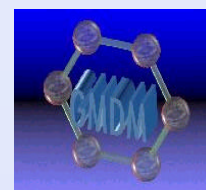




Structural and electronic effects of the interaction of metal cations with Benzene



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Introduction :

Synthesis of Carbon Nanotubes (CN) is usually carried out with high-energy methods, because of its high production rate. These methods produce perfect and long CN, but recently, Current-Voltage measurements of defected CN have shown a clear rectifying character.[1] These results show the need for finding new synthesis methods for CN with defects, that can be reached with low-energy methods, where the catalysts play a key-role. Therefore, a detailed study of the interaction of the usual catalysts in CN synthesis and the graphitic components is needed.

In this context, this work focuses attention on the interaction of transition metal cations with benzene as building block of dehydropolycondensation.[2] We have selected a family of seven first-row metal cations, with atomic numbers ranging from 23 to 29. As the first step, the cations were chosen to have closed-shell electronic configuration, resulting in the following cations: V^+ Cr^{++} Mn^+ Fe^{++} Co^+ Ni^{++} Cu^+

Methodology :

Ab-initio Density Functional Theory (DFT) theoretical calculations of the six benzene-cation complexes were performed with the Gaussian98 [3] software package. The basis set used was 6-311+G*, and the functional used was the Becke's three parameter hybrid functional B3LYP, accurate enough to describe electronic and magnetic properties of graphitic systems, [4] although the presence of metal cations in the complexes made necessary the inclusion of diffuse functions.

The optimized geometry and the electronic properties of the complexes were analyzed in terms of various parameters, and the electronic density was analyzed in terms of the Bader analysis, [5] with the help of the AIMPACK [6] software package. The Electronic Localization Function (ELF) [7] was also analyzed with the TOPMOD package. [8]

The ring deformation was analyzed by the Puckering Amplitude (PA), and the difference between bond lengths.

FIGURE 1: Representation of the electronic density and its laplacian in the symmetry plane containing C_6 carbon atoms, for complexes 1 and 7, respectively the most and the least interacting.

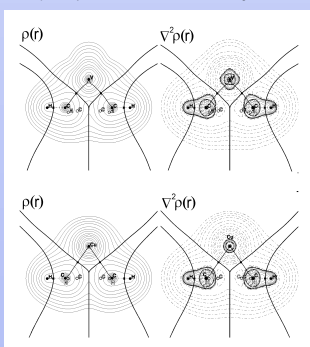
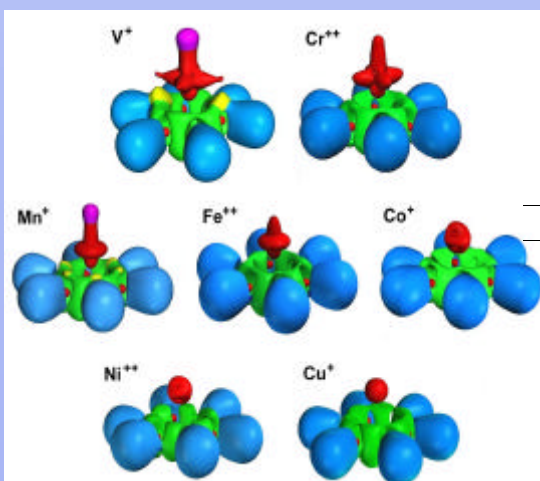


FIGURE 2: Colour-coded ELF diagram at 0.63 value for complexes 1-7



Results and Discussion :

The interaction energy did not correlate with the benzene ring deformation observed, as shown in Table 1. Complexes 3, 4 and 7 showed no benzene ring deformation, however, complexes 1, 2, 5 and 6 revealed a boat-like disposition. The divalent ion complexes showed larger DH than the monovalent complexes. Also, for the divalent cation complexes, a net gain of electronic charge in the cation was observed, while in the monovalent metal-ion complexes a net loss of charge occurred.

In Figure 2 can be observed that the cations in complexes with benzene ring deformation presented stronger asymmetry, the other cations having cylindrical symmetry, thus preserving the symmetry of the ring.

Complexes 1 and 5 showed large benzene ring bond differentiation, and medium to low interaction energy, and consequently presented good properties as catalysts in dehydropolycondensation processes of polyaromatic hydrocarbons.

The electronic data for complex 1 are somewhat different to the other complexes, yielding the greatest values for the density, laplacian and ellipticity. These data is compatible with the length of this bond, the shortest one (1.386 Å), and a certain double bond character. In addition, structure 1 showed the largest difference between C_a-C_a and C_a-C_b bond lengths and the greater ring deformation ($PA=0.218$ Å).

