# The Crystal Structures of 1,5,12,16,23,26,29,32,35-nonaoxa[13³·¹⁴]-[5.5]orthocyclophane and its Complex with Rubidium Picrate

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The crystal structures of the macrobicyclic polyether (Ic) systematically named in the title, and of its complex with rubidium picrate have been determined from observations collected on a CAD4 diffractometer. Crystals of the uncomplexed ether are monoclinic with four molecules in a unit cell having a = 8.859(4), b = 11.555(10), c = 25.325(11) Å and β = 102.49(4)° and space group $P2_1/c$. The structure was solved by direct methods and refined by full matrix least squares to R 0.068 for 3 285 observed reflections. The molecules take up a folded conformation, with the aliphatic bridge much nearer one benzene ring than the other. There are several unexpected values for the torsion angles. The rubidium picrate complex is triclinic with space group $P\bar{1}$. In the unit cell a = 16.280(4), b = 16.660(5), c = 16.077(3) Å, α = 111.62(2), β = 116.29(2), γ = 91.32(2)°, there are two crystallographically independent rubidium ions, ligand molecules (Ic), picrate ions, and water molecules. One rubidium, Rb(1), is nine-co-ordinated by the oxygen atoms of (Ic) (1) with Rb–O ranging from 2.952(7) to 3.368(11) Å, giving a complex cation [Rb(1)(Ic)(1)]⁺. The second rubidium, Rb(2), is eleven-co-ordinated by the nine oxygen atoms of (Ic)(2) [Rb–O 2.922(11)—3.277(15) Å], by a nitro-oxygen atom from picrate(2) [Rb–O 2.933(16) Å], and by a water molecule on a centre of symmetry [Rb–O 3.077(2) Å]. This water molecule bridges two complexed ion pairs so that the entity is {[Rb(2)(Ic)(2)picrate(2)]₂H₂O}⁰. There may be hydrogen bonding contacts between the second water molecule, the co-ordinating picrate(2) and the unco-ordinated picrate(1). Disorder is evident in the aliphatic chains of each ligand and in the picrate(1). Least squares refinement in two blocks of full matrices gave R 0.105 for 4 746 observed reflections. The conformations of the complexed forms of the macrobicyclic molecule are similar and differ markedly from that of the uncomplexed molecule.

THE synthesis of macrobicyclic polyethers having high complexing ability with Group Ia salts [1] has provided new tools for studying the behaviour of alkali-metal cations. Complexes of (Ia—c) and (II) [2,3] with alkali metal halides crystallise with large, and non-stoicheiometric amounts of water and, in general, crystalline complexes are difficult to obtain free of solvent. Use of

(I)

a ; n = 1
b ; n = 2
c ; n = 3

(II)
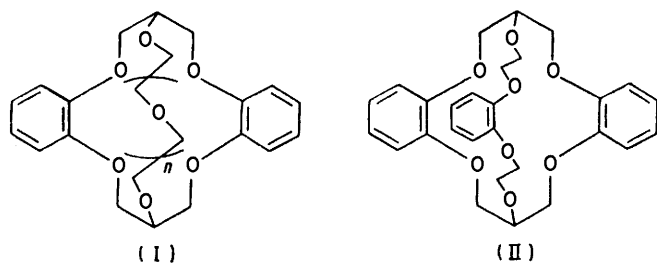
a larger anion, the picrate, allowed crystallisation [4] of a rubidium complex which showed only a very weak hydroxy-stretching frequency in the i.r. spectrum. To investigate the co-ordination of the rubidium ion we carried out a crystal structure analysis of the complex; preliminary X-ray photographs and the density revealed the additional interest that there are two independent complexes in the asymmetric unit.

For comparison the dimensions of the uncomplexed macrobicyclic molecule have also been determined by crystal structure analysis. The numbering of the atoms is shown in Figure 1.

EXPERIMENTAL

Procedures common to both crystals are described first, then those for the individual analyses. Approximate unit cell dimensions were obtained from preliminary photographs. One crystal of each compound was mounted on a CAD4 diffractometer. Accurate unit cell dimensions were obtained from 22 (25 for the complex) accurately centred reflections having high 2θ values. Intensities were collected with the ω—2θ scan procedure, and reduced to structure amplitudes by the CAD4 processor program.[5] Structure solution and refinement were carried out with the SHELX [6] suite, and stereopairs were drawn using ORTEP.[7] All these calculations were performed on the System 4 computer. Geometry calculations were performed on an IBM 1130 computer.[8]

Scattering factors for Rb⁺, C, N, and O were calculated using the analytical approximation in Table 2.2B of ref. 9, and the real and imaginary parts of the anomalous dispersion correction were from Table 2.3.1 of ref. 9. Observed and calculated structure factors have been deposited.

Uncomplexed Molecule (Ic).—*Crystal data.* $C_{26}H_{34}O_9$, M = 490.6. Monoclinic, a = 8.859(4), b = 11.555(10), c = 25.325(11) Å, β = 102.49(4)°, U = 2 531 Å³, D_m = 1.29, Z = 4, D_c = 1.29 Mg m⁻³, $F(000)$ = 1 048, space group $P2_1/c$ (C_{2h}^5, No 14). No molecular symmetry required, Mo-K_α radiation, graphite monochromator, λ = 0.7107 Å (1 Å $\equiv$ 10⁻¹⁰ m), μ = 0.091 mm⁻¹, no absorption correction applied. A crystal 0.95 × 0.50 × 0.60 mm was used to collect data for 5 053 planes with 1.5 < θ < 26°. No correction for crystal deterioration was necessary. A total of 4 943 independent planes were obtained, of which 3 285 had $|F_o| \geqslant 4\sigma(F_o)$ and were classed as observed.

The phase problem was solved using multisolution direct methods,[6] and all non-hydrogen atoms refined with anisotropic temperature factors. Hydrogen atoms were placed in positions calculated from the geometry of the rest of the molecule, with a C–H distance of 0.98 Å. They were given
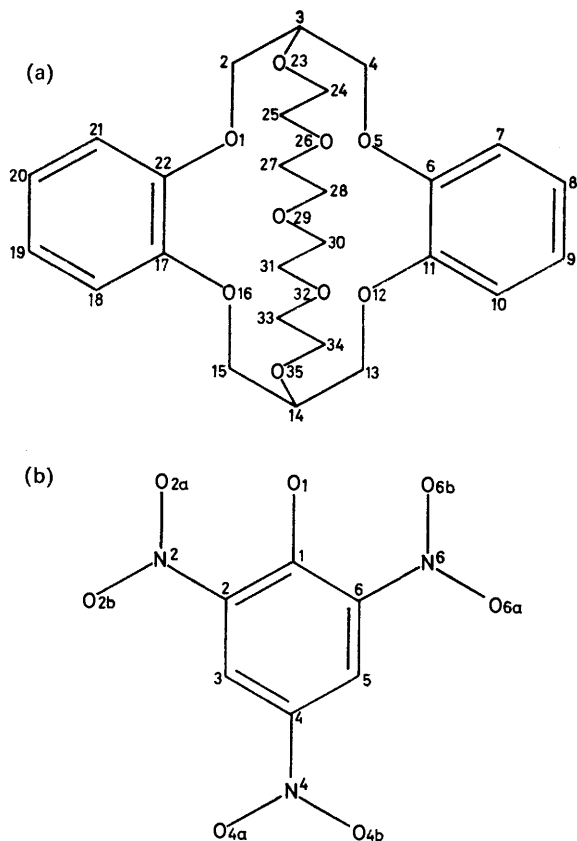
FIGURE 1 (a) The numbering of the atoms in the uncomplexed molecule (Ic). In the complexes the atoms are designated by three digits, the first being either 1 or 2 denoting the ligand to Rb(1) or Rb(2) respectively. For comparison of dimensions the first digit is defined as n. The value of n for the uncomplexed molecule is taken as 0. Hydrogen atoms have the same designations as the carbon atoms, those on methylene groups being distinguished by the letters a and b. (b) Atom numbering in the picrate anions. Atoms have two digits, the first being either 1 or 2 for picrate(1) or (2). Nitro-oxygen atoms are denoted by letters, and the other atoms are primed in the Tables and in the text to avoid confusion with atoms of the uncomplexed ligand. The alternative position for picrate(1) gives rise to further atoms O(15)′ on C(15)′ and O(16)c and O(16)d on N(16)′

a common isotropic temperature factor which refined to a value of $U_{iso} = 0.078(2)$ Å². Full matrix refinement gave a final $R = 0.068$, and $R' = 0.093$ using weights w calculated from the expression $w = 0.309/[\sigma^2(F_o) + 0.025 \ F_o^2]$. The largest peak on the final difference map was 0.7 e Å⁻³, close to O(32), one of the bridge atoms with very anisotropic thermal motion.

