Co-ordination of Alkali Metals by Open-chain Polyethers in Transition-metal Complexes. Part 1. *X*-Ray Crystal and Molecular Structure of Tetrakis[1-*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethanato-(1−)]dipotassiumcobalt(II), a Trinuclear Potassium–Cobalt–Potassium Complex

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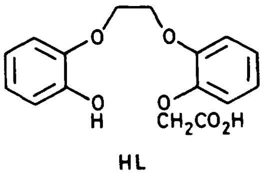
The synthesis and *X*-ray crystal structure of tetrakis[1-(*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)-ethanato(1 −)]dipotassiumcobalt(II), $[Co(L_2K)_2]$, a novel neutral K–Co–K complex, is reported. The cobalt(II) ion is tetrahedrally co-ordinated by four carboxyl oxygens, one from each of four open-chain polyether hydroxy-acid anion ligands L^-. The polyether ligands are held in the correct positions to co-ordinate two potassium ions, each potassium being co-ordinated by ten oxygen atoms. Four interligand hydrogen bonds from hydroxy groups to carboxy oxygens add further stability to the $[Co(L_2K)_2]$ structure. Crystals are monoclinic, a = 17.052(4), b = 14.263(4), c = 26.226(6) Å, β = 106.71(2)°, and Z = 4. R = 0.069 for 2 338 reflections.

There have been several studies of the interaction of transition-metal ions with cyclic polyethers,[1] and the crystal structures which have been determined for some of the isolated compounds illustrate a considerable variation in the complexing role of the polyether. In some cases the co-ordination of the transition metal is by water and anions, which are then hydrogen-bonded to the ether oxygens. Thus, penta-aquanitratomanganese(II)–18-crown-6 nitrate monohydrate,[2] hexa-aquamanganese(II)–18-crown-6 perchlorate,[3] and hexa-aquacobalt tetrachlorocobaltate–18-crown-6 acetone [4] are all examples where the cyclic polyether does not directly co-ordinate the transition metal. In contrast, structures of dichloro-(12-crown-4)copper(II),[5] (12-crown-4)dinitratocobalt(II),[6] and diaqua(15-crown-5)cobalt dinitrate [6] show the transition metal to be co-ordinated by all the oxygens of the polyether, and the remaining co-ordination sites filled either by anions or by water molecules.

Holt *et al.*[6] have previously suggested that the smaller rings 12-crown-4 and 15-crown-5 with cavity diameters 1.2—1.5 Å and 1.7—2.2 Å respectively [7] should be more favourable for binding Co^{II} (ionic diameter 1.48 Å) than the larger 18-crown-6 with cavity diameter 2.6—3.2 Å.[7] Because of the constraints of the macrocyclic ring, distorted co-ordination geometries of the transition metal are often observed, and this must lead to a reduction in stability of the complex. Thus, copper(II)–12-crown-4 chloride shows the copper in a plane of two oxygens and two chlorines, but the angle subtended at copper by the two apical oxygens completing the irregular octahedron is 135.2°.[5]

We decided therefore to investigate the co-ordination chemistry of transition metals with some open-chain polyethers, where a more flexible molecule may form a regular co-ordination pattern around the transition-metal ion. We have recently reported the syntheses and solution studies of some hydroxy acid polyethers,[8] and we now describe the crystal structure of the product obtained on reacting the potassium salt of 1-(*o*-carboxymethoxyphenoxy)-2-(*o*-hydroxyphenoxy)ethane (HL) with cobalt(II) chloride.



HL

EXPERIMENTAL

Cobalt(II) chloride hexahydrate was dehydrated by treatment with refluxing thionyl chloride for 16 h, followed by drying *in vacuo* at 50 °C. Anhydrous cobalt(II) chloride (0.127 g) and the potassium salt of HL (0.684 g) were refluxed together in acetonitrile (15 cm^3) giving a blue solution, and blue-mauve crystals were slowly deposited. Reflux was continued for 6 h, then the solution was allowed to cool to room temperature, and the crystals collected on a sinter and washed with acetonitrile (5 cm^3). Yield 0.55 g, m.p. 240—242 °C. These crystals were used for *X*-ray analysis without further treatment, but the bulk sample was contaminated with potassium chloride. A pure sample of this compound was isolated as follows. Cobalt(II) acetate tetrahydrate (0.125 g) and HL (0.304 g) were refluxed together in ethyl alcohol (50 cm^3) and a pale red solution resulted. This was filtered hot, and the filtrate refluxed with the potassium salt of HL (0.2 g) for 1 h. During this time the solution became dark blue, and a crystalline blue solid was deposited. This was collected on a sinter and washed with ethyl alcohol (10 cm^3). Yield 0.37 g, m.p. 241–242 °C (Found: C, 56.65; H, 4.5. $C_{64}H_{60}CoK_2O_{24}$ requires C, 56.95; H, 4.5%).

