Dhaka Univ. J. Sci. 67(1): 63-68, 2019 (January)

DFT and TD-DFT Study of [Tris(dithiolato)M]$^{3-}$ Complexes[M= Cr, Mn and Fe]: Electronic Structures, Properties and Analyses

Mohammad A. Matin[1], Mohammad Alauddin[2], Tapas Debnath[2], M. Saiful Islam[2] and Mohammed A. Aziz[2,*]

[1]*Centre for Advanced Research in Sciences (CARS), Dhaka University, Dhaka-1000, Bangladesh*
[2]*Department of Theoretical and Computational Chemistry, Dhaka University, Dhaka-1000, Bangladesh*

(Received: 17 November 2018; Accepted: 28 January 2019)

Abstract

Using Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) methods, transition metal complexes of benzene-1, 2-dithiolate (L^{2-}) ligand from Cr to Fe have been studied theoretically. The ground state geometries, binding energies, UV-Visible spectra (UV-Vis), frontier molecular orbitals (FMOs) analysis, charge analysis and natural bond orbital (NBO) have been calculated. The structural parameters are in good accord with the experimental data. The metal-ligand binding energies are one (1) order of magnitude higher than the physisorption energy of a benzene-1, 2-dthiolate molecule on a metallic surface. In accordance with experiment the calculated electronic spectra of these tris complexes show bands at 565, 559 and 546 nm for Cr^{3+}, Mn^{3+}, and Fe^{3+} respectively which are mainly qualified to ligand-to metal charge transfer (LMCT) transitions. The electronic properties analysis demonstrate that the highest occupied molecular orbital (HOMO) is mostly centered on metal coordinated sulfur atoms whereas the lowest unoccupied molecular orbital (LUMO) is mainly located on the metal surface. By calculating natural bond orbital (NBO), the intramolecular interactions and electron delocalization was obtained. The results of NBO analysis illustrated the significant charge transfer from sulfur to central metal ions, as well as to the benzene of the complex. The calculated charges on metal ions are also reported at various charge schemes. The calculations show encouraging agreement with the available experimental data.

Keywords: Transition metal, TD-DFT, binding energy, spectroscopy, electronic properties, tris-dithiolate, coordination complex.

I. Introduction

A metalloligand complex contains several potential donor groups. The chemistry of dithiolene complexes has increased tremendously since 1960s.[1] The geometries,[2] redox properties,[3-5] and magnetic properties[6] of this class of complexes are focused primarily from early state which arise from the noninnocent property[7] of dithiolenes. By Jørgeson definition, " The innocent ligands allow oxidation states of the central metal atoms''.[8] According to Ward and McCleverty[7] the noninnocent is applied properly when it combines with the metal and ligand.

The dithiolene ligands can be distinguished in two classes, the non-benzenoid dithiolenes [9] and benzenoid systems.[10] When coordinated to transition metals, dithiolene referred to as noninnocent.[11-13] The dithiolene (L) ligand shown in the scheme 1a and 1b of Figure 1,[14] leveled as monoanionic radical $(L\bullet)^{1-}$, or as dianionic, closed-shell $(L^{Red})^{2-}$ ligand or as neutral 1,2- dithioketone $(L^{Ox})^{0}$ is used.[13] No dianion containing ligand as shown in scheme 2(a)[14] in Figure 1 has been isolated before. The reduced trianionic form with S = 3/2 ground state has been synthesized[15-16] (as shown in scheme 2 (b)[14] in Figure 1).

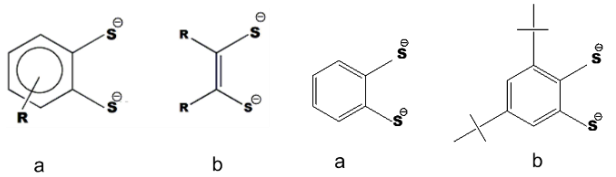

Fig. 1. Binding schemes of metals coordination complexes.

The electronic structures for the $[Cr(L)_3]^z$ (z=0, 1-, 2-, 3-)[17-18] series have been successfully revealed by Sproules et al. The trianion is a rudimentary Werner-type compound with three closed-shell dithiolates surrounding a Cr(III) ion. The dianionic manganese(IV) complexes of $[PPh_4]_2[Mn(mnt)_3]$ and $[N(nBu)_4]_2[Mn(Cl_4\text{-}bdt)_3]$ have been isolated which has S = 3/2 ground state.[16,19-20] The first structurally characterized complex of manganese was $(PNP)_2[Mn(bdt)_3]$ (PNP^+= bis(triphenylphosphine)iminium).[21] These are isoelectronic with the corresponding trianions $[Cr(dithiolene)_3]^{3-}$. Milsmann et al. reported on a similar series of iron(III) complexes with a low-spin ferric ion in octahedral monocations manner.[22] The bis(dithiolate) metal and tris(dithiolate) metal complexes have been extensively studied.[2]

In this study, we have performed systematically a theoretical exploration on the structures, binding energies, spectroscopic and electronic properties of $[M(bdt)_3]^{3-}$ (M=Cr, Mn and Fe) which contains bdt^{2-}=benzene-1,2-dithiolate ligand (as shown in scheme 2(a) of Figure 1) in gas phase applying the first principles HF/DFT hybrid approach. The NBO analysis on these tris complexes is also reported. These calculated results help us to know the thermodynamic behavior of each system as a function of the quantum chemistry descriptors.

II. Computational Methods

We have studied the [tris(bdt)M]$^{3-}$complexes where M=Cr^{3+}, Mn^{3+} and Fe^{3+} with the bdt^{2-}=benzene-1,2-dithiolate ligand (Figure 2). The dithiolene was taken to be oxidized (dithiolate). The compounds are examined by theoretically using HF/DFT hybrid approach B3LYP[23] with the 6-311G(d,p) basis sets in gas phase. All investigations were done using Gaussian09 program[24] and Gauss View 5.0.8 was

*Author for correspondence. e-mail: azizttma@yahoo.com

used for visualization. We have considered dithiolate as a weak-field ligand, thus the metal complex was assumed to have been high spin complex. Geometry optimization was performed and considered the maximum atomic force less than 0.00045 Hartree/Bohr and without imaginary frequency. We did not use any symmetry in any of the calculations. The metal-ligand binding energies were calculated according to equation (1) that was used successfully by others,[25,2]

$$\Delta E = -\frac{(E_{complex} - E_{metal} - E_{ligand})}{3} \quad (1)$$

Where $E_{complex}$, E_{metal}, and E_{ligand} are the energies of the tris(dithiolate) coordination complex, the metal ion and dithiolate ligand, respectively. Therefore, the binding energy ΔE, refers to the binding energy per ligand. The geometry of each species was optimized separately.

Electronically excited state calculations were performed to compute the UV-Vis of the $[M(dithiolate)_3]^{3-}$ complexes of Cr^{3+}, Mn^{3+} and Fe^{3+}. Using the time-dependent DFT, the vertical excited energies were calculated at the level of CAM B3LYP/6-311+G(d,p)[27] after the ground state optimization.

III. Results and Discussion

Structural Analysis

After full optimization, the geometