THEORETICAL STUDY OF THE [Fe(en)$_2$(NCS)$_2$] COMPLEX WITH REPARAMETERIZED DENSITY FUNCTIONALS

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ABSTRACT

Quantum chemical studies have been carried out on the Fe(en)$_2$(NCS)$_2$ (en = ethylenediamine) complex both in low and high spin states (S = 0 and S = 2) using hybrid exchange-correlation functional (B3LYP) and non-hybrid method (BLYP). Calculations were performed in vacuum and in methanol to study the effect of cis-trans geometry on the structure and energy difference between low-spin (LS) and high-spin (HS) states of iron (II) complexes. Full geometry optimizations of the complexes show that hybrid method consistently gives higher energy difference between LS and HS states than the nonhybrid methods. Calculations with reparameterized density functional theory that showed more reasonable electronic energy splittings in previous research was also carried out. In addition, the computational study of Fe(en)$_2$(NCS)$_2$ in vacuum and methanol with PCM method showed that the complexes tend to adopt cis geometry. This geometry showed much less charge transfer in the substitutions of NCS$^-$ ligands compare to trans geometry.

INTRODUCTION

Density functional theory (DFT) methods based on the seminal work of Hohenberg, Kohn and Sham are promising alternatives to the traditional *ab initio* methods for characterizing transition metal containing system because they include electron correlation in the exchange-correlation functional [1-3]. DFT methods have been proved to give accurate results for many properties of transition metal compounds (such as geometries, relative stability among isomers, dipole moments, etc.) with moderate computational expenses [4-5]. However, the accuracy is still not sufficient to allow predictions of the transition temperature between low-spin and high-spin states [6], which means that mainstream DFT methods poorly predict the energy differences among different multiplicities of complexes.

To obtain reliable energetic for reactions with transition-metal compounds, density functional calculations must give correct multiplicity for the ground state. This is most obvious for those compounds with small energy differences, $\Delta E^e_{LS/HS}$ between the low-spin (LS) and the high-spin (HS) state at their equilibrium structure. Example of this class of compounds are furnished by Fe(II) complexes in a weak ligands such as amines. In the simple picture of ligand field theory we find Fe(II) to be a d^6 case, where all six d electrons may occupy t_{2g} orbitals (in the idealized picture of octahedral symmetry) or are also distributed over the e_g orbitals (Fig. 1). In the former case we would have a singlet
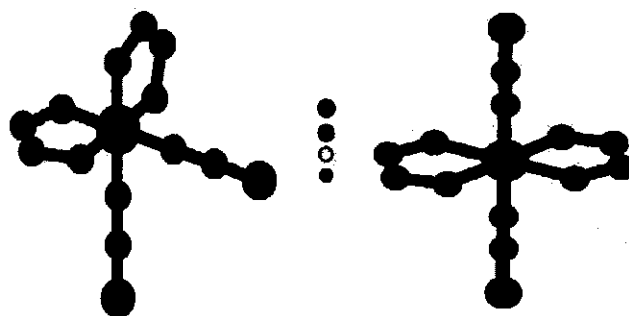

Figure 1. Structure of complexes [Fe(en)$_2$(NCS)$_2$] on *cis* and *trans* configuration

state and thus a low-spin complex, while in the latter case a quintet ground state, thus, a high-spin complex. The low spin compound is characterized by singlet multiplicity with total spin quantum number $S = 0$, while the high-spin analogue is described by quintet multiplicity with total spin quantum number $S = 2$. In very weak ligand, many of the spin crossover compounds [7-8] consist of Fe(II) metal ion which surrounded by a pseudo-octahedral system of six nitrogen atoms as in [Fe(phen)$_2$(NCS)$_2$]. However, the Fe(II)-N complexes, which are considered in this study, are not of the spin crossover type.

We used non local DFT, the gradient-corrected Becke-Lee-Yang-Parr (BLYP) and hybrid functional B3LYP. Becke introduced a hybrid functional where the exchange correlation energy is defined as follows:

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$$E_{xc}^{B3LYP} = (1-a)E_x^{LSD} + aE_x^{HF} + bE_x^{B88} + cE_c^{LYP} + (1-c)E_c^{LSD} \quad (1)$$

with the semiempirical parameters $a = 0.2$; $b = 0.72$ and $c = 0.81$. In its ability to predict the ground state multiplicity of iron(II) complexes, B3LYP usually fails. Instead, pure DFT methods predict the correct ground state but they exceed in favoring the LS state [6]. Reiher et al ascribed this behavior to the admixture of Hartree-Fock exchange and proposed a reparameterization of the B3LYP method by setting $a = 0.15$. First application of this new method, called B3LYP*, suggest that reduced admixture of Hartree-Fock exchange leads to more accurate results for the energy splitting between states with different spin multiplicity [9-10].

