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Computational study of cesium cation–humic substance interactions. A neutral analogue ligand molecules approach

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Abstract. Interactions between the cesium cation (Cs^+) and humic substances were studied by the calculations of complexes between Cs^+ and small ligand molecules mimicking different moieties in humic substances. The cesium cation gas-phase affinities (CsCAs) and basicities (CsCBs) of 52 model compounds (mainly aromatic) were calculated using the density functional method. The most common binding patterns of Cs^+ are discussed. The CsCAs are mainly governed by ion-induced dipole π-type interaction (CsCA around 11 kcal/mol) in unsubstituted fused aromatic systems. The cesium cation tends to form a more localized type of bond in substituted aromatic compounds via the lone pairs of electronegative atoms (O, N) of substituents resulting in enhanced CsCA (around 20 kcal/mol). If the model compound is able to form chelate-type complexes with the Cs cation, CsCA may be even higher (20–28 kcal/mol).

Key words: cesium cation basicity, cesium cation affinity, humic substances, DFT calculations.

INTRODUCTION

Humic substances are the most significant fraction of decomposed natural organic matter. Being present in particulate and dissolved forms in soils, waters, and sediments, they are formed by the decomposition of plant, animal, and microbial material through an array of chemical and microbial transformations. This produces mixtures of complex, acidic organic molecules of high molecular

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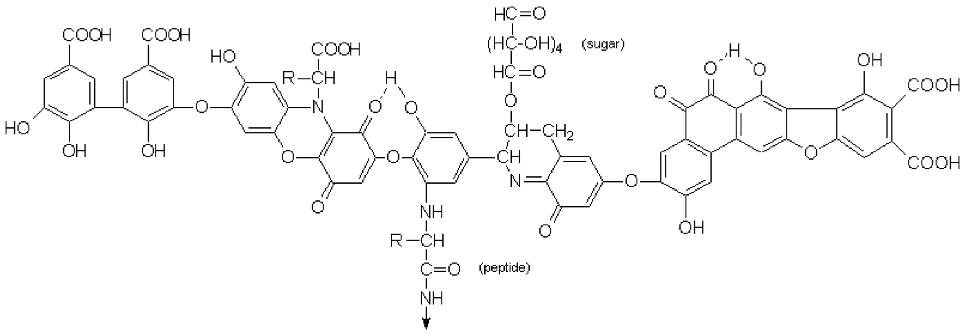
weight, which are abundant and persistent in the biosphere and immediate subsurface.

Humic acids are generally thought to be complex aromatic (about 19–25% aromaticity) macromolecules with amino acids, sugars, peptides, and aliphatic compounds involved in the cross-linking between the aromatic groups [1, 2]. It appears that humic substances consist of a heterogeneous mixture of compounds for which no single structural formula exists. A variety of structural models for humic acids have been proposed, the one below being just one example [3]:



The role of humic substances in the natural environment and their ability to play a role under different environmental conditions are of greatest interest. In that respect cation–humic acids interactions and cation binding are important concerns of this research. Some aspects of environmental issues involving humic substances for which cation binding is important are plant nutrient control (binding of iron and phosphate), soil and water acidification (binding of protons and aluminium cations), ecosystem buffering (control of H^+ and metal ion concentrations), to name a few. Besides, the possible role of humic substances in the transport and fixation of metals of economic interest (Au, Pt, Pd, U) has been pointed out [4], and further geochemical studies in this field are encouraged.

A hypothetical humic acid molecule may contain a wide variety of different functional groups. With regard to the binding of metal cations, the weakly acidic proton dissociating groups (carboxyl –COOH, phenolic –OH groups) are of particular importance. Besides, nitrogen and sulphur containing functional groups, though far less abundant in humic substances, may play an important role in creating strong binding sites for certain cations, especially for soft and polarizable metal cations such as mercury and other heavy metals.

Several authors have suggested that the most abundant metal cation and proton binding sites in humic substances may be similar to simple organic ligands such as benzoic acid, *o*-phthalate, and salicylate [5–7]. In fact, this idea has been carried further to develop various mathematical models (the so-called analogue models), which predict cation–humic substances interactions based on the equating of binding sites in the humic substance with simple low molecular weight organic compounds that, acting together, have binding properties similar to those of humic substances [8, 9].

The speciation of heavy toxic metals such as Cd, Hg, and radioactive Cs is a key factor of their transport, retention, and bioavailability in the environment, and humic substances are known to play a major part in determining the uptake of these metals. After the Chernobyl accident in 1986, an increased level of radioactive cesium in the environment was detected. Soil activities of ^{137}Cs in excess of 30 Bq/cm^3 still persist over large areas in Russia and the Ukraine. Several other European regions (French Alps, northern Finland, etc.) were also polluted by radioactive cesium. There is a considerable interest in remediation of sites contaminated by Cs radioisotopes. To accomplish this task, an understanding of the mechanism of Cs uptake, distribution, binding, and release in the biosphere is of vital importance.

In the current paper we attempted to investigate the Cs cation complexation with simple organic molecules (as presented in references [4, 7]), which could be pictured as simple building blocks to macromolecular humic substances. In this respect the Cs cation basicities and affinities, typical binding patterns, as well as charge distribution of Cs–organic molecule complexes were studied using computational techniques.

