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Cu^+ association to some Ph–X (X = OH, NH_2, CHO, COOH, CF_3) phenyl derivatives. A comparison with Li^+ complexes

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This paper is dedicated to Prof. D.K. Bohme on the occasion of his 65th birthday.

Abstract

The complexes of Cu^+ with phenol, aniline, benzaldehyde, benzoic acid, and trifluromethyl-benzene were investigated through the use of MP2 and density functional theory (DFT) methods. Both harmonic vibrational frequencies and optimized geometries were obtained at the B3LYP/6-311G(d,p) and MP2(full)/6-311G(d,p) levels of theory. Final energies were obtained through single point B3LYP/6-311+G(3df,2p)//B3LYP/6-311G(d,p) calculations. The interactions of Cu^+ with these aromatic compounds have a non-negligible covalent character, which clearly differentiate Cu^+-complexes from the corresponding Li^+-complexes. These dissimilarities are reflected in the geometries, binding energies and infrared spectra of the most stable adducts. For Li^+ only conventional π-complexes should be expected when interacting with aniline, while Cu^+ attaches preferentially to the *para* carbon atom. For phenol, besides the conventional π-complexes, a 12% of oxygen attached species are expected to be found upon Li^+ association. Conversely, no oxygen attached species should be formed in reactions of phenol with Cu^+. For benzoic acid and benzaldehyde, Li^+ aligns with the dipole moment of the base, interacting exclusively with the carbonyl oxygen in the plane of the molecule. This is also the case in Cu^+–benzoic acid complex, while in the Cu^+–benzaldehyde complex the metal ion also interacts with the aromatic π-system. Cu^+ binding enthalpies (BEs) are systematically larger (about 1.3 times) than Li^+ BEs. The covalent character of Cu^+ interactions is associated with electron donations from bonding (π) orbitals or lone-pairs of the base toward the 4s empty orbital of the metal and with back-donations from the occupied d orbitals of the metal toward antibonding (π^*) empty orbitals of the base. This non-negligible covalent character is also reflected in a rough correlation between the calculated Cu^+ BEs and the available experimental proton affinities that does not exist for Li^+ BEs.

Keywords: Phenyl derivatives; Cu^+ binding energies; Li^+ binding energies; Density functional calculations

1. Introduction

The association of metal cations to unsaturated organic compounds attracted much attention because cation–π interactions are important in many phenomena and they act, in some specific cases, as the driving force of non-covalent interactions [1–8]. These complexes are frequently involved in molecular recognition processes [5] and may play an important role in removing metal cations from contaminated media, as well. These interactions are also expected to be involved in many important biological processes [9–12] as well as in catalytic mechanisms [13,14]. For instance, transition metals, such as Cu^+, play important roles in oxidation, dioxygen transport and electron transfer processes [15,16], and the tendency of different metal ions to bind to different small biochemical molecules was used to gain insight into the reactivity of more complicated biological systems, through the use of different mass spectrometry techniques [17–19]. In this respect, the work of Bohme et al. [20–22] on the reactivity of different metal monocations complexed with small biochemical systems or to other neutral molecules of biological relevance can be consider seminal in this field.

In our group we have paid particular attention to the interaction of transition metal monocations, such as Cu^+ and Ni^+ to different α,β-unsaturated and aromatic compounds containing

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Si, and Ge as heteroatoms. All these systems had in common that they bind Cu^+ and Ni^+ much more strongly than their carbon analogs [23–25] reflecting the ability of SiH_3 and GeH_3 groups to strongly interact with transition metal monocations, through agostic-type linkages [26]. These agostic-type interactions involve electron donations from the $\sigma_{X\text{–}H}$ (X = Si, Ge) bonding orbitals toward the 4s empty orbital of the metal, and back-donations from d occupied orbitals of the metal toward the corresponding $\sigma_{X\text{–}H}{}^*$ antibonding orbitals of the base [23,24,27,28].

The aim of this paper is to investigate whether similar mechanisms may be involved in the interactions of Cu^+ with aromatic systems containing more electronegative substituents. For this purpose we have chosen as suitable model systems: phenol, aniline, benzaldehyde, benzoic acid and trifluoromethyl-benzene. For the sake of comparison we have included in this survey the corresponding Li^+ complexes, where the aforementioned orbital interactions do not take place, and the bonding is essentially ionic.

