

# Interactions between alkaline earth cations and oxo ligands. DFT study of the affinity of the $Mg^{2+}$ cation for phosphoryl ligands

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**Abstract** DFT (B3LYP/6-31+G(d)) calculations of  $Mg^{2+}$  affinities for a set of phosphoryl ligands were performed. Two types of ligands were studied: a set of trivalent [O = P (R)] and a set of pentavalent phosphoryl ligands [O = P (R)<sub>3</sub>] (R = H, F, Cl, Br, OH, OCH<sub>3</sub>, CH<sub>3</sub>, CN, NH<sub>2</sub> and NO<sub>2</sub>), with R either bound directly to the phosphorus atom or to the *para* position of a phenyl ring. The affinity of the  $Mg^{2+}$  cation for the ligands was quantified by means of the enthalpy for the substitution of one water molecule in the [Mg(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> complex for a ligand. The enthalpy of substitution was correlated with electronic and geometric parameters. Electron-donor groups increase the interaction between the cation and the ligand, while electron-acceptor groups decrease the interaction enthalpy.

**Keywords** Magnesium ion · Phosphoryl ligands · Substituent effect · DFT · Interaction enthalpy

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## Introduction

The coordination chemistry of earth alkaline cations has developed rapidly in the last few decades due to its importance in prokaryotes and higher life forms [1–6]. Magnesium divalent ions ( $Mg^{2+}$ ) form many coordination compounds of biological importance [1]. In the plant and monera kingdoms it is present in chlorophyll and bacteriochlorophyll, respectively. The insertion of the  $Mg^{2+}$  cation into the protoporphyrin IX molecule is an important stage in the biosynthesis of these pigments [3]. Photosynthetic organisms require these pigment molecules to harness light energy and to transform water and carbon dioxide into carbohydrates and oxygen [3].  $Mg^{2+}$  is the most abundant cation in living cells, and it plays a vital role in many cellular processes: in the composition of enzymes that control carbohydrate, fat, protein, and electrolyte metabolism, and in the regulation of cell permeability, neuromuscular excitability and vascular tone [1]. It also has a structural function, as it stabilizes the structures of the DNA and RNA chains in the nucleus of the cell [4].

Many drug molecules interact with DNA in a specific and  $Mg^{2+}$ -dependent manner [5]. Mithramycin, for example, is a member of the aureolic acid group of antitumor antibiotics that are effective against a wide selection of human tumors. It acts by inhibiting the transcription of DNA as a result of complex formation in the presence of  $Mg^{2+}$ . The cation coordinates to both mithramycin and DNA, stabilizing the system in a conformation that hides the site for DNA transcriptase [5]. Quinolones are antibacterial drugs that either inhibit the bacterial DNA topoisomerase or bind to the DNA molecule directly, thereby stopping cell division and avoiding the unfolding of DNA. The amount of norfloxacin and other quinolones that bind to DNA is

modulated by the concentration of  $\text{Mg}^{2+}$  [5]. This cation acts as a bridge between the phosphate groups of the nucleic acid and the carbonyl and carboxyl moieties of the quinolones [6].

Another class of antibiotics associated with the  $\text{Mg}^{2+}$  cation are the ionophore compounds [7–9]. These are hydrophobic molecules that carry ions through the lipidic bilayers of the cell membranes [7]. Their inner structures are composed of polar groups that form octahedral coordination compounds with the  $\text{Mg}^{2+}$  cation [8]. Many antibiotics like valinomycin [9] and beauvericin [9], which are produced by various strains of microorganisms, selectively bind to a metal ion, increasing cell permeability and thus killing Gram-positive bacteria.

In these and other examples [10–22], the key point is the interactions between the  $\text{Mg}^{2+}$  cation and the ligands, which determine the properties of the complex. These interactions modulate the biological effects of the molecules. Therefore, it is worth attempting to enhance our knowledge of the intensity and features of those interactions in order to optimize the drug's potency.

