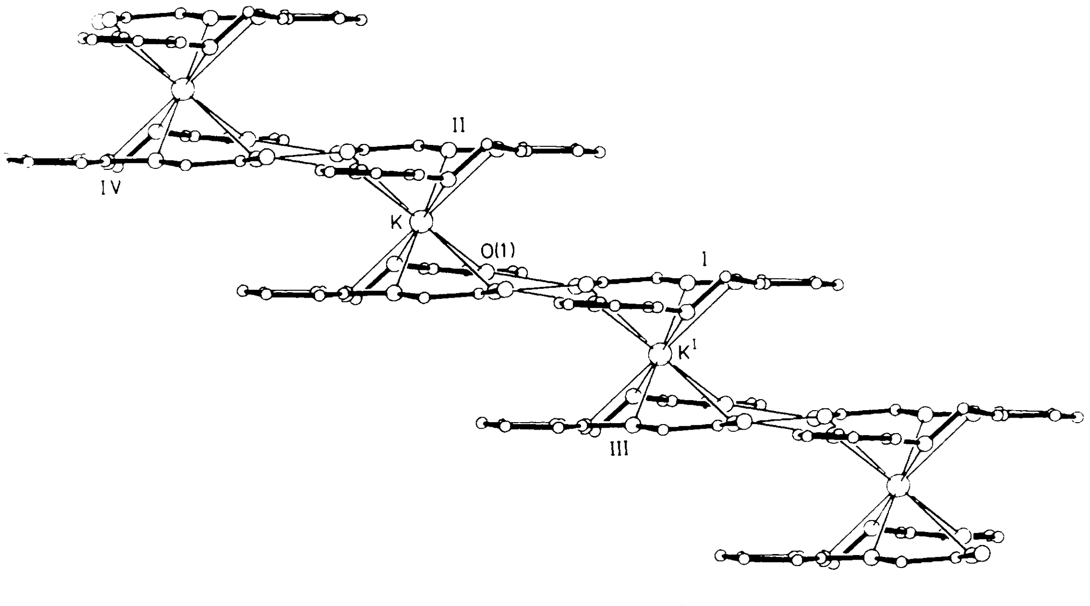

Figure 2. The step-polymer formation of KHL_2, showing the linking of hydrogen-bonded HL_2^- anions through co-ordinated K^+ ions

Table 3. Potassium co-ordination dimensions in KHL_2

(*a*) K–O bond lengths (Å)

K–O(1)	2.710(13)	K–O(18)	2.788(14)
K–O(8)	2.873(15)	K–O(21)	3.187(14)
K–O(11)	2.819(14)		

(*b*) Angles (°) subtended at the potassium ion, O_a–K–O_b *

O_a \ O_b	O(8)	O(11)	O(18)	O(21)	$O(1^{II})$	$O(8^{II})$	$O(11^{II})$	$O(18^{II})$	$O(21^{II})$
O(1)	56.4	93.2	102.3	66.9	180.0	123.6	86.8	77.8	113.1
O(8)		57.6	105.0	112.1		180.0	122.4	75.0	67.9
O(11)			53.2	94.7			180.0	126.8	85.3
O(18)				53.3				180.0	126.7
O(21)									180.0

* Roman numeral superscript II denotes the symmetry-related molecule at $1 - x$, $1 - y$, $1 - z$. E.s.d.s are *ca.* 0.4°.

Table 4. Bond lengths (Å) in KHL_2 and HL

	KHL_2	HL
O(1)–C(2)	1.366(22)	1.366(2)
C(2)–C(3)	1.371(28)	1.383(2)
C(2)–C(7)	1.384(26)	1.379(3)
C(3)–C(4)	1.399(34)	1.378(3)
C(4)–C(5)	1.310(33)	1.361(3)
C(5)–C(6)	1.392(32)	1.385(3)
C(6)–C(7)	1.375(30)	1.382(2)
C(7)–O(8)	1.373(25)	1.372(2)
O(8)–C(9)	1.399(28)	1.424(2)
C(9)–C(10)	1.443(30)	1.497(2)
C(10)–O(11)	1.389(26)	1.430(2)
O(11)–C(12)	1.364(22)	1.370(2)
C(12)–C(13)	1.382(29)	1.382(2)
C(12)–C(17)	1.427(26)	1.394(2)
C(13)–C(14)	1.373(32)	1.392(2)
C(14)–C(15)	1.330(30)	1.368(3)
C(15)–C(16)	1.421(29)	1.386(3)
C(16)–C(17)	1.367(26)	1.378(2)
C(17)–O(18)	1.369(22)	1.377(2)
O(18)–C(19)	1.479(24)	1.412(2)
C(19)–C(20)	1.492(28)	1.509(2)
C(20)–O(21)	1.278(24)	1.288(2)
C(20)–O(22)	1.247(25)	1.226(2)
O(1)–H(1a)		0.91(4)
O(1)–H(1b)		0.96(7)
O(21)–H(21)		0.95(4)