2. Computational details

The geometries of the neutral compounds under investigation and those of their Cu^+ complexes were optimized using the B3LYP density functional theory (DFT) approach as implemented in the Gaussian-03 suite of programs [29]. The B3LYP method includes the Becke's three-parameter non-local hybrid exchange potential [30] and the non-local correlation functional of Lee et al. [31]. This functional has been shown to be well suited for the study of complexes involving singly charged transition metal ions [32–36] and alkali metal ions [37,38]. The geometries of the stationary points of the different potential energy surfaces (PESs) were optimized by using a 6-311G(d,p) basis set expansion, using an ultrafine grid. Harmonic vibrational frequencies were obtained at the same level of theory to classify the stationary points as local minima or transition states and to estimate the corresponding zero point energies (ZPE), which were scaled by the empirical factor 0.9806 [39].

Not always DFT and MP2 approaches yield the same results as far as the optimized geometries of complexes between aromatic systems and transition metal cations are concerned. For example, while both B3LYP and BLYP DFT methods predict the C_s benzene–Cu^+ complexes in which Cu^+ interacts specifically with two carbons of the aromatic ring to be local minima of the PES [40] these minima are not found at the HF and MP2 levels [40,41] and only the C_{6v} conventional π-complex is predicted to be stable. A similar behavior was recently reported for phenylsilane–Cu^+ and phenylgermane–Cu^+ complexes [42]. Hence, we have decided to carry out also the geometry optimizations of the Cu^+-complexes under investigation at the MP2(full)/6-311G(d,p) level for the sake of completeness. Aniline–Cu^+ and benzene–Cu^+ complexes were taken as suitable examples for measuring the influence of correlation effects beyond second order.

For all the local minima, final energies were obtained, on the aforementioned B3LYP/6-311G(d,p) optimized geometries, by using a 6-311+G(3df,2p) basis set expansion, that includes diffuse functions on all heavy atoms, as well as high angular momentum functions, that may be important when describing π-complexes. For Cu the 6-311+G(3df,2p) basis set corresponds actually to the (14s9p5d/9s5p3d) Wachters–Hay [43,44] basis supplemented with a set of (1s2p1d) diffuse functions and with two sets of f functions (rather than d) and one set of g functions (rather than f).

The same theoretical procedure was adopted for the study of the corresponding Li^+ complexes. Phenol was excluded because its Li^+ complexes were already reported in the literature [38] at the same level of theory employed in this work. The complexes between aniline and Li^+ were also studied theoretically and experimentally before [45] but the level of theory used was different from that adopted in this paper and therefore this compound and its Li^+-complexes were included in our survey, together with benzaldehyde, benzoic acid and trifluoromethyl-benzene.

Cu^+ and Li^+ binding enthalpies (BEs), were evaluated by subtracting from the B3LYP energy of the complex the energy of the neutral and that of the metal cation, after including the corresponding B3LYP/6-311G(d,p) thermal corrections.

The base–Cu^+ interactions were identified by analyzing the donation from occupied orbitals of the neutral toward vacant orbitals of Cu^+, and/or from occupied orbitals of Cu^+ toward antibonding orbitals of the neutral, through a second order perturbation NBO analysis [46]. This analysis will be complemented with that carried out in terms of the atoms in molecules (AIM) theory [47]. For this purpose we have evaluated the contour maps of the energy density, defined as

$$H(\vec{r}) = \frac{1}{4}\nabla^2\rho(\vec{r}) - G(\vec{r})$$

where $\nabla^2\rho(\vec{r})$ and $G(\vec{r})$ are the Laplacian of the electron density and the kinetic energy density, respectively.

Bonding regions in which the energy density is negative correspond to covalent linkages [24,48]. Conversely, typical ionic bonds are associated with regions where the energy density is clearly positive. These analyses will be complemented with that carried out in terms of the lengthening or shortening of the bond lengths and in terms of the shifting of the corresponding stretching frequencies.

3. Results and discussion

3.1. Structure and bonding

The structures of the complexes of phenol, aniline, benzoic acid, benzaldehyde and CF_3–Ph with Cu^+ are presented in Fig. 1. This figure contains also the Li^+ complexes that to the best of our knowledge were not reported before in the literature. Their total energies, relative enthalpies, relative free energies, and the corresponding binding energies are summarized in Table 1.