Crystals obtained from acetonitrile are mauve-blue, finely formed rhombus-shaped plates, many of which were found to be split and/or twinned. A rare single crystal, 0.14 × 0.21 × 0.26 mm, was mounted in epoxy-resin on a glass fibre. Preliminary *X*-ray photographs suggested a triclinic cell, which was reduced by Delaunay's method to a C-centred monoclinic cell. Cell dimensions were refined from the settings of 25 reflections (having θ in the range 8.0—9.7°) on an Enraf-Nonius CAD4 diffractometer.

Crystal Data.—$C_{64}H_{60}CoK_2O_{24}$, *i.e.* $[Co(L_2K)_2]$ where L = $C_{16}H_{15}O_6$, M = 1 350.3, monoclinic, a = 17.052(4), b = 14.263(4), c = 26.226(6) Å, β = 106.71(2)°, U = 6109.2 Å^3, space group $C2/c$, D_m = 1.465 (by flotation), Z = 4, D_c = 1.468 g cm^{-3}, $F(000)$ = 2 804, μ(Mo-K_α) = 5.0 cm^{-1}, λ(Mo-K_α) = 0.710 69 Å.

Intensity data were measured on the diffractometer for reflections in the range $1.3 \leqslant \theta \leqslant 20.0°$, with monochromated Mo-$K_\alpha$ radiation. There was no significant change in the intensities of the two control reflections, and some sample ψ-scans indicated that the determination of an absorption factor was not required. The data were therefore corrected only for Lorenz and polarization effects. From the measured intensities, systematic absences showed the space group to be either $C2/c$ or Cc; the centrosymmetric group, $C2/c$, was proved the correct one by the structure analysis. Structure amplitudes of 2 856 independent reflections were calculated.

There was some uncertainty at this stage as to what 'heavy' atoms were present in the crystal, and in what ratio they were present. Microanalysis suggested that chlorine was present, the colour confirmed cobalt, and there was the possibility of some potassium to balance the ionic changes. From density and analytical measurements, it was estimated that there should be two ligands and the equivalent of about two cobalt atoms in the asymmetric unit of the centrosymmetric space group.

Peaks from the Patterson map did not appear to produce a clear, unique solution, and electron-density maps phased by various combinations of the heavier atoms in several trial positions in both possible space groups did not lead to a ready solution. It was evident, however, that there were prominent planes of atoms normal to the *b*-axis in the structure.