COMPUTATIONAL DETAILS

The density functional calculations were carried out using the Gaussian 03 program package [10] to obtain model structures, thermodynamic data and natural bond orbital (NBO) charges for the neutral humic acids and their complexes with the Cs cation. Full geometry optimizations were performed with B3LYP functional using the Dunning–Huzinaga valence double-zeta (D95V) [11] basis with a single set of polarization functions for carbon, hydrogen, oxygen, and nitrogen. For calculations involving the cesium cation, the Stuttgart–Dresden (SDD) effective core potential and the accompanying basis set [12] were used. A single polarization (d) function was added to the SDD basis for Cs atom with an exponent of 0.19 as suggested by Glendening et al. [13]. Vibrational frequency analysis was performed at the same level with the geometry optimizations to obtain the thermodynamic data (enthalpies and Gibbs free energies), no scaling of the vibrational frequencies was applied.

The gas-phase cesium cation affinities and basicities were computed according to the following thermodynamic equilibrium:

$$B + Cs^+ \rightarrow [B\text{–}Cs^+], \tag{1}$$

where the Cs cation basicity (CsCB) is associated with the negative Gibbs free energy change (CsCB = $-\Delta G_{\mathrm{Cs}^+}$) and cesium cation affinity (CsCA) as the negative enthalpy change (CsCA = $-\Delta H_{\mathrm{Cs}^+}$) of the association reaction (1). The calculated CsCA and CsCB are given in Table 1. Raw computational data (energies and geometries) are available from authors upon request.

Table 1. Calculated gas-phase cesium cation affinities (CsCA, in kcal/mol) and basicities (CsCB, in kcal/mol) at 298 K at DFT B3LYP D95V(d,p) level

Model compound	CsCA	CsCB
Benzene	10.7	5.4
Naphthalene	11.3	5.6
Anthracene	11.5	5.8
Phenanthrene	11.5	5.5
Pyrene	11.3	5.6
Perylene	11.0	5.7
Benzoic acid	18.9	12.8
Salicylic acid	18.4	12.3
o-Phthalic acid	25.8	17.8
m-Phthalic acid	21.3	14.8
p-Phthalic acid	16.9	10.8
Methyl salicylate	19.3	13.2
3-Hydroxybenzoic acid	19.4	13.4
3,4-Dihydroxybenzoic acid	19.7	13.8
3-Hydroxycinnamic acid	28.0	19.9
Caffeic acid	26.3	18.4
Ferulic acid	21.7	14.7
Vanillic acid	19.5	13.7
Gallic acid	17.5	11.4
Pyrogallol	20.4	13.8
3,4-Dimethylbenzoic acid	21.0	14.7
3,5-Dimethylbenzoic acid	20.4	14.3
2,3-Dimethylbenzoic acid	20.5	14.3
2,5-Dimethylbenzoic acid	20.1	13.8
2,4-Dimethylbenzoic acid	19.6	13.5
2,6-Dimethylbenzoic acid	19.4	13.5
2,4,6-Trimethylbenzoic acid	21.1	13.3
Catechol	18.2	11.8
Hydroquinone	14.8	9.3
Quinone	13.6	8.7
2-Hydroxyacetophenone	16.5	10.7
β-Naphthol	11.8	5.0
Coumarin	22.2	16.3
Chromone	21.8	15.5
Xanthone	19.3	13.9
Kojic acid*	20.3	14.3
3-Quinolinol	15.2	9.2
Oxalic acid*	16.6	10.2
Malonic acid*	22.4	16.3
Diethylmalonic acid	23.1	16.4
Succinic acid	24.4	16.2
Fumaric acid	14.7	8.4
Maleic acid	23.5	16.8
Acetic acid	16.5	10.3
Propionic acid	16.6	10.1
2-Hydroxy-2-methylpropionic acid	22.6	15.4
3-Hydroxybutyric acid	21.6	14.7
Acetylacetone*	18.5	13.2
Malic acid*	22.9	15.8
3-Aminoglutaric acid	27.8	20.9

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* The most stable conformers for free model compound and metallated compound are different.

RESULTS AND DISCUSSION

For interpreting the results of the current work, certain precaution should be expressed towards predicting the complexing ability of humic substances with the cesium cation on the basis of gas-phase Cs cation affinity of simple organic molecule analogues to humic acids. Besides the heterogeneous nature, this is also due to an extreme complexity of the structure of humic matter, which may be altered by the change in pH, ionic strength of the medium, and metal loading. Also, because of the multidentate nature of humic substances, it can be expected that the folding of the macromolecules (much like proteins) can bring various functional groups into the proximity of each other and, thereby, create binding sites that may significantly change the mechanism and strength of the metal cation speciation to humic substances. Nevertheless, the current paper should provide basic introductory data about the subject, hoping that computational data on molecules resembling real humic substances, but more importantly experimental results, will be available in the near future.

