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Electron Paramagnetic Resonance Studies of the Effects of π-donor Ligand and $B_{18}N_{18}$ Nanoring Field on Energy Gaps

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ABSTRACT

To investigation non-bonded interaction of the $[CuF_4]^{2-}$ complex inside nanoring, we focus on the single wall boron-nitride $B_{18}N_{18}$ nanoring. Thus, the geometry of $B_{18}N_{18}$ nanoring has been optimized by B3LYP method with EPR-II basis set and geometry of the $[CuF_4]^{2-}$ complex has been optimized at B3LYP method with Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential. Also electronic delocalization between donor and acceptor bonds has been calculated 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 $B_{18}N_{18}$-$[CuF_4]^{2-}$ nanosystem, and the coefficients and hybrids of s, p and d orbitals of Cu and F involved in systemscan be distinguished based on these NBO data. The second order perturbation theory analysis of fock matrix in NBO of the molecules and the systems have been investigated at B3LYP method and Lewis σ-type (donor) and non-Lewis σ*-type (acceptor) and ΔE in different loops of the nanorings have been calculated. The Gaussian quantum chemistry package is used for all calculations.

Keyword: DFT; Dipole moment; ECP; EPR-II basis set; HOMO; LUMO; NICS.

Abbreviations and Notations

Abbreviations and notations:
DFT, Density functional theory
EPR, Electron paramagnetic resonance
HOMO, Highest occupied molecular orbital
LUMO, Lowest unoccupied molecular orbital
ECP, Effective core potential
NICS, Nuclear independent chemical shift

1. 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

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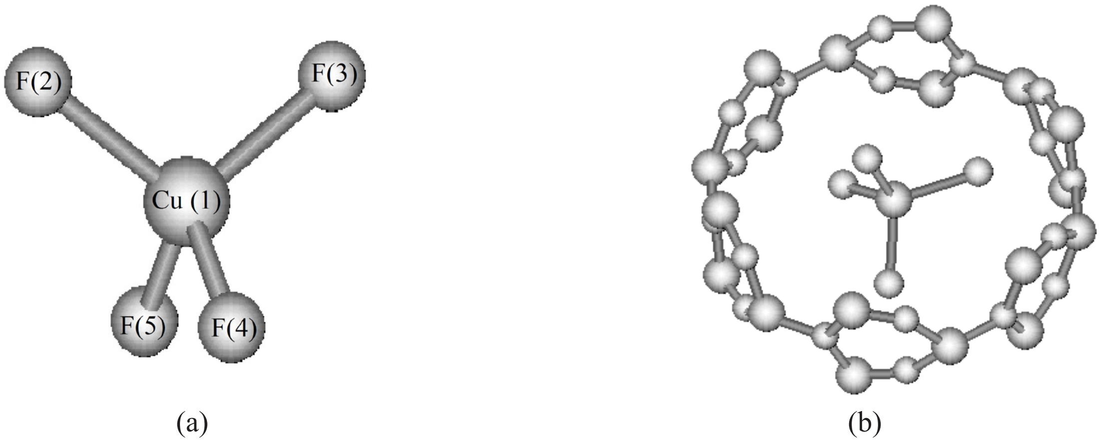
***Table 1:** Optimized parameters of octahedral symmetric Cu (II) coordination compounds and four π-donor ligands.*

Compound	Bond ID	Bond length	Bond angle
$[CuF_4]^{2-}$	Cu(1)-F(2)	2.068	-
	Cu(1)-F(3)	2.068	-
	Cu(1)-F(4)	1.954	-
	Cu(1)-F(5)	1.954	-
	F(2)-Cu(1)-F(3)	-	105.771
	F(2)-Co(1)-F(4)	-	112.555
	F(2)-Co(1)-F(5)	-	112.555
	F(3)-Co(1)-F(4)	-	112.548
	F(3)-Co(1)-F(5)	-	112.548
	F(4)-Co(1)-F(5)	-	101.075

** See Figure 1 for more details.*

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]. There has been a particular notice in experimental studies of B_nN_m clusters that can be found in the literature, and several research groups have described the exhibition of boron nitride-based nano-structures [3-5]. Recently, various cages and $(BN)_n$ cubes have been synthesized [6, 7], BN polyhedral have also been successfully synthesized by reaction of BCl_3 with NH_3 in a laser beam [8, 9]. To introduce physical properties of $B_{24}C_{12}N_{24}$ molecule [10] and the $B_{12}N_{12}$, $B_{16}N_{16}$ and $B_{28}N_{28}$ molecules, the experimental synthesis and various spectrometers are needed for their structural stabilities confirmation [11-13]. The schematic of $B_{18}N_{18}$ is displayed in the Figure 1. In present work we present the non-bonded interaction of the $[CuF_4]^{2-}$ embedded in $B_{18}N_{18}$ nanoring. The basic purpose of this investigation was the study of the electromagnetic interactions within the



