Simple Charge–Transfer Model for Metallic Complexes

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Simple Charge-Transfer Model for Metallic Complexes

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In the chemistry of metallic complexes, two important concepts have been used to rationalize the recognition and selectivity of a host by a guest: preorganization and complementarity. Both of these concepts stem from geometrical features. Less explored in the literature has been the interactional complementarity, where mainly the electronic factors in the intermolecular forces are involved. Because the charge transfer between a species rich in electrons (ligand) and another deficient in them (cation) is one of the main intermolecular factors that control the binding energies in metallic complexes, for such systems, we propose a simple model based on density functional theory. We define an interactional energy in which the geometrical energy changes are subtracted from the binding energies and just the electronic factors are taken into account. The model is tested for the complexation between bidentate and cyclic ligands and Ca, Pb, and Hg metal dications. The charge-transfer energy described by our model fits nicely with the interactional energy. Thus, when the geometrical changes do not contribute in a significant way to the complexation energy, the interactional energy is dominated by charge-transfer effects.

1. Introduction

The complexation phenomenon is observed and studied in several fields of chemistry: the interactions of a metal ion with a ligand,[1,2] a supramolecular host with a guest,[3−5] and an enzyme with a substrate,[6,7] are some examples. The understanding of this kind of interaction can be used to design the perfect couple between a host and a guest, which is quite relevant in several fields, such as environmental chemistry, where heavy metals need to be trapped selectively.

In metallic complexes, the recognition and selectivity of a host by a guest have been rationalized mainly in terms of two important concepts: the preorganization and complementarity principles.[8] The former refers to the conformational changes that a metal-free ligand undergoes when a complex is built. If a metal-free ligand has the same geometrical conformation as the metallic complex, one can say that it is highly preorganized for that specific metal ion. On the other hand, a ligand is complementary to a specific metal ion if it has an ideal cavity size and shape, that is, when the donor atoms in the ligand have an ideal spatial distribution to reach an ideal donor−metal distance. As can be seen, the preorganization and complementarity concepts stem from geometrical features, and some proposals have been made to rationalize them in terms of energy changes to be used in ligand design.[9,10]

Another concept that has been less explored in the literature for the design of selective ligands is interactional complementarity.[11] This concept takes into account electronic factors involved in the intermolecular forces present in the interaction between a host and a guest. These factors can be related to charge-transfer processes and electrostatic or van der Waals interactions because, in many cases, hydrogen bonds are present.[9−12] Knowledge of the driving forces that induce host−guest interactions is crucial to understanding the complexation phenomenon. The consideration of electronic factors

leads to a double complementarity principle[13] that involves both energetic and geometric features.

In a metal ion−ligand interaction, the charge transfer from the donor atoms to the metal ion is expected to play a very important role in stabilizing the complex, due to the fact that one of the species is deficient in electrons and the other is rich in them. The object of the present work is to analyze this situation by using a simple charge-transfer model based on density functional theory (DFT)[14,15] to study the formation of metallic complexes. Crown and aza-crown ethers are commonly used to trap metal ions in many fields of chemistry, because of their ability to strongly coordinate with cations.[16] On the other hand, the complexation of Ca^{2+}, Hg^{2+}, and Pb^{2+} has been widely studied[16−27] because of the importance of these cations in biological and environmental problems. Thus, we chose the complexation of these dications with crown and aza-crown ethers, and with their bidentate ligands analogues, to compare the energy change predicted by the simple charge-transfer model with the energy change associated to the interactional complementarity.

2. Charge-Transfer Model

The formation energy of a complex by a metal and a ligand can be expressed as

$$\Delta E_f = E_{complex} - (E_{ligand} + E_{metal}) \qquad (1)$$

where $E_{complex}$, E_{ligand}, and E_{metal} represent the energies of the ground-state structures of the complex, the ligand, and the metal, respectively, when they are isolated from each other. By using standard quantum chemistry methods, one can evaluate all of the terms involved in eq 1.

Now, on the basis of the discussion in the Introduction, the formation energy of a complex can be divided into two steps. The first involves the geometrical changes of the ligand related to the preorganization and complementarity principles,[8] ΔE_{reorg},
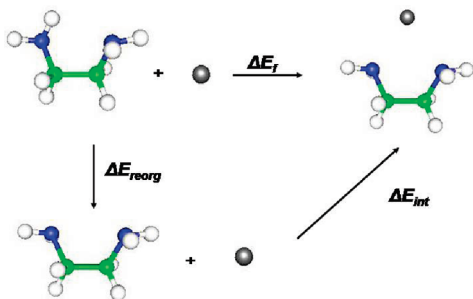
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7946 *J. Phys. Chem. A, Vol. 114, No. 30, 2010*

Ramírez-Ramírez et al.

