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Computational Study of Cesium Cation Interactions with Neutral and Anionic Compounds Related to Soil Organic Matter

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The gas-phase cesium cation affinities (CsCAs) and basicities (CsCBs) for 56 simple neutral compounds (mostly aromatic molecules) and 41 anions (carboxylates and phenolates) were calculated using density functional theory (DFT), in the context of the interaction of Cs^+ with soil organic matter (SOM). The B3LYP/def2-TZVP method gives in general CsCAs and CsCBs in a good agreement with experimental data. The strong deviations in case of NO_3^- and $CsSO_4^-$ anions need further experimental investigations as the high-level CCSD(T) calculations support B3LYP results. Different cesium cation complexation patterns between Cs^+ and the neutral and anionic systems are discussed. As expected, the strongest CsCAs are observed for anions. The corresponding quantities are approximately by 4−5 times higher than for the neutral counterparts, being in the range 90−118 kcal/mol. The weakest cesium cation bonding is observed in the case of unsubstituted aromatic systems (11−15 kcal/mol).

1. Introduction

Cesium, the heaviest alkali metal possessing a stable isotope, is toxic to plants, even as the stable isotope ^{133}Cs. This element is taken up by roots and mainly accumulated in the rapidly growing parts (roots, leaves, and other selected tissues and organs),[1,2] causing a decrease in the growth of biomass and in tissue hydration, as well as potassium starvation via competitive interaction with vital K^+ binding sites in proteins,[3] suppressing their activities. Nonetheless, the main concern with cesium arises from the long-range transport and deposition of radioactive ^{137}Cs in the biosphere, e.g. after the fallout following the Chernobyl accident (April 26, 1986) and from atmospheric nuclear weapons test from 1945 to 1980. The subsequent transfer of ^{137}Cs to the terrestrial food chain poses a serious radiological hazard. Certain crops (e.g., onion, cress, and mushrooms) are prone to cesium accumulation. Elevated uptake of this radionuclide by the cuticle of the mushroom "bay boletus" has been attributed to norbadione A. This natural substance comprises the carboxylate and hydroxyl groups in favorable positions and exhibits highly selective chelating power toward Cs^+,[4] as shown by theoretical calculations and mass spectrometry experiments. In fact, various approaches are foreseen to find possible ways of utilizing plants for removing cesium from highly polluted areas (phytoremediation).[5]

The mobility and bioavailability of metal cations (including their radioactive isotopes, such as ^{137}Cs) in the environment is strongly influenced by their complexation with soil organic matter (SOM). Several functional groups have been identified in SOM, i.e. the oxygen containing groups (carbonyl, carboxyl and hydroxyl), as well as nitrogen, phosphorus, and sulfur containing groups.[6,7] In fact, some of these groups (in particular −COOH and −OH) play an important role in creating strong binding sites, when ionized and favorably situated to constitute polydentate potential chelators for certain metal cations.[8] Indeed, at soil natural pH values, the most acidic functional groups are deprotonated, drastically enhancing the metal cation binding ability by SOM and consequently increasing the metal loading in soil, especially in the upper layers. The role of low molecular weight carboxylic acids in metal cation transport in soil in close contact with plant roots (rhizosphere) has also been invoked,[9] although the complex role of these small organic acids molecules is not yet completely understood.[10] The need for a better description of the influence of SOM and humic substances[11] (principally humic and fulvic acids, the fractions of SOM, which can be extracted using strong base, but also small organic molecules, in particular low molecular weight carboxylic acids) on cesium cation transport in soils, and the bioavailability, retention and distribution of cesium in organic soils,[12] prompted our groups to study the interaction between Cs^+ and organic functionalities present in SOM, starting from the most fundamental and simple aspect, i.e. the intrinsic interaction in the gas phase.[13−16] In fact, alkali metal ions were the first metal cations studied in the gas phase for their Lewis acid properties.[17] This possibility of measuring accurate alkali metal cation affinities (enthalpies) and basicities (Gibbs free energies), by means of different experimental techniques (equilibrium constant determination by high pressure mass spectrometry, HPMS,[18] or ion cyclotron resonance, ICR;[19] unimolecular dissociation of excited cation bound dimers, also called the Cooks kinetic method;[20] threshold collision-induced dissociation, TCID;[21] photodissociation and radiative association kinetics[22]), has stimulated a growing interest in the study of these interactions. However, cesium has been much less studied as compared to lighter alkali metals: lithium, sodium, and potassium. Our recent review of cesium cation affinities (CsCAs) and cesium cation basicities (CsCBs)[23] revealed that experimental data are available for fewer than 20 organic molecules, and no carboxylic acids

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or their anions have been studied. CsCA is defined as the negative of the enthalpy change for the association reaction 1 ($CsCA = -\Delta H_{(1)}$) and CsCB as the negative of the corresponding Gibbs free energy change ($CsCB = -\Delta G_{(1)}$):

$$B^n + Cs^+ \rightarrow [B-Cs]^{n+1} \qquad (1)$$

Besides, understanding the interactions between cesium cation and different Lewis bases (both neutral and anionic) is important in several fields like, among others, analytical mass spectrometry,[24−26] chiral recognition,[27] the effect of the chemical environment on the ^{133}Cs NMR chemical shifts,[28] and extraction of cesium from nuclear wastes.[29]

To complement and interpret the results of the experimental techniques, it is nowadays standard practice to approach the structures and energetics of metal ion adducts by using quantum chemical calculations.[21d] A few examples relevant to the present study are cited here. Amicangelo and Armentrout have applied threshold collision-induced dissociation technique and theoretical MP2 calculations for determining the bond dissociation energies and geometries of mono- and bis-complexes of alkali metal cations (including Cs^+) with benzene.[30] Similar studies were performed by Amunugama and Rodgers with toluene,[31] fluorobenzene,[32] aniline,[33] phenol,[34] anisole,[35] and naphthalene.[36] Generally, an electrostatic nature of the Cs^+ bonding was documented for these complexes. Hoyau and Ohanessian studied the complexes formed by alkali metal cations (Li^+ to Cs^+) and glycine using ab initio quantum chemical methods.[37] Computed binding energies indicate that the cation affinities decrease with the increase of the cation radius. The same conclusion can be drawn from experimental bond dissociation energies.[21d] The formation of cesium cation clusters with aromatic acidic molecules (phenol, benzoic, salicylic, and phthalic acids) and simpler diacids (maleic, fumaric, oxalic, and malonic acids) by means of electrospray ionization mass spectrometry (ESI-MS) was studied by Maria, Gal et al.[13,14,16] Calculations of structures and bonding energetics (thermodynamic basicities and affinities) of adducts formed between Cs^+ and neutral molecules,[15,16] as well as of small anion/Cs^+ clusters,[13,14,16] were carried out using DFT methods.