The final atomic co-ordinates are given in Table 1, and the anisotropic temperature factors have been deposited with the structure factors in Supplementary Publication No. SUP 23167 (49 pp.).*

Rubidium Picrate Complex RbC₆H₂N₃O₇, (Ic).—*Crystal data.* C₃₂H₃₆N₃O₁₆Rb,0.75H₂O, $M = 817.7$. Triclinic, $a = 16.280(4)$, $b = 16.660(5)$, $c = 16.077(3)$ Å, $\alpha = 111.62$-(2), $\beta = 116.29(2)$, $\gamma = 91.32(2)°$, $U = 3\ 542$ Å³, D_m (flotation) $= 1.50$, $Z = 4$, $D_c = 1.533$ Mg m⁻³, $F(000) =$

TABLE 1

Fractional co-ordinates ($\times 10^4$) for uncomplexed (Ic) (with estimated standard deviations in parentheses)

Atom	x	y	z
O(1)	926(2)	932(2)	1 613(1)
C(2)	1 494(3)	1 826(3)	2 003(1)
C(3)	186(3)	2 258(2)	2 240(1)
C(4)	654(4)	3 381(3)	2 543(1)
O(5)	2 125(3)	3 242(2)	2 911(1)
C(6)	2 091(3)	3 019(3)	3 442(1)
C(7)	1 480(4)	3 804(3)	3 750(2)
C(8)	1 528(5)	3 590(4)	4 291(2)
C(9)	2 226(5)	2 607(4)	4 533(2)
C(10)	2 871(5)	1 824(3)	4 229(2)
C(11)	2 804(4)	2 018(3)	3 683(1)
O(12)	3 492(3)	1 285(2)	3 375(1)
C(13)	3 021(4)	98(3)	3 360(1)
C(14)	4 287(3)	−601(3)	3 196(1)
C(15)	4 545(3)	−336(3)	2 644(1)
O(16)	3 098(2)	−489(2)	2 261(1)
C(17)	3 141(3)	−339(3)	1 724(1)
C(18)	4 199(4)	−912(3)	1 488(1)
C(19)	4 156(5)	−795(3)	945(2)
C(20)	3 056(4)	−115(3)	631(2)
C(21)	1 989(4)	456(3)	863(1)
C(22)	2 041(3)	368(3)	1 407(1)
O(23)	−195(2)	1 381(2)	2 579(1)
C(24)	−1 730(4)	1 446(3)	2 673(2)
C(25)	−1 735(4)	1 432(3)	3 256(2)
O(26)	−1 299(3)	327(2)	3 483(1)
C(27)	−1 278(6)	352(5)	4 038(2)
C(28)	−748(7)	−771(5)	4 291(2)
O(29)	853(4)	−809(3)	4 407(2)
C(30)	1 401(8)	−1 853(6)	4 651(2)
C(31)	3 167(7)	−1 788(5)	4 818(2)
O(32)	3 930(5)	−1 665(3)	4 383(1)
C(33)	4 027(7)	−2 683(5)	4 100(2)
C(34)	4 811(5)	−2 466(4)	3 645(2)
O(35)	3 897(3)	−1 804(2)	3 219(1)

Fractional co-ordinates ($\times 10^3$) for H atoms in uncomplexed (Ic)

Atom	x	y	z
H(2)a	228	151	229
H(2)b	192	244	183
H(3)	−71	242	196
H(4)a	−12	359	274
H(4)b	74	398	229
H(7)	99	449	358
H(8)	109	414	450
H(9)	227	246	491
H(10)	338	115	440
H(13)a	286	−15	371
H(13)b	208	0	309
H(14)	523	−39	344
H(15)a	530	−86	256
H(15)b	489	45	263
H(18)	498	−139	171
H(19)	490	−119	79
H(20)	301	−5	25
H(21)	122	94	65
H(24)a	−222	214	251
H(24)b	−230	78	251
H(25)a	−275	162	331
H(25)b	−101	200	343
H(27)a	−55	92	421
H(27)b	−229	55	409
H(28)a	−116	−137	404
H(28)b	−113	−87	461
H(30)a	97	−197	496
H(30)b	110	−248	440
H(31)a	355	−247	502
H(31)b	343	−112	504
H(33)a	455	−328	434
H(33)b	299	−293	394
H(34)a	508	−319	350
H(34)b	574	−204	380

1 698, space group $P\bar{1}$ (C_i, No. 2) from structure analysis, two formula units in the asymmetric unit, Mo-K_α radiation, graphite monochromator, $\lambda = 0.7107$ Å, $\mu = 1.44$ mm^{-1}, absorption correction applied.

Intensities were collected for 6 588 reflections in the range $1.5 < \theta < 20°$. Two intensity control reflections, 041 and 728, were measured after every 50 reflections and no deterioration in the crystal was shown. Diffraction measurements in the ψ scan mode of 31 reflections and their Friedel equivalents were made and used to apply a semi-empirical absorption correction.[10]

The structure was determined from Patterson and electron density difference maps. The R factor fell from 0.49 for the two rubidium atoms only to 0.107 with those atoms allowed anisotropic vibration and all the non-hydrogen atoms with isotropic vibration. These atoms consisted of two ligand molecules (1) and (2), two picrate anions (1) and (2), one water molecule in a general position, Wat(1), and one on a centre of symmetry, Wat(2). At this stage the difference electron density map showed a second orientation for picrate(1) and anisotropic vibration and/or disorder in the aliphatic chains of both ligands. When anisotropic vibration was allowed the parameters were not physically reasonable. Attempts to fit the electron density with alternative conformations of atoms in the aliphatic chains while possible for O(129)–C(130)–C(131)–O(132)–C(133) did not lead on refinement to improvement in R or to physically reasonable bond lengths, angles, and U_{iso} values. No plausible scheme could be deduced for O(223) $\cdots$ C(227). For picrate(1), the alternative position corresponds to rotation about the C(13)$'$ $\cdots$ C(16)$'$ direction, and the relative site occupation factors refined to 0.80 and 0.20(1). [Although the possibility that the true space group is $P1$ with four independent rubidium ions, four (Ic) molecules, four picrate ions, and three water molecules in the unit cell cannot be disproved, it would still not account for the 0.8 : 0.2 ratio without disorder.] The many parameters necessitated refinement in two blocks, the first consisting of the scale, both rubidium ions, and all the atoms of ligand(1), picrate-(1), and Wat(1) giving 237 parameters, and the second consisting of the scale, both rubidium ions, and all the atoms of ligand(2), picrate(2), and Wat(2), giving 226 parameters. The final R value was 0.105 for 4 746 observed reflections [$|F_o| \geqslant 5\sigma(F_o)$] with weights from the counting statistics. (Limitation of computer time prevented the use of the weaker reflections and the addition of hydrogen atoms.) Atomic co-ordinates are in Table 2.

The R factor is high because of the unresolved disorder and because of the omission of 75 hydrogen atoms per asymmetric unit, as indicated by it being largest at low values of $\sin\theta$. The standard deviations are approximately as expected for two heavy atoms in the asymmetric unit. High correlation coefficients between the x and z co-ordinates of several atoms result from the large β angle in the Delaunay reduced cell. An alternative cell also has all lengths ca. 16 Å with angles 89, 68, and 116°, still far from 90°. Although the standard deviations in the bond lengths and angles calculated by the SHELX program will have allowed for the correlation between one atom and another in the same block, there is no allowance for correlation between the complexes. Photographs show that the intensities fall off most rapidly along the b^* axis. This is not the effect of absorption, for which a correction was applied, and, as shown later, the vibration parameters are qualitatively reasonable in relation to the structure.