Figure 1. Schematic representation of the energy contributions (ΔE_{reorg}, reorganization energy; ΔE_{int}, interaction energy) to the formation energy (ΔE_{f}).

whereas the second is related to the electronic energy change when the metal ion and the ligand interact at the fixed final geometry, ΔE_{int}, which is precisely the energy change associated with the interactional complementarity. Thus, the formation energy can be written as

$$\Delta E_{\text{f}} = \Delta E_{\text{reorg}} + \Delta E_{\text{int}} \qquad (2)$$

Figure 1 depicts the two steps and the energy changes involved in the host−guest interaction.

Because the energy change ΔE_{reorg} is related to the redistribution of the electron density due to the reorganization of the nuclei at constant number of electrons, it can be determined from[9,10] the expression

$$\Delta E_{\text{reorg}} = E_{\text{ligand at complex}} - E_{\text{ligand}} \qquad (3)$$

where $E_{\text{ligand at complex}}$ is the energy of the ligand at the complex geometry. That is, the energy change in eq 3 measures how well-organized the isolated ligand is to bind to the guest. Both terms in eq 3 can also be obtained by standard quantum chemistry methods.

In this way, ΔE_{int} can be obtained from eq 2 as

$$\Delta E_{\text{int}} = \Delta E_{\text{f}} - \Delta E_{\text{reorg}} \qquad (4)$$

by evaluating previously ΔE_{f} through eq 1 and ΔE_{reorg} through eq 3. It is worth noting that only the electronic contribution is measured in this term, because the changes due to structural rearrangement are subtracted from the complex formation energy.

This separation of the energy into different steps can be compared with density-based[28] or orbital-based[29−33] energy decomposition analysis schemes. In particular, if we compare it with the density based scheme,[28] one can see that ΔE_{reorg} corresponds to what they call the preparation energy, while ΔE_{int} corresponds to the sum of what they call the electrostatic interactions, the Pauli repulsion, the polarization and the charge-transfer contributions. Because the objective of the present work is to compare directly the energy change associated with the interactional complementarity with the energy change determined from a simple charge-transfer model, we will not decompose ΔE_{int} into the different contributions of the density based analysis.

Now, to study the role of charge transfer in the complexation through a simple model, one can make use of density functional theory.[14] In density functional theory, the chemical potential, μ, is identified[34] with the first derivative of the energy with

respect to the number of electrons, N, at constant external potential (fixed geometry), and the chemical hardness, η, is identified[35] with the second derivative of the energy with respect to the number of electrons, also at constant external potential. That is

$$\mu^{\pm} = (\partial E/\partial N)_v^{\pm} \qquad (5)$$

and

$$\eta^{\pm} = (\partial^2 E/\partial N^2)_v^{\pm} = (\partial \mu/\partial N)_v^{\pm} \qquad (6)$$

where the $\pm$ signs indicate that the left derivative $(-)$ that describes the charge removal process is different from the right derivative $(+)$ that describes the charge addition process.[36−39]

In terms of these derivatives, the energy changes related to the charge donation or charge acceptance process, at constant external potential, which corresponds to a fixed position of the nuclei, can be described through the quadratic model[14,35,40]

$$\Delta E^{\pm} = \mu^{\pm}\Delta N^{\pm} + \frac{1}{2}\eta^{\pm}(\Delta N^{\pm})^2 \qquad (7)$$

where the values of μ^+, μ^-, η^+, and η^- can be determined from the two conditions provided by the energy differences associated with the first ionization potential I, the electron affinity A, and two additional conditions. The usual ones come from the assumption that the left and right derivatives are equal, that is, $\mu^+ = \mu^- = \mu$ and $\eta^+ = \eta^- = \eta$, leading to[14,35]

$$\mu = -(I + A)/2 \quad \text{and} \quad \eta = I - A \qquad (8)$$

However, if one differentiates the response to charge donation from the response to charge acceptance through the chemical potentials μ^+ and μ^- and assumes that $\eta^- = \eta^+ = \eta$ and that $\eta = \mu^+ - \mu^-$, one finds that[40]

$$\mu^- = -\frac{1}{4}(3I + A), \quad \mu^+ = -\frac{1}{4}(I + 3A),$$
$$\text{and} \quad \eta = \frac{1}{2}(I - A) \qquad (9)$$

