Co-ordination of Alkali Metals by Open-chain Polyethers in Transition-metal Complexes. Part 2.† An Explanation for Alkali-metal Selectivity from the *X*-Ray and Molecular Structure of Tetrakis[1-(*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)-ethanato(1–)]dirubidiumcobalt(II) and Comparison with the Dipotassium Analogue ‡

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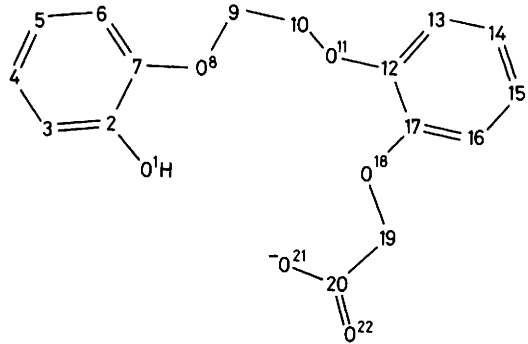
The synthesis and *X*-ray crystal structure of the title compound $[Co(L_2Rb)_2]$, containing the trifunctional centre Rb–Co–Rb, is reported and compared with the analogous $[Co(L_2K)_2]$ structure. The selectivity of the moiety $[CoL_4]^{2-}$ between alkali metals and, in particular, for potassium is discussed on the basis of this comparison. Crystals of $[Co(L_2Rb)_2]$ are triclinic, $a = 14.352(4)$, $b = 14.911(3)$, $c = 16.772(3)$, $\alpha = 93.16(2)$, $\beta = 106.75(2)$, $\gamma = 110.91(2)°$, and $Z = 2$. The structure was refined to $R = 0.055$ for 3 585 reflections.

It has been known for some time that transition-metal complexes such as [Cu^{II}(salen)] [salen = *NN'*-ethylenebis(salicylideneiminate)] may themselves act as partial co-ordinating spheres for alkali metals.[1] Recently, however, there has been much interest in the use of these bifunctional centres for activating small molecules. For example, Fachinetti and Floriani [2] have been studying the reactions of [Co^{I}(salen)Na] with carbon dioxide, where the carbon atom of CO_2 is co-ordinated to cobalt and one of the oxygens is co-ordinated to sodium. Similarly, a co-ordinated carbon monoxide molecule has been activated by a lithium ion which itself is co-ordinated by polyether oxygens of the bifunctional molecule $[M(CO)_4\{Ph_2P(OCH_2CH_2)_3OPPh_2\}]$ (M = Cr, Mo, or W) and hence, on the addition of LiR, lithium acylates may be isolated.[3] An earlier example of carbon monoxide being co-ordinated by both a transition metal and an alkali metal had been reported by Floriani and co-workers.[4]

In a recent paper,[5] we reported a multifunctional K–Co^{II}–K neutral complex where four open-chain polyethers (L^-, Figure 1) are each co-ordinated at one end by a carboxylate oxygen to the cobalt ion, and, by hydrogen bonding, form two cavities for potassium ions. We now report the structure of the corresponding Rb–Co–Rb complex and explain by comparison with the K–Co–K structure the high selectivity of this co-ordinating system between the alkali metals.

Experimental

Preparation of $[Co(L_2Rb)_2]$.—Cobalt(II) acetate tetrahydrate (0.125 g) and HL (0.304 g) were refluxed together in ethanol (50 cm^3) to give a dark pink solution. This solution was filtered hot, and RbL (0.19 g) added. Reflux was continued for 16 h, but no crystallisation occurred. Further RbL was added (0.15 g) and reflux continued for another 16 h. Large blue-mauve crystals were formed which were collected on a sinter and washed with ethanol, m.p. 196—197 °C (Found: C, 53.3; H, 4.10. $C_{64}H_{60}CoO_{24}Rb_2$ requires C, 53.25; H, 4.20%).



L^-

Figure 1. The hydroxy-acid anion ligand, with the non-hydrogen atoms numbered, *n*. In the crystal analysis of complex $[Co(L_2Rb)_2]$ (1R), the atoms of the four anion ligands are numbered (*n*)a and (*n*)b about Rb(1), (*n* + 40)a and (*n* + 40)b about Rb(2), *e.g.* the four phenolic oxygen atoms are O(1)a, O(1)b, O(41a), and O(41)b. Hydrogen atoms have the same numbers and suffices as their bonded C or O atoms; methylene H atoms have an additional suffix, 1 or 2

Attempted Preparation of $[Co(L_2Na)_2]$.—Cobalt(II) acetate tetrahydrate (0.125 g) and HL (0.304 g) were refluxed together in ethanol (30 cm^3) to give a red solution. This solution was filtered hot and when NaL (0.304 g) was added the solution slowly darkened to mauve. Reflux was continued for 2 d but no further colour change occurred and, on cooling, NaL was recovered.

