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Interaction between alkaline earth cations and oxo-ligands. DFT study of the affinity of the Ca^{2+} cation for carbonyl ligands

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Abstract The affinity of the Ca^{2+} ion for a set of substituted carbonyl ligands was analyzed with both the DFT (B3LYP/ 6-31+G(d)) and semi-empirical (PM6) methods. Two types of ligands were studied: a set of monosubstituted [O=CH (R)] and a set of disubstituted ligands [O=C(R)$_2$] (R=H, F, Cl, Br, OH, OCH$_3$, CH$_3$, CN, NH$_2$ and NO$_2$), with R either directly bound to the carbonyl carbon atom or to the *para* position of a phenyl ring. The interaction energy was calculated to quantify the affinity of the Ca^{2+} cation for the ligands. Geometric and electronic parameters were correlated with the intensity of the metal-ligand interaction. The electronic nature of the substituent is the main parameter that determines the interaction energy. Donor groups make the interaction energy more negative (stabilizing the complex formed), while acceptor groups make the interaction energy less negative (destabilizing the complex formed).

Keywords Calcium ion · Carbonyl ligands · Substituent effect · DFT · Interaction energy

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Introduction

The coordination chemistry of alkaline and alkaline earth cations is a subject of continuous interest [1, 2] mainly because of their human body importance. A vital cation is the Ca^{2+} that is essential for formation of the bone structures of mammals [3], acts as a second messenger in signal transduction and in the transmission of nerve impulses [4]. The Ca^{2+} ion is also associated with ionophore compounds [5–7] and inorganic chemical scaling [8–13]. The inner part of ionophores is made of polar groups that, generally, form octahedral coordination compounds with alkaline and alkaline earth cations [6]. Many antibiotics, like monensin [7] and salinomycin [7], produced by various strains of Streptomyces, selectively bind to a given metal ion, increasing its cell permeability and acting as a killer of gram positive bacterias.

The calcium cation is also involved in chemical scaling formation, which occurs in almost every process where water is used: laundry detergents, water treatment, industrial heat exchangers, steam generation equipment *etc*. [8]. The two inorganic compounds mainly associated with scaling formation are calcium sulfate and calcium carbonate, because their solubility limits often exceed the saturation levels, leading to crystallization on surfaces [9]. The resulting surface blockage causes a decline in the permeate flux, reducing the process efficiency and increasing operational

costs. Chemicals that inhibit the scaling process have been in use for more than a century [10]. During the past two decades, considerable efforts in the development of chemical additives have been made, which leads to antiscalant molecules like polycarboxylates, polyacrylates and polyphosphonates [9, 11, 12]. These compounds adsorb onto formed crystals or complex with cations that form the crystals, inhibiting the scale formation [9].

It is also worth to note the importance of calcium compounds in the petroleum industry. In petroleum platforms the first form of recovering the oil is by its natural pressure. When oil is exhausted a second recuperation method is to inject seawater in the oil well to cause a physical displacement in the oil for further recuperation in the production line. In this process precipitation of calcium sulfate is common due to chemical incompatibility of the injection water of the platform (rich in sulfate anions) and the formation water of the rock reservoir (rich in alkaline earth cations) [13]. Chemical scaling causes damage in the drilling pipe, heating equipment, down-hole pumps, tubing, casing and other production facilities. To minimize these difficulties, the petroleum industry has been using compounds that inhibit the process of chemical scaling. These compounds capture the Ca^{2+} cation, hindering interactions with sulfate anions and thereby avoiding formation of calcium sulfate [9].

In the examples cited above and others [14–19], the key point is the interaction between the cation and the ligands, which determines the properties of the complex. Continuing our previous studies on interactions of phosphoryl ligands with the Ca^{2+} cation [14], in the present work we determine the intensity of the binding energy of several carbonyl ligands to a cationic Ca^{2+} aquocomplex and analyze how the neighborhood of the carbonyl group can affect that interaction. Another objective is to continue the determination of the ability of the semi-empirical PM6 method to qualitatively reproduce the interaction energy between the Ca^{2+} cation and the ligands.

