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Dual Cation and Anion Acceptor Molecules. The Case of the (η^6-C_6H_6)($\eta^6C_6F_6$)Cr(0) Complex

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In this manuscript we report high-level ab initio (RI-MP2(full)/6-31++G**) and DFT (B3LYP/ 6-31++G** and MPWB1K/6-31++G**) calculations on complexes between the bis(arene)chromium complex (η^6-C_6H_6)($\eta^6C_6F_6$)Cr(0) (**1**) and cations/anions. This interesting molecule **1**, which is synthetically available, exhibits a dual binding mode to anions and cations, with interaction energies similar to those previously reported for benzene with cations and hexafluorobenzene with anions. In addition, the simultaneous interaction with cations and anions is also studied.

Introduction

In modern chemistry, noncovalent interactions are crucial, especially in the field of supramolecular chemistry and molecular recognition.[1] In particular, interactions involving aromatic rings are key processes in both chemical and biological recognition. They have been recently reviewed by Meyer et al.[2] A classical example is the interaction of cations with aromatic systems, namely cation−π interactions,[3] which are supposed to be an important factor to the ion selectivity in potassium channels.[4] Such interactions are also important for the binding of acetylcholine to the active site of the enzyme acetylcholine esterase.[5] Recently, the importance of cation−π interactions in neurotransmitter receptors has been demonstrated.[6] Anion−π interactions[7] are also important noncovalent forces that have attracted considerable attention in the last 3 years. They have been observed experimentally, supporting the theoretical predictions and the promising proposal for the use of anion receptors based on anion−π interactions in molecular recognition.[8] In addition, π-acidic oligonaphthalendiimide rods have been recently proposed as transmembrane anion−π slides.[9]

The cation−π and anion−π interactions are dominated by electrostatic and ion-induced polarization terms.[10] The nature of the electrostatic term can be rationalized by means of the permanent quadrupole moment of the arene. The favorable face-to-face interaction of the benzene-hexafluorobenzene complex has been explained emphasizing the important role of the large and opposite permanent quadrupole moments of the two molecules.[11] The π−π interaction in the benzene dimer is governed by dispersion effects.[12] Some of us have studied the dual binding mode of some molecules to form stable complexes with both cations and anions.[10c,13,14,15] Two examples are the triazine and trifluorobenzene rings, and the dual behavior is explained by means of the small quadrupole moment of these molecules. The interaction is thus dominated by polarization effects and the electrostatic contribution to the interaction energy is negligible. As a consequence the binding energies of the complexes of these compounds with ions is small compared with benzene (cation−π complexes) or hexafluorobenzene (anion−π complexes), but recent reports have described the complexes formed between nitrate and π face of triazine in solid phase.[16]

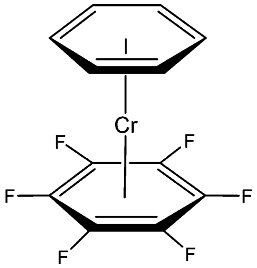

Figure 1. Schematic representation of (η^6-C_6H_6)($\eta^6C_6F_6$)Cr(0) (**1**).

In the present study, we investigate the dual binding mode of a molecule that itself is a sandwich complex of benzene, hexafluorobenzene and chromium(0). This complex was first synthesized by Middletown et al. in 1973 via a condensation procedure.[17] The resulting bis(arene)chromium (η^6-C_6H_6)(η^6-C_6F_6)Cr(0) (**1**) is stable and neutral, and exhibits a lower reactivity than hexafluorobenzene. Compound **1** exhibits two faces that in principle should be able to selectively interact with cations and anions. In order to demonstrate this issue, we have carried out a theoretical study where we optimized complexes of **1** with several anions and cations, and computed the interaction energies using high level ab initio and DFT calculations.

