





DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS

65

**DFT STUDY OF THE CESIUM CATION  
CONTAINING COMPLEXES RELEVANT  
TO THE CESIUM CATION BINDING  
BY THE HUMIC ACIDS**

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## LIST OF ORIGINAL PUBLICATIONS

- I Peeter Burk, Jaana Tammiku-Taul, Sven Tamp, Pierre-Charles Maria, Jean-François Gal, Charly Mayeux, Computational study of cesium cation interactions with model compounds of humic substances, *J. Mol. Struct. THEOCHEM*, submitted.
- II Peeter Burk, Sven Tamp, Jaana Tammiku-Taul, Pierre-Charles Maria, Jean-François Gal. Computational study of cesium cation-humic substance interactions. A neutral analogue ligand molecules approach. *Proc. Estonian Acad. Sci. Chem.* 54(2), 2005, 70–84
- III Pierre-Charles Maria, Jean-François Gal, Lionel Massi, Peeter Burk, Jaana Tammiku-Taul, Sven Tamp. Investigations of cluster ions formed between cesium cations and benzoic, salicylic and phthalic acids by electrospray mass spectrometry and density-functional theory calculations. Toward a modeling of the interaction of Cs<sup>+</sup> with humic substances. *Rapid Comm. Mass Spectrom.* **19**, 2005, 568–573.
- IV Peeter Burk, Sven Tamp. A theoretical study of gas-phase basicities and proton affinities of alkali metal oxides and hydroxides. *J. Mol. Struct. THEOCHEM* **638** (1–3), 2003, 119–128.

### Author's contribution

- Paper I: Responsible for most of the relevant calculations. Significant participation in manuscript preparation.
- Paper II: Responsible for most of the relevant calculations. Significant participation in manuscript preparation.
- Paper III: Responsible for around half of the performed calculations. Minor participation in manuscript preparation.
- Paper IV: Responsible for all of the relevant calculations and manuscript preparation.

# 1. INTRODUCTION

Alkali metal ion binding to ligand is one of the many types of ion-molecule noncovalent bonding interactions in chemistry. Although much weaker than covalent bonding, this is of great significance in chemistry and related disciplines as a result of their widespread occurrence as well as potential technological applications. For example, there has been a great deal of interest in lithium polymer electrolytes for their potential applications in fuel cells and other electrochemical devices where ion-polymer and ion-ion interactions in these materials play an important role in the ion transport mechanism.  $\text{Na}^+$  and  $\text{K}^+$  are abundant metal ions in biological systems where they are involved in a variety of processes including osmotic balance, the stabilization of the conformations of biomolecules and information transfer via differential  $\text{Na}^+/\text{K}^+$  ion pumps and ion channels [1].

Similar data on heavier alkali ions like  $\text{Cs}^+$  is rather limited. This may well be because of more modest applications as well as scientific attractiveness in chemistry and related fields as compared to the lighter alkali elements. Nevertheless, many useful applications have been found and are developed, exploiting the coordinating properties of the cesium cation. Among these is the use of Cs as a cationizing agent in mass spectrometry for 1) quantitative analysis of biomolecules (carbohydrates) [2,3], polymers (polyethyleneglycol, polymethylmethacrylate) [4,5] and mass calibration of mass spectrometer by the generation of high molecular weight Cs ion clusters by electrospray (ES) ionization mass spectrometry [6].

On the downside, Cs also poses a major radiological hazard on the environment. The uptake and transfer of radioisotope  $^{137}\text{Cs}$  by plants, fungi and ultimately to all living organisms is largely associated with soil organic matter (SOM), particularly by complexation with humic or fulvic substances. Hence, sequestration of Cs contaminants is significantly affected by SOM chemistry. In that respect, fundamental knowledge about the different types and strength of interaction between Cs cation and a variety of organic compounds as ligands is clearly necessary.

Characterizing these interactions in the absence of solvent or counterion species necessitates solid thermochemical data of alkali ion binding to an array of organic compounds. This permits to evaluate the effects of solvation on structure and possibly provide an initial guess for future solvation calculations. A wealth of such data is available for  $\text{Li}^+$  and  $\text{Na}^+$  (though less for heavier alkali ions –  $\text{K}^+$ ,  $\text{Cs}^+$ ) and can be found in the famous “Webbook” (National Institute of Standard and Technology, NIST) [7] and other sources.

Parallel to obvious experimental gas-phase studies on ion-molecule systems, high level theoretical calculations can provide excellent complement in this field. It is even expected that with advances in computational power such calculations (Gaussian-2 and -3, coupled-cluster (CC) theory) are able to yield

data in even better agreement with experiment. Besides, a strong advantage of calculations is to provide accurate structural information about the systems under study, which is often difficult if not impossible to obtain with experimental techniques.

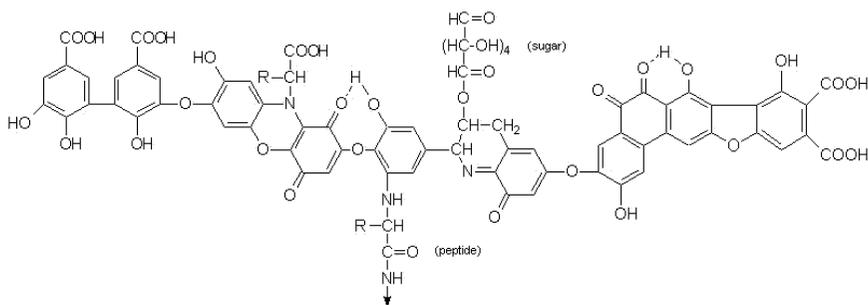
This thesis presents a compilation of our work on the use of theoretical calculations to get an insight into the intrinsic binding modes and bonding energetics of Cs<sup>+</sup> cation interacting with some organic aliphatic and aromatic compounds.

## **1.1. The toxicity of Cs in relation to soil organic matter**

### **The main objectives of the study**

The phytotoxicity of a stable Cs isotope (<sup>133</sup>Cs) is expressed in its accumulation in the rapidly growing parts (roots, leaves and other organelles) of plants, causing a decrease in the growth of biomass, in tissue hydration and potassium starvation via competitive interaction with vital K<sup>+</sup> binding sites in proteins [8]. But a major threat lies in the deposition of radionuclide <sup>137</sup>Cs in the biosphere and its subsequent transfer into the food chain through fauna which poses a serious radiological hazard. The major fallouts soon after the Chernobyl accident in 1986 caused elevated concentrations of that radioisotope over large areas in Russia, Belarus and Ukraine as well as some other European regions. Relative increased uptake of Cs by certain crops (onions, cress, mushrooms) have been reported. Just as an example, more detailed studies of this phenomena have revealed the presence of natural organic compounds (like “norbadione A” in mushroom “bay boletus”) that constitute carboxylate and hydroxyl groups in favorable spatial arrangement, exhibiting highly selective chelating power towards Cs [9]. In fact, scientific research is carried out to design ligands as materials that selectively bind radioactive elements, e.g. <sup>137</sup>Cs and thus remove them from waste streams.

It is known that humic and fulvic substances [10] may play an important role in the mobility and bioavailability of Cs in the environment. These are complex macromolecules (molecular weight up to several kDa-s) containing substituted, partly oxidized aromatic rings linked by various size aliphatic chains (amino acids, sugars, peptides, etc.). Especially carboxylic and hydroxylic functional groups create strong binding sites (especially when ionized or favourably located to constitute potential chelators) for certain metal cations [11]. A typical model of a humic acid macromolecule is presented on Figure 1:



**Figure 1.** One of the proposed structural models for humic acids

To understand the mechanism of Cs uptake and distribution in the biosphere, fundamental information about the binding patterns and energetics of  $\text{Cs}^+$  to natural organic substances is of profound importance. To acquire a better understanding of the interaction of cesium ion with these relatively high molecular-weight macromolecules, knowledge of the intrinsic structure and energetics of the binding to smaller model systems is required.

The following main tasks were put on to the current thesis:

1) To study the  $\text{Cs}^+$  complexation with organic aromatic and aliphatic compounds which can be envisaged as constituent units of humic and fulvic substances. Under most natural conditions however, soil organic matter will be deprotonated because there are abundant functional groups (e.g. carboxylic acids) with pKa-s around 4. This was considered by broadening the study in case of carboxylic acids and phenolic compounds to their deprotonated anionic carboxylate and phenolate forms, respectively as model compounds.

In this respect, the  $\text{Cs}^+$  cation basicities (CsCB) and affinities (CsCA) as well as typical binding patterns within the complexes were studied using computational techniques. The CsCB-s and CsCA-s were computed according to the following thermodynamic equilibrium (1),



where B = neutral or anionic base and  $n=0$  or  $-1$  for neutral or anionic bases, respectively. The  $\text{Cs}^+$  cation basicity (CsCB) is associated with the negative Gibbs free energy change ( $\text{CsCB} = -\Delta G_{(1)}$ ) and cesium cation affinity (CsCA) with the negative enthalpy change ( $\text{CsCA} = -\Delta H_{(1)}$ ) of the association reaction.

2) Estimate the strength of  $\text{Cs}^+$  binding (CsCA, CsCB) to organic acid cesium ion pairs (or salts  $\text{Cs}^+ \text{A}^-$ ) where  $\text{A}^-$  is benzoate, salicylate or phthalate anion.

3) Provide basic validation of the chosen computational procedure by comparing results with previously published experimental and higher level ab initio calculation values for a small number of reference compounds available.

## 2. LITERATURE OVERVIEW

### 2.1. Sources of Cs<sup>+</sup> Complexation from Experimental Studies

A short overview of the working principles of the most common experimental techniques and studies relevant to intrinsic Cs<sup>+</sup> complexation thermochemistry follows.

#### Ligand exchange equilibrium technique by FT-ICR

Ion-molecule reaction equilibria and kinetics have been studied frequently using FT-ICR. In its simplest description, the cyclotron frequencies of low kinetic energy ions (a few tens of eV) trapped electrically and magnetically within a cell are measured and converted into *m/z*. The method is compact in a sense that ionization, ion selection-interaction and product mass analysis stages can all be carried out in a single cell and a variety of experiments performed using different pulse sequences. The main advantage of the technique is its high to ultrahigh mass resolution without the sacrifice in the loss of sensitivity, and high speed because all the ions can be excited simultaneously with a single radiofrequency (rf) pulse.

Gibbs free energy changes of ligand exchange can in principle be measured for metal cation M<sup>+</sup>, provided that reaction conditions favor equilibrium for the following reaction (2):



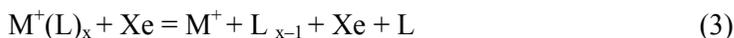
where A and B are neutral ligands. This is sometimes difficult to achieve, either because of the low vapour pressures of A and B or their widely different quantitative binding for M<sup>+</sup>. If this is the case, relative gas phase ion affinities can be measured by bracketing ion transfer reactions in FT-ICR method in which an ion is reacted with a series of reference molecules having a variation in the measured thermochemical parameter like basicity or affinity. The experimentally measured equilibrium constants can then be related to the endo- or exothermicity of the relevant reactions and relative thermochemical parameters be derived.

FT-ICR is well suited for measurement of rate and equilibrium constants for molecular systems exhibiting molecular recognition. In that respect, crown ethers have been extensively studied because they bind alkali ions selectively in solution. Following the kinetics of ligand exchange reaction, the relative Cs cation binding to a series of various size crown ethers has been studied using FT-ICR [12,13] as well as the effect of substitution of cyclohexyl groups in dicyclohexano-18-crown-6 (DC18C6) in alkali ion (Li-Cs) binding relative to unsubstituted 18-crown-6 and the rates of formation of 2:1 ligand-metal

complexes [14]. The higher cation affinity of DC18C6 vs. 18-crown-6, though decreasing with increasing ionic radii was attributed to the higher polarizability of DC18C6. The relative CsCA of dibenzo-18-crown-6 was found to be between that of 15-crown-5 and 18-crown-6 in the bracketing FT-ICR gas phase studies of selected crown ethers.

### Collision-induced dissociation threshold (CIDT) technique

Metal cation-ligand bond dissociation energies can be measured by CIDT experiment. The method involves accelerating the reactant ion  $M^+L$  to known kinetic energies and determining the energy threshold for the fragmentative dissociation of  $M^+L$  by collision with a third body, usually a noble gas Xe:



The measured threshold for the above reaction, corresponding to the highest energy along the reaction path for dissociation is equal to the bond dissociation energy assuming that the reverse ion-molecule association reaction is largely exothermic and proceeds without an activation energy. Armentrout and coworkers [15] have specifically designed a guided ion-beam tandem mass spectrometer for such experiments which has proved to give sufficiently accurate thermodynamic data regarding alkali ion-molecule complexes. In their construction, ions are created in the ion source, mass selected, retarded to the desired kinetic energy and injected into an rf octopole passing through a collision gas cell where the fragmentation of the ion adducts take place. The product and unreacted ions are drifted to the end of the octopole, focused into a quadrupole mass filter and ultimately ion intensities measured by standard techniques. Bond dissociation energies (at 0 K) are obtained as a parameter by fitting ion intensity vs. kinetic energy data to known mathematical expressions.