In parallel to their use as a complementary tool for experimental physicochemical studies, computational molecular modeling (ab initio as well as molecular 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.[38] Theoretical calculations coupled with Fourier transform ion cyclotron resonance mass spectrometry and nuclear magnetic resonance spectrometry data allowed a consistent picture of humic acid to be set up.[39−41]

A variety of oxygen-containing organic compounds (the most common being phenols and polyphenols, aliphatic and aromatic mono- and polycarboxylic acids) have been proposed as a simple analogue model, mimicking specific interaction sites for complexation with metal cations (including radioactive cesium) in SOM.[42] We decided to investigate a series of such compounds. The choice of organic molecules on which CsCA and CsCB calculations were carried out (Figure 1) was mostly based on the list reported in a review by Wood on the role of humic substances in the transport and fixation of metals, including the thermodynamic modeling of the cation binding.[43] The compounds in Figure 1 are also present in a longer list of so-called "precursor molecules", established in the context of molecular modeling of humic acid, that were selected from a library of molecular fragments derived from spectroscopic data.[38a] Noteworthy, some molecules in Figure 1 (bearing in particular phenol and carboxylic acid functions) are present in plants and soils.

The aim of the current research was to study the Cs^+ cation complexation with simple aromatic and aliphatic organic compounds as their neutral form (Figure 1) or in their anionic forms (deprotonated), when they were likely to be ionized in soil. As mentioned above, several functional groups present in SOM (particularly carboxylic groups) are acidic enough to be considerably deprotonated at pH conditions occurring in soils. In this respect, the Cs^+ cation affinities and basicities of anionic systems were examined, as well as typical binding patterns and charge distribution in the complexes, using computational techniques. Of course, the same work was carried out on neutral molecules. A word of caution should be expressed toward predicting the complexing ability of SOM with the cesium cation on the basis of gas-phase CsCA of simple organic molecule mimicking certain functionalities of SOM. Besides the heterogeneous nature of real complexation equilibria between Cs^+ and SOM, the complexity of the structure of the latter, which may be altered by the medium (pH change, ionic strength, polarity) and metal loading, should be underlined. However, reliable data for smaller molecules are needed before moving further to more complex SOM models, and the authors expect that the present work will be a step toward a better appraisal of cesium interactions with its environment.

2. Computational Details

All calculations were carried out using the Gaussian 03[44] program package. The B3LYP hybrid density functional,[45] which includes Becke's exchange functional and the correlation part due to Lee, Yang and Parr, was used with the def2-TZVP triple-ζ basis set,[46] developed by Ahlrichs and co-workers from previous Karlsruhe bases ("def-SV(P)", etc.). The basis sets were obtained from EMSL Basis Set Library.[47] For calculations involving the cesium cation, the corresponding 46 electron effective core potential[48] was used. This basis set was designed to give similar errors all across the periodic table.

Full conformational searches, geometry optimizations and vibrational analyses were performed for the neutral and anionic systems and their complexes with Cs^+. In the case of anionic systems all possible OH groups were considered as possible deprotonation sites. All stationary points were found to be true minima (NImag = 0). Vibrational frequency analysis was used to obtain thermodynamic data such as enthalpies and Gibbs free energies. The natural bond orbital (NBO) charges[49] were calculated for some of the studied species.

The cesium cation affinities (CsCAs) and basicities (CsCBs) as defined for reaction 1 in the Introduction, were computed at the reference temperature of 298.15 K. The energies of the most stable conformers of bases and complexes were used.

3. Results and Discussion

3.1. Calibration of the B3LYP/def2-TZVP Method for Calculation of CsCA and CsCB Values. The experimental CsCAs and CsCBs for several neutral and anionic bases are available.[23] We have used these experimental results to benchmark the performance of the B3LYP/def2-TZVP computational model. Corresponding CsCAs and CsCBs are given in Table 1.

Comparison of the experimental and calculated values for neutral bases indicates that for those systems our calculation method performs rather well. The error in calculated CsCBs