Computational methods

The interactions between the Ca^{2+} cation and two types of carbonyl ligands, a set of monosubstituted [O=CH(R)] and a set of disubstituted ligands [O=C(R)$_2$], were investigated.

Following our studies on interactions of phosphoryl ligands with the Ca^{2+} cation, we choose a set of simple and most common substituents, having different properties for resonance and inductive effects [20]. The substituents H, F, Cl, Br, OH, OCH$_3$, CH$_3$, CN, NH$_2$ and NO$_2$ were calculated. For each set of monosubstituted (Fig. 1a and c) and disubstituted (Fig. 1b and d) ligands there are two pattern of binding, one with the R group directly bound to
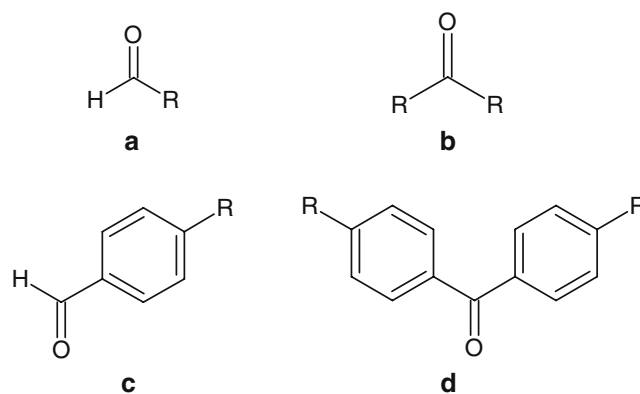
Fig. 1 General scheme for the substitution pattern

the carbon atom of the carbonyl group (Fig. 1a and b) and a second set with the R group bound to the *para* position of a phenyl ring (Fig. 1c and d).

Experimental observations show that the most common coordination number of the Ca^{2+} cation is 6 [21–23]. Based on this fact, the cation was surrounded by six water molecules to determine the energy for substitution of one of these water molecules by a ligand, as shown in Eq. 1. The heat of reaction for Eq. 1 gives the interaction or substitution energy for a given ligand. The same approach has been used in other works [14–18, 24] to determine the interaction energy between metal cations and ligands. With this model we consider the specific electronic effect of a given substituent, steric effects and possible reciprocal interactions between the ligand and the water molecules.

$$\left[Ca(H_2O)_6\right]^{2+} + L \rightarrow \left[Ca(H_2O)_5L\right]^{2+} + H_2O \qquad (1)$$
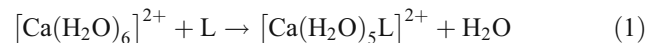
Molecular parameters that could show correlation with the substitution energy were also computed. The following electronic and geometric parameters were analyzed: the bond length between the Ca^{2+} cation and the oxygen atom of the carbonyl group; the C=O bond length in the carbonyl group; Mulliken charge densities on the Ca^{2+} cation, on the oxygen atom of the carbonyl group and on the ligand; the Hammett σ_p constant and the HOMO energy of the ligand. With the charge decomposition analysis (CDA) method [25] we calculated the amount of electron donation, back-donation and interaction energy between the metal center and the ligand.

Density functional calculations (DFT) were carried out with Gaussian 03 W [26], using the B3LYP [27] method and the 6–31+G(d) basis set [28]. It has been shown that this combination of method and basis set is able to yield structures in reasonable agreement with those obtained at higher level of theory [29]. The MOPAC 2007 software [30] was used for semi-empirical calculations using the PM6 method [31].

The geometries of all species investigated were fully optimized with both the semi-empirical PM6 and the B3LYP/6-31+G(d) methods, without any restriction. We calculated the structures of several conformers for each molecule, obtained by rotation around single bonds, to confirm that the final structure is the most stable one. Only the most stable conformer in each case was considered for energy and properties calculations. After geometry optimization with the B3LYP functional, the second order force constant matrix was calculated to confirm that optimized geometry as a genuine minimum on the potential energy surface.

