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Theoretical Study of electronic Structure of $[CoF_6]^{3-}$ Complex embedded in Nano-Ring

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ABSTRACT

Density functional theory calculations (DFT), as well as hybrid methods (B3LYP) for $B_{18}N_{18}$-$[CoF_6]^{3-}$ complex have been carried out to study the non-bonded interaction. The geometry of the $B_{18}N_{18}$ has been optimized at B3LYP method with EPR-II basis set and geometry of the $[CoF_6]^{3-}$ have been optimized at B3LYP method with Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential. The electromagnetic interactions of the $[CoF_6]^{3-}$ molecule embedded in the $B_{18}N_{18}$ nano ring have been investigated at B3LYP and total atomic charges, spin densities, dipole moment and isotropic Fermi coupling constants parameters in different loops and bonds of the $B_{18}N_{18}$-$[CoF_6]^{3-}$ system have been calculated. Also NBO analysis such as electronic delocalization between donor and acceptor bonds has been studied by DFT method. Then we have been investigated the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) for the lowest energy have been derived to estimate the structural stability of the $B_{18}N_{18}$-$[CoF_6]^{3-}$ system. The Gaussian quantum chemistry package is used for all calculations.

Keywords: DFT; Dipole moment; EPR-II basis set; HOMO; LUMO; Hyperfine properties

INTRODUCTION

Molecular orbital theory was developed, in the years after valence bond theory had been established (1927), primarily through the efforts of Friedrich Hund, Robert Mulliken, John C. Slater, and John Lennard-Jones. The first accurate calculation of a molecular orbital wave function was that made by Charles Coulson in 1938 on the hydrogen molecule. By 1950, molecular orbitals were completely defined as wave functions of the self-consistent field Hamiltonian and it was at this point that molecular orbital theory became fully rigorous and consistent[1]. This rigorous approach is known as the Hartree–Fock method for molecules although it had its origins in calculations on atoms. This led to the development of many ab initio quantum chemistry methods. Parallel to this rigorous development, molecular orbital theory was applied in an approximate manner using some empirically derived parameters in methods now known as semi-empirical quantum chemistry methods [2]. We report the non-bonded interaction of the $[CoF_6]^{3-}$ embedded in $B_{18}N_{18}$ nano ring. Stability structure of CoF_6 under the different loops and bonds of $B_{18}N_{18}$ nano ring have been calculated. For further structural information, the lowest unoccupied molecular orbital and the highest occupied molecular orbital differences, namely band gaps have been reported to explore the ability of the $[CoF_6]^{3-}$ to create a stable $B_{18}N_{18}$-$[CoF_6]^{3-}$ system.

COMPUTATIONAL DETAILS

In chemistry, molecular orbital theory (MO theory) is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. In this theory, each molecule has a set of molecular orbitals, in which it is assumed that the molecular orbital

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wave function ψ_j may be written as a simple weighted sum of the n constituent atomic orbitals χ_i, according to the following equation:

$$\psi_j = \sum_{i=1}^{n} c_{ij}\chi_i$$

The c_{ij} coefficients may be determined numerically by substitution of this equation into the Schrodinger equation and application of the variational principle. This method is called the linear combination of atomic orbitals approximation and is used in computational chemistry. Molecular orbital (MO) theory uses a linear combination of atomic orbitals (LCAO) to represent molecular orbitals involving the whole molecule. These are often divided into bonding orbitals (σ, π), anti-bonding orbitals (σ*, π*), and non-bonding orbitals or lone pairs orbitals (n), that σ* - almost never occupied in the ground state, π* - very rarely occupied in the ground state, n –lone pairs, π - always occupied in compounds with multiple bonds (Pi Bond), σ - at least one occupied in all molecules (Sigma Bond). The $[CoF_6]^{3-}$ complex including octahedral symmetric Co (III) coordination compounds and six π-donor ligands. The geometry of the $[CoF_6]^{3-}$ have been optimized at B3LYP method with Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential. Effective Core Potential operators are sums of products of polynomial radial functions, Gaussian radial functions and angular momentum projection operators. ECP input therefore specifies which potential to use on each atomic center, and then includes a collection of triplets of: (coefficient, power of R, exponent) for each potential for each term in each angular momentum of the ECP. Since only the first few angular momentum components have different terms, the potential is expressed as (1) terms for the general case, typically d or f and higher projection, and (2) the extra terms for each special angular momentum. Thus for an LP-31G potential, which includes special s and p projected terms, the input includes the general (d and higher) term, the s-d term (i.e., what to add to the general term to make the s component) and the p-d term.