Rodgers & Amunugama [14–18] investigated the absolute binding energies of alkali metal cations (from Li up to Cs) to several substituted (methyl, fluoro, amino, hydroxyl, and methoxy) benzene ligands. With electronegative substituents present in the aromatic ring, the question of the relative stability of the cation–ligand π-type vs. σ-type complex arises, because the alkali cation may interact with the π-electron cloud of the aromatic ring (mainly electrostatic ion–induced dipole type interaction, which is denominated as π-binding) or form a more localized type of bond with free electron pairs on electronegative substituent atoms such as oxygen, nitrogen, and halogen (which is denominated as σ-binding). It is proposed that the relative stability of these different types of complexes varies with the size of the cation, for the lighter alkali metals the π-type complex being more favoured. So, at the MP2(full)–6-311+G(2d,2p) level of theory, the σ-binding conformers of Li^+ and K^+ were found to be 7.5 and 1.5 kJ/mol less stable than the corresponding π-complexes. For Rb^+ and Cs^+ the σ- and π-binding complexes were found to be at least as stable, if not in slight favour for σ-type binding. A conclusion was drawn that in general Rb^+ and especially Cs^+ show a great flexibility in the type of complexing pattern, allowing various conformations depending on the local environment, whereas the smaller alkali metal cations (with stronger polarizing power) such as Li^+ and Na^+ would preferentially bind via cation–π interaction.

Rodgers & Amunugama suggested that the calculations underestimate the binding energy in the cases of toluene and fluorobenzene, when effective core potentials (ECPs) are used for heavier alkali metals like Rb^+ and Cs^+. Our calculations also involve the use of ECPs for the cesium cation. Unfortunately, no experimental binding energies of Cs^+ to similar model systems (as presented in this paper) are available to us, thus, the validation of the current computational results could not be done.

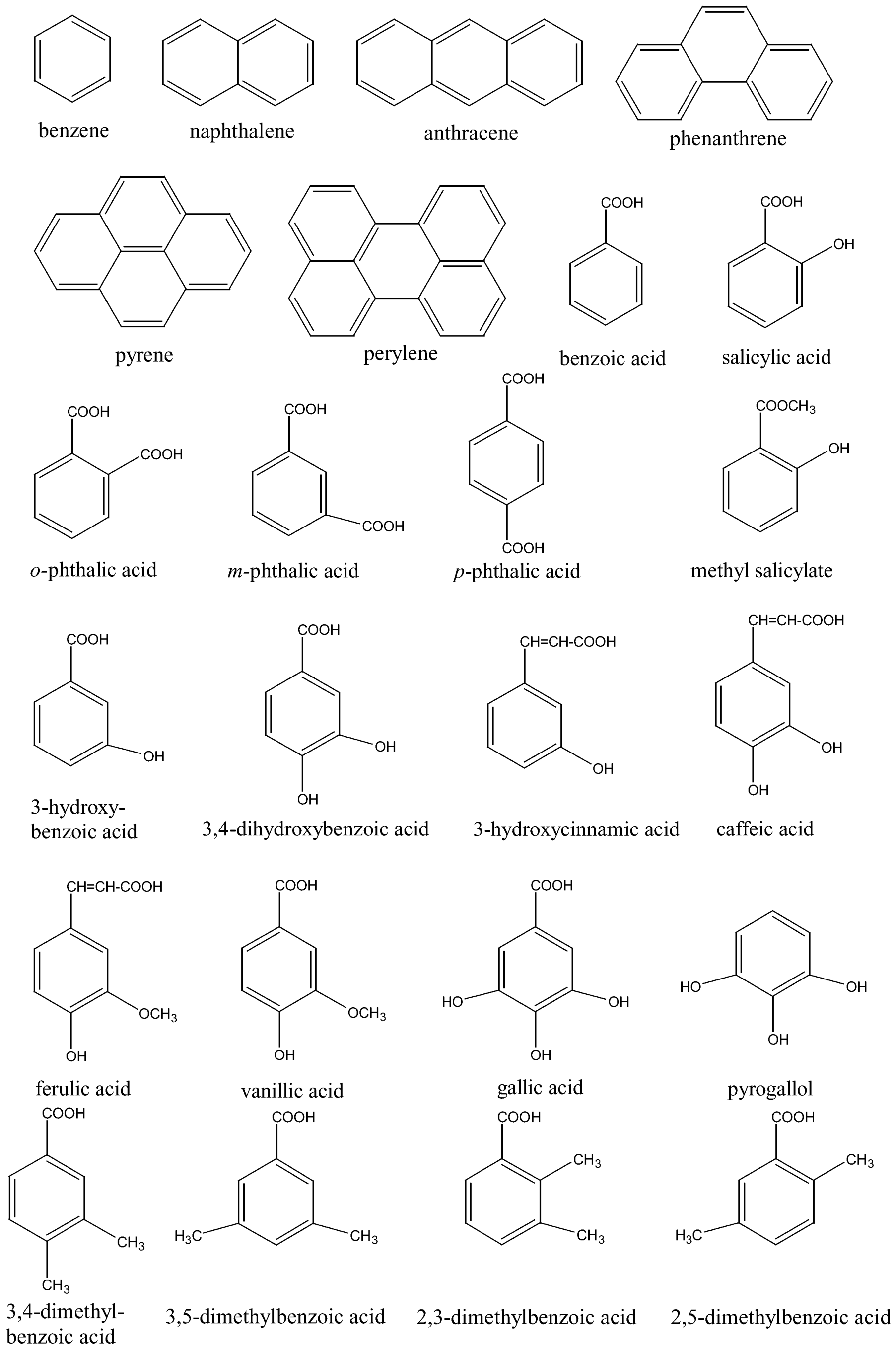
Previous experimental findings [6] also suggest that metal cation binding is mainly governed by weakly acidic carboxyl and phenolic hydroxyl groups, most abundantly present in humic substances. Our calculations based on small organic molecule analogues to humic substances also support this hypothesis.