Table 5. Valence angles (°) in KHL_2 and HL

	KHL_2	HL
O(1)–C(2)–C(3)	122.0(19)	121.4(2)
O(1)–C(2)–C(7)	117.0(18)	118.8(1)
C(3)–C(2)–C(7)	120.6(21)	119.8(2)
C(2)–C(3)–C(4)	117.8(24)	120.6(2)
C(3)–C(4)–C(5)	119.8(29)	119.6(2)
C(4)–C(5)–C(6)	125.0(29)	120.6(2)
C(5)–C(6)–C(7)	115.0(25)	120.1(2)
C(2)–C(7)–C(6)	121.6(22)	119.4(2)
C(2)–C(7)–O(8)	117.8(19)	115.0(1)
C(6)–C(7)–O(8)	120.6(21)	125.5(2)
C(7)–O(8)–C(9)	117.5(18)	117.8(1)
O(8)–C(9)–C(10)	110.5(23)	107.8(1)
C(9)–C(10)–O(11)	112.0(21)	108.4(1)
C(10)–O(11)–C(12)	116.8(17)	117.5(1)
O(11)–C(12)–C(13)	126.7(20)	124.3(2)
O(11)–C(12)–C(17)	113.9(17)	115.6(1)
C(13)–C(12)–C(17)	119.2(22)	120.1(1)
C(12)–C(13)–C(14)	115.9(26)	119.7(2)
C(13)–C(14)–C(15)	127.1(29)	120.1(2)
C(14)–C(15)–C(16)	117.6(26)	120.3(2)
C(15)–C(16)–C(17)	118.0(22)	120.2(2)
C(12)–C(17)–C(16)	121.8(20)	119.5(2)
C(12)–C(17)–O(18)	112.7(18)	115.0(1)
C(16)–C(17)–O(18)	125.4(19)	125.5(2)
C(17)–O(18)–C(19)	114.9(17)	118.3(1)
O(18)–C(19)–C(20)	111.9(19)	113.1(1)
C(19)–C(20)–O(21)	120.3(21)	112.2(1)
C(19)–C(20)–O(22)	114.2(21)	122.8(1)
O(21)–C(20)–O(22)	125.4(20)	125.0(2)
H(1a)–O(1)–C(2)		107.6(25)
H(1b)–O(1)–C(2)		114.7(39)
C(20)–O(21)–H(21)		113.9(23)

and Rb, are amongst the shortest of the co-ordination contacts; in these complexes, O(21) is considered to carry the anionic charge and, in fact, bridges the M and Co ions. In KHL_2, however, the charge on O(21) is formally only $-\frac{1}{2}$ and the atom is involved in the strong hydrogen bond across the centre of symmetry.

The step-polymer chains run parallel to the *a* axis. Interactions between adjacent chains are at van der Waals distances.

Description of the structure of HL.—In contrast to the ligand in KHL_2 and in the cobalt complexes, the free acid molecule (Figure 3) is not restrained by metal co-ordination to approximate planarity. All the torsion angles in HL, Table 6, are close to expected values for an unstrained molecule, *i.e.* with *trans* configurations for C–O–C–C bonds and *gauche* about the central O–CH_2–CH_2–O bond. In complexes involving L, we have found that there is always at least one torsion angle which is not close to normal *trans* or *gauche* values. In Co(KL_2)$_2$ the aberrant angle is 113° for C(10)–O(11)–C(12)–C(17) in each of the two independent ligands.[9] In the rubidium analogue, the angle C(2)–C(7)–O(8)–C(9) is *ca.* −100° in three of the ligands (in the fourth, there is unresolved disorder),[10] and the ligand in KHL_2 shows an angle of −123° in the same place. There are also slight differences in the carboxylate groups in these last two complexes; whereas in Co(RbL_2)$_2$, the carboxylate group bends in towards the Co and Rb ions, in KHL_2 the group bends out towards the hydrogen-bonding groups of the HL_2^- unit.