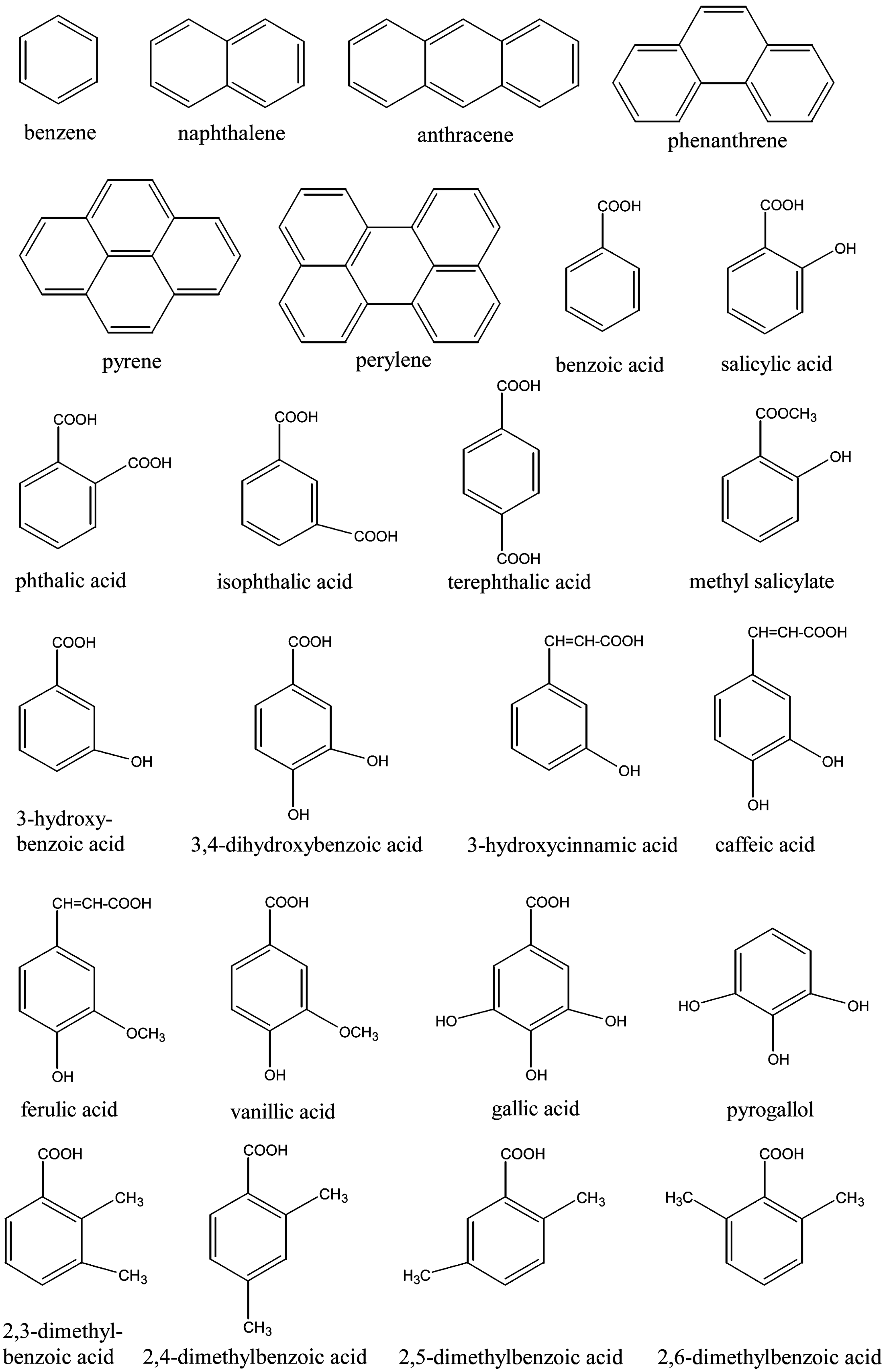
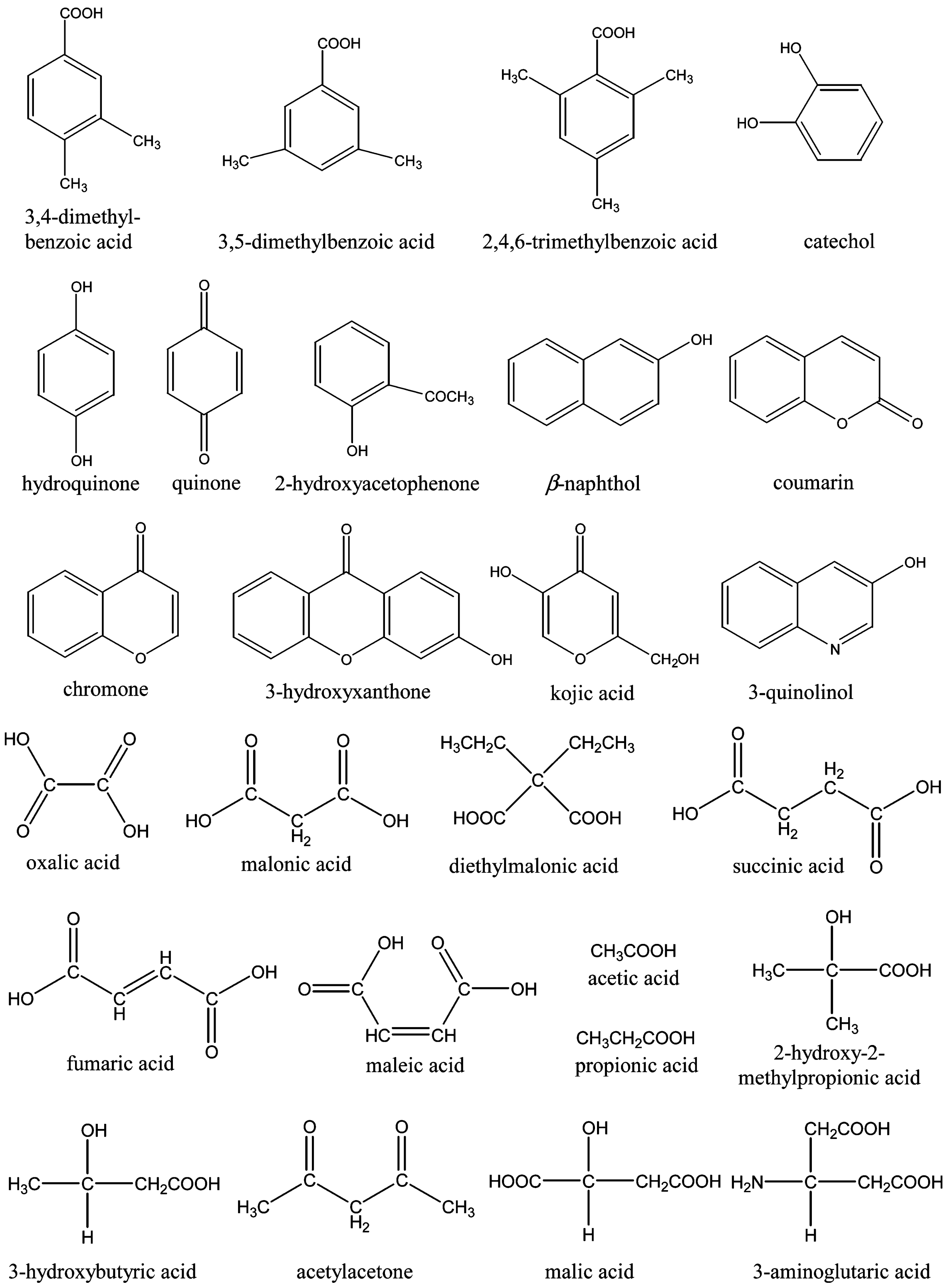


Figure 1. Part 1 of 3. Structures of neutral model compounds referred to in Table 1.

for neutral bases is usually less than 2.4 kcal/mol (1 kcal/mol = 4.184 kJ/mol), and the mean absolute deviation between experiment and calculations is 1.1 kcal/mol. The largest error, −3.0 kcal/mol, corresponds to benzene. For CsCAs the mean absolute deviation between experiment and calculations is 2.3 kcal/mol and the errors are still within 3.8 kcal/mol, except for 1,2-dimethoxyethane with the error of 9.3 kcal/mol. However, for that compound the large difference can be attributed to the



3,4-dimethylbenzoic acid, 3,5-dimethylbenzoic acid, 2,4,6-trimethylbenzoic acid, catechol

hydroquinone, quinone, 2-hydroxyacetophenone, *β*-naphthol, coumarin

chromone, 3-hydroxyxanthone, kojic acid, 3-quinolinol

oxalic acid, malonic acid, diethylmalonic acid, succinic acid

fumaric acid, maleic acid, acetic acid, propionic acid, 2-hydroxy-2-methylpropionic acid

3-hydroxybutyric acid, acetylacetone, malic acid, 3-aminoglutaric acid

Figure 1. Part 2 of 3.

adduct formation with retaining the structure of the most stable (*all-trans*) conformer of neutral ligand resulting in unidentate complex instead of the most stable bidentate one.[50] Using the corresponding conformation (1,2-dimethoxyethane in the *all-trans* form) of the complex gave us CsCA of 12.6 kcal/mol, in good agreement with experiment (experimental CsCA = 13.6 kcal/mol).

The CsCAs of anionic bases are at first glance somewhat less accurately described by the method used with the errors up to 18 kcal/mol and the mean absolute deviation between experiment and calculations being 7.1 kcal/mol. We have further investigated the large error in cases of NO_3^- and $CsSO_4^-$ ions using full geometry optimization and frequency calculations with B3LYP and Møller–Plesset second order perturbation theory

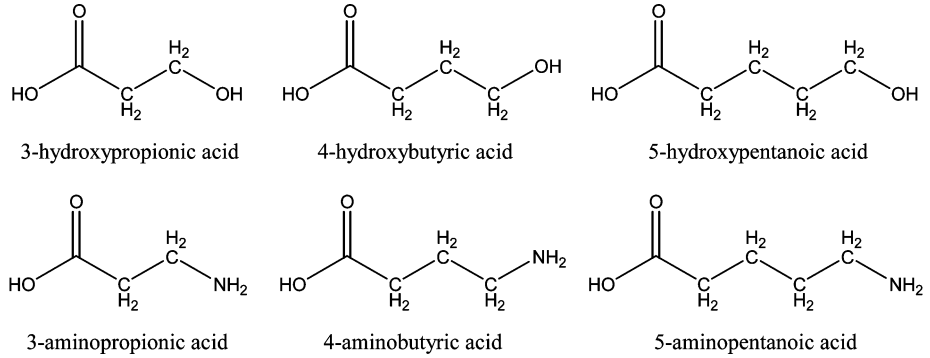

3-hydroxypropionic acid
4-hydroxybutyric acid
5-hydroxypentanoic acid
3-aminopropionic acid
4-aminobutyric acid
5-aminopentanoic acid

Figure 1. Part 3 of 3.