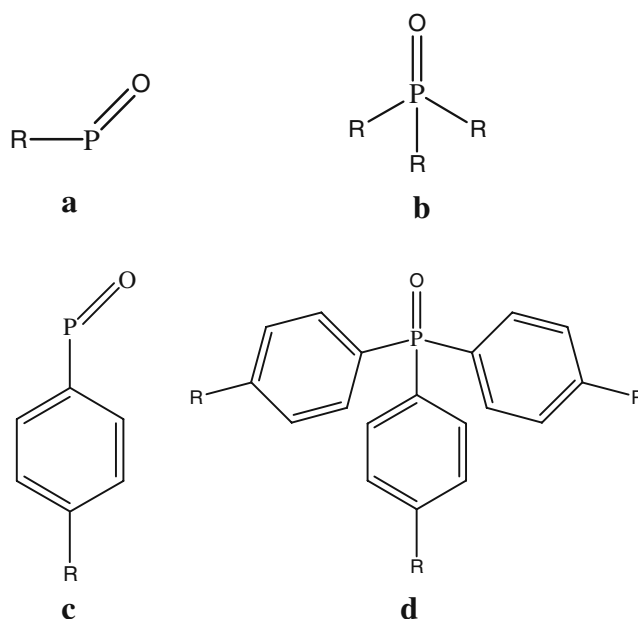
Continuing our previous investigations of the effects of substituents on the interactions between oxo ligands and alkaline earth cations [10, 11], in the present work we quantify the binding enthalpies of several phosphoryl ligands to a cationic  $\text{Mg}^{2+}$  aquo complex and analyze how the neighborhood of the phosphoryl group affects these interactions.

## Computational methods

The interactions between the  $\text{Mg}^{2+}$  cation and two types of phosphoryl ligands, a set of trivalent  $[\text{O} = \text{P}(\text{R})]$  and a set of pentavalent  $[\text{O} = \text{P}(\text{R})_3]$  phosphorus compounds, were investigated (Fig. 1).

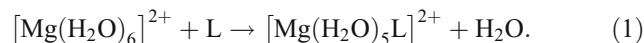
Following our previous studies on the interactions of oxo ligands with the  $\text{Ca}^{2+}$  cation, we chose a set of simple and common substituents that had different resonance and inductive effects [23]. The substituents H, F, Cl, Br, OH,  $\text{OCH}_3$ ,  $\text{CH}_3$ , CN,  $\text{NH}_2$  and  $\text{NO}_2$  were selected. For each set of trivalent (Fig. 1a and c) and pentavalent (Fig. 1b and d) phosphoryl derivatives there are two patterns of binding: one with the R group directly bound to the phosphoryl group (Fig. 1a and b), and a second set with the R group in the *para* position of a phenyl ring bound to the phosphoryl group (Fig. 1c and d).

Experimental observations and theoretical calculations show that the most common coordination number of the  $\text{Mg}^{2+}$  cation in water solution is 6 [24–26]. Given this information, we surrounded the  $\text{Mg}^{2+}$  cation with six water molecules and determined the enthalpy (the electronic energy at 0 K combined with the zero-point vibrational energy and the thermal correction term at 298 K) for the substitution of one of these water molecules for a ligand, as



**Fig. 1** Structures of the phosphoryl ligands

shown in Eq. 1. The heat of reaction for Eq. 1 gives the interaction or substitution enthalpy for a given ligand as compared to water, and this is a parameter that quantifies the affinity of the cation for the ligand. The same approach has been used in other works [10–18, 20] to calculate the interaction energy between metal cations and ligands. With this equation, the specific electronic effect of a given substituent, steric effects and possible reciprocal interactions between the ligand and the water molecules are considered. Additionally, as the products and reactants in Eq. 1 both have the same type and number of atoms, it avoids the need to determine the basis set superposition error correction, a common requirement when the interaction energy is calculated directly as a dissociation process.



Molecular parameters that could show correlations with the substitution enthalpy were also computed. The following geometric parameters were analyzed: the distance between the  $\text{Mg}^{2+}$  cation and the oxygen atom of the phosphoryl group, and the P=O bond length.