A similar reaction to that above for thallium yielded only unreacted TlL.

Preparation of $[Co(L_2K)_2]$ *using* KI.—Cobalt(II) acetate tetrahydrate (0.125 g) and HL (0.304 g) were refluxed together in ethanol (30 cm^3) to give a red solution. This was filtered hot and potassium iodide (0.165 g) added. Reflux was continued for 30 min, during which time dark blue crystals were deposited. These were collected on a sinter and washed with a small amount of ethanol. Yield 0.155 g. These crystals were confirmed [5] as $[Co(L_2K)_2]$, m.p. 240 °C.

Similar reactions using potassium bromide and potassium thiocyanate also produced $[Co(L_2K)_2]$ in good yield.

Attempted Preparation of $[Co(L_2Rb)_2]$ *using* RbBr.—Cobalt(II) acetate tetrahydrate (0.125 g) and HL (0.304 g) were

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† For Part 1, see ref. 5.

‡ *Supplementary data available* (No. SUP 23543, 32 pp.): thermal parameters, H-atom co-ordinates, ligand bond parameters, inter- and intra-molecular contacts, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

refluxed together in ethanol (30 cm^3), the clear solution was filtered hot, and rubidium bromide (0.165 g) added. On reflux no visible reaction occurred, but after reflux for 24 h and cooling to room temperature, RbL was isolated. Yield 0.15 g.

A similar reaction using caesium iodide instead of rubidium bromide yielded unreacted caesium iodide.

Attempted Preparation of $[Co(L_2Na)_2]$ *using* NaSCN.—Cobalt(II) acetate tetrahydrate (0.125 g) and HL (0.304 g) were refluxed in ethanol (30 cm^3), the resulting clear solution filtered hot, and dried sodium thiocyanate (0.095 g) added to give a blue solution. Heating was continued for 45 min during which time a flocculent white precipitate was formed. This was collected on a sinter, washed with ethanol (2 cm^3), and dried *in vacuo*. The product, m.p. 248—251 °C, was shown to be the sodium salt of the hydroxy-acid, NaL, obtained in good yield (0.245 g).

A similar reaction performed in acetonitrile also gave crystals of NaL.

Competition Reaction of NaBr *and* KBr *with* $[CoL_2]$.—Cobalt(II) acetate tetrahydrate (0.125 g) and HL (0.304 g) were refluxed together in ethanol (30 cm^3) to give a red solution. This was filtered hot, and sodium bromide (0.102 g) added to the filtrate. Reflux was continued for 4 h during which time the solution became blue. No crystallisation occurred on cooling. Potassium bromide (0.119 g) was added, and reflux continued for 24 h. On cooling, chunky blue crystals were formed, which were collected on a sinter and washed with water. These were confirmed as $[Co(L_2K)_2]$ by their melting point, 241 °C, and *X*-ray photographs. The filtrate produced NaL on cooling.

The complexes $[Co(L_2K)_2]$ and $[Co(L_2Rb)_2]$ are denoted (1K) and (1R) respectively.

Crystal-structure Determination of Complex (1R).—Crystals of (1R) are very similar in appearance to those of complex (1K),[5] blue-mauve plates; many, with rhombus-shaped faces, are twinned and/or split. Single crystals are more often smaller and elongated plates. The crystal selected (from many photographed) was 0.05 × 0.08 × 0.24 mm. Refinement of cell dimensions from the diffractometer settings of 25 centred reflections (with $7 < \theta < 9°$) revealed a triclinic cell, some of whose dimensions are similar to those of complex (1K).

Crystal data. $C_{64}H_{60}CoO_{24}Rb_2$, $M = 1\,443.0$, Triclinic, $a = 14.352(4)$, $b = 14.911(3)$, $c = 16.772(3)$ Å, $\alpha = 93.16(2)$, $\beta = 106.75(2)$, $\gamma = 110.91(2)°$, $U = 3\,160.0$ Å^3, space group $P\bar{1}$ (no. 2), $Z = 2$, $D_c = 1.516$ g cm^{-3}, $F(000) = 1\,474$, $\mu(\text{Mo-}K_\alpha) = 18.4$ cm^{-1}, $\lambda(\text{Mo-}K_{\bar{\alpha}}) = 0.710\,69$ Å (1 Å = 10^{-10} m).