Freedom from co-ordination restraints also allows the HL molecule to adopt an extended form, rather than being folded round to approximate a cyclic ligand. In this elongated form, with a phenolic group at one end and a carboxylic acid group at the other, the molecule is able to form intermolecular hydrogen bonds and connect molecules in long chains. These bonds can be seen in the packing diagram, Figure 4. Both are formed around centres of symmetry; the acidic group is involved in two bonds, in the normal pattern for carboxylic acids, with the acid group of molecule I at $(1 - x, 1 - y, - z)$, while the phenolic group hydrogen-bonds with the phenolic group of molecule II at $(1 - x, 2 - y, 1 - z)$. In this latter contact, the phenolic hydrogen atoms are arranged either as shown in Figure 4, *i.e.* forming the sequences of bonds O(1$^{\text{II}}$)-H(1a$^{\text{II}}$) · · · O(1)-H(1b) · · · O(11$^{\text{II}}$), or in the opposite direction, O(1)-H(1a) · · · O(1$^{\text{II}}$)-H(1b$^{\text{II}}$) · · · O(11); this is the cause of the apparent disorder of the phenolic hydrogen atom. The hydrogen bonding dimensions in Table 7 suggest that H(1a) is involved in a bifurcated bond, contacting also O(8). It should be noted that in HL there are no phenol–carboxyl interactions, which is in sharp contrast with the hydrogen-bonding schemes found in KHL_2, $Co(KL_2)_2$,[9] and $Co(RbL_2)_2$.[10]

Other intermolecular contacts are all at van der Waals distances. The catechol group O(1),C(2)—C(7),O(8) is parallel to the same groups (*i*) in neighbouring cells $(x \pm 1)$ and (*ii*) related by the centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$. The interplanar spacings of the rings are normal stacking distances, 3.35 and 3.55 Å respectively, but none of the carbon and oxygen atoms in these groups quite overlaps any other ring. Similarly, the catechol group O(11),C(12)—C(17),O(18) has parallel groups in neighbouring cells $(x \pm 1)$ at 3.40 Å distant, and again the rings do not quite overlap; the group related by inversion at $(1, 1, \frac{1}{2})$ has its plane only 3.00 Å away, but it is displaced laterally.

Discussion

The crystal structure of the open-chain polyether hydroxy acid, HL, shows the molecule to be in an extended, open form, with normal torsion angles. Earlier work had suggested that a series of such hydroxy acids did not show any enhanced stability constants on complexation with alkali metals over and above an average value of that for the parent diols and diacids,[8] although they might have been expected to wrap around the alkali-metal ion by using intramolecular hydrogen bonds in the same way as the antibiotic monensin.[17] In more recent work,[9] we demonstrated that, in ethanol in the presence of the transition-metal ion Co$^{\text{II}}$, cavities may be generated in the complex which are specific for potassium. The ligands forming these cavities are held together by the central cobalt ion, and by hydrogen bonding from one L ligand to

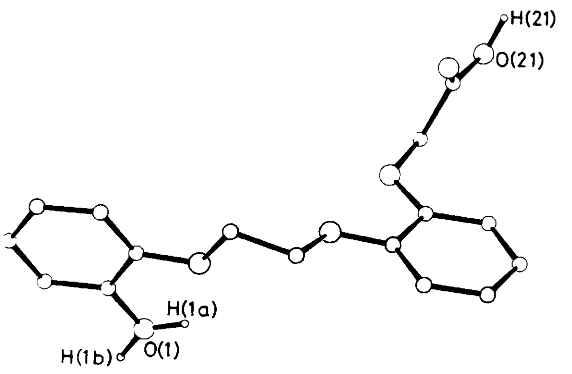

Figure 3. A molecule of HL, the free hydroxy acid. The atomic-numbering scheme of L is as in Figure 1. The two sites for the disordered phenolic hydrogen atom, H(1a) and H(1b), are shown