A number of works utilizing CIDT has involved the studies of bond dissociation energies of Cs complexes with various neutral ligands. These include simple ethers (dimethylether, 1,2-dimethoxyethane [16]) as well as cyclic crown ethers[17,18] and a set of aromatic compounds measured by Rodgers et. al. [19–24]

### High Pressure Mass Spectrometry (HPMS)

Pulsed electron high pressure mass spectrometry can be used to study thermodynamic properties of ion-molecule association:



or clustering equilibria:



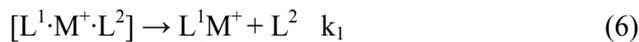
The alkali ions are typically created by thermionic emission from a heated filament or by electrospraying salt solutions containing the appropriate metal ion. The ions are reacted with neutral ligands and the association-clustering equilibria is achieved by collision with a third body collision gas (M) to thermalize the exothermically formed ion adducts. The gas is allowed to effuse through a small exit slit in the wall of the ion source, followed by ions capture by electric fields. Ion adducts sampling is achieved by acceleration and subjection to mass analysis either with a magnetic sector or quadrupole filter. The equilibrium constant for the corresponding equilibrium reactions may be determined from the ion intensities and neutral ligand pressures. The experimental determination of the enthalpy and entropy changes for the reactions can be obtained from van't Hoff plots by measuring equilibrium constant over a range of temperatures.

As regards to HPMS technique, several studies have been devoted to solvation phenomena of alkali cations (including  $\text{Cs}^+$ ) in the gas phase. In a series of works, Kebarle has measured equilibrium constants of  $\text{Cs}^+$  hydration equilibria with up to six water molecules [25], the sequential hydration energies and entropies with up to four water molecules for singly charged  $\text{Cs}^+\text{L}_n$  clusters [26] as well as Gibbs energy changes for ligand exchange equilibria in  $\text{Cs}^+$  competitive solvation by water and methanol [27] using ES ionization source. As a rule, the hydration energies decreased with increasing alkali ion size for bare  $\text{M}^+$  and  $(\text{MXM})^+$  charged cluster (M – alkali ion, X – halogen ion) though the latter had lower energies due to repulsive interaction between X and the solvent molecule. The decreased preference of  $\text{Cs}^+$  solvation by methanol (vs. water) was found, being in accord with increased distance between the metal ion and the ligands. Consequently, the larger dipole moment of water relative to the larger polarizability of methanol was realised to be more important for determining bonding in ion-solvent clusters. Equilibrium constants and the associated Gibbs free energies for mixed clustering of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{SO}_2$  to several positively charged ions, including  $\text{Cs}^+$  were reported by Banic and Iribarne [28]. The ions were produced in ion source at atmospheric pressure using aqueous solutions by evaporation from the surface of charged droplets – in fact an earlier version of modern ES ionization technique.

### **Kinetic method**

A method, referred to as the kinetic method was developed, based on the unimolecular dissociation of ion adducts. Although this method has largely been used for the study of the thermodynamics of proton transfer (relative acidities, basicities), many have investigated its applicability to the determination of affinities for alkali-metal cations by FT-ICR mass spectrometry.

The principle of the method relies on competitive dissociation (either by metastable decomposition, collisionally activated dissociation or by some other process) of an ion-bound heterodimer in the form  $[\text{L}^1 \cdot \text{M}^+ \cdot \text{L}^2]$ :



where L are appropriate ligands,  $M^+$  may be a proton, metal ion etc. and  $k_1$  and  $k_2$  are the rate constants for the respective competitive dissociation reactions (6) and (7). The natural logarithm of the fragment ion intensities ( $\ln[L^1 M^+]/[L^2 M^+]$ ) can be equated with  $\ln k_1/k_2$  if dissociation is treated as a quasiequilibrium process. In its simplest form, assuming negligible entropy differences of the competitive dissociation channels and negligible activation energies of the reverse association reactions, the ratio of the fragment ion intensities can be related to the differences in ion affinities of the two ligands:

$$\ln \frac{k_1}{k_2} = \ln \left[ \frac{[L^1 M^+]}{[L^2 M^+]} \right] \approx \frac{\Delta(\Delta H)}{R \cdot T_{eff}} \quad (8)$$

In practice, ion intensity ratios are plotted for a series of ion bound heterodimers comprised on ligand under study against a series of ligands with known ion affinities which gives a direct relative measure of the  $M^+$  affinity for the unknown ligand. The attractiveness of the method lies in a wide variety of thermochemical quantities that can be determined as well as in its high sensitivity to small differences in measured values.

Relative alkali ion affinity ladders were constructed for crown ethers of various sizes and their acyclic analogs using the kinetic method [29]. For small and middle sized crown ethers (12-crown-4, 15-crown-5) their acyclic analogs showed greater affinity for heavier alkali Rb and Cs, which was attributed to their greater conformational adaptability to maximize multiple bonding interactions with the metal ion. In a similar study on gas-phase size selectivities of crown ethers by the kinetic method [30], the collisional dissociation of crown ether complexes with two different alkali ions (crown ether mixed alkali metal halide dimer complexes in the form  $(C+M \cdot M \cdot X)^+$ ) were observed. In all cases the formation of  $Cs^+$  – crown ether complexes were disfavoured following collisional activation of the crown ether/mixed alkali metal adduct. This was presumably due to difficulty of the crown ether macrocycle to maximize the  $Cs^+$ /crown attractive interaction with the relatively large  $Cs^+$ . The relative alkali ion affinities of arginine in its canonical free acid as well as zwitterionic salt bridge form and corresponding methyl ester were studied by the kinetic method [31]. The relative ion affinities were found to be in the order – free acid < ester < zwitterion. The structural determination of  $M^+$  adducts of arginine revealed that  $[Arg]K^+$  and  $[Arg]Cs^+$  contained both the zwitterionic form of arginine (i.e. a salt-bridged structure) as opposed to  $[Arg]Li^+$  and  $[Arg]Na^+$  complexes which contained arginine in its free acid form. It was found that  $Cs^+$ , due to its higher polarizability and lower charge density can favourably interact with both O-atoms of carboxylate thus stabilizing anion-cation attractive forces.

## 2.2. Sources of Cs<sup>+</sup> Complexation from theoretical calculations

There have been a number of computational studies of the structures and bonding energies (including enthalpies, gibbs free energies) of Cs cation binding to different neutral ligands at various levels of theory. The objective of the current chapter is to give a compact overview of the different computational approaches in view of the systems under study.

To be useful, such calculations need to be performed at a fairly high level of theory. In general, structures involving noncovalent interactions need methods that include electron correlation (such as MP2) and basis set of at least double-zeta quality, including polarization functions. For final energetics, commonly single-point energy calculations are performed using even larger basis set (of triple-zeta quality) including additional polarization and diffuse functions. Another approach, although less frequently used concerning Cs, is density functional theory (DFT) that has attracted interest in the last decades. DFT offers advantage of less drastic scaling with the size of the system than traditional *ab initio* methods. Especially hybrid density functionals (like B3LYP) provide the best overall precision and occasionally have been reported to be of same (or even surpass) the quality of MP2 or Gaussian-2 (G2) levels.

From the computational perspective, Cs is a more challenging element as compared to the lighter alkali metals – it contains a large number of inner-shell (core) electrons that are inert in a chemical sense. Secondly, as a 6-th period element, cesium exhibits rather strong relativistic effects that ordinary basis set do not account for. In practice, most calculations involving Cs use effective core potentials (ECP-s) where core electrons are treated by appropriate mathematical function and only valence electrons are treated separately by the accompanying basis set [32]. For definition, "small core" ECP-s treat also the outermost (n-1) shell (prior to valence shell) electrons explicitly by the basis set for expected added precision in calculations. As a bonus, the ECP-s are also designed to account for the relativistic mass-velocity effects known to significantly contribute to describing heavier elements like Cs.

A number of studies involving Cs have made use of a hybrid basis set reported by Glendening and Feller. For convenience, it is defined as a "Glendening-Feller hybrid basis set" in the following overview of computational studies. It consists of a 6-31+G\* basis set for oxygen and 6-31G\* for carbon and hydrogen. Cesium is described by the quasi-relativistic "small-core" Hay-Wadt ECP with split valence basis set augmented by additional 6-term d-type polarization function [33]. Also an additional polarization function with an exponent of 0,19 has been added to Cs basis set as suggested by Glendening [34].

Ionic clusters composed of a single Cs cation and up to 6 [35,36] or 8 [37] water molecules have been studied at the restricted Hartree-Fock and correlated MP2 level of theory using Glendening's hybrid basis or augmented correlation

consistent (aug-cc-pVDZ) basis on water and Stuttgart small core ECP for Cs [38]. RHF method was found to be adequate for clusters containing up to 3 water molecules. This was attributed to lower need of correlated treatment of energy within smaller clusters where electrostatic interactions dominate. Correlated MP2 level of theory was however needed for larger clusters due to higher degree of dispersion forces present in the hydrogen-bonded networks and thus a more balanced description of all interactions within the cluster. Basis set of at least triple-zeta quality was found to be in need for more accurate description of the relatively higher polarizability of Cs cation and more accurate water-water distances within clusters composed of up to 8 water molecules [39].

Examining alkali cation interactions with short-chain ethers as ligands can give prerequisite data for binding of these metals to cyclic crown ethers. Hill and Glendening have studied the structures of the complexes and binding enthalpies of  $\text{Cs}^+$  with up to four molecules of dimethyl ether [40] and up to two molecules of 1,2-dimethoxyethane [41] at the RHF and MP2 level using a hybrid Glendening-Feller basis as defined above.  $\text{Cs}^+$  complex with a single dimethylether (DME) ligand was found to be in a trigonal planar form having a  $C_{2v}$  symmetry, but a strongly bent conformation of  $C_2$  symmetry with two ligands was realized to be characteristic for heavier alkalis, including Cs. The calculation of a  $\text{Cs}^+[\text{DME}]_3$  revealed its pyramidalized structure where  $\text{Cs}^+$  is located 0.68 Å above the plane formed by three oxygens of the ether molecules. Although the calculated bond dissociation energies for lighter alkali metal complexes were in very good agreement with the experimental CIDT values (within 1 kcal/mol), the overestimation of as much as 14 kcal/mol, as compared to experimental values, were uncovered for 1,2-dimethoxyethane complexes with heavier Rb and Cs. Such high discrepancy in energies was partly reasoned by a possible presence of higher energy conformers in the dissociation channel in the CIDT experiment and consequently lower measured thresholds for dissociation of these complexes.

Having studied acetone complexes with a variety of mono and divalent cations, Song et al. [42] found that the corresponding complex with  $\text{Cs}^+$  is linear which, according to the authors, is a direct evidence of near zero charge transfer from metal cation to the acetone, also confirmed by natural bond orbital (NBO) analysis. The authors concluded that the type of bonding within the clusters is electrostatic. The calculations were performed at the MP2 level with aug-cc-pVDZ basis set on acetone and Stuttgart-Dresden relativistic ECP on Cs.

The interaction of  $\text{Cs}^+$ , among other metal cations has been studied [43] with important DNA bases adenine and guanine at the HF and MP2 levels of theory with Christiansen's ECP on  $\text{Cs}^+$  and 6-31G\*\* basis set on the rest of the elements. The binding to guanine was stronger due to its higher dipole moment and favorable position of the carbonyl oxygen and the nitrogen atom of the 5-member heterocycle resulting in a chelation interaction within the Cs-guanine complex.

Macrocyclic crown ethers have received considerable attention because of their ability to selectively bind alkali cations in solution, determined by a balanced equilibrium in competition between the crown ether and solvent molecules for the cation. Besides experimental studies, the field has also attracted interest among computational chemists as crown ethers represent the smallest systems for studying host-guest interactions both intrinsically and also in the presence of solvent molecules.

Glendening et.al. [33] have studied, besides other alkalis, the  $\text{Cs}^+$  binding to 18-crown-6 at the HF and MP2 levels using Glendening-Feller hybrid basis. The calculated geometries generally compared favorably with reported crystal structure data, although the calculated Cs-O distances with a lower quality 3-21G basis were up to 0,15Å shorter as compared to Glendening-Feller basis. In the calculated lowest energy  $\text{Cs}^+$ -18-crown-6 complex the  $\text{Cs}^+$  resides above the cavity of the crown at a distance of 1,6Å. The binding enthalpy at the MP2 level was however overestimated at least by 9 kcal/mol as compared to experimental CIDT result. The binding enthalpy of  $\text{Cs}^+$  to 15-crown-5 and the effect of a larger correlation consistent aug-cc-pVDZ basis set was studied by Hill and Feller [44] using the same levels of theory. The calculated binding enthalpy compared rather poorly with the experimental CIDT result – the MP2 level in conjunction with Glendening-Feller basis overestimated the experimental value by 18 kcal/mol. Though the use of a larger aug-cc-pVDZ basis resulted in a reduction of the binding enthalpy by 5 kcal/mol, the difference of 12,5 kcal/mol with experiment still remained. One possible explanation for such a large discrepancy between theory and experiment in both these works again assumed that the CIDT technique measured dissociation of alkali metal/crown complexes that were trapped in higher energy lying conformations.