THE LOCATION OF THE CESIUM CATION IN MODEL COMPOUNDS

The structures of compounds used as structural models of humic acids are presented in Fig. 1. Unsubstituted aromatic molecules interact with the cesium cation preferably via their π-systems as evidenced by the location of the Cs cation above the centre of one of the benzene rings at a distance of ca 3.0 Å (1 Å = 0.1 nm). The symmetrical position of the Cs cation above the central benzene ring in anthracene (Fig. 2a) and phenanthrene is only marginally preferred (0.04–0.2 kcal/mol more stable compared to the position above peripheral rings; 1 cal = 4.184 J), in contrast with results obtained by Gal et al. [19], who found the energy differences to be in the range of 2 kcal/mol. Very small differences between different cation attachment positions (above different benzene rings, ΔH = 0.04–0.3 kcal/mol) lead to the conclusion that the cesium cation binds to the different benzene rings in complexes with naphthalene, anthracene, phenanthrene, pyrene, and perylene with approximately equal probability.

For most of the studied substituted aromatic compounds the Cs cation is preferentially attached to the carboxyl (–COOH) or hydroxyl (–OH) groups via an electrostatic interaction with the lone-pair electrons on electronegative oxygen atoms. When both groups are present in the compound, the carbonyl group (C═O) as the binding centre is preferable to the hydroxyl group. The most typical binding pattern can be illustrated on the basis of 3,4-dimethylbenzoic acid for which two of the most stable complexes are presented in Fig. 2b and c. In the first complex (b) the Cs^+ is bonded only to the carbonyl oxygen. The second complex (c), where the Cs^+ interacts with the lone-pair electrons of both oxygen atoms and is lying at an almost equal distance from them in the plane of the benzene ring, is energetically less stable by 1.4 kcal/mol. Complexing patterns of this type are quite common for the similar compounds with single or isolated carboxyl groups attached to the benzene ring such as benzoic, *p*-phthalic, 3-hydroxybenzoic, 3,4-dihydroxybenzoic, gallic, etc. acids. The binding pattern via carbonyl oxygen is only typical for quinone, coumarin, chromone, xanthone, and kojic acids.

Among the studied compounds, caffeic (Fig. 2d) and ferulic acids reveal a slightly different type of complexing pattern with the Cs cation. It appears that the end-carboxyl group of the side chain is strongly deflected from the plane of the benzene ring and the Cs^+ ion (bonded to the carbonyl oxygen) lies almost above the plane of the benzene ring, the sight of π-electron cloud. The complexation of the Cs cation with 3-quinolinol is also different – it attaches to the nitrogen atom, which is a stronger complexing centre as compared to the oxygen atom (Fig. 2e).