(a) (b)

***Figure 1:** The optimized geometrical structure of the a) $[CuF_4]^{2-}$ complex and b) $B_{18}N_{18}$-$[CuF_4]^{2-}$ system at the level of B3LYP/EPR-II theory.*

Table 2: *Natural atomic orbitals of $[CuF_4]^{2-}$ complex with four π-donor ligands.*

Natural atomic orbital			
Atom	$[CuF_4]^{2-}$		
	Atomic Orbital	Energy	Occ
Cu^{2+} (1)	4s	1.20359	0.13054
	3dxy	-0.15055	1.99863
	3dxz	-0.15444	1.99954
	3dyz	-0.06337	1.34980
	3dx2y2	-0.15006	1.99862
	3dz2	-0.19652	1.99887
F (2)	2s	-1.63875	1.99390
	2px	0.05311	1.98075
	2py	0.06223	1.98981
	2 pz	0.07197	1.97281
F (3)	2s	-1.640	1.99390
	2px	0.0531	1.98183
	2py	0.06016	1.98877
	2 pz	0.07093	1.97285
F (4)	2s	-1.74075	1.99053
	2px	-0.0036	1.99961
	2py	-0.01613	1.96271
	2 pz	-0.01545	1.86171
F (5)	2s	-1.74075	1.99053
	2px	-0.0036	1.99961
	2py	-0.01613	1.96271
	2 pz	-0.01545	1.86171

Table 3: *Molecular orbital diagram of $[CuF_4]^{2-}$ complex with four π-donor ligands.*

Compound	Molecular orbital diagram		
	Natural Bond Orbitals	Energy (a.u.)	Occupancy
$[CuF^{4]2-}$	BD(1)Cu 1-F4	-0.04230	0.95892
	BD(1)Cu 1-F5	-0.04230	0.95892
	LP (1)Cu 1	-0.09662	0.99994
	LP (2)Cu 1	-0.06565	0.99989
	LP (3)Cu 1	-0.06362	0.99934
	LP (4)Cu 1	-0.05673	0.99917
	LP (2) F 4	-0.23355	0.99983
	LP (3) F 4	-0.61245	0.99629
	LP (2) F 5	-0.23355	0.99983
	LP (3) F 5	-0.61245	0.99629
	BD^*(1)Cu 1-F4	0.38671	0.08602
	BD^*(1)Cu 1-F5	0.38671	0.08602
	LP (1) F 2	-0.62919	0.99990
	LP (3) F 2	-0.13492	0.98309
	LP (1) F 3	-0.62919	0.99990
	LP (3) F 3	-0.13554	0.98311

$B_{18}N_{18}$-$[CuF_4]^{2-}$ system. For further evaluation about electromagnetic interactions, stability structure of $[CuF_4]^{2-}$ complex under the different loops of nanoring have been determined. For further structural information, the lowest unoccupied molecular orbital and the highest occupied molecular orbital differences, namely band gaps and the hybrids on atom have been reported to explore the ability of the $[CuF_4]^{2-}$ to create a stable $B_{18}N_{18}$-$[CuF_4]^{2-}$ system.

2. COMPUTATIONAL DETAILS

Molecular orbital 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 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:

$$\Psi_j = \sum_i^n c_{ij}\chi_i \qquad (1)$$

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),

Table 4: *Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at the level of B3LYP theory and EPR-II basis set for F atom and Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential for Cu (II).*

Compound	Natural bond orbital (NBO) analysis				
	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
$[CuF_4]^{2-}$	BD (1)Cu 1- F 4	BD*(1)Cu 1- F 4	2.31	0.43	0.041
	BD (1)Cu 1- F 4	BD*(1)Cu 1- F 5	8.38	0.43	0.077
	BD (1)Cu 1- F 5	BD*(1)Cu 1- F 4	8.38	0.43	0.077
	BD (1)Cu 1- F 5	BD*(1)Cu 1- F 5	2.31	0.43	0.041
	LP (3) F 4	BD*(1)Cu 1- F 4	1.01	1.00	0.042
	LP (3) F 4	BD*(1)Cu 1- F 5	0.99	1.00	0.041
	LP (3) F 5	BD*(1)Cu 1- F 4	0.99	1.00	0.041
	LP (3) F 5	BD*(1)Cu 1- F 5	1.01	1.00	0.042
	LP (1) F 2	BD*(1)Cu 1- F 4	0.49	1.02	0.029
	LP (1) F 2	BD*(1)Cu 1- F 5	0.49	1.02	0.029
	LP (2) F 2	BD*(1)Cu 1- F 4	0.05	0.38	0.006
	LP (2) F 2	BD*(1)Cu 1- F 5	0.05	0.38	0.006
	LP (3) F 2	BD*(1)Cu 1- F 4	6.00	0.52	0.073
	LP (3) F 2	BD*(1)Cu 1- F 5	6.00	0.52	0.073
	LP (1) F 3	BD*(1)Cu 1- F 4	0.49	1.02	0.029
	LP (1) F 3	BD*(1)Cu 1- F 5	0.49	1.02	0.029
	LP (2) F 3	BD*(1)Cu 1- F 4	0.05	0.38	0.006
	LP (2) F 3	BD*(1)Cu 1- F 5	0.05	0.38	0.006
	LP (3) F 3	BD*(1)Cu 1- F 4	5.99	0.52	0.073
	LP (3) F 3	BD*(1)Cu 1- F 5	5.99	0.52	0.073