Among the several approaches proposed to describe the solvent effect at the *ab initio* level, continuum models are quite popular, due to their flexibility and efficiency. In such models, solute molecule is placed in cavity surrounded by a polarizable continuum, whose reaction field modifies the energy and the properties of the solute. In this paper, we used Conductor-like PCM (CPCM-COSMO) to study electrostatic interaction between solute and solvent. PCM has been widely used since its appearance in 1981 for the study of many chemical processes [11-13].

The present study aims to investigate how the choice of the DFT method influences the accuracy of the calculated total energy differences and the electronic ground band of unsubstituted tris-ethylenediamine Fe(II) (I), [Fe(en)₂(NCS)₂] complexes with NCS⁻ ligands substituted at *cis* position (II) and at *trans* position (III). We also investigate how the medium (vacuum and methanol) influence the properties of those complexes.

COMPUTATIONAL METHOD

All calculations have been performed with the Gaussian 03, Revision E.01 package [14] with 6-31G(d) basis set. We have calculated and compared results from density functional calculation with Hartree-Fock (HF) method. DFT calculations were performed using pure density functionals BLYP (Becke's exchange and

LYP correlation functional), hybrid functional B3LYP (Becke's exchange functional together with the local spin density correlation functional III and the non-local correlation functional) and the reparameterized version, B3LYP* (i.e., B3LYP with successive $a = 0.12$; 0.13; 0.14 and 0.15). We omit the counter ions in our calculations. To take solvent effect into account, a polarizable continuum model, PCM, has been used which methanol was chosen as a solvent.

RESULT AND DISCUSSION

Substituent Effects on Some Geometry Parameters of the Complexes

Calculated structure of Fe(en)₂(NCS)₂ in *cis* and *trans* geometry in vacuum are presented in Figure 1. For simplification, hydrogen atoms are not shown here. Generally, HF, BLYP and B3LYP methods give the same accuracy in the geometry optimization so, we choose B3LYP results to explore molecular structures. Selected geometrical parameters are compared in Table 1. Variation of the iron-ligand bond distance is 0.2 Å greater in HS state for all methods (HF, BLYP and B3LYP) but hybrid functionals (B3LYP) show good agreement with experimental data. The B3LYP* structural parameters are close to the B3LYP parameters. Generally, the metal-ligands bond distance in *trans* configuration was greater than *cis* configuration.

Solvent Effect on Conformation and Energy

Calculations employing the PCM-COSMO model have been performed with B3LYP method. Table 2 summarizes dipole moments and the total electronic energy difference HS-LS (ΔE_{el}) in vacuum and in methanol. The same as in vacuum, variation of the metal-ligand bond distance in methanol were 0.2 Å. Based on those data, can be seen that in vacuum, complex I with B3LYP method gives reasonable ΔE_{el}.

Table 1. Comparison of substituent effects on coordination-bond lengths (Å), bond angles and torsional angles (°).

Comp.	Fe-N$_m$[a]		Fe-N$_c$[b]		A$_m$		D$_m$		C-C$_m$	
	LS	HS	LS	HS	LS	HS	LS	HS	LS	HS
I	2,06	2,27	--	--	92,9	110	51,9	-41,4	1,52	1,52
II	2,02	2,25	1,85	2,04	124.	109.	-52,2	-48.6	1,53	1.53
Exp.[*]	--	2,11	--	2,04	--	108.	--	-52,4	--	1,49
III	2,02	2,25	1,93	2,06	114	117	0,0	0,0	1,55	1,56

[a] Fe-N$_m$ expresses the bond length between Fe and N of main ligand.
A$_m$ expresses the bond angle N-Fe-N between main ligand and Fe.
D$_m$ expresses torsional angle between Fe and main ligand
C-C$_m$ expresses bond length C-C of main ligand.
[b] Fe-N$_c$ expresses bond length between Fe and N of counter-ion NCS⁻.
[*] Exp.   Experimental data from ref. [16].

Table 2. Calculated total energy difference ΔE_{el} in kJ mol⁻¹ and dipole moments (Debye) with basis set 6-31G(d).