RESULT AND DISCUTION

The $[CoF_6]^{3-}$ complex including octahedral symmetric Co (III) coordination compounds and six π-donor ligands. The geometry of the $[CoF_6]^{3-}$ have been optimized at B3LYP method with Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential. Optimized parameters of $[CoF_6]^{3-}$ such as bond length and bond angle have been reported in Table 1. We can view the Co-F(4) and Co-F(5) bond lengths are less than other bond lengths, because the octahedral symmetric Co (III) coordination compounds and six π-donor ligands are High-spin d^6 electronic configuration ($S = 2$) exhibit the Z-in Jahn–Teller distortion. The different energy levels of metal-ligands bonding in $[CoF_6]^{3-}$ complex and three different loops have been reported in Table 2-3. We can view the metal t_{2g} orbitals are now slightly antibonding (π*) therefore it is less energetically favourable to fill them. Note the effect on the t_{2g} d-orbitals in comparison to the σ-only case. These t_{2g} orbitals have risen in energy, closer to the e_g level, resulting in a reduction of Δ_{oct}.

Table 1. Optimized parameters of octahedral symmetric Co (III) coordination compounds and six π-donor ligands

Bond ID	bond length	bond angle
Co(1)-F(2)	2.065	-
Co(1)-F(3)	2.065	-
Co(1)-F(4)	1.945	-
Co(1)-F(5)	1.945	-
Co(1)-F(6)	2.065	-
Co(1)-F(7)	2.065	-
F(2)-Co(1)-F(3)	-	90.000
F(2)-Co(1)-F(4)	-	90.010
F(2)-Co(1)-F(5)	-	89.990
F(2)-Co(1)-F(6)	-	90.000
F(2)-Co(1)-F(7)	-	179.981
F(3)-Co(1)-F(4)	-	89.986
F(3)-Co(1)-F(5)	-	90.014
F(3)-Co(1)-F(6)	-	179.996
F(3)-Co(1)-F(7)	-	90.000
F(4)-Co(1)-F(5)	-	180.000
F(4)-Co(1)-F(6)	-	90.010
F(4)-Co(1)-F(7)	-	90.010
F(5)-Co(1)-F(6)	-	89.990
F(5)-Co(1)-F(7)	-	89.990
F(6)-Co(1)-F(7)	-	90.000

* See Figure 1 for more details.

Table 2. Molecular orbital diagram of O_h complex with π-donor ligands

Natural Bond Orbitals	Energy (a.u.)
σ^*_{t1u}	0.56761
σ^*_{a1g}	0.54690
σ^*_{eg}	0.54612
π^*_{t2g}	0.31682
σ^*_{t1u}	0.31164
n.b.	0.18824
n.b.	0.18824
n.b.	0.18793
n.b.	0.18787
n.b.	0.18519
n.b.	0.18513
n.b.	0.18513
n.b.	0.18513
n.b.	0.16829
n.b.	0.16451
n.b.	0.16438
n.b.	0.16386
π_{t2g}	0.13537
σ_{t1u}	0.07407
σ_{eg}	0.07110
σ_{a1g}	0.02385

Δ_{oct} =0.2293 a.u.

