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Nature of the metal–ligand bond in trivalent neodymium complexes with neutral π-donor ligands. A theoretical study

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Abstract

The nature of bonding and energetics in trivalent rare earth π-donor ligand complexes [$NdCl_3$–πL] and [$NdCp_2$–πL]$^+$ have been investigated theoretically by employing Hartree–Fock (HF) and density functional theory (DFT) based methods. Acetylene, ethylene, butadiene, and benzene served as model π-ligands. Geometries and binding energies are reported. The analysis presented in this study clearly indicates the essentially electrostatic character of that binding interaction in terms of a cation–π-ligand interaction. The lanthanide to π-ligand bonding was predicted to be weak, accompanied with a slight distortion of the ligand's geometry upon coordination. The role of electron correlation does not appear to be crucial in correctly predicting the metal–ligand interaction energy and the ligand distortion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Neodymium; Olefin; Coordination bond; DFT calculation

1. Introduction

The subject of lanthanide chemistry has been of interest to both experimental [1] and theoretical chemists [2] for many years. From the theoretical point of view, there is the challenge of predicting accurate molecular properties (geometries, bond dissociation energies, etc.) in lanthanide complexes that, due to the large number of electrons in s, p and f shells, are particularly difficult to describe. Furthermore, there is great interest in understanding the role of metal–ligand interactions in catalytic processes, in which those complexes are often involved.

Unfortunately, a precise evaluation of molecular properties is still far from being a routine task, especially when f electrons are involved. The theoretical investigation of rare earth complexes, even at a semi-quantitative level, requires a sufficiently accurate treatment of relativistic effects and of electron correlation, which can contribute to a similar amount. Different relativistic contributions play a significant role in heavy metal chemistry [3] and different theoretical approaches are proposed to account for them [2,4]. The most popular and computationally least expensive methodology for incorporating scalar relativistic effects is the relativistic effective core potential (RECP) approach [5]. It has been demonstrated in numerous studies that standard non-empirical methods using RECPs give accurate geometries and bond energies of heavy-atom complexes [6]. The recent development of accurate functionals, including gradient corrections, makes the methods based on the density functional theory (DFT) the most powerful non-empirical alternative to conventional Hartree–Fock (HF) and post-HF methods. It has been proven in a number of studies that DFT based methods are advantageous in studying transition metal complexes [7]. They provide an accurate description of metal–ligand interactions without losing the simple chemical interpretation arising from a single-determinant scheme with an effort comparable to the HF method and are therefore much less expensive than post-HF methods.

On the other hand, the theoretical examination of the bonding situation in lanthanide complexes is challenging. In fact, only a few investigations have yet been

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carried out [2,8], most of them have been on small model systems. Particularly, a theoretical understanding of the rare earth-π-donor bonding in trivalent lanthanide complexes is still lacking.

In this paper we report a systematic theoretical investigation on the bonding interaction of neutral π-donors (πL) with neutral and cationic Nd^{III} model complexes with the aim to get valuable insight into the nature of this bond and to predict theoretically the binding energies. An important question in this regard is whether this bond can be described as a donor–acceptor interaction in terms of the familiar Dewar–Chatt–Duncanson model [9] of synergetic ligand → MX_n donation and ligand ← MX_n back-donation, similar to that observed for πL interaction with low-valent transition metal complexes, or whether the lanthanide–ligand bond is substantially if not predominantly electrostatic in nature. There are no theoretical studies employing non-empirical methods known to us, which address this question.

Acetylene, ethylene, butadiene and benzene were chosen as sample π-donor ligands πL that interact with cationic, i.e. $[NdCp_2]^+$, and neutral, i.e. $NdC1_3$, Nd^{III} model complexes. The mode of ligand coordination was considered such that the interaction of its π-face with the Nd^{III}, moiety is maximized. Thus, a η^2-coordination is considered for acetylene and ethylene, a η^4-coordination for butadiene, while benzene is η^6-coordinated. In order to probe the importance of electron correlation, the investigations were performed with both HF and gradient-corrected DFT methods.