TABLE 2

Fractional co-ordinates ($\times 10^3$) for the rubidium picrate complex and isotropic thermal parameters $\times 10^3$ (Å^2) (with estimated standard deviations in parentheses). The temperature factor is of the form: $\exp[-8\pi^2 U \sin^2\theta / \lambda^2]$. For the rubidium ions the equivalent isotropic parameter is defined as: $\sum\limits_{i=1}^{3} \sum\limits_{j=1}^{3} U_{ij} a_i^* a_j^* (a_i a_j)$

Atom	x	y	z	U
Rb(1)	184.2(1)	156.6(1)	414.3(1)	73
O(101)	376(1)	237(1)	590(1)	45(2)
C(102)	397(1)	241(1)	691(1)	52(4)
C(103)	337(1)	162(1)	675(1)	57(4)
C(104)	362(1)	73(1)	633(1)	67(5)
O(105)	337(1)	50(1)	527(1)	62(3)
C(106)	363(1)	−23(1)	480(1)	52(4)
C(107)	390(1)	−86(1)	520(1)	70(5)
C(108)	412(1)	−162(1)	462(1)	76(5)
C(109)	406(1)	−171(1)	370(1)	81(5)
C(110)	379(1)	−108(1)	332(1)	65(5)
C(111)	358(1)	−32(1)	387(1)	52(4)
O(112)	329(1)	33(1)	358(1)	54(3)
C(113)	337(1)	29(1)	268(1)	62(4)
C(114)	305(1)	106(1)	247(1)	61(4)
C(115)	364(1)	199(1)	324(1)	54(4)
O(116)	360(1)	220(1)	420(1)	48(2)
C(117)	417(1)	297(1)	499(1)	41(4)
C(118)	466(1)	364(1)	494(1)	57(4)
C(119)	521(1)	441(1)	583(1)	60(4)
C(120)	528(1)	452(1)	676(1)	58(4)
C(121)	481(1)	384(1)	683(1)	53(4)
C(122)	424(1)	309(1)	595(1)	46(4)
O(123)	242(1)	161(1)	618(1)	63(3)
C(124)	177(1)	101(1)	618(1)	93(6)
C(125)	86(1)	128(1)	588(1)	91(6)
O(126)	46(1)	104(1)	481(1)	97(4)
C(127)	−43(2)	128(1)	445(2)	113(7)
C(128)	−86(2)	95(1)	335(2)	115(7)
O(129)	−32(1)	150(1)	313(1)	132(5)
C(130)	−84(2)	131(2)	199(3)	198(13)
C(131)	−43(3)	197(3)	204(3)	234(16)
O(132)	54(1)	171(1)	202(1)	173(7)
C(133)	50(2)	101(2)	122(2)	119(7)
C(134)	149(1)	105(1)	132(2)	100(6)
O(135)	209(1)	99(1)	226(1)	73(3)
C(11)$'$	462(1)	106(1)	1 088(1)	73(5)
C(12)$'$	426(1)	103(1)	991(1)	78(5)
C(13)$'$	474(1)	114(1)	945(1)	66(5)
C(14)$'$	570(1)	132(1)	1 000(1)	59(4)
C(15)$'$	617(1)	135(1)	1 099(1)	62(4)
O(15)$'$	695(6)	146(5)	1 138(6)	128(28)
C(16)$'$	560(1)	120(1)	1 138(1)	68(5)
O(11)$'$	416(1)	102(1)	1 132(1)	115(6)
N(12)$'$	319(2)	75(2)	919(2)	164(9)
O(12)a	280(2)	57(2)	954(2)	244(12)
O(12)b	291(2)	89(2)	850(2)	233(11)
N(14)$'$	628(1)	147(1)	954(1)	103(5)
O(14)a	586(1)	154(1)	878(1)	141(6)
O(14)b	711(1)	159(1)	1 006(1)	136(5)
N(16)$'$	619(2)	127(2)	1 246(2)	137(7)
O(16)a	694(2)	169(2)	1 300(2)	
O(16)b	563(2)	78(2)	1 253(2)	157(6)
O(16)c	672(7)	80(7)	1 267(7)	
O(16)d	606(7)	182(6)	1 312(7)	
Wat(1)	288(1)	243(1)	88(1)	138(5)
Rb(2)	39.8(1)	485.5(1)	825.5(1)	63
O(201)	171(1)	404(1)	749(1)	56(3)
C(202)	263(1)	396(1)	820(1)	56(4)
C(203)	254(1)	388(1)	909(1)	64(4)
C(204)	195(1)	308(1)	887(1)	70(5)
O(205)	97(1)	303(1)	818(1)	66(3)
C(206)	31(1)	231(1)	784(1)	64(4)
C(207)	55(1)	165(1)	824(1)	88(6)
C(208)	−22(1)	92(1)	783(2)	99(6)
C(209)	−110(1)	84(1)	713(2)	100(6)
C(210)	−134(1)	150(1)	675(1)	78(5)
C(211)	−58(1)	222(1)	712(1)	60(4)

TABLE 2 (continued)

Atom	x	y	z	U
O(212)	−72(1)	288(1)	679(1)	60(3)
C(213)	−162(1)	270(1)	585(1)	70(5)
C(214)	−161(1)	349(1)	558(1)	62(4)
C(215)	−90(1)	364(1)	522(1)	59(4)
O(216)	5(1)	385(1)	607(1)	58(3)
C(217)	76(1)	394(1)	586(1)	56(4)
C(218)	60(1)	394(1)	491(1)	63(4)
C(219)	142(1)	405(1)	481(1)	72(5)
C(220)	230(1)	412(1)	554(1)	65(5)
C(221)	244(1)	413(1)	647(1)	57(4)
C(222)	167(1)	403(1)	661(1)	47(4)
O(223)	228(1)	471(1)	954(1)	83(3)
C(224)	275(1)	506(1)	1 065(1)	80(5)
C(225)	267(2)	596(2)	1 106(2)	128(8)
O(226)	183(1)	611(1)	1 068(1)	157(6)
C(227)	164(2)	699(2)	1 112(3)	200(13)
C(228)	127(2)	733(2)	1 047(2)	137(8)
O(229)	37(1)	682(1)	964(1)	120(5)
C(230)	−46(2)	692(2)	960(2)	158(10)
C(231)	−126(2)	661(2)	861(2)	136(8)
O(232)	−139(1)	564(1)	808(1)	101(4)
C(223)	−221(1)	533(1)	712(2)	101(6)
C(234)	−229(1)	439(1)	656(1)	94(6)
O(235)	−147(1)	430(1)	638(1)	72(3)
C(21)'	481(1)	641(1)	868(1)	50(4)
C(22)'	412(1)	641(1)	773(1)	52(4)
C(23)'	321(1)	641(1)	743(1)	55(4)
C(24)'	288(1)	637(1)	807(1)	53(4)
C(25)'	344(1)	633(1)	901(1)	49(4)
C(26)'	436(1)	638(1)	927(1)	46(4)
O(21)'	565(1)	639(1)	895(1)	67(3)
N(22)'	446(1)	649(1)	702(1)	83(4)
O(22)a	524(1)	672(1)	730(1)	100(4)
O(22)b	383(1)	620(1)	612(1)	130(5)
N(24)'	191(1)	634(1)	778(1)	87(4)
O(24)a	140(1)	639(1)	696(1)	139(5)
O(24)b	157(1)	623(1)	828(1)	99(4)
N(26)'	499(1)	643(1)	1 033(1)	76(4)
O(26)a	468(1)	593(1)	1 055(1)	116(5)
O(26)b	574(1)	696(1)	1 085(1)	95(4)
Wat(2)	0	500	1 000	202(12)

RESULTS AND DISCUSSION

In the crystal the uncomplexed molecule is held by van der Waals forces; there are only two intermolecular O · · · H contacts <2.5 Å, these are O(1) · · · H(7) 2.35 Å and O(35) · · · H(24)a 2.43 Å. There are no stackings of parallel planes of benzene rings.