Medium	$\Delta E_{el}^{gasphase}$			CPCM – B3LYP	
	HF	BLYP	B3LYP	$\Delta E_{el}^{methanol}$	μ^{a}
I	-43,67	-115,38	-42,85	-351,00	0,03
II	335,17	17,38	-296,99	-34,82	21,23
III	-285,83	34,29	30,51	-56,05	0,08

μ^{a} : Dipole moments at high-spin state.

Table 3. Low-spin/high-spin splittings ΔE_{el} in kJ mol⁻¹ in complex II with reparameterization of B3LYP functional.

Method	ΔE_{el}
BLYP	17,38
B3LYP (a = 0,12)	15,75
B3LYP (a = 0,13)	7,76
B3LYP (a = 0,14)	7,69
B3LYP (a = 0,15)	7,58
B3LYP	-296,99
HF	335,17

In addition, ethylenediamine ligand with sp^3 systems tend to stablilize steric effect from incoming ligand thus kind of substituent and it's configuration inadequate to influence ΔE_{el}.

In methanol, results shows that complex I dan III has a zero dipole moment meanwhile methanol as polar solvent tend to stabilized complex II through electrostatic solute-solvent interactions so this complex show reasonable ΔE_{el}. cis configuration make easily intermolecular interaction trough intermolecular hydrogen contacts S.....H-C which involving S atoms from NCS⁻ ligands [15]. The data shows that pure DFT method (BLYP) overprediction of ΔE_{el} and B3LYP method give too low ΔE_{el}.

Dependence of ΔE_{el} on E_{ex}^{HF}

The HF method without correlation correction favors the LS spin state by several hundreds kJ/mol (Table 3), which is far from reasonable. An energy splitting of this size is the reason why this uncorrelated methods are considered incapable to describe spin transition in transition metal complexes [10], while correlated methods based on HF wave function (like MP2 and CCI) are computationally too expensive. Pure density functional methods (BLYP) also predict the LS state as ground state, 17.8 kJ/mol lower from HS state. However, as ethylenediamine and NCS⁻ are known as weak ligands, we intuitively predict that the complex favor the HS state. Hybrid functionals (B3LYP) correctly give the high-spin state as the lowest-energy state, but the difference with LS state is too large.

The calculations with the reparameterized version of B3LYP, denoted by B3LYP*, with successive $a = 0.12$; 0.13; 0.14 and 0.15 revealed that they predict the energy difference between HS and LS state better than nonhybrid method (BLYP) and hybrid method (B3LYP). However, this method was incorrectly predict LS state as the ground state of the complex, contrary to the findings of Reiher for another iron(II) complex, so it can be said that the proposed parameter values from Reiher cannot be generalized to other iron(II) complexes. Although in our case B3LYP* still favors the low-spin state, this hybrid functional can still be recommended for general use in DFT calculations on transition metal compounds because it is applicable to a wide range of transition metal complexes (Reiher et al., 2001) and represent the smallest modification to the original B3LYP functional.

Substituent Effects on Frontier Molecular Orbital Components

Frontier molecular orbitals, in particular, HOMO and LUMO are very important because they are related not only to spectral properties, but also reaction active sites and characteristics of excited states of complexes. Some frontier molecular orbital compositions (or atomic orbital population) have been analyzed. The atomic orbital populations for a varied type of atomic orbitals (i.e. s, p, d orbitals) in specific molecular orbitals (i.e. NHOMO, HOMO, LUMO and NLUMO) are approximately expressed as a square sum of the atomic orbital coefficient in the type of atomic orbitals and corrected by normalizing factor. The results are shown in Table 4. The stereographs of HOMO and LUMO of three complexes are shown in Fig. 2 in order to understand their characteristics in detail.

Some interesting population trends of the frontier molecular orbitals of complexes I, II and III can be seen from Table 2 and Fig. 2. For I and II complexes, the components of HOMO and LUMO come mainly from d orbitals of the center metal ion, i.e. they may be characterized by d orbitals of the metal ion. Substitutions of two NCS- counter-ion at cis position have no significance influences to change orbitals composition. As its consequences, no electronic grounds bands are available for these complexes. For trans configuration (III), the components of HOMO and NHOMO come mainly from d orbitals of the center metal ion and the components of LUMO and NLUMO come mainly from p_z and p_y orbitals of C atom in NCS⁻ ligands, i.e. they may be characterized by p orbitals of the ligands. Hence the electronic ground bands and the next ground bands are all assigned to singlet metal-to-ligand charge-transfer (^{1}MLCT).