2. Computational details

The HF and DFT calculations were performed by using the program package TURBOMOLE [10], developed by Ahlrichs et al. at the University of Karlsruhe. The DFT calculations were carried out using Slater exchange [11] and the VWN parameterization [12] of the LDA correlation energy, with the gradient corrections of Becke [13] for exchange and of Perdew [14] for correlation (denoted as BP86), which were added variationally within the SCF procedure. Additionally, Becke's three-parameter hybrid functional [15], together with the correlation functional of Lee, Yang and Parr [16] (denoted as B3LYP) was used.

For Nd the relativistic effective core potential (ECP) developed by Dolg et al. [5b] was used together with (7s6p5d)/[5s4p3d] valence basis functions throughout this paper. This ECP treats $[Kr]4d^{10}4f^3$ as a fixed core, whereas $5s^25p^66s^25d^16p^0$ shells are taken into account explicitly. Partially filled 4f orbitals are believed to be unimportant in the chemical behavior of lanthanide–ligand bonds. Because of their small size they cannot contribute to the valence region and therefore, they are included in the ECP. The various studies by Dolg et al. [2,17] confirmed this assumption.

The TZVP basis set of Ahlrichs et al. [18] was used for main group elements, consisting of a (73211/6111/1) contracted set for chlorine, a (62111/411/1) contracted set for carbon, and a (311/1) contracted set for hydrogen. In addition, basis set saturation effects were verified by single-point calculations at the optimized geometries by adding a single f-type function ($\zeta_f = 0.586$) on neodymium.

The geometries of the complexes were fully optimized by using gradient techniques at the Hartree–Fock and DFT level. The bonding situation of the complexes was analyzed with the help of the natural bond orbital (NBO) analysis [19] and charge decomposition analysis (CDA) [20] partitioning scheme. The CDA decomposes the wave function or the Kohn–Sham determinant of a complex [ML] in terms of fragment orbitals of the chosen ligand L and the metal fragment [M]. The [M] ← L donation is then given by mixing of the occupied orbitals of L and the vacant orbitals of [M]. The [M] → L back-donation is given by the mixing of the occupied orbitals of [M] and vacant orbitals of L. Mixing of occupied orbitals of both fragments gives the repulsive polarization (r) and the residual term (Δ) of mixing the unoccupied orbitals should vanish. Bond orders, expressed in terms of the NAO basis, were calculated using the method of Wiberg [21].

3. Results and discussion

3.1. Structures

At first we shall start with a brief examination of the molecular shape of the $NdC1_3$ and $[NdCp_2]^+$ molecules. There has been an extensive debate in the literature about the true conformation of LnX_3 species (with Ln = lanthanide, X = halide) [22]. Unfortunately, the interpretations of the experimental data from IR-spectra or electron diffraction are sometimes contradictory [22b], owing to the flexible nature of these molecules. At the HF level we found the planar (D_{3h} symmetry) structure, while the DFT methods agreed in predicting a pyramidal (C_{3v} symmetry) equilibrium structure. The energy required for planarity amounts to less than 0.5 kcal mol^{-1}. Similar to LnX_3, experimental studies were not conclusive for $LnCp_2$ with respect to the equilibrium structures of the isolated molecules [23]. They can be characterized by low bending potentials, which were confirmed by a thorough theoretical study [17f]. Our calculations predict for $[NdCp_2]^+$ a bent equilibrium structure both at the HF and DFT levels of computation. Important geometrical parameters for the optimized structures of $[NdCp_2]^+$ are summarized in Table 1 (Fig. 1). The metal–(ring centroid) distance

Table 1
Geometrical parameters (Å and °) of $[NdCp_2]^+$

Method	Symmetry	*d* [a]	<α [b]
HF	C_s	2.491	138.8
BP86	C_s	2.441	131.7
B3LYP	C_s	2.459	133.2

[a] Metal to (ligand-centroid) distance, see Fig. 2.
[b] Bending angle (ring-centroid)–metal–(ring-centroid).