In this context, the charge-transfer process between two chemical species, the host H and the guest G, can be expressed in terms of the quadratic model as

$$\Delta E = \Delta E_G + \Delta E_H \qquad (10)$$

with

$$\Delta E_G = \mu_G^+\Delta N_G^+ + \frac{1}{2}\eta_G^+(\Delta N_G^+)^2 \qquad (11)$$

and

$$\Delta E_H = \mu_H^-\Delta N_H^- + \frac{1}{2}\eta_H^-(\Delta N_H^-)^2 \qquad (12)$$

Simple Charge-Transfer Model for Metallic Complexes

J. Phys. Chem. A, Vol. 114, No. 30, 2010 **7947**

where it has been explicitly assumed that the guest will accept the charge donated by the host, so that

$$\Delta N_G^+ = -\Delta N_H^- = \Delta N \qquad (13)$$

and

$$\Delta E = (\mu_G^+ - \mu_H^-)\Delta N + \frac{1}{2}(\eta_G^+ + \eta_H^-)(\Delta N)^2 \qquad (14)$$

By minimizing the energy change with respect to the charge transferred, one finds that

$$\Delta N_{ct} = \frac{\mu_H^- - \mu_G^+}{\eta_G^+ + \eta_H^-} \qquad (15)$$

and

$$\Delta E_{ct} = -\frac{1}{2}\frac{(\mu_H^- - \mu_G^+)^2}{\eta_G^+ + \eta_H^-} \qquad (16)$$

Note that, in these relationships, the evaluation of the chemical potentials and the hardnesses can be done through eq 8 or through eq 9. When eq 8 is used, the directional derivatives for the chemical potentials and for the hardnesses are not differentiated; that is, $\mu^+ = \mu^- = \mu$ and $\eta^+ = \eta^- = \eta$, and eqs 15 and 16 become equal to those of the original quadratic charge-transfer model.[35,41] In contrast, when eq 9 is used, the directional derivatives for the chemical potentials are differentiated, $\mu^+ \neq \mu^-$, and the directional derivatives for the hardnesses are not differentiated, $\eta^+ = \eta^- = \eta$.

It is important to mention that, in many cases, eq 7 has been used together with eq 8 to qualitatively describe and understand fundamental aspects of chemical interactions driven by donor−acceptor processes.[14,35,41−55] However, recently, the differentiation of directional derivatives has been used to introduce the electron-donating and electron-accepting powers, which have been used successfully in the analysis of the charge transfer of antioxidants[56,57] and to establish the net electrophilicity concept, which has proven to be quite useful in the analysis of thermoneutral, exothermic, endothermic, and cycloaddition reactions.[58] The differentiation of chemical potentials has also been used successfully in the study of redox reactions.[59]

Equations 15 and 16 are used in this work to analyze the contribution of the charge-transfer process to ΔE_f and its relation with ΔE_{int} in the complexes formed by six ligands, namely, three bidentate ligands (ethylene glycol, EG; ethanolamine, EA; and ethylenediamine, ED) and three crown ethers (12-crown-O$_4$, 12-crown-O$_2$N$_2$, and 12-crown-N$_4$), with the three metal ions Ca^{2+}, Hg^{2+}, and Pb^{2+}.

Thus, although in a density- or orbital-based energy decomposition analysis, one determines the different contributions with greater precision, the present approach might be useful to estimate in a very simple way the interactional complementarity between a given host and a given guest.

3. Methodology

The bidentate ligands and crown ether complexes were fully optimized within DFT using the generalized gradient ap-

proximation to the exchange correlation functional from Becke, Lee, Yang, and Parr (BLYP).[60,61] For the ligands, we used the polarized triple-ζ basis set TZVP,[62] and the relativistic effective core potential proposed by the Christiansen−Ermler[63,64] group (CRENBL) was used for each metal. The selection of this theoretical level was discussed in a previous work.[65] The initial conformation for each ligand was taken from previous work,[66−70] and all of them were reoptimized with BLYP/TZVP. However, no previous geometrical conformation was found for the 12-crown-O$_2$N$_2$ ligand. Thus, for this reason, the most stable conformation for this ligand was determined through a conformational search by using the MM3 force field,[71−73] and then its most stable conformation was reoptimized with BLYP/TZVP.