TABLE 1: Comparison of Calculated (B3LYP/def2-TZVP) Cesium Cation Affinities and Basicities with Experimental Data[23] (All Values in kcal/mol)

	experimental		calculated	
	CsCA	CsCB	CsCA	CsCB
	Neutral Bases			
H_2O	13.7	7.9	14.6	8.7
MeCN	19.2	13.7	19.0	13.1
CO_2	6.2	2.4	5.8	1.0
anisole	16.9	10.2	13.2	7.8
aniline	15.9	8.6	15.4	8.7
phenol	15.8	7.4	12.5	6.6
fluorobenzene	12.1	5.3	10.6	5.8
toluene	15.5	7.3	12.3	5.2
SO_2	10.9	5.2	11.2	5.9
MeOH	15.4	9.1	14.8	8.9
Me_2O	13.6		14.0	8.5
1,2-dimethoxyethane[a]	13.6		22.9	15.8
1,2-dimethoxyethane[b]			12.6	7.2
benzene	15.5	9.3	11.2	6.3
naphthalene	16.6	9.0	13.3	8.1
MAD[c]			2.3	1.1
	Anionic Bases			
OH^-	137.4		144.7	138.3
F^-	131.1		141.1	136.0
Cl^-	111.1		113.1	108.4
Br^-	107.2		105.3	100.7
I^-	99.9		97.9	93.4
NO_3^-	123.7		105.8	99.5
CsO^-	138.8		144.7	134.8
BO_2^-	101.7		103.6	95.4
$CsSO_4^-$	139.3		123.8	116.4
MAD[c]			7.1	

[a] CsCA and CsCB calculated using the most stable (cyclic) structure of the complex. [b] CsCA and CsCB calculated using the structure of the complex where 1,2-dimethoxyethane is in the *all-trans* form corresponding to the most stable conformation of the neutral base. [c] The mean absolute deviation between experiment and theory.

(MP2) methods with the quadruple-ζ def2-QZVPP basis set. Single point calculations at MP2 optimized geometries were also performed with CCSD(T) theory, which is called "the effective gold standard for single reference computations"[51] emphasizing its comparability with experimental data, and hence predictive power, using the same def2-QZVPP basis. The results of those additional calculations are presented in Table 2. Our best estimates of CsCA of NO_3^- and $CsSO_4^-$ anions (see Table 2) at CCSD(T)/def2-QZVPP level (using MP2 frequencies) are still far away from the experimental predictions. So, we believe that a careful re-examination of experimental data is warranted, and this is under way in our laboratories. Thus, our DFT calculation results should be considered reliable.

TABLE 2: Comparison of Cesium Cation Affinities Calculated at Different Levels with Experimental Data[23] (All Values in kcal/mol) for NO_3^-, $CsSO_4^-$, F^-, and OH^- Anions

method	basis	CsCA
	NO_3^-	
B3LYP	def2-TZVP	105.8
B3LYP	def2-QZVPP	105.7
MP2	def2-QZVPP	108.2
CCSD(T)[a]	def2-QZVPP	107.9
expt		123.7
	$CsSO_4^-$	
B3LYP	def2-TZVP	123.8
B3LYP	def2-QZVPP	125.0
MP2	def2-QZVPP	128.8
CCSD(T)[a]	def2-QZVPP	128.5
expt		139.3
	F^-	
B3LYP	def2-TZVP	141.1
B3LYP	def2-QZVPP	137.0
MP2	def2-QZVPP	135.5
CCSD(T)[a]	def2-QZVPP	135.7
expt		131.1
	OH^-	
B3LYP	def2-TZVP	144.7
B3LYP	def2-QZVPP	139.2
MP2	def2-QZVPP	139.4
CCSD(T)[a]	def2-QZVPP	139.0
expt		137.4

[a] Single-point energy calculations at MP2/def2-QZVPP geometries using MP2/def2-QZVPP frequencies.

If one excludes the very strongly deviating NO_3^- and $CsSO_4^-$ anions, it can be seen that the larger errors are associated with smaller anions (OH^- and F^-), where there is a high concentration of negative charge in anion. This is further confirmed by the calculations with much advanced def2-QZVPP basis (see Table 2), which lead to considerably smaller errors for the F^- and OH^- anions. Considering the theoretical results for polyatomic anions, it can be expected that the precision of the B3LYP/def2-TZVP method is comparable to that for neutral bases, and appropriate for our purpose.

3.2. Geometries of Cs^+/Neutral Ligand Complexes and the Corresponding Affinities and Basicities. The structures of neutral molecules investigated in the present work are presented in Figure 1, and the corresponding gas-phase cesium cation affinities and basicities are given in Table 3. A rapid perusal at the $-T\Delta S$ term shows that entropy effects are relatively constant, at least within series of similar compounds. The $-T\Delta S$ values for bifunctional aliphatic compounds for the longer alkyl chains appear to be systematically larger than for monofunctional or short chain bifunctional compounds.

TABLE 3: Calculated Gas-Phase Cesium Cation Affinities (CsCA, in kcal/mol) and Basicities (CsCB, in kcal/mol) of Neutral Model Compounds at 298.15 K

model compound	CsCA	CsCB	$-T\Delta S$
unsubstituted aromatic compounds	11.2−15.2	6.3−10.2	4.9−6.5
benzene	11.2	6.3	4.9
naphthalene	13.3	8.1	5.2
anthracene	14.8	9.6	5.2
phenanthrene	15.0	10.2	4.8
pyrene	15.2	10.0	5.2
perylene	14.5	8.0	6.5
substituted aromatic compounds	13.2−25.3	6.6−19.0	5.6−6.8
benzoic acid	18.1	12.2	5.9
salicylic acid	14.2	8.6	5.6
phthalic acid	25.3	19.0	6.3
isophthalic acid	19.9	13.0	6.9
terephthalic acid	16.1	10.0	6.1
methyl salicylate	17.8	11.5	6.3
3-hydroxybenzoic acid	19.4	13.5	5.9
3,4-dihydroxybenzoic acid	19.4	13.7	5.7
3-hydroxycinnamic acid	20.9	14.5	6.4
caffeic acid	20.3	14.1	6.2
ferulic acid	22.5	15.9	6.6
vanillic acid	18.5	12.7	5.8
gallic acid	18.0	12.3	5.7
pyrogallol	19.5	12.6	6.9
2,3-dimethylbenzoic acid[a]	18.5	12.0	6.5
2,4-dimethylbenzoic acid[a]	18.7	12.1	6.6
2,5-dimethylbenzoic acid	18.3	11.5	6.8
2,6-dimethylbenzoic acid[a]	18.1	12.4	5.7
3,4-dimethylbenzoic acid[a]	20.1	14.0	6.1
3,5-dimethylbenzoic acid	19.5	13.3	6.2
2,4,6-trimethylbenzoic acid[a]	19.2	13.2	6.0
catechol	17.5	10.8	6.7
hydroquinone	13.9	8.4	5.5
quinone	15.5	9.8	5.7
2-hydroxyacetophenone	16.0	10.3	5.7
β-naphthol	13.2	6.6	6.6
substituted heteroaromatic compounds	17.6−24.7	11.5−18.4	5.8−6.3
coumarin	24.7	18.4	6.3
chromone	24.5	18.1	6.3
3-hydroxyxanthone	23.8	18.0	5.8
kojic acid[a]	22.9	17.0	5.9
3-quinolinol	17.6	11.5	6.1
aliphatic compounds	16.2−30.9	10.0−22.9	6.1−8.8
acetic acid	16.7	10.6	6.1
propionic acid	16.9	10.6	6.3
oxalic acid[a]	17.8	11.5	6.3
malonic acid[a]	24.0	17.5	6.5
diethylmalonic acid	24.3	17.9	6.4
succinic acid[a]	23.6	16.6	7.0
fumaric acid	16.2	10.0	6.2
maleic acid	24.3	17.6	6.7
2-hydroxy-2-methylpropionic acid[a]	21.8	14.6	7.2
3-hydroxybutyric acid[a]	22.3	15.4	6.9
acetylacetone[a]	20.9	13.4	7.5
malic acid[a]	22.5	15.4	7.1
3-aminoglutaric acid[a]	28.7	21.6	7.1
3-hydroxypropionic acid	21.9	15.1	6.8
4-hydroxybutyric acid	26.0	18.4	7.6
5-hydroxypentanoic acid	27.1	18.6	8.5
3-aminopropionic acid	29.8	21.4	8.4
4-aminobutyric acid	30.9	22.9	8.0
5-aminopentanoic acid	30.6	21.8	8.8