Anderson et.al. have studied the dibenzo-18-crown-6 complexation with alkali cations, including Cs cation with HF, MP2 and density functional B3LYP methods [17]. The hybrid Glendening-Feller basis set with minor modifications was used for the crown ether and optionally a LanL2 DZ ECP for  $\text{Cs}^+$ . The calculated binding enthalpies with HF and DFT/B3LYP methods were somewhat closer, though still up to 10 kcal/mol overestimated as compared to experimental value while the MP2 method resulted in an even higher binding enthalpy.

Alkali cation- $\pi$  interactions exhibit importance in molecular biology, serving an important role in protein structural organization, functioning of ionic channels etc. [45]. Aromatic structural units are also of immense importance in drugs. Alkali metal (from Li to Cs) ion binding to benzene has been studied by Nicholas et.al. [46] with HF, MP2 and DFT (local SVWN and non-local BP86 functionals) levels using Hay-Wadt ECP on  $\text{Cs}^+$  and 6-311G\* basis set on benzene. The authors concluded that consideration of electron correlation is necessary for calculating binding enthalpies for such type of noncovalently bonded systems. While the geometries at the DFT and MP2 level agreed well,

the calculated  $\text{Cs}^+$  binding enthalpy for benzene was by 2 kcal/mol higher at the DFT/SVWN level, and roughly lower by the same margin at the DFT/BP86 level as compared to the MP2 value (11,6 kcal/mol). It was also noticed that the C-C distances in benzene were higher by 0,003 Å at the RHF and MP2 level upon complexation with  $\text{Cs}^+$ , as compared to DFT results. Besides, the hydrogen atoms were forced out of the plane of the benzene ring by 2–3° within the metallated complex. An analogous study was later repeated by the same group [47] on a higher level of calculation – MP2 and CCSD(T) using a collection of correlation-consistent basis set up to quadrupole-zeta quality for benzene and a Hay-Wadt ECP for  $\text{Cs}^+$ . The estimated Cs cation binding enthalpy of benzene at the MP2 level in the complete basis set limit was in relatively good agreement, being 2,6 kcal/mol lower than the experimental value (15,1 kcal/mol). Higher order correlation effects, estimated at the CCSD(T) level had a negligible contribution to the binding enthalpy however.

Rodgers and Amunugama have studied the geometries and type of interactions predominant in alkali cation (from Li to Cs) complexes with a number of substituted benzene derivatives – toluene [19], fluorobenzene [20], aniline [21], phenol [22], anisole [23] and also naphthalene [24] using Glendening-Feller hybrid basis at MP2 and DFT/B3LYP levels of theory. Binding energies were determined from single point calculations at the MP2(full)/6–311+G(2d,2p) (including corrections for ZPE and BSSE) and, for comparison, exclusively for toluene at the B3LYP/6–311+G(2d,2p) level. In general, the calculated binding energies agreed rather well but were systematically lower than experimental CIDT values by up to 1,7 kcal/mol at the MP2 level (including zero point energies). However, including correction for BSSE lowered the binding energies even further and thus widened the discrepancies between experiment and theory to ca. 3 kcal/mol. At the DFT/B3LYP level the agreement with experimental values was far worse, underestimating the binding energy for toluene almost to 6 kcal/mol.

The authors also analyzed the structural features of the complexes. They revealed that the metal cation can bind to the  $\pi$ -face of the aromatic ring resulting in cation- $\pi$  complex (naphthalene, toluene) or, alternatively interact with the lone pairs of the electronegative atom of the substituent group in case of substituted benzene derivatives, resulting in the so-called “ $\sigma$ -complex”. It was generally found that in contrast to lighter alkali ions (Li) the heavier  $\text{Cs}^+$  showed an intermediate behaviour and greater flexibility upon complexation in sense that  $\sigma$  and  $\pi$ -complexes were nearly degenerate in energy (fluorobenzene, phenol, anisole). In some cases, like for aniline a lowest energy conformation was found for the complex where probably both  $\sigma$  and  $\pi$ -type of binding modes are operative. Metal cation binding to these compounds resulted mainly from ion-(induced) dipole and ion-quadrupole interaction, associated with the polarizability and influence of the local stereoelectronic effect of the substituent on the  $\pi$ -electron density of the substituted aromatic compound, respectively.

Gal et.al. [48] have recently reviewed gas phase experimental and theoretical studies relevant to  $\text{Cs}^+$ , including data on experimental CsCA-s and CsCB-s for different neutral ligands compiled from various sources. Besides, CsCA-s for a small number of negatively charged ligands obtained from thermochemical cycle (by applying Hess law using tabulated enthalpies of formation) was also included for comparison. A more compact form of this data (limited to ion-molecule complexes with only one ligand) is included in the current work (Table 1.)

**Table 1.** Cesium cation affinities (CsCA) and basicities (CsCB) of neutral ligands

Ligand	CsCA <sup>a</sup>	CsCB <sup>a</sup>	Technique <sup>b</sup>
18-crown-6	40,6 (2)		CIDT
dibenzo-18-crown-6	32,5 (8)		Bracketing
CsOH	28,3		HL
15-crown-5	24,1 (1)		CIDT
12-crown-4	20,6 (2)		CIDT
indole	19,7 (0,7)		CIDT
acetonitrile	19,2 (0,1)	13,7 (0,1)	HPMS
aniline	16,9 (1)	10,2 (2)	CIDT
naphtalene	16,6 (1)	9 (2)	CIDT
anisole	15,9 (1)	8,6 (2)	CIDT
phenol	15,8 (0,8)	7,4 (2)	CIDT
toluene	15,5 (1)	7,3 (2)	CIDT
benzene	15,5 (1)	9,3 (2)	CIDT
MeOH	15,4	9,1	HPMS
dimethylether	13,6 (1)		CIDT
1,2-dimethoxyethane	13,6 (1)		CIDT
fluorobenzene	12,1 (1)	5,3 (2)	CIDT
H <sub>2</sub> O	11,9 (1)	7,6 (3)	DT
SO <sub>2</sub>	10,8 (1)	5,2 (2)	DT
CO <sub>2</sub>	6,2 (1)	1,9 (0,8)	DT

<sup>a</sup> Experimental cesium cation affinities and basicities with exp. uncertainties in brackets (in kcal/mol), from reference 48.

<sup>b</sup> Techniques:

CIDT: Collision Induced Dissociation Threshold

DT: Diffusion Tube

HL: Hess law using enthalpies of formation of relevant species

HPMS: High Pressure Mass Spectrometry

Evidently, the CsCA-s range between 6,2 kcal/mol (CO<sub>2</sub>) and 40,6 kcal/mol (18-crown-6) among the selected neutrals, being the weakest interactions in the alkali cation series. Just for comparison – the lithium cation affinity (LCA) is 34 kcal/mol for H<sub>2</sub>O and 36,8 kcal/mol for benzene. The monotonic lowering of

alkali ion affinities and basicities is in accord with the trends in increase in ionic radius, polarizability and lowering of charge density in the series Li to Cs.

In general, the alkali ion-neutral ligand complexation is mainly of electrostatic nature – a balanced action of ion-dipole, ion-quadrupole and ion-(induced) dipole interactions. The relatively higher CsCA of crown ethers can be explained by the favorable interaction of  $\text{Cs}^+$  with multiple oxygen atoms.

### 3. COMPUTATIONAL METHOD

The gas-phase calculations were carried out using the Gaussian 03 [49] program. All geometry optimizations were done by means of the density functional theory with hybrid B3LYP functional and Dunning/Huzinaga valence double-zeta basis set, augmented with polarization functions (D95V(d,p) on hydrogen and first period atoms (Articles I, II and III). Besides, diffuse basis functions were added for both neutral and anionic compounds (including the corresponding  $\text{Cs}^+$  complexes ( in Article I) but only to anionic compounds and their  $\text{Cs}^+$  complexes (in Article III). For all calculations involving the cesium cation, the Stuttgart-Dresden (SDD) effective core potential and the accompanying basis set was used. A single set of polarization (d) functions was added to the SDD basis for  $\text{Cs}^+$  with an exponent of 0,19.

Following the geometry optimizations of the neutral and anionic systems, including their complexes with  $\text{Cs}^+$ , the frequency calculations were conducted at the same level of theory to ensure that the relevant species represent the true minima on the potential energy surface. The frequency calculations were necessary to obtain Gibbs free energies and enthalpies for calculation of thermochemical quantities (i.e. CsCA-s and CsCB-s) according to ion-molecule equilibrium (1).

## 4. SUMMARY OF ORIGINAL PUBLICATIONS

### 4.1. Computational study of cesium cation interactions with model compounds of humic substances

In Articles I and II we discuss the intrinsic Cs<sup>+</sup> complexation (CsCA-s, CsCB-s) and the most typical binding modes to 50 organic compounds. These primarily include unsubstituted aromatic, substituted (hetero)aromatic as well as some aliphatic compounds – a variety of which can be envisaged as simple constituents to macromolecular humic and fulvic substances. To mimic the natural soil pH conditions under which at least some of the acidic groups can be considered deprotonated, the Cs<sup>+</sup> complexation to carboxylate and phenolate anionic systems were also studied.

The weakest interactions among studied bases towards metal cation involve Cs<sup>+</sup> complexation with unsubstituted aromatic compounds (CsCA constantly around 10 kcal/mol). Within these  $\pi$ -type complexes, Cs<sup>+</sup> binds via the  $\pi$ -electron density and is located about 3,5 Å above the plane of the aromatic ring(s). There is a characteristic lengthening of C-C bond distances (at least by 0,003 Å) upon complexation with Cs<sup>+</sup>, consistent with donation of electron density from the ring to the cation. It may be concluded that Cs<sup>+</sup> cation can move quite freely above the aromatic rings in condensed ring aromatics. There is little enthalpy difference (up to 0,2 kcal/mol) in Cs<sup>+</sup> attachment to different benzene rings in condensed aromatic systems (anthracene, phenanthrene, etc.).

Cs<sup>+</sup> binding is stronger and spanning a wider range (CsCA between 10,6–27,1 kcal/mol) for substituted aromatics. Generally Cs<sup>+</sup> is bound to the electronegative atoms, possibly via cation-lone pair interaction, with the common substituents. In fact, no  $\pi$ -type bonding corresponding to stable conformations of the complexes were detected. In overall, the carboxylic (–COOH) group seems to be the strongest binding center for Cs<sup>+</sup>, followed by sp<sup>2</sup> nitrogen atom, hydroxylic (–OH) and carbonyl (=O) groups. This can be roughly seen in the decreasing CsCA values for the following compounds: benzoic acid (CsCA 15,1 kcal/mol), 3-quinolinol (14 kcal/mol), hydroquinone (13,6 kcal/mol) and quinone (12,8 kcal/mol).

The metal cation binds to carboxylic group, the most common substituent within the set of compounds essentially in two ways. Cs<sup>+</sup> may be aligned along the axis of the carbonyl group and the hydroxylic proton is in cis position relative to the carbonyl group (as in gallic acid-Cs complex, illustrated on Figure 2 below). Alternatively Cs<sup>+</sup> may lie at almost equal distance from both oxygen atoms, bisecting the O-C-O angle while the hydroxylic proton in trans position, respectively (as in vanillic acid-Cs complex, Figure 2). In general, there tend to be a preference for the first type of binding pattern (i.e. the linear complex) but the difference in enthalpies are rather small (0.04–1,4 kcal/mol for

the series of methyl substituted aromatic acids) and thus both conformers of the complexes may be of similar abundance.

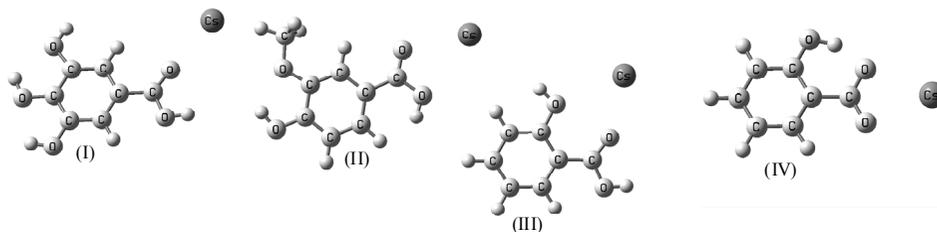
Adjacent ortho positions of electronegative functional groups can result in metallated chelate complexes where  $\text{Cs}^+$  is more or less symmetrically between two oxygen atoms of neighbouring oxygen groups like in salicylic acid (Figure 2, adjacent  $-\text{COOH}$  and  $-\text{OH}$  groups), methyl salicylate (adjacent ester and  $-\text{OH}$  groups), pyrogallol and catechol (adjacent  $-\text{OH}$  groups). This may lead to enhanced binding of  $\text{Cs}^+$ , an example being o-phtalic acid (CsCA 24,4 kcal/mol) vs. p-phtalic acid (CsCA 15,7 kcal/mol) for the lack of chelate type binding in the latter, obviously because of greater carbonyl oxygen distances.