Intensity data were measured on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation. Of 4 333 independent reflections in the rather limited range of θ 1.2—18° (there were very few measurable reflections beyond this point), 3 177 were considered observed, having $I \geqslant 2\sigma(I)$. There was no apparent deterioration in the crystal during observation. During processing, data were corrected by Lorentz and polarisation factors, but not for absorption effects.

By analogy with the structure of complex (1K), a vector pattern for the linear arrangement Rb ··· Co ··· Rb seemed a probable solution to the Patterson map, and after the pseudo-symmetry was broken (the cobalt co-ordinates were *ca.* 0, $\frac{1}{4}$, $\frac{1}{4}$), the remainder of the structure was found, from successive electron-density maps, to correspond closely to that of (1K) [except that there is no crystallographic symmetry within the molecule of (1R)].

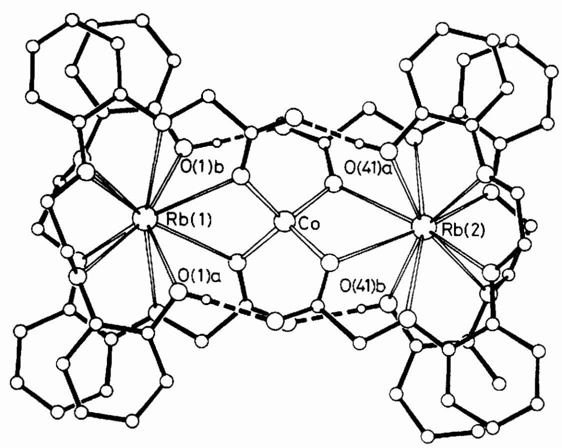

Figure 2. View of the complex molecule $[Co(L_2Rb)_2]$ (1R). The *b* axis is almost parallel with the direction of view

Refinement of the structure could not be performed satisfactorily in the SHELX system [6] because there were too many atomic parameters; recourse was made to a vintage block-diagonal least-squares program,[7] recently updated for compatability with SHELX. Scattering factors were taken from ref. 8. Refinement progressed smoothly except that the anisotropic thermal parameters for one O atom, O(48)a (see Figure 1 for the atomic numbering scheme), were unrealistic, and the torsion angle about the adjacent CH_2–CH_2 bond was *ca.* 0°. This region was examined carefully with difference and electron-density maps, but the precise arrangements of the sites of the disordered atoms (for we believe the problem to be one of disorder) were not fully elucidated. In the final stages of refinement all the non-hydrogen atoms O(41)a—O(51)a were refined anisotropically, whereas in the remainder of the molecule only the Co, Rb, and O atoms have anisotropic thermal parameters.

Three of the four phenolic H atoms were located in difference maps, in hydrogen-bonding arrangements similar to those in complex (1K); the co-ordinates of the fourth were calculated correspondingly. These H atoms were refined independently. The co-ordinates of all other H atoms were calculated for idealised bonding, and these atoms were set to ' ride ' on their bonded C atoms.

In the final stages of refinement, 3 585 reflections with $I > \sigma(I)$ were used, and the procedure was terminated with R 0.055 and R' 0.046; the weighting scheme used was $w = \sigma(F)^{-2}$.

Co-ordinates for the non-hydrogen atoms are in Table 1, bond lengths and angles in Table 2.

Results

Description of the Molecular and Crystal Structure.—As in complex (1K), four hydroxy-acid anionic ligands are each bound through a carboxylate O atom to the central Co atom. The ligands are arranged in two pairs, each pair forming a roughly planar hydrogen-bonded dimer layer, with each phenolato H atom bonded to the non-co-ordinated carboxylate O atom of the other ligand. The two layers are arranged one on each side of the Co atom, and enclose also the two rubidium ions; each ligand co-ordinates a Rb^+ ion through five O atoms (all except the hydrogen-bonding acceptor atom). In crystals of (1R) there is no precise intramolecular symmetry [whereas the (1K) molecules contain a crystallographic two-fold symmetry axis], but views of the two complexes show remarkable similarity (Figure 2, and Figure 1 of ref. 5).