In the rubidium picrate complex the crystallographically independent units are not chemically equivalent. There is a complex cation [Rb(1),Ic(1)]$^+$, a picrate ion [pic(1)]$^-$, a water molecule Wat(1), and a neutral entity [pic(2)Rb(2),Ic(2)H$_2$O(2)] which, with the water molecule Wat(2) on a crystallographic centre of symmetry, is a μ-aquo complex, Rb(2) and Rb(2^I) being equidistant from it. Relation I is −x, 1 − y, 2 − z from the co-ordinates in Table 2.

Comparison of dimensions between the uncomplexed molecule and the two independent complexed molecules are given in Table 3. There are no significant differences in the bond lengths which are in the usual range for monocyclic polyethers. The most significant difference in the bond angles in the uncomplexed molecule is C(17)–C(22)–O(1) which at 122.2(3)° is larger than the three corresponding ones in the same molecule and than any of those in the complex. The torsion angle C(17)–C(22)–O(1)–O(2) is 67.0(4)° (Table 3c), compared with −126.6,

TABLE 3

Bond lengths in the ligands (Å)

a.

	$n = 0$	$n = 1$	$n = 2$
O(n01)–C(n02)	1.443(4)	1.47(2)	1.47(2)
O(n01)–C(n22)	1.376(4)	1.38(2)	1.38(2)
C(n02)–C(n03)	1.500(4)	1.50(2)	1.55(3)
C(n03)–C(n04)	1.519(4)	1.54(2)	1.45(3)
C(n04)–O(n05)	1.439(4)	1.46(2)	1.47(2)
O(n05)–C(n06)	1.376(4)	1.37(2)	1.36(2)
C(n06)–C(n07)	1.381(5)	1.41(3)	1.44(3)
C(n06)–C(n11)	1.394(5)	1.40(3)	1.36(2)
C(n07)–C(n08)	1.384(6)	1.42(3)	1.44(3)
C(n08)–C(n09)	1.372(6)	1.39(3)	1.34(3)
C(n09)–C(n10)	1.389(5)	1.40(3)	1.43(3)
C(n10)–C(n11)	1.388(5)	1.41(2)	1.44(3)
C(n11)–O(n12)	1.380(4)	1.35(2)	1.38(2)
O(n12)–C(n13)	1.431(4)	1.48(2)	1.48(2)
C(n13)–C(n14)	1.511(4)	1.51(3)	1.53(3)
C(n14)–C(n15)	1.496(4)	1.53(2)	1.57(3)
C(n15)–O(n16)	1.442(4)	1.47(2)	1.45(2)
O(n16)–C(n17)	1.380(4)	1.35(1)	1.36(2)
C(n17)–C(n18)	1.384(4)	1.40(3)	1.43(3)
C(n17)–C(n22)	1.386(4)	1.42(2)	1.39(2)
C(n18)–C(n19)	1.375(5)	1.39(2)	1.44(3)
C(n19)–C(n20)	1.365(5)	1.40(3)	1.36(2)
C(n20)–C(n21)	1.383(5)	1.42(3)	1.41(3)
C(n21)–C(n22)	1.372(5)	1.38(2)	1.39(3)
C(n03)–O(n23)	1.416(3)	1.39(2)	1.47(2)
O(n23)–C(n24)	1.432(4)	1.45(3)	1.45(2)
C(n24)–C(n25)	1.475(6)	1.48(3)	1.44(3)
C(n25)–O(n26)	1.418(5)	1.43(3)	1.29(3)
O(n26)–C(n27)	1.402(5)	1.43(3)	1.49(4)
C(n27)–C(n28)	1.478(8)	1.45(3)	1.28(6)
C(n28)–O(n29)	1.386(6)	1.47(4)	1.43(2)
O(n29)–C(n30)	1.394(7)	1.53(4)	1.34(4)
C(n30)–C(n31)	1.532(9)	1.23(7)	1.42(3)
C(n31)–O(n32)	1.418(6)	1.68(6)	1.47(3)
O(n32)–C(n33)	1.389(6)	1.35(3)	1.41(2)
C(n33)–C(n34)	1.491(6)	1.54(4)	1.46(3)
C(n34)–O(n35)	1.424(4)	1.44(3)	1.49(3)
O(n35)–C(n14)	1.436(4)	1.43(2)	1.41(2)

b. Bond angles (°) in the uncomplexed compound. The corresponding ones in the complexes are given if the difference is more than the sum of the standard deviations

	$n = 0$	$n = 1$	$n = 2$
C(n22)–O(n01)–C(n02)	115.2(2)		
O(n01)–C(n02)–C(n03)	109.1(2)		
C(n02)–C(n03)–C(n04)	109.7(2)	115.2(16)	118.4(12)
C(n02)–C(n03)–O(n23)	108.1(2)		103.7(14)
C(n04)–C(n03)–O(n23)	112.3(3)		114.7(17)
C(n03)–C(n04)–O(n05)	110.0(2)	108.2(14)	
C(n04)–O(n05)–C(n06)	116.6(2)		118.3(13)
O(n05)–C(n06)–C(n07)	121.5(3)		
O(n05)–C(n06)–C(n11)	118.7(3)	114.7(15)	117.9(17)
C(n07)–C(n06)–C(n11)	119.6(3)	122.4(15)	
C(n06)–C(n07)–C(n08)	120.6(4)	117.7(19)	115.6(15)
C(n07)–C(n08)–C(n09)	120.3(4)		
C(n08)–C(n09)–C(n10)	119.4(4)		
C(n09)–C(n10)–C(n11)	120.8(4)		116.4(15)
C(n10)–C(n11)–C(n06)	119.2(3)		122.5(18)
C(n10)–C(n11)–O(n12)	122.3(3)	125.7(17)	
C(n06)–C(n11)–O(n12)	118.4(3)	115.8(13)	115.9(15)
C(n11)–O(n12)–C(n13)	116.2(2)	114.3(12)	
O(n12)–C(n13)–C(n14)	106.9(2)		
C(n13)–C(n14)–C(n15)	114.8(3)	118.6(11)	117.2(15)
C(n13)–C(n14)–O(n35)	107.9(3)		113.5(16)
C(n15)–C(n14)–O(n35)	108.8(3)	111.1(13)	106.0(12)
C(n14)–C(n15)–O(n16)	108.1(2)		
C(n15)–O(n16)–C(n17)	116.0(2)		
O(n16)–C(n17)–C(n18)	122.1(3)	126.1(15)	
O(n16)–C(n17)–C(n22)	118.6(3)	114.5(14)	
C(n18)–C(n17)–C(n22)	119.3(3)		
C(n17)–C(n18)–C(n19)	120.7(3)		116.0(13)
C(n18)–C(n19)–C(n20)	120.1(3)		123.2(20)
C(n19)–C(n20)–C(n21)	119.6(3)		
C(n20)–C(n21)–C(n22)	120.9(3)		
C(n21)–C(n22)–O(n01)	118.3(3)	125.3(16)	124.6(12)
C(n21)–C(n22)–C(n17)	119.4(3)	120.6(16)	122.2(17)

TABLE 3 (*continued*)

	n = 0	n = 1	n = 2
C(n17)-C(n22)-O(n01)	122.2(3)	114.0(10)	113.2(16)
C(n03)-O(n23)-C(n24)	115.1(2)		111.9(13)
O(n23)-C(n24)-C(n25)	111.9(3)	108.9(18)	109.3(18)
C(n24)-C(n25)-O(n26)	110.9(3)	105.7(19)	116.5(17)
C(n25)-O(n26)-C(n27)	109.4(3)		121.5(18)
O(n26)-C(n27)-C(n28)	110.6(4)	107.8(21)	
C(n27)-C(n28)-O(n29)	109.6(4)		113.7(28)
C(n28)-O(n29)-C(n30)	111.4(4)		126.2(20)
O(n29)-C(n30)-C(n31)	108.5(5)	98.8(26)	116.9(30)
C(n30)-C(n31)-O(n32)	114.9(4)	104.6(36)	108.8(22)
C(n31)-O(n32)-C(n33)	114.1(4)	121.3(18)	108.7(16)
O(n32)-C(n33)-C(n34)	110.3(4)		
C(n33)-C(n34)-O(n35)	113.1(3)	106.2(21)	107.5(17)
C(n34)-O(n35)-C(n14)	116.6(3)	112.4(17)	112.8(11)