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, σ- at least one occupied in all molecules. To determination electromagnetic interactions of the $[CuF_4]^{2-}$ complex including tetrahedral symmetric Cu (II) coordination compounds and four π-donorligands, the geometry of the $[CuF_4]^{2-}$ have been optimized at B3LYP method with Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential. The geometry of the $B_{18}N_{18}$ nanoring and $[CuF_4]^{2-}$ complex have been optimized at B3LYP method with EPR-II basis set using ab initio GAUSSIAN quantum chemical package. Vibrational frequencies have been calculated at B3LYP method with EPR-II basis set to analyze the thermochemical functions including enthalpies and Gibbs free energies [14].

The natural bond orbital (NBO) analysis [15, 16] has also been applied to study the intermolecular orbital interactions in the complexes [17]. Also, NBO data such as coefficients and hybrids of s, p and d orbitals of atoms, donor, acceptor bonds and ΔE in $[CuF_4]^{2-}$ complex in different loops of the $B_{18}N_{18}$ nanoring have been calculated.

3. RESULTS AND DISCUTION

Density functional theory (DFT) calculations, as well as hybrid methods (B3LYP) for $B_{18}N_{18}$-$[CuF_4]^{2-}$ complex have been carried out to study the non-bonded interaction. The geometry of the $B_{18}N_{18}$ have been optimized at B3LYP method with EPR-II basis set and geometry of the $[CuF_4]^{2-}$ complex have been optimized at B3LYP method with Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential. The non-bonded electromagnetic interactions of the $[CuF_4]^{2-}$ complex inside nanoring have been investigated at B3LYP in different loops of the $B_{18}N_{18}$ nanoring. Optimized parameters of $[CuF_4]^{2-}$ such as bond lengths and bond angles have been reported in Table 1. In accordance with the occupancy values of metal Cu (II)

Table 5: *Natural bond orbital (NBO) analysis: Bond orbital/ Coefficients/ Hybrids of* $[CuF_4]^{2-}$ *at the level of B3LYP theory and EPR-II basis set for F atom and Def2-TZVP basis set and Stuttgart RSC 1997 Effective Core Potential for Cu (II).*

Compound	Natural bond orbital (NBO) analysis	
	Bond orbital	Coefficients/ Hybrids
$[CuF_4]^{2-}$	BD (1)Cu 1- F 4	0.3763*Cu 1 ($sp^{0.02}$ $d^{1.02}$)+ 0.9265* F 4 (s $p^{61.83}$)
	BD (1)Cu 1- F 5	0.3763*Cu 1 ($sp^{0.02}$ $d^{1.02}$)+0.9265* F 5 (s $p^{61.83}$)
	LP (1)Cu 1	($sp^{0.}$00d99.99)
	LP (2)Cu 1	($sp^{0.00}d^{1.00}$)
	LP (3)Cu 1	($sp^{0.00}d^{1.00}$)
	LP (1) F 2	($sp^{0.27}$)
	LP (2) F 2	($sp^{26.92}$)
	LP (3) F 2	($sp^{4.74}$)
	LP (1) F 3	($sp^{0.27}$)
	LP (2) F 3	($sp^{26.44}$)
	LP (3) F 3	($sp^{4.74}$)
	LP (1) F 4	($sp^{1.00}$)
	LP (2) F 4	($sp^{2.62}$)
	LP (3) F 4	($sp^{0.41}$)
	LP (1) F 5	($sp^{1.00}$)
	LP (2) F 5	($sp^{2.62}$)
	LP (3) F 5	(sp 0.41)
	BD*(1)Cu 1- F 4	0.9265*Cu 1 ($sp^{0.02}d^{1.02}$)-0.3763* F 4 ($sp^{61.83}$)
	BD*(1)Cu 1- F 5	0.9265*Cu 1 ($sp^{0.02}d^{1.02}$) -0.3763* F 5 ($sp^{61.83}$)

Table 6: *Relative energies (ΔE), radial coordinate of dipole moment (r) and band gap of* $[CuF_4]^{2-}$ *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 Cu (II).*