benzene

naphthalene

anthracene

phenanthrene

pyrene

perylene

benzoic acid

salicylic acid

o-phthalic acid

m-phthalic acid

p-phthalic acid

methyl salicylate

3-hydroxy-benzoic acid

3,4-dihydroxybenzoic acid

3-hydroxycinnamic acid

caffeic acid

ferulic acid

vanillic acid

gallic acid

pyrogallol

3,4-dimethyl-benzoic acid

3,5-dimethylbenzoic acid

2,3-dimethylbenzoic acid

2,5-dimethylbenzoic acid

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

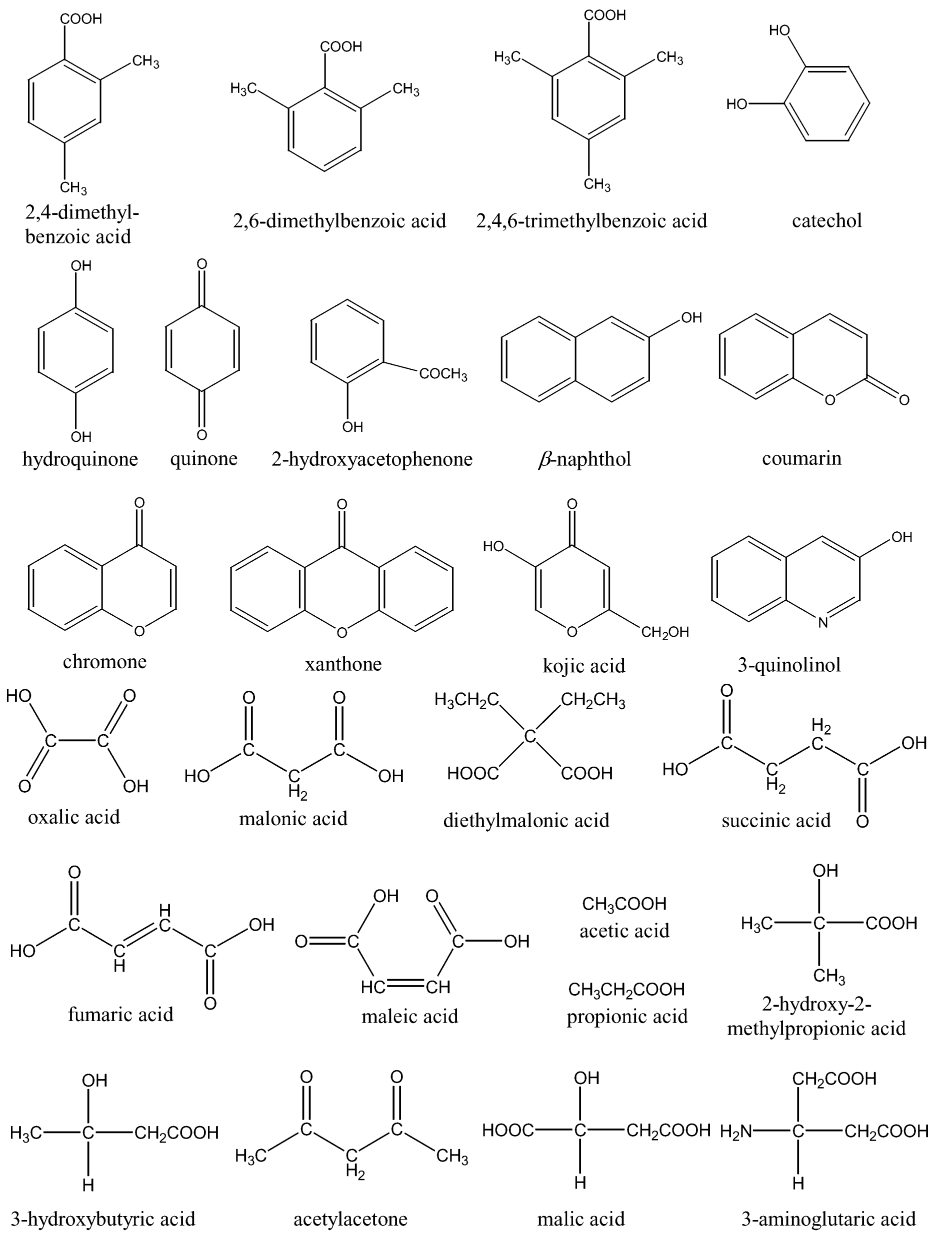

2,4-dimethylbenzoic acid
2,6-dimethylbenzoic acid
2,4,6-trimethylbenzoic acid
catechol
hydroquinone
quinone
2-hydroxyacetophenone
β-naphthol
coumarin
chromone
xanthone
kojic acid
3-quinolinol
oxalic acid
malonic acid
diethylmalonic acid
succinic acid
fumaric acid
maleic acid
CH_3COOH acetic acid
CH_3CH_2COOH propionic acid
2-hydroxy-2-methylpropionic acid
3-hydroxybutyric acid
acetylacetone
malic acid
3-aminoglutaric acid

Fig. 1. *Continued.*

β-Naphthol is an exceptional compound as Cs^+ is located above one of the benzene rings and is not directly interacting with hydroxyl group. The difference in enthalpy between the benzene rings in *β*-naphthol is only 0.5 kcal/mol, close to

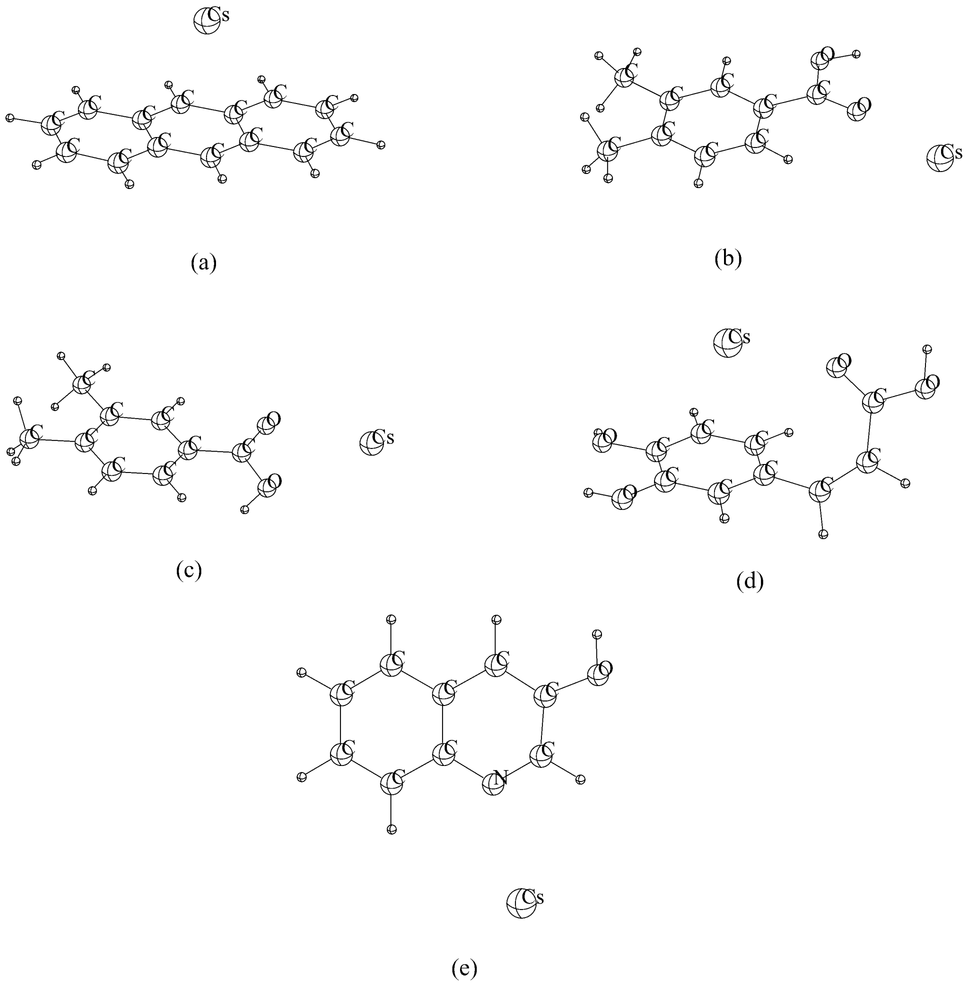

(a) (b) (c) (d) (e)