[a] The most stable conformation of the free compound differs significantly from that in the complex with Cs^+ cation. For acetylacetone, the complex with Cs^+ is in keto form, but the free compound exists as an enol tautomer.

Unsubstituted Aromatic Molecules. The CsCAs of unsubstituted aromatic molecules lie in the range 11.2 to 15.2 kcal/mol. A conclusion can be made for a series benzene to anthracene/phenanthrene: more benzene rings in a compound means a larger CsCA (CsCB) value. However, this effect is quickly saturated: pyrene and perylene have practically the same CsCAs as phenanthrene. These aromatic compounds interact with Cs^+ via their π-systems (Figure 2a). The importance of cation/π interactions in various fields of molecular recognition and biochemistry was advocated by Ma and Dougherty.[52] A complete discussion of the role of electrostatic and "nonelectrostatic" interactions in noncovalent complexes involving aromatics and alkali metal cations can be found in their review.

There are very small CsCA differences (δCsCA = 0.10 to 0.53 kcal/mol) between cation attachment positions above the central or peripheral benzene rings at a distance ~3.5 Å (calculated average distance between cesium cation and carbon atoms of the ring), which leads to the conclusion that Cs^+ 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^+ affinities,[53] where energy differences in a 2 kcal/mol range were found in the cases of anthracene and phenanthrene.

Substituted Aromatic and Heteroaromatic Compounds. The range of calculated CsCAs for substituted aromatic and heteroaromatic compounds is relatively large: 13.2 to 25.3 kcal/mol. For most of the studied systems, Cs^+ 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 center (i.e., in 3-hydroxybenzoic acid; 3,4-dihydroxybenzoic acid; 3,4,5-trihydroxybenzoic acid, also known as gallic acid; *trans*-cinnamic acid derivatives: *trans*-3-hydroxycinnamic acid, *trans*-3,4-dihydroxycinnamic acid, also known as caffeic acid; *trans*-3-methoxy-4-hydroxycinnamic acid, also known as *trans*-ferulic acid; 2-hydroxyacetophenone). The cinnamic acid derivatives can also exist in a *cis*-form. Although the *cis*-configuration is less stable and less common in a natural environment, it was expected that Cs^+ chelation might be enhanced by this geometry. Indeed, the *cis*-forms of the isolated neutral acids were found to be less stable by 2.8−7.6 kcal/mol than the *trans*-forms. But contrary to our expectations, the *cis*-complexes with cesium cation were also less stable (by 2.4−5.1 kcal/mol) as compared to the *trans*-forms. A type of Cs^+ binding pattern, that we call "monocoordinated", is illustrated in the case of gallic acid in Figure 2b: the Cs^+ is bonded only to the carbonyl oxygen (C, O, and Cs^+ are in almost linear arrangement) and the hydroxylic proton is in *cis* position relative to the carbonyl group. This monocoordinated type of complexation is also favored for benzoic and terephthalic (or 1,4-dicarboxylic) acids. But aromatic carboxylic acids can complex with Cs^+ 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. This form will be called a "dicoordinated carboxyl complex" in the following. For example, methyl salicylate and vanillic acid (Figure 2c) give such a dicoordinated complex. Both types of complexes are found for the series of dimethylbenzoic acids (except for 2,6-dimethylbenzoic acid) and 2,4,6-trimethylbenzoic acid. The enthalpy differences between these two kinds of complexes range from 0.01 kcal/mol (2,3-dimethylbenzoic acid) to 1.3 kcal/mol (3,4-dimethylbenzoic acid) in favor of a linear monocoordinated complex. However, there is no general conclusion that can be drawn about the energetically more favorable structure.