The first conspicuous fact of Fig. 1 is that besides the conventional π-complexes, X1, in which the metal cation locates above the aromatic ring at a distance of about 1.8 Å from its center, there are other conformers which, in some cases, are more stable than the π-complex, in particular when the attacking ion is

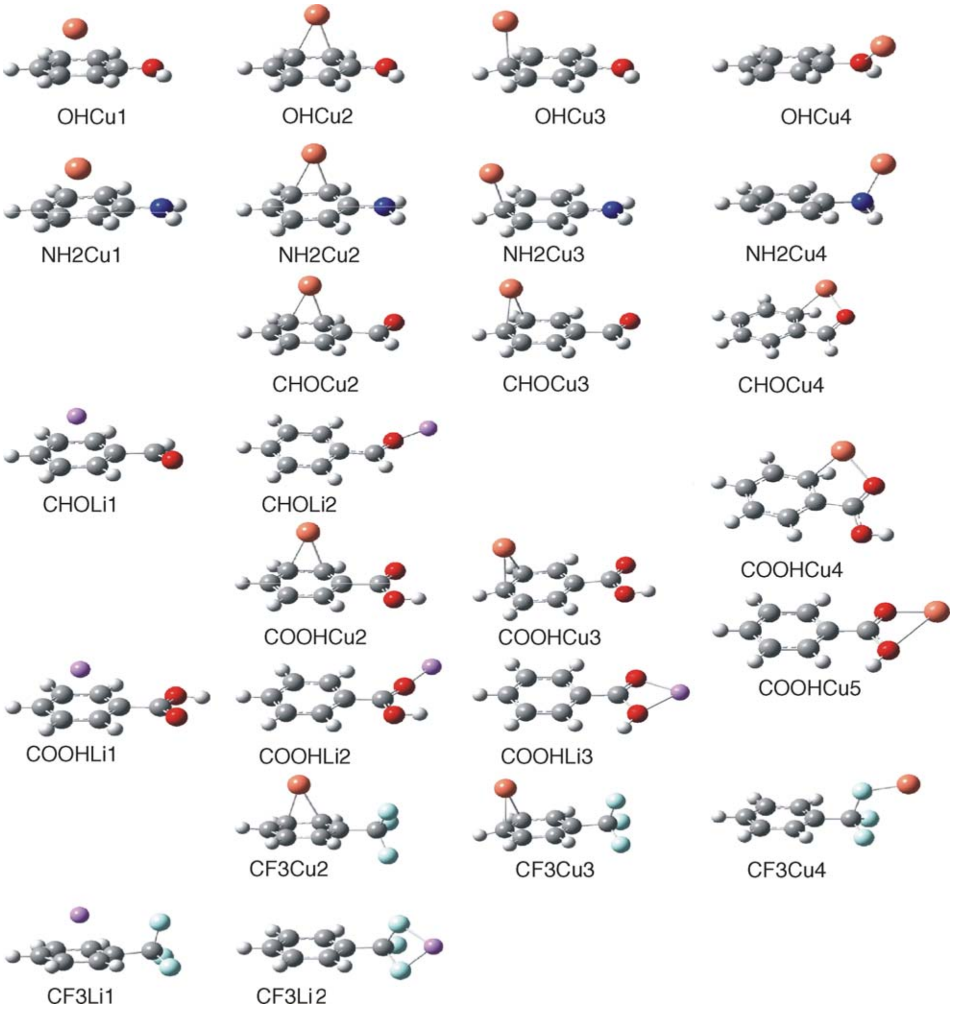
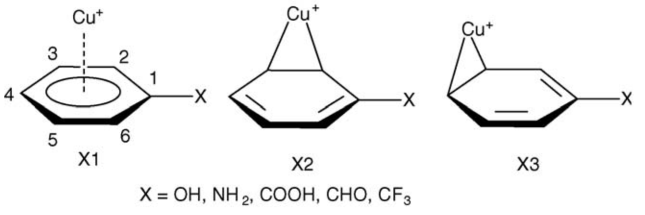


Fig. 1. B3LYP/6-311G(d,p) optimized structures of Cu^+- and Li^+-complexes with Ph–X (X = OH, NH_2, CHO, COOH, CF_3) benzene derivatives.

Cu^+. Hence, although the global minima of the phenol–Li^+ [38] and aniline–Li^+ [45] systems corresponds to the conventional π-complexes, Cu^+ interacts also with the *ortho* and *meta* or with the *meta* and *para* pairs of carbon atoms of the six-membered ring, to yield complexes of the X2- and X3-type shown in Scheme 1, which are of similar stability or more stable than the conventional X1-type complexes.

For benzaldehyde and trifluoromethyl-benzene the X1 conventional π-complexes are local minima at the MP2 level, but they evolve to the X3-type structures when optimized at the B3LYP level. For aniline, X2- and X3-type complexes were not found at the MP2 level as they collapse to the conventional π-complex, NH2Cu1. However, for X = CHO, COOH, CF_3, either X2 or both X2- and X3 (X = OH)-type of complexes were found to be local minima of the PES also at the MP2 level of theory.