Table 4. Main atomic orbital population (%) of some frontier molecular orbitals in $[Fe(en)_3]^{2+}$ and its substituted derivates*.

Comp.		Fe			N_m		C_m		N_c		C_c	
		s	p	d	s	p	s	p	s	p	s	p
I	NH	0,0	0,0	86,5	1,9	7,8	2,3	1,5	--	--	--	--
	H	0,0	0,4	94,3	1,9	3,2	0,3	0,2	--	--	--	--
	L	62,4	0,0	0,42	31,0	0,51	3,1	2,6	--	--	--	--
	NL	0,0	82,2	0,0	13,2	4,6	0,0	0,0	--	--	--	--
II	NH	2,5	0,0	80,0	4,6	4,5	1,6	1,5	2,7	0,5	1,4	0,7
	H	0,0	0,0	82,9	0,1	0,0	2,1	0,4	7,3	1,3	3,7	1,7
	L	0,0	74,2	3,2	10,0	0,6	8,5	1,7	1,7	0,7	0,1	1,2
	NL	0,0	64,3	0,0	9,1	1,4	9,1	3,2	0,1	0,9	0,0	11,9
III	NH	0,8	0,0	74,5	1,9	3,0	0,1	0,2	10,0	1,2	5,8	2,5
	H	0,0	0,0	78,2	2,8	10,9	5,4	2,7	0,0	0,0	0,0	0,0
	L	0,0	31,0	0,0	6,3	1,0	2,0	0,5	0,0	13,7	0,0	45,5
	NL	0,0	22,1	0,0	6,5	0,0	2,0	0,5	0,0	17,5	0,0	51,4

) Calculated at HS state with level theory/basis set: B3LYP/6-31G(d).
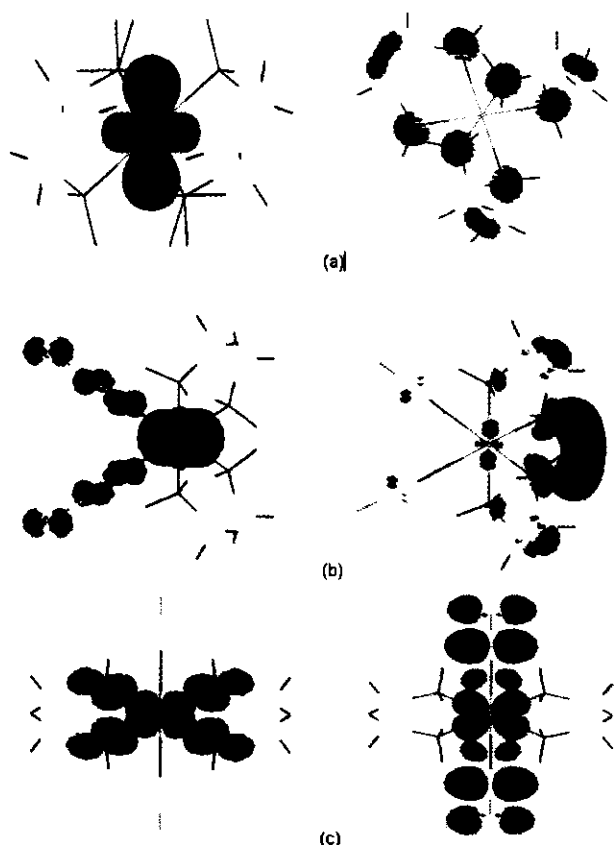

Figure 2. Stereographs of HOMO and LUMO of complexes (I-III) [(a) I, (b) II, (c) III; and HOMO on left, LUMO on right].

CONCLUSION

Full geometry optimizations of the complexes shows that the nonhybrid method consistently gives higher energy; and the hybrid method give too high energy difference between LS and HS although it predict correctly that the complexes favor HS state. We have demonstrated that the prediction of low-spin/high-spin energy splitting for $Fe(en)_2(NCS)_2$ can be improved within precision of the method by adjusting the admixture parameter for exact exchange in B3LYP from a = 0.13 to 0.15 (B3LYP*). However, the parameter values from Reiher can not be generalized for all iron(II) complexes. Computational study $Fe(en)_2(NCS)_2$ in vacuum and in methanol showed that complexes tend to adopt *cis* geometry with high-spin state. As far as charge distributions are concerned, there is much less charge transfer in the substitutions of NCS⁻ ligands on the *cis* configuration of the complexes compare to the *trans* configuration.

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