Table 6. Selected torsion angles (°) in KHL_2 and HL

	KHL_2	HL
O(1)–C(2)–C(7)–O(8)	0(3)	0.3(2)
C(2)–C(7)–O(8)–C(9)	−123(2)	−176.1(1)
C(7)–O(8)–C(9)–C(10)	173(2)	173.9(1)
O(8)–C(9)–C(10)–O(11)	−56(3)	71.6(2)
C(9)–C(10)–O(11)–C(12)	−175(2)	175.2(1)
C(10)–O(11)–C(12)–C(17)	−179(2)	−170.9(1)
O(11)–C(12)–C(17)–O(18)	5(3)	−0.8(2)
C(12)–C(17)–O(18)–C(19)	−176(2)	176.1(1)
C(17)–O(18)–C(19)–C(20)	−176(2)	−77.2(2)
O(18)–C(19)–C(20)–O(21)	−7(3)	174.8(1)
O(18)–C(19)–C(20)–O(22)	169(2)	−6.2(2)
C(7)–C(2)–O(1)–H(1a)		−6(3)
C(7)–C(2)–O(1)–H(1b)		170(5)
C(19)–C(20)–O(21)–H(21)		178(3)
O(22)–C(20)–O(21)–H(21)		−1(3)

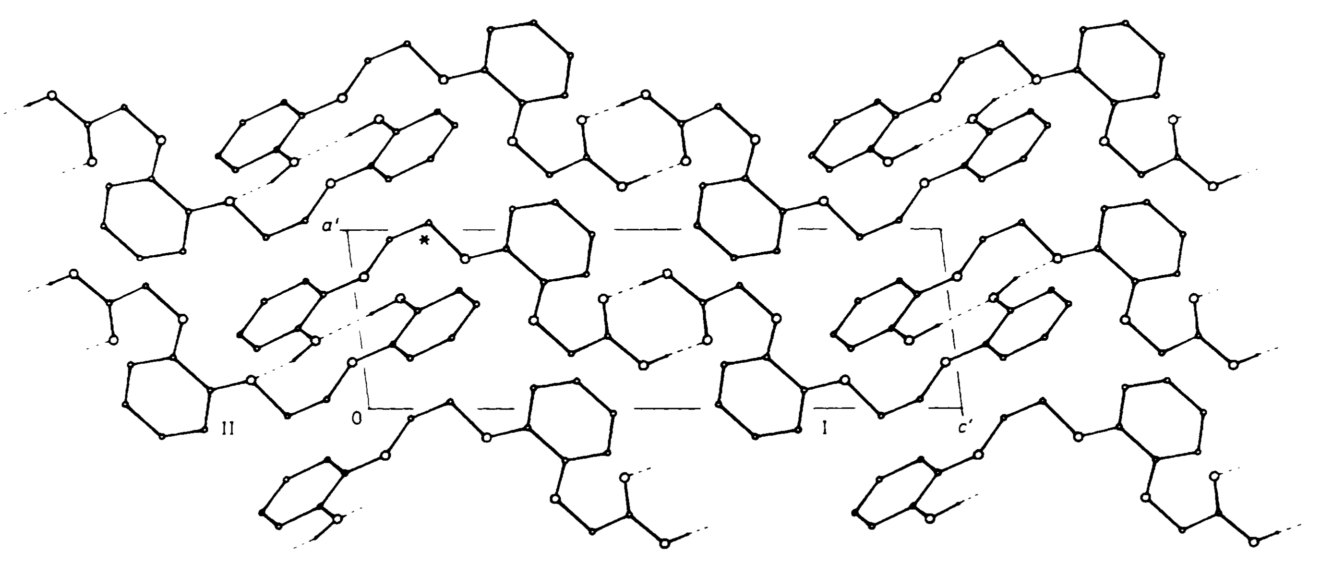

Figure 4. Packing diagram of HL, viewed down the *b* axis. The molecule with co-ordinates of Table 2 is marked with an asterisk. The intermolecular hydrogen bonds linking the molecules in chains are shown with dashed lines

Table 7. Proposed hydrogen-bonding scheme dimensions

(*a*) In KHL_2 (Roman numerical superscript I denotes the symmetry-related molecule at $2 - x, 1 - y, 1 - z$)

	O···O/Å	C–O···O/°
$O(1)–H \cdots O(22^I)$	2.54(2)	113(1)
$O(21) \cdots H \cdots O(21^I)$	2.45(3)	116(1)

(*b*) In HL (Roman numeral superscripts I and II denote symmetry-related molecules at $1 - x, 1 - y, 1 - z$ and $1 - x, 2 - y, -z$ respectively)