The charge decomposition analysis (CDA), proposed by Dapprich and Frenking [25], was used to rationalize the nature of the metal-ligand interactions. This method decomposes a molecule into a set of fragments, and uses a linear combination of fragment orbitals to form the molecular orbitals of the complex [32]. We chose the $Ca(H_2O)_5^{2+}$ moiety as the first fragment and the ligand L as the second fragment. The CDA method used is the 2.19 version of the AOMix 6.44 package [32, 33].

Results and discussion

Energy trend analysis

The geometries of the 37 substituted $[Ca(H_2O)_5L]^{2+}$ complexes were fully optimized using both the PM6 and the DFT methods. Figures 2 and 3 show graphical representations of the substitution energies, calculated according to Eq. 1 (see supplementary material for Tables with these and other data).

The B3LYP/6-31+G(d) data given in Figs. 2 and 3 show negative values for substitution energy for almost all ligands, with the exception of the electron-attractor F, Cl, Br, and CN groups, when they are directly bound to the carbonyl carbon. This indicates that the carbonyl ligands investigated in the present work bind more strongly to the
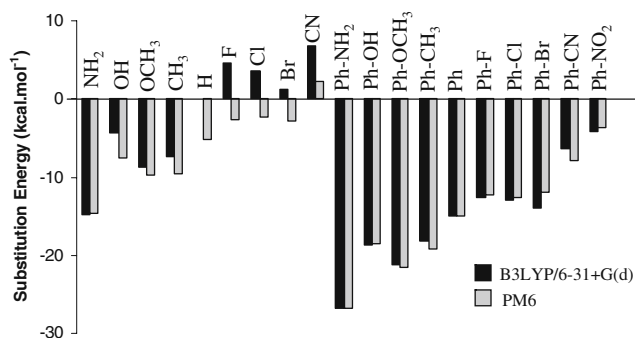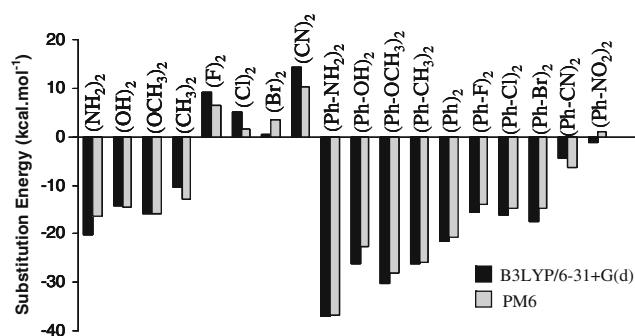
Fig. 3 Interaction energies calculated according to Eq. 1, using the B3LYP/6-31+G(d) and the PM6 methods for the disubstituted carbonyl ligands

cationic center than the aquo ligand, even when substituted with some electron-attractor groups in the *para* position of the aromatic ring. As a general trend, ligands with a phenyl group bound to the carbonyl carbon atom have more negative substitution energies than those where the R group is bound directly to the carbonyl carbon atom. Additionally, disubstituted carbonyl ligands lead to more negative substitution energies than the corresponding ones with monosubstituted carbonyl ligands. These are essentially the same trends observed in our previous studies of interactions of the Ca^{2+} cation with phosphoryl ligands. It must be added, however, that the phosphoryl ligands lead to more negative substitution energies than the carbonyl ligands, which may be attributed to the difference in electron polarizability between the phosphorous and the carbon atoms [34]. The phosphorous atom is bigger and has a more easily polarizable electronic cloud. This makes the electron donation from the ligand to the metallic center more efficient in the phosphoryl case than in the complexes with the carbonyl group (see discussion below). The substitution energies for the trivalent phosphoryl ligands are, on average, 4 kcal mol^{-1} more negative than those for the corresponding monosubstituted carbonyl ligands. As in both cases there is only one R group for each ligand, the difference in the substitution energy may be attributed to the higher polarizability of the phosphorous atom as compared to that of the carbon atom. In contrast, substitution energies for the pentavalent phosphoryl ligands are about 12 kcal mol^{-1} more negative than the corresponding values for the disubstituted carbonyl ligands. In this case, in addition to the electronic effect inherent to the phosphorous atom, the number of R groups in the phosphoryl ligands (3) is bigger than in the carbonyl ligands (2), therefore increasing the electronic effect in the first case.