Bidentate complexes are also common for aliphatic compounds if functional groups as binding centers are in close proximity, or favorable conformational preferences upon complexation with the metal cation. The CsCA-s of the aliphatic compounds range from 13,4 to 25,6 kcal/mol. A good example of enhanced  $\text{Cs}^+$  binding by adjacent carboxylic functions (resulting in a chelate complex) is maleic acid (CsCA 21,9 kcal/mol). The fumaric acid, which is the trans isomer of maleic acid with unfavourable location of carboxylic groups for bidentate binding of  $\text{Cs}^+$ , forms a much weaker complex (CsCA 13,4 kcal/mol).

The distances between  $\text{Cs}^+$  and the corresponding binding centers of aliphatic and substituted (hetero)aromatic compounds are within 2,8–3,6 Å. In overall, the bonding of  $\text{Cs}^+$  to neutral bases can be considered electrostatic. This is supported by the NBO charge analysis, which reveals that  $\text{Cs}^+$  carries a positive charge from 0,9 to 0,99 a.u.

The CsCA-s of anionic substituted aromatic compounds range from 89,4 to 111,6 kcal/mol and for anionic aliphatic compounds from 91,1 to 114,8 kcal/mol – thus being roughly 5 times higher than their neutral counterparts. Among the carboxylic anions the  $\text{Cs}^+$  binds electrostatically to the carboxylate group, almost bisecting the O-C-O angle and the distances between  $\text{Cs}^+$  and the oxygen atoms are slightly shorter (around 2,8–2,9 Å) as compared to neutral bases. The internal hydrogen bond by nearby hydroxylic or carboxylic protons to the carboxylate group (both in the free anion as well as within the metallated complex) are preserved, if possible (as in salicylate- $\text{Cs}^+$  complex, Figure 2). It was, however, observed that internal hydrogen bonding may also lead to slightly lower CsCA and CsCB values.

The  $\text{Cs}^+$  affinities and basicities of phenolate type anions were calculated for deprotonated hydroxyl substituted organic compounds without carboxyl functions (pyrogallol, catechol, 2-hydroxyacetophenone etc.) and are comparable with the rest of the compounds where the carboxylate anion acts as a basicity center for  $\text{Cs}^+$ .



**Figure 2.** The optimized structures of cesium cation complexes with gallic acid (I), vanillic acid (II), salicylic acid (III) and salicylate anion (IV)

## 4.2. Investigations of cluster ions formed between cesium cation and benzoic, salicylic and phthalic acids by density functional theory calculations.

A part of the computational studies in Article III is concerned with the validation of the chosen computational procedure. All calculations have been performed at the density functional level (for details, see the "Computational Method" chapter or Article III).

The CsCA-s and CsCB-s were calculated for a small number of substituted aromatic compounds and compared with available experimental data as well as earlier theoretical calculations at the MP2 level using a large basis set (6-311++G(2d,2p)) for C, H, O, F and N. Our calculated CsCA values are systematically lower by 3 kcal/mol than the experimental ones. This also holds for higher level MP2 results, although the discrepancies are somewhat smaller (around 2 kcal/mol). As an additional test, the CsCA-s and CsCB-s were calculated for small neutral ligands ( $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{CO}_2$ ) and anions ( $\text{F}^-$ ,  $\text{OH}^-$ ), and compared with experimental values. Again our calculated CsCA-s are smaller than experimental, with an overall error of around 2 kcal/mol. A very good match between theory and experiment (within 0,1 kcal/mol) was found for the CsCA of  $\text{H}_2\text{O}$ . In conclusion, the chosen computational level can be considered fairly good in terms of quality vs. efficiency and being well suited for the systems under study.

In the main theme of the project, the calculations were performed to obtain gas-phase Cs affinities and basicities of organic acids, AH (A= benzoic(Bz), salicylic(Sal), phthalic acid (PhtH), phenol); their deprotonated anionic forms ( $\text{A}^-$ ) and cesium salts (i.e. ion pairs in the form  $\text{Cs}^+\text{A}^-$ ). As expected, the strongest  $\text{Cs}^+$  affinities are observed for anions, being around 100 kcal/mol. The strength of  $\text{Cs}^+$  binding to cesium ion pairs is intermediate between that of anionic and neutral systems, and comparable to binding to cesium nitrate ( $\text{CsNO}_3$ ). On the basis of the order of calculated  $\text{Cs}^+/\text{Cs}^+\text{A}^-$  interaction energies

relative to that of  $\text{Cs}^+/\text{Cs}^+\text{NO}_3^-$ , the formation and existence of such small clusters in the process of the fragmentation of larger ion adducts in the general form  $[(\text{CsNO}_3)_n(\text{CsA}^-)_m\text{Cs}]^+$  may be estimated. The latter adducts are generally formed during the electrospray ionization of the mixed solutions containing cesium nitrate and the organic acid of interest. According to studies, the interaction energy of  $\text{Cs}^+$  with  $\text{CsNO}_3$  is larger than the interaction energies with  $\text{CsBz}$  and  $\text{CsSal}$  but lower than the interaction of  $\text{Cs}^+$  with  $\text{CsPhtH}$ . This agrees with experimentally observed  $\text{Cs}^+/\text{Cs}^+\text{NO}_3^-$  ion pair abundances in the ES-MS spectra. For salicylic and benzoic acid, cluster ions comprised of several  $\text{CsNO}_3$  ion pairs were in significant abundance while for phthalic acid the similar clusters were almost not observed. Despite a stronger interaction between  $\text{Cs}^+$  and cesium phenolate relative to  $\text{Cs}^+/\text{Cs}^+\text{NO}_3^-$ , no clusters involving PhOCs were detected in the ES-MS spectrum. This controversy can be attributed to a low concentration of phenolate ions in solution due to fact that phenol is significantly weaker acid than any of the carboxylic acids used in this study.

### **4.3. A theoretical study of gas-phase basicities and proton affinities of alkali metal oxides and hydroxides**

In article IV we present our extensive study of gas-phase basicities and proton affinities (PA) of heavier alkali metal (K – Cs) oxides and hydroxides – one of the strongest "traditional" bases in the gas phase, utilizing different computational schemes. The calculations were carried out at the DFT level with PBE0 and B3LYP functionals and different effective core potentials for alkali metals. The basis set accompanying the ECP-s for  $\text{Cs}^+$  was augmented with a set of Glendening's polarization functions. The Dunning basis set of double-zeta quality was used for oxygen and hydrogen atom. Furthermore, the effect of additional set of polarization and/or diffuse functions on oxygen and hydrogen atom on the basicities, proton affinities and geometries of the relevant species was studied. The results were compared with rather scarce experimental data of gas phase basicities and affinities available for these compounds. It is generally accepted that the basicities and proton affinities of the alkali hydroxides are more precisely determined from experiment and thus more amenable for comparison and validation of computational models.

As a rule, the calculated PA-s and basicities were significantly overestimated as compared to the available experimental data, though in better overall agreement for the alkali hydroxide series. It was concluded that addition of polarization and diffuse functions to oxygen atom markedly lowered the values of PA-s and basicities, thus bringing them closer to experimental values. The best overall agreement was achieved with the B3LYP functional in combination with small core CRENBL and Stuttgart ECP-s for alkali cations. The

geometries of both metal oxides and hydroxides were linear at all levels of computation which is consistent with similar spectral observations. The best agreement with calculated and experimental bond lengths was achieved with the PBE0 functional, including polarization functions on all atoms and additionally a set of diffuse functions on the oxygen atom.

## 5. CONCLUSIONS

The primary objective of the current thesis was to reveal the intrinsic binding modes and energetics of Cs cation complexation (affinities and basicities) to selected (un)substituted (hetero)aromatic and aliphatic compounds by means of theoretical gas-phase calculations. Data on Cs<sup>+</sup> binding to these compounds as constituent units of humic and fulvic substances (primarily responsible for the mobility of radioisotope <sup>137</sup>Cs in the biosphere) serve as a link toward a detailed understanding of these interactions within more complex macromolecular systems. The calculations were performed at the density functional level, using a Stuttgart-Dresden relativistic effective core potential on Cs<sup>+</sup>. Based on the validation of the selected computational model, the theory may be expected to underestimate experimental CsCA-s and CsCB-s with an average error of 2–3 kcal/mol.

The weakest interaction involves Cs<sup>+</sup> binding to the unsubstituted aromatic systems and  $\beta$ -naphthol, resulting in a metal cation- $\pi$  complex. The CsCA-s of these neutral ligands are constantly around 10 kcal/mol. In case of variously substituted aromatic and aliphatic compounds the binding is always stronger and spanning a wider range (CsCA-s 10–27 kcal/mol). Most commonly, Cs<sup>+</sup> forms a more localized type of bond with various substituent groups. The variation in the binding strength involves the type of functional group (the carboxyl group seemed to be the most attractive binding (basicity) center among the studied compounds in our case) but also a favourable formation of bidentate Cs<sup>+</sup> complexes, which in several cases lead to stronger binding of the cesium cation.

It is known that metal cation binding to natural organic matter occurs essentially via carboxylic functions which are to a large extent dissociated at usual soil pH. Most of the calculations involving Cs<sup>+</sup> cation complexation with the deprotonated anionic ligands were devoted to carboxylates but some examples of interactions between phenolate oxygen and Cs<sup>+</sup> were also considered. In most cases, the Cs<sup>+</sup> binds to carboxylate anions in a symmetric bidentate way, bisecting the O-C-O angle. The CsCAs are in the range 90 to 115 kcal/mol.

In overall, cesium cation binding to neutral and anionic molecules is considered to be largely electrostatic with a very little degree of charge transfer. This is also supported by the evidence that the metal cation can interact with more than one electronegative atom by forming stable chelate-type complexes.

The gas phase CsCA-s and CsCB-s of Cs<sup>+</sup> salts (i.e. ion pairs in the form Cs<sup>+</sup>A<sup>-</sup> where A<sup>-</sup> is a benzoate, salicylate or phtalate anion, respectively) were studied. The CsCA-s range between 27–40 kcal/mol, apparently higher than those for substituted aromatic and aliphatic compounds. The order of calculated Cs<sup>+</sup>/Cs<sup>+</sup>A<sup>-</sup> interaction energies in the gas phase lends support to the trend

observed for the formation of such small clusters during the ES ionization process.

Finally, some overall comments regarding  $\text{Cs}^+$  complexation to humic and fulvic substances can be made. Most likely, cesium cation binding to deprotonated (carboxylate) groups is expected to dominate, though weaker interactions involving carboxylate salts or  $\text{Cs}^+$  binding to neutral compounds via their functional groups (ion-(induced)dipole interactions) may be of significant abundance depending on the natural soil pH conditions.

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## SUMMARY IN ESTONIAN

### DFT arvutus Cs katiooni interaktsioonidest humiinühenditega orgaaniliste mudelühendite baasil

Tseesiumi kui radioaktiivse raskmetalli ladestumine ja transport biosfääris on olulisel määral reguleeritud looduslikes vetes ja mullakihis leiduvate humiin- ja fulvohapete poolt. Seetõttu on oluline teada Cs-katiooni keemilise seostumise mehhanisme ja tugevust nimetatud looduslike makromolekulaarsete ühenditega.

Käesoleva töö peamiseks eesmärgiks oli uurida leelismetalli Cs katiooni seostumise tugevust (aluselisus(CsCB), afiinsus(CsCA) ja metall-ligand komplekside geometriaid ca. 50 asendamata ja asendatud aromaatsete ning alifaatsete ühendite näitel. Ühendite valikus lähtuti sellest, et enamikke neist võiks vaadelda kui mudelühendeid humiin- ja fulvohapetele. Tulemused põhinevad kvantkeemilistel tihedusfunktsionaali teooria arvutustel gaasifaasis, mistõttu tuleb rõhutada töö pigem fundamentaalset kui praktilist käsitlust ja tähtsust.

Valitud arvutusmeetodi valideerimine, tuginedes eksperimentaalsetel afiinsuste väärtustel väikesele arvule testühenditele näitas, et teoreetilised väärtused on keskmiselt 2–3 kcal/mol alahinnatud eksperimendi andmetega võrreldes.