The formation energy for each complex was calculated using eq 1, and the reorganization and interaction energies were determined using eqs 3 and 4, respectively.

The vertical ionization energy and the electronic affinity were computed for each metal and for each ligand, and the resulting values were used to estimate the chemical potential and the hardness either from eq 8 or from eq 9. All of the calculations were done with the NWChem v4.5 code.[74,75]

4. Results and Discussion

4.1. Geometries of Bidentate and Cyclic Ligand Complexes. The structural parameters for the complexes of Ca^{2+}, Hg^{2+}, and Pb^{2+} with EG, EA, and ED are reported in Table 1. These results show that the structures of the complexes of each metal with the same ligand are very similar to each other. For example, the M−O and M−N distances have a little variation from one complex to another, just 0.11 Å from the shortest M−O distance to the largest and 0.23 Å for the M−N distance. In the same table, the structural parameters of the complexes of Ca^{2+}, Hg^{2+}, and Pb^{2+} with 12-crown-O$_4$, 12-crown-O$_2$N$_2$, and 12-crown-N$_4$ are reported. We can observe that the variations in the M−O and M−N distances are very similar to those in the bidentate complexes. As for the bidentate ligand complexes, the largest variations are in the donor−metal−donor angles. This observation is in agreement with the idea that, at least structurally, bidentate ligands are good models for more complex ligands.

The shortest metal−donor distances are observed in the mercury complexes, and the same is observed for the largest donor−donor distances and the largest donor−metal−donor angles. These structural features are mapped on the complex formation energy.

4.2. Reorganization and Interaction Energies. The formation (ΔE_f), reorganization (ΔE_{reorg}), and interaction (ΔE_{int}) energies determined through eqs 1, 3, and 4 are reported in Table 2 for the Ca^{2+}, Hg^{2+}, and Pb^{2+} complexes with the ligands EG, EA, ED, 12-crown-O$_4$, 12-crown-O$_2$N$_2$, and 12-crown-N$_4$.

The ΔE_f values show that the most stable complexes are formed with the ligands in which a nitrogen atom is present in their structures (ED for the bidentate ligands and 12-crown-N$_4$ for the cyclic ones). This behavior is in agreement with the fact that nitrogen is a better electron donor than oxygen. This characteristic is exacerbated when one goes from the bidentate ligands to the cyclic ones, because the N atoms in the cyclic ligands are secondary amines, which are better Lewis bases than the primary amines in the bidentate ligands. On the other hand, one can observe that the Hg^{2+} complexes are more stable than the Ca^{2+} and Pb^{2+} complexes, as expected, because this is the metal ion that shows the shortest distances with the ligands, as discussed before.

In the same table, one can notice that the ΔE_{reorg} values are larger for the crown ligands than for the bidentate ligands. This

TABLE 1: Main Distances and Angles for the Complexes between Ligands and Metal Cations, Optimized at the BLYP/TZVP Level in Combination with CRENBL RECPs[a,b]

ligand	$D(M-O)$	$D(M-N)$	$D(O-O)$	$D(O-N)$	$D(N-N)$	$\angle O-M-O$	$\angle O-M-N$	$\angle N-M-N$
			Ca^{2+}					
EG	2.38		2.76			70.9		
EA	2.37	2.54		2.90			72.4	
ED		2.53			3.08			74.8
			Pb^{2+}					
EG	2.47		2.71			66.6		
EA	2.46	2.59		2.84			68.5	
ED		2.58			2.99			70.9
			Hg^{2+}					
EG	2.36		2.86			74.7		
EA	2.46	2.36		3.01			77.2	
ED		2.38			3.09			80.9
			Ca^{2+}					
12crnO$_4$	2.44		2.80			69.9		
12crnO$_2$N$_2$	2.43	2.56	2.78	2.93	3.10	69.9	71.8	74.4
12crnN$_4$		2.55			3.08			74.1
			Pb^{2+}					
12crnO$_4$	2.57		2.83			67.0		
12crnO$_2$N$_2$	2.58	2.65	2.82	2.93	3.04	66.1	68.2	70.3
12crnN$_4$		2.66			3.03			69.5
			Hg^{2+}					
12crnO$_4$	2.43		2.97			75.4		
12crnO$_2$N$_2$	2.46	2.40	2.95	3.02	3.12	73.5	76.9	81.1
12crnN$_4$		2.44			3.09			78.8

[a] M represents the metal cation Ca^{2+}, Pb^{2+}, or Hg^{2+}. [b] Distances are in angstroms, and angles are in degrees.