Scheme 1.

As indicated above, the fact that DFT methods favor the association of Cu^+ to a C–C bond, while the MP2 approach favors the conventional π-complex was analyzed by Dargel et al. [40]. Nevertheless, the critical question of which of the two methods is more reliable is still without answer. Hence, we have decided to take a step further and try to verify if the inclusion of correlation effects beyond second order can change the description obtained at the MP2 level. For this purpose, we have used the complexes of benzene and aniline with Cu^+ as suitable model systems, whose geometry was optimized at the QCISD/6-311G(d,p) level of theory, that is correct at least at fourth order. These results showed that for benzene, besides the η^6 conventional π-complex, the η^2 one obtained at the DFT level, in which the metal cation interacts with a specific C–C bond, is also a local minimum of the PES, in contrast with the predictions based on MP2 calculations, although this local minimum is slightly less stable than the conventional π-complex. The situation is rather similar for aniline–Cu^+ complexes. At the QCISD level, both the conventional π-complex, obtained at the MP2 level, and the complex

Table 1
Total energies (E, hartrees), relative enthalpies (ΔH, kJ mol^{-1}), relative free energies (ΔG, kJ mol^{-1}), binding enthalpies (BE, kJ mol^{-1}) and proton affinities (PA, kJ mol^{-1})

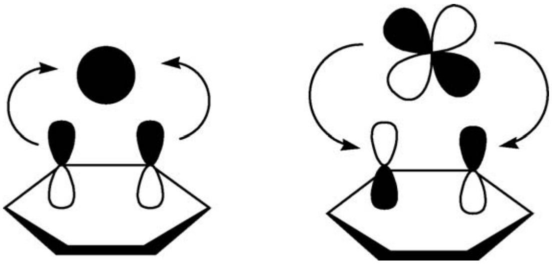
System	E[a]	ΔH	ΔG	BE (Cu^+)	BE (Li^+)	PA (exp.)[b]
OH	−307.58086			218.0	164.0[b]	817
OHCu1	−1947.83862	5.0	3.3			
OHCu2	−1947.84000	3.2	3.8			
OHCu3	−1947.84118	0.0	0.0			
OHCu4	−1947.82578	40.7	37.2			
NH2	−287.70823			250.1	184.9	882
NH2Cu1	−1927.97593	11.2	13.2			
NH2Cu2	−1927.97597	12.8	14.3			
NH2Cu3	−1927.98113	0.0	0.0			
NH2Cu4	−1927.97837	11.1	12.0			
CHO	−345.69299			218.4	204.1	834
CHOCu2	−1985.93922	36.6	34.1			
CHOCu3	−1985.93772	39.8	36.1			
CHOCu4	−1985.95331	0.0	0.0			
COOH	−420.97734			234.0	196.4	821
COOHCu2	−2061.22649	44.4	45.2			
COOHCu3	−2061.22549	46. 4	46.5			
COOHCu4	−2061.24001	8.8	11.9			
COOHCu5	−2061.24386	0.0	0.0			
CF3	−569.49879			174.4	126.9	
CF3Cu2	−2209.74225	0.0	0.0			
CF3Cu3	−2209.74206	0.1	−1.1			
CF3Cu4	−2209.72453	46.2	43.0			
OHLi1	−314.9287[c]	0.0	0.0			
OHLi2	−314.92416[c]	10.0[c]	5.0[c]			
NH2Li1	−295.06590	0.0	0.0			
NH2Li2	−295.05994	14.2	16.5			
CHOLi1	−353.02660	81.2	84.2			
CHOLi2	−353.05814	0.0	0.0			
COOHLi1	−428.31476	63.0	67.1			
COOHLi2	−428.33889	0.0	0.0			
COOHLi3	−428.33582	4.8	5.3			
CF3Li1	−576.83225	2.9	5.7			
CF3Li2	−576.83241	0.0	0.0			

[a] Values calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-311G(d,p) level.
[b] Values taken from Ref. [53].
[c] Values taken from Ref. [38] calculated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d) level.