c. Torsion angles

	n = 0	n = 1	n = 2
C(n22)-O(n01)-C(n02)-C(n03)	-173.1(2)	178(1)	-174(1)
C(n17)-C(n22)-O(n01)-C(n02)	67.0(4)	169(1)	169(1)
O(n01)-C(n02)-C(n03)-C(n04)	-166.1(2)	71(2)	68(2)
O(n01)-C(n02)-C(n03)-O(n23)	71.1(3)	-58(2)	-60(2)
C(n02)-C(n03)-C(n04)-O(n05)	-50.5(3)	-70(2)	-66(2)
O(n23)-C(n03)-C(n04)-O(n05)	69.7(3)	57(2)	57(2)
C(n02)-C(n03)-O(n23)-C(n24)	-157.5(3)	-166(1)	-141(1)
C(n04)-C(n03)-O(n23)-C(n24)	81.4(3)	64(2)	89(2)
C(n03)-C(n04)-O(n05)-C(n06)	-98.2(3)	174(1)	177(2)
C(n04)-O(n05)-C(n06)-C(n11)	122.7(3)	-166(1)	-173(2)
O(n05)-C(n06)-C(n11)-O(n12)	-1.0(5)	1(2)	1(2)
C(n06)-C(n11)-O(n12)-C(n13)	-126.6(3)	172(1)	167(1)
C(n11)-O(n12)-C(n13)-C(n14)	-158.7(3)	-179(1)	-177(1)
O(n12)-C(n13)-C(n14)-C(n15)	-63.0(3)	67(2)	68(2)
O(n12)-C(n13)-C(n14)-O(n35)	175.6(2)	-60(2)	-56(2)
C(n13)-C(n14)-C(n15)-O(n16)	-55.8(3)	-67(2)	-65(2)
O(n35)-C(n14)-C(n15)-O(n16)	65.1(3)	59(2)	63(2)
C(n13)-C(n14)-O(n35)-C(n34)	-109.0(3)	-128(2)	-70(2)
C(n34)-O(n35)-C(n14)-C(n15)	126.0(3)	100(2)	160(1)
C(n14)-C(n15)-O(n16)-C(n17)	-176.7(2)	173(1)	176(1)
C(n15)-O(n16)-C(n17)-C(n22)	-131.1(3)	-170(1)	-172(1)
O(n16)-C(n17)-C(n22)-O(n01)	0.8(4)	3(2)	-2(2)
C(n03)-O(n23)-C(n24)-C(n25)	-127.3(3)	160(1)	165(2)
O(n23)-C(n24)-C(n25)-O(n26)	-70.0(4)	72(2)	52(3)
C(n24)-C(n25)-O(n26)-C(n27)	178.5(3)	180(2)	174(3)
C(n25)-O(n26)-C(n27)-C(n28)	-177.0(4)	-174(2)	121(3)
O(n26)-C(n27)-C(n28)-O(n29)	82.5(5)	-70(2)	63(4)
C(n27)-C(n28)-O(n29)-C(n30)	179.5(5)	-169(2)	91(4)
C(n28)-O(n29)-C(n30)-C(n31)	-174.5(5)	162(3)	157(3)
O(n29)-C(n30)-C(n31)-O(n32)	-63.4(6)	84(3)	62(3)
C(n30)-C(n31)-O(n32)-C(n33)	-77.4(6)	59(4)	177(2)
C(n31)-O(n32)-C(n33)-C(n34)	178.7(4)	169(2)	175(2)
O(n32)-C(n33)-C(n34)-O(n35)	-70.3(5)	62(2)	-64(2)
C(n33)-C(n34)-O(n35)-C(n14)	102.2(4)	-178(2)	-161(2)

-131.1, and 122.7° for the three corresponding ones in the uncomplexed molecule and *ca.* 180° in the complex. A similar increase of bond angle for the $C(sp^2)$-$C(sp^2)$-O was found [11] for (Ia and b) accompanied by a corresponding torsion angle of *ca.* 60°.

Many torsion angles in the uncomplexed molecule

differ significantly from 180 or 60° and the effect of these variations is to cause the aliphatic chain to be bent almost on top of one of the benzene rings as shown in Figure 2. The conformation is such that the hydrogen atoms of C(13) are in the cavity; neither the distances to the nearest oxygen atoms [H(13)a $\cdots$ O(32) 2.49 Å, H(13)b $\cdots$ O(16) 2.53 Å] nor the angles subtended at the hydrogen atoms suggest that these might be hydrogen-bonded.

The torsion angles in the dibenzo-14-crown-4 entities of the complexed molecules do not differ significantly and are the same as those in the corresponding part of the potassium complex of (II),[3] and approximate to 0, 60, or 180°. Not surprisingly, the aliphatic chain from O(23) and O(35), which is subject to disorder, also exhibits some different torsion angles in the two ligands.

The mean planes through various groups of atoms are shown in Table 4. In the uncomplexed molecule the planes shown are those of the two benzene rings and an approximate plane, c, consisting of five oxygen atoms which can be seen as forming an open face in the free ligand. These are O(1) and O(16) on one benzene ring, and O(23), O(26), and O(35) on the aliphatic chain. The angle between the normals to the benzene rings is 22.8(3)°. In both complexes this angle has increased to *ca.* 60° [a(1) to b(1) and a(2) to b(2)] and there is a similar angle to the normal of a plane, c, defined in the complexes as the plane through the five aliphatic oxygen atoms, giving a three dimensional instead of a rather flat molecule.

Co-ordination about the Rubidium Ions.—The co-ordination geometry is shown in the stereopairs, Figures 3a and b, and dimensions are given in Table 5. Rb(1) is nine-co-ordinated yielding a complex cation of most unusual geometry. The five aliphatic oxygen atoms are roughly coplanar with Rb(1), plane c(1) of Table 4 with Rb-O in the range 2.95—3.25 Å. The rubidium ion has its maximum mean square amplitude of vibration (0.115 Å²) at 21.2° to the normal to this plane. On either side of this plane are the oxygen atoms from the catechol rings, those from ring A, O(105) and O(112), being further from the rubidium than those from ring B, O(101) and O(116). The only contact <4.0 Å to any atom outside the complex [Rb(1)Ic(1)]⁺ is at 3.64 Å to C(209) at -x, -y, 1 - z from the co-ordinates in Table 2.

Two additional contacts give eleven co-ordination for
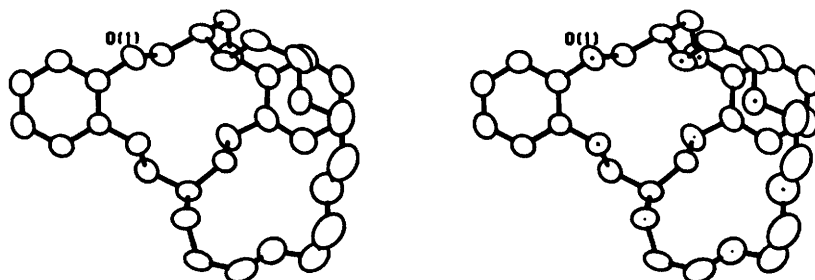

FIGURE 2 Stereoview of uncomplexed molecule drawn by ORTEP with thermal ellipsoids at the 50% level. Oxygen atoms have central spots

TABLE 4

Deviations of atoms from mean planes ($\times 10^3$ Å). Atoms not used in calculation of the plane in italics