	O···O/Å	O–H/Å	H···O/Å	O–H···O/°
O(8)	2.618(2)		2.09(4)	116(3)
O(1)–H(1a)		0.91(4)		
$O(1^{II})$	2.968(3)		2.13(4)	152(3)
$O(1)–H(1b) \cdots O(11^{II})$	3.177(2)	0.96(7)	2.28(7)	155(6)
$O(21)–H(21) \cdots O(22^I)$	2.681(2)	0.95(4)	1.74(4)	177(3)

the next, and the crystalline complex $[Co(ML_2)_2]$, once formed, is not rapidly attacked by water.

We therefore attempted to repeat the above reaction by mixing cobalt acetate with HL and potassium bromide, but in water rather than alcohol. Instead of the blue complex $Co(KL_2)_2$, a white solid was deposited. The same compound is isolated when HL and potassium bromide (or potassium chloride or potassium iodide) are refluxed together in aqueous alcohol in the absence of cobalt ions, proving that this compound is not a transition-metal complex, nor requires to pass through a transition-metal complex as an intermediate. The i.r. spectrum (see below) suggested that the white solid was an acid salt, KHL_2, and this hypothesis was supported by the isolation of the same compound from a mixture of HL and KL in refluxing ethanol. Similar acid salts of sodium, rubidium, and caesium cannot be obtained from reactions of HL with the halides of these alkali metals, HL being recovered unchanged, but the reaction of HL with RbL did lead to the isolation of $RbHL_2$. The unit HL_2^- is therefore highly selective in its preference for potassium over the other alkali metals. A similar selectivity has been reported previously by Duax and co-workers [18] who showed that catechol diacetic acid reacts with potassium chloride (but not lithium, sodium, or caesium chlorides), to give an acid salt. Each potassium ion in the structure of this acid salt has an irregular pentagonal-antiprism ten-co-ordination, but oxygens from four different ligands contribute. The overall structure is a two-dimensional polymer held together by hydrogen bonds, and a change in size of the alkali-metal cation was thought likely to affect these hydrogen bonds and be sufficient to prevent the structure from forming.

Our ligand system HL_2^- possesses enough oxygen atoms to provide all ten co-ordinating atoms within one unit, or at least five oxygen atoms from each of two L ligands, and hence may be expected to give a complex more stable in water, and possibly more selective. We therefore undertook the crystal structure determination of KHL_2, which shows the compound to be a step polymer, where HL_2^- units are held together by ion-dipole interactions with potassium ions, which they sandwich (Figure 2). The HL_2^- units in this structure are held together by three hydrogen bonds, as previously described. The individual L ligands are thus held in a dimeric cyclic structure by inter-, not intra-ligand hydrogen bonds, fixing five possible co-ordinating oxygen atoms in each ligand in a reasonable plane. Each L ligand is now able to become half of a sandwich for a potassium ion, and the resulting co-ordination is a not too irregular pentagonal antiprism. The chelating O–K–O angles are regularly spaced (53.2—57.6°) with the exception of O(1)–K–O(21) which is 66.9°. This compares with those obtained in the structure of the dibenzo-30-crown-10 * complex of KI [19] which lie in the range 52—60°. This results in a good co-ordination sphere for a potassium ion, one which may be able to expand slightly to take a rubidium ion, but is likely to be unsuited for sodium or caesium ions. The 'chelate effect' of five oxygen donors from each ligand will also contribute to the stability of the potassium acid salt in comparison, say, with that formed by catechol diacetic acid.[18]

The short oxygen-oxygen distance, 2.45 Å, across the centre of symmetry of HL_2^- and the equivalence of the two L ligands in HL_2^- indicate that the acid salt is that defined as Type A.[16] In accordance with this, the i.r. spectrum shows a broad band centred at 1 720 cm^{-1}, and no sign of either the carboxyl stretch of the free acid (sharp peak at 1 700 cm^{-1}) or of the carboxylate stretch of KL (~1 620 cm^{-1}). This is similar to the corresponding band at 1 725 cm^{-1} found in the spectrum of the potassium acid salt of *o*-nitrobenzoic acid, which is isomorphous with the rubidium acid salt whose structure has been determined as that of Type A.[20] The hydroxyl regions of the spectrum of KHL_2, however, are more complex. There are broad absorption bands in the region 3 500—2 500 cm^{-1}, as expected for the longer O···O hydrogen bonds (2.54 Å), but there is no sign of the very broad bands in the range 1 400 600 cm^{-1} generally found in Type A acid salts. Further, there is no discernible change in the i.r. spectrum on recrystallising KHL_2 from D_2O. It is possible that the peak is so broad that it is obscured by the fingerprint region of the open-chain polyether, or that we have a special case of pseudo-Type A acid salt,[20] in which there is disorder (not definable in our crystal structure) about the centre of symmetry.