Table 3. Molecular orbital diagram of $B_{18}N_{18}$-$[CoF_6]^{3-}$ complex

Loop 1			Loop 2			Loop 5		
Natural Bond Orbitals	**Occupancy**	**Energy (a.u.)**	**Natural Bond Orbitals**	**Occupancy**	**Energy (a.u.)**	**Natural Bond Orbitals**	**Occupancy**	**Energy (a.u.)**
σ* Co37- F38	0.12000	0.48593	σ* Co37- F40	0.09360	0.46672	σ* Co37- F39	0.11563	0.49034
σ* Co37- F40	0.12472	0.48057	σ* Co37- F43	0.14748	0.45776	σ* Co37- F41	0.09262	0.48451
σ* Co37- F42	0.10996	0.46740	σ*Co37- F39	0.12361	0.45734	σ* Co37- F43	0.14411	0.47456
LP*(3)Co37	0.12104	0.29613	σ* B 3- F41	0.16992	0.32027	σ* B23- F40	0.17435	0.31086
LP*(2)Co37	0.13666	0.28513	LP*(3)Co37	0.13535	0.27152	LP*(3)Co37	0.13709	0.27947
σ* B35- F39	0.17427	0.26574	LP*(2)Co37	0.15214	0.26640	LP*(2)Co37	0.14509	0.27831
LP (3) F38	0.96630	0.16111	-	-	-	-	-	-
LP (3) F43	0.96630	0.16111	LP (3) F42	0.94655	0.15575	LP (3) F42	0.96169	0.15811
LP (1) F38	0.99934	0.15703	LP (3) F39	0.95838	0.15035	LP (3) F39	0.94969	0.15788
LP (1) F43	0.99934	0.15703	LP (3) F40	0.94528	0.14238	LP (1) F42	0.99956	0.15162
LP (3) F42	0.97002	0.15562	LP (3) F38	0.96939	0.14157	LP (3) F41	0.94536	0.15062
LP (2) F42	0.98682	0.15498	LP (3) F43	0.96939	0.14157	LP (3) F43	0.97012	0.14652
LP (3) F40	0.94981	0.14245	LP (2) F43	0.97324	0.14074	LP (3) F38	0.97012	0.14652
LP (2) F40	0.97417	0.14021	LP (2) F38	0.97324	0.14074	LP (2) F43	0.97191	0.14597
LP (2) F39	0.98593	0.13484	LP (1) F40	0.99963	0.13297	LP (2) F38	0.97191	0.14597
LP (2) F41	0.96999	0.12005	LP (1) F39	0.99924	0.11946	LP (2) F39	0.98888	0.13791
LP (3) F41	0.96058	0.11429	LP (2) F42	0.99358	0.10999	LP (1) F41	0.99931	0.13027
LP (3) F39	0.94812	0.10644	LP (3) F41	0.97061	0.09838	LP (3) F40	0.96976	0.10396
LP (1)Co37	0.99872	0.10413	LP (1)Co37	0.99785	0.09003	LP (1)Co37	0.99546	0.10092
σ B35- F39	0.90554	0.08444	σ Co37- F43	0.98069	0.04480	σ B23- F40	0.92357	0.05402
σ Co37- F42	0.98799	0.05458	σ B 3- F41	0.92439	0.03962	σ Co37- F43	0.98191	0.04850
σ Co37- F38	0.99224	0.04854	σ Co37- F39	0.99210	0.03119	σ Co37- F39	0.99126	0.04510
σ Co37- F40	0.98460	0.00176	σ Co37- F40	0.98887	-0.00414	σ Co37- F41	0.98823	0.00563