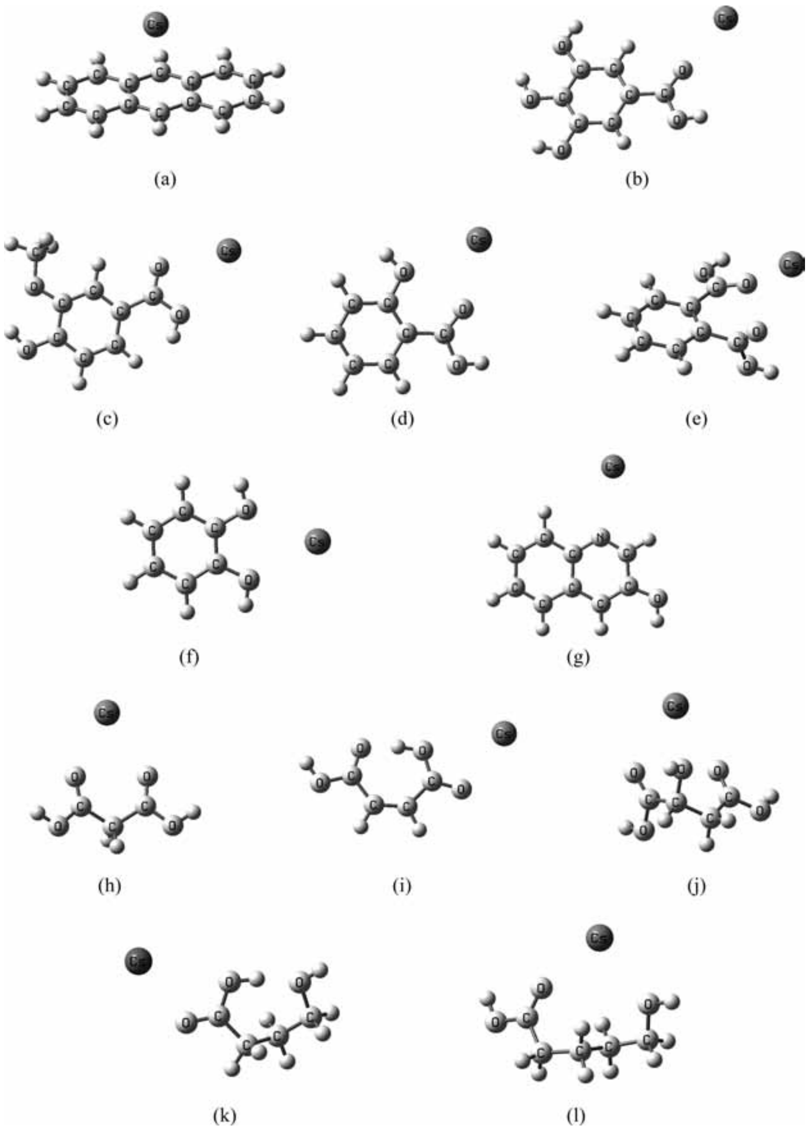


Figure 2. The optimized structures of cesium cation complexes with (a) anthracene, (b) gallic acid, (c) vanillic acid, (d) salicylic acid, (e) phthalic acid, (f) catechol, (g) 3-quinolinol, (h) malonic acid, (i) maleic acid, (j) malic acid, (k) 4-hydroxypropionic acid, and (l) 5-hydroxypentanoic acid.

The above-mentioned *trans*-ferulic, vanillic, and gallic acids were also expected to form a true bidentate (chelate-type) complex in a way where Cs^+ is interacting with another functional group(s) ($-OH$, $-OCH_3$), but the complexation enthalpies of such complexes are, respectively, by 9.8, 5.4, and 1.0 kcal/mol less stable than the simple Cs^+ bonding to the carbonyl group. The tendency for the formation of chelate-type complexes is greater when an electron-rich functional group is in ortho position relative to another such functional group. In these chelate-type complexes the most favorable position for Cs^+ is, if possible, more or less symmetrical between two oxygen atoms of the neighboring oxygen-containing groups, like in salicylic acid (Figure 2d, adjacent $-COOH$ and $-OH$ groups), phthalic and isophthalic acids (Figure 2e, $-COOH$ groups), pyrogallol and catechol (Figure 2f, $-OH$ groups). It is worth mentioning that an intramolecular hydrogen bond should be broken to form these Cs^+ chelates.

For compounds in which a carbonyl group is a part of a rigid six-membered cycle (quinone, coumarin, chromone, 3-hydroxyxanthone, kojic acid), a monocoordinated binding pattern with an angle $C{=}O{-}Cs^+$ close to 180° is typical, together with a rather large CsCA.

The complexation of Cs^+ with β-naphthol is similar to the phenol/Cs^+ interaction.[13,34] As for phenol, we found that there are three conformers relatively close in energy. The Cs^+ 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 β-naphthol is only 0.7 kcal/mol in favor of the unsubstituted benzene ring and the interaction of Cs^+ with the oxygen atom of hydroxyl group is only by 0.3 kcal/mol weaker than with the unsubstituted ring. Calculations by Amunugama and Rodgers and by Maria et al. lead to the conclusion that the phenol π-complex and the oxygen-bonded complex are very close in energy. In the complex of 3-quinolinol the cation attaches to the nitrogen atom (Figure 2g), which appears to be a stronger basic center as compared to the oxygen atom (δCsCA = 6.8 kcal/mol). Likewise, it has been observed that pyridine is a stronger base than phenol toward Li^+ [54,55] and Na^+.[21d]

The distances between Cs^+ and the corresponding bonding centers of substituted aromatic and heteroaromatic compounds are 2.8−3.2 Å in monocoordinated and bidentate complexes and somewhat longer (2.9−3.7 Å) in dicoordinated complexes, where Cs^+ interacts with both oxygens of the carboxylic group.

Aliphatic Compounds. The CsCAs for aliphatic compounds bearing carboxylic acid functions are in the 16.2−30.9 kcal/mol range. In most cases a dicoordinated or a bidentate complex is favored, except for acetic, propionic, and fumaric acids, where Cs^+ is monocoordinated to the carbonyl oxygen of the carboxyl group. In the case of bifunctional compounds, one of the possible Cs^+ adducts has a symmetric bonding with two carbonyl oxygens of different functional groups, like for oxalic, malonic (Figure 2h), succinic acids, and acetylacetone (in its keto form; the most stable tautomer for acetylacetone in the gas phase is the enol form),[56] which give the most stable complexes. Another possibility is the Cs^+ dicoordination (diethylmalonic, maleic (Figure 2i), 3-aminoglutaric acids) or chelation (e.g., in 2-hydroxy-2-methylpropionic, 3-hydroxybutyric acids). The Cs^+ interacts even with three oxygen atoms in the complex formed with malic acid (Figure 2j). For the aliphatic acids studied, the distances between cesium cation and oxygen atoms are in a range of 2.9 to 3.5 Å.

The chelating ability of two electronegative groups (carboxyl and hydroxyl or amino groups) separated by an alkyl chain $(-CH_2-)_n$, $n = 2-4$, was also examined. All possible rotamers (rotations by 120 degrees steps around C−C and C−O or C−N single bonds) were considered. In fact, it was found that the Cs^+ was preferably bound as a dicoordinated complex to the two oxygens of a carboxyl group (like for diethylmalonic, maleic, and 3-aminoglutaric acids) in most cases. The chelated structures (Cs^+ bound to both carboxyl and hydroxyl or amino groups) were by 2.3−7.7 kcal/mol less stable. This is caused by the tendency of the carboxyl group to form an intramolecular hydrogen bond with the electronegative hydroxyl or amino group (Figure 2k) in the studied acids. The only exceptions were 3-hydroxypropionic and 5-hydroxypentanoic acids for which the chelate forms (Figure 2l) were more stable by 0.1 and 2.1 kcal/mol, respectively, than the structures with an intramolecular hydrogen bond and the cesium dicoordinated to the carboxyl group. For several aliphatic compounds, the $-T\Delta S$ term tends to be significantly larger than the average. The corresponding decrease in the entropy change for reaction 1, $\Delta S(1)$, is attributed to a partial freezing of conformational freedom due to Cs^+ attachment.

The most significant comparison concerning the chelate effect, i.e. cesium cation binding simultaneously to the two substituents, can be done in the phthalic (benzene dicarboxylic) acid series. The CsCA value is highest in the case of the ortho compound (phthalic acid), for which the bidentate-type complex is the strongest. This chelate effect is largely attenuated for the meta (isophthalic) acid, and is completely absent for the para (terephthalic) acid, because of a greater distance of two carbonyl oxygen atoms, and a continuous lowering of the affinities in the series phthalic, isophthalic, terephthalic, 25.3, 19.9, and 16.1 kcal/mol, is observed. Another comparison that shows the large stabilization due to the bidentate bonding and intramolecular hydrogen bond is the case of maleic acid (*cis*-isomer of 2-butenedioic acid), where the Cs^+ can simultaneously interact with two oxygen atoms of the same carboxyl group and the intramolecular hydrogen bond is conserved. The corresponding CsCA is 24.3 kcal/mol, almost 8.1 kcal/mol larger than in the case of fumaric acid (*trans*-isomer of 2-butenedioic acid), for lack of this kind of stabilization.