Compound	Basis sets for Cu^{2+}			
$B_{18}N_{18}$-$[CuF_4]^{2-}$	Def2-TZVP, Stuttgart RSC 1997 ECP			
	Band gap (Hartree)	ΔE (Hartree)	Dipole moment (Debye)	NICS
loop 1-$[CuF_4]^{2-}$	0.05469	-831.7449534	3.8929	-9.8094
Bond 1-$[CuF_4]^{2-}$	0.04897	-671.6756222	34.6191	
loop 2-$[CuF_4]^{2-}$	0.02378	-830.0046387	43.2226	-9.8196
Bond 2-$[CuF_4]^{2-}$	0.10199	-672.3802177	6.8162	
loop 3-$[CuF_4]^{2-}$	0.07624	-831.7465563	5.2806	-9.8051
Bond 3-$[CuF_4]^{2-}$	0.00255	-651.314292	124.5741	
loop 4-$[CuF_4]^{2-}$	0.06172	-831.7607891	4.1019	-9.8196
Bond 4-$[CuF_4]^{2-}$	0.07443	-672.3417425	5.3989	
loop 5-$[CuF_4]^{2-}$	0.0559	-831.7458498	4.8725	-9.8196
Bond 5-$[CuF_4]^{2-}$	0.09745	-672.3291818	2.9317	
loop 6-$[CuF_4]^{2-}$	0.03108	-831.7554394	2.7438	-9.8051
Bond 6-$[CuF_4]^{2-}$	0.05616	-672.3152578	7.6188	

Table 7: *Molecular orbital diagrams of $B_{18}N_{18}$-$[CuF_4]^{2-}$ complex at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II).*

Loop 1		Loop 2		Loop 3	
Natural Bond Orbitals	Energy (a.u.)	Natural Bond Orbitals	Energy (a.u.)	Natural Bond Orbitals	Energy (a.u.)
BD (1)Cu37- F39	-0.05623	BD (1)Cu37- F38	-0.02077	BD (1)Cu37- F41	-0.07620
LP (1)Cu37	-0.09308	LP (1)Cu37	-0.00365	LP (1)Cu37	-0.11045
LP (2)Cu37	-0.09087	LP (2)Cu37	0.01271	LP (2)Cu37	-0.08962
LP (3)Cu37	-0.08588	LP (3)Cu37	0.01774	LP (3)Cu37	-0.07984
LP (4)Cu37	-0.07665	LP (4)Cu37	0.04832	LP (4)Cu37	-0.07500
LP (1) F39	-0.02934	LP (1) F38	-0.16392	LP (1) F41	-0.05920
LP (2) F39	-0.03078	LP (2) F38	-0.64811	LP (2) F41	-0.17536
LP (3) F39	-0.81087	LP (3) F38	0.00412	LP (3) F41	-0.68166
BD*(1)Cu37- F39	0.13933	BD*(1)Cu37- F38	0.12221	BD*(1)Cu37- F41	0.13531
LP (1) F38	-0.62548	LP (1) F39	-24.14896	LP (1) F38	-0.06539
LP (2) F38	-0.00754	LP (2) F39	-0.52753	LP (2) F38	-0.85317
LP (3) F38	-0.20067	LP (3) F39	0.00110	LP (3) F38	-0.04069
LP (1) F40	-0.38165	LP (1) F40	-0.47334	LP (1) F39	-0.06404
LP (2) F40	-0.50677	LP (2) F40	-0.47372	LP (2) F39	-0.45366
LP (3) F40	-0.02000	LP (3) F40	-0.05262	LP (3) F39	-0.30577
LP (1) F41	-0.14561	LP (1) F41	-0.05201	LP (1) F40	-0.43630
LP (2) F41	-0.50047	LP (2) F41	-0.82102	LP (2) F40	-0.06125
LP (3) F41	-0.18278	LP (3) F41	-0.01779	LP (3) F40	-0.36032