Theoretical Methods

The geometries of all compounds studied in this work were fully optimized using the MPWB1K/6-31+G** and B3LYP/6-31++G** levels of theory within the Gaussian 03 package.[18] The minimum nature of the complexes was evaluated performing frequency analyses at the same level. The DFT optimized geometries were used as starting points for the optimization using the resolution of the identity MP2 (RI-MP2) level and the 6-31++G** basis set. The RI-MP2(full) calculations were done using the program TURBOMOLE version 5.7.[19] The

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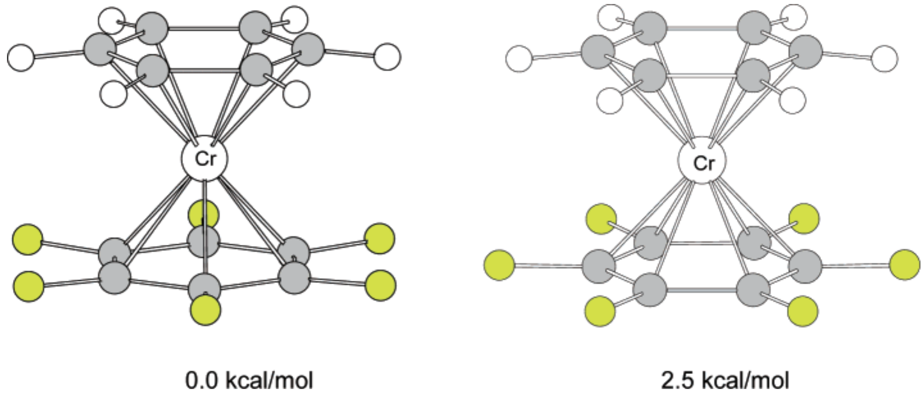

Figure 2. RI-MP2(full)/6-31++G** optimized staggered and eclipsed conformations of **1**.

TABLE 1: Interaction Energies with the BSSE Correction (E_{CP}, kcal mol) and Equilibrium Distances (R_e, Å) Computed at the RI-MP2/6-31++G, B3LYP/ 6-31++G**, and MPWB1K/6-31++G** Levels of Theory for Complexes 2−19**

	RI-MP2[a]		B3LYP		MPWB1K	
compound	E_{CP} (NImag)	R_e	E_{CP} (NImag)	R_e	E_{CP} (NImag)	R_e
2 (**1**···Li^+)	−28.6 (0)	1.87	−31.7 (1)	1.84	−34.3 (0)	1.84
	−26.2	*1.87*				
3 (**1**···Na^+)	−17.5 (0)	2.34	−19.2 (1)	2.42	−21.2 (0)	2.33
4 (**1**···K^+)	−10.9 (0)	2.84	−10.5 (1)	2.87	−12.7 (0)	2.82
5 (**1**···F^-)	−15.5 (3)	2.48	−14.9 (2)	2.56	−15.6 (2)	2.52
	−12.9	2.49				
6 (**1**···Cl^-)	−8.9 (0)	3.06	−7.4 (0)	3.28	−8.5 (0)	3.21
7 (**1**···Br^-)	−8.6 (0)	3.24	−5.4 (2)	3.30	−6.7 (1)	3.23
8 (Li^+···**1**···F^-)	−112.5 (2)	1.75/2.27	−114.2 (2)	1.73/2.33	−117.2 (2)	1.73/2.30
	−109.9	*1.75/2.27*				
9 (Na^+···**1**···Cl^-)	−83.5 (2)[b]	2.25/2.89	−82.1 (2)	2.22/3.00	−85.5 (0)	2.22/2.96
10 (K^+···**1**···Br^-)	−71.0 (0)	2.69/3.06	−65.7 (2)	2.71/3.10	−69.9 (0)	2.67/3.06
11 (BEN···Li^+)	−33.7	1.91	−37.2 (0)	1.84	−39.1 (0)	1.86
12 (BEN···Na^+)	−21.4	2.39	−24.1 (0)	2.40	−26.5 (0)	2.32
13 (BEN···K^+)	−14.9	2.90	−15.5 (0)	2.94	−17.8 (0)	2.92
14 (HFB···F^-)	−18.8	2.57	−17.5 (2)	2.66	−19.7 (0)	2.62
15 (HFB···Cl^-)	−13.1	3.15	−11.0 (0)	3.31	−13.0 (0)	3.30
16 (HFB···Br^-)	−12.7	3.28	−9.4 (2)	3.37	−11.9 (1)	3.41
17 (Li^+···BEN···F^-)	−113.3	1.78/2.41	−117.4 (2)	1.77/2.47	−121.7 (2)	1.73/2.35
18 (Na^+···BEN···Cl^-)	−84.8	2.27/3.01	−87.7 (2)	2.29/3.11	−91.4 (2)	2.27/3.12
19 (K^+···BEN···Br^-)	−71.5	2.76/3.21	−70.5 (3)	2.77/3.30	−74.5 (3)	2.65/3.20