The dicoordinated and bidentate complexes are not always more stable than the monocoordinated complexes, e.g. for the ferulic acid the monocoordinated complex is by 8.3 kcal/mol more stable than the bidentate complex of salicylic acid. The CsCA values of dicoordinated and bidentate complexes vary in a large range, from 14.2 to 30.9 kcal/mol (respectively salicylic acid and 4-aminobutyric acid).

A NBO analysis revealed that the Cs^+ carries a positive charge of ca. 0.99 electron unit in all the studied Cs^+/neutral molecule complexes. This small amount of charge transfer toward Cs^+ is a general characteristic of adducts between alkali metal cations and neutral molecules, and accordingly, the interaction is considered as mostly electrostatic. This is consistent with the fact that the complex formed with a polar molecule has a tendency to adjust its geometry such as the metal−ligand bond is aligned with the permanent dipole of the molecule.[21d] In the case of nonpolar (or weakly polar) aromatic compounds, the more complex cation/π interaction[52] is dominant.

3.3. Geometries of Cs^+/Anion Ligand Complexes and the Corresponding Affinities and Basicities. In the usual range of organic soil pH, it is expected that acidic functional groups (−COOH, −OH, −SH, etc.) of SOM macromolecules may be weakly to totally ionized, thus, contributing significantly to metal complexation and transport in the biosphere. Hence, complexes of Cs^+ cation with anions of organic acids were studied and the calculated CsCAs and CsCBs are listed in Table 4. The corresponding quantities are approximately 4−5 times larger than for the neutral counterparts, being in the range of 90−118 kcal/mol. Examination of the $-T\Delta S$ term shows that, as for neutral molecules, entropy effects are relatively constant.

In cases of acids bearing both hydroxyl and carboxyl groups, both carboxylate and phenolate anions were considered, as the electron delocalization in the π-orbitals of the anion extending over the entire molecule, plus stabilization of the charge by hydrogen bonding whenever possible, lead to very similar acidities of hydroxyl and carboxyl groups in the gas phase.[57,58] However, our calculations indicate that although in several cases (e.g., anions of caffeic and gallic acids) the phenolic form of anion is more stable, the Cs^+ cation always prefers to bind to carboxylate rather than phenolate form (where both phenolate and carboxylic binding sites were tested) of an anion.

The CsCAs for anionic *substituted aromatic compounds* range from 90.1 to 112.6 kcal/mol and for anionic *aliphatic compounds* from 95.8 to 118.0 kcal/mol. There is no direct comparison possible with experimental values for such anions, but published anion CsCAs[23] are in the range 100−140 kcal/mol. The Cs^+ binds in a rather similar way to almost all anions studied in this work. For the carboxylate group, Cs^+ is bonded in a symmetric dicoordinated way, i.e. the cesium cation interacts with both oxygen atoms of the group. Intramolecular hydrogen bonding tends to be preserved in the complex whenever possible, for example by a nearby hydroxyl (e.g., in salicylate, Figure 3a) or carboxyl group (e.g., in phthalate, Figure 3b). The hydrogen bond donor group may also be in a farther position, for instance the amino group in 3-aminoglutarate (Figure 3c). The distances between Cs^+ and the oxygen atoms are about 2.5−3.0 Å as compared to 2.8−3.7 Å in the complexes with neutral molecules.

A notable exception is the complex between Cs^+ and oxalate anion, where the cation interacts with the two oxygen atoms of the two different carboxyl groups (Figure 3d). This type of complex is more favorable by 3.8 kcal/mol (δCsCA) compared with the usual way of binding to a single carboxylate group. This is attributable to the energetically favorable formation of an intramolecular hydrogen bond between the remaining proton and the carboxylate oxygen.

Cs^+ affinities and basicities of phenolate anions were studied for some hydroxyl substituted benzenic compounds without carboxyl functions: anionic forms of methyl salicylate, pyro-

TABLE 4: Calculated Gas-Phase Cesium Cation Affinities (CsCA, in kcal/mol) and Basicities (CsCB, in kcal/mol) of Anionic Model Compounds at 298.15 K

anion of model compound[a]	CsCA	CsCB	$-T\Delta S$
substituted aromatic compounds	90.1−112.6	84.6−105.3	5.5−8.0
benzoic acid	111.9	105.3	6.6
salicylic acid	102.7	96.0	6.7
phthalic acid	93.9	88.2	5.7
isophthalic acid	108.3	101.1	7.2
terephthalic acid	107.3	100.3	7.0
methyl salicylate	112.6	104.8	7.8
3-hydroxybenzoic acid	110.6	103.5	7.1
3,4-dihydroxybenzoic acid	97.0	90.2	6.8
3-hydroxycinnamic acid	108.5	102.6	5.9
caffeic acid	90.1	84.6	5.5
ferulic acid[b]	111.4	105.3	6.1
vanillic acid	112.0	104.9	7.1
gallic acid	92.2	86.1	6.1
pyrogallol	98.9	93.1	5.8
2,3-dimethylbenzoic acid	111.0	103.8	7.2
2,4-dimethylbenzoic acid	112.0	105.1	6.9
2,5-dimethylbenzoic acid	111.6	103.6	8.0
2,6-dimethylbenzoic acid	109.2	102.1	7.1
3,4-dimethylbenzoic acid	110.3	104.6	5.7
3,5-dimethylbenzoic acid	112.5	104.7	7.8
2,4,6-trimethylbenzoic acid	109.7	102.8	6.9
catechol	100.2	93.5	6.7
hydroquinone	107.0	99.9	7.1
2-hydroxyacetophenone	106.6	99.3	7.3
aliphatic compounds	95.8−118.0	89.5−111.6	5.2−8.1
acetic acid	118.0	111.6	6.4
propionic acid	116.8	110.1	6.7
oxalic acid	104.6	97.2	7.4
malonic acid	97.9	90.6	7.3
diethylmalonic acid	96.3	89.9	6.4
succinic acid	97.4	90.1	7.3
fumaric acid	108.3	101.2	7.1
maleic acid	95.8	89.5	6.3
2-hydroxy-2-methylpropionic acid	108.0	101.3	6.7
3-hydroxybutyric acid	108.6	102.0	6.6
3-aminoglutaric acid[b]	99.1	92.9	6.2
3-hydroxypropionic acid	109.3	102.7	6.6
4-hydroxybutyric acid	108.4	101.7	6.7
5-hydroxypentanoic acid	111.2	103.1	8.1
3-aminopropionic acid	112.9	106.0	6.9
4-aminobutyric acid	112.4	106.3	6.1
5-aminopentanoic acid	111.1	105.9	5.2

[a] The deprotonation has taken place at the carboxyl group, if present, or otherwise at the phenolic hydroxyl group. [b] The most stable conformation of the free compound differs significantly from that in the complex with Cs^+ cation. For ferulic acid, the complex with Cs^+ is in *trans*-form but free compound exists as a *cis*-form. (For 3-hydroxycinnamic and caffeic acids, the complexes and free compounds exist as *trans*-forms.)

gallol (the dissociation of the central −OH group is favored), catechol, hydroquinone, and 2-hydroxyacetophenone. The CsCA and CsCB values are comparable with the compounds for which the carboxylate anion acts as a coordination center for Cs^+. The cesium cation is also chelated more or less symmetrically between the phenolate oxygen and the carbonyl of $-COOCH_3$ or $-COCH_3$ groups for the anionic forms of methyl salicylate (Figure 3e) and 2-hydroxyacetophenone. For the other compounds, several possible structures exist. The Cs^+ may bound to substituted phenolate (i) by a bidentate interaction with the oxygen atoms of the phenolate and hydroxyl (as for pyrogallol and catechol anions) or (ii) by only the phenolate oxygen, in a linear $C-O-Cs^+$ arrangement (as for hydroquinone anion, see Figure 3f) or (iii) by the phenolate oxygen but located out of plane (exists for all the three anions, see Figure 3g for hydroquinone anion). In the last case, the complex may be additionally stabilized by cation/π interaction. The complexation enthalpy corresponding to the third conformation (iii) for catechol anion is larger by 0.8 kcal/mol than the first (bidentate) conformer (i), while for pyrogallol anion the bidentate complex is preferred, being more stable by 0.6 kcal/mol than the third conformer. The linear complex is favored by 1.4 kcal/mol for hydroquinone anion relative to the third conformer, where the cation is located out of plane.

