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The rubidium salt of an ω-hydroxycarboxylic acid with six ethereal O atoms

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The title compound, aqua[2-({2-[2-(2-{2-[2-(2-hydroxyethoxy)phenoxy]ethoxy}phenoxy)ethoxy]phenoxy}methyl)benzoato]rubidium monohydrate, $[Rb(C_{32}H_{33}O_{10})]\cdot H_2O$, shows a monomeric structure. The polyether chain encloses Rb^+ and adopts an S-like conformation. The Rb^+ centre is ninefold coordinated by one O atom of the carboxylate group, the O atom of the terminal hydroxy group, six ethereal O atoms and one water molecule. An intermolecular hydrogen bond was observed between the terminal hydroxy group and the hydrate water molecule.

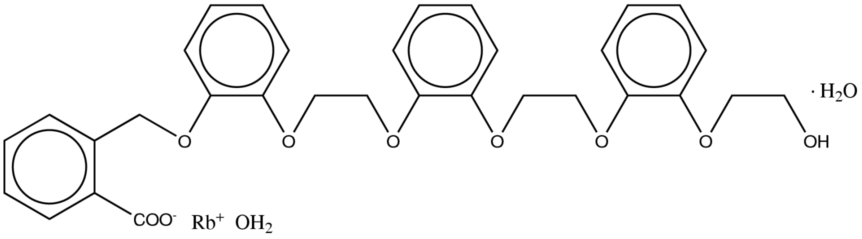
Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.006 Å
R factor = 0.040
wR factor = 0.115
Data-to-parameter ratio = 16.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

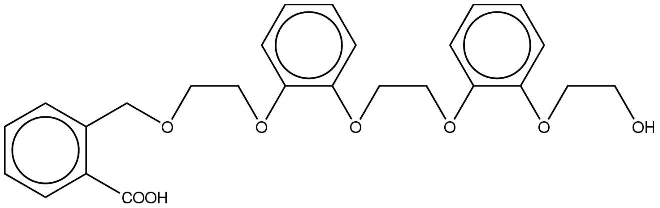
Naturally occurring acid ionophores are known to mediate active ion transport through lipophilic membranes by formation of hydrophobic complexes with ions (Taylor *et al.*, 1982, and references therein) and their structures were studied to provide information on their function (Duesler & Paul, 1983, and references therein). We have synthesized a series of relatively simple ω-hydroxycarboxylic acids as model compounds for the naturally occurring ionophores to investigate the relationship between the primary molecular structures and ion-transport properties (Kuboniwa *et al.*, 1982, 1985; Yamazaki *et al.*, 1978, 1979; Yamaguchi *et al.*, 1988, 1989).



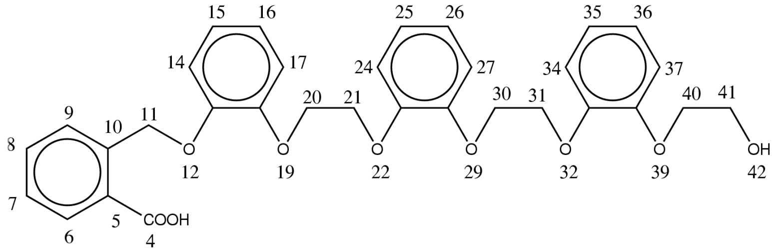
(I)

The model compounds, (1)–(3), transport K^+ over Na^+ through the $ClCH_2CH_2Cl$ membrane using the pH gradient of outer aqueous phases. The competitive ion-transport experiments show that the amount of transported ions, as well as K^+ selectivity over Na^+, increases in the order of (1) → (2) → (3) (Kuboniwa *et al.*, 1985; Yamaguchi *et al.*, 1988). The model compound, (1), having five ethereal O atoms, forms a 2:2 dimer with K^+. The polyether chain of (1) encloses K^+ and adopts an S-like conformation. One hydroxy group, six ethereal O atoms including one from the polyether chain of the dimer, and two water molecules coordinate to K^+ and the cation has ninefold coordination. Two O atoms of the carboxylate group do not coordinate to the cation. Solvent water molecules are located between the K salt molecules