Ligands with electron-donor groups make the substitution more exothermic, while ligands with electron-attractor groups yield less exothermic substitutions, in agreement with Senapati's work [24]. This behavior is better analyzed considering the σ_P Hammett constant of each R group.

Fig. 2 Interaction energies calculated according to Eq. 1, using the B3LYP/6-31+G(d) and the PM6 methods for the monosubstituted carbonyl ligands

Figure 4 shows the correlation between the B3LYP/6-31+G (d) substitution energy and the σ_P Hammett constant for the *para* substituted ligands. The correlation coefficient between these two properties is $r^2=0.951$ for the monosubstituted and $r^2=0.960$ for the disubstituted ligands. Therefore, at least for the *para*-substituted ligands, the electron-donor or electron-attractor feature of the R group, quantified by the σ_P Hammett constant, is an important property determining the substitution energy. This trend is analogue to that found by Lanznaster et al. when studying metalloenzymes complexes [35]. For those ligands with the R group directly bound to the carbon atom, a visual inspection confirms that electron-donor substituents lead to ligands that bind more strongly to the metal center than those with electron-attractor substituents.

We also calculated the interaction energy between the ligand and the metal center using the CDA method. This energy can be defined as the energy difference between the energy of the complex, $[Ca(H_2O)_5L]^{2+}$, and that of each fragment, $[Ca(H_2O)_5]^{2+}$ and L, at the geometries they have in the complex. The substitution energy calculated according to Eq. 1 also gives a measure of the direct interaction energy between the ligand and the metal center. The correlation coefficient between the substitution energy and the interaction energy is $r^2=0.974$ for the monosubstituted carbonyl compounds and $r^2=0.990$ for the disubstituted ones, evidencing that these properties are strongly correlated.

The ability of the semi-empirical PM6 method to quantitatively reproduce the B3LYP/6–31+G(d) substitution energy for the carbonyl systems was also evaluated. Some recent works suggested that the PM6 parametrization is able to give results close to that obtained with hybrid DFT calculations [14, 36, 37]. Data in Figs. 2 and 3 show that for the *para*-substituted ligands the differences between
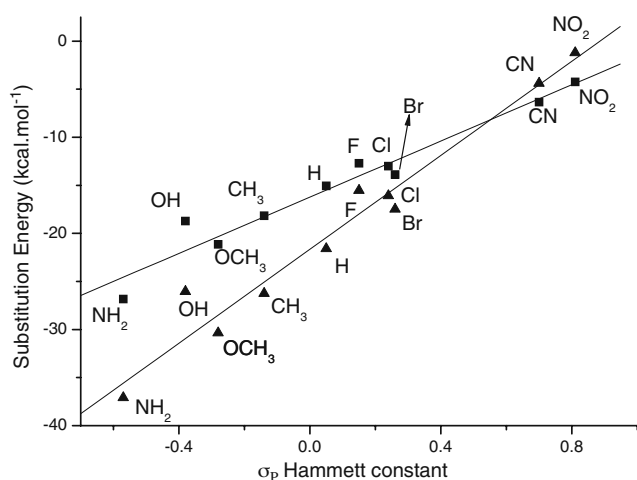
the B3LYP/6-31+G(d) and the PM6 values are below 3 kcal mol^{-1}, while for the ligands where the R group is directly bound to the carbonyl carbon atom, the differences between the B3LYP and the PM6 values are a bit higher, amounting up to 6 kcal mol^{-1}. Comparing with our previous studies the differences between PM6 and DFT values are smaller. The correlation between both values using all the data yields a correlation coefficient of 0.927 for ligands with the R group directly bound to the carbonyl carbon atom and of 0.976 when the R group is bound to the phenyl ring. Observe that, while individual differences between the PM6 and the B3LYP values are bigger for the phosphoryl case, the two values are more intimately correlated than in the carbonyl case. This is due to the fact that the PM6 substitution energies for the phosphoryl ligands are always more negative than the corresponding B3LYP values. In contrast, for the carbonyl ligands the differences between the PM6 and the B3LYP substitution energies oscillate between positive and negative values, leading, as a consequence, to a smaller correlation.

