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Density Functional Theory Investigation of EPR Parameters for of Mn(II), Fe(II), Co(II) and Cd(II) complexes based on a tetradentate ONNO donor Schiff base ligand

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ABSTRACT

Characterization of a tetradentate ONNO Schiff base ligand namely (1, 1'-(pyridine-2, 3-dimethyliminomethyl) naphthalene-2, 2'-diol) and hereafter denotes as "SL" and selected metal complexes including Mn(II), Fe(II), Co(II) and Cd(II) as a central metal was studied. In this paper, the calculation was done to determine the magnetic exchange of the studied molecules, Schiff base complexes via DFT calculations. Using the ZORA approach with the BP86 functionals and appropriate basis set def2-tzvp and Coulomb fitting, the optimized geometries were obtained with reliable accuracy and precision. The dipole moment was calculated. The EPR parameters were also reported.

Introduction

Designing materials with two or more potential functions derived from diverse physical properties has been a significant approach in chemistry and materials research[1]. Numerous constituent molecules may provide for an unanticipated combination of magnetic, spectroscopic, and biological properties in the same compound[2]. (Affectionately referred to as multifunctional materials). Complexes of transition metals, most notably iron or manganese, are an intriguing example of a multifunctional material. The metal core in these compounds may exist in two separate spin states, low-spin (LS) and high-spin (HS), which can be changed through external stimuli such as temperature, pressure, light irradiation, or solvents, while the photoactive fragments can glow[3]. The employment of an appropriate metal-ligand combination enables the formation of systems with mixed properties. Due to their capacity to form stable complexes with a wide variety of transition metals, Schiff bases complexes have been intensively researched in order to determine their potential contribution to the development of coordination chemistry and biological systems [4]–[6].

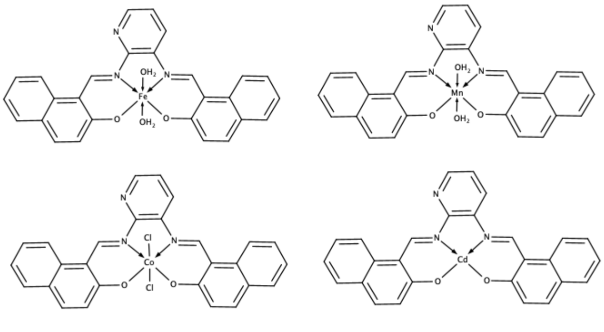

Figure 1: Structures of the transition metal containing SL complexes

Numerous scientists are intrigued by the presence of the pyridine ring in the structure of Schiff bases, since it plays a critical function in biological systems [7], [8] Additionally, the synthesis of Schiff bases from 2-hydroxy-1-naphthaldehyde and other primary amines has been intensively investigated owing to their use in

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medicine and the high stability of the complexes formed. This Schiff base family includes donors that are bidentate, tridentate, tetradentate, or hexadentate in structure. The use of Co(II) and Mn(II) complexes comprising tetradentate Schiff bases with two nitrogen and two oxygen donor atoms as oxygen carriers and catalysts in water-splitting systems has been widely addressed [4]–[6]. When Fe(II) was complexed with tetradentate ONNO donor Schiff bases in an Oh geometry, the presence of different pyridine derivatives as ligands in the axial position revealed spin transition properties [9], [10]. According to the study, pyridine derivatives have sparked considerable attention due to their potential uses in a range of fields, including medicine and chemical synthesis [11]. Due to the existence of transition metal atom/ion bonds with two nitrogen and two oxygen atoms in the structure of Schiff base complexes, an unusually intricate form of coordination with metal ions at four active sites is obtained. For example, when a metal atom or ion is present, non-spherical symmetry and the Jahn–Teller phenomenon are predicted; the stereochemistry of transition metal-containing Schiff base complexes is characterized by non-rigid structures and encompasses a variety of deformed geometries[4], [12]. In some circumstances, this outcome gets more difficult. The electron paramagnetic resonance is a frequently utilized technique for analyzing such complicated molecules (EPR). The technique is centered on identifying two spin Hamiltonian parameters that describe the EPR spectrum of the unpaired electron: the g factor and the hyperfine coupling constant (HFCC), denoted by A, between the unpaired electron and nuclei. This method of examining tetradentate Schiff bases has generated much debate.

To investigate the structural characteristics of such Schiff base complexes, it is necessary to develop methodologies for interpreting experimental data and correlating the structures of specific Schiff base complexes molecules. Recent years have seen an explosion of interest in density functional theory (DFT). Calculations on large molecules may be performed effectively if the appropriate functional and basis sets are used. Regrettably, there are presently no standards for choosing the optimal DFT procedure for most systems in order to gain the greatest agreement with experimental data: While an efficient functional is important, it is dependent on the molecular/spectroscopic characteristics of the metal being investigated; the basis set must be sufficiently broad to incorporate polarization and diffuse functions, as well as relativistic effects, if necessary. Scalar relativistic (SR) contributions are negligible or nonexistent for the first row of transition metal complexes, but they should be included for the second and third series components. As a consequence, the optimal approach for doing a DFT calculation must be decided on a case-by-case basis using current knowledge from the literature, and there are no criteria for deciding which level of theory would produce the best agreement with the experiment in issue. When analyzing EPR findings, quantitative agreement with experimental data is possible.