Loop 4		Loop 5		Loop 6	
Natural Bond Orbitals	Energy (a.u.)	Natural Bond Orbitals	Energy (a.u.)	Natural Bond Orbitals	Energy (a.u.)
BD (1)Cu37- F39	-0.02312	BD (1)Cu37- F38	-0.05808	BD (1)Cu37- F40	-0.05070
BD (1)Cu37- F40	-0.03843	-	-	BD (1)Cu37- F41	-0.06640
LP (1)Cu37	-0.09017	LP (1)Cu37	-0.09464	LP (1)Cu37	-0.10813
LP (2)Cu37	-0.06391	LP (2)Cu37	-0.10278	LP (2)Cu37	-0.07982
LP (3)Cu37	-0.06750	LP (3)Cu37	-0.08226	LP (3)Cu37	-0.07192
LP (4)Cu37	-0.06236	LP (4)Cu37	-0.07621	LP (4)Cu37	-0.07389
LP (1) F39	-0.15022	LP (1) F38	-0.01988	LP (1) F40	-0.16831
LP (2) F39	-0.19471	LP (2) F38	-0.01666	LP (2) F40	-0.62545
LP (3) F39	-0.47825	LP (3) F38	-0.83793	LP (3) F40	-0.08199
LP (1) F40	-0.11709	BD*(1)Cu37- F38	0.13872	LP (1) F41	-0.12177
LP (2) F40	-0.35692	LP (1) F39	-0.54552	LP (2) F41	-0.69398
LP (3) F40	-0.38104	LP (2) F39	-0.00546	LP (3) F41	-0.09084
BD*(1)Cu37- F39	0.34461	LP (3) F39	-0.24507	BD*(1)Cu37- F40	0.37225
BD*(1)Cu37- F40	0.35151	LP (4) F39	-0.00121	BD*(1)Cu37- F41	0.36672
LP (1) F38	-0.20263	LP (1) F40	-0.54478	LP (1) F38	-0.36282
LP (2) F38	-0.63388	LP (2) F40	-0.08729	LP (2) F38	-0.28767
LP (3) F38	-0.02299	LP (3) F40	-0.24194	LP (3) F38	-0.09849
LP (1) F41	-0.43363	LP (1) F41	-0.48068	LP (1) F39	-0.64343
LP (2) F41	-0.35158	LP (2) F41	-0.41393	LP (2) F39	-0.00584
LP (3) F41	-0.08100	LP (3) F41	-0.02217	LP (3) F39	-0.14656

Table 8: *Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II)in Loop 1-*$[CuF_4]^{2-}$ *system.*

Compound	Natural bond orbital (NBO) analysis				
	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
Loop 1-$[CuF_4]^{2-}$	BD (1)Cu37- F39	LP*(5)Cu37	0.27	0.58	0.016
	LP (3) F39	LP*(5)Cu37	2.19	1.33	0.071
	BD*(1)Cu37- F39	LP*(5)Cu37	7.24	0.38	0.137
	LP (1) F38	LP*(5)Cu37	1.02	1.15	0.045
	LP (2) F38	LP*(5)Cu37	0.04	0.53	0.006
	LP (3) F38	LP*(5)Cu37	7.65	0.72	0.098
	LP (3) F38	BD*(1)Cu37- F39	0.32	0.34	0.014
	LP (4) F38	LP*(5)Cu37	5.25	0.51	0.066
	LP (4) F38	BD*(1)Cu37- F39	1.69	0.13	0.019
	LP (1) F40	LP*(5)Cu37	1.11	0.90	0.042
	LP (2) F40	LP*(5)Cu37	4.87	1.03	0.093
	LP (2) F40	BD*(1)Cu37- F39	0.16	0.65	0.014
	LP (3) F40	LP*(5)Cu37	0.63	0.54	0.024
	LP (3) F40	BD*(1)Cu37- F39	0.53	0.16	0.012
	LP (4) F40	LP*(5)Cu37	8.89	0.56	0.091
	LP (4) F40	BD*(1)Cu37- F39	0.30	0.18	0.010
	LP (1) F41	LP*(5)Cu37	0.72	0.67	0.029
	LP (2) F41	LP*(5)Cu37	1.57	1.02	0.053
	LP (3) F41	LP*(5)Cu37	7.10	0.71	0.093
	LP (3) F41	BD*(1)Cu37- F39	0.72	0.32	0.021
	LP (4) F41	LP*(5)Cu37	8.46	0.54	0.086
	LP (4) F41	BD*(1)Cu37- F39	0.31	0.15	0.009

Table 9: *Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II) in Loop 2-*$[CuF_4]^{2-}$ *system.*