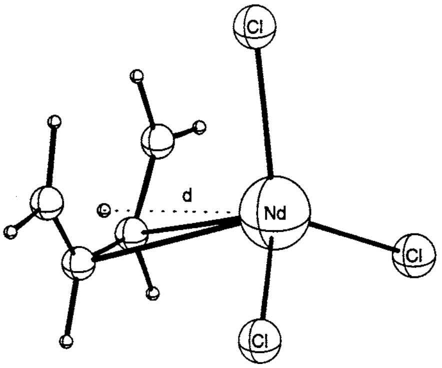

Fig. 1. Important geometric parameter for $[NdC1_3–\pi L]$ with $\pi L =$ *cis*-butadiene.

decreases in the order HF > B3LYP > BP86, thus as a common phenomenon, the metal Cp bond shrinks with inclusion of electron correlation.

Upon ligand coordination the $NdC1_3$ and $[NdCp_2]^+$ moieties are readily distorted at low energetic costs, in order to minimize the repulsive interaction of the ligand's π-system with the Cl^-/Cp anions. This distortion, however, is not regarded to be important for the understanding of the nature of the Nd^{III}–πL interaction. Therefore, the bonding interaction is analyzed in terms of deformation of the ligand's carbon framework Δ(C=C) and of metal–(ligand centroid) distance *d*, which are summarized for $[NdC1_3–\pi L]^+$ and $[NdCp_2–\pi L]^+$ complexes in Tables 2 and 3 (Fig. 2), respectively.

Because of the well balanced basis set we used in the DFT calculations, the basis set superposition error (BSSE) calculated for the TZVP basis set with the counterpoise correction method is negligible ($0.2 + 0.1 = 0.3$ kcal mol^{-1}) for the interaction energy in the case of the $[NdCp_2–(ethen)]^+$ system.

The metal–ligand distances *d* are calculated to be in the range of 2.70–3.20 Å and they are for a given ligand always larger for $[NdCp_2–\pi L]^+$ complexes than for $[NdC1_3–\pi L]$ complexes. This results from steric congestion of the ligand with the bulky Cp ligands, which, however, best can be observed by comparing the structural data of $[NdC1_3–benzene]$ and $[NdCp_2–benzene]^+$ complexes. The metal–ligand distances are predicted to be largest at the HF level of computation and become shorter with the inclusion of electron correlation via DFT methods. The generally observed trend, with respect to the computational level, shows the order HF ≫ B3LYP > BP86. This can be understood from a theoretical point of view, since some portion of the exact HF exchange contributes to the B3LYP functional.

The distortion of the ligand's carbon framework is calculated to be very small for all complexes. It never exceeds 0.12 Å (Tables 2 and 3, respectively). Different from the observed dependence of the predicted Nd^{III}–πL distance from the computational level employed, there is no noticeable influence of them on the Δ(C=C) values. It is well known from theoretical studies on transition metal complexes that inclusion of

Table 2
Geometrical parameters (Å and °) of optimized structures and binding energies (kcal mol^{-1}) for the $[NdC1_3]$–πL interaction

πL	Method	Symmetry	*d* [a]	C=C [b]	D_e [c]
C_2H_2	HF	C_s	3.017	1.186 (0.005)	13.4(13.0)
	BP86		2.921	1.214 (0.005)	13.6(13.5)
	B3LYP		2.955	1.203 (0.004)	13.6(13.3)
C_2H_4	HF	C_s	3.067	1.325 (0.011)	14.0(13.5)
	BP86		2.966	1.345 (0.011)	13.7(13.5)
	B3LYP		3.007	1.337 (0.010	13.7(13.4)
cis-C_4H_6	HF	C_s	2.918	1.327/1.482 (0.008/0.004)	18.3 (17.5)
	BP86		2.789	1.352/1.472 (0.008/0.003)	18.1 (17.9)
	B3LYP		2.849	1.342/1.474 (0.007/0.006)	17.5(17.2)
trans-C_4H_6	HF	C_1	2.912	1.326/1.467 (0.006/0.009)	17.4 (16.7)
	BP86		2.787	1.354/1.472 (0.008/0.007)	17.1 (16.8)
	B3LYP		2.854	1.342/1.462 (0.006/0.007)	16.9 (16.3)
C_6H_6	HF	C_{3v}	2.840	1.389 (0.005)	22.4 (21.9)
	BP86		2.768	1.405 (0.006)	22.2 (22.0)
	B3LYP		2.826	1.397 (0.004)	22.0 (21.6)