The geometries of all species investigated were fully optimized with the DFT method, without any restriction. For each ligand, the structures of several conformers obtained by rotating around single bonds were calculated. The reported structure is that of the most stable conformer among the several calculated. After geometry optimization with the B3LYP functional, the second-order force constant matrix was calculated to confirm that the optimized geometry was a genuine minimum on the potential energy surface.

The charge decomposition analysis (CDA) method proposed by Frenking and Dapprich [27] and the energy decomposition analysis (EDA) method [28, 29] were employed to rationalize the nature of the metal–ligand interactions. In these methods, the molecule is divided into fragments and, using a linear combination of each fragment's orbitals, the molecular orbitals of the complex are formed. In our case, the molecule was divided in two fragments: the first was the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  moiety and the second was the ligand L. In the CDA method, the interaction between fragments is obtained by combining three main terms: (i) the mixing between the occupied orbitals of the first fragment and the empty orbitals of the second fragment, which indicates electron back-donation; (ii) the mixing between the occupied orbitals of the second fragment and the empty orbitals of the first fragment, which gives the donation; and (iii) the mixing between the occupied orbitals of both fragments, which indicates the charge polarization in the binding region. The amount of electron donation and back-donation between fragments was analyzed with this method [27].

The EDA approach also treats the molecule as a sum of fragments and divides the interactions between the fragments into three main terms, as shown in Eq. 2: the total Pauli repulsion due to the repulsion of the electronic cloud of fragments; the total orbital interaction due to the overlap of the orbitals of the fragments, counted as the covalent part of the interaction; and the electrostatic interaction, due to the attraction of the charges of the fragments, which is counted as the ionic part of the interaction [28, 29].

$$\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{orb}} \quad (2)$$

Using the EDA calculations, we aimed to work out the relative strengths of the ionic and covalent interactions in the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  complexes and how the relative contribution of each interaction changes with the substituent.

Geometry optimizations and enthalpy calculations were carried out with the Gaussian 03W software [30], using the B3LYP [31] functional and the 6-31+G(d) basis set [32]. It has been shown that this combination of method and basis set can yield structures that are in reasonable agreement with those obtained at a higher level of theory [10, 15, 21, 33]. The CDA method used is the 2.19 version of the AOMix 6.46 package [34, 35]. The EDA calculations were done with the ADF software [36] using the B3LYP functional and the DZP basis set.

## Results and discussion

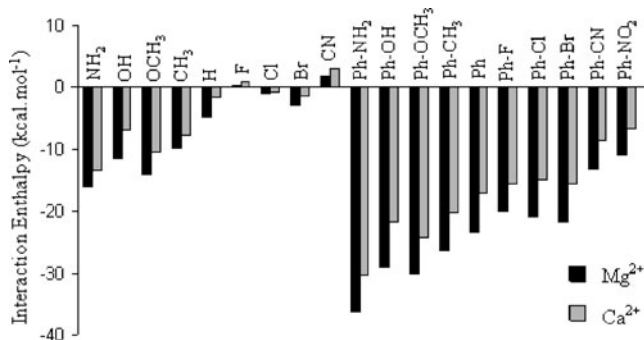
### Interaction enthalpy

The geometries of the 38 substituted  $[\text{Mg}(\text{H}_2\text{O})_5\text{L}]^{2+}$  complexes were fully optimized using the DFT method

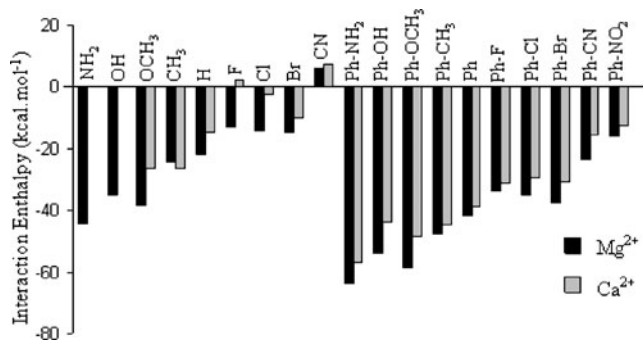
and the substitution enthalpies were calculated according to Eq. 1. Figures 2 and 3 show graphical representations of the substitution enthalpies (see the “Electronic supplementary material” for tables with these and other data). For comparison purposes, the corresponding data obtained with the  $\text{Ca}^{2+}$  cation [10] are also given in Figs. 2 and 3.