Kõige nõrgem interaktsioon (CsCA ca. 10 kcal/mol) realiseerub asendamata aromaatses süsteemides (benseen, antratseen, fenantreen jne.) kus toimub Cs<sup>+</sup> seostumine aromaatses tuuma tasandi kohale (~ 3,5Å) π-elektronsüsteemi kaudu. Asendatud aromaatsete (karboksüül, hüdroksüül, ester rühmad) kui ka alifaatsete ühendite korral moodustub pigem lokaliseerunud side Cs katiooni ja vastavate asendusrühmade elektronegatiivsete aatomite (vabade elektronpaaride) vahendusel. Selline side on reeglina tugevam kation-π interaktsioonist ja CsCA väärtused ulatuvad valitud ühendite korral ca. 27 kcal/mol-ni. Leiti et Cs<sup>+</sup> seostumise afiinsus sõltub funktsionaalrühmast (reeglina suurem karboksüül-rühma korral, võrreldes hüdroksüül-, ketorühmaga või N aatomi kui aluselise tsentriga). Sõltuvalt asendusrühmade suhtelisest asendist või ühendite soodsast konformatsioonist võivad paljudel juhtudel realiseeruda multidentaatsed metallokompleksid, kus esineb Cs<sup>+</sup> interaktsioon enama kui ühe elektronegatiivse aatomiga, mis mitmetel juhtudel seotud ka kõrgema CsCA väärtustega. Samas näitas NBO laenguanalüüs, et Cs<sup>+</sup> side antud ühenditega on valdavalt elektrostaatiline ning elektrontiheduse ülekannet tseesiumi katioonile kompleksis praktiliselt ei esine.

Samuti uuriti ka vastavate ühendite deprotoneeritud anioonsete vormide (peamiselt karboksülaatide) tseesiumafiinsust ja aluselisust. Vastavad väärtused osutusid ca. 5 korda suuremateks võrreldes laenguta neutraalühenditega, jäädes CsCA vahemikku 90–115 kcal/mol. Tüüpiline on Cs<sup>+</sup> seostumine sümmeetriliselt karboksülaatanioonile, kus C-O vahekaugused ~ 2,8–2,9Å.

Olulist rolli metallioonide sidumistsentritena looduslikes orgaanilistes ühendites võivad omada juba primaarsel komplekseerumisel tekkinud metall katioon-anioon ioonpaarid. Antud töö raames uuriti ka  $\text{Cs}^+$  seostumise tugevust ( $\text{CsCA}$ ,  $\text{CsCB}$ )  $\text{Cs}$ -sooladele ( $\text{Cs}^+\text{A}^-$ ), kus happejäägina ( $\text{A}^-$ ) bensoaat, salitsülaat ja ftalaat.  $\text{Cs}^+$  afiinsuste väärtused jäid vahemikku 27–40 kcal/mol, olles kõrgemad vastavate neutraalvormis hapete  $\text{CsCA}$  väärtustest.

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## **PUBLICATIONS**





Peeter Burk, Jaana Tammiku-Taul, Sven Tamp, Pierre-Charles Maria,  
Jean-François Gal, Charly Mayeux, Computational study of cesium cation  
interactions with model compounds of humic substances,  
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# COMPUTATIONAL STUDY OF CESIUM CATION INTERACTIONS WITH MODEL COMPOUNDS OF HUMIC SUBSTANCES

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## ABSTRACT

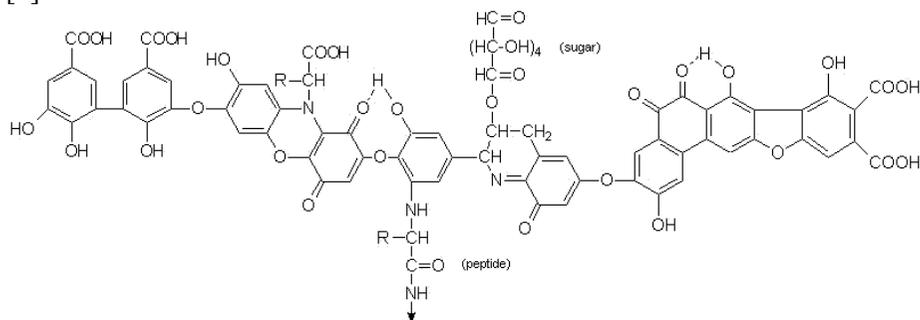
Density functional theory (DFT) calculations were carried out on the interactions of cesium cation with small neutral or anionic species taken as model systems for humic substances. Different cesium cation complexation patterns are discussed. The gas-phase cesium cation affinities (CsCAs) and basicities (CsCBs) for 50 simple neutral compounds (mainly aromatic) and 35 anionic compounds are reported. As expected, the strongest CsCAs are observed for anions. The corresponding quantities are approximately by 5 times higher than for the neutral counterparts, being around 100 kcal/mol. The weakest cesium cation bonding is observed in the case of unsubstituted aromatic systems (around 10 kcal/mol).

*Keywords:* Cesium cation basicity; Cesium cation affinity; Humic substances; DFT calculations

## 1. INTRODUCTION

The mobility and bioavailability of metal ions (for example toxic metals such as Cd, Hg, and radioactive isotopes, such as those of Cs) in the environment is strongly influenced by their complexation with humic and fulvic substances (HS, FS) [1,2], which constitute an important part of soil organic matter (SOM). Humic substances are generally thought to be complex aromatic (about 19–25% aromaticity) oxidized macromolecules coupled with amino acids, sugars, and peptides, being linked by carbon and oxygen atoms. They have a large range of

molecular weights that may vary from a few hundreds Da for fulvic acids to over 2 kDa for humic acids. A variety of structural models for humic acids have been proposed [3,4] and one of them is presented in Scheme 1 as an example [4]:



**Scheme 1.** One of the proposed structural models for humic acids.

Several functional groups have been identified in HS, e.g.  $-C=O$ ,  $-COOH$ ,  $-OH$ , as well as nitrogen, phosphorus, and sulfur containing groups [4,5]. In fact, some of these (in particular  $-COOH$  and  $-OH$ ) groups play an important role in creating strong binding sites (especially when ionized and favorably situated to constitute polydentate potential chelators) for certain metal cations [3]. At soil natural pH values the most acidic functional groups are deprotonated, drastically enhancing the metal cation binding ability by these natural substances and consequently the metal loading in SOM.

Although the Chernobyl accident took place in 1986, the radionuclide cesium-137, a major fall-out contamination of that accident, is still persistent in the environment. Soil activities of  $^{137}\text{Cs}$  in excess of  $30 \text{ Bq/cm}^3$  still persist over large areas in Russia, Belarus, and Ukraine, as well as some European regions (French Alps, northern Finland, etc.) that were also polluted by radioactive cesium [6,7].

Even as a stable isotope  $^{133}\text{Cs}$ , cesium is toxic to plants – it is taken up by roots and mainly accumulated in the rapidly growing parts (roots, leaves, and other selected tissues and organs) [8,9], causing a decrease in the growth of biomass, in tissue hydration and potassium starvation via competitive interaction with vital  $\text{K}^+$  binding sites in proteins [10], suppressing their activities. But the main problem is the deposition of  $^{137}\text{Cs}$  in the biosphere, and its subsequent transfer to the terrestrial food chain through fauna, that poses a serious radiological hazard. Certain crops (e.g. onion, cress, and mushrooms) are more prone to accumulation of cesium. Elevated uptake of this radionuclide by mushroom ‘bay boletus’ has been attributed to norbadione A, a natural substance comprised of carboxylate and hydroxyl groups in favorable positions, exhibiting highly selective chelating power towards  $\text{Cs}^+$  [11] as shown by theoretical calculations. In fact, scientific research projects are being carried out

to find possible ways of utilizing plants for phytoremediation of highly polluted areas [12].

The computational molecular modeling (ab initio as well as mechanics) techniques have become in modern geochemistry an integral part of SOM research, often complementing “real world” field geochemical studies and laboratory experiments. A critical stage in this theoretical approach is a realistic description of the system to be modeled. Structural models for SOM have been built using a molecular modeling approach [13]. Theoretical calculations coupled with FTICR mass spectrometry and NMR spectrometry data allowed to set up a more reliable picture of humic acid [14,15,16].

A variety of organic compounds (the most common are derivatives of phenol and polyphenols, benzoic and phthalic acids) have been proposed as simple analogue models, mimicking specific interaction sites for complexation with metal cations (including radioactive cesium) in HS macromolecules [17].

Amunugama and Rodgers have employed threshold collision-induced dissociation techniques and theoretical studies (MP2 and B3LYP methods) to determine the bond dissociation energies and geometries of alkali metal cations (including Cs<sup>+</sup>) mono and bis complexes of toluene [18], fluorobenzene [19], aniline [20], phenol [21], anisole [22], and naphthalene [23]. Generally, an electrostatic nature of the Cs<sup>+</sup> bonding, specifically an ion/(induced) dipole (or ion/quadrupole) interaction was documented for these complexes. As regards to the corresponding computational results, the theory underestimated the bond dissociation energies of complexes between Rb<sup>+</sup> or Cs<sup>+</sup> cation and ligands by 0.5...3 kcal/mol and MP2 was found superior to the B3LYP method.

Hoyau and Ohanessian have studied the complexes formed by alkali metal cations (Li<sup>+</sup>–Cs<sup>+</sup>) and glycine using ab initio quantum chemical methods. Computed binding energies showed a decrease of cation affinities with the increase of radius of cation [24].

The formation of cesium cation clusters with aromatic (phenol, benzoic, salicylic, and phthalic acids) and simpler (maleic, fumaric, oxalic, and malonic acids) subunits of HS in water/methanol solutions by means of electrospray ionization mass spectrometry (ESI-MS) were conducted by Maria, Gal et al. [25,26]. Calculations of structures and bonding energetics (thermodynamic basicities and affinities) of Cs<sup>+</sup> cation complexes with these compounds were carried out using DFT methods, and compared with the stability of the Cs<sup>+</sup> adducts.

For more accurate prediction of Cs<sup>+</sup> cation binding to natural organic acids, fundamental gas-phase data revealing intrinsic intermolecular forces between the metal cation and ligand-molecule for a broader range of compounds is clearly lacking. Our recent review on the cesium cations report about 20 Cs<sup>+</sup> cation affinities (CsCAs) or basicities (CsCBs) for neutral organic compounds, and only 10 for inorganic anions [27]. The aim of the current research was to study the Cs<sup>+</sup> cation complexation with the simple aromatic and aliphatic

organic compounds presented in Fig. 1, which could be pictured as building blocks of macromolecular humic-fulvic substances. In this respect, the  $\text{Cs}^+$  cation affinities and basicities, as well as typical binding patterns and charge distribution of the complexes were studied using computational techniques. In addition,  $\text{Cs}^+$  cation complexation with the anionic forms of some of the above-mentioned ligands was also studied in the same manner.

Certain precaution should be expressed towards predicting the complexing ability of HS with the cesium cation on the basis of gas-phase CsCA of simple organic molecule mimicking certain functionalities of humic acids. Besides the heterogeneous nature of real complexation equilibria between  $\text{Cs}^+$  and HS, it is also due to an extreme complexity of the structure of humic matter, which may be altered by the medium (pH change, ionic strength, polarity) and metal loading. Nevertheless, reliable data for smaller molecules are needed before moving further to more complex models. The authors hope that the present work should provide basic introductory data about the subject.

## 2. COMPUTATIONAL DETAILS

All calculations were carried out using the Gaussian 03 [28] program package. The B3LYP hybrid density functional [29], which includes Becke's exchange functional and the correlation part due to Lee, Yang and Parr was used with Dunning-Huzinaga valence double-zeta basis set augmented with polarization functions (D95V(d,p)) [30] on hydrogen and first period atoms (C, N, O). Diffuse basis functions [31] were added to all non-hydrogen atoms to allow for better description of the distribution of electron density. For calculations involving the cesium cation, the Stuttgart-Dresden (SDD) effective core potential [32] and the accompanying basis set was used. A single set of polarization (d) functions was added to the SDD basis for Cs atom with an exponent of 0.19 as suggested by Glendening et al. [33].

Full conformational searches, geometry optimizations, and vibrational analyses were performed for the neutral and anionic systems and their complexes with  $\text{Cs}^+$ . All stationary points were found to be true minima (NImag=0). Vibrational frequency analysis was used to obtain the thermodynamic data (enthalpies and Gibbs free energies). The natural bond orbital (NBO) charges [34] were calculated for some of the studied species.

The cesium cation affinities and basicities were computed according to the following thermodynamic equilibrium (B = neutral or anionic base):



where  $n = 0$  or  $-1$  (for neutral or anionic systems, respectively). The  $\text{Cs}^+$  cation basicity (CsCB) is associated with the negative Gibbs free energy change

(CsCB =  $-\Delta G_{(1)}$ ) and cesium cation affinity (CsCA) with the negative enthalpy change (CsCA =  $-\Delta H_{(1)}$ ) of the association reaction. The calculated CsCAs and CsCBs, at the reference temperature of 298.15 K, for neutral and anionic compounds are given in Table 1 and 2, respectively. Raw computational data (energies, thermochemical data, and geometries) are available from authors upon request.

### 3. RESULTS AND DISCUSSION

#### 3.1. Geometries of Cs<sup>+</sup>/neutral ligand complexes and the corresponding affinities and basicities

The structures of neutral molecules, used in a current work as simple models of humic acids, are presented in Fig. 1 and the corresponding gas-phase cesium cation affinities and basicities are given in Table 1.