Fig. 2. Structures of some cesium cation complexes: anthracene with Cs^+ (a), 3,4-dimethylbenzoic acid with Cs^+ (b and c), caffeic acid with Cs^+ (d), and 3-quinolinol with Cs^+ (e).

that found in unsubstituted aromatic compounds. In the case of β-naphthol, the hydroxyl group is a relatively weak electron-releasing substituent, contributing to a slight increase of π-electron density, and presumably to the strengthening of the Cs cation–π interaction. The interaction of the Cs cation with the oxygen atom of the hydroxyl group is by ca 1.0 kcal/mol weaker. Generally, however, no stable conformers arising from a significant amount of metal cation–π interaction could be found for other complexes of Cs^+ with –OH or –COOH substituted compounds.

According to our calculations, and considering the ionic nature of the M^+ in the complex, the cesium cation may form stable bidentate-type chelate complexes with ligands that have adjacent functional groups with lone-pair electrons. In these chelate-type complexes the most favourable position for Cs^+, when possible, is more or less symmetrical between the two oxygen atoms of the neighbouring oxygen-containing group, like in *m*-phthalic acid (Fig. 3a), *o*-phthalic acid (Fig. 3b), pyrogallol (Fig. 3c), or salicylic acid (Fig. 3d). The tendency for the

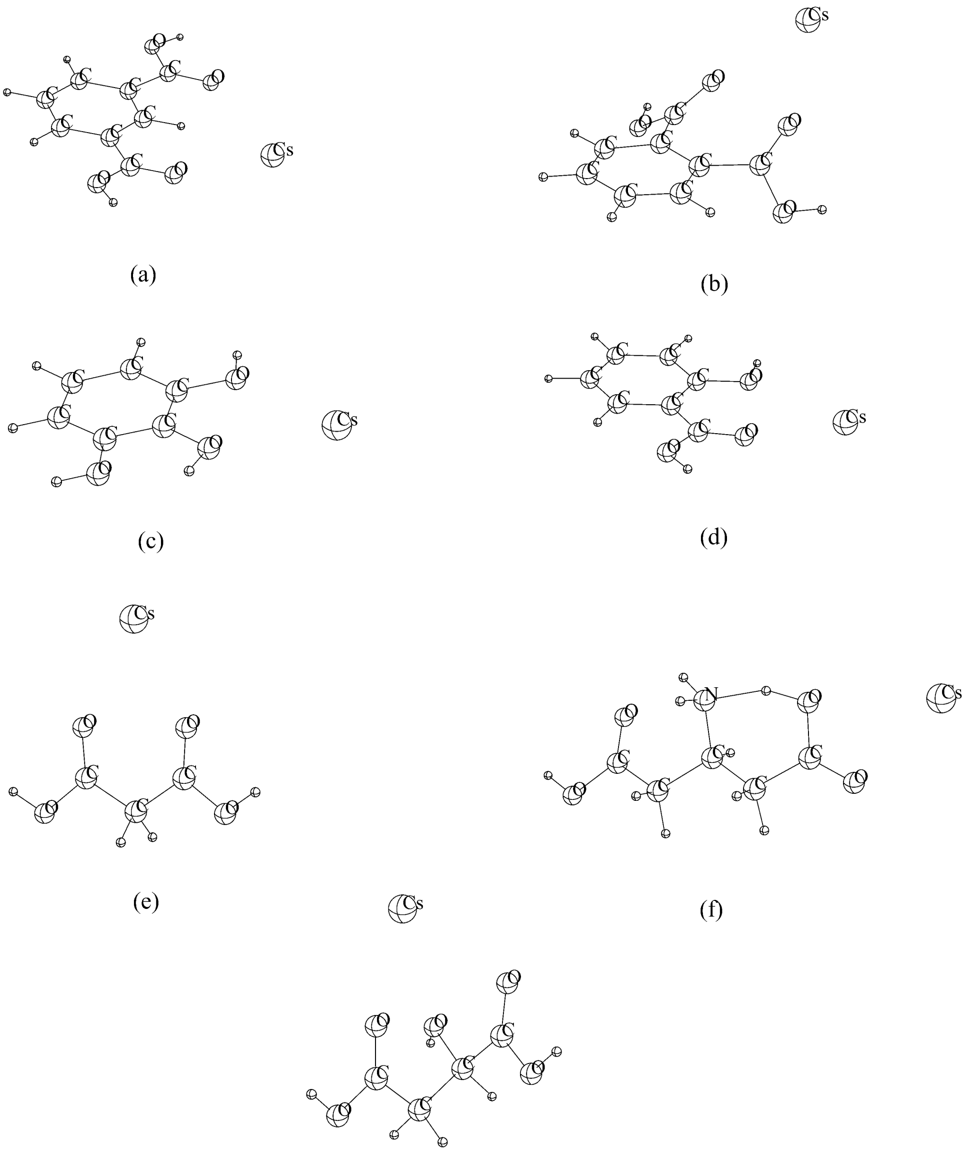


Fig. 3. Structures of some cesium cation complexes: *m*-phthalic acid with Cs^+ (a), *o*-phthalic acid with Cs^+ (b), pyrogallol with Cs^+ (c), salicylic acid with Cs^+ (d), malonic acid with Cs^+ (e), 3-aminoglutaric acid with Cs^+ (f), and malic acid with Cs^+ (g).