Table 1. Atomic parameters of complex (1R). Co-ordinates are fractional (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Co	−77(1)	2 396.9(9)	2 578.7(7)				
Rb(1)	98.3(7)	2 539.6(7)	4 838.3(5)				
Rb(2)	−191.7(7)	2 381.1(7)	351.7(5)				
O(1)a	1 638(5)	4 338(4)	4 673(3)	C(12)a	−1 813(7)	3 312(6)	5 557(5)
H(1)a	1 744(66)	4 332(61)	4 250(51)	C(13)a	−2 255(8)	3 363(7)	6 215(7)
C(2)a	2 559(7)	4 727(6)	5 346(5)	C(14)a	−3 342(8)	2 953(8)	5 987(7)
C(3)a	3 536(7)	5 124(7)	5 264(6)	C(15)a	−3 978(9)	2 505(8)	5 226(6)
C(4)a	4 423(9)	5 487(7)	5 978(6)	C(16)a	−3 567(8)	2 424(7)	4 576(6)
C(5)a	4 325(9)	5 459(8)	6 769(7)	C(17)a	−2 477(7)	2 832(6)	4 761(5)
C(6)a	3 341(8)	5 048(7)	6 853(7)	O(18)a	−1 967(4)	2 810(4)	4 183(3)
C(7)a	2 446(7)	4 689(7)	6 145(6)	C(19)a	−2 589(7)	2 540(7)	3 319(5)
O(8)a	1 471(5)	4 232(4)	6 229(4)	C(20)a	−1 888(7)	2 667(6)	2 786(5)
C(9)a	979(7)	4 901(7)	6 322(6)	O(21)a	−951(4)	2 744(4)	3 134(3)
C(10)a	−67(7)	4 376(7)	6 422(6)	O(22)a	−2 291(5)	2 678(5)	2 024(4)
O(11)a	−768(5)	3 719(5)	5 666(3)				
O(1)b	−1 483(4)	639(4)	3 857(3)	C(12)b	2 134(7)	1 988(6)	6 391(5)
H(1)b	−1 678(52)	528(49)	3 278(41)	C(13)b	2 678(8)	2 186(7)	7 270(6)
C(2)b	−2 306(6)	325(6)	4 144(5)	C(14)b	3 756(8)	2 736(7)	7 556(7)
C(3)b	−3 346(7)	−158(6)	3 616(6)	C(15)b	4 311(8)	3 067(7)	7 035(6)
C(4)b	−4 155(8)	−441(7)	3 954(6)	C(16)b	3 784(7)	2 865(6)	6 161(5)
C(5)b	−3 956(8)	−279(7)	4 803(6)	C(17)b	2 698(7)	2 342(6)	5 856(5)
C(6)b	−2 929(7)	186(7)	5 335(6)	O(18)b	2 071(4)	2 127(4)	5 013(3)
C(7)b	−2 115(7)	467(6)	5 009(5)	C(19)b	2 588(6)	2 314(6)	4 400(5)
O(8)b	−1 084(5)	981(4)	5 550(3)	C(20)b	1 766(7)	2 123(6)	3 534(5)
C(9)b	−591(7)	381(6)	5 971(6)	O(21)b	869(4)	2 082(4)	3 504(3)
C(10)b	478(7)	1 000(7)	6 533(5)	O(22)b	2 051(5)	2 005(5)	2 922(3)
O(11)b	1 090(4)	1 460(5)	6 031(3)				
O(41)a	−1 720(5)	3 136(5)	650(4)	C(52)a	1 777(7)	4 442(7)	−281(5)
H(41)a	−1 835(56)	3 049(51)	1 095(43)	C(53)a	2 276(8)	4 759(7)	−881(7)
C(42)a	−2 596(7)	2 739(7)	−67(6)	C(54)a	3 375(8)	5 157(8)	−616(7)
C(43)a	−3 579(8)	2 289(7)	−19(6)	C(55)a	3 960(8)	5 272(7)	198(6)
C(44)a	−4 426(8)	1 879(8)	−778(7)	C(56)a	3 465(7)	4 976(6)	793(6)
C(45)a	−4 257(8)	1 917(8)	−1 545(7)	C(57)a	2 388(7)	4 555(6)	549(5)
C(46)a	−3 267(8)	2 377(9)	−1 565(6)	O(58)a	1 813(4)	4 216(4)	1 085(3)
C(47)a	−2 429(7)	2 785(8)	−831(6)	C(59)a	2 405(7)	4 418(6)	1 957(5)
O(48)a	−1 412(6)	3 195(8)	−832(5)	C(60)a	1 690(7)	4 003(6)	2 462(5)
C(49)a	−1 043(8)	3 837(8)	−1 236(7)	O(61)a	756(4)	3 397(4)	2 075(3)
C(50)a	33(8)	4 271(8)	−1 126(6)	O(62)a	2 083(5)	4 302(5)	3 232(3)
O(51)a	709(5)	4 041(5)	−474(4)				
O(41)b	1 465(4)	1 758(4)	1 216(3)	C(52)b	−2 143(7)	255(6)	−1 320(5)
H(41)b	1 632(58)	1 849(54)	1 682(45)	C(53)b	−2 673(7)	−50(7)	−2 199(6)
C(42)b	2 323(6)	2 072(6)	954(5)	C(54)b	−3 769(8)	−419(7)	−2 486(7)
C(43)b	3 356(7)	2 391(6)	1 485(6)	C(55)b	−4 346(9)	−498(7)	−1 976(6)
C(44)b	4 189(8)	2 694(7)	1 171(6)	C(56)b	−3 836(7)	−211(7)	−1 091(6)
C(45)b	3 996(8)	2 690(7)	330(6)	C(57)b	−2 732(7)	182(6)	−797(5)
C(46)b	2 972(7)	2 389(6)	−218(6)	O(58)b	−2 127(4)	522(4)	59(3)
C(47)b	2 136(7)	2 070(6)	90(5)	C(59)b	−2 649(7)	290(6)	667(5)
O(48)b	1 107(4)	1 794(4)	−450(3)	C(60)b	−1 845(7)	727(6)	1 550(5)
C(49)b	644(7)	817(6)	−895(6)	O(61)b	−981(4)	1 378(4)	1 595(3)
C(50)b	−438(7)	610(7)	−1 466(5)	O(62)b	−2 124(5)	407(4)	2 139(3)
O(51)b	−1 088(4)	608(4)	−964(3)				