Figures 2 and 3 show negative values for the substitution enthalpy for almost all ligands, with the exception of the strong electron-withdrawing CN group directly bound to the phosphoryl group. There are some features that follow the same pattern as those obtained in our previous studies [10, 11]: the phosphoryl ligands bind more strongly to the cationic center than the aquo ligand, a common behavior, as already reported [10, 11, 16, 17]; ligands with a phenyl group bound to the phosphoryl group lead to more negative substitution enthalpies than those where the R substituent is bound directly to the phosphoryl group, which may be attributed to the fact that the aromatic ring is a strong electron source [19]; the pentavalent phosphoryl ligands lead to more negative substitution enthalpies than the corresponding trivalent phosphoryl ligands—a direct effect of the greater number of contributing R groups. Comparison of the abilities of the  $\text{Ca}^{2+}$  and the  $\text{Mg}^{2+}$  cations to coordinate the phosphoryl ligands shows that the  $\text{Mg}^{2+}$  cation leads to more negative substitution enthalpies, in agreement with previous works [20]. This may be attributed to the polarizing powers of both cations. Although they carry the same charge,  $\text{Mg}^{2+}$  is smaller than  $\text{Ca}^{2+}$  [37] and is thus a stronger Lewis acid, with stronger power to polarize the ligand. The ionic charge/ionic radius ratios for the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations are 2.1 and 3.1, respectively [37]. Therefore, the  $\text{Mg}^{2+}$  cation leads to complexes with stronger interaction enthalpies, a result in agreement with the Irving–Williams series [38].

The substitution energies for the trivalent phosphoryl ligands with the R group directly bound to the phosphorus atom are on average 3 kcal mol<sup>-1</sup> more negative for complexes with  $\text{Mg}^{2+}$  than for the corresponding com-

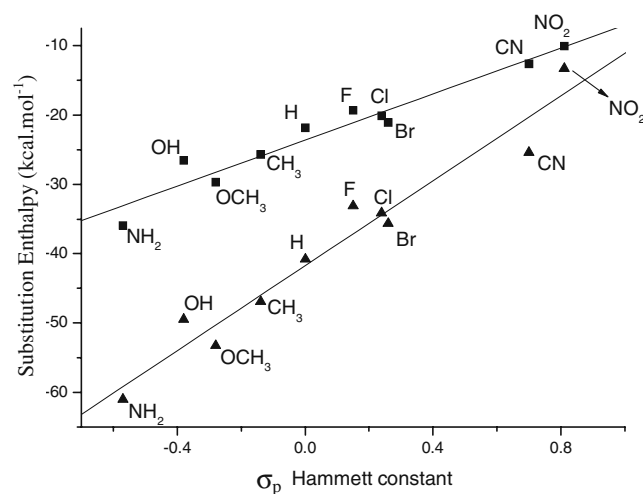


**Fig. 2** B3LYP/6-31G(d) substitution enthalpies, calculated according to Eq. 1, for complexes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  [10] cations with trivalent phosphoryl ligands