[a] Values in intalics correspond to the complexes using the eclipsed geometry of **1**. [b] Very small degenerate frequencies (9 cm^{-1})

frequency analysis of these complexes was carried out at the MP2(full)/6-31G*//RI-MP2(full)/ 6-31++G** level of theory. The RI-MP2 method[20] applied to the study of cation−π and anion−π interactions is considerably faster than that of the MP2, and the interaction energies and equilibrium distances are almost identical for both methods.[21] The binding energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys−Bernardi counterpoise technique.[22] The optimization of the complexes has been performed imposing C_{6v} symmetry, unless noted otherwise. The charge transfer from the ion to the aromatic rings has been evaluated using the Merz−Kollman (M−K) scheme for deriving atomic charges.[23] This method derives the charges from a least-squares fit to the electrostatic potential calculated in a large number of points around the molecule. The M−K method differs from other electrostatic potential methods in the choice of the points where the potential is calculated. In particular, it uses points on nested Connolly surfaces with a density of 1 point Å and it samples points at 1.4, 1.6, 1.8, and 2.0 times the van der Waals radius of the atoms. The "atoms-in-molecules" analysis[24] has been performed by means of the AIM2000 version 2.0 program[25] using the MP2/ 6-31++G**//RI-MP2/6-31++G** wavefunctions.

Results and Discussion

First of all, several considerations regarding the geometry of **1** should be mentioned. At the RI-MP2/6-31++G** level of theory the staggered geometry is 2.5 kcal/mol more stable than the eclipsed geometry, see Figure 2. Moreover, the optimization of a C_1 geometry (skewed), converges to the staggered (C_{6v}) geometry. At the DFT level of theory, both conformations have the same energy. Therefore, the optimization of complexes of **1** with ions has been performed using the staggered conformation and imposing C_{6v} symmetry.

In Table 1, we summarize the binding energies and equilibrium distances obtained for complexes **2**−**19** (see Figure 3) where, in addition to complexes of **1** with ions (**2**−**10**), complexes of benzene (BEN) with cations (**11**−**13**), complexes of hexafluorobenzene (HFB) with anions (**14**−**16**), and complexes of BEN with both cations and anions simultaneously (**17**−**19**) are also included for comparison purposes. From the inspection of the results several interesting points arise. First, the DFT interaction energies of cation−π complexes are overestimated compared to the MP2 ones. In particular, the MPWB1K functional, which is assumed to give good results for weak noncovalent interactions,[26] predicts interaction energies 2−6 kcal/mol more negative than the MP2 for complexes where a cation−π interaction is present. In addition, for the systems

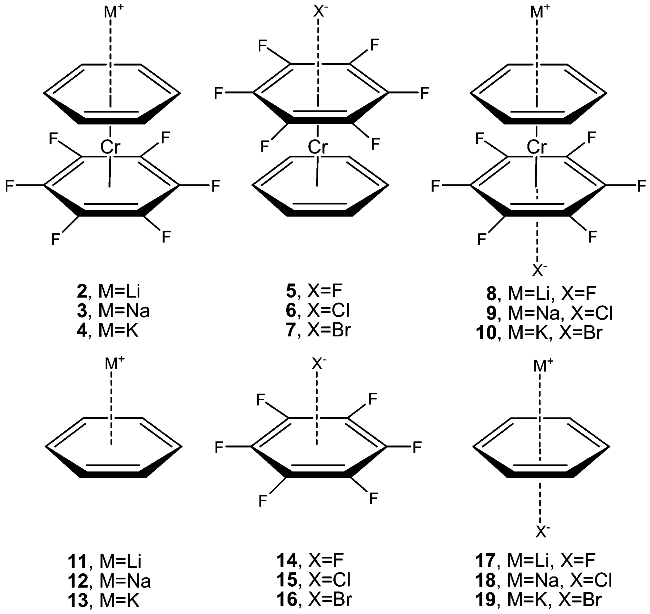

Figure 3. Cation$-\pi$ and anion$-\pi$ complexes **2**$-$**19**.