The direct methods routines, EEES and TANG, in the SHELX program system [9] were also run with little success. The *E* values were recalculated with the NORMAL routine of the MULTAN suite,[10] taking into account that the ligand L^- was known to contain two rigid catechol groups (in unknown orientation and position). Eventually, from two runs of TANG, using reflections having $|E| \geqslant 1.8$ and (*i*) $\theta \leqslant 20°$ and (*ii*) $\theta \leqslant 15°$, two sets of starting reflections (five reflections from each run) were obtained. Two of these reflections were selected as the origin-determining reflections, and the signs of the other eight were systematically varied in a run of the centrosymmetric routine EEES. Of the six *E*-maps produced, the fifth in order of PARACHOR value [9] [but having the highest M(ABS) value [9]] showed top peaks corresponding to those of one of the favoured sets from the Patterson searches; there were also indications of recognisable fragments of the ligand molecules. This *E*-map was therefore contoured and drawn on Perspex sheets, and found to show double images of parts of the structure. The vector separating the two images was a prominent Patterson peak and was also thought to separate pairs of the heavier atoms.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) for $[Co(L_2K)_2]$, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Co	5 000	641(1)	2 500
K	2 950(1)	630(1)	2 640.3(7)
O(1)	4 071(4)	1 854(6)	3 414(3)
C(2)	3 844(5)	1 792(6)	3 869(3)
C(3)	4 375(5)	1 624(6)	4 367(3)
C(4)	4 068(6)	1 561(6)	4 798(4)
C(5)	3 253(5)	1 657(6)	4 744(4)
C(6)	2 724(5)	1 809(6)	4 245(3)
C(7)	3 014(5)	1 882(5)	3 810(3)
O(8)	2 557(3)	2 025(5)	3 295(2)
C(9)	1 710(5)	2 166(6)	3 186(3)
C(10)	1 367(5)	2 394(6)	2 620(3)
O(11)	1 463(3)	1 609(4)	2 306(2)
C(12)	1 130(5)	1 695(6)	1 771(3)
C(13)	274(6)	1 690(7)	1 552(4)
C(14)	−58(7)	1 732(7)	1 008(4)
C(15)	413(5)	1 792(6)	676(4)
C(16)	1 259(5)	1 801(6)	887(3)
C(17)	1 616(5)	1 741(5)	1 430(3)
O(18)	2 443(3)	1 710(4)	1 679(2)
C(19)	2 954(4)	1 746(6)	1 336(3)
C(20)	3 846(5)	1 609(6)	1 641(4)
O(21)	4 022(3)	1 345(4)	2 119(2)
O(22)	4 324(3)	1 745(6)	1 377(3)
O(31)	3 092(4)	−531(5)	1 789(3)
C(32)	2 395(5)	−609(6)	1 382(3)
C(33)	2 378(6)	−630(7)	857(4)
C(34)	1 624(6)	−699(7)	469(4)
C(35)	918(6)	−716(7)	603(4)
C(36)	927(6)	−705(7)	1 129(4)
C(37)	1 669(5)	−644(6)	1 526(3)
O(38)	1 772(4)	−629(5)	2 060(2)
C(39)	1 153(6)	−935(8)	2 264(4)
C(40)	1 445(6)	−1 149(8)	2 822(4)
O(41)	1 908(3)	−428(4)	3 129(2)
C(42)	2 217(5)	−619(6)	3 661(4)
C(43)	1 678(6)	−730(7)	3 967(4)
C(44)	2 002(7)	−932(8)	4 498(4)
C(45)	2 807(6)	−1 022(7)	4 731(4)
C(46)	3 348(6)	−880(6)	4 423(3)
C(47)	3 039(5)	−690(6)	3 884(3)
O(48)	3 519(3)	−564(4)	3 544(2)
C(49)	4 376(5)	−713(7)	3 769(3)
C(50)	4 851(5)	−479(6)	3 381(3)
O(51)	4 488(3)	−73(4)	2 953(2)
O(52)	5 574(3)	−715(6)	3 524(3)
H(1)	4 466(39)	1 813(51)	3 493(28)
H(3)	4 963	1 551	4 413
H(4)	4 446	1 444	5 152
H(5)	3 047	1 618	5 056
H(6)	2 136	1 865	4 200
H(9)a	1 452	1 595	3 269
H(9)b	1 607	2 686	3 403
H(10)a	1 656	2 936	2 532
H(10)b	784	2 542	2 547
H(13)	−83	1 658	1 785
H(14)	−655	1 718	859
H(15)	162	1 828	290
H(16)	1 606	1 851	649
H(19)a	2 788	1 251	1 068
H(19)b	2 889	2 359	1 160
H(31)	3 437(63)	−620(81)	1 708(43)
H(33)	2 888	−595	755
H(34)	1 608	−737	93
H(35)	395	−737	323
H(36)	412	−740	1 224
H(39)a	737	−442	2 212
H(39)b	908	−1 501	2 072
H(40)a	1 787	−1 713	2 866
H(40)b	971	−1 274	2 952
H(43)	1 086	−665	3 808
H(44)	1 627	−1 014	4 717
H(45)	3 015	−1 184	5 109
H(46)	3 941	−915	4 588
H(49)a	4 571	−314	4 085
H(49)b	4 469	−1 373	3 873

Mean positions of the atoms in the pair of images were calculated. Three of the four catechol groups were clear, with two heavier atoms (one of which was located on a two-fold axis) corresponding to the alternative favoured set from the Patterson map. Subsequent structure factor calculations and electron-density maps showed that a Co atom was on the symmetry axis; the second heavy atom, surrounded by ten oxygen atoms, was identified as a potassium ion, and the ionic charges in the complex $[Co(L_2K)_2]$ were thus balanced (assuming anionic ligands, L^-). There was

