

X-ray analysis of the structure of an assembly of cationic aminomethylated calix[4]resorcinarene and the zinc tetrachloride anion

Aidar T. Gubaidullin, Yuliya E. Morozova, Asiya R. Mustafina, Ella Kh. Kazakova, Igor A. Litvinov and Alexander I. Kononov*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420083 Kazan, Russian Federation. Fax: +7 8432 752 253; e-mail: aidar@iopc.kcn.ru

The first X-ray crystallographic data on an ionic host–guest self-assembling system with water-soluble tetraprotonated macrocyclic 2,4,14,20-tetramethyl-5,11,17,23-(*N,N*-dimethylamino)methylenecalix[4]resorcinarene as a host and zinc tetrachloride as a guest are presented.

Because of their high flexibility, host calixarene molecules are affected by the nearest environment, and this fact gives new unexpected opportunities for coordination chemistry. Metal complexes with host molecules can be effectively used for making self-assembling systems and offer the opportunity to compare the conformational modifications of the macrocycles induced by the complexation. Few crystal structures of actinide complexes with deprotonated calixarenes have been reported to date. The complexes described are the inclusion compounds of thorium in *p*-*tert*-butylcalix[8]arene¹ and of the uranyl ion in *p*-*tert*-butylcalix[5]arene.² In the latter case, one protonated triethylamine molecule is located inside and the other, outside the calixarene cavity. Lanthanide elements form complexes with water-soluble *p*-sulfonatocalix[5]arene; the crystal structure includes pyridine *N*-oxide and water as guest species.³ The transition metal complexes of *p*-sulfonatocalix[5]arene also include 2-*N,N*-dimethylacetamide and 15 water molecules as guest species.⁴ In the last two cases, an interesting clay-like bilayer supramolecular structure of solid compounds was discussed. In all of these examples, calixarenes occurred as anions.

Heretofore only five X-ray entries for calix[4]resorcinarene with free OH groups^{5–9} and no data on their metal complexes are included in the Cambridge Crystallographic Database.¹⁰ Here we report the crystal and molecular structure of the ionic compound $2(C_{44}H_{64}O_8N_4)^{4+}(ZnCl_4)^{2-} \cdot 6Cl^- \cdot 4H_2O$, which was obtained from aminomethylated calix[4]resorcinarene and zinc chloride in an aqueous HCl solution.[†] This is the first example of X-ray data for a metal complex in which a calixarene exists in the protonated cationic form.

The calixarene molecule has a twofold axis of symmetry and lies on the C_2 symmetry axis of the crystal. The Zn atom is located at the intersection of two twofold axes. The asymmetric unit contains only one half of the macrocycle, one quarter of the anion $[ZnCl_4]^{2-}$, a Cl^- anion and a water molecule. Water molecules are disordered (Figure 1). The anion $[ZnCl_4]^{2-}$ is statistically disordered, as can be seen from the amplitudes and forms of thermal parameters of the Cl atom. The calixarene

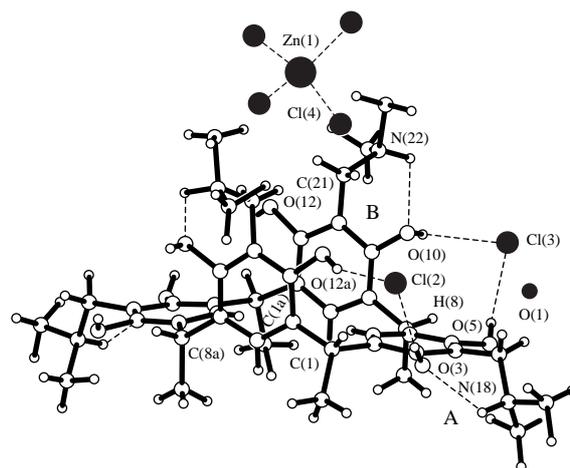


Figure 1 The crystal structure of the complex $2(C_{44}H_{64}O_8N_4)^{4+}(ZnCl_4)^{2-} \cdot 6Cl^- \cdot 4H_2O$. Dashed lines indicate hydrogen bonds.

molecule exhibits a 1,3-diplanar shape with the two opposite phenolic rings bearing the dimethylamino groups almost parallel to one another. The least squares plane formed by the methyne carbon atoms C(1a)–C(1)–C(8a)–C(8) is generally chosen as a reference plane for the molecule. The dihedral angle between

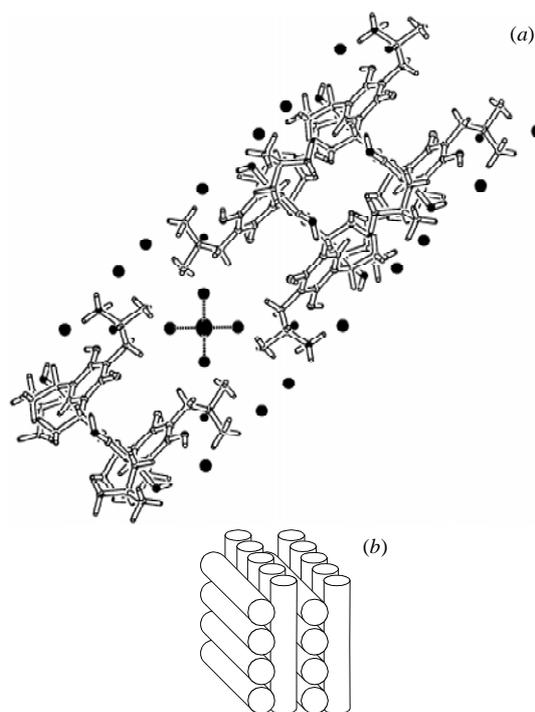


Figure 2 (a) A fragment of molecular packing and (b) arrangement of sticks in the crystal.