	$n = 0$	$n = 1$	$n = 2$
Plane A			
C(n06)	−7(3)	−3(15)	6(16)
C(n07)	11(4)	1(18)	10(19)
C(n08)	−7(4)	−2(20)	−12(23)
C(n09)	−2(4)	5(20)	−8(23)
C(n10)	6(4)	−6(18)	21(18)
C(n11)	−2(3)	5(16)	−17(16)
O(n05)	77(5)	−64(21)	44(23)
O(n12)	66(5)	−25(23)	−28(23)
Rb(n)		−1 439(34)	1 457(39)
Plane B			
C(n17)	−6(3)	−3(15)	−2(16)
C(n18)	−3(3)	8(18)	−4(17)
C(n19)	6(4)	1(18)	15(18)
C(n20)	0(4)	−14(18)	−15(18)
C(n21)	−10(3)	17(17)	8(16)
C(n22)	13(3)	−8(15)	−1(14)
O(n01)	−33(4)	33(19)	28(20)
O(n16)	−90(5)	−24(21)	−9(22)
Rb(n)		−1 732(27)	1 526(33)
Plane C			
O(n01)	−255(2)		
O(n23)	424(2)	O(n23) 249(11)	−26(14)
O(n26)	−231(3)	O(n26) −574(15)	−294(23)
O(n35)	37(2)	O(n29) 288(19)	567(17)
O(n16)	25(2)	O(n32) 802(22)	−443(14)
		O(n35) −244(15)	136(13)
		Rb(n) 396(7)	73(7)
Plane D			
Picrate ions			
C(n1)′		18(20)	0(16)
C(n2)′		−3(20)	−14(16)
C(n3)′		−13(17)	9(16)
C(n4)′		13(16)	10(16)
C(n5)′		−1(18)	−21(15)
C(n6)′		−16(18)	16(14)
O(n1)′		129(29)	−64(22)
O(n5)′		−21(90)	
N(n2)′		−170(38)	42(25)
N(n4)′		28(29)	7(26)
N(n6)′		0(34)	119(23)
Rb(n)			−2 094(36)

Plane E	N(n2)–O(n2)a–O(n2)b
Plane F	N(n4)–O(n4)a–O(n4)b
Plane G	N(n6)–O(n6)a–O(n6)b
Plane H	N(16)–O(16)c–O(16)d

Angles between normals to planes (°)
Uncomplexed molecule, $n = 0$.
A to B 22.8(3), B to C 15.8(3), A to C 27.6(2)

In the complex with rubidium picrate (standard deviations 0.5—0.7°)

	B(1)	C(1)	D(1)	A(2)	B(2)	C(2)	D(2)
A(1)	54.3	60.7	71.5	95.9	67.6	58.2	62.5
B(1)		115.0	125.2	120.7	121.6	90.2	116.3
C(1)			12.7	63.3	8.5	54.8	6.6
D(1)				52.9	4.2	69.8	9.0
A(2)					56.0	118.0	56.8
B(2)						62.0	5.4
C(2)							61.4

In the picrate ions (standard deviations 2—6°)

	E(n)	F(n)	G(n)	H(n)
D(n) $n = 1$	12	10	27	57
$n = 2$	22	5	136	

Rb(2), a water molecule, Wat(2), and picrate(2) through the nitro-oxygen O(24)b, not the usual phenolate oxygen; possibly there is insufficient space for a chelating ligand to be introduced. As shown in Table 5 the bond angles subtended by Ic(2) at Rb(2) differ by a maximum of 15° from those subtended at Rb(I) by Ic(1). The aliphatic oxygen atoms form an approximate plane, c(2), of Table 4, about Rb(2) with Rb–O in the range 2.92—3.28 Å; the additional contacts can be seen as being on opposite sides of this plane and in the direction away from that occupied by the four catechol oxygen atoms. This results in a more uniform co-ordination sphere than that of Rb(1) and possibly accounts for the more nearly isotropic vibration of Rb(2). The two pairs of catechol oxygen atoms are more nearly equidistant from the rubidium although there is still a tendency for those on ring A to be further away. While it is often found that a co-ordinated water molecule has a shorter M–O distance than a multidentate ligand, the Rb(2)–Wat(2) distance is of the same order as the others.

We have assigned the co-ordination numbers because these are discrete molecules. However, some of the actual Rb $\cdots$ O distances would not be considered as corresponding to co-ordination in continuous structures. Examples of rubidium ions in discrete cationic complexes are known with co-ordination numbers for oxygen ranging from 6, in each of the two independent centrosymmetric complexes of prolinomycin (Rb–O 2.80—3.01 Å),[12] to 10 in the complex with dibenzo-30-crown-10 (Rb–O 2.96—3.19 Å).[13] Discrete cationic complexes formed by polyether derivatives of quinolin-8-ol with seven co-ordination (2 N and 5 O at 2.88—3.04 Å)[14] and ten co-ordination (2 N and 8 O at 2.95—3.12 Å)[15] have been reported. In these examples there are no additional contacts. A more difficult case is the rubidium thiocyanate complex of cyclo-1-prolylglycyl; the authors[16] quoted six co-ordination (Rb–O 2.78— 3.02 Å), but there is another oxygen at 3.23 Å.

Co-ordination of rubidium by an oxygen from an aromatic nitro-group has been found in the 4-nitrobenzo-18-crown-6 complex of rubidium isothiocyanate;[17] this Rb–O contact, 3.09 Å, completes eight co-ordination, the other seven atoms being the nitrogen atom (Rb–N 2.90 Å) of the thiocyanate anion, and six oxygen atoms of one polyether, Rb–O 2.95—3.08 Å. For unsubstituted benzo-18-crown-6[18] and for 18-crown-6 itself,[19] the rubidium thiocyanate complexes are dimeric, eight co-ordination being achieved by the rubidium ions sharing two thiocyanate anions. Additional substitution to give dibenzo-18-crown-6 yields a seven-co-ordinated complex, six oxygen atoms and an unshared thiocyanate ion.[20]

Dimensions of the Picrate Anions.—Picrate(2) has the distribution of bond lengths and angles found in many examples of picrate[21] (as opposed to neutral picric acid). All the N–O bonds are in the range 1.21—1.24 Å except for N(22)′–O(22)a which is 1.13(2) Å; this last bond may be a recipient of a hydrogen bond from Wat(1), extension along N(22)′–O(22)a giving a shorter contact to Wat(1).

TABLE 5

Co-ordination geometry

	$n = 1$	$n = 2$
Rb(n)–O(n01)	2.952(7)	3.029(12)
Rb(n)–O(n05)	3.341(11)	3.168(11)
Rb(n)–O(n12)	3.368(11)	3.147(8)
Rb(n)–O(n16)	2.977(11)	3.057(11)
Rb(n)–O(n23)	2.953(12)	2.922(11)
Rb(n)–O(n26)	3.113(18)	3.277(15)
Rb(n)–O(n29)	3.132(16)	3.225(15)
Rb(n)–O(n32)	3.229(22)	3.163(15)
Rb(n)–O(n35)	3.035(14)	2.984(9)
Rb(2)–O(24)b		2.933(16)
Rb(2)–Wat(2)		3.077(2)

Angles (°) subtended at Rb(1), in the form A–Rb(1)–B

	O(105)	O(112)	O(116)	O(123)	O(126)	O(129)	O(132)	O(135)
O(101)	53.4(2)	72.5(2)	50.8(3)	55.8(3)	111.0(3)	150.3(4)	138.1(5)	105.4(3)
O(105)	—	44.9(3)	75.9(3)	53.3(3)	91.5(4)	139.9(4)	145.4(4)	95.9(3)
O(112)		—	53.0(3)	98.0(3)	125.3(3)	137.1(3)	102.1(5)	51.1(3)
O(116)			—	106.0(3)	161.7(3)	142.4(5)	91.9(5)	56.8(2)
O(123)				—	55.8(3)	107.0(5)	158.7(5)	149.0(3)
O(126)					—	53.7(5)	105.7(5)	139.3(3)
O(129)						—	52.6(6)	99.5(4)
O(132)							—	51.7(5)

Angles (°) subtended at Rb(2) in the form A–Rb(2)–B

	O(205)	O(212)	O(216)	O(223)	O(226)	O(229)	O(232)	O(235)	O(24)b	Wat(2)
O(201)	54.4(3)	77.0(3)	50.0(2)	54.9(3)	103.0(4)	135.7(4)	155.0(3)	104.8(3)	70.7(3)	136.0(2)
O(205)	—	48.5(2)	75.9(3)	56.0(3)	98.5(4)	147.3(4)	135.7(4)	103.5(3)	121.9(4)	88.5(3)
O(212)		—	54.5(3)	104.3(3)	140.1(5)	146.9(4)	95.7(3)	55.3(3)	137.6(4)	96.4(3)
O(216)			—	104.5(3)	150.5(5)	136.3(4)	106.4(3)	55.1(3)	83.5(3)	150.5(2)
O(223)				—	52.0(4)	101.4(3)	149.0(3)	156.3(3)	78.8(4)	86.3(3)
O(226)					—	51.5(4)	97.8(4)	151.3(4)	75.0(5)	55.6(5)
O(229)						—	52.8(3)	102.0(3)	67.9(5)	64.8(4)
O(232)							—	53.5(3)	102.1(4)	67.9(3)
O(235)								—	107.6(4)	106.4(3)
O(24)b									—	125.9(3)