in which the metal cation is attached to the *para* carbon atom, obtained at the DFT level, are predicted to be local minima of the PES with practically identical energy. We can then conclude that the inclusion of correlation effects beyond second order in the ab initio geometry optimizations clearly stabilizes the type of complexes predicted using DFT approaches. It would be desirable to know if the inclusion of triple excitations would substantially modify this picture, but QCISD(T) geometry optimizations, for systems of this size, are still prohibitively expensive. Taking into account these results, from now on we will discuss exclusively the DFT results. We have also considered of interest to compare Cu^+ with the other coinage metals. With this goal in mind, we performed B3LYP calculations on aniline–M^+ and phenol–M^+ (M = Ag, Au) complexes using a 6-311G(d,p) basis set for first and second row atoms and the Stuttgart RSC 1997 ECP for the metal. In agreement with previous findings concerning benzene–M^+ (M = Cu, Ag, Au) complexes [40,41], any attempt to find conventional π-complexes for Ag^+ or Au^+ failed, since they evolved to structures in which the metal ion is attached either to the *ipso*, *ortho* or *para* carbon atoms.

In general these non-conventional complexes are stabilized through dative bonds from the bonding π-orbitals of the aromatic ring towards the 4s empty orbital of the metal, and by back-donations from the occupied d orbitals of the metal into the antibonding π^*-orbitals of the aromatic ring (see Scheme 2).

For both aniline and phenol, our results indicate that Cu^+ attaches preferentially to the *para* carbon atom (X3-complexes), the conventional π-complexes being 5 and 11 kJ mol^{-1} less



Scheme 2.

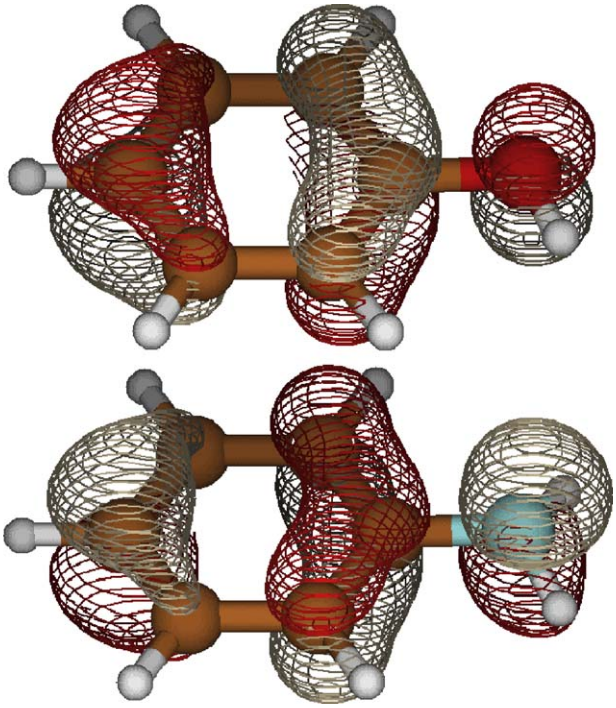


Fig. 2. Phenol's and aniline's highest occupied molecular orbitals showing the important contribution of C3, C4 and C5 p-atomic orbitals.

stable, respectively. The enhanced stability of X3 complexes can be readily explained in terms of second order NBO population analysis, that indicates that, in OH- and NH_2-complexes, the strongest donation into the empty 4s orbital and backdonation from 3d orbitals of the metal, come from the C4–C5 π-bonding and π^*-antibonding orbitals (197 and 73 kJ mol^{-1}), respectively or from the p-atomic orbital centered in C4 (374 and 88 kJ mol^{-1}) (for comparison, the average donation and backdonation energies in X1 complexes are of 40 and 16 kJ mol^{-1} in phenol and 43 and 15 kJ mol^{-1} in aniline). This picture is consistent with the shape of the HOMO in both phenol and aniline which presents a strong contribution from the C3, C4 and C5 p-atomic orbitals (see Fig. 2), which at the same time are the centers bearing the highest negative natural charge (−0.178, −0.239, −0.179). The depopulation of these bonding orbitals upon Cu^+ interaction, and the concomitant population of the corresponding antibonding orbitals are reflected in a lengthening of the C3–C4 and C4–C5 bonds by about 0.043 Å. This is clearly at variance with Li^+ complexes, where as mentioned above, the conventional π-complex is the global minimum of the PES, and no complexes of the X2- or X3-type are stable as they collapse to the X1 structure. As shown in Table 1, both Li^+ and Cu^+ association to the oxygen atom of phenol or to the nitrogen atoms of aniline is less favorable than the interaction with the aromatic π-system. However, while upon Cu^+ attachment one should expect to find 67.5% of OHCu3, 18.2% of OHCu1 and 14.3% of OHCu2, but no oxygen attached complexes, upon Li^+ association 12% of the formed complexes should correspond to the oxygen attached species, and therefore only 88% will be conventional π-complexes. Once more the behavior of aniline is different and only one type of complex, NH2Cu3 in the case of reactions with Cu^+ and NH2Li1, in the case of reactions with Li^+ should be found.