TABLE 2: Reorganization (ΔE_{reorg}), Interaction (ΔE_{int}), and Formation (ΔE_f) Energies for the Complexes between the Ligands and the Metal Cations[a]

ligand	ΔE_{reorg}	ΔE_{int}	ΔE_f
	Ca^{2+}		
EG	0.35	−4.35	−4.00
EA	0.37	−4.61	−4.24
ED	0.28	−4.85	−4.57
12-crown-O$_4$	0.73	−7.36	−6.63
12-crown-O$_2$N$_2$	0.78	−7.97	−7.19
12-crown-N$_4$	0.90	−8.44	−7.54
	Pb^{2+}		
EG	0.39	−4.80	−4.41
EA	0.39	−5.28	−4.89
ED	0.27	−5.71	−5.44
12-crown-O$_4$	0.69	−7.97	−7.28
12-crown-O$_2$N$_2$	0.72	−8.85	−8.12
12-crown-N$_4$	0.86	−9.47	−8.61
	Hg^{2+}		
EG	0.53	−7.77	−7.24
EA	0.38	−9.10	−8.72
ED	0.32	−10.23	−9.91
12-crown-O$_4$	0.62	−11.58	−10.96
12-crown-O$_2$N$_2$	0.68	−13.26	−12.58
12-crown-N$_4$	0.85	−14.57	−13.72

[a] All quantities are in electronvolts.

result indicates that the cyclic ligands are more sensitive to distortion than the bidentate ligands. The smallest ΔE_{reorg} values among the bidentate ligands corresponds to the ED complexes. In the cases of Ca^{2+} and Pb^{2+}, the ΔE_{reorg} values for the EG and EA complexes have almost the same value, but the value is not the same for Hg^{2+}, where the EG complex has the largest value of ΔE_{reorg}. In the case of the cyclic ligands, the ΔE_{reorg} values grow up from 12-crown-O$_4$ to 12-crown-N$_4$ for each metal. It is important to note that ΔE_{reorg} does not contribute in a relevant way to ΔE_f. For the Ca^{2+} complexes, ΔE_{reorg} is

approximately 7.9% of ΔE_f for the bidentate ligands and 11.3% for the cyclic ligands. Similarly, for the Pb^{2+} complexes, the contribution of ΔE_{reorg} is 7.3% and 9.5% for the bidentate and cyclic ligands, respectively. However, for the Hg dication, the contribution of ΔE_{reorg} is the smallest, at approximately 5% for bidentate ligands and 5.8% for cyclic ligands. Thus, the major contribution to ΔE_f comes from ΔE_{int}, which means that the energy related to the intermolecular forces is responsible for the stabilization of the complexes in the systems studied here.

4.3. Charge Transfer and Interactional Complementarity. To evaluate ΔN_{ct} and ΔE_{ct} in eqs 15 and 16, we need to determine the first ionization potential and the electron affinity, to calculate the chemical potentials and the hardnesses through eq 8 or through eq 9. In Table 3, the values of I, A, μ, η, μ^-, and μ^+ are reported for the ions and ligands. For the ligands, these values are determined at the geometry they have in the complex. Now, if one compares the values of μ and η for the dications, using the calculated I and A results, with the values obtained using the experimental I and A data (within parentheses),[35] one finds small differences for Ca^{2+}, but rather large differences for Hg^{2+} and Pb^{2+}. Thus, we decided to use the experimental values of I and A for the dications in order to determine μ, η, and μ^+. If one compares the values of the chemical potentials of the ligands (μ_H or μ_H^-) with those of the cations (μ_G or μ_G^+), one can see that the former are larger than the latter, indicating that the flow of charge will occur from the ligands to the cations, as expected.