The CsCAs of *unsubstituted aromatic molecules* lie in the narrow range: 9.8...10.6 kcal/mol (1 kcal/mol = 4.184 kJ/mol). These aromatic systems interact with Cs<sup>+</sup> preferably via their  $\pi$ -systems (ion/induced dipole  $\pi$ -type interaction, Fig. 2a). There are very small energy differences between cation attachment positions above the central or peripheral benzene rings at a distance  $\sim 3.5$  Å (1 Å = 0.1 nm) ( $\Delta H = 0.06...0.25$  kcal/mol), which lead to the conclusion that Cs<sup>+</sup> binds to the different benzene rings in the studied compounds with approximately equal probability in contrast with results obtained by Gal et al. for Li<sup>+</sup> affinities [35], where energy differences in a 2 kcal/mol range were found in case of anthracene and phenanthrene.

The range of calculated CsCAs for *substituted (hetero)aromatic compounds* is rather large: 10.6...24.4 kcal/mol. For most of the studied systems Cs<sup>+</sup> is preferentially attached to the oxygen atoms of carboxyl (–COOH) or hydroxyl (–OH) group. When both functional groups are present in the compound, the carbonyl oxygen is the preferred binding centre (e.g. in 3-hydroxybenzoic acid, 3,4-dihydroxybenzoic acid, *trans*-3-hydroxycinnamic acid, *trans*-caffeic acid, *trans*-ferulic acid, gallic acid, and 2-hydroxyacetophenone). 3-hydroxycinnamic, caffeic, and ferulic acids can also exist in a *cis*-form. However, the *cis*-forms are less stable both as neutral acids (by 2.7...7.3 kcal/mol) and complexes with cesium cation (by 2.5...5.1 kcal/mol) compared to the *trans*-forms. The above-mentioned type of Cs<sup>+</sup> binding pattern is illustrated on the basis of gallic acid in Fig. 2b, where the Cs<sup>+</sup> is bonded only to the carbonyl oxygen (C, O, and Cs<sup>+</sup> are in almost linear arrangement) and the hydroxylic proton is in *cis* position relative to the carbonyl group. The above-described complexation is also favored due to the presence of carboxyl group(s) (e.g. in benzoic acid and *p*-phthalic acid). But aromatic carboxylic acids can complexate with Cs<sup>+</sup> in another way – the cation is interacting with the

lone-pairs of both oxygen atoms of the same carboxyl group and is lying at almost equal distance from these atoms. For example, *m*-phthalic acid and vanillic acid (Fig. 2c) give such kind of bidentate complex. Both type of complexes are found for the series of dimethylbenzoic acids and 2,4,6-trimethylbenzoic acid. The enthalpy differences between these two kinds of complexes are ranging from 0.04 kcal/mol (2,6-dimethylbenzoic acid) to 1.4 kcal/mol (3,4-dimethylbenzoic acid) in favor of a linear complex. For 2,4,6-trimethylbenzoic acid, which is sterically the most crowded with three relatively bulky methyl groups, the bidentate complex is only by 0.12 kcal/mol more stable compared to the unidentate structure. However, there is no general conclusion that can be drawn about the energetically more favorable structure.

The above-mentioned *trans*-ferulic, vanillic, and gallic acids are also able to form a bidentate complex in a way where Cs<sup>+</sup> is interacting with the other(s) adjacent functional group(s) (–OH, –OCH<sub>3</sub>) but the complexation enthalpies are, respectively, by 10.2, 5.5 and 1.4 kcal/mol less stable than the Cs<sup>+</sup> bonding to carbonyl group.

The tendency for the formation of chelate-type complexes in case of substituted aromatic compounds is greater when an electronegative functional group is in ortho position relative to another such functional group. In these chelate-type complexes the most favorable position for Cs<sup>+</sup>, if possible, is more or less symmetrically between two oxygen atoms of neighboring oxygen-containing group like in salicylic acid (Fig. 2d, adjacent –COOH and –OH groups), *o*-phthalic acid (Fig. 2e, adjacent –COOH groups), methyl salicylate (adjacent –COOCH<sub>3</sub> and –OH groups), pyrogallol and catechol (Fig. 2f, adjacent –OH groups).

The binding pattern via single oxygen of a carbonyl group (the angle C-O-Cs<sup>+</sup> is close to linear) is typical for quinone, coumarin, chromone, 3-hydroxyxanthone, and kojic acid.

The complexation of Cs<sup>+</sup> with  $\beta$ -naphthol and 3-quinolinol is exceptional. In the case of  $\beta$ -naphthol, the Cs<sup>+</sup> is preferentially located above one of the benzene rings and is not directly interacting with the hydroxyl group. The difference in enthalpy of bonding between the benzene rings in  $\beta$ -naphthol is only 0.5 kcal/mol, and the interaction of Cs<sup>+</sup> with the oxygen atom of hydroxyl group is only by 0.8 kcal/mol weaker. In the complex of 3-quinolinol the cation attaches to the nitrogen atom (Fig. 2g), which seems to be a stronger basic center by 6.5 kcal/mol ( $\Delta H$ ), as compared to the oxygen atom. The distances between Cs<sup>+</sup> and the corresponding binding centers of substituted (hetero)aromatic compounds are 2.8...3.6 Å.

The CsCAs for *aliphatic compounds* are in the 13.4...25.6 kcal/mol range. In most cases a bidentate complex is favored, except for acetic, propionic, and fumaric acids, where Cs<sup>+</sup> is connected with the carbonyl oxygen of the carboxyl group (the C-O-Cs<sup>+</sup> angle is almost linear). One of the possible adducts of Cs<sup>+</sup> has again a symmetric binding with two carbonyl oxygens of different carboxyl

groups like in oxalic, malonic (Fig. 2h), succinic acids, and acetylacetone (in its keto form; the most stable tautomer for acetylacetone itself is the enol form) which gives the most stable complex. Another possibility is the Cs<sup>+</sup> location close to two oxygen atoms of carbonyl and hydroxyl groups of the same carboxyl group (e.g. in diethylmalonic, maleic (Fig. 2i), 3-aminoglutaric acids) or of the different carboxyl groups (e.g. in 2-hydroxy-2-methylpropionic, 3-hydroxybutyric acids). The Cs<sup>+</sup> interacts even with three oxygen atoms in malic acid forming polydentate complex (Fig. 2j). All the distances between cesium cation and oxygen atoms are in a range of 2.9...3.4 Å.

There is a very little amount of charge transfer in the Cs<sup>+</sup> ion/molecule complexes, thus, the association between Cs<sup>+</sup> and the neutral molecule can be considered as electrostatic. To support this, the NBO analysis revealed that the Cs<sup>+</sup> carries a positive charge from 0.9 up to 0.99 electron unit in all the studied Cs<sup>+</sup>/neutral molecule complexes. This is in full agreement with the results of Rodgers for all M<sup>+</sup>(C<sub>6</sub>H<sub>5</sub>X) complexes (M = alkali metal from Li to Cs) [18–23]. It seems from those studies that the partial charge does not depend markedly on the type of alkali metal and substituent groups in the aromatic benzene ring.

The primary conclusions about CsCAs (and CsCBs) as regard to the complexation patterns are the following:

1. The Cs<sup>+</sup> cation exhibits the weakest affinity towards the unsubstituted aromatic systems and β-naphthol. The CsCAs are constantly around 10...11 kcal/mol for those compounds. The formed complexes are of pure π-type.
2. The Cs<sup>+</sup> cation interaction with the oxygen atom of a hydroxyl group (e.g. in hydroquinone) and the sp<sup>2</sup> nitrogen atom (e.g. in 3-quinolinol) is usually weaker compared to the oxygen atom of carbonyl or carboxyl group.
3. The bidentate complexes are not always more stable than the unidentate complexes. The corresponding values vary in a large range, from 13.3 to 25.6 kcal/mol for CsCAs (respectively salicylic acid and 3-aminoglutaric acid).
4. It is easier to compare similar compounds, for instance in the series of phthalic acids it can be realized that the CsCA is highest in case of *o*-phthalic acid, for which the bidentate-type complex is the strongest. This particular type of complex is weaker for the *m*-phthalic acid and completely absent for the *p*-phthalic acid because of a greater distance of two carbonyl oxygen atoms. Obviously, this results in a continuous lowering of the affinities in this series. The CsCAs are respectively 24.4, 19.6 and 15.7 kcal/mol in the series ortho, meta, para. Moreover, the stabilization due to the bidentate binding and intramolecular hydrogen bond is particularly apparent in case of maleic acid (*cis*-isomer of 2-butenedioic acid), where the Cs<sup>+</sup> can simultaneously interact with

adjacent oxygen atoms of carboxyl group. The corresponding CsCA is 21.9 kcal/mol, that is almost 8.5 kcal/mol higher than in case of fumaric acid (*trans*-isomer of 2-butenedioic acid) for lack of this kind of stabilization.

### 3.2. Geometries of Cs<sup>+</sup>/anion ligand complexes and the corresponding affinities and basicities

Due to slightly acidic natural pH values of soils, it is expected that acidic functional groups (–COOH, –OH, –SH, etc.) of SOM macromolecules may be weakly to totally dissociated, thus, contributing significantly to metal complexation and transport in the biosphere. Hence, complexes of Cs<sup>+</sup> cation with anions of organic acids were studied and the calculated CsCAs and CsCBs are listed in Table 2. The corresponding quantities are approximately by 5 times higher than for the neutral counterparts, being in the range of 100 kcal/mol. In cases when acid had both hydroxyl and carboxyl groups, only carboxylate anions were considered because the carboxyl is much more acidic both in the gas phase [36] and in solution [25].

The CsCAs for anionic *substituted aromatic compounds* range from 89.4 to 111.6 kcal/mol and for anionic *aliphatic compounds* from 91.1 to 114.8 kcal/mol. The Cs<sup>+</sup> binds in a rather similar way to almost all anions studied in this work: the complex is formed between carboxylate group of the acid and Cs<sup>+</sup> in a symmetric bidentate way, i.e. the cesium cation interacts electrostatically with both oxygens of the carboxylate group. The intramolecular hydrogen bond tends to be preserved whenever possible, for example by a nearby hydroxyl group (e.g. in salicylate in Fig. 3a) or carboxylic proton (e.g. in *o*-phthalate in Fig. 3b). The hydrogen bond donor group may also be in a farther position, for instance the amino group in 3-aminoglutarate (Fig. 3c). The distances between Cs<sup>+</sup> and the oxygen atoms are about 2.8...2.9 Å.

A notable exception is the complex between Cs<sup>+</sup> and oxalate anion, where the cation interacts with two oxygen atoms, although each binding site pertains to the different carboxyl groups (Fig. 3d). This type of complex is more favorable by 3.4 kcal/mol ( $\Delta H$ ) compared with the binding to a single carboxylate group in a symmetrical way as usual, due to the close proximities of adjacent carboxyl groups.

Examples of phenolate anion Cs<sup>+</sup> affinities and basicities can be found for hydroxyl substituted organic compounds without carboxyl functions, e.g. anionic methyl salicylate, pyrogallol, catechol, hydroquinone, and 2-hydroxyacetophenone. The CsCA and CsCB values are comparable with the rest of the compounds where the carboxylate anion acts as a basicity centre for Cs<sup>+</sup>. The cesium cation is also located more or less symmetrically between phenolate oxygen and the oxygen of –COOCH<sub>3</sub> or –COCH<sub>3</sub> groups like for the anionic forms of methyl salicylate (Fig. 3e) and 2-hydroxyacetophenone. For the other

compounds, several possible structures exist. The  $\text{Cs}^+$  may have, as usual, (i) a bidentate interaction with phenolate and hydroxyl (exists for pyrogallol and catechol anions) oxygens or (ii) the  $\text{Cs}^+$  may be bound to the phenolate oxygen close to linear arrangement (exists for all three anions, see Fig. 3f for anionic catechol) or (iii) the  $\text{Cs}^+$  is still bound to the phenolate oxygen but located out of plane (exists for all three anions, see Fig. 3g for anionic catechol). In the last case the complex may be additionally stabilized by cation/aromatic  $\pi$ -electron interaction [37].

The complexation enthalpies corresponding to the third conformer (stabilized by  $\pi$ -interaction) for pyrogallol and catechol anions are higher by 0.3 and 1.8 kcal/mol, respectively, over those of the first (bidentate) conformer, and by 3.4 and 1.0 kcal/mol, respectively, over those of the second conformer (linear bond for  $\text{Cs}^+$ -phenolate group), while for the hydroquinone anion the linear complex is preferred, being more stable by 1.0 kcal/mol than the third conformer.

The NBO charge density analysis showed that the Cs atom is carrying an average 0.96...0.97 positive charge and both oxygens an average 0.8 negative charge in all the studied complexes.

A general observation is that the formation of an internal hydrogen bond, for example when a function  $-\text{O}^-$  or  $-\text{COO}^-$  is close to an  $-\text{OH}$  or  $-\text{COOH}$  group, decreases the CsCA and CsCB.