The interaction between the Ca^{2+} cation and a ligand is predominantly electrostatic [38, 39], however some degree of covalent interaction may also be present. Although the covalent interaction is not the major component, it may be important to determine the relative affinity of the ligand. The electrostatic interaction arises mainly from ion-dipole and ion-induced dipole interactions, while the covalent component is due to charge transfer from the ligand to the metal center, and may be important, mainly for ligands with strongly electron donating groups [17]. Analysis of the substitution energy revealed that it is strongly influenced by the ability of the ligand to donate or to attract electrons, indicating that electron transfer is a relevant parameter to distinguish the affinity of each ligand for the Ca^{2+} cation. Therefore, parameters that can quantify electron transfer between the two subunits, the cation and the ligand, should contain quantitative information of the variation of the substitution energy and should correlate with it. Three parameters associated with electron transfer were analyzed: the amount of electron donation from the ligand to the metal center, calculated by the CDA approach; the amount of charge transfer from the ligand to the metal center as a consequence of complexation and the HOMO energy of the ligand.

With CDA it is possible to calculate both the donation and the back-donation from the delta in charge transfer before and after complexation. As the Ca^{2+} ion does not possess available high-energy occupied d orbitals, back-donation is negligible. Similar results for the Ag^+ cation were found by Ma et al. [17]. In the present case, the amount of electron transfer from the $[Ca(H_2O)_5]^{2+}$ fragment to the ligand is close to zero, even in the case of the strongly electron-attracting substituents [14]. Thus, the only
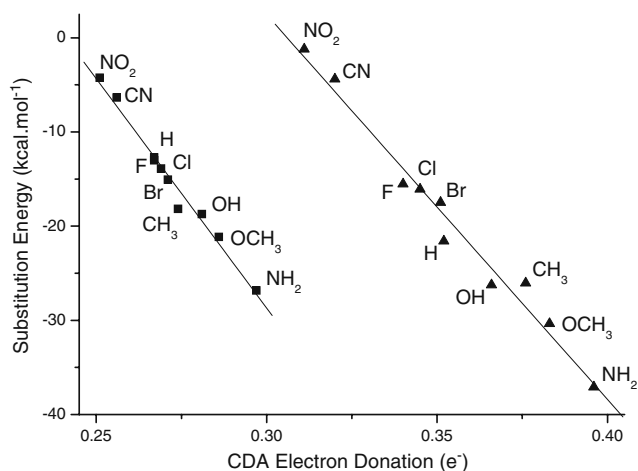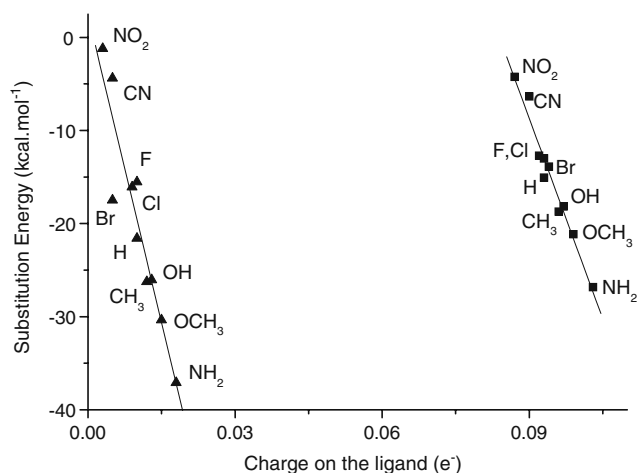