Compound	Natural bond orbital (NBO) analysis				
	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
Loop 2-$[CuF_4]^{2-}$	LP*(4)Cu37	BD*(1)Cu37- F38	0.69	0.07	0.014
	LP (1) F38	LP*(5)Cu37	0.46	0.79	0.025
	LP (2) F38	LP*(5)Cu37	2.42	1.27	0.072
	LP (3) F38	LP*(4)Cu37	2.77	0.04	0.016
	LP (3) F38	LP*(5)Cu37	0.83	0.62	0.029
	BD*(1)Cu37- F38	LP*(5)Cu37	4.34	0.50	0.135
	LP (1) F39	LP*(4)Cu37	0.05	0.35	0.007
	LP (1) F39	LP*(5)Cu37	0.61	0.93	0.031
	LP (1) F39	BD*(1)Cu37- F38	0.04	0.43	0.005
	LP (2) F39	LP*(4)Cu37	0.04	0.58	0.008
	LP (2) F39	LP*(5)Cu37	3.55	1.15	0.083
	LP (3) F39	LP*(4)Cu37	1.06	0.05	0.011
	LP (3) F39	LP*(5)Cu37	0.06	0.62	0.008
	LP (3) F39	BD*(1)Cu37- F38	0.30	0.12	0.008
	LP (4) F39	LP*(4)Cu37	3.45	0.06	0.019
	LP (4) F39	LP*(5)Cu37	8.41	0.63	0.095
	LP (4) F39 .	BD*(1)Cu37- F38	1.20	0.13	0.016
	LP (1) F40	LP*(4)Cu37	0.23	0.52	0.017
	LP (1) F40	LP*(5)Cu37	1.24	1.10	0.048
	LP (1) F40	BD*(1)Cu37- F38	0.13	0.60	0.012
	LP (2) F40	LP*(4)Cu37	0.31	0.52	0.019
	LP (2) F40	LP*(5)Cu37	3.81	1.10	0.084
	LP (2) F40	BD*(1)Cu37- F38	0.31	0.60	0.018
	LP (3) F40	BD*(1)Cu37- F38	1.17	0.17	0.019
	LP (4) F40	LP*(4)Cu37	7.22	0.14	0.045
	LP (4) F40	LP*(5)Cu37	7.99	0.72	0.096
	LP (4) F40	BD*(1)Cu37- F38	1.39	0.21	0.022
	LP (1) F41	LP*(4)Cu37	0.17	0.10	0.006
	LP (1) F41	LP*(5)Cu37	0.14	0.68	0.013
	LP (2) F41	LP*(4)Cu37	0.65	0.87	0.036
	LP (2) F41	LP*(5)Cu37	3.95	1.45	0.099
	LP (3) F41	LP*(4)Cu37	0.23	0.07	0.006
	LP (3) F41	LP*(5)Cu37	0.04	0.64	0.006
	LP (3) F41	BD*(1)Cu37- F38	0.97	0.14	0.016
	LP (4) F41	LP*(4)Cu37	18.15	0.09	0.055
	LP (4) F41	LP*(5)Cu37	8.33	0.67	0.100
	LP (4) F41	BD*(1)Cu37- F38	0.12	0.17	0.006

Table 10: *Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II) in Loop 3-*$[CuF_4]^{2-}$ *system.*

Compound	Natural bond orbital (NBO) analysis				
	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
Loop 3-$[CuF_4]^{2-}$	BD (1)Cu37- F41	LP*(5)Cu37	0.38	0.60	0.020
	LP (2) F41	LP*(5)Cu37	0.44	0.70	0.023
	LP (3) F41	LP*(5)Cu37	3.51	1.20	0.086
	BD*(1)Cu37- F41	LP*(5)Cu37	6.90	0.39	0.134
	LP (1) F38	LP*(5)Cu37	0.10	0.59	0.010
	LP (2) F38	LP*(5)Cu37	3.65	1.37	0.093
	LP (2) F38	BD*(1)Cu37- F41	0.24	0.99	0.021
	LP (3) F38	LP*(5)Cu37	3.49	0.56	0.058
	LP (3) F38	BD*(1)Cu37- F41	2.27	0.18	0.027
	LP (4) F38	LP*(5)Cu37	0.98	0.58	0.031
	LP (4) F38	BD*(1)Cu37- F41	0.07	0.19	0.005
	LP (1) F39	LP*(5)Cu37	0.28	0.59	0.017
	LP (2) F39	LP*(5)Cu37	1.07	0.98	0.043
	LP (3) F39	LP*(5)Cu37	4.15	0.83	0.077
	LP (3) F39	BD*(1)Cu37- F41	0.10	0.44	0.009
	LP (4) F39	LP*(5)Cu37	10.12	0.52	0.093
	LP (4) F39	BD*(1)Cu37- F41	1.32	0.14	0.018
	LP (1) F40	LP*(5)Cu37	1.30	0.96	0.047
	LP (2) F40	LP*(5)Cu37	0.40	0.58	0.020
	LP (3) F40	LP*(5)Cu37	5.86	0.88	0.095
	LP (3) F40	BD*(1)Cu37- F41	0.06	0.50	0.007
	LP (4) F40	LP*(5)Cu37	11.23	0.54	0.099
	LP (4) F40	BD*(1)Cu37- F41	1.85	0.16	0.022

Table 11: *Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II) in Loop 4-*$[CuF_4]^{2-}$ *system.*