Slight differences are discerned in the cation co-ordination patterns where the pentagonal antiprismatic arrangement for the K^+ ions is more regular than for the Rb^+ ions. The side views of the complexes, Figure 3, show other differences; in (1R) the ligand planes are distorted rather more from parallel formations.

The K/Rb · · · O distances are in Table 2, with mean values of 2.830 Å in complex (1K) and 2.949 Å in (1R). Correspondingly, the distances between layers of the complexes, *i.e.* between the mean planes of the ten co-ordinating O atoms in each layer, are 2.97 Å in (1K) and 3.29 Å in (1R).

The geometries of three of the four ligands in complex (1R) are very similar; the fourth ligand suffers from disorder which we cannot accurately describe. Torsion angles are compared with those of the two ligands of (1K) in Table 3. The differences in the central region should be noted; whereas the orientations of the carboxylate groups are similar in both complexes, the twists about the C(9)–C(10) type bonds are positive *gauche* for the (1K) ligands but negative in (1R). There are corresponding differences about the C(7)–O(8) and O(11)–C(12) bonds.

Another small difference between complexes (1K) and (1R), in the accommodation of the rather larger Rb^+ ions, is in the hydrogen-bonding O · · · O dimensions, which in (1R) are in the range 2.674(8)—2.721(8) with a mean value 2.701 Å [*cf.* in (1K) the two O · · · O distances are 2.637(9) and 2.643(9)

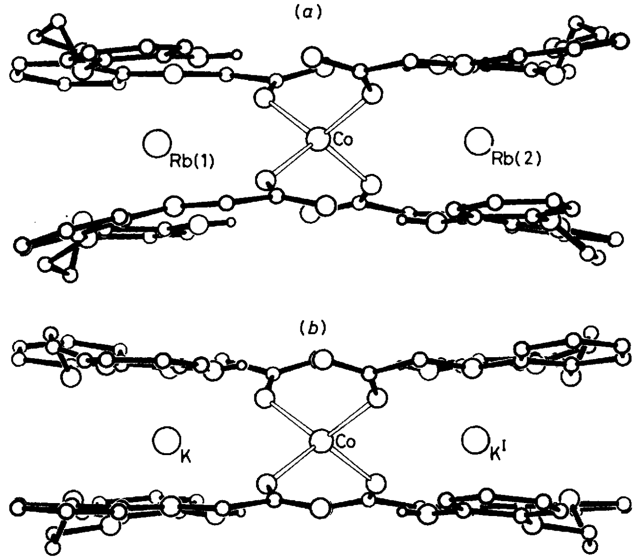

Figure 3. Side views of the complexes (1R) (*a*) and (1K) (*b*). The plane of the paper is almost the plane of *b–c* in (1R) and of *a–b* in (1K)