Fig. 4 The relationship between the substitution energy and the σ_P Hammett constant (■ monosubstituted carbonyl ligands; ▲ disubstituted carbonyl ligands)

Fig. 5 The relationship between electron donation from the ligand to the $[Ca(H_2O)_5]^{2+}$ fragment and the substitution energy for the *para* substituted compounds (■ monosubstituted carbonyl ligands; ▲ disubstituted carbonyl ligands)
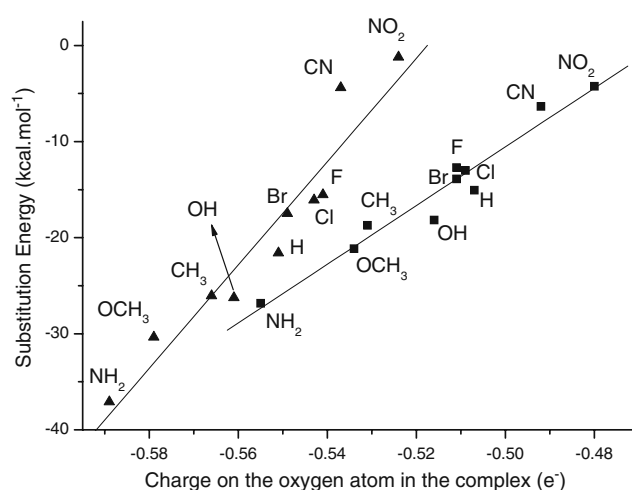

Fig. 7 The relationship between charge on the carbonyl oxygen and substitution energies for the *para* substituted compounds. (■ monosubstituted carbonyl ligands; ▲ disubstituted carbonyl ligands)

process of charge transfer calculated is that due to electron donation from the ligand to the $[Ca(H_2O)_5]^{2+}$ fragment. A graphical representation of the correlation between the substitution energy and the amount of electron donation calculated by CDA for the *para* substituted compounds is shown in Fig. 5. The correlation coefficient between these two properties is $r^2=0.908$ for the monosubstituted compounds and $r^2=0.877$ for the disubstituted ones, considering both the species with the R group directly bound to the carbonyl carbon atom and those with the R group bound to the *para* position of the phenyl ring.

Charge density analysis

Charge transfer from the ligand to the metal center may also be quantified by direct analysis of charge densities on the

atoms in the complex. The relationship between the Mulliken charge densities on the whole ligand in the complex and the substitution energy for the *para* substituted ligands is shown in Fig. 6.

Ligands that more strongly transfer charge density to the metal center are also those that bind more strongly. The correlation coefficient for the monosubstituted compounds with the R group directly bound to the carbonyl group is $r^2=0.824$ and for the *para* substituted compounds $r^2=0.964$. For the disubstituted species $r^2=0.893$ for the compounds with the R group directly bound to the carbonyl group and $r^2=0.882$ for the compounds substituted in the *para* position. Observe that, as reported before [14], charge density on the Ca^{2+} cation is essentially constant for all members of the set. Therefore, charge transferred to the Ca^{2+} cation is dispersed to the other (aquo) ligands.
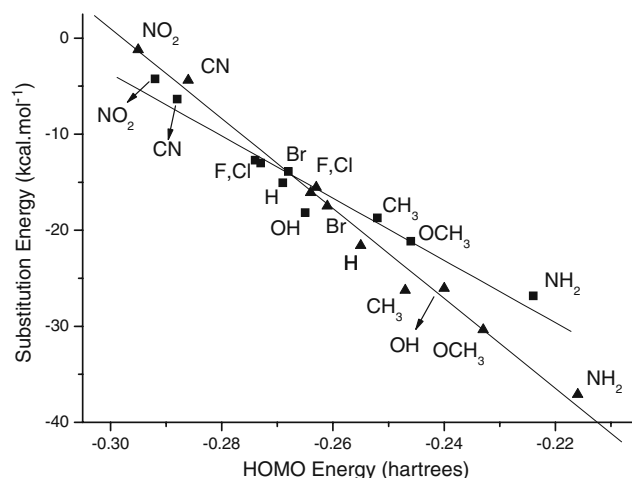