TABLE 2

Bond distances (Å) and angles (°) with e.s.d.s in parentheses

(*a*) Distances

Co · · · K	3.619(2)	K–O(1)	2.931(8)
Co–O(21)	1.957(5)	K–O(8)	2.833(6)
Co–O(51)	1.952(5)	K–O(11)	2.806(5)
		K–O(18)	2.867(5)
		K–O(21)	2.773(5)
		K–O(31)	2.845(7)
		K–O(38)	2.795(6)
		K–O(41)	2.897(6)
		K–O(48)	2.852(6)
		K–O(51)	2.705(5)
O(1)–C(2)	1.359(10)	O(31)–C(32)	1.355(10)
C(2)–C(3)	1.378(11)	C(32)–C(33)	1.369(11)
C(2)–C(7)	1.385(10)	C(32)–C(37)	1.397(11)
C(3)–C(4)	1.379(12)	C(33)–C(34)	1.395(12)
C(4)–C(5)	1.363(12)	C(34)–C(35)	1.348(12)
C(5)–C(6)	1.377(12)	C(35)–C(36)	1.376(13)
C(6)–C(7)	1.372(11)	C(36)–C(37)	1.391(12)
C(7)–O(8)	1.365(9)	C(37)–O(38)	1.361(10)
O(8)–C(9)	1.404(9)	O(38)–C(39)	1.383(10)
C(9)–C(10)	1.467(11)	C(39)–C(40)	1.435(12)
C(10)–O(11)	1.426(10)	C(40)–O(41)	1.403(11)
O(11)–C(12)	1.358(9)	O(41)–C(42)	1.369(10)
C(12)–C(13)	1.407(11)	C(42)–C(43)	1.392(12)
C(12)–C(17)	1.384(10)	C(42)–C(47)	1.358(11)
C(13)–C(14)	1.377(13)	C(43)–C(44)	1.375(13)
C(14)–C(15)	1.347(12)	C(44)–C(45)	1.339(13)
C(15)–C(16)	1.389(11)	C(45)–C(46)	1.406(13)
C(16)–C(17)	1.380(11)	C(46)–C(47)	1.387(11)
C(17)–O(18)	1.375(9)	C(47)–O(48)	1.384(9)
O(18)–C(19)	1.422(8)	O(48)–C(49)	1.425(9)
C(19)–C(20)	1.512(11)	C(49)–C(50)	1.508(11)
C(20)–O(21)	1.260(9)	C(50)–O(51)	1.257(9)
C(20)–O(22)	1.227(10)	C(50)–O(52)	1.229(9)

(*b*) Angles

O(21)–Co–O(51)	96.5(2)
O(21)–Co–O(21^{I})	118.3(2)
O(21)–Co–O(51^{I})	114.9(2)
O(51)–Co–O(51^{I})	117.1(2)
O(1)–C(2)–C(3)	124.5(7)
O(1)–C(2)–C(7)	115.7(7)
C(3)–C(2)–C(7)	119.7(8)
C(2)–C(3)–C(4)	119.1(8)
C(3)–C(4)–C(5)	121.7(9)
C(4)–C(5)–C(6)	118.9(9)
C(5)–C(6)–C(7)	120.6(8)
C(2)–C(7)–C(6)	120.0(8)
C(2)–C(7)–O(8)	113.6(7)
C(6)–C(7)–O(8)	126.4(7)
C(7)–O(8)–C(9)	119.0(6)
O(8)–C(9)–C(10)	109.0(7)
C(9)–C(10)–O(11)	109.4(7)
C(10)–O(11)–C(12)	116.3(6)
O(11)–C(12)–C(13)	119.8(8)
O(11)–C(12)–C(17)	121.5(7)
C(13)–C(12)–C(17)	118.7(8)
C(12)–C(13)–C(14)	119.5(9)
C(13)–C(14)–C(15)	121.9(10)
C(14)–C(15)–C(16)	119.1(9)
C(15)–C(16)–C(17)	120.7(8)
C(12)–C(17)–C(16)	120.1(7)
C(12)–C(17)–O(18)	114.5(7)
C(16)–C(17)–O(18)	125.4(7)
C(17)–O(18)–C(19)	115.5(6)
O(18)–C(19)–C(20)	111.5(6)
C(19)–C(20)–O(21)	118.7(7)
C(19)–C(20)–O(22)	114.3(8)
O(21)–C(20)–O(22)	127.0(8)
Co–O(21)–K	98.3(2)
O(31)–C(32)–C(33)	123.6(8)
O(31)–C(32)–C(37)	115.8(8)
C(33)–C(32)–C(37)	120.6(8)
C(32)–C(33)–C(34)	118.9(9)
C(33)–C(34)–C(35)	121.1(10)
C(34)–C(35)–C(36)	120.6(10)
C(35)–C(36)–C(37)	119.8(10)
C(32)–C(37)–C(36)	119.0(8)
C(32)–C(37)–O(38)	114.6(7)
C(36)–C(37)–O(38)	126.4(8)
C(37)–O(38)–C(39)	120.4(7)
O(38)–C(39)–C(40)	112.4(9)
C(39)–C(40)–O(41)	113.7(9)
C(40)–O(41)–C(42)	115.3(7)
O(41)–C(42)–C(43)	119.0(8)
O(41)–C(42)–C(47)	120.0(8)
C(43)–C(42)–C(47)	121.0(9)
C(42)–C(43)–C(44)	117.9(10)
C(43)–C(44)–C(45)	122.9(11)
C(44)–C(45)–C(46)	118.8(11)
C(45)–C(46)–C(47)	119.6(9)
C(42)–C(47)–C(46)	119.7(8)
C(42)–C(47)–O(48)	116.2(7)
C(46)–C(47)–O(48)	124.1(7)
C(47)–O(48)–C(49)	116.1(6)
O(48)–C(49)–C(50)	111.9(7)
C(49)–C(50)–O(51)	118.8(7)
C(49)–C(50)–O(52)	114.9(8)
O(51)–C(50)–O(52)	126.3(8)
Co–O(51)–K	100.8(2)