Table 2. Co-ordination dimensions about the Co and alkali-metal cations in complexes (1K) and (1R). E.s.d.s are in parentheses

(1K)		(1R)			
(*a*) Distances (Å)					
(*i*) From Co					
O(21)	1.957(5)	O(21)a	1.947(5)	O(61)a	1.954(6)
O(51)	1.952(5)	O(21)b	1.947(5)	O(61)b	1.948(5)
K	3.619(2)	Rb(1)	3.714(1)	Rb(2)	3.689(1)
(*ii*) From M = K		M = Rb(1)		M = Rb(2)	
O(1)	2.931(8)	O(1)a	2.891(6)	O(41)a	2.943(6)
O(8)	2.833(6)	O(8)a	2.974(6)	O(48)a	2.873(9)
O(11)	2.806(5)	O(11)a	2.976(6)	O(51)a	2.973(7)
O(18)	2.867(5)	O(18)a	3.029(6)	O(58)a	3.041(6)
O(21)	2.773(5)	O(21)a	2.911(5)	O(61)a	2.877(5)
O(31)	2.845(7)	O(1)b	2.938(6)	O(41)b	2.891(6)
O(38)	2.795(6)	O(8)b	2.892(6)	O(48)b	2.921(6)
O(41)	2.897(6)	O(11)b	2.995(6)	O(51)b	2.967(6)
O(48)	2.852(6)	O(18)b	3.044(5)	O(58)b	3.035(6)
O(51)	2.705(5)	O(21)b	2.914(5)	O(61)b	2.892(5)
(*b*) Angles (°) subtended at the Co					
O(21)–Co–O(21^{I})	118.3(2)	O(21)a–Co–O(21)b	101.9(2)		
O(21)–Co–O(51)	96.5(2)	O(21)a–Co–O(61)a	117.3(2)		
O(21)–Co–O(51^{I})	114.9(2)	O(21)a–Co–O(61)b	109.4(2)		
O(51)–Co–O(51^{I})	117.1(2)	O(21)b–Co–O(61)a	109.4(2)		
		O(21)b–Co–O(61)b	117.9(2)		
		O(61)a–Co–O(61)b	101.6(2)		

In complex (1K) the superscript I denotes atoms generated by the two-fold symmetry axis which relates the two halves of the molecule.

Å]. In the carboxylate groups, the O(22)-type atoms (the hydrogen-bond acceptor atoms, not bonded to the Co or alkali-metal ions) in all ligands of both (1K) and (1R) have rather higher thermal parameters than the other oxygen atoms. That these atoms are the carbonyl oxygen atoms and the O(21) atoms take (most of) the anionic charge is reflected in the consistently longer C(20)–O(21) than C(20)–O(22) bond lengths; mean values for the six ligands are 1.258 and 1.233 Å respectively.

Molecules of (1K) and (1R) pack in almost identical sheets; in (1K) these sheets form the *a–b* plane of the crystal, and in (1R) the *b–c* plane. It is only in stacking of these sheets (Figure 4) that notable differences are found: in complex (1K), Figure 4(*b*), the molecules 1, 2, 3, 4... have co-ordinates + − + − ... with respect to a plane normal to *b*, whereas in (1R), Figure 4(*a*), they progress + + + + ... Along the *b* axis in both complexes, molecules are stacked at van der Waals distances; adjacent molecules are related by screw axes in (1K), and by inversion centres in (1R), but the distances between neighbouring molecules in both cases are *ca.* 4.1 Å (between the planes of co-ordinating O atoms).

Benzene rings overlap to varying degrees, both within and between molecules, with separations of planes of 3.3—3.8 Å. The more parallel arrangements are found in complex (1K), with angles between the normals of overlapping rings of *ca.* 6°; in (1R) these angles lie in the range 5.6(3)—15.8(4)° (mean 10.8°). In (1R) every benzene ring has an approximately parallel, partially overlapping ring on each side of it; however, one pair of rings between adjacent molecules of (1K), *viz.* the rings of C(12)—C(17) and C(42′)—C(47′) (and *vice versa*), do not overlap, but the methylene atom H(19)b points towards the centre of the ring of C(42′)—C(47′) and, similarly, H(49)b points towards C(12″)—C(17″).