[a] Metal to (ligand–centroid) distance, see Fig. 1.
[b] C–C distance of the ligand's carbon backbone. Values in parenthesis refer to changes relative to the free ligand.
[c] Values in parenthesis are obtained with an additional f-function on Nd.

Table 3
Geometrical parameters (Å and °) of optimized structures and binding energies (kcal mol^{-1}) for the $[NdCp_2]^+$–πL interaction

πL	Method	Symmetry	d [a]	C=C [b]	D_e [c]
C_2H_2	HF	C_s	3.188	1.185 (0.004)	11.1 (11.1)
	BP86		3.082	1.213 (0.004)	11.4 (11.4)
	B3LYP		3.120	1.202 (0.003)	11.5 (11.5)
C_2H_4	HF	C_s	3.193	1.324 (0.010)	12.8(12.7)
	BP86		3.084	1.344 (0.010)	12.4(12.4)
	B3LYP		3.134	1.336 (0.009)	12.7(12.7)
cis-C_4H_6	HF	C_s	2.951	1.328/1.483 (0.009/0.005)	20.2(20.1)
	BP86		2.776	1.356/1.472 (0.012/0.003)	20.8 (20.9)
	B3LYP		2.833	1.344/1.473 (0.009/0.005)	20.5(20.4)
trans-C_4H_6	HF	C_1	2.966	1.328/1.471 (0.008/0.005	19.4(19.2)
	BP86		2.828	1.354/1.462 (0.009/0.009)	20.1(20.1)
	B3LYP		2.883	1.344/1.461 (0.008/0.006)	19.7(19.7)
C_6H_6	HF	C_s	3.033	1.388 (0.004)	18.8(18.8)
	BP86		2.874	1.405 (0.006)	19.8(20.0)
	B3LYP	2.945		1.398 (0.005)	19.0 (19.2)

[a] Metal to (ligand–centroid) distance, see Fig. 2.

[b] C–C distance of the ligand's carbon backbone. Values in parenthesis refer to changes relative to the free ligand.

[c] Values in parenthesis are obtained with an additional f-type function on Nd.

electron correlation strengthens the back-donation component and therefore causes a larger ligand distortion. Owing to the nearly identical very small ligand distortion predicted at HF and DFT level of computation, the back-donation component, as expected for the electron-deficient Nd^{III} center, should not significantly contribute to the metal–πL bonding.

3.2. Binding energies

The metal–ligand binding energies for the $[NdCl_3$–πL] and $[NdCp_2$–πL$]^+$ complexes are shown in the last column of Table 2 and Table 3, respectively. They indicate weak Nd^{III}–πL bonds. This agrees with the experimental characterization of lanthanide(III) complexes of neutral olefins, alkynes, and arenes as generally quite labile [24]. The calculated binding energy for a given complex is nearly identical, regardless of the theoretical method employed. This corresponds to the predicted geometrical deformation of the ligand's carbon framework upon coordination, as discussed above. A supplemental f-function on Nd only negligibly influences the energetics.

The energetic stabilization of the Nd^{III}–πL interaction will now be analyzed in detail for the BP86 results (cf. Table 2 and Table 3). The ligand's binding energy is ordered as benzene > butadiene ≫ ethylene ∼ acetylene for $[NdCl_3$–πL] and benzene ∼ butadiene ≫ ethylene ∼ acetylene for $[NdCp_2$–πL] complexes. Surprisingly, for an individual ligand the complexation energy is predicted to be on the same order of magnitude for both cationic and neutral model complexes. This needs some explanation and we will return to this issue below.