For benzoic acid and benzaldehyde, the most stable complexes upon Cu^+ interaction correspond to structures where the metal interacts with the substituent, namely complexes COOH5 and CHO4. In the former the metal interacts only with the oxygen of the carbonyl group while in the latter Cu^+ is bonded simultaneously to the *ortho* carbon atom of the aromatic moiety and to the carbonyl oxygen atom of the substituent. These complexes are also found to be the global minima at the MP2 level. In contrast, the most stable Li^+-complexes correspond to the association of the metal cation exclusively to the carbonyl oxygen, in the plane of the molecule. This reflects the significant differences between Cu^+ and Li^+ bonding. It is well established that for Li^+ the interactions are essentially electrostatic [8,49–51]. This is mirrored in the energy density map of Fig. 3b, which shows that the energy density between Li^+ and the carbonyl oxygen in complex CHOLi2 is clearly positive as it corresponds to a typically ionic bond. For the Cu^+ complex, the situation is markedly different (see Fig. 3a). In this case, $H(r)$ is negative between the metal cation and the carbonyl oxygen and between the metal cation and the carbon atoms of the aromatic ring, showing that the interaction has a non-negligible covalent character. This picture is consistent with a second order perturbation NBO analysis of the orbital interactions in these complexes. In both benzoic acid–Cu^+ and benzaldehyde–Cu^+ complexes, strong donations from the carbonyl oxygen lone-pairs and in the case of the benzaldehyde also from the C1–C2 π-bonding orbital towards the 4s empty orbital of Cu^+ are observed. Concomitant much weaker backdonations from the occupied d orbitals of the metal toward the empty C–O and C1–C2 π^*-antibonding orbital of the base also take place. Obviously, these interactions are not possible in Li^+ complexes where the first empty 2s orbital of the metal cation lies very high in energy. These donations and backdonations have a clear effect on the geometry of the complexes. In benzaldehyde–Cu^+ the C=O, C1–C2 and C2–C3 bonds become weaker and lengthen by 0.025, 0.027, 0.007 Å, respectively, while in benzoic acid the C=O lengthens by 0.036 Å and the C–OH bond becomes slightly reinforced and shortens by 0.026 Å. This latter reinforcement can be explained in terms of the BAR (bond activation-reinforcement) rule [34]. The donation from the carbonyl group to the metal ion enhances the electronegativity of this carbon atom that polarizes the C–OH bond. As a consequence, the charge density in the C–OH bonding region increases and the bond becomes reinforced. The same mechanism leads to a reinforcement of the C–H bond in benzaldehyde.

For trifluoromethyl-benzene, our results indicate that upon Cu^+ attachment a similar proportion of complexes of the X2- and X3 (39% and 61%, respectively)-type should be formed, while the association to the CF_3 group is less favorable by more than 40 kJ mol^{-1} (see Table 1). This clearly reflects that the CF_3 group is a poorer electron donor than the aromatic moiety. In contrast, Li^+ association takes place preferentially at the substituent, even though the conventional π-complex lies only 5.7 kJ mol^{-1} higher in terms of free energies, and therefore one should expect to find 90% of CF3Li2 species and 10% of the

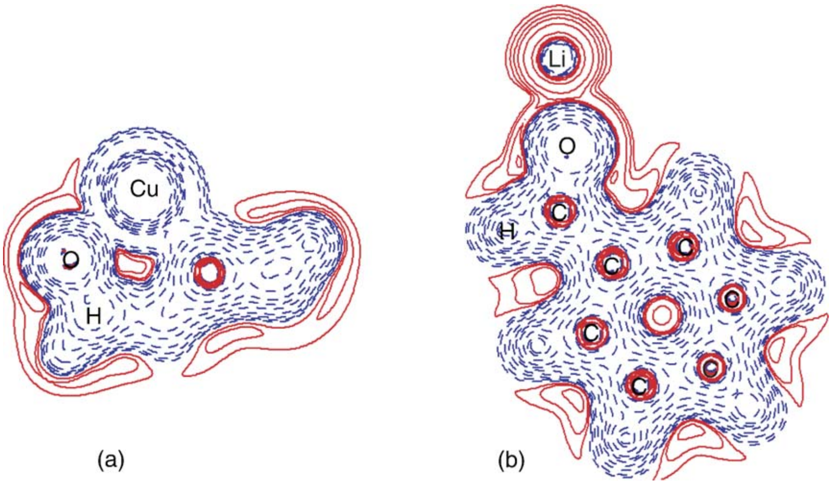


Fig. 3. Energy density contour map for CHOCu4 and CHOLi2 complexes. Solid red lines correspond to positive values of the energy density and dashed blue lines to negative values.