#### 4. CONCLUSIONS

We have computationally studied the gas-phase cesium cation affinities (CsCAs) and basicities (CsCBs) of various aromatic and aliphatic compounds, which can be envisaged as simple models for the building blocks of macromolecular humic substances. It is known that metal cation binding occurs essentially via carboxylic functions within natural organic matter, which are to a large extent dissociated at usual soil pH. Thus, most of the  $\text{Cs}^+$  cation complexation calculations were devoted to the anionic (deprotonated) forms of carboxylic acid. In addition, some examples of interactions between phenolate oxygen and  $\text{Cs}^+$  were considered.

The cesium cation affinities are the weakest (around 10 kcal/mol) for all the unsubstituted aromatic systems studied and for  $\beta$ -naphthol. The complexes are of pure cation/ $\pi$ -type. The  $\text{Cs}^+$  cation tends to form a more localized type of bond in substituted aromatic compounds via the lone pair of the electronegative atoms (O, N) borne by the substituents. When the carboxyl and hydroxyl groups are present in the compound, the carbonyl oxygen is preferred to the hydroxyl group as the binding centre. The model compounds are also able to form chelate-type complexes when electronegative functional groups are in adjacent positions in the aromatic ring. The most favorable position for the  $\text{Cs}^+$  is

essentially a symmetrical binding to two oxygen atoms of functional groups in aliphatic systems. The oxygen-containing neutral molecules show approximately 1.5...2 times stronger CsCAs than unsubstituted aromatic systems. In most cases, the Cs<sup>+</sup> binds to carboxylate anions in a symmetric bidentate way. The CsCAs are in the range 90 to 115 kcal/mol.

The cesium cation binding to neutral and anionic molecules is considered to be largely electrostatic with a very little degree of charge transfer. This is also supported by the evidence that the metal atom can interact with more than one electronegative atom by forming stable chelate-type complexes.

## ACKNOWLEDGEMENTS

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**Table 1.** Calculated gas-phase cesium cation affinities (CsCAs, in kcal/mol) and basicities (CsCBs, in kcal/mol) of neutral model compounds at 298.15 K

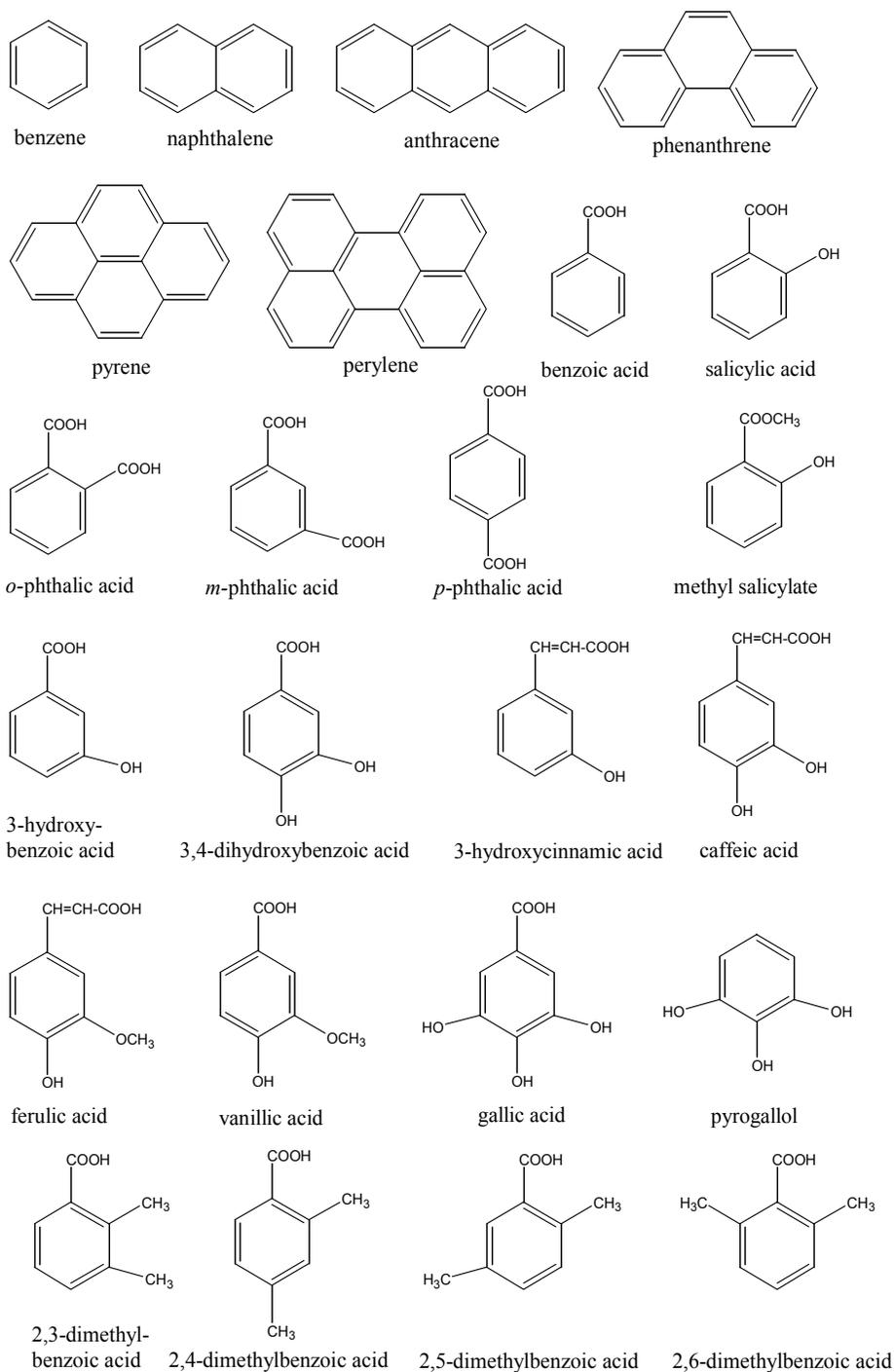
<b>Model compound (B)</b>	<b>CsCA</b>	<b>CsCB</b>
Unsubstituted aromatic compounds	9.8–10.6	4.6–5.0
benzene	9.8	4.6
naphthalene	10.5	5.0
anthracene	10.1	4.8
phenanthrene	10.6	5.0
pyrene	10.4	5.0
perylene	10.0	4.7
Substituted aromatic compounds	10.6–24.4	4.1–17.5
benzoic acid	15.1	8.9
salicylic acid	13.3	7.3
<i>o</i> -phthalic acid	24.4	17.5
<i>m</i> -phthalic acid	19.6	13.5
<i>p</i> -phthalic acid	15.7	9.6
methyl salicylate	17.4	11.2
3-hydroxybenzoic acid	18.2	12.2
3,4-dihydroxybenzoic acid	18.9	12.8
<i>trans</i> -3-hydroxycinnamic acid	21.6	15.3
<i>cis</i> -3-hydroxycinnamic acid	23.4	16.5
<i>trans</i> -caffeic acid	22.2	15.8
<i>cis</i> -caffeic acid	27.1	19.7
<i>trans</i> -ferulic acid	22.1	15.8
<i>cis</i> -ferulic acid	19.8	13.2
vanillic acid	18.1	12.6
gallic acid	17.6	11.8

pyrogallol	18.8	12.0
2,3-dimethylbenzoic acid	19.4	13.3
2,4-dimethylbenzoic acid	18.4	12.4
2,5-dimethylbenzoic acid	18.9	12.8
2,6-dimethylbenzoic acid	17.7	12.0
3,4-dimethylbenzoic acid	19.9	13.6
3,5-dimethylbenzoic acid	19.3	13.7
2,4,6-trimethylbenzoic acid	18.9	12.5
catechol	16.9	10.3
hydroquinone	13.6	8.1
quinone	12.8	7.9
2-hydroxyacetophenone	15.7	9.9
$\beta$ -naphthol	10.6	4.1
Substituted heteroaromatic compounds	14.0–21.5	7.9–15.1
coumarin	21.5	15.1
chromone	21.1	14.6
3-hydroxyxanthone	18.6	12.4
kojic acid*	19.9	13.7
3-quinolinol	14.0	7.9
Aliphatic compounds	13.4–25.6	7.3–18.8
acetic acid	15.2	9.1
propionic acid	15.1	8.7
oxalic acid*	15.2	9.0
malonic acid*	21.2	14.9
diethylmalonic acid	21.1	14.6
succinic acid*	22.2	14.0
fumaric acid	13.4	7.3
maleic acid	21.9	15.3
2-hydroxy-2-methylpropionic acid*	20.8	13.8
3-hydroxybutyric acid*	19.7	12.8
acetylacetone*	17.1	12.7
malic acid*	21.0	14.1
3-aminoglutaric acid	25.6	18.8

\*The most stable conformation of the free compound differs from that in the complex with Cs<sup>+</sup> cation.

**Table 2.** Calculated gas-phase cesium cation affinities (CsCAs, in kcal/mol) and basicities (CsCBs, in kcal/mol) of anionic model compounds at 298.15 K

<b>Anion of model compound (B)</b>	<b>CsCA</b>	<b>CsCB</b>
Substituted aromatic compounds	89.4–111.6	82.4–104.6
benzoic acid	107.8	101.1
salicylic acid	98.2	91.4
<i>o</i> -phthalic acid	89.4	82.4
<i>m</i> -phthalic acid	107.5	100.3
<i>p</i> -phthalic acid	105.9	98.8
methyl salicylate	110.5	102.7
3-hydroxybenzoic acid	110.6	103.3
3,4-dihydroxybenzoic acid	111.0	103.6
<i>trans</i> -3-hydroxycinnamic acid	111.0	103.7
<i>cis</i> -3-hydroxycinnamic acid	108.9	101.7
<i>trans</i> -caffeic acid	111.6	103.7
<i>cis</i> -caffeic acid	107.8	100.4
<i>trans</i> -ferulic acid	111.2	104.0
<i>cis</i> -ferulic acid	105.7	98.4
vanillic acid	110.3	103.1
gallic acid	109.7	102.6
pyrogallol	95.8	88.8
2,3-dimethylbenzoic acid	109.6	102.4
2,4-dimethylbenzoic acid	110.7	103.4
2,5-dimethylbenzoic acid	107.1	100.1
2,6-dimethylbenzoic acid	107.6	99.9
3,4-dimethylbenzoic acid	109.0	103.0
3,5-dimethylbenzoic acid	111.2	104.1
2,4,6-trimethylbenzoic acid	108.2	101.0
catechol	98.2	91.5
hydroquinone	104.2	97.1
2-hydroxyacetophenone	104.8	97.3
Aliphatic compounds	91.1–114.8	84.4–107.4
acetic acid	114.4	107.2
propionic acid	114.8	107.4
oxalic acid	100.2	93.0
malonic acid	93.3	86.1
diethylmalonic acid	91.1	84.4
succinic acid	95.5	88.8
fumaric acid	104.0	96.6
maleic acid	91.1	84.4
2-hydroxy-2-methylpropionic acid	106.2	99.6
3-hydroxybutyric acid	106.6	100.0
3-aminoglutaric acid	97.6	90.9