(*c*) Selected torsion angles

O(1)–C(2)–C(7)–O(8)	0(1)
C(2)–C(7)–O(8)–C(9)	−177(1)
C(7)–O(8)–C(9)–C(10)	175(1)
O(8)–C(9)–C(10)–O(11)	64(1)
C(9)–C(10)–O(11)–C(12)	176(1)
C(10)–O(11)–C(12)–C(17)	113(1)
O(11)–C(12)–C(17)–O(18)	−1(1)
C(12)–C(17)–O(18)–C(19)	179(1)
C(17)–O(18)–C(19)–C(20)	−174(1)
O(18)–C(19)–C(20)–O(21)	11(1)
O(18)–C(19)–C(20)–O(22)	−172(1)
O(31)–C(32)–C(37)–O(38)	−2(1)
C(32)–C(37)–O(38)–C(39)	−161(1)
C(37)–O(38)–C(39)–C(40)	162(1)
O(38)–C(39)–C(40)–O(41)	51(1)
C(39)–C(40)–O(41)–C(42)	−178(1)
C(40)–O(41)–C(42)–C(47)	114(1)
O(41)–C(42)–C(47)–O(48)	0(1)
C(42)–C(47)–O(48)–C(49)	−175(1)
C(47)–O(48)–C(49)–C(50)	−175(1)
O(48)–C(49)–C(50)–O(51)	10(1)
O(48)–C(49)–C(50)–O(52)	−170(1)

no chloride ion in the crystal; later examination showed that the bulk sample contained an impurity of KCl.

Thereafter full-matrix least-squares refinement (with SHELX) was rapid. The Co, K, and O atoms were refined with anisotropic thermal parameters, the C atoms isotropically. Co-ordinates of H atoms were calculated at 0.98 Å from their bonded C atoms, and $U_{\text{iso.}}$ values for these H atoms were set at *ca.* 0.005 Å^2 above, and to 'ride' on, those of the bonded C atoms. The two phenolic H atoms were located in a difference map and were refined independently and satisfactorily.

Scattering factors for Co^{2+}, K$^+$, C, O, and H were taken from ref. 11. The scheme in which all reflections were equally weighted was found to be the most satisfactory. Convergence was reached with $R = 0.069$ and $R' = 0.067$ for 2 338 reflections (all those with a positive net intensity).

The refined atomic co-ordinates are in Table 1. Isotropic thermal parameters $U_{\text{iso.}}$ or $U_{\text{eq.}}$ and anisotropic thermal parameters for the Co, K, and O atoms havc been deposited with a listing of observed and calculated structure factors in Supplementary Publication No. SUP 23287 (18 pp.).*

All bonding dimensions are in Table 2.

Computing.—The diffractometer data were processed in the program CAD4.[12] The crystal structure was determined using a part of the MULTAN suite [10] in conjunction with the SHELX program,[9] which was also used for the least-squares refinement and analysis of results. Additional geometrical calculations were made with GEOM,[13] a suite of interactive programs adapted or written by Dr. J. D. Owen. All these programs were run on our Prime 550 computer. The diagrams were drawn by ORTEP [14] on Rothamsted's ICL System 4 computer.

DISCUSSION

The product expected from the reaction of the potassium salt of hydroxy-acid (HL) with cobalt(II) chloride was one where the chlorines had been replaced to give a $Co^{II}L_2$ species. Co-ordination was expected from the oxygens of two multidentate ligands, where the carboxyl groups would co-ordinate cobalt, and ether oxygens would also be available, as proposed in the isolated complexes of tetrahydrofuroic and tetrahydrofuranic acids.[15] The crystal structure of our isolated blue-mauve complex, however, showed that, although the chlorine atoms had been replaced, an oxygen atom of the carboxylate from each of four different hydroxy-acid ligands was co-ordinating the cobalt in a tetrahedral arrangement and no ether oxygens were involved in bonding to cobalt. The electronic absorption bands of a solution of the complex in methylene chloride and also of the diffuse reflectance spectrum of the solid are shown in Figure 1. The spectra are similar to those obtained for other tetrahedral cobalt(II) complexes with oxygen donors.[16-18] The highly interesting feature of the complex, however, was the presence of two potassium ions per molecule, giving a virtually linear potassium–cobalt–potassium grouping (K · · · Co 3.619 Å). Each potassium ion is co-ordinated by ten oxygen atoms.