CF3Li1 conventional π-complex in gas-phase reactions between trifluoromethyl-benzene and Li^+.

3.2. Vibrational frequencies

Let us summarize the most significant features of the calculated infrared spectra of the most stable complexes.

Conventional π-complexes, as those that Li^+ forms with phenol and aniline, are characterized by the presence of a quite intense band at about 380–390 cm^{-1} that corresponds to a vertical displacement of the metal cation with respect to the benzene ring. Also a blue shifting of about 20 cm^{-1}, of all the out-of-plane C–H bending modes of the aromatic rings, similar to the ones already reported for other phenyl-derivatives–Li^+ complexes [38] is observed, due to the presence of the metal cation above the aromatic ring. The π-charge withdrawal caused by metal cation association leads to a 25 cm^{-1} red-shifting of C–C stretching frequencies of the benzene ring. In benzoic acid–Li^+ and benzaldehyde–Li^+ complexes, the O–Li^+ stretching frequency appears coupled with C–C–C bending modes at 675 and 616 cm^{-1}, respectively. The C═O stretch is red shifted by about 110 cm^{-1}, while changes in the C–C or C–H stretching or bending frequencies are rather small.

As mentioned in previous sections, Cu^+ attaches preferentially to the *para* carbon atom of phenol and aniline. As a consequence, the depopulation of C–C π-bonding orbitals together with the population of C–C π^*-antibonding orbitals results in a red-shifting, by about 65 cm^{-1}, of the C3–C4 and C4–C5, and by about 16 cm^{-1} of the C2–C3 and C5–C6 stretches. Cu^+ association affects also to the O–H out of plane bending mode in the case of phenol, which appears blue shifted by 103 cm^{-1} and to the NH_2 wagging in the case of aniline which in this case is red-shifted by 206 cm^{-1}. In both complexes, the C–O and the C–N stretching frequencies are shifted to the blue by 46 and 80 cm^{-1}, respectively. This can be explained again in terms of the BAR rule [34]. The electronegativity enhancement of the aromatic carbons leads to a polarization of the charge density of the atoms bonded to them into the corresponding bonding region, with the result that the bonds reinforce slightly and their stretching frequencies increase.

The most significant changes in the case of benzaldehyde and benzoic acid affect the C═O stretching frequency which appears shifted to the red by 131 and 130 cm^{-1}, respectively. In the case of benzaldehyde, in addition all C–C stretching frequencies of the aromatic ring are also red shifted from 11 to 47 cm^{-1}. In agreement with the reinforcement of the C–OH bond in the case of the benzoic acid–Cu^+ complex, its stretching frequency appears 272 cm^{-1} blue shifted.

3.3. Binding energies

The non-negligible covalent character of Cu^+-complexes is reflected in enhanced binding energies which are systematically larger than the corresponding Li^+ binding energies (see Table 1). Quite interestingly, as shown in Fig. 4, there is a quite good correlation between Li^+ and Cu^+ BEs for those cases in which the metal interacts preferably with the aromatic system, i.e., NH_2, OH, CF_3, the Cu^+ BEs being about 1.3 times larger than the Li^+ BEs. However benzoic acid and benzaldehyde deviate significantly from this correlation, reflecting that, actually, the Li^+ BEs of these two compounds are larger than expected for aromatic systems, because of the high dipole moment of both benzoic

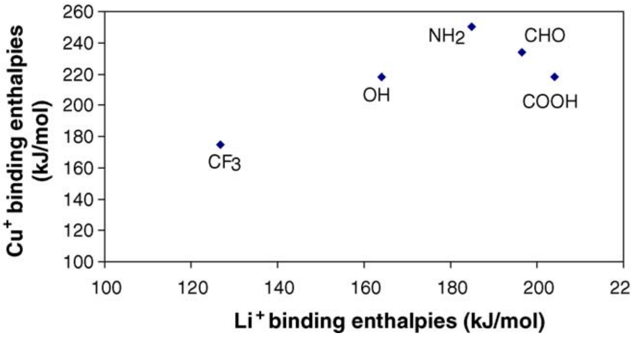


Fig. 4. Correlation between Cu^+ and Li^+ binding enthalpies of Ph–X (X = OH, NH_2, CHO, COOH, CF_3) benzene derivatives.

acid and benzaldehyde, and the fact that Li^+ does not form conventional π-complexes, but aligns with the dipole moment of the neutral molecule. It is also worth noting that the Li^+ BEs of these two compounds are reversed with respect to their Cu^+ BEs.