In Table 4, we report the values of ΔE_{ct} calculated from eq 16. In this table, there are two values for each complex: ND indicates that the left and right derivatives of the chemical potential are equal (eq 8), and D indicates that the left and right derivatives of the chemical potential are different (eq 9). Thus, ND uses μ, and D uses μ^- and μ^+. From this table, one can observe that, within each column, the ordering of the ΔE_{ct} values

TABLE 3: Ionization Potentials, Electronic Affinities, Hardnesses, and Chemical Potentials of the Metal Cations and the Ligands Calculated by Finite Differences[a]

metal	I	A	η_G	μ_G	μ_G^+
Ca^{2+}	50.63	12.11	38.52 (39.04)	−31.37 (−31.39)	−21.74 (−21.63)
Pb^{2+}	30.90	12.81	18.09 (16.91)	−21.86 (−23.49)	−17.33 (−19.26)
Hg^{2+}	35.22	19.07	16.15 (15.44)	−27.15 (−26.48)	−23.11 (−22.62)

ligand	I	A	η_H	μ_H	μ_H^-
			Ca^{2+} complexes		
EG	9.36	−2.87	12.22	−3.24	−6.30
EA	8.76	−3.20	11.96	−2.78	−5.77
ED	8.32	−3.48	11.79	−2.42	−5.37
12-crown-O_4	7.66	−2.59	10.25	−2.53	−5.10
12-crown-O_2N_2	7.03	−2.77	9.80	−2.13	−4.58
12-crown-N_4	6.52	−2.90	9.42	−1.81	−4.17
			Hg^{2+} complexes		
EG	9.39	−2.94	12.33	−3.22	−6.31
EA	8.37	−3.27	11.64	−2.55	−5.46
ED	7.99	−3.58	11.57	−2.21	−5.10
12-crown-O_4	7.81	−2.65	10.46	−2.58	−5.20
12-crown-O_2N_2	6.88	−2.87	9.75	−2.00	−4.44
12-crown-N_4	6.35	−2.99	9.34	−1.68	−4.02
			Pb^{2+} complexes		
EG	9.34	−2.85	12.20	−3.25	−6.29
EA	8.65	−3.22	11.87	−2.71	−5.68
ED	8.15	−3.52	11.67	−2.32	−5.23
12-crown-O_4	7.71	−2.61	10.31	−2.55	−5.13
12-crown-O_2N_2	6.95	−2.82	9.77	−2.07	−4.51
12-crown-N_4	6.39	−2.94	9.33	−1.72	−4.06

[a] All quantities are in electronvolts.

TABLE 4: ΔE_{ct} (in eV) for Complexes of Ca^{2+}, Hg^{2+}, and Pb^{2+} with the Bidentate and Cyclic Ligands

ligand	Ca^{2+} ND	Ca^{2+} D	Pb^{2+} ND	Pb^{2+} D	Hg^{2+} ND	Hg^{2+} D
EG	−7.73	−4.59	−7.04	−5.77	−9.74	−9.59
EA	−8.03	−4.93	−7.50	−6.41	−10.58	−10.88
ED	−8.26	−5.20	−7.84	−6.88	−10.91	−11.36
12-crown-O_4	−8.45	−5.55	−8.05	−7.33	−11.03	−11.73
12-crown-O_2N_2	−8.77	−5.95	−8.60	−8.16	−11.89	−13.11
12-crown-N_4	−9.03	−6.29	−9.03	−8.81	−12.41	−13.97

is equal to the ordering of the ΔE_{int} values in both cases, ND and D. However, ND fails to predict the horizontal ordering (rows).

According to ND, the Ca^{2+} complexes are more stable than the Pb^{2+} complexes, whereas ΔE_{int} shows the opposite ordering. This behavior is reversed when the directionality of the derivatives is taken into account. Thus, D predicts the same ordering as presented by ΔE_{int}. A plot of ΔE_{ct} vs ΔE_{int} is presented in Figure 2, where the symbols represent the complexes formed with Ca^{2+} (squares), Pb^{2+} (triangles), and Hg^{2+} (circles). We have distinguished the bidentate ligands (solid symbols) from the crown ethers (blank symbols). It is clear from this plot that there is an approximately linear

relationship between the charge-transfer energy and the interaction energy. The correlation coefficient for the linear relationship between the three metals and the bidentate ligands is 0.97, and that of the three metals with the cyclic ligands is 0.96.

In Table 5, we report the amount of charge transferred during complex formation. In this case, the trends for D and ND are the same, but the D values are larger. Additionally, one can see that the trend with respect to the hardness of the acid in the complex is correctly described for both D and ND, in agreement with previous work, where the charge transferred is related to the principle of hard and soft acids and bases.[76] That is, according to Table 3, Ca^{2+} is much harder than Pb^{2+} and Hg^{2+}, and therefore, one expects that the amount of charge transferred will be smaller[77] for Ca^{2+} than for Pb^{2+} and Hg^{2+}, as can be observed in Table 5.