For further to determination non-bonded interaction of the $[CoF_6]^{3-}$ complex embedded in nano ring, we focus on the single wall boron-nitride an armchair $B_{18}N_{18}$ nanotube with chirality n=m=6, and the schematic of optimized structure of the $B_{18}N_{18}$-$[CoF_6]^{3-}$ system have been displayed in Fig.1. The geometry of $B_{18}N_{18}$ nano ring have been optimized by Becke's hybrid three-parameter exchange functional and the non-local correlation functional of Lee, Yang and Parr (B3LYP) method [3,4] with EPR-II basis set of Barone [5]. The Gaussian quantum chemistry package is used for all calculations. EPR-II is a double zeta basis set with a single set of polarization functions and an enhanced s part: (6,1)[6,7] for H and (10,5,1)[6,8,9] for B to F. Also in this case the s-part is improved to better describe the nuclear region: (6,2)[10,8] for H and [6,8,11,12] for B to F. Vibration frequencies have been calculated at the level of B3LYP/ EPR-II theory to verify that the geometry was a real minimum without any imaginary frequency and analyze the thermo chemical functions including enthalpies and Gibbs free energies [13]. To check the accuracy of relative energy values, we employed the techniques concerning weak intermolecular interactions. The standard quantum chemical calculations usually give exaggerated values of the binding energies of weakly bonded complexes.

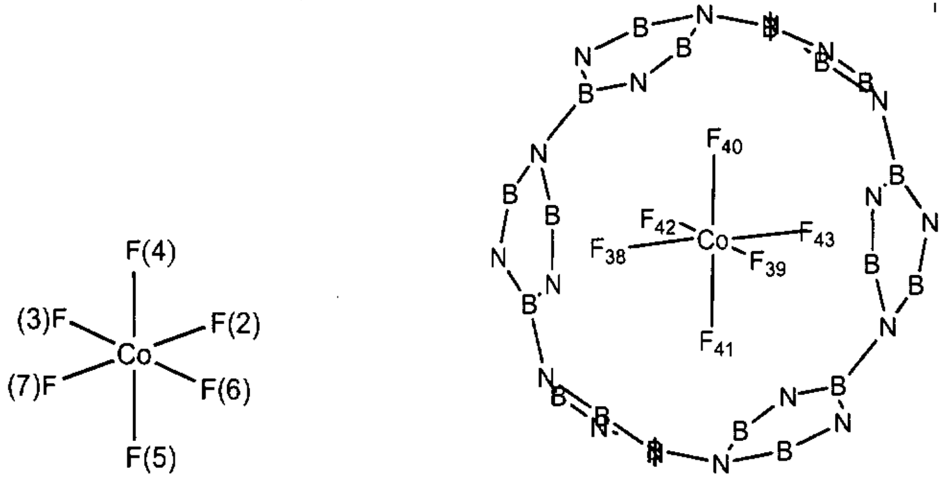

Fig. 1. The optimized geometrical structure of the [CoF6]3- complex and B18N18-[CoF6]3- system at the level of B3LYP/EPR-III theory.

The geometry of $B_{18}N_{18}$ nano-ring and $[CoF_6]^{3-}$ have been optimized by B3LYP method [14] with EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential for Co (III). The electron paramagnetic resonance (EPR) spectra and the paramagnetic parameters derived therefrom provide stringent tests of quantitative molecular orbital calculations. So it is notable that the obtained energy of mentioned basis set and ECP for $B_{18}N_{18}$ nano- ring and $[CoF_6]^{3-}$ were -1434.1167014 and -743.7823343, (Hartree) respectively. According to the frequency calculation at the level of B3LYP/EPR-II theory, obtaining thermo chemical functions such as ΔG= -67.7929 kcal/mol and ΔH= -124.4012 kcal/mol confirmed the structural stability of $B_{18}N_{18}$ nano ring. This effect is probably due to the large dipole moments of the B-N bonds, which preferentially enhance the ring stability.