Two main reasons seem to be responsible for the fact that neither benzoic acid nor benzaldehyde yield conventional π-complexes when they interact with Li^+, and that for trifluoromethyl-benzene only 10% of these complexes are formed. The first one is that these substituents deactivate significantly the aromatic system, because they are strong electron withdrawing systems. The second one is that they lead to a significant increase in the dipole moment of the corresponding compound, which lies in the plane of the molecule.

Unfortunately, no much experimental information is available on Li^+ binding energies, and to the best of our knowledge only those of phenol [38] and aniline [45] have been reported in the literature so far. The good agreement between theoretical estimates and experimental values for phenol has been already discussed in Ref. [38]. Our calculated value for the aniline–Li^+ BE (184.9 kJ mol^{-1}) is smaller than the experimental reported value [45] (191.5 ± 22.4 kJ mol^{-1}), but it must be noted that the experimental estimate is affected by a large error due to the difficulties in measuring cross-sections for Li^+.

Although, as far as we know, the Cu^+ binding energies of the phenyl derivatives investigated are not known, it is worth mentioning that the experimental Cu^+ binding energy of benzene is 217.6 ± 21 kJ mol^{-1} [52] and therefore our calculations predict aniline and benzoic acid to be stronger bases than benzene when the reference acid is Cu^+, while phenol and benzaldehyde have almost the same basicity as benzene. Obviously, CF_3–Ph should be much less basic. From a more quantitative point of view, it can be observed that although there is no correlation at all between our calculated Li^+ BEs and the corresponding experimental proton affinities (PAs) when available [53] Cu^+ binding energies vary grosso modo as PAs do (see Table 1). This can be taken, as pointed out before in the literature [54] as an indirect indication of the non-negligible covalent character of Cu^+–base interactions. It should be noticed however that Cu^+ BEs for benzaldehyde and benzoic acid appear reversed with respect to their PAs. A second order NBO analysis reveals that the donation from the lone-pairs of the carbonyl oxygen into the 4s orbitals of the metal cation is significantly stronger in benzoic acid (orbital interaction energy 164 kJ mol^{-1}) than in benzaldehyde (orbital interaction energy 124 kJ mol^{-1}). A stabilizing electrostatic interaction between the negatively charged hydroxyl oxygen (natural charge −0.656) and the metal cation (natural charge +0.872) is likely a second factor that contributes to the stability enhancement of the benzoic acid–Cu^+ complex, with respect to benzaldehyde–Cu^+ complex.

4. Conclusions

The interactions of Cu^+ with phenol, aniline, benzoic acid, benzaldehyde and trifluoromethyl-benzene have a non-negligible covalent character, which clearly differentiate Cu^+-complexes from the corresponding Li^+-complexes. These dissimilarities are reflected in the geometries of the most stable adducts. For Li^+ only conventional π-complexes should be expected when interacting with aniline, while Cu^+ attaches preferentially to the *para* carbon atom. For phenol, conventional π-complexes are favored when interacting with Li^+, although a small proportion (12%) of oxygen attached species should be present. Conversely, no oxygen attached species should be found upon Cu^+ attachment, which would yield a mixture of OHCu1 (18.2%), OHCu2 (14.3%) and OHCu3 (67.5%) complexes. For benzoic acid and benzaldehyde Li^+ aligns with the dipole moment of the base, interacting exclusively with the carbonyl oxygen in the plane of the molecule. A similar structure is found in the benzoic acid–Cu^+ complex, while for benzaldehyde Cu^+ interacts with the carbonyl oxygen and additionally with the aromatic π-system. Also, Cu^+ BEs are systematically larger (about 1.3 times) than Li^+ BEs. Only for benzoic acid and benzaldehyde this gap is smaller, likely because these two systems present enhanced Li^+ binding energies. The covalent character of Cu^+ interactions is associated with electron donations from bonding π-orbitals or lone-pairs of the base toward the 4s empty orbital of the metal and with back-donations from the occupied d orbitals of the metal toward antibonding π^*-empty orbitals of the base. This non-negligible covalent character is also reflected in a rough correlation between the calculated Cu^+ BEs and the available experimental proton affinities, which does not exist for Li^+ BEs.

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