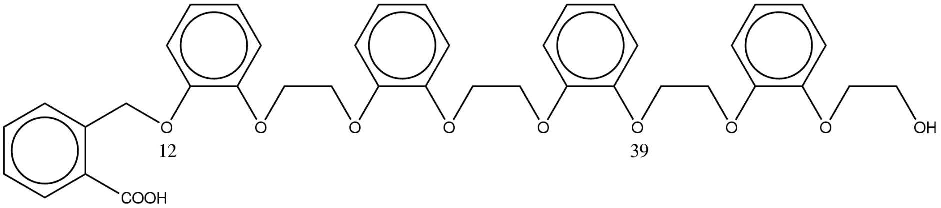
(Kasuga *et al.*, 1995). Compound (3), having eight ethereal O atoms, forms 1:1 salts with K^+, Rb^+ and Cs^+. The conformation of the three alkali metal salts of (3) are very similar to each other. The backbone of the three salts of (3) forms a pseudocyclic ring by head-to-tail hydrogen bonding between the terminal carboxylate and hydroxy groups. The main chain of (3) is bent at O12 and O39 and wraps the cation like the seam of a tennis ball to give a complex with a lipophilic exterior. One hydroxy group, eight ethereal O atoms of the main chain and one O atom of the carboxylate group participate in the coordination and K^+ is tenfold coordinated. The chloroform molecules, used as the recrystallization solvent, fill the space between the salt molecules in the crystals (Kuboniwa *et al.*, 1988; Kasuga *et al.*, 1991). Slow evaporation of a chloroform solution of the Rb salt of (2), which has six ethereal O atoms and shows ion-transport properties intermediate between those of (1) and (3), afforded single crystals. This paper reports the structure of the Rb salt of (2), *i.e.* (I).



(1)



(2)



(3)

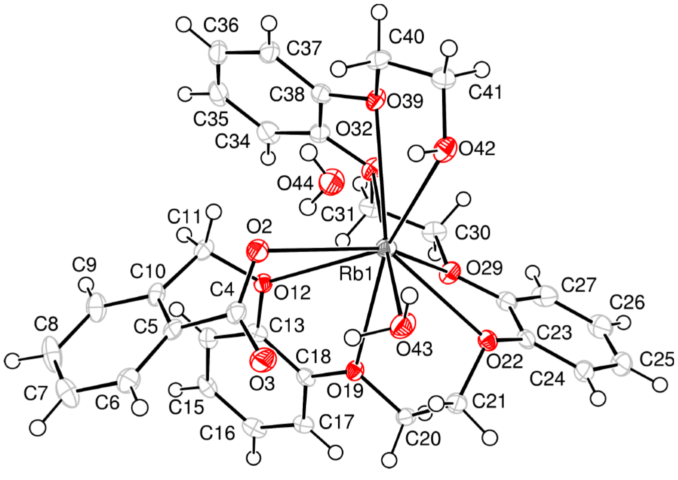


Figure 1

An *ORTEP*-3 drawing (Farrugia, 1997) of (I) with 50% probability displacement ellipsoids.

The molecular structure of (I) (Fig. 1) reveals that the salt forms a 1:1 monomeric structure. The Rb—O distances [2.877 (3)–3.147 (3) Å] indicate that one O atom of the carboxylate group, six ethereal O atoms, the terminal hydroxy group and a water molecule coordinate to Rb^+. As a result, Rb^+ is ninefold coordinated. Water coordination to the cation is observed in the structure of the K salt of (1), but not in the structure of the K salt of (3). In (I), another water molecule (O44) lies near the coordinating water molecule (O43), with an O43···O44 distance of 3.151 (4) Å. The O42···O44 distance of 2.724 (4) Å shows that intermolecular hydrogen bonding is formed between the terminal hydroxy group and the solvent water molecule. The head-to-tail hydrogen bonding seen in the structure of the K salt of (3) is not observed in (I). Generally, $Csp^3—Csp^3—O—Csp^2$(quaternary) torsion angles are near 180°, $Csp^2—Csp^2$(quaternary)$—O—Csp^3$ are 0° and $O—Csp^3—Csp^3—O$ are *gauche*. In (I), this rule also holds except for four torsion angles, C10—C11—O12—C13 [−65.0 (4)°], C14—C13—O12—C11 [−22.4 (5)°], C20—C21—O22—C23 [70.4 (4)°] and C24—C23—O22—C21 [69.8 (4)°]. Consequently, the backbone bend of (2) in (I) occurs in a shorter period (O12 and O22) compared with that in the alkali metal salts of (3) (O12 and O39).

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In conclusion, the three-dimensional structure of the Rb salt of (2) is intermediate between that of the K salt of (1) and that of the alkali metal salts of (3).

Experimental

Model compound (2) was synthesized using successive Williamson's methods (Kuboniwa *et al.*, 1985). An ion-transport experiment using (2) through a $ClCH_2CH_2Cl$ liquid membrane was carried out in a U-tube apparatus as described previously (Yamaguchi *et al.*, 1988), however, transported ions were analyzed by atomic absorption spectrometry instead of flame analysis. The analysis showed that 22% of Na^+ and 73% of K^+ were transported by (2) with errors of about 5% in 5 d. A solution of RbOH in MeOH (0.54 ml, 3.74 m*M*) was added to the solution of (2) (11.3 mg) in 20 ml MeOH and the mixture was stirred overnight. After removal of the solvent, the solid was dried *in vacuo*. Compound (2) and its Rb salt were characterized by EA, IR, ^{1}H and ^{13}C NMR. A chloroform solution of the Rb salt of (2) was slowly evaporated to give single crystals of (I). Crystals of the K salt of (2) were also obtained from chloroform solution, however, the quality of the reflection data was not good.