**Fig. 1.** Structures of neutral model compounds referred to in Table 1.

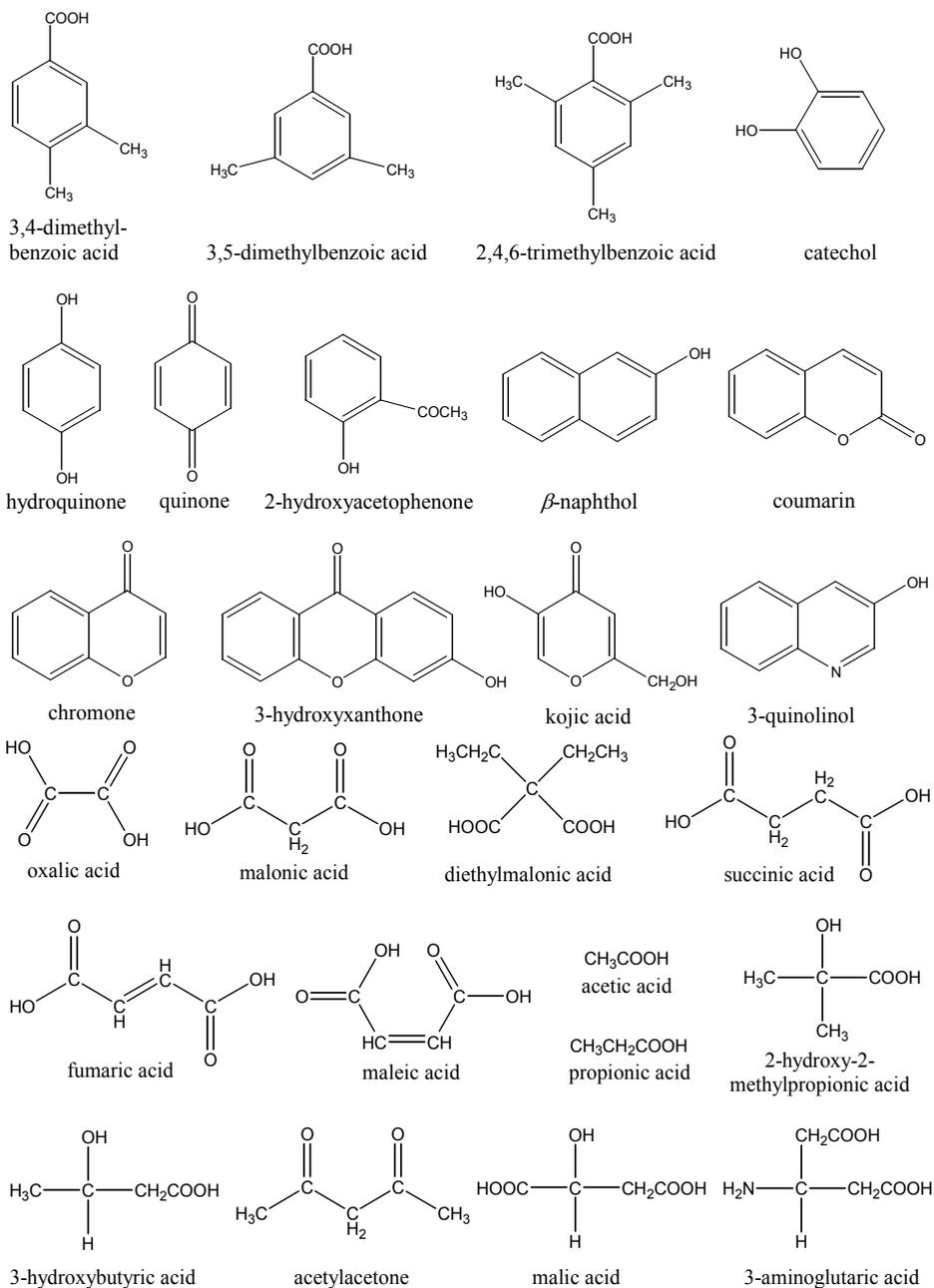
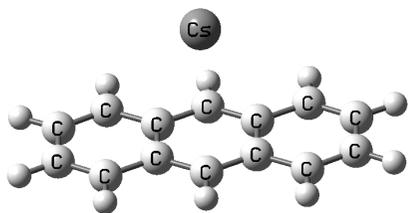
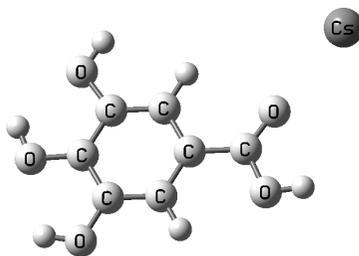


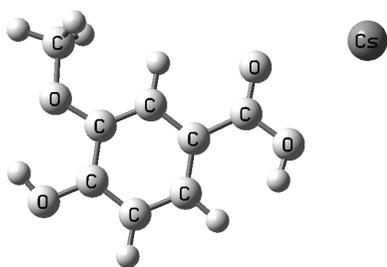
Fig. 1. Continued.



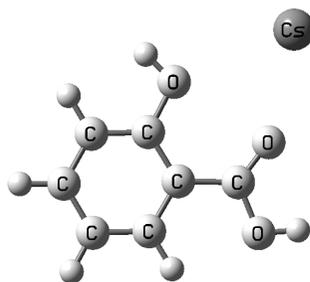
(a)



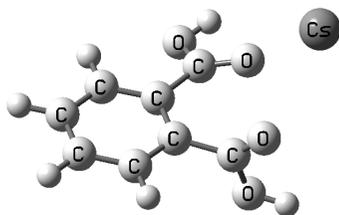
(b)



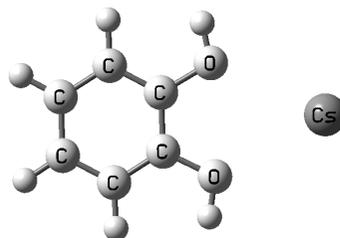
(c)



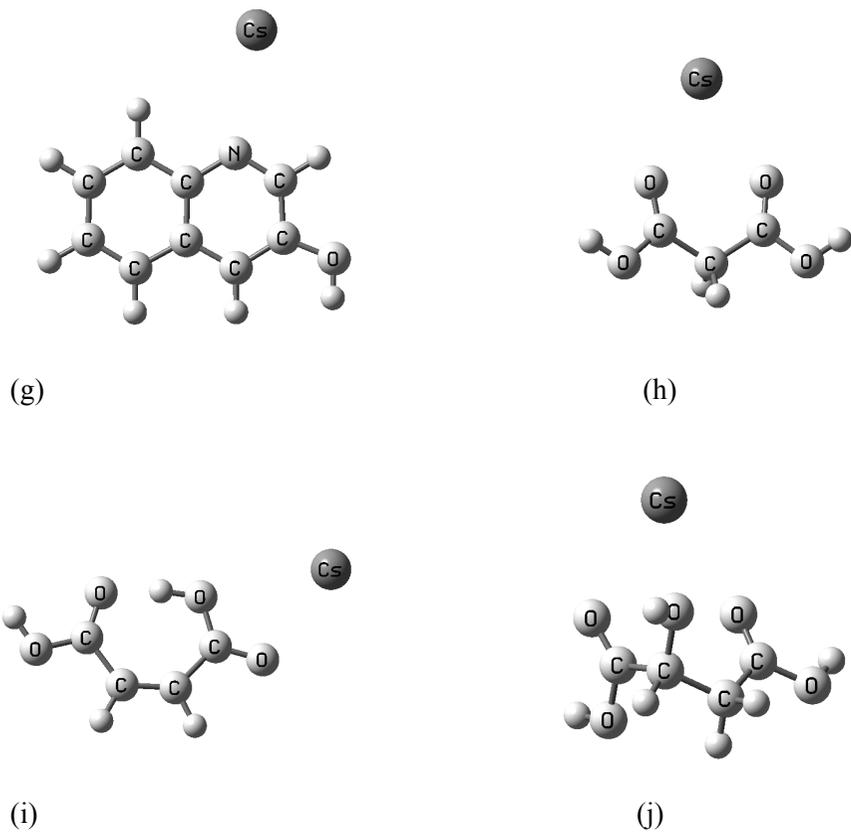
(d)



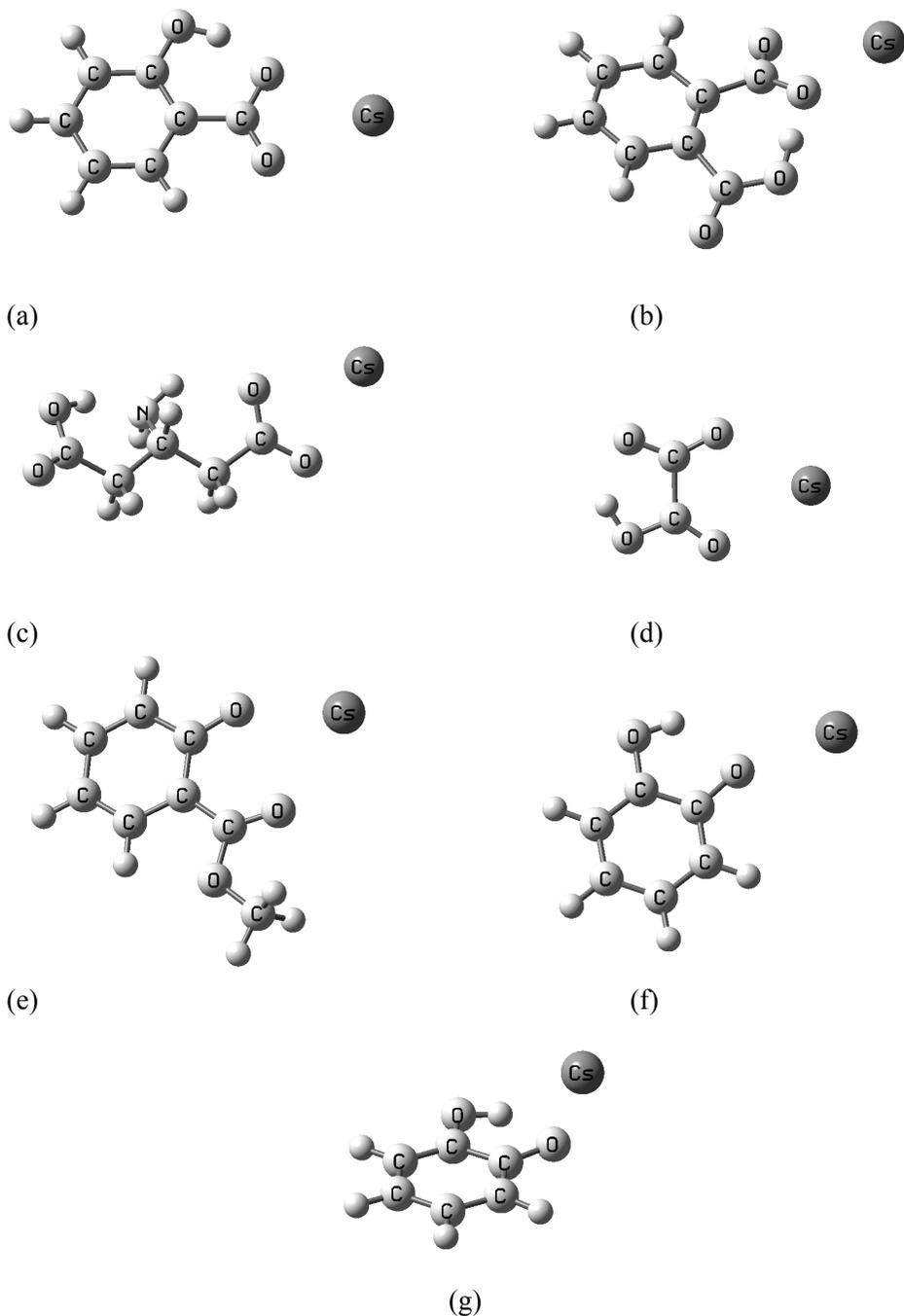
(e)



(f)



**Fig. 2.** The optimized structures of cesium cation complexes with anthracene (a), gallic acid (b), vanillic acid (c), salicylic acid (d), *o*-phthalic acid (e), catechol (f), 3-quinolinol (g), malonic acid (h), maleic acid (i), and malic acid (j).



**Fig. 3.** The optimized structures of cesium cation complexes with salicylate (a), *o*-phthalate (b), 3-aminoglutarate (c), oxalate (d), methyl salicylate (e) and catechol anions (f and g).



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Jean-Francois Gal. Computational study of cesium cation-humic substance  
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# CURRICULUM VITAE

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- I Peeter Burk, Jaana Tammiku-Taul, Sven Tamp, Pierre-Charles Maria, Jean-François Gal, Charly Mayeux, Computational study of cesium cation interactions with model compounds of humic substances, *J. Mol. Struct. THEOCHEM*, submitted.
- II Peeter Burk, Sven Tamp, Jaana Tammiku-Taul, Pierre-Charles Maria, Jean-François Gal. Computational study of cesium cation-humic substance interactions. A neutral analogue ligand molecules approach. *Proc. Estonian Acad. Sci. Chem.* 54(2), 2005, 70–84
- III Pierre-Charles Maria, Jean-François Gal, Lionel Massi, Peeter Burk, Jaana Tammiku-Taul, Sven Tamp. Investigations of cluster ions formed between cesium cations and benzoic, salicylic and phthalic acids by electrospray mass spectrometry and density-functional theory calculations. Toward a modeling of the interaction of Cs<sup>+</sup> with humic substances. *Rapid Comm. Mass Spectrom.* **19**, 2005, 568–573.
- IV Peeter Burk, Sven Tamp. A theoretical study of gas-phase basicities and proton affinities of alkali metal oxides and hydroxides. *J. Mol. Struct. THEOCHEM* **638** (1–3), 2003, 119–128.

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## Tähtsamad teaduspublikatsioonid

- I Peeter Burk, Jaana Tammiku-Taul, Sven Tamp, Pierre-Charles Maria, Jean-François Gal, Charly Mayeux, Computational study of cesium cation interactions with model compounds of humic substances, *J. Mol. Struct. THEOCHEM*, submitted.
- II Peeter Burk, Sven Tamp, Jaana Tammiku-Taul, Pierre-Charles Maria, Jean-Francois Gal. Computational study of cesium cation-humic substance interactions. A neutral analogue ligand molecules approach. *Proc. Estonian Acad. Sci. Chem.* 54(2), 2005, 70–84
- III Pierre-Charles Maria, Jean-Francois Gal, Lionel Massi, Peeter Burk, Jaana Tammiku-Taul, Sven Tamp. Investigations of cluster ions formed between cesium cations and benzoic, salicylic and phthalic acids by electrospray mass spectrometry and density-functional theory calculations. Toward a modeling of the interaction of Cs<sup>+</sup> with humic substances. *Rapid Comm. Mass Spectrom.* **19**, 2005, 568–573.
- IV Peeter Burk, Sven Tamp. A theoretical study of gas-phase basicities and proton affinities of alkali metal oxides and hydroxides. *J. Mol. Struct. THEOCHEM* **638** (1–3), 2003, 119–128.

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