[†] The crystals exhibited extreme sensitivity to solvent losses and were protected in a glass capillary during the collection of X-ray diffraction data with an 'Enraf-Nonius CAD4' four-circle diffractometer (graphite monochromator, $CuK\alpha$ radiation, $\omega/2\theta$ scan, $\theta \leq 74.3^\circ$). Twenty-five-centered reflections gave a refined tetragonal unit cell of the dimensions $a = 14.894(4) \text{ \AA}$, $c = 23.395(6) \text{ \AA}$, $V = 5190.0(2) \text{ \AA}^3$, $Z = 4$, $\rho = 1.37 \text{ g cm}^{-3}$. A total of 6027 reflections were measured, of which 4032 were unique with $I > 3\sigma(I)$. The structure was solved in the uniquely assignable space group $P-4n2$ by direct methods using SIR¹¹ and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, while the thermal and positional parameters of hydrogen atoms were fixed. The final R values were $R = 0.054$, $R_w = 0.064$ for 3633 unique reflections with $F^2 \geq 3\sigma(I)$. All calculations were carried out on a 'DEC Alpha Station 200' computer with the MolEN¹² system. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 1999. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/35.

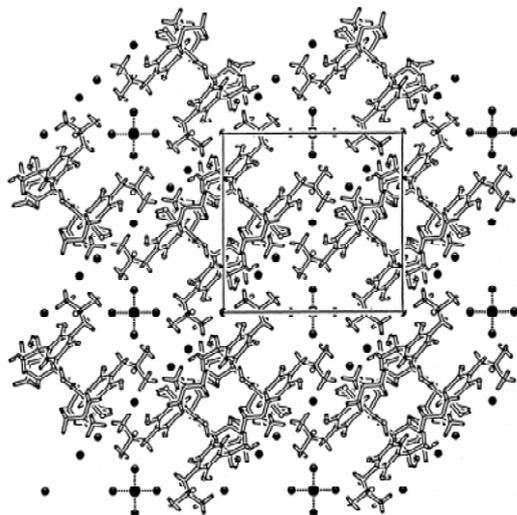


Figure 3 The monolayer arrangement in the crystal. View along the *c* axis.

opposite resorcinolic rings (A) lying in the least squares plane is $171.3(4)^\circ$. The other pair of resorcinolic rings (B) perpendicular to the least squares plane constitute the dihedral angle of $31.2(2)^\circ$ with each other. The neighbouring resorcinolic rings make angles $70.5(2)^\circ$ with each other. The dimethylamino groups of rings (B) together with OH groups form hydrophilic host cavities.

The N(18)–H(18)···O(3) 2.35(3) Å (A rings), N(22)–H(22)···O(10) 2.57(3) Å (B rings) distances suggest the formation of intramolecular hydrogen bonds between the amino protons and one of the hydroxyl oxygens of the resorcinol moiety (Figure 1). The remaining hydroxyl protons also take part in hydrogen bonding with the bridging methylene hydrogen C(8)–H(8)···O(5) 2.53(4) Å (A rings) and with the methylene hydrogen of CH₂NH⁺Me₂ groups C(21)–H(21)···O(12) 2.44(5) Å (B rings). The two Cl[−] anions participate in the intermolecular hydrogen bonding with resorcinol groups: O(3)–H(3)···Cl(2) 2.24(4) Å (A rings), O(12)–H(12)···Cl(2) 2.47(4) Å (B rings), O(5)–H(5)···Cl(3) 2.50(6) Å (A rings), O(10)–H(10)···Cl(3) 2.77(5) Å (B rings). The chlorine anions are also stabilized by additional weak interactions with the bridging methylene hydrogen C(1)–H(1)···C(2) 2.65(4) Å and the protons at the nitrogen atoms N(18)–H(18)···Cl(3) 2.63(3) Å of the A rings. Protons at the nitrogen atom also interact with a water molecule N(22)–H(22)···O(1) 1.89(4) Å.

The crystal superstructure is rather interesting (Figure 2). Two calixarene molecules are faced each other with their planar resorcinol A rings to form lipophilic regions [Figure 2(a)]. On the other hand the resorcinol B rings form a supercavity, which is large enough to encompass the anion [ZnCl₄]^{2−}. This motif is organized into infinite one-dimensional sticks, which are

surrounded by a hydrophilic layer that consists of NH⁺Me₂ and OH groups, Cl[−] and H₂O, which form a solvate shell. The coplanar sticks are packed to form a monolayer (Figure 3). Each subsequent monolayer is swung 90° to the preceding layer [Figure 2(b)]. This is the reason why all guests have a lipophilic covering. One Cl[−] anion is placed on the *C*₂ axis and forms an anion pseudochannel. Hydrogen bonding forms a three-dimensional network; the directions of hydrogen bonds do not coincide with the directions of sticks and monolayers.

Thus, protonated aminomethylated calixarenes can serve as cationic host ligands for ionic self-assembling systems. In contrast to the complexes described in refs. 3 and 4 the aminomethylated calixarene fragments are not involved in the first coordination sphere of the metal ion. Electrostatic forces and the size of an anion are important in this case.

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