**Fig. 3** B3LYP/6-31G(d) substitution enthalpies, calculated according to Eq. 1, for complexes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  [10] cations with pentavalent phosphoryl ligands

plexes with the  $\text{Ca}^{2+}$  cation. For the pentavalent phosphoryl ligands with the R group directly bound to the phosphorous atom, the energy difference is on average  $7 \text{ kcal mol}^{-1}$ , while for the *para*-substituted compounds, complexes with  $\text{Mg}^{2+}$  are on average  $5 \text{ kcal mol}^{-1}$  more stable than the corresponding complexes with  $\text{Ca}^{2+}$ . Recently, we also reported calculations for the interaction between carbonyl ligands and the  $\text{Ca}^{2+}$  cation [11]. The interaction between the  $\text{Mg}^{2+}$  cation and phosphoryl ligands is stronger than the interaction between the  $\text{Ca}^{2+}$  cation and carbonyl ligands. As observed previously [10, 11, 17], ligands with electron-donor groups lead to more exothermic substitution enthalpies, while ligands with electron-withdrawing groups yield less exothermic substitution enthalpies. This behavior is better analyzed by considering the Hammett constant  $\sigma_p$  of each R substituent. Figure 4 shows the correlation between the B3LYP/6-31+G(d) substitution enthalpy and  $\sigma_p$  for the *para*-substituted ligands. The high correlation coefficient between these two properties reinforces the previous



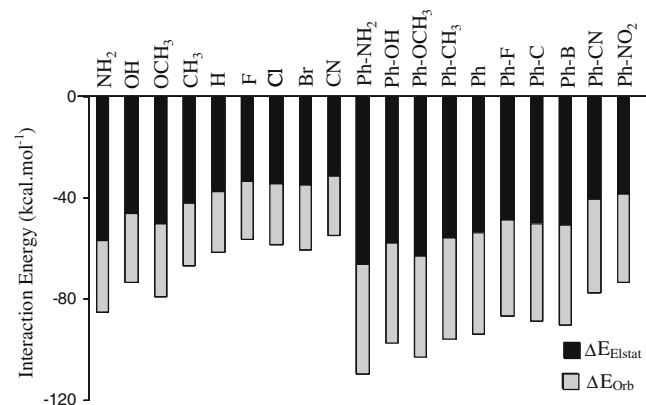
**Fig. 4** The relationship between the substitution enthalpy and the Hammett constant  $\sigma_p$  (squares trivalent phosphoryl ligands,  $r^2=0.945$ ; triangles pentavalent phosphoryl ligands,  $r^2=0.951$ )

finding that the electron-donating or electron-attracting character of the R group, as quantified by  $\sigma_p$ , is an important influence on the substitution enthalpy [22, 39].

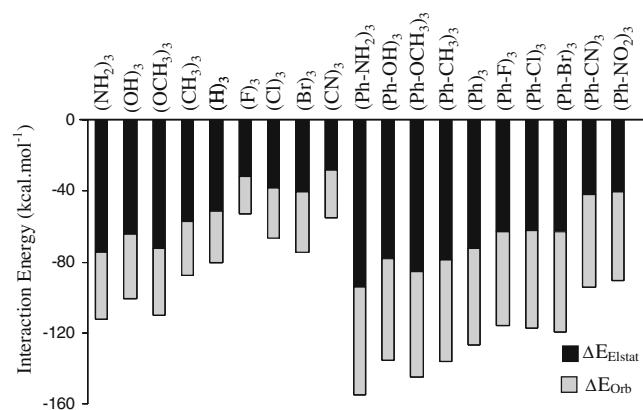
#### Analysis of the $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}\text{L}$ interaction

The nature of the interaction between the  $\text{Mg}^{2+}$  cation and the ligands is predominantly electrostatic, although it also has some covalent character (this nonelectrostatic term is the difference between the total interaction energy and the sum of the Pauli repulsion term and the electrostatic energy) [12, 18, 20, 40, 41]. Based on the amount of charge transferred from the ligand L to the  $[\text{Ca}(\text{H}_2\text{O})_5]^{2+}$  moiety, we suggested in our previous studies [10, 11] that, in spite of the high ionic character of the interaction, the covalent contribution could be the component responsible for the different substitution enthalpies for the various complexes. Using the EDA approach, it is possible to quantify the relative individual ionic and covalent contributions to the stabilization of each complex [28, 29]. The electrostatic component associated with the ionic 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 [28, 29]. Figures 5 and 6 give the ionic and covalent contributions to the interaction between the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  and L (ligand) fragments as a function of the R group for the trivalent and pentavalent phosphoryl ligands, respectively.