formation of chelate-type complexes in the case of substituted aromatic compounds is greater when functional groups are in ortho positions (salicylic acid, pyrogallol, catechol). Although *m*-phthalic acid cannot be strictly considered a typical chelate-type complex with the Cs cation, it is likely that both carbonyl oxygen atoms in meta positions, interacting with the Cs cation, contribute to the stabilization of the complex.

The distances between Cs^+ and the corresponding binding centres of substituted aromatic compounds are 2.8–3.0 Å.

Unsurprisingly, the Cs cation is connected with the electronegative oxygen atom in aliphatic compounds. The most favourable position for Cs^+, when possible, is also more or less symmetrical between the two oxygen atoms of carbonyl groups, like in oxalic, malonic (Fig. 3e), and succinic acids and acetylacetone, or between the two oxygen atoms of carbonyl and hydroxyl groups like in maleic, diethylmalonic, 2-hydroxy-2-methylpropionic, 3-hydroxybutyric, and 3-aminoglutaric acids. In the latter case, a hydrogen bond is formed in the compound besides the interaction with Cs^+ (Fig. 3f). The Cs cation has an interaction with three oxygen atoms in malic acid (Fig. 3g). All the distances between the cesium cation and oxygen atoms are in the range 2.8–3.3 Å.

CALCULATED CESIUM CATION AFFINITIES AND BASICITIES

The NBO analysis [20] reveals that the cesium cation carries a positive partial charge from 0.9 up to 0.99 electron unit in all the studied complexes of the Cs cation with simple humic acid analogue ligands. This is in full agreement with the results of Rodgers & Amunugama [14–18] for all $M^+(C_6H_5X)$ complexes. It seems that the partial charge does not depend markedly on the type of alkali metal and the substituent groups in the aromatic benzene ring. Especially, there is a very small degree of charge transfer in the complex for heavier alkali metal atoms, and the bond to the ligand molecule can be considered ionic.

The variation in calculated cesium cation affinities (CsCA) for most of the carboxylic acids (acting as O-bases) is not very large, being generally around 20 kcal/mol (see Table 1) and governed mainly by the cesium cation binding to carboxyl groups according to the patterns discussed above.

The cesium cation affinity towards compounds with single or isolated hydroxyl groups (or quinone-type oxygen atoms) is slightly lower, being around 15 kcal/mol. However, if there is a possibility for Cs^+ to interact simultaneously with several hydroxyl groups (as in catechol, pyrogallol) by forming chelate-type complexes, the affinity is obviously higher and comparable to the molecules with carboxyl groups present.

Also, the cesium cation affinities are higher if there is a possibility for the formation of chelate-type complexes with neighbouring carbonyl (C═O) groups. For instance, in the series of phthalic acids (*o*-, *m*-, and *p*-forms) it can be seen that the CsCA value is highest in the case of *o*-phthalic acid, for which the Cs^+–bidentate-type complex is also the strongest. This particular type of complex is weaker in *m*-phthalic acid and completely absent in *p*-phthalic acid because of a greater distance of the two carbonyl oxygen atoms. Obviously, this results in a continuous lowering of the affinities in this series. The CsCA is 25.8, 21.3, and 16.9 kcal/mol for *o*-, *m*-, and *p*-phthalic acids, respectively. Moreover, the stabilization due to multidentate binding is particularly apparent in the case of maleic acid (where Cs^+ can simultaneously interact with adjacent carbonyl oxygen atoms) with the CsCA 23.5 kcal/mol being almost 9 kcal/mol higher than in the case of fumaric acid for lack of this kind of stabilization.

Among the studied compounds, 3-hydroxycinnamic and caffeic acids have the highest calculated CsCA – 28 and 26 kcal/mol, respectively. The somewhat higher cesium cation affinities for these compounds may partially be explained by a slightly different Cs^+ binding pattern (see in the discussion above), resulting in increased stabilization of the complex by allowing more favourable conformations of the more bulky side chain of these ligands, leading to an additional Cs cation interaction with the π-electron density of the benzene ring. This is also supported by the calculated Cs cation–benzene ring centroid distances for 3-hydroxycinnamic acid (3.45 Å) and caffeic acid (3.48 Å), which are quite close to the Cs cation–benzene centroid distance calculated by Rodgers & Amunugama [17] for the $Cs^+(C_6H_5OH)$–π complex (3.49 Å). Therefore, in the case of more bulky substituent groups attached to the benzene ring, the relative population of the Cs cation–π complexes may be significantly higher and experimentally detectable Cs cation–neutral ligand complexes may contain both conformers of similar probability.