Complex 1 and 5 yielded geometrical and electronic data that agreed with Vanadium and Cobalt ions as good catalysts. This possibility was confirmed also by the ELF data. The $V(C-C)$ basins had markedly different electron populations (2.96 e for $V(C_a-C_b)$ and 2.42 e for $V(C_a-C_b)$ in 1, and 2.89 e for $V(C_a-C_a)$ and 2.71 e for $V(C_a-C_b)$ in 5). All this data agrees with an extremely large bond discrimination in the aromatic ring, with medium to small interaction energy, proposing vanadium and cobalt ions as good candidates to act as a catalysts.

For 1, the bonds between vanadium and the C_b atoms are clearly presented by two basins with large volume and population. The presence of this two bonds caused the C_a-C_a bonds to be shorter and to have a relative double bond character. In complexes 1 and 3, there is a large basin (in magenta) but with very small population.

Conclusions :

All the data agrees with complex 6 being the one with the strongest interaction and large geometrical and electronic ring differentiation. However, complex 1 and 5 showed also very large geometrical and electronic differentiation with low DH , being suitable as catalysts in dehydropolycondensation processes.

References:

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TABLE 1: Energetic and Geometric data for complexes 1-7, the calculated interaction energy $DH = E_{\text{complex}} - E_{\text{cation}} - E_{\text{benzene}}$ (kcal mol⁻¹), (B3LYP/6-311+G*), distance between the ring and the cation D_p , bond lengths and Puckering amplitude (Å)

Complex	Cation	E_{complex}	DH	D_p	C_a-C_a	C_a-C_b	PA
1	V^+	-1175.981805	-76.69	1.746	1.386	1.435	0.218
2	Cr^{++}	-1275.984176	-167.25	1.785	1.428	1.410	0.109
3	Mn^+	-1382.972803	-176.83	1.531	1.417	1.417	0.000
4	Fe^{++}	-1495.224652	-199.02	1.587	1.417	1.417	0.000
5	Co^+	-1614.748761	-79.22	1.603	1.432	1.409	0.095
6	Ni^{++}	-1739.821948	-230.36	1.724	1.459	1.404	0.135
7	Cu^+	-1872.557555	-50.17	1.845	1.414	1.414	0.001
C_6H_6	-	-232.300705	-	-	1.395	1.395	0

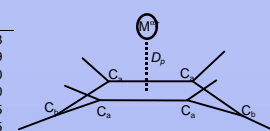


TABLE 2: Numerical data resulting from the AIM and ELF analyses in the complexes 1-7, relatives to the metal position and C-C bonds: properties of Bond Critical Points (if applicable) electronic density $r(r)$ (e a_0^{-3}), its laplacian $\nabla^2 r(r)$ (e a_0^{-5}) and ellipticity ϵ , ELF basin population N_e , standard deviation $s(W)$ and relative fluctuation $l(W)$

fluctuation $I(W)$							fluctuation $I(W)$								
	r	$\nabla^2 r$	e	\tilde{N}_e	$s(W)$	$I(W)$		r	$\nabla^2 r$	e	\tilde{N}_e	$s(W)$	$I(W)$		
1	C(V)	-	-	-	21.62	1.120	0.058	5	C(Co)	-	-	-	25.58	1.146	0.05
	$V(C_a-C_b)$	0.311	-0.854	0.225	2.96	1.186	0.476		$V(C_a-C_b)$	0.286	-0.725	0.181	2.89	1.208	0.50
	$V(C_a-C_b)$	0.282	-0.707	0.196	2.42	1.102	0.502		$V(C_a-C_b)$	0.301	-0.807	0.183	2.71	1.152	0.48
	$V(C_b-V)$	0.074	0.198	1.447	0.54	0.665	0.826								
2	C(Cr)	-	-	-	22.38	1.023	0.047	6	C(Ni)	-	-	-	26.49	1.080	0.04
	$V(C_a-C_b)$	0.289	-0.752	0.163	2.65	1.146	0.495		$V(C_a-C_b)$	0.276	-0.701	0.083	2.50	1.125	0.50
	$V(C_b-C_b)$	0.301	-0.819	0.156	2.69	1.144	0.487		$V(C_b-C_b)$	0.306	-0.850	0.150	2.71	1.147	0.48
3	C(Mn)	-	-	-	23.23	1.299	0.073	7	C(Cu)	-	-	-	27.87	0.813	0.02
	$V(C-C)$	0.293	-0.759	0.206	2.62	1.136	0.493		$V(C_a-C_b)$	0.297	-0.793	0.177	2.74	1.155	0.48
	$V(C-Mn)$	0.081	0.275	1.645	0.21	0.443	0.929		$V(C_b-C_b)$	0.297	-0.793	0.177	2.73	1.153	0.48
4	C(Fe)	-	-	-	24.30	1.227	0.062	C_6H_6	$V(C-C)$	0.308	-0.851	0.195	2.75	1.138	0.47
	$V(C-C)$	0.297	-0.800	0.142	2.68	1.151	0.493								