Figures 5 and 6 show that both the electrostatic and the covalent components make strong contributions to the interaction enthalpy, with the electrostatic component clearly being the most important. Additionally, while the covalent component is essentially constant across the series, the electrostatic contribution gradually drops upon moving from the more electron-releasing to the more electron-withdrawing groups. Therefore, it is the ionic component



**Fig. 5** Electrostatic ( $\Delta E_{\text{Elstat}}$ ) and orbital ( $\Delta E_{\text{Orb}}$ ) components of the interaction enthalpy for trivalent phosphoryl ligands



**Fig. 6** Electrostatic ( $\Delta E_{\text{EIstat}}$ ) and orbital ( $\Delta E_{\text{Orb}}$ ) components of the interaction enthalpy for pentavalent phosphoryl ligands

that makes the difference, leading ligands with electron-releasing groups to bind more strongly to the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  moiety.

The higher electrostatic contributions calculated for the ligands with electron-releasing groups are due to their ability to increase the negative charge on the oxygen atom of the phosphoryl group, thereby increasing the ionic interaction. Although the covalent contribution also varies among the different compound classes (see, for example, the trivalent vs. pentavalent derivatives), it is the electrostatic contribution that changes more strongly within a given class (see the individual values in the tables of the “Electronic supplementary material”).

The Pauli repulsion term must be added to the ionic and covalent contributions to obtain the total interaction energy, according to Eq. 2. The Pauli repulsion is positive and helps to reduce the interaction energy to a value close to that computed in the dissociation process. The Pauli repulsion term is essentially constant within a given class of ligand.

The EDA results discussed above indicate that the electrostatic contribution between the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  and the ligand moieties is the main parameter that modulates the ability of the ligand to bind to the cation. Therefore, the charge density at the oxygen atom of the phosphoryl group may be an important parameter in the interaction. The Mulliken atomic charge densities on the oxygen atom of the phosphoryl group in the complexes show a high correlation with the electrostatic contribution, reinforcing the facts discussed above.

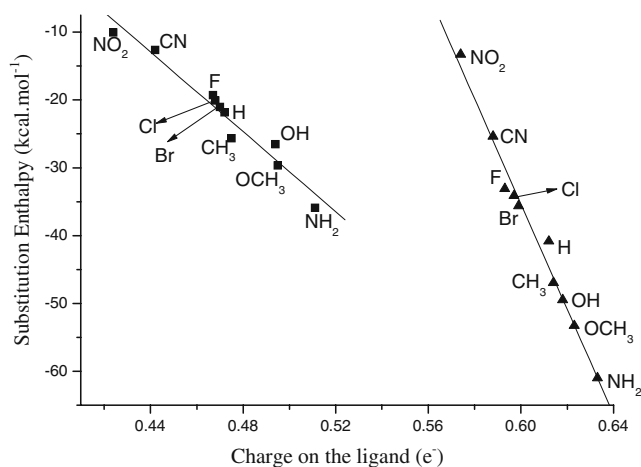
Charges on the oxygen atom for the pentavalent phosphoryl ligands are always more negative than the corresponding ones for trivalent phosphoryl ligands, resulting in a higher binding energy for the first class of ligands. Electron-donating groups increase the charge density on the oxygen atom, while electron-withdrawing groups reduce the

charge density on the oxygen atom. Additionally, the charge on the oxygen atom for the *para*-substituted ligands is more negative than it is when the R group is bound directly to the phosphoryl group, in good agreement with the EDA analysis.