In the studied compounds, the Cs cation is expressing the weakest affinity towards the unsubstituted fused aromatic systems (naphthalene, anthracene, phenanthrene, etc.), being constantly around 11 kcal/mol. They can be considered as pure π-type complexes. Therefore, we infer that at least for heavier alkali metal (like Cs^+) complexes with aromatic compounds, the σ-type interaction of the alkali metal with electronegative (donor) atoms in functional groups (if present in the molecule) predominates, while the metal cation–π interaction is much weaker.

CONCLUSIONS

We have studied computationally the cesium cation affinities (CsCA) and basicities (CsCB) of various aromatic compounds. These could be envisioned as simple units to macromolecular humic acids and the results should provide a fair insight into the types of binding patterns and affinities of the cesium cation to real humic matter.

Humic acids contain a significant amount of aromatic character with a wide variety of functional groups. Among them, carboxyl (–COOH) and hydroxyl (–OH) groups are the most abundant and potential binding sites to alkali metal cations. So, the relative stability of cesium cation–π complexation (with the aromatic π-electron cloud) vs. the σ-type binding (with the lone-pair electrons of electronegative atoms of substituent groups) arises.

The cesium cation affinity is the weakest (around 11 kcal/mol) for the unsubstituted fused aromatic compounds (naphthalene, anthracene, perylene, etc.). In these complexes the cesium cation–π interaction predominates and the cation is located just above one of the aromatic rings. However, σ-binding predominates in the case the substituents of aromatic ring contain electronegative atoms with lone-pair electrons and the cesium cation lies close to the plane of the benzene ring. This is the most typical binding pattern for the majority of the studied compounds, and is clearly more favoured as indicated by a stronger CsCA of about 20 kcal/mol. For certain model compounds with bulkier substituent groups (caffeic, ferulic acids) stable conformers were found where a significant amount of cesium cation–π interaction is also present.

The cesium cation binding to neutral model compounds is largely ionic (the metal atom carrying a positive charge from 0.9 up to 0.99 electron unit) as indicated by the NBO charge analysis. This is supported by the evidence that the metal atom can interact with more than one electronegative atom by forming stable chelate-type complexes. This type of complex formation is favoured when there are electronegative atoms of functional groups substituted in adjacent positions in the aromatic ring (like in *o*-phthalic acid, pyrogallol, catechol, maleic acid, etc.). The extra stabilization of the Cs cation–neutral ligand complex by chelate formation is also reflected in the somewhat higher cesium cation affinities as opposed to ordinary complexes, where the chelate-type complex formation is weaker or completely absent. This is especially apparent in the case of *o*-phthalic acid (as compared to *m*- or *p*-forms) and maleic acid (as opposed to fumaric acid).

In order to validate the current computational results, further experimental data concerning the Cs cation binding energies, affinities, and basicities on smaller model systems, resembling real humic substances, seem highly desirable.

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Humiinhapete ja tseesiumikatiooni vaheliste interaktsioonide modelleerimine tihedusfunktsionaaliteooria arvutustega neutraalsete mudelühendite baasil

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Tseesiumi kui radioaktiivse metalli ladestumine ja transport biosfääris on olulisel määral reguleeritud vetes ja mullas leiduvate humiin- ja fulvohapete poolt. Seetõttu on oluline teada Cs-katiooni seostumise eripära ja tugevust nimetatud looduslike makromolekulaarsete ühenditega. Artiklis on uuritud Cs-katiooni afiinsust (CsCA), aluselisust (CsCB) ja tüüpilisi seostumisvõimalusi erinevate, peamiselt aromaatsete mudelühendite baasil, mida võib teatud lähenduses vaadelda kui lihtsaid “ehituskive”, millest humiinhapped põhiliselt koosnevad. Tulemused põhinevad tihedusfunktsionaaliteooria (DFT) arvutustel. Ilmneb, et Cs-katioon võib seostuda aromaatse tuuma π-elektronsüsteemi kaudu (π-tüüpi interaktsioon), mis realiseerub asendamata kondenseerunud tuumadega aromaatsetes ühendites, mille korral Cs-katiooni seostumise tugevus (afiinsus) on nõrgim (CsCA = ~11 kcal/mol). Asendusrühmade (–COOH, –OH jt) olemasolu korral moodustub pigem lokaliseerunud side ehk Cs-katioon interakteerub funktsionaalrühmade erinevate elektronegatiivsete aatomite (O, N) vabade elektronipaaridega (σ-tüüpi interaktsioon). Sellisel juhul on ka CsCA suurem (~20 kcal/mol). Sõltuvalt asendusrühmade iseloomust ning paigutusest võivad moodustuda veel kelaatsed kompleksid, kus esineb interaktsioon enama kui ühe elektronegatiivse aatomiga. Eriti iseloomulik on selliste komplekside moodustumine benseenituumas 1- ja 2-asendis paiknevate funktsionaalrühmade korral, olles ka termodünaamiliselt eelistatud (CsCA = 20–28 kcal/mol). Sõltuvalt asendusrühmade mahukusest ja paindlikkusest võivad realiseeruda ka vähem tüüpilised kompleksid (nt Cs^+-kompleks kohvhappega), kus esineb tõenäoliselt nii σ- kui ka π-interaktsioon.