Compound	Natural bond orbital (NBO) analysis				
	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
Loop 4-$[CuF_4]^{2-}$	BD (1)Cu37- F39	BD*(1)Cu37- F39	1.21	0.37	0.028
	BD (1)Cu37- F39	BD*(1)Cu37- F40	5.11	0.37	0.058
	BD (1)Cu37- F40	BD*(1)Cu37- F39	4.80	0.38	0.057
	BD (1)Cu37- F40	BD*(1)Cu37- F40	1.05	0.39	0.027
	LP (3) F39	BD*(1)Cu37- F39	0.80	0.82	0.035
	LP (3) F39	BD*(1)Cu37- F40	1.03	0.83	0.039
	LP (3) F40	BD*(1)Cu37- F39	1.90	0.73	0.050
	LP (3) F40	BD*(1)Cu37- F40	1.49	0.73	0.045
	LP (1) F38	BD*(1)Cu37- F39	0.06	0.55	0.008
	LP (1) F38	BD*(1)Cu37- F40	0.35	0.55	0.019
	LP (2) F38	BD*(1)Cu37- F39	1.01	0.98	0.042
	LP (2) F38	BD*(1)Cu37- F40	2.04	0.99	0.060
	LP (3) F38	BD*(1)Cu37- F39	0.07	0.37	0.007
	LP (4) F38	BD*(1)Cu37- F39	1.52	0.37	0.031
	LP (4) F38	BD*(1)Cu37- F40	10.68	0.37	0.082
	LP (1) F41	BD*(1)Cu37- F39	0.89	0.78	0.036
	LP (1) F41	BD*(1)Cu37- F40	0.22	0.79	0.018
	LP (2) F41	BD*(1)Cu37- F39	2.77	0.70	0.059
	LP (2) F41	BD*(1)Cu37- F40	1.31	0.70	0.041
	LP (3) F41	BD*(1)Cu37- F39	2.87	0.43	0.047
	LP (3) F41	BD*(1)Cu37- F40	1.94	0.43	0.039
	LP (4) F41	BD*(1)Cu37- F39	11.63	0.35	0.082
	LP (4) F41	BD*(1)Cu37- F40	0.92	0.36	0.023

Table 12: *Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II) in Loop 5-$[CuF_4]^{2-}$ system.*

Compound	Natural bond orbital (NBO) analysis				
	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
Loop 5-$[CuF_4]^{2-}$	BD (1)Cu37- F38	LP*(5)Cu37	0.27	0.58	0.016
	LP (3) F38	LP*(5)Cu37	2.16	1.36	0.071
	BD*(1)Cu37- F38	LP*(5)Cu37	6.96	0.38	0.136
	LP (1) F39	LP*(5)Cu37	0.96	1.07	0.042
	LP (2) F39	LP*(5)Cu37	0.17	0.53	0.012
	LP (3) F39	LP*(5)Cu37	4.70	0.77	0.079
	LP (3) F39	BD*(1)Cu37- F38	0.25	0.38	0.013
	LP (4) F39	LP*(5)Cu37	9.25	0.52	0.088
	LP (4) F39	BD*(1)Cu37- F38	0.46	0.14	0.011
	LP (1) F40	LP*(5)Cu37	1.35	1.07	0.050
	LP (2) F40	LP*(5)Cu37	0.35	0.61	0.019
	LP (3) F40	LP*(5)Cu37	9.90	0.76	0.114
	LP (3) F40	BD*(1)Cu37- F38	0.58	0.38	0.020
	LP (4) F40	LP*(5)Cu37	5.06	0.52	0.065
	LP (4) F40	BD*(1)Cu37- F38	1.81	0.13	0.020
	LP (1) F41	LP*(5)Cu37	0.88	1.00	0.039
	LP (2) F41	LP*(5)Cu37	5.82	0.94	0.097
	LP (2) F41	BD*(1)Cu37- F38	0.36	0.55	0.019
	LP (3) F41	LP*(5)Cu37	1.10	0.54	0.032
	LP (3) F41	BD*(1)Cu37- F38	0.15	0.16	0.007
	LP (4) F41	LP*(5)Cu37	7.65	0.56	0.085
	LP (4) F41	BD*(1)Cu37- F38	0.22	0.18	0.008

Table 13: *Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Co (III) in Loop 6-$[CuF_4]^{2-}$ system.*

Compound	Natural bond orbital (NBO) analysis				
	Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(j)-E(i) a.u.	F(i,j) a.u.
Loop 6-$[CuF_4]^{2-}$	BD (1)Cu37- F40	BD*(1)Cu37- F40	1.85	0.42	0.036
	BD (1)Cu37- F40	BD*(1)Cu37- F41	7.24	0.42	0.071
	BD (1)Cu37- F41	BD*(1)Cu37- F40	8.49	0.44	0.079
	BD (1)Cu37- F41	BD*(1)Cu37- F41	2.40	0.43	0.042
	LP (2) F40	BD*(1)Cu37- F40	0.75	1.00	0.036
	LP (2) F40	BD*(1)Cu37- F41	0.81	0.99	0.037
	LP (3) F40	BD*(1)Cu37- F40	0.66	0.45	0.023
	LP (3) F40	BD*(1)Cu37- F41	0.70	0.45	0.023
	LP (2) F41	BD*(1)Cu37- F40	0.76	1.07	0.038
	LP (2) F41	BD*(1)Cu37- F41	0.74	1.06	0.037
	LP (1) F38	BD*(1)Cu37- F40	0.44	0.74	0.024
	LP (1) F38	BD*(1)Cu37- F41	0.39	0.73	0.022
	LP (2) F38	BD*(1)Cu37- F40	0.42	0.66	0.022
	LP (2) F38	BD*(1)Cu37- F41	0.39	0.65	0.021
	LP (3) F38	BD*(1)Cu37- F40	4.56	0.47	0.061
	LP (3) F38	BD*(1)Cu37- F41	5.97	0.47	0.069
	LP (4) F38	BD*(1)Cu37- F40	3.39	0.37	0.046
	LP (4) F38	BD*(1)Cu37- F41	0.79	0.36	0.022
	LP (1) F39	BD*(1)Cu37- F40	0.53	1.02	0.031
	LP (1) F39	BD*(1)Cu37- F41	0.40	1.01	0.026
	LP (2) F39	BD*(1)Cu37- F40	0.14	0.38	0.010
	LP (2) F39	BD*(1)Cu37- F41	0.09	0.37	0.008
	LP (3) F39	BD*(1)Cu37- F40	5.19	0.52	0.068
	LP (3) F39	BD*(1)Cu37- F41	5.55	0.51	0.070
	LP (4) F39	BD*(1)Cu37- F40	2.97	0.35	0.042
	LP (4) F39	BD*(1)Cu37- F41	0.21	0.35	0.011