Fig. 6 Correlation between charge on the ligands and substitution energies for the *para* substituted compounds (■ monosubstituted carbonyl ligands; ▲ disubstituted carbonyl ligands)

Fig. 8 The relationship between the HOMO energy of the ligand and the substitution energy for the *para* substituted compounds (■ monosubstituted carbonyl ligands; ▲ disubstituted carbonyl ligands)

Figure 7 shows a plot of the charge densities on the oxygen atom of the carbonyl group in the complex as a function of the substitution energy.

Charges on the oxygen atom for disubstituted ligands (Fig. 7) are always more negative than the corresponding ones for monosubstituted ligands. Electron-donating groups increase charge densities on the oxygen atom, while electron-withdrawing groups reduce charge density on the oxygen atom. Additionally, charges on the oxygen atom for the *para*-substituted ligands are more negative than those where the R group is bound directly to the carbonyl carbon atom. When considering the whole set of compounds the correlation between the charge on the carbonyl oxygen and the substitution energy has an r^2 value of 0.883. The charge densities on the carbonyl oxygen for the isolated ligand show the same trend.

Another parameter that should correlate with the substitution energy is the energy difference between the HOMO of the donor fragment (the ligand) and the LUMO of the acceptor fragment (the $[Ca(H_2O)_5]^{2+}$ moiety). As the electron accepting fragment ($[Ca(H_2O)_5]^{2+}$) is always the same, the important point is the energy of the HOMO of the ligand. It may be predicted that ligands with highest energy values for the HOMO are good electron donors while the ones that have low energy values for the HOMO are poor electron donors [19, 40]. Figure 8 shows the correlation between the HOMO energy of the ligand and the substitution energy. As can be seen these two properties correlate nicely.

Trends in geometric parameters

In our previous study with phosphoryl ligands we have shown that the Ca-O distance does not show any significant correlation with the substitution energy, while the P=O distance increases for the more strongly electron donor substituents. Contrary to this fact, in the present study we found that the C=O distance is essentially constant along the set while the Ca-O distance changes from 2.28 to 2.52 A, but without any significant correlation with the substitution energy, in agreement with previous studies [41]. Qualitatively electron donor substituents result in shorter Ca-O distances. The carbonyl group is harder than the phosphoryl group, disfavoring stretching of the C=O bond.

Conclusions

In this study we analyzed the complexation efficiency of carbonyl ligands with the Ca^{2+} cation in the reaction for exchange of a water molecule in the system $[Ca(H_2O)_6]^{2+}$ by a carbonyl ligand. 37 carbonyl ligands were tested, being 19 compounds with monosubstituted carbonyl group $[O=C(H)R]$ and 18 compounds with disubstituted carbonyl

group $[O=C(R_2)]$, to evaluate the energetic influence of the R substituent in the complex formation.

The DFT and PM6 methods presented a good correlation for calculation of the substitution energies, in such a way that the semi-empirical method can be used for calculations of substitution energies with low computational cost and reasonable confidence. It was observed that the electron donor groups lead to the more negative substitution energies whereas electron withdrawing groups are associated with less negative substitution energies. The substitution energy is strongly correlated with the σ_p Hammett constant.

While the interaction between the Ca^{2+} cation and the ligands is predominantly electrostatic, covalent interactions may be important to determine the relative affinity of each ligand for the Ca^{2+} cation. The intensity of charge transfer from the ligand to the cation is an important component of the metal ligand interaction. Charges on the oxygen atom of the carbonyl group in the complex, charges on the ligand in the complex, the HOMO energy of the ligand, charges on the oxygen atom of the carbonyl group in the ligand and the degree of electron donation from the ligand to the metal center all are parameters that correlate with the substitution energy.

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