Within CDA it is possible to calculate the amount of electron donation and back-donation based on the change in charge transfer before and after complexation. As the  $\text{Mg}^{2+}$  ion does not possess available low-energy *d* orbitals, back-donation is negligible. The CDA results confirm this hypothesis. Back-donation from the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  fragment to the ligand is close to zero for all ligands investigated, including those with electron-withdrawing substituents. Similar results were found previously for the  $\text{Ag}^+$  [12] and  $\text{Ca}^{2+}$  cations [10, 11]. In contrast, electron donation from the ligand to the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  fragment is significant.

Figure 7 shows the correlation between the amount of charge transferred from the ligand to the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  moiety and the substitution enthalpy for the *para*-substituted ligands. Of course, as was the case for the systems studied in our previous works, some degree of charge transfer should also be observed in the present systems. This can be quantified by simply assessing the net electronic charge on the ligand after complexation, which is obtained as the net atomic charge summed over all atoms in the ligand, or by the CDA approach.

The correlation shown in Fig. 7 indicates that ligands that are able to transfer more charge have more negative substitution enthalpies. When compared to the  $\text{Ca}^{2+}$  case studied before, it is apparent that more charge is transferred for the complexes with the  $[\text{Mg}(\text{H}_2\text{O})_5]^{2+}$  moiety, which correlates with the stronger interaction enthalpy calculated for the  $\text{Mg}^{2+}$  case, as commented above.



**Fig. 7** Correlation between charge on the ligand and substitution enthalpy for *para*-substituted compounds (squares trivalent phosphoryl ligands,  $r^2=0.955$ ; triangles pentavalent phosphoryl ligands,  $r^2=0.980$ )



## Analysis of geometrical parameters

The geometrical parameters that are relevant in the complexation process are the Mg–O and the P=O distances. In our previous study with phosphoryl ligands [10], we showed that the Ca–O distance does not show any significant correlation with the substitution enthalpy. In contrast, we found in the present study that the Mg–O distance is correlated with the substitution enthalpy, as found before in other studies [13, 19, 20].

The Mg–O distances are about 0.300 Å shorter than the Ca–O distances in complexes with the same ligand. The shorter Mg–O distance increases the electrostatic component of the interaction and reflects a more negative substitution enthalpy. The higher polarizing power of the Mg<sup>2+</sup> cation, as compared to Ca<sup>2+</sup>, may be the reason for the better correlation found in the present case.

As observed for the Ca<sup>2+</sup> case, the P–O distance in the [Mg(H<sub>2</sub>O)<sub>5</sub>L]<sup>2+</sup> complex also depends on the electron-releasing or electron-withdrawing power of the substituent. The P=O distance increases for more strongly electron-releasing substituents, as seen before. The P=O distances in the [Mg(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> complexes are on average 0.010 Å shorter than the corresponding ones in the [Ca(H<sub>2</sub>O)<sub>5</sub>]<sup>2+</sup> complexes.

## Conclusions

The ability of phosphoryl ligands to complex the Mg<sup>2+</sup> cation was analyzed in terms of the reaction where a water molecule in the [Mg(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> complex was exchanged for a ligand. In this work, 38 phosphoryl ligands were studied: 19 compounds with a trivalent phosphorus atom [O = P(R)] and 19 compounds with a pentavalent phosphorus atom [O = P(R)<sub>3</sub>]. Electron-donating substituents attached to the phosphoryl group stabilize the complex, leading to a stronger interaction between the cation and the ligand, while electron-withdrawing substituents have the opposite effect. The Hammett constant  $\sigma_p$  is strongly correlated with the substitution enthalpy. Using the EDA approach, we were able to show that the differences in the abilities of the ligands to complex the cation are mainly due to differences in the electrostatic component of the interaction enthalpy. This is related to the higher charge density on the oxygen atom of the phosphoryl group in ligands with electron-releasing substituents. This finding was confirmed by analyzing the charge transfer between the ligand and the cation.

The interaction of the Mg<sup>2+</sup> cation with phosphoryl ligands is stronger than the corresponding interaction between the Ca<sup>2+</sup> cation and phosphoryl ligands. Geometric parameters such as the Mg–O and P=O distances also change systematically across the series of ligands and correlate with the substitution enthalpy.

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