in $[CuF_4]^{2-}$ complex in Table 2, it was elaborated that $3d_z2$ orbitals have the least value of energy and the 4S orbital have no electron. For instance, in F(2) and F(4) that are in one direction related to Cu(II), $2p_x$ has a lower energy level equal to 0.05 and in F(3) and F(5) equal to -0.003 and $2p_y$ and $2p_z$ have higher energy levels (Figure 1). The different energy levels of metal-ligands bonding in $[CuF_4]^{2-}$ complex have been reported in Table 3. In the NBO analysis, second order perturbation theory analysis of fock matrix in NBO basis at the level of B3LYP theory and EPR-II basis set for F atom and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II) in $[CuF_4]^{2-}$ complex have been reported in Table 4. Bond orbital, Coefficients and Hybrids of $[CuF_4]^{2-}$ complex at the level of B3LYP theory and EPR-II basis set for F atom and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II) have been reported in Table 5. It has been found that the bonding and anti-bonding coefficients of s, p and d orbitals of Cu-F bonds were 0.3 and 0.9 respectively.

To determination non-bonded interaction of the $[CuF_4]^{2-}$ complex embedded in nanoring, we focuson the $B_{18}N_{18}$ nanoring and the schematic of optimized structure of the $B_{18}N_{18}$-$[CuF_4]^{2-}$ system have been displayed in Figure 1. The geometry of $B_{18}N_{18}$ nanorings have been optimized by B3LYP method with EPR-II basis set. According to the frequency calculation of $B_{18}N_{18}$ nanorings such as ΔG= -67.7929 kcal/mol and ΔH= -124.4012 kcal/mol, confirmed the structural stability of nanorings. Radial coordinate of dipole moments of complex under different loops of nanorings have been reported in Table 6.

In accordance with the electron paramagnetic resonance (EPR) study, it is notable that the obtained energy of mentioned basis set and ECP for single $B_{18}N_{18}$ nanoring and single $[CuF_4]^{2-}$ complex were -1434.1167014 and -592.9067459 (Hartree) respectively. To investigate the non-bonded interaction of $[CuF_4]^{2-}$ we focused onsix different loops of $B_{18}N_{18}$ nanorings. So, quantities values such as the relative energies (ΔE), radial coordinate of dipole moment (r), nuclear repulsion energy, NICS and band gap of $[CuF_4]^{2-}$ under different loops of nanorings at the level of B3LYP theory have been reported in Table 6. Molecular orbital diagrams of $B_{18}N_{18}$-$[CuF_4]^{2-}$ complex at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II) have been reported in Table 7. Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis at the level of B3LYP theory and EPR-II basis set for B,N,F atoms and Def2-TZVP basis set and Stuttgart RSC 1997 ECP for Cu (II) in different Loops-$[CuF_4]^{2-}$ system have been reported in Tables 8-13.

4. CONCLUSIONS

In this study, Density functional theory calculations with EPR basis sets have been used to determination electrostatic non-bonded interaction. Relative energies and HOMO-LUMO bond gaps of complex in different loops have been employed to detect and characterize the hyperfine structural properties of nanoring complex system. In accordance with Table 1, $[CuF_4]^{2-}$ complex with four π-donor ligands exhibit the Jahn-Teller distortion. It has been found at Table 5 that the bonding coefficients of s, p and d orbitals were 0.3 and anti-bonding coefficients of Cu-F bonds were 0.9. In accordance with NICS values of Table 8, it's elaborated that loops 1, 3 and 6 have similar NICS values that is equal to -9.8094 and loops 2, 4 and 5 have similar NICS values that is equal to -9.8196. So, that if the NICS values would be more negative, the aromaticity and magnetism of the loop is more.

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