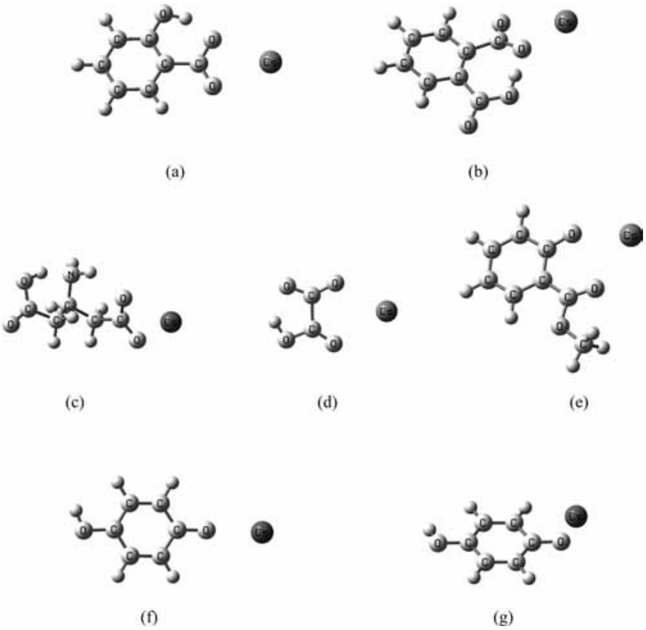


Figure 3. The optimized structures of cesium cation complexes with (a) salicylate anion, (b) phthalate anion, (c) 3-aminoglutarate anion, (d) oxalate anion, (e) methyl salicylate anion, and (f, g) hydroquinone anion.

Studies on the carboxylate anions with hydroxyl or amino groups separated by an alkyl chain $(-CH_2-)_n$, $n = 2-4$, were carried out in a similar way. Here the Cs^+ was in all cases bound to both carboxylate oxygens in a more or less symmetric dicoordinated mode (differences in Cs−O distances were less than 0.11 Å). All hydroxycarboxylate complexes displayed also intramolecular hydrogen bonding between the hydroxyl group hydrogen and one of the carboxylate oxygens (O···H distances were in the range of 1.7 to 1.9 Å). However, in the case of aminocarboxylate anions, only 3-aminopropanoate had a similar hydrogen bond (O···H(N) distance 2.3 Å), while in the other cases the *all-trans* structure of carbon−carbon backbone was preferred for complexes (the cyclic form was by 0.9 and 1.4 kcal/mol less stable for complexes involving the anions of 4-aminobutyric acid and 5-aminopentanoic acid, respectively). For the last two aliphatic anions in Table 4, the $-T\Delta S$ terms are smaller than for the other systems. The corresponding increase in the entropy change for reaction 1, $\Delta S(1)$, may be attributed to a relaxation of the conformational restraint due to the intramolecular hydrogen bond initially present in the anion.

In all the studied complexes with anionic bases, a NBO charge density analysis showed that the Cs atom is carrying an average 0.96−0.97 positive charge and both oxygen atoms have an average 0.7−0.8 negative charge, while the rest of the anion has an average 0.6 positive charge.

A general observation is that the existence of an internal hydrogen bond, for example when a function $-O^-$ or $-COO^-$

is close to a −OH or −COOH group, decreases CsCA and CsCB, with the exception of oxalate, where the hydrogen bond is formed between oxygens which are not involved in Cs^+ binding.

4. Conclusions

In the context of the interaction of cesium with organic functions governing the complexing ability of soil organic matter, intrinsic intermolecular forces between the metal cation and neutral or anionic molecule were studied by DFT, in the form of Cs^+ affinities and basicities, as well as geometries of the complexes.

The B3LYP/def2-TZVP method gives in general CsCAs and CsCBs in a good agreement with experiment. The strong deviations in the case of NO_3^- and $CsSO_4^-$ anions need further experimental investigations as the high-level CCSD(T)/def2-QZVPP calculations support B3LYP results.

The enthalpies of interaction for Cs^+/neutral molecule (CsCAs) fall in the range 11−31 kcal/mol. The smallest values correspond to π-complexes with aromatic systems. This study reveals that phenols bind Cs^+ with similar energy on the π-system or on the oxygen atom, in agreement with literature data. The Cs^+ cation tends to form a more localized type of bond in substituted aromatic compounds via the lone pair of the electronegative oxygen atoms borne by the substituents. The oxygen-containing neutral molecules show approximately 1.5−2 times larger CsCAs than unsubstituted aromatic systems. When the carboxyl and hydroxyl groups are present in the compound, the carbonyl oxygen is preferred to the hydroxyl group as the binding center. Diacids with carboxylic functions in favorable position for chelation exhibit a large cesium cation affinity. For bifunctional molecules, the bidentate complexes are not always the most stable form, because internal hydrogen bonding competes with cesium complexation. The variations in Cs^+ affinities and basicities are rather parallel. However, entropy effects are apparent in flexible systems, due to change in internal degrees of freedom induced by Cs^+ complexation.

As metal cation binding with natural organic matter basically occurs via carboxylic functions that are to a large extent ionized at usual soil pH, most of the calculations on Cs^+ complexation with anions were devoted to the carboxylate forms of the acids, already studied in their neutral form, and to a few phenolates, which were selected for comparison. The CsCAs of the oxygen anions considered in this study are in the range 90 to 118 kcal/mol. The presence of a second (neutral) function able to form a strong hydrogen bond with the negatively charged site tends to diminish the cation affinity. Therefore, the largest CsCAs pertain to the monofunctional anions, or to anion in which the other(s) function(s) cannot interact with the negative charge.

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.

Although still oversimplified if we consider all the effects that are not taken into account, the present calculations give the order of magnitudes and trends of the elementary interactions that are virtually unknown experimentally. The main structural features of the complexes are also offered by such calculations. Considering the scarcity of data, we hope that this work will stimulate further joint experimental and theoretical studies on the interaction between the cesium cation and organic matter.

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Supporting Information Available: Energies, enthalpies, free energies, and structures of the most stable forms of studied acids, corresponding anions, and their complexes with cesium cation. This material is available free of charge via the Internet at http://pubs.acs.org.

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