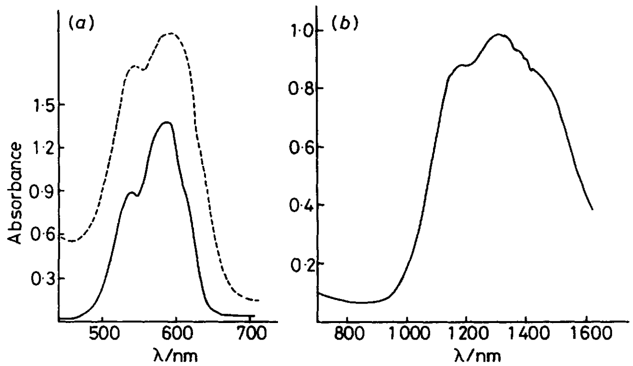


FIGURE 1 (*a*) Absorption (——) (20 mg/5 cm^3 methylene chloride) and diffuse reflectance (— — — —) spectra of the complex $[Co(L_2K)_2]$; (*b*) absorption spectrum (20 mg/1 cm^3 methylene chloride) of the complex $[Co(L_2K)_2]$

Description of the Structure.—A view of the whole complex molecule is in Figure 2 (K · · · O contacts are not shown), and the upper half of this molecule is shown, with atom numbering, in Figure 3. A two-fold symmetry axis, parallel to the viewing (*b*) axis, passes through the Co atom. The upper and lower halves of the molecule are approximately related by *pseudo*-two-fold axes of symmetry in the plane of the paper, one along the K · · · Co · · · K^I axis, the other normal to it and through the Co atom. The atoms of the ligand in the lower half are, therefore, crystallographically independent of those in Figure 3 and are named O(31), C(32), O(31^I), *etc.* with numbers ($n + 30$) with respect to those shown in Figure 3.

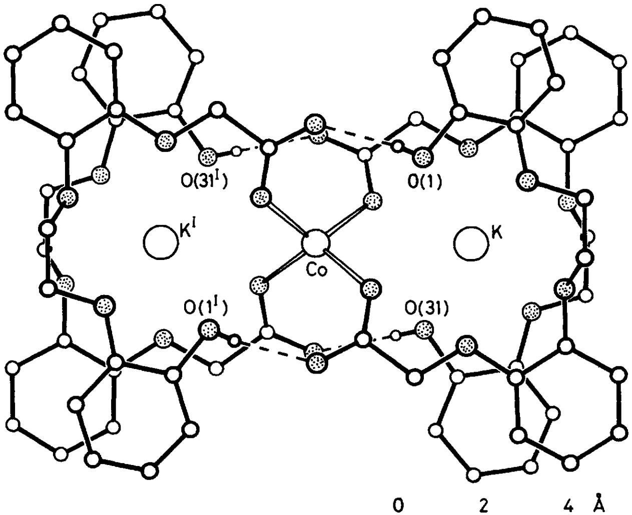


FIGURE 2 The whole complex molecule $[Co(L_2K)_2]$, viewed down the *b* axis. Superscript I denotes the symmetry relation $1 - x, y, \frac{1}{2} - z$ with respect to the co-ordinates *x*, *y*, *z* of Table 1

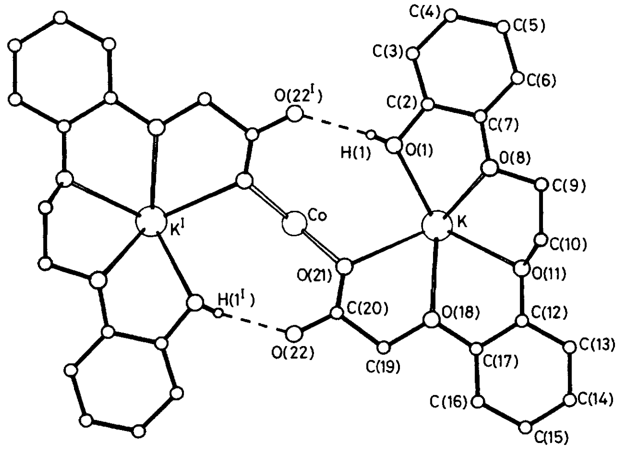


FIGURE 3 The upper half of the molecule of Figure 2. The atomic naming scheme for one ligand and the hydrogen-bonding contacts between the symmetry-related halves of the dimer pair are shown

The layered nature of the molecule and crystal is shown in Figure 4. In the molecule A, the atoms numbered 1—