The purpose of this study is to describe complexes with a broad variety of geometrical and spin structures, their spin-state characterizations, and magnetic properties. Numerous studies on the calculation of EPR parameters, g, and A values for Schiff base complexes have been published in recent years, but to our knowledge, the only thorough analysis is that of Neese [13], [14] utilizing the B3LYP functional. This study reports on the DFT prediction of g and A values for two Fe(II), and Mn(II) Schiff base complexes with two unique spin states, HL and SL. The Fe(II) and Mn(II) complexes were then carefully examined for the magnetic investigation, and several recommendations for boosting prediction accuracy were made. Finally, the g and A values for Fe(II) and Mn complexes were calculated using the best computational parameters.

Experimental

All the calculations were done using the Orca 4.2.1 at DFT level using the method and basis set developed and implemented into the package [15]. The numerical thresholds were gradually raised by utilizing the "TightOpt," "TightSCF," "Grid5", and "FinalGrid6" options, in a methodical manner. We thoroughly investigated the accuracy and precision of our calculations by changing the basis set and functionalities, which were all included in the ORCA package, in a systematic manner.

The Resolution of Identity (RI) approximation (also called Density Fitting) for the two- electron integrals was employed. Full geometry optimizations were performed within the framework of the BP86/def2-TZVP computational procedure which utilized the BP86 functional and the balanced polarized triple-zeta basis set (def2-TZVP) along with associated Weigend's “universal" Coulomb fitting (def2/J) basis sets and the D3 Becke–Johnson damping (BJ) for the dispersion correction. Geometry and energy convergence were reached by allowing all the atoms to relax, choosing the lowest-energy spin states.

For the DFT calculation of EPR parameters, the g and A tensors of the metal center for each complex were calculated utilizing a developed and implemented package method. The A tensor was obtained by summing the contributions of three terms: the isotropic Fermi contact (AFC), the anisotropic dipolar (ADx,y,z), and the spin-orbit coupling term (ASOx,y,z). For an accurate estimate of AFC, the unrestricted Kohn-Sham (UKS) formalism was required to include the appropriate spin polarization. We confirm the performance of the all-electron ZORA-DFT calculation for the Fe2+ and Mn2+ with the SL ligands in this study by employing the benchmarking-validated methods. Population analyses to molecular orbitals, such as spin population and bond overlap population, are utilized to investigate the origin of its selectivity towards ligands. This is the first attempt to investigate the bonding of four complexes containing three types of donor atoms (S, N, and O). We anticipate that a comprehensive understanding of transition metal selectivity as it relates to donor atoms will lead to the prediction of separation behavior and the design of novel separation materials that incorporate the effective functional group and donor atom.

Results and discussion

The geometric and electronic characteristics of the SL molecule were altered to investigate the geometric and electronic parameters that may affect its electron donation. The structure of the optimized SL ligand is planar, with four donating groups (2 hydroxyl and two imino) facing each other around the molecule's center point. The square planar and tetrahedral geometries are defined in Fig 1 depending on the angle. To preserve the structure, hydrogen interaction between the hydroxyl and imino groups was identified. This orientation indicated that the ligand might be connected in a single plane to the metal ions, resulting in the formation of complexes with square planar and octahedral geometries. The planar form was associated with the symmetrical charge distribution among the atoms. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbital occupations indicated that electrons are distributed throughout the molecule, with an estimated energy gap of 8.65 eV.

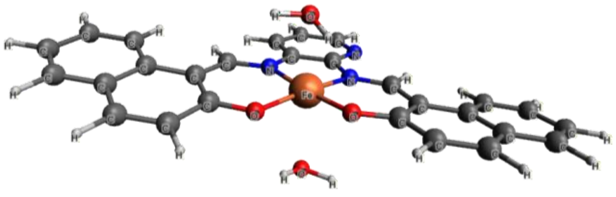

Figure 2: The optimized structure of the Fe-SL complexes

When the SL complexes containing Fe^{2+}, Mn^{2+} and Co^{2+} is optimized, they are assigned at two different spin, the high spin state and low spin state which are summarized in Table 1. The obtained structures of the Fe-SL were illustrated in Fig 2. Geometry and energy convergence were reached by allowing all the atoms to relax, choosing the lowest-energy spin states.