KHL_2 is rapidly converted to $Co(KL_2)_2$ when refluxed with cobalt acetate in ethanol, and is therefore a possible intermediate in the normal preparation of the cobalt complex.[9] A comparison of the ligand dimer units in KHL_2 (Figure 1) and $Co(KL_2)_2$ (Figure 3 of ref. 9) shows great similarities. The hydrogen bonds joining phenolic to carbonyl oxygens are present in both, but in KHL_2 a hydrogen bridges the other carboxyl oxygens in a short hydrogen bond, whereas in $Co(KL_2)_2$ the bridging ion is cobalt(II). However, whereas in the $Co(KL_2)_2$ structure, pairs of L_2 dimer units (bound by cobalt and potassium ions) form discrete molecules with a bilayer, sandwich arrangement, the neighbouring dimer units

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* 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]decaoxacyclotriacontine.

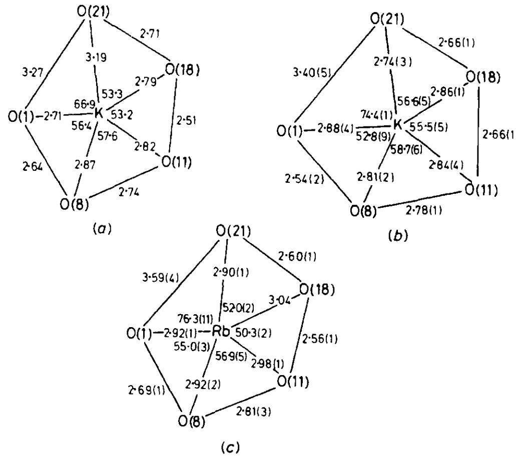

Figure 5. Dimensions (distances in Å and angles in degrees) in one half of the co-ordination sandwiches in (*a*) KHL_2, (*b*) $Co(KL_2)_2$, and (*c*) $Co(RbL_2)_2$. In (*a*), e.s.d.s are, for K–O distances ~0.014 Å, O ··· O ~0.021 Å, and O–K–O ~0.4°. In (*b*) and (*c*), the values are weighted means from the independent ligands (two in the K complex, four in the Rb analogue), and e.s.d.s are in parentheses

in the KHL_2 structure only half overlap and form a step polymer. Furthermore, the ligands are related by pseudo-two-fold symmetry axes in the cobalt complex, and each potassium ion sees two ligands having the same folding direction. In the KHL_2 structure, however, the ligands are related by centres of symmetry, and are folded about the potassium ion in opposite directions. In the conversion of KHL_2 to $Co(KL_2)_2$, therefore, we propose that dissociation occurs at the potassium ions, thus leaving intact the hydrogen-bonded dimer units common to both intermediate and product. Cobalt replaces the central proton of one dimer unit, and then binds a second unit in the right orientation, ejecting its proton at the same time. This process would be controlled by the simultaneous binding of one or both potassium ions.

Although it is possible to isolate the analogous complex $Co(RbL_2)_2$ under certain conditions,[10] the reaction of $RbHL_2$ with cobalt acetate only yields RbL, illustrating the high specificity of the cobalt complex for potassium ions. Figure 5 shows the O–M–O angles and O ··· O distances in half of the pentagonal antiprism co-ordination spheres of KHL_2, $Co(KL_2)_2$, and $Co(RbL_2)_2$. The most regular spatial co-ordination is found in KHL_2, and the angle O(1)–M–O(21) becomes larger on going to $Co(KL_2)_2$ and $Co(RbL_2)_2$. This may be a further contributing factor in the isolation of potassium complexes, and the difficulty of forming the corresponding rubidium compounds. It has already been noted that the hydrogen bonds are longer, and therefore weaker, in $Co(RbL_2)_2$ in comparison with those in $Co(KL_2)_2$.[10]

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