Discussion

Although alkali-metal complexes with cyclic polyethers have been extensively studied, complexation and decomplexation is difficult to control. It is necessary to look for a system which may change conformation when the external conditions are changed slightly. Our studies are now centred on the complexation of alkali metals by open-chain polyethers containing functional groups, these ligands being themselves held in place by co-ordination to a transition metal.

In a recent structure determination of $[Co(L_2K)_2]$ (1K),[5] we showed that hydrogen bonding is important for holding the ligands in place and thus forming cavities for cations. The crystal structure of $[Co(L_2Rb)_2]$ (1R), reported here, also shows these hydrogen-bonding interactions between the carboxyl oxygen of one ligand and the phenolic hydroxyl hydrogen of an adjacent ligand.

A comparison of the structures (1K) and (1R) shows clearly that, whilst the two cavities formed by the transition-metal complex $[CoL_4]^{2-}$ are exactly the right size and shape for co-ordinating potassium ions, the larger rubidium ions do not complex so well. Thus the spatial arrangement of the K–O bonds in (1K) is much more regular than that of the Rb–O bonds in (1R), and also the ligands L are twisted outwards in the latter (Figure 3). This has the effect of moving the overlapping benzene rings further out of the plane in complex (1R), leading to a less favourable energy. The hydrogen bonds in this complex are also lengthened with respect to those in (1K), and hence the forces holding the complex structure in place are weakened.

These structural findings are reflected in the easier preparation of complex (1K) with respect to (1R), and also in the reactions of potassium bromide and rubidium bromide with the possible intermediate $[CoL_2]$ as illustrated in equations (i) and (ii).