If the π-donor ligands interact with the Nd^{III} moiety essentially in a donor–acceptor fashion, then one would expect, that the strength of that interaction goes along with the donor–acceptor ability of the individual ligands. Since back-donation does not play an important role we focus on the ligands donor strength. Following a simple frontier orbital approach, according to the ligand's HOMO energies (Table 4, where the DFT calculated eigenvalues are given, which cannot be interpreted as ionization energies in the sense of the Koopmans' theorem), their donation ability is generally ordered as butadiene > benzene > ethylene > acetylene. However, that is not consistent with the trends in the binding energy expressed in Table 2 and Table 3. In particular, the very similar binding energies calculated for ethylene and acetylene and the stronger energetic stabilization of benzene than of butadiene (at least for

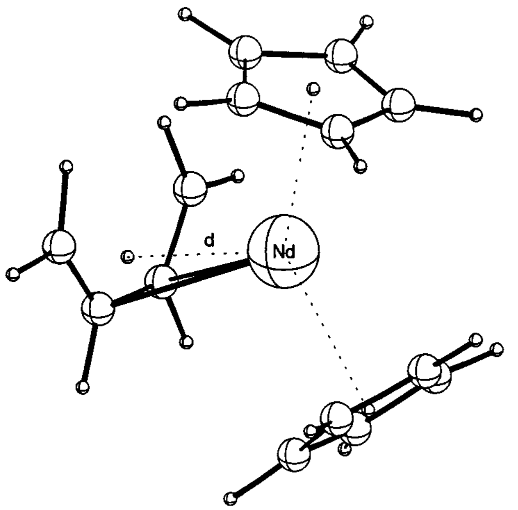

Fig. 2. Important geometric parameter for $[NdCp_2$–πL$]^+$ with πL = *cis*-butadiene.

Table 4
HOMO and LUMO energies [a], quadrupole moment (Q_{zz}) [b], and electrostatic potential EP [c] for π-ligands calculated at BP86 level

π-ligand	HOMO(π) [a]	LUMO(π*) [a]	Q_{zz} [b]	EP [c]
C_2H_2	−7.22	−0.33	−10.18	−7.7
C_2H_4	−6.80	−1.06	−11.70	−7.9
cis−C_4H_6	−5.83	−2.21	−21.61	−9.5
trans-C_4H_6	−5.89	−1.96	−21.65	−9.1
C_6H_6	−6.37	−1.24	−29.71	−11.2

[a] In electron volts.

[b] Component of quadrupole moment perpendicular to the molecular plane (π-face mode) (in atomic units).

[c] Electrostatic potential in kilocalories per mole, see text.

Table 5
Charge decomposition analyses [a] calculated at BP86 level

Complex	$\pi L \rightarrow Nd^{III}$	$Nd^{III} \rightarrow \pi$	r	Δ
$[NdC1_3–C_2H_2]$	0.272	−0.018	−0.098	−0.017
$[NdC1_3–C_2H_4]$	0.225	−0.045	−0.098	−0.015
[NdC1$_3$–*cis*-C_4H_6]	0.290	−0.074	−0.187	−0.023
[NdC1$_3$–*trans*–C_4H_6]	0.244	−0.049	−0.184	−0.018
$[NdC1_3–C_6H_6]$	0.407	−0.084	−0.205	−0.034
$[NdCp_2–C_2H_2]^+$	0.332	−0.018	−0.056	−0.019
$[NdCp_2–C_2H_4]^+$	0.292	−0.029	−0.066	−0.012
[NdCp$_2$–*cis*-C_4H_6]$^+$	0.491	0.004	−0.162	−0.023
[NdCp$_2$–*trans*-C_4H_6]$^+$	0.419	−0.004	−0.133	−0.018
$[NdCp_2–C_6H_6]^+$	0.455	−0.019	−0.190	−0.030

[a] Donation $\pi L \rightarrow Nd^{III}$, back-donation $Nd^{III} \rightarrow \pi L$, repulsive part r, and residual term Δ.