that we consider in this work, it does not represent an improvement over the B3LYP functional. In contrast, both functionals give interaction energies for the anion$-\pi$ complexes comparable to those for the RI-MP2. Second, the interaction energies of complexes of **1** with cations are comparable to those of the complexes of benzene with cations, indicating that the binding ability of benzene ring is to a minor extend affected when it is forming the sandwich system **1**. In the same way, the interaction energies of complexes of **1** with anions are comparable to those of the complexes of hexafluorobenzene with anions. These results indicate that **1** can behave as a dual binding unit for cations and anions with the same characteristics as benzene and hexafluorobenzene. Third, we have examined the simultaneous interaction of **1** with anions and cations. At the RI-MP2(full)/6-31++G** level of theory, the interaction energies of $X^-\cdots$**1**$\cdots M^+$ complexes **8**$-$**10** are almost identical to those of the $X^-\cdots$BEN$\cdots M^+$ complexes **17**$-$**19**, confirming that **1** is able to interact simultaneously with anions and cations, behaving almost the same as in the corresponding benzene complexes. Last, we have computed three complexes (**2**, **5** and **8**) using the eclipsed geometry of **1** at the RI-MP2(full)/6-31++G** level of theory. The binding energies (referred to the staggered geometry of **1**) and equilibrium distances are present in parenthesis in Table 1. For both staggered and eclipsed geometries, the equilibrium distances are very similar. Moreover, the interaction energies are 2.4$-$2.6 kcal/mol more positive for the complexes using the eclipsed conformation of **1**. Consequently the cation/anion binding ability of **1** does not depend upon the conformation of **1**, since this difference corresponds to the conformational eclipsed-staggered energy change.

We have analyzed the geometrical features of **1** and its complexes with ions including charge-transfer effects. In Table 2 we summarize the optimized distances between the Cr atom and the ring centroids in compounds **1**$-$**10** and the Merz$-$Kollman (M$-$K) computed charges. We have used the M$-$K method for deriving atomic charges since it is considered to give high-quality charges.[27] Moreover, we have successfully used them to study charge-transfer effects in ion$-\pi$ interactions.[10c,28] In compound **1** the Cr$-C_6F_6$ distance is 0.04 Å shorter than the Cr$-C_6H_6$ distance, in agreement with the reported[29] X-ray structure of a pentafluoro derivative of **1**, where the Cr$-C_6F_5$ distance is 0.07 Å shorter than the Cr$-C_6H_6$ distance. However, this fact is reversed in the complexes of **1** with either anions or cations, where the Cr$-C_6F_6$ distances are longer than the Cr$-C_6H_6$ distances. This behavior can be explained by means of analyzing the atomic charges in the complexes. In **1** the Cr atom and the C_6H_6 ring are slightly positive and the negative part of the molecule corresponds to the C_6F_6 ring. In the complexes **2**$-$**10** the charge distribution in both rings is the opposite. In addition, the charge separation in the ternary complexes **8**$-$**10** is very important, and consequently, the very favorable interaction energies observed in these complexes are probably due to important electrostatic interactions. In those complexes where a simultaneous interaction with an anion and a cation occurs, **8**$-$**10** and **17**$-$**19**, the distance between the ions to the aromatic rings is considerably shorter than in binary complexes **2**$-$**7**. These results indicate a Coulombic interaction between the ions across the aromatic rings.

We have used the Bader's theory of "atoms-in-molecules" (AIM), which has been widely used to characterize a great variety of interactions,[30] to analyze the noncovalent interactions of the complexes. The AIM analysis is summarized in Table 3, and it gives some helpful information regarding the strength of the noncovalent interactions involved in the complexes. It has been demonstrated that the value of the electron charge density at the (3,+3) critical point (CP) that it is generated in ion$-\pi$ complexes can be used as a measure of the bond order.[10] In Figure 4 we show the distribution of CPs in complexes **3**, **6**, and **9**, as representative examples of **1**$\cdots M^+$, **1**$\cdots X^-$, and $M^+\cdots$**1**$\cdots X^-$ complexes, respectively. In all complexes, six bond CPs and six ring CPs describe the Cr$-C_6H_6$/Cr$-C_6F_6$ interactions. The bond CPs connect the Cr atom with the carbon atoms of the C_6H_6/C_6F_6 ring and the ring CPs connect the Cr atom with the middle of the C$-$C bonds of the aromatic rings. The anion$-\pi$ and cation$-\pi$ interactions are described by six bond CPs, six ring CPs, and one (3,+3) CP. The bond CPs connect the anion/cation with the six carbon atoms of the ring and the ring CPs connect the anion/cation with the middle of the six