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

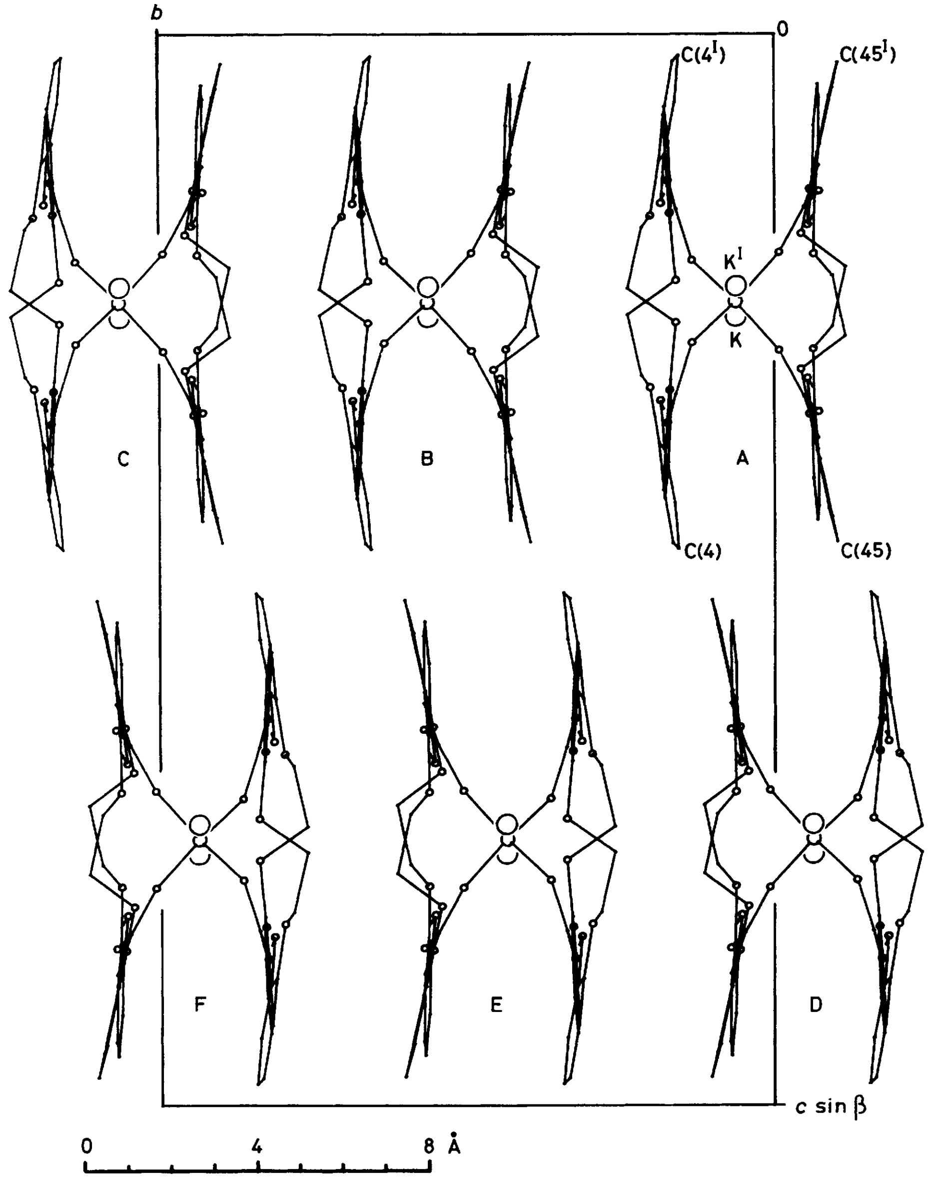

FIGURE 4 Packing diagram, viewed down the *a* axis. The Co atoms of molecules A, C, D, and F are at $x = 0.5$; those of molecules B and E are at $x = 0.0$

22 are to the left of the K · · · Co · · · K^I group, while those **31**—**52** are to the right.

Each of the four ligands of the complex molecule is bound through the anionic O atom of the carboxylate group to the central Co atom. The Co–O distances are *ca.* 1.955 Å and are normal for this type of bonding; the angles about the Co atom indicate a rather flattened tetrahedral co-ordination.

The second O atom of each carboxylate group is the acceptor atom of a hydrogen bond from the phenolic group of the symmetry-related ligand, *i.e.* the two ligands in the same layer are hydrogen-bonded. We find, therefore, that in this crystal, the open-chain ligand is *not* cyclised by formation of an intraligand hydrogen-bond but that a much larger cyclic unit, a hydrogen-bonded dimer-pair, is created; hydrogen-bond dimensions are in Table 3. This observation agrees with conclusions drawn from our previous studies on hydroxy-acids,[8] diacids,[19] and diols,[20] that no intramolecular hydrogen bonds were found. However, a recent paper by Chaker and Saenger [21] shows such a hydrogen bond in the co-ordination of sodium with a polyether zwitterion.

The potassium ions lie sandwiched between the two layers, interacting with five O atoms from each layer in an approximately pentagonal antiprismatic arrangement. The ten K · · · O distances lie in the range 2.705—2.931 Å, with the shortest two contacts to the pair of anionic O atoms, O(21) and O(51).

The dimensions within the ligands do not differ greatly between the two molecules and are, generally, close to values expected in polyether molecules. The distances between O(38) and O(41), however, are rather shorter than normal, with C(39)–C(40) at 1.435 Å especially short; the temperature factors of these atoms are a little higher than those of the corresponding atoms O(8)—O(11).