$$2[CoL_2] + 2KBr \longrightarrow [Co(L_2K)_2]\downarrow + CoBr_2 \qquad (i)$$

$$[CoL_2] + 2RbBr \longrightarrow 2RbL\downarrow + CoBr_2 \qquad (ii)$$

The larger caesium ion is not co-ordinated in the cavity,

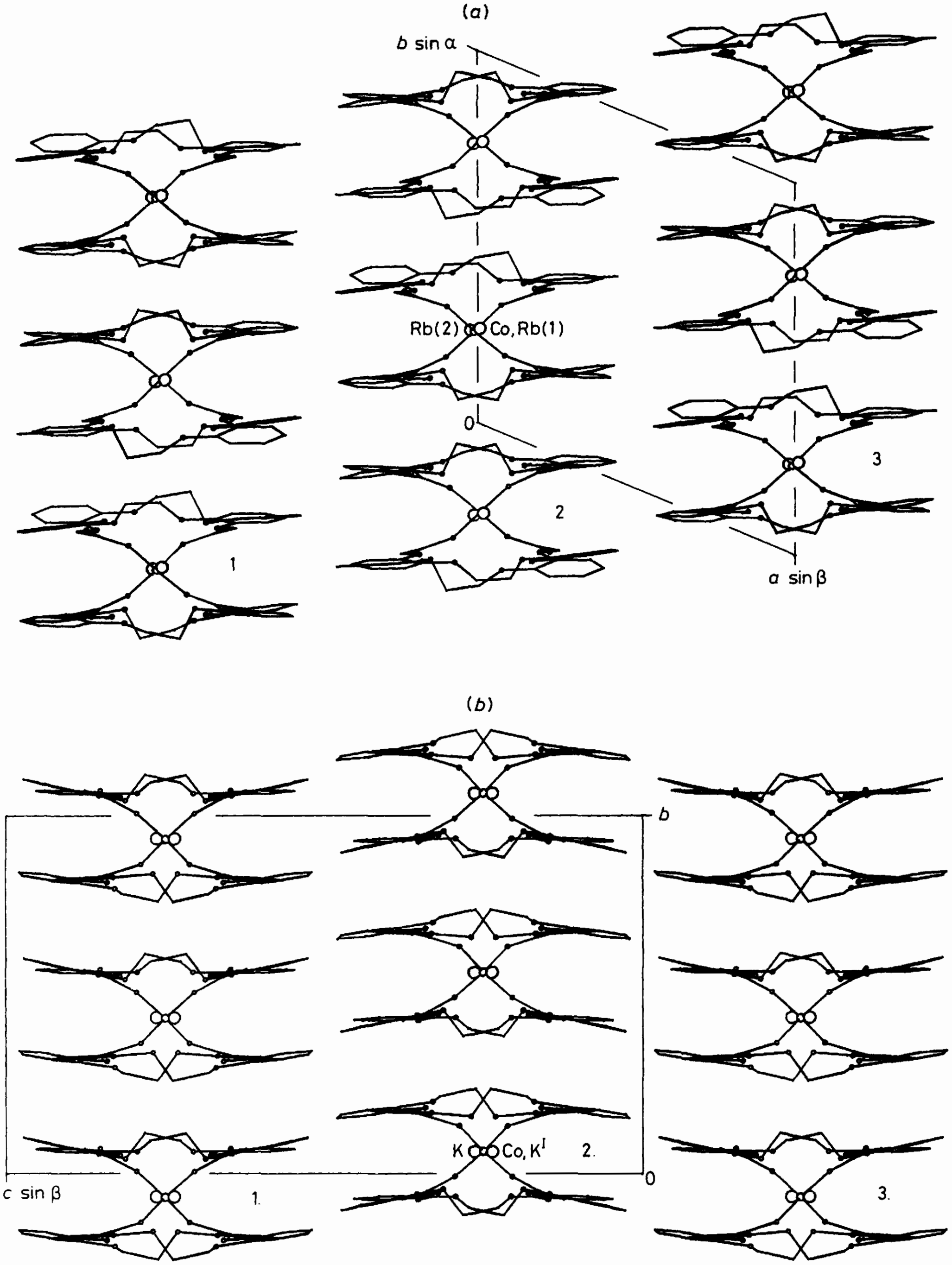

Figure 4. Corresponding packing views of complexes (1R) (a) and (1K) (b)

and reaction with thallium(I) gives the salt TlL. The smaller cation sodium does not form isolable crystals of $[Co(L_2Na)_2]$ and, in fact, in an equimolar solution of sodium and potassium ions, $[CoL_2]$ selects exclusively for potassium. The selectivity is likely to arise because of two factors. Firstly, the size of the sodium cation, being smaller than potassium, would tend to pull the open-chain ligands inwards, causing increased non-bonded interactions. Secondly, it is unusual, although not unknown, for sodium to adopt 10-fold co-ordination.

The above selectivity suggests possible transport and extraction applications. Indeed, $[Co(L_2K)_2]$ may be stored under water without decomposition in excess of 2 d, and may also be dissolved in methylene chloride without change.

The linear arrangement of M^I–M^{II}–M^I where M^I are alkali metals and M^{II} is a transition metal also has wide possibilities for activation of small molecules by initial co-ordination to the transition metal followed by interaction of the alkali metal as a Lewis acid.

Our research is now continuing both in attempting to change the central transition-metal ion ' cement ' and also the ligand arms of the complex cavity. We believe this will lead to interesting variations in cation selectivity. For example, changing the transition-metal co-ordination geometry from tetrahedral to square planar would alter the ' bite ' of the co-ordinating ligands, generating smaller cavities more suitable for sodium complexation.

Table 3. Torsion angles (°) in complexes (1K) and (1R). The atoms defining the angle are numbered as in Figure 1; the ligands are identified by a representative atom. E.s.d.s are 1°, except where shown otherwise in parentheses

	(1K)		(1R)			
Ligand of:	O(1)	O(31)	O(1)a	O(1)b	O(41)a	O(41)b
H(1)-O(1)-C(2)-C(7)	179(7)	167(10)	−175(7)	−179(5)	−174(6)	−172(7)
O(1)-C(2)-C(7)-O(8)	0	−2	4	4	2(2)	3
C(2)-C(7)-O(8)-C(9)	−177	−161	−95	−104	−131	−100
C(7)-O(8)-C(9)-C(10)	175	162	−179	−179	174	−179
O(8)-C(9)-C(10)-O(11)	64	51	−66	−65	−7(2)	−68
C(9)-C(10)-O(11)-C(12)	176	−178	−167	−173	−178	−167
C(10)-O(11)-C(12)-C(17)	113	114	168	174	150	174
O(11)-C(12)-C(17)-O(18)	−1	0	2	3	1	2
C(12)-C(17)-O(18)-C(19)	179	−175	−165	−170	−173	−167
C(17)-O(18)-C(19)-C(20)	−174	−175	174	−175	−179	180
O(18)-C(19)-C(20)-O(21)	11	10	17	17	14	17
O(18)-C(19)-C(20)-O(22)	−172	−170	−164	−162	−166	−164

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