TABLE 2: Merz$-$Kollman (MK) Charges Computed at the MP2/6-31++G// RI-MP2/6-31++G** Level of Theory and Cr$-C_6H_6$ and Cr$-C_6F_6$ Distances for Complexes 1$-$19**

	R_e (Å)		Q (M$-$K, e)				
compound	**Cr$-C_6H_6$**	**Cr$-C_6F_6$**	**Cr**	X^-	M^+	**C_6H_6**	**C_6F_6**
1	1.538	1.501	0.189			0.139	-0.328
2 (**1**$\cdots Li^+$)	1.492	1.551	0.236		0.904	-0.358	0.216
3 (**1**$\cdots Na^+$)	1.492	1.536	0.191		0.939	-0.298	0.166
4 (**1**$\cdots K^+$)	1.503	1.534	-0.094		0.949	-0.084	0.410
5 (**1**$\cdots F^-$)	1.515	1.544	0.155	-1.002		-0.309	0.156
6 (**1**$\cdots Cl^-$)	1.521	1.542	0.217	-0.989		-0.267	0.036
7 (**1**$\cdots Br^-$)	1.522	1.540	0.172	-0.989		-0.219	0.036
8 ($Li^+\cdots$**1**$\cdots F^-$)	1.471	1.592	0.119	-0.969	0.887	-0.739	0.702
9 ($Na^+\cdots$**1**$\cdots Cl^-$)	1.474	1.582	0.283	-0.913	0.922	-0.700	0.406
10 ($K^+\cdots$**1**$\cdots Br^-$)	1.485	1.581	0.186	-0.898	0.911	-0.541	0.346

TABLE 3: Interaction Energies (E_{CP}, kcal/mol) and Electron Charge Density (ρ, au) Computed at the (3, +3) Critical Point for Complexes 2−10, and Electron Charge Density Computed at the Cr−π Bond Critical Points (ρ, au) for 1−10 and Its Variation upon Complexation ($\Delta\rho$, au) for Complexes 2−10

complex	E_{CP}	$10^2\rho$(3,+3)[a]	$10^2\rho$ (3,-1) Cr-C_6H_6	$10^2\Delta\rho$ (3,-1) Cr-C_6H_6	$10^2\rho$ (3,-1) Cr-C_6F_6	$10^2\Delta\rho$ (3,-1) Cr-C_6F_6
1			8.3896		7.7669	
2 (**1**···Li^+)	−28.6	1.1884	7.9866	−0.40	7.7945	0.03
3 (**1**···Na^+)	−17.5	0.8707	8.0086	−0.38	7.7975	0.03
4 (**1**···K^+)	−10.9	0.6872	7.9246	−0.47	7.7987	0.03
5 (**1**···F^-)	−15.5	0.8818	7.8803	−0.50	8.0110	0.24
6 (**1**···Cl^-)	−8.9	0.6996	7.8240	−0.56	8.0078	0.24
7 (**1**···Br^-)	−8.6	0.6564	7.8175	−0.57	8.0122	0.25
8 (Li^+···**1**···F^-)	−112.5	1.3329/1.1376	8.1973	−0.19	7.5456	−0.22
9 (Na^+···**1**···Cl^-)	−83.5	0.9701/0.8728	8.1924	−0.20	7.5890	−0.18
10 (K^+···**1**···Br^-)	−71.0	0.8294/0.8209	8.1108	−0.28	7.5883	−0.18

[a] $10^2\rho$ (3,+3) values of **11**, **12**, **13**, **14**, **15**, and **16** are: 1.153, 0.809, 0.622, 0.828, 0.629, and 0.688 au, respectively.