TABLE 3

Hydrogen-bond dimensions

	O–H/Å	O···O/Å
O(1)–H(1)···O(22$^{\text{I}}$)	0.65(6)	2.637(9)
O(31)–H(31)···O(52$^{\text{I}}$)	0.69(10)	2.643(9)

	H···O/Å	O–H···O/°
O(1)–H(1)···O(22$^{\text{I}}$)	2.00(6)	171(8)
O(31)–H(31)···O(52$^{\text{I}}$)	1.96(10)	173(13)

Table 4 records some mean-plane data. In each ligand, four of the five O atoms bonded to the K$^+$ ion form a good plane; in each case, the fifth atom, O(18) and O(48), is *ca.* 0.6 Å removed from this plane, away from the K$^+$ ion.

The separation of the ligand layers is *ca.* 3.6 Å; the *b* cell length is 14.3 Å. There is partial overlap of approximately parallel benzene rings in adjacent layers, both within the molecule [the rings C(2)—C(7) and C(42)—C(47) are partly overlapping, as are C(12)—C(17) and C(32)—C(37)], and between molecules [where the paired rings are C(2)—C(7) and C(32$^{\text{II}}$)—C(37$^{\text{II}}$)]. Distances between the paired ring systems are all at normal van der Waals stacking distances, in the range 3.5—3.7 Å. Angles between the normals to these planes are in Table 4.

TABLE 4

Mean plane data [a]

(*a*) Deviations (Å) from mean planes [b]

Plane A. Four O atoms of the first ligand

O(1) −0.079(8), O(8) 0.056(7), O(11) −0.031(6), O(21) 0.017(6), O(18) * 0.612(8), Co * −1.082(7), K * −1.424(4)

Plane B. Four O atoms of the second ligand

O(31) −0.029(8), O(38) 0.027(7), O(41) −0.014(7), O(51) 0.008(6), O(48)* −0.647(9), Co *1.029(7), K *1.391(4)

Plane C. Benzene ring C(2)—C(7)

C(2) 0.005(8), C(3) −0.005(9), C(4) −0.001(10), C(5) 0.007(10), C(6) −0.006(9), C(7) 0.000(8), O(1) * −0.020(13), O(8) * −0.021(12), K * −2.13(2)

Plane D. Benzene ring C(12)—C(17)

C(12) 0.005(8), C(13) 0.004(10), C(14) −0.009(11), C(15) 0.000(9), C(16) 0.007(8), C(17) −0.008(8), O(11) * −0.048(12), O(18) * −0.052(12), K * −1.46(2)

Plane E. Benzene ring C(32)—C(37)

C(32) 0.001(8), C(33) 0.004(10), C(34) −0.011(11), C(35) 0.012(11), C(36) −0.005(11), C(37) −0.001(9), O(31) * 0.031(13), O(38) * −0.021(13), K * 1.64(2)

Plane F. Benzene ring C(42)—C(47)

C(42) −0.007(9), C(43) 0.010(11), C(44) 0.001(12), C(45) −0.014(11), C(46) 0.011(9), C(47) −0.002(8), O(41) * −0.015(13), O(48) * −0.015(13), K * 1.18(2)

Plane G. Carboxylate group of first ligand

C(19) −0.003(10), C(20) 0.014(7), O(21) −0.002(5), O(22) −0.003(9), Co * −0.706(11), K * −0.58(2)

Plane H. Carboxylate group of second ligand

C(49) −0.000(11), C(50) 0.001(7), O(51) −0.000(5), O(52) −0.000(9), Co * 0.548(10), K * 0.24(2)

(*b*) Angles (°) between normals to mean planes [c]

A—B	11.7(3)	B—E	7.5(4)	C—F	6.2(8)
A—C	21.6(2)	B—F	21.3(2)	D—E	5.5(3)
A—D	17.3(2)	B—H	37.6(2)	E—F	14.3(3)
A—G	30.2(2)	C—D	8.2(4)	C—E$^{\text{II}}$	6.6(4)

[a] Atoms were weighted according to their positional e.s.d.s in the calculation of the equations for the mean planes. [b] Atoms marked (*) were not included in the determination of the plane. [c] Superscript II denotes the symmetry relation $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$, *i.e.* part of molecule B of Figure 4.

Contacts between molecules in the *ac* plane are also at normal van der Waals distances.

Conclusion.—The observed crystal structure of the complex $[Co(L_2K)_2]$ introduces the possibility of a class of compounds where a number of open chain polyether ligands are co-ordinated to a transition metal and thus held in a suitable orientation for further co-ordination to an alkali metal. Because the oxidation state and the co-ordination geometry of the transition metal may be changed, it may be possible to complex and decomplex the alkali metal under reversible conditions which would be more easily controlled than with the cyclic or open-chain polyethers themselves.

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