$[NdC1_3−\pi L]$ complexes, where steric congestion does not play an important role) contradict the picture of an essentially donor–acceptor dominated interaction. The calculated bonding energy, which does not remarkably depend on whether the HF or DFT method is employed [25], reinforces the evidence of a negligible back-donation and donation bonding component, since it is well known that inclusion of electron correlation significantly improves the energetics of M–L donor–acceptor interactions with transition metals are involved.

The significance of the cation π-interaction as an important noncovalent binding force has come to be appreciated in recent years [26a]. It was argued, that to first-order, the major aspect of the cation π-interaction is electrostatic in nature, involving the interaction of the cation with the permanent quadrupole moment of π-ligands [26]. Two approaches are used to probe whether an electrostatic cation π-interaction may explain the trend of the calculated bonding energies. First the quadrupole moment (Q_{zz}) of the free ligands are considered (Table 4), and secondly the electrostatic potential (EP) was used as a meter to evaluate the bonding. To this end, we replaced the Nd-moiety of the optimized $[NdCl_3−\pi L]$ complexes by a positive point charge and evaluated the interaction energy (Table 4). The order of increasing quadrupole moments and also the EP values match well the trend of calculated binding energies. Although the two approaches do not allow estimation of the electrostatic contribution to overall binding, they provide insights helpful for a closer understanding of the $Nd^{III}–\pi L$ interaction. They indicate the crucial role that electrostatic bonding components play for the $Nd^{III}–\pi L$ bonding, similar to that already found for alkali metal–arene complexes.

The very similar complexation energies of a given ligand calculated for complexes $[NdCl_3−\pi L]$ and $[NdCp_2−\pi L]^+$ can be explained by considering two different effects, which may energetically compensate each other.

According to the electrostatic nature of bonding the metal–ligand interaction should be stronger in cationic complexes, since the formal positive charge of the metal can be expected to be larger for the $[NdCp_2]^+$ moiety when compared to $[NdCl_3]$ (see Section 3.3). On the other hand, the bulkier Cp ligands increase the steric repulsion about the neodymium and prevent a closer interaction of both fragments. This can best be observed for benzene and gives rise to nearly identical binding energies of benzene and butadiene in cationic complexes, although of a somewhat stronger electrostatic metal–benzene than metal–butadiene interaction, as detected for $[NdCl_3−\pi L]$ complexes.

3.3. Analysis of the charge distribution

To obtain a thorough understanding of the nature of the $Nd^{III}–\pi L$ bond, the electron density distribution and their changes upon ligand coordination will be analyzed with the help of the NBO analysis and the CDA partioning scheme at BP86 level.

Following the picture of an essentially donor–acceptor dominated metal–ligand interaction, the complex formation should be mainly due to donation of π-electron density from the ligands to the electron-deficient metal center, since the Nd^{III} has formally no valence electrons. However, because of the remarkable size of the ion and its relatively low ionisation energies, the electron donation to the metal should be weak.

The results of the CDA method, which has been proven to be helpful for the analysis of donor–acceptor interactions [20a,b], are collected in Table 5. It was emphasized, that the absolute values for the donation and back-donation are not important; however their ratio is relevant [20b]. Furthermore, there is no direct correlation between the amount of donated electron density and the energetic effect of that component to the binding. The most important result is the finding that $\pi L \rightarrow Nd^{III}$ donation is always dominant and the back-donation for all complexes is negligible. The CDA method suggests that all ligands act as pure donors.

Table 6
Natural orbital population analysis (NPA): metal charges Q(Nd) and total π-ligand charges Q(πL) together with Wiberg bond indices P(Nd–C) and P(C=C) calculated at BP86 level.