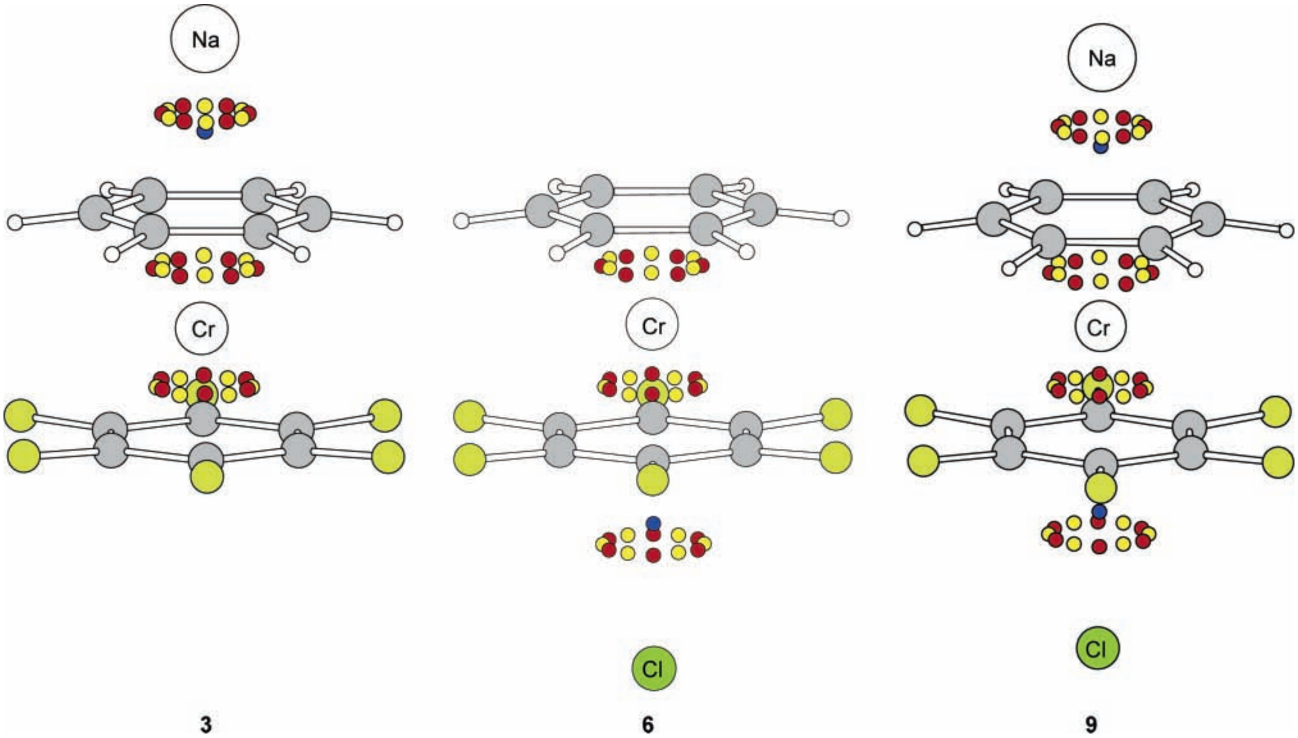

Figure 4. Schematic representation of the location of bond (red), ring (yellow), and (3,+3) (blue) CPs in complexes **3**, **6**, and **9**.

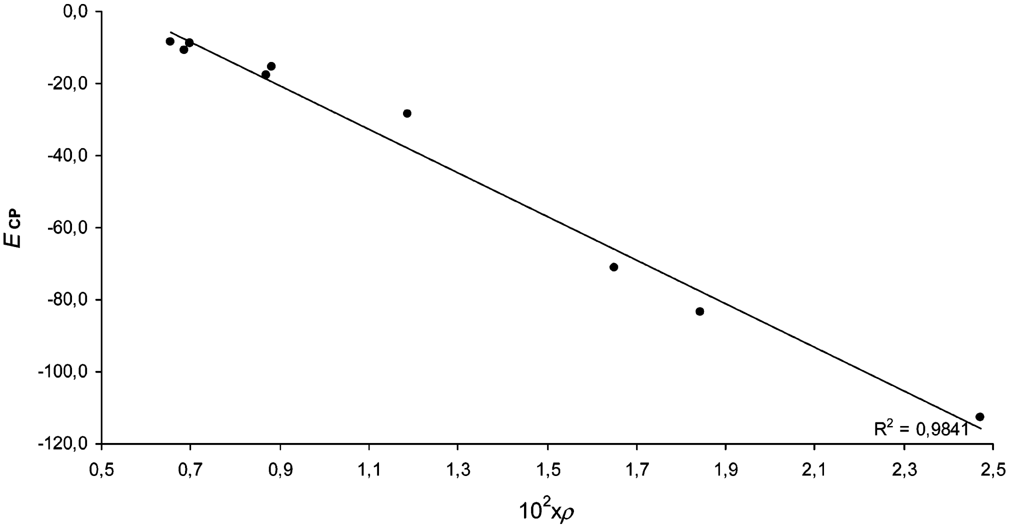

Figure 5. Plot of the linear regression of E_{CP} and $10^2\rho$.

