Supplementary Material (ESI) for Chemical Communications

Supplementary information for "Pyrogallarenes as alkali metal receptors: The role of cation-π interactions for complexation"

Antti Åhman and Maija Nissinen*

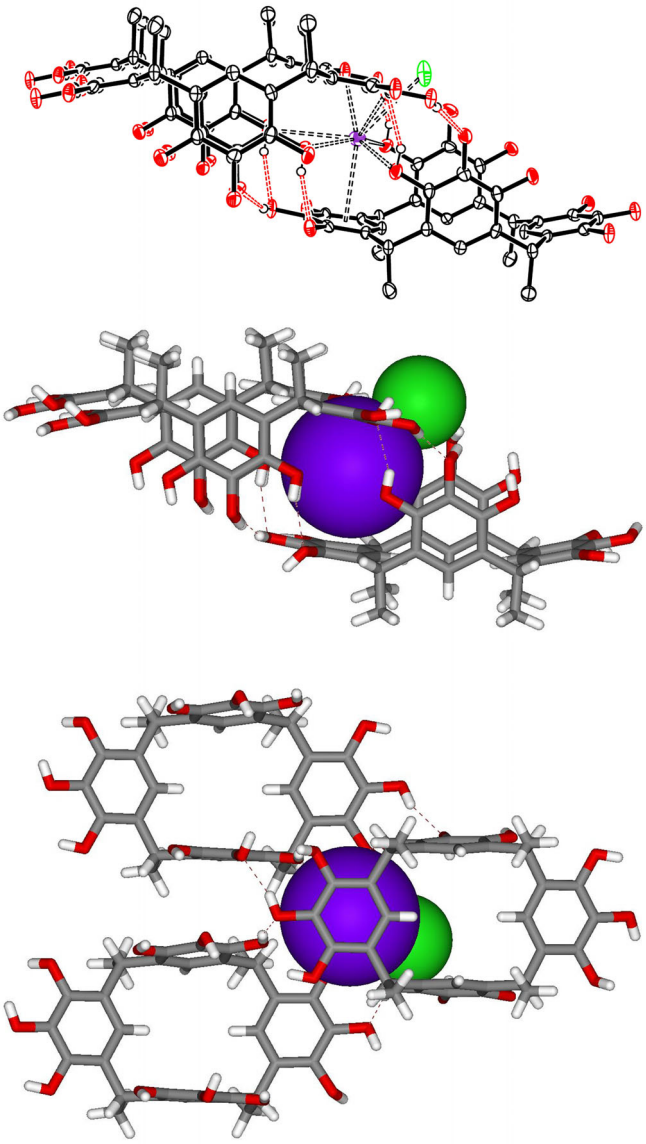

Fig. 1 Crystal structure of the RbCl complex of **1** drawn as Ortep plot (50% probability level) and as VDW/stick presentations (chloride: green). Solvents and non-hydrogen bonding hydrogens from the Ortep plot are excluded for clarity. The structure is isomorphous to CsBr complex.

Table 1. The closest and coordinative distances (Å) between the alkali metal cation and pyrogallarene receptor.

	KBr	**RbCl**	**CsBr**
Aromatic ring 1:			
C8	3.323 (7)	3.500 (5)	3.626 (8)
C9	3.284 (7)	3.474 (5)	3.590 (8)
C10	3.225 (7)	3.478 (5)	3.568 (8)
C11	3.136 (7)	3.480 (5)	3.536 (8)
C12	3.102 (7)	3.412 (5)	3.464 (7)
C13	3.228 (7)	3.444 (5)	3.537 (7)
Centroid 1	2.900 (7)	3.173 (5)	3.269 (8)
Aromatic ring 2:			
C22	3.214 (7)	-	-
C23	3.214 (7)	-	-
C24	3.190 (7)	-	-
C25	3.152 (7)	-	-
C26	3.165 (7)	-	-
C27	3.187 (7)	-	-
Centroid 2	2.792 (7)	-	-
Halide	**No contact** 6.607 (2)	3.489 (2)	3.627 (1)
O4	2.756 (5)	3.062 (4)	3.209 (6)
O20	2.793 (5)	3.027 (5)	3.178 (6)
O6[a]	2.845 (5)	3.431 (4)	3.471 (6)
O18[a]	2.781 (5)	2.922 (4)	3.084 (5)
O25[a]	-	2.954 (4)	3.133 (6)
O27[a]	-	3.358 (4)	3.410 (6)

[a] oxygens from different asymmetric unit

Experimental details of X-ray structure determination

Data were recorded on a Nonius Kappa CCD diffractometer with Apex II detector using graphite monochromatized MoK_α radiation [$\lambda(MoK\alpha) = 0.71073$ Å] and temperature of 173.0 ± 0.1 K. The data were processed with Denzo-SMN v0.97.638.[1] The structures were solved by direct methods (SHELXS-97[2]) and refinements based on F^2, were made by full-matrix least-squares techniques (SHELXL-97[3]). The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times

the C temperature factor) and refined as riding atoms. No hydrogens were determined for water molecules in the structures of **1**·RbCl, **1**·CsBr and resorcinarene **2**.

Absorption correction[4] was made to all structures but not used in the final refinement since it worsens the quality of the structure.

In the structure **1**·KBr the temperature factor of carbon C26 were fixed (EADP) with the anisotropic displacement parameters of carbon C19. The hydrogen of methanol oxygen O53 is disordered over two positions.

In the structure **1**·RbCl methanol molecules were refined isotropically with population parameters of 1 and 0.75. In one of them the oxygen is disordered over two position with site occupancy factors 0.25:0.50 and the other isotropic methanol molecule is totally disordered in two positions (0.40:0.60) and both disordered oxygen atoms are disordered second time over two positions (0.15:0.25 and 0.20:0.40). Disordered water/methanol molecule with occupancy factor 0.25:0.75 is positioned in the cavity of **1**.

In the structure **1**·CsBr oxygen atoms of methanol molecules with population parameters 1.0 and 0.75 are disordered over two positions with site occupancy factors 0.35:0.40 and 0.50:0.50. Disordered water/methanol molecule with occupancy factors 0.25:0.75 is positioned in the cavity of **1**. The final difference maps displayed electron density of 1.07-1.42 e.Å^{-3} near Cs^{+} and Br^{-}.

In the structure of resorcinarene **2** oxygen atom of methanol molecule is disordered over two positions with site occupancy factors 0.4:0.6.

1 Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology,* vol. 276, *Macromolecular Crystallography*, *Part A*, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press. New York, 1997, pp. 307-326.

2 G. M. Sheldrick, *Acta Crystallogr*., *Sect A*, 1990, **46**, 467.

3 G. M. Sheldrick, *A program for crystal structure refinement*, 1997, University of Göttingen, Germany.

4 R. H. Blessing, *Acta Crystallogr*., *Sect. A*, 1995, **51**, 33.