Bond angles (°) subtended at oxygen atoms

	$n = 1$	$n = 2$
Rb(n)–O(n01)–C(n02)	120.6(8)	120.4(9)
Rb(n)–O(n01)–C(n22)	116.0(7)	121.7(8)
C(n22)–O(n01)–C(n02)	114.2(9)	113.8(13)
Rb(n)–O(n05)–C(n04)	115.4(9)	116.7(8)
Rb(n)–O(n05)–C(n06)	127.2(8)	121.1(9)
C(n06)–O(n05)–C(n04)	115.9(13)	118.3(13)
Rb(n)–O(n12)–C(n11)	126.1(11)	121.7(6)
Rb(n)–O(n12)–C(n13)	116.5(8)	118.8(9)
C(n13)–O(n12)–C(n11)	114.3(12)	116.5(11)
Rb(n)–O(n16)–C(n15)	120.8(6)	119.4(10)
Rb(n)–O(n16)–C(n17)	117.0(10)	118.8(6)
C(n15)–O(n16)–C(n17)	115.4(13)	115.9(13)
Rb(n)–O(n23)–C(n03)	116.0(11)	115.0(7)
Rb(n)–O(n23)–C(n24)	113.4(8)	125.0(11)
C(n03)–O(n23)–C(n24)	114.6(14)	111.9(13)
Rb(n)–O(n26)–C(n25)	114.9(11)	116.1(15)
Rb(n)–O(n26)–C(n27)	117.7(16)	116.6(15)
C(n25)–O(n26)–C(n27)	109.5(18)	121.5(18)
Rb(n)–O(n29)–C(n28)	114.7(12)	113.3(14)
Rb(n)–O(n29)–C(n30)	118.1(20)	115.5(12)
C(n28)–O(n29)–C(n30)	110.2(20)	126.2(20)
Rb(n)–O(n32)–C(n31)	106.4(20)	118.8(12)
Rb(n)–O(n32)–C(n33)	110.6(16)	119.0(12)
C(n31)–O(n32)–C(n33)	121.3(18)	108.7(16)
Rb(n)–O(n35)–C(n34)	126.9(12)	115.2(9)
Rb(n)–O(n35)–C(n14)	114.5(8)	114.4(8)
C(n14)–O(n35)–C(n34)	112.4(17)	112.8(11)
Rb(2)–O(24)b–N(24)′		140.3(9)

The observed dimensions of picrate(1) are consistent with one-fifth of the anions being rotated through 180° about a line through N(16)′, C(16)′, C(13)′. In both picrate ions the substituents are significantly out of the benzene planes, D(1) and D(2). In picrate(1) the N(16)′ group in either orientation and in picrate(2) the N(26)′ group are

TABLE 6

a. Bond lengths in the picrate anions

	$n = 1$	$n = 2$
C(n1)′–O(n1)′	1.25(4)	1.24(2)
C(n1)′–C(n2)′	1.39(3)	1.44(2)
C(n2)′–C(n3)′	1.33(3)	1.34(2)
N(n2)′–C(n2)′	1.54(3)	1.50(3)
C(n3)′–C(n4)′	1.37(2)	1.37(3)
C(n4)′–C(n5)′	1.40(3)	1.40(2)
C(n4)′–N(n4)′	1.51(4)	1.43(2)
C(n5)′–C(n6)′	1.40(3)	1.37(2)
C(n6)′–C(n1)′	1.40(2)	1.45(3)
C(n6)′–N(n6)′	1.53(3)	1.51(2)
N(n2)′–O(n2)a	1.12(6)	1.13(2)
N(n2)′–O(n2)b	1.11(5)	1.24(2)
N(n4)′–O(n4)a	1.17(3)	1.24(3)
N(n4)′–O(n4)b	1.19(2)	1.21(3)
N(n6)′–O(n6)a	1.15(3)	1.21(3)
N(n6)′–O(n6)b	1.27(4)	1.21(2)
N(n6)′–O(n6)c	1.19(11)	
N(n6)′–O(n6)d	1.23(11)	
C(n5)′–O(n5)′	1.11(9)	

TABLE 6 (continued)