Now, to compare the charge-transfer values with those obtained through other methods, we performed a natural population analysis (NPA) in the complexes to estimate the amount of charge transferred by considering the initial charge of the cation to be 2+. The values are reported in parentheses in Table 5. It is clear that these NPA values follow the same tendency as ΔN_{ct}: the greatest charge transfer is observed in mercury complexes, and it grows from EG to ED and from 12-

TABLE 5: ΔN_{ct} (in Atomic Units) for the Complexes between Ca^{2+}, Hg^{2+}, and Pb^{2+} and Bidentate and Cyclic Ligands, along with Natural Population Analysis Charge Transfer (in Parentheses)

ligand	Ca^{2+} ND	Ca^{2+} D	Pb^{2+} ND	Pb^{2+} D	Hg^{2+} ND	Hg^{2+} D
EG	0.55	0.60 (0.03)	0.70	0.89 (0.16)	0.84	1.18 (0.62)
EA	0.56	0.62 (0.07)	0.72	0.94 (0.22)	0.88	1.27 (0.78)
ED	0.57	0.64 (0.11)	0.74	0.98 (0.29)	0.90	1.30 (0.80)
12-crown-O_4	0.59	0.67 (0.07)	0.77	1.04 (0.29)	0.92	1.35 (0.67)
12-crown-O_2N_2	0.60	0.70 (0.12)	0.80	1.11 (0.40)	0.97	1.44 (0.75)
12-crown-N_4	0.61	0.72 (0.16)	0.83	1.16 (0.52)	1.00	1.50 (0.80)

7950 *J. Phys. Chem. A, Vol. 114, No. 30, 2010*

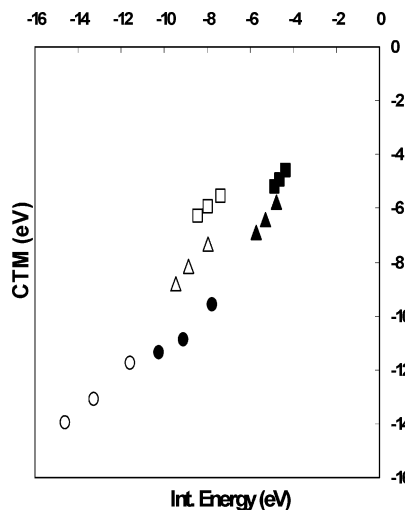Ramírez-Ramírez et al.

Figure 2. ΔE_{ct} versus ΔE_{int} for the 18 complexes formed by Ca^{2+} (squares), Pb^{2+} (triangles), and Hg^{2+} (circles) with bidentate (solid symbols) and crown ether (open symbols) ligands.

crown-O_4 to 12-crown-N_4. However, NPA predicts almost the same values for bidentate and cyclic ligands and does not follow the binding energy tendency of ΔN_{ct}. It can also be observed that the values of charge transferred according to NPA are smaller than those predicted by the model presented in this work.

Thus, the results presented indicate that, in these cases, charge transfer has the most significant effect on the interactional energies and, consequently, on the formation energies. Additionally, the fact that the order of the complexation energy is correctly described only when one differentiates the left and right derivatives indicates that it is important, at least in the present systems, to take into account the fact that the response of a system to charge acceptance is different from the response to charge donation.

5. Conclusions

We have presented a very simple approach for analyzing geometrical and electronic effects on the formation energy of some metal complexes, for some dications interacting with bidentate and cyclic ligands. The geometrical factors in these cases do not contribute to the formation energy more than 12%; rather, the main effects are due to electronic rearrangements when the complex is formed. Thus, we have seen that interactional complementarity, which measures these latter effects, can be related to charge transfer when the directionality of the derivative for the chemical potential is taken into account. In this way, the formation energy of the complex when a dication interacts with a ligand can be estimated through the energy change associated with the charge transferred, which, in our model, can be determined from the ionization potentials and the electron affinities of the isolated host (at the geometry it will have in the complex) and guest.

It is important to mention that the strength of the present approach, based on global properties that do not depend on the position within the molecule, is its simplicity in providing an estimate of the interactional complementarity. However, further developments at the local level, through reactivity indexes defined in DFT, that depend on the position within the molecule, such as the Fukui function[78] or the local softness,[79] would be required to take into account retrodonating effects from the metal to the ligand. These local descriptors could also be used to try to get a better understanding of the structural features of the systems studied. We are presently working in this direction.

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