Complex	Q(Nd)	Q(πL)	P(Nd–C) [a]	P(C=C) [b]
$[NdC1_3–C_2H_2]$	1.604	0.085	0.098	2.894 (3.000)
$[NdC1_3–C_2H_4]$	1.602	0.096	0.099	1.950 (2.052)
$[NdCl_3$–*cis*-$C_4H_6]$	1.557	0.130	0.066/0.073	1.822/1.120 (1.894/1.126)
$[NdC1_3$–*trans*-$C_4H_6]$	1.556	0.122	0.060/0.076	1.808/1.114 (1.871/1.154)
$[NdC1_3–C_6H_6]$	1.493	0.157	0.055	1.422 (1.444)
$[NdCp_2–C_2H_2]^+$	1.796	0.088	0.079	2.923 (3.000)
$[NdCp_2–C_2H_4]^+$	1.808	0.100	0.087	1.971 (2.052)
$[NdCp_2$–*cis*-$C_4H_6]^+$	1.723	0.140	0.082/0.099	1.797/1.123 (1.894/1.126)
$[NdCp_2$–*trans*-$C_4H_6]^+$	1.760	0.157	0.084/0.075	1.801/1.136 (1.871/1.154)
$[NdCp_2–C_6H_6]^+$	1.787	0.170	0.056	1.417 (1.444)

[a] For butadiene two values are given for terminal/central carbons, respectively.

[b] Values in parenthesis refer to free π-ligands.

Table 6 shows the results of the NBO analysis and the Wiberg bond indices. The neodymium ion carries large positive charges. Very similar for all ligands investigated, the neodymium atom has a formal charge of about 1.4 $|e^-|$ in $[NdC1_3–\pi L]$ compounds and a somewhat larger one of about 1.9 $|e^-|$ in $[NdCp_2–\pi L]^+$ compounds. Overall, the ligands are nearly neutral; thus indicating a low charge transfer toward the metal fragment upon complex formation. The very small metal–ligand bond orders together with the negligible changes of the ligand C=C bond orders, when compared with the free ligands, reinforce the evidence for a weak contribution of electron donation to bonding. The picture of the Nd^{III}–πL interaction provided by the NBO analysis is consistent with the above mentioned geometrical and energetical features.

4. Conclusions

The nature of the bonding interaction of neutral π-donor ligands (πL) with Nd^{III} complexes was studied theoretically. This was performed by using the Hartree–Fock (HF) method and density functional theory (DFT) based methods on cationic $[NdCp_2–\pi L]^+$ and neutral $[NdC1_3–\pi L]$ model complexes, with acetylene, ethylene, butadiene, and benzene chosen as πL-donor ligands. Geometric, energetic, and electronic aspects of the metal–ligand interaction were investigated.

All the results presented here provide a consistent picture of the Nd^{III}–πL–ligand interaction as predominantly electrostatic in nature, in terms of a cation–πL interaction, and ligand → metal donation of electron density does contribute to a minor extent to bonding. The lanthanide πL–ligand bonding was predicted to be weak, accompanied with a slight distortion of the ligand upon coordination. The similar binding energies of a given ligand calculated for both $[NdC1_3–\pi L]$ and $[NdCp_2–\pi L]^+$ complexes can be attributed to an interplay of reduced metal–ligand interaction due to steric congestion with the bulky Cp ligands, which is compensated by a stronger electrostatic bonding component. In the absence of steric congestion the bond strength is ordered as acetylene < ethylene < butadiene < benzene. These findings agree with the experimental observation of a strongly decreasing activity of the lanthanide-mediated polymerization of olefines or dienes when the reaction medium changes from aliphatic to aromatic solvents. In the latter the olefin or diene cannot compete with the solvent for coordination, which therefore causes a loss in activity.

The role of electron correlation does not appear to be crucial in correctly predicting the metal–ligand interaction energy and the ligand distortion, since both quantities were calculated to be very similar at HF and DFT level of computation. Additionally, higher angular momentum functions (ζ_f on Nd) possess a negligible role.

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