C−C bonds of the ring. Finally, the interaction is further described by a (3,+3) CP that connects the anion/cation with the center of the ring. In Table 3, we show the values of the electron charge density (ρ, a.u.) computed at the (3,+3) CPs for complexes **2**−**10**. These values give information about the strength of the noncovalent interactions involved in the complexes. First, it is worth mentioning that the values of the charge density computed at the (3,+3) CPs in complexes **2**−**7** are comparable to those computed for cation−π and anion−π complexes of BEN and HFB (see footnote of Table 3), indicating that the bond order of the interaction is maintained in **1**···M^+ and **1**···X^- complexes. Second, we have found a strong ($R^2 = 0.984$) relationship between the interaction energies computed for complexes **2**−**10** and electron charge density (ρ) at the (3, +3) critical point (see Figure 4). For complexes **8**−**10** we have used the sum of the charge density value at the two (3, +3) CPs. It is worth mentioning the importance of this relationship, since there are cation−π, anion−π and cation−π−anion complexes in the same representation. Therefore the value of the electron density at the (3, +3) CP can be used as a bond order of the ion−π complexes, regardless of the sign of the ion. Third, we have also included in Table 3 the value of the charge density at the six bond CPs that connect the Cr atom with the aromatic rings and its variation upon complexation of the ions ($\Delta\rho$) in order to study the Cr−C_6H_6 and Cr−C_6F_6 interactions and the effect of the complexation on the Cr-π bonding. In **1** the strongest interaction corresponds to Cr−C_6H_6. In the cation−π complexes **2**−**4** the Cr−C_6H_6 interaction weakens and the Cr−C_6F_6 interaction is almost unaltered. In contrast, in the anion−π complexes **5**−**7** the Cr−C_6H_6 interaction is weakened and the Cr−C_6F_6 interaction is strengthened. A likely explanation is that in cation−π complexes the π-cloud of the C_6H_6 ring looses electron density due to the interaction of the cation, giving rise to a debilitation of the Cr−C_6H_6 interaction. In contrast, in anion−π complexes the π-cloud of the C_6F_6 ring gains electron density and reinforces the Cr−C_6F_6 interaction. As a consequence of this reinforcement, the other interaction (Cr−C_6H_6) weakens. In the cation−**1**-anion complexes both interactions are weakened. It should be mentioned that in these complexes the ion−π interactions are very strong and the equilibrium distances are very short (see Table 1). For instance in complex **8,** the R_e distance of the lithium cation is 1.75 Å and the R_e distance of the fluoride anion is 2.27 Å, considerably shorter than 1.87 Å and 2.48 Å obtained for the **1**−Li^+ and **1**−F^- distances in complexes **2** and **5**, respectively. In theory, the Cr-π interaction that should be reinforced the most is the Cr−C_6H_6 interaction since the cation is always located at a shorter distance to the benzene ring than the anion to the hexafluorobenzene ring. Probably, an internal reorganization is produced in the C_6H_6−Cr−C_6F_6 system that minimizes both effects resulting in a small weakness of both interactions, as deduced by the negative values of $\Delta\rho$.

Conclusion

In summary, the results derived from the theoretical calculations reported in this study reveal the suitability of (η^6-C_6H_6)($\eta^6$$C_6F_6$)Cr(0) complex **1** for interacting with anions and cations. Moreover, the cation/anion binding ability of **1** is comparable to benzene with cations and hexafluorobenzene with anions. Therefore, **1** can be used in molecular recognition as a binding unit for the construction of ditopic receptors. From the AIM analysis we conclude that the density at the (3,+3) critical point generated upon complexation of the ion is a useful parameter to measure the strength of the interaction, even when comparing cation−π, anion−π and cation−π−anion complexes.

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