b. Bond angles in the picrate anions

|	$n = 1$	$n = 2$
C(n6)′–C(n1)′–C(n2)′	112(2)	109(1)
O(n1)′–C(n1)′–C(n2)′	127(2)	127(2)
O(n1)′–C(n1)′–C(n6)′	121(2)	124(1)
C(n1)′–C(n2)′–C(n3)′	128(2)	127(2)
N(n2)′–C(n2)′–C(n3)′	113(2)	116(2)
N(n2)′–C(n2)′–C(n1)′	119(2)	117(1)
C(n2)′–C(n3)′–C(n4)′	117(2)	118(2)
C(n3)′–C(n4)′–C(n5)′	123(2)	124(2)
N(n4)′–C(n4)′–C(n3)′	120(2)	120(2)
N(n4)′–C(n4)′–C(n5)′	118(2)	115(2)
C(n4)′–C(n5)′–C(n6)′	115(2)	114(2)
C(n5)′–C(n6)′–C(n1)′	125(2)	128(1)
N(6)′–C(n6)′–C(n1)′	124(2)	117(1)
N(n6)′–C(n6)′–C(n5)′	111(2)	115(2)
O(n2)a–N(n2)′–C(n2)′	113(3)	122(2)
O(n2)b–N(n2)′–C(n2)′	117(3)	113(2)
O(n2)a–N(n2)′–O(n2)b	129(3)	125(2)
O(n4)a–N(n4)′–C(n4)′	114(2)	117(2)
O(n4)b–N(n4)′–C(n4)′	116(2)	123(2)
O(n4)a–N(n4)′–O(n4)b	130(3)	120(2)
O(n6)a–N(n6)′–C(n6)′	123(3)	116(1)
O(n6)b–N(n6)′–C(n6)′	102(2)	117(2)
O(n6)a–N(n6)′–O(n6)b	135(3)	127(2)
O(n6)c–N(n6)′–C(n6)′	124(5)	
O(n6)d–N(n6)′–C(n6)′	115(5)	
O(n6)c–N(n6)′–O(n6)d	121(7)	
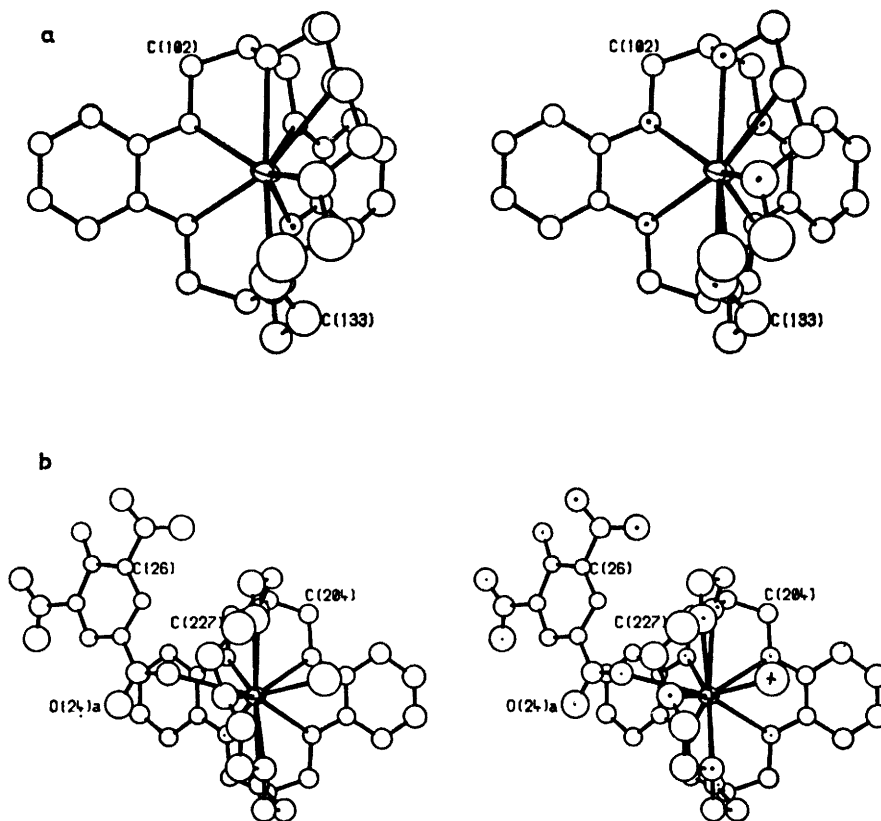
FIGURE 3 (a) Stereoview of the complex cation [Rb(1)L(1)]⁺. Vibration ellipsoids are at the 30% level. Oxygen atoms have central spots. Rb(1) appears to vibrate most in a direction perpendicular to the aliphatic chain. (b) Stereoview of the surroundings of Rb(2) in the complexed ion pair. Oxygen atoms have central spots. The water molecule Wat(2) and the picrate ion (2) are shown as co-ordinated. One benzene ring O(2) is nearly parallel to picrate(2) as shown in the stereo-diagram and in Table 4. Wat(2) is on a centre of symmetry and shared by Rb(2ᴵ) at $-x$, $1 - y$, $2 - z$ relative to x, y, z in Table 2
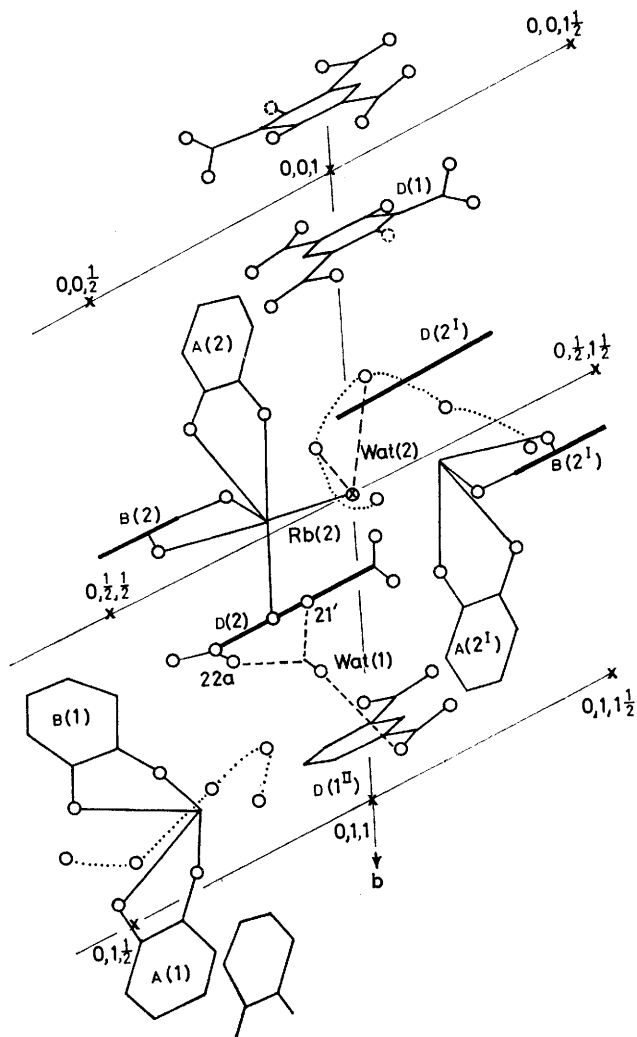
FIGURE 4 Part of the structure of the rubidium complex projected normal to the (100) plane, centres of symmetry are marked by crosses. Planes are designated as in Table 4, those shown for A(2), B(2), D(1), and D(2) are in the crystal chemical unit with co-ordinates in Table 2. The alternative site O(15)′ is shown by a broken circle for one picrate(1); the alternatives O(16)c and O(16)d overlap O(16)b and O(16)a respectively in this projection. Stacking between the two equivalent picrate ions D(1) is shown at 0,0,1. Stacking between D(2) and D(1^{II}) may be reinforced by the hydrogen bonding from water Wat(1) to O(12)a and a bifurcated bond to O(22a) and O(21)′ as indicated by broken lines. For the ligand of Rb(2) the aliphatic oxygen atoms have been omitted; they are shown connected by dots for the symmetry related Rb(2^{I}) with the suggested hydrogen bonding from Wat(2) shown by broken lines. For the picrate ion D(2) all the oxygen atoms are shown, for D(2^{I}) only the plane is indicated. D(2^{I}) stacks with D(1) in the unit cell below that shown, i.e. at $x - 1, y, z$. For Rb(1) and its ligand the cation shown is at $-x, 1 - y, 1 - z$ compared with that in Table 2. The oxygen atoms of the aliphatic chain are shown joined by a dotted line, the approximate plane through them constitutes plane c(1). Stacking between A(1) and its symmetry equivalent can be visualized with the operation of the centre of inversion shown here at 0,1,½. The diagram shows how the parallel planes B(2), D(2), D(1), and c(1) cut the b axis at intervals of ca. 0.25

both significantly twisted out of plane D as is usually found for one of the ortho-nitro-groups in picrates.

Electrostatic Interactions and Hydrogen Bonding.—The [Rb(1)Ic(1)]$^{+}$ has as neighbours with C $\cdots$ C, C $\cdots$ O or O $\cdots$ O distances <3.5 Å, five contacts to four different picrate(1) anions, one to an O(15) in a fifth, five contacts to four different picrate(2) anions, and one to a Ic(2) ligand. The {[pic(2)Rb(2)Ic(2)]$_2$Wat(2)}° moiety makes two intermolecular contacts of this kind from Ic(2) to each of two further picrate(2) anions. The picrate anions, apart from the contacts mentioned, have, as their main environment, other picrate ions. As shown in Figures 3b and 4 and Table 4, the picrate ions are nearly parallel and also parallel to ring B of the complex 2 and ring c of complex 1. These planes are all parallel within 2.5—10.6° to the (010) plane in the unit cell. The centroids are at y/b 0.12, 0.40, 0.64, and 0.14, so that the separations are close to 0.25, and the reflection (040) is by far the strongest. The centroids of the benzene rings of D(1) and its symmetry equivalent at $1 - x, -y, 2 - z$ are 3.64(1) Å apart and those of D(2) and of D(1^{II}) at $1 - x, 1 - y, 2 - z$ from D(2) in Table 2 are 3.71(1) Å apart. These represent a stacking of ions of like charge and the actual separation is little greater than in a molecular complex. Within these relationships, picrate(1) in the major orientation makes one pair of contacts <3.5 Å long across the centre of symmetry, while the minor orientation makes five such pairs of contacts. Pic(1) also makes three contacts to picrate(2^{II}), and the major and minor orientations make another two and five such contracts respectively. This is consistent with the minor orientation being less favourably situated.

Stacking of picrate anions is not uncommon. In particular it has been found in the red thallium picrate [22] with which the rubidium salt is isomorphous. Stacking which corresponds to repetition of the unit cell gives separations of the order of 4.5 Å, but shorter distances are found where there is stacking between symmetry related ions as in the potassium [23] salt or that with 2-thiocytosine.[24]

A discrete system of hydrogen bonding may be postulated; statistically it is centrosymmetrical at the position of Wat(2). If Rb-Wat(2) is taken as fixing one direction, the two hydrogen atoms could point towards O(226)^{I} and O(229)^{I} at 2.97 and 3.38 Å. Rb(2) is co-ordinated by picrate(2) at the phenolic end of which is a water molecule, Wat(1), at distances of 2.91(2) and 2.96(2) Å to O(21)′ and O(22)a respectively. The angle subtended by these at Wat(1) is 55°, so if one hydrogen atom forms a bifurcated hydrogen bond to picrate(2), the other would then be suitably placed to form a hydrogen bond to O(12)a of picrate(1). This is the only attractive interaction we can postulate for the picrate(1)

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