Table 1: Selected bond distance (Å) for some transition metal containing SL complexes

Parameters	Structures	High spin	Low spin
Fe-O1	Octahedral	1.922	1.896
Fe-O2		1.956	1.894
Fe-N1		2.012	1.879
Fe-N2		2.046	1.973
Mn-O1	Octahedral	1.959	1.919
Mn-O2		1.940	1.911
Mn-N1		2.012	1.908
Mn-N2		2.017	1.915
Co-O1	Octahedral	2.423	1.923
Co-O2		2.416	1.926
Co-N1		1.867	1.867
Co-N2		1.885	1.859
Co-Cl1		2.416	2.416
Co-Cl2		2.423	2.423
Cd-O1	Planar	1.906	
Cd-O2		1.920	
Cd-N1		1.955	
Cd-N2		1.946	

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When the Cd^{2+} ion complex is optimized using the SL Schiff base ligand, the lowest energy structure has a square planar shape with the chemical formula [CdSL]. Protonation of the hydroxyl groups neutralizes the Cd^{2+} ion, resulting in this form. The formation of two six-membered rings between the Cd and the ligand stabilized this combination. The addition of two chloride ions in a perpendicular plane to the SL Schiff base ligand resulted in the formation of an octahedral $[SL(Cl)_2Co]$ complex with the ligand's donor groups bound in a single plane. Through analysis the MOs, the protons rotated in opposite directions to prevent the steric interaction between the Co^{2+} and hydroxyl groups of SL. When the atomic charge distributions of the two complexes are compared, it is obvious that the ligand in the Co(II) complex is more neutral than the ligand in the Cd(II) complex, which exhibits greater charge interaction between the ligand and the metal than the ligand in the Co(II) complex, which exhibits neutral atomic charges. Even though the optimum structures of Fe^{2+} and Mn^{2+} were octahedral, the ligand was deprotonated inside the coordination and the octahedral geometry was satisfied by two water molecules. According to optimization findings, water molecules are coordinated in a plane perpendicular to the M-SL plane. Additionally, it was shown that the ligand's donor groups are coordinated with the metal center in a single plane in both Mn (II) and Fe(II) complexes.

Table 2: Calculated HOMO, LUMO, energy gap (E) of studied complexes. All units are in eV

Complexes	Spin	HOMO	LUMO	ΔE	μ
Fe-SL	1	-5.070	-3.057	2.013	1.36
	2	-5.499	-4.032	1.467	2.37
Mn-SL	1/2	-4.067	-2.939	1.128	0.48
	5/2	-5.160	-3.627	1.533	2.22
Co-SL	1/2	-4.679	-2.734	1.945	2.54
	3/2	-5.655	-3.783	1.872	3.67
Cd-SL	0	-5.099	-3.121	1.978	2.56

Calculating the universal chemical reactivity descriptors revealed the relative stability and chemical reactivity of the produced SL Schiff base and its complexes (HOMO, LUMO, energy gap, dipole moment). Presented in Table 2 is a property that indicates the stability and reactivity of a chemical system. According to frontier molecular orbitals, chemical hardness is equal to the energy difference between HOMO and LUMO. As the energy gap grows, the molecule becomes harder and less reactive. The calculated differences between $[SL(Cl)_2Co]$ and [SLCd] complexes were rather small. As a consequence of these discoveries, both complexes looked to be quite stable. Significant difference between the ΔE of the low and high spin state of each complexes agree well with the literature values.

Table 3: Calculated g tensor of complexes with the SL ligand

	Spin	g_x	g_y	g_z
Fe-SL	1	2.008	2.032	2.171
	2	2.018	2.061	2.221
Mn-SL	1/2	2.010	2.042	2.251
	3/2	2.001	2.001	2.101

Table 4: Calculated spin Hamiltonian parameters of the SL complexes. Here the values of A are reported in 10^{-4} cm^{-1}

	Spin	A_x	A_y	A_z
Fe-SL	1	10.3	11.8	3.6
	2	17.3	14.8	3.3
Mn-SL	1/2	7.1	8.1	4.6
	3/2	9.9	8.7	13.1

Conclusion

Complexes comprising transition metals serve a key role in chemistry, biology, and medicine, along with several metal species. Here a tetradentate ONNO Schiff base ligand namely (1, 1′- (pyridine-2, 3-dimethyliminomethyl) naphthalene-2, 2′-diol) and selected metal complexes including Mn(II), Fe(II), Co(II) and Cd(II) as a central metal was studied. Several instrumental approaches are available for their characterization, but in the case of paramagnetic species, EPR is the most commonly employed technique since the values of spin Hamiltonian parameters, gz and Az, are largely dependent on the equatorial donors bound to the metal. In certain circumstances, however, the interpretation of the spectra is not simple since the variation of gz and Az is not always clearly anticipated and can be affected by several factors, such as the geometry's distortion and the presence of ligands in the axial positions. Typically, such complexity falls within this

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range of scenarios. The computational methods, particularly those based on DFT, have shown to be very valuable for confirming experimental findings or for generating ideas to explain spectroscopic measurements. In this paper, we proposed a straightforward method for predicting the spin Hamiltonian of species containing transition metals and explored how to circumvent the most challenging situations. Results indicated that, within the context of DFT calculations, it is not viable to provide a general technique for achieving a sufficient agreement with experimental data. In calculating Az and gz for the compounds investigated in this study, the functionals BP86 and ZORA settings achieve the highest performance. They can be combined with a triple- zata basis set to provide a good fit with experimental data. These computational settings could also be used to elucidate the coordination environment of larger transition metal complexes and other biological systems. In conclusion, we would like to emphasize that when the quality of the optimization is poor, the prediction of Az deteriorates dramatically, and a larger basis set or the solvent effect must be taken into account.

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