To investigate the non-bonded interaction on $[CoF_6]^{3-}$ with six different segments including six loops and six connecting bonds of $B_{18}N_{18}$ nano ring, first the five hexagon loops have been freezed and the electrostatic interaction of $[CoF_6]^{3-}$ with the one remained active loop have been considered. Other loops have been examined one by one in the same way and the changes of all the following calculated quantities have been explored. Next, we were focused on each bond of $B_{18}N_{18}$ individually and evaluated the interaction of $[CoF_6]^{3-}$ with each six connecting bonds of $B_{18}N_{18}$ ring and repeated the calculations along each bond. As a check on the quality of the calculated geometrical parameters and their stability with respect to the level of theory, the HOMO and the LUMO differences have been explored. The HOMO corresponds to a combination of lone-pair orbitals on the N atoms as well as LUMO which is characterized by large contributions from vacant p orbitals on B atoms with some admixture of N-based orbitals have been calculate. For further structural information, the lowest unoccupied molecular orbital and the highest occupied molecular orbital differences, namely band gaps have been reported to explore the ability of the suitable $[CoF_6]^{3-}$ forms to create a stable $B_{18}N_{18}$-$[CoF_6]^{3-}$ system. So, quantities values such as the relative energies (ΔE), radial coordinate of dipole moment (r) and band gaps of $B_{18}N_{18}$-$[CoF_6]^{3-}$ system have been reported in Table 4.

To justify the structural stability of various $B_{18}N_{18}$-$[CoF_6]^{3-}$ systems, the HOMO-LUMO band gap as the differences between highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital (LUMO) has been found as a measure of the structural stability and semi-conducting properties for the purpose. DFT methods (particularly B3LYP) with EPR-II basis sets seemed as a suitable theoretical model for the computation of hyperfine coupling constants. Total atomic charges, spin densities, and isotropic fermi coupling constants of $[CoF_6]^{3-}$ in different loops and bonds of $B_{18}N_{18}$-$[CoF6]^{3-}$ system with EPR-II basis sets have been reported in Table 5.

CONCLUSION

In this study, we used DFT methods with EPR basis sets to determination electrostatic non-bonded interaction among nano-systems. So the results of hybrid DFT with EPR quantum-chemical calculations were useful for assignment of the provided a basis for description of electromagnetic non-bonded interaction between $B_{18}N_{18}$ nano ring and $[CoF_6]^{3-}$ octahedral complex. Because of the electrostatic and hyperfine characteristics of $B_{18}N_{18}$-$[CoF_6]^{3-}$ system, those techniques dealing with electron distributions around nuclei including relative energies, HOMO-LUMO band gaps, total atomic charges, spin densities, of $[CoF_6]^{3-}$ in different loops and bonds have been employed to detect and characterize the hyperfine structural properties of $B_{18}N_{18}$-$[CoF_6]^{3-}$ system. In this study, first, we have discussed the different aspects of electronic structure of the $B_{18}N_{18}$-$[CoF_6]^{3-}$ system for further validation of theoretical results to increase there usefulness in practical applications or for pre-experimental modeling. Second, we have explored the electromagnetic nature of the $B_{18}N_{18}$-$[CoF_6]^{3-}$ system through calculating the following parameters which provide valuable information on the interaction characteristics.

Table 4. relative energies (ΔE), radial coordinate of dipole moment (r) and band gap of $[CoF_6]^{3-}$ under different loops and bonds of $B_{18}N_{18}$ at EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential for Co (III)

Compound	**Basis sets for Co^{3+}**		
	Def2-TZVP , Stuttgart RSC 1997 ECP		
$B_{18}N_{18}$-$[CoF_6]^3$	**band gap (Hartree)**	**ΔE (Hartree)**	**Dipole moment (Debye)**
loop 1-$[CoF_6]^{3-}$	0.03659	-982.65042	6.6680
Bond 1-$[CoF_6]^{3-}$	0.08516	-823.24785	7.9548
loop 2-$[CoF_6]^{3-}$	0.04825	-982.66282	8.1198
Bond 2-$[CoF_6]^{3-}$	0.03138	-823.22981	13.6766
loop 3-$[CoF_6]^{3-}$	0.02648	-982.60022	13.0825
Bond 3-$[CoF_6]^{3-}$	0.07568	-823.2076	7.4861
loop 4-$[CoF_6]^{3-}$	0.03664	-982.65055	6.6633
Bond 4-$[CoF_6]^{3-}$	0.08492	-823.24791	7.9731
loop 5-$[CoF_6]^{3-}$	0.0441	-982.66281	7.3290
Bond 5-$[CoF_6]^{3-}$	0.03139	-822.69026	10.6949
loop 6-$[CoF_6]^{3-}$	0.02434	-982.60002	13.0791
Bond 6-$[CoF_6]^{3-}$	0.07569	-823.20760	7.4862