Crystal data

$[Rb(C_{32}H_{33}O_{10})]\cdot H_2O$
$M_r = 681.07$
Triclinic, $P\bar{1}$
$a = 10.0948\ (10)$ Å
$b = 11.2408\ (10)$ Å
$c = 14.055\ (3)$ Å
$\alpha = 85.524\ (11)^\circ$
$\beta = 71.679\ (11)^\circ$
$\gamma = 89.852\ (14)^\circ$
$V = 1509.0\ (4)$ Å^3

$Z = 2$
$D_x = 1.50$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1053 reflections
$\theta = 2.3$–13.7°
$\mu = 1.70$ mm^{-1}
$T = 123\ (2)$ K
Platelet, colorless
0.30 × 0.10 × 0.05 mm

Data collection

Rigaku R-AXIS–RAPID Imaging Plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.616$, $T_{max} = 0.919$
12 683 measured reflections

6684 independent reflections
4520 reflections with $I > 2\sigma(I)$
$R_{int} = 0.054$
$\theta_{max} = 27.3^\circ$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.115$
$S = 0.94$
6684 reflections
413 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—Rb1	3.020 (3)	O32—Rb1	3.012 (3)
O12—Rb1	2.958 (2)	O39—Rb1	3.037 (2)
O19—Rb1	2.945 (2)	O42—Rb1	2.994 (3)
O22—Rb1	2.877 (3)	O43—Rb1	3.023 (3)
O29—Rb1	3.147 (3)		
C10—C11—O12—C13	−65.0 (4)	C24—C23—O22—C21	69.8 (4)
C21—C20—O19—C18	178.4 (3)	C27—C28—O29—C30	5.6 (5)
C20—C21—O22—C23	70.4 (4)	C34—C33—O32—C31	0.7 (5)
C31—C30—O29—C28	−178.8 (3)	C37—C38—O39—C40	−2.9 (5)
C30—C31—O32—C33	−170.6 (3)	O19—C20—C21—O22	65.6 (4)
C41—C40—O39—C38	−175.0 (3)	O29—C30—C31—O32	−64.8 (4)
C14—C13—O12—C11	−22.4 (5)	O39—C40—C41—O42	62.6 (4)
C17—C18—O19—C20	−1.5 (5)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O42—H42···O44	0.807 (19)	1.93 (2)	2.724 (4)	169 (4)

H atoms attached to C atoms were included in idealized positions and refined using a riding model (C—H = 0.93 Å). H atoms attached to O atoms were found in the difference Fourier maps and their positional parameters were refined with restraints on the O—H distances. The O—H distances were 0.803 (18)–1.00 (4) Å.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Molecular Structure Corporation and Rigaku, 2001); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Duesler, E. N. & Paul, I. C. (1983). *Polyether Antibiotics Naturally Occurring Acid Ionophores*, Vol. 2, edited by J. W. Westley, pp. 87–195. New York: Marcel Dekker.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.

Kasuga, N. C., Yamaguchi, K. & Ohashi, Y. (1995). *Acta Cryst.* C**51**, 1816–1819.

Kasuga, N., Nakahama, S., Yamazaki, K., Ohashi, Y. & Hori, K. (1991). *Bull. Chem. Soc. Jpn*, **64**, 3548–3556.

Kuboniwa, H., Nagami, S., Yamaguchi, K., Hirao, A., Nakahama, S. & Yamazaki, N. (1985). *J. Chem. Soc. Chem. Commun.* pp. 1468–1469.

Kuboniwa, H., Yamaguchi, K., Hirao, A., Nakahama, S. & Yamazaki, N. (1982). *Chem. Lett.* pp. 1937–1940.

Kuboniwa, H., Yamaguchi, K., Nakahama, S., Hori, K. & Ohashi, Y. (1988). *Chem. Lett.* pp. 923–926.

Molecular Structure Corporation & Rigaku (2001). *CrystalStructure*. Version 2.00. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA, and Rigaku Corporation, Tokyo, Japan.

Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Taylor, R. W., Kauffman, R. F. & Pfeiffer, D. R. (1982). *Polyether Antibiotics Naturally Occurring Acid Ionophores*, Vol. 1, edited by J. W. Westley, pp. 103–184. New York: Marcel Dekker.

Yamaguchi, K., Kuboniwa, H., Murakami, N., Hirao, A., Nakahama, S. & Yamazaki, N. (1989). *Bull. Chem. Soc. Jpn*, **62**, 1097–1101.

Yamaguchi, K., Negi, S., Kozakai, S., Nagano, R., Kuboniwa, H., Hirao, A., Nakahama, S. & Yamazaki, N. (1988). *Bull. Chem. Soc. Jpn*, **61**, 2047–2054.

Yamazaki, N., Hirao, A. & Nakahama, S. (1979). *J. Macromol. Sci. Chem.* A**13**, 321–349.

Yamazaki, N., Nakahama, S., Hirao, S. & Negi, S. (1978). *Tetrahedron Lett.* **27**, 2429–2432.

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