Table 5. Different quantities of $[CoF6]^{3-}$ under different loops and bonds of $B_{18}N_{18}$ system at EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential for Co (III)

Compound		Basis sets of Co (III)				
		Def2-TZVP , Stuttgart RSC 1997 ECP				
$B_{18}N_{18}$-$[CoF_6]^3$		Total atomic charges	Total atomic spin densities	Isotropic Fermi Coupling MHz	Dipole orientation θ	Dipole orientation φ
loop 1	B(1)	-0.0147	0.000482	-0.02005	90.0	78.3841
	B(2)	-0.0147	0.000482	-0.02005		
	N(4)	-0.2045	0.002077	0.74944		
	N(34)	-0.0560	-0.00043	-0.04480		
	B(35)	0.00498	-0.00221	0.10523		
	N(36)	-0.0560	-0.00043	-0.04480		
bond1	B(3)	-0.1742	0.701884	145.7426	90.0	89.3726
	N(4)	-0.2476	-0.50058	-8.87115		
loop 2	B(3)	-0.0612	0.128319	21.72458	90.0	134.1474
	N(5)	-0.0577	-0.00816	4.53021		
	B(6)	-0.0107	0.020216	5.62525		
	N(7)	-0.0577	-0.00816	4.53021		
	N(8)	-0.1872	0.000635	-0.54826		
	B(9)	-0.0107	0.020216	5.62525		
bond2	N(8)	-0.3675	0.749001	3.70693	90.0	153.4938
	B(11)	-0.2672	0.027679	5.38088		
loop 3	N(10)	-0.1211	0.117485	24.71548	90.0	179.6831
	B(11)	-0.2008	0.660697	151.6903		
	B(12)	-0.0749	0.076154	38.72004		
	N(13)	-0.1211	0.117485	24.71548		
	B(14)	-0.0749	0.076154	38.72004		
	N(16)	-0.2682	0.316657	10.38782		
bond3	B(15)	-0.1976	0.728356	119.0673	90.0	145.3154
	N(16)	-0.2151	0.909943	2.37329		
loop 4	B(15)	0.00472	-0.00264	-0.09924	90.0	101.4969
	N(17)	-0.0558	-0.00054	-0.09082		
	B(18)	-0.0147	0.000314	-0.06153		
	N(19)	-0.0558	-0.00054	-0.09082		
	N(20)	-0.2045	0.002317	0.71227		
	B(21)	-0.0147	0.000314	-0.06153		
bond4	N(20)	-0.2484	-0.49697	-8.85807	90.0	90.5899
	B(23)	-0.1750	0.702430	145.6761		
loop 5	N(22)	-0.0525	0.000928	2.33986	90.0	43.8833
	B(23)	-0.0486	0.055562	8.96248		
	B(24)	-0.0072	0.005769	2.27783		
	N(25)	-0.0525	0.000928	2.33986		
	B(26)	-0.0072	0.005769	2.27783		
	N(28)	-0.1758	0.003718	-0.00196		
bond5	B(27)	-0.0194	0.449654	56.78421	90.0	158.7584
	N(28)	0.49895	0.477640	0.77829		
loop 6	B(27)	-0.1995	0.656312	150.4633	90.0	0.50099
	N(29)	-0.1217	0.115522	24.52702		
	B(30)	-0.0753	0.075448	38.40351		
	N(31)	-0.1217	0.115522	24.52702		
	N(32)	-0.2684	0.312433	10.28485		
	B(33)	-0.0753	0.075448	38.40351		
bond6	N(32)	-0.2151	0.910001	2.37307	90.0	34.6964
	B(35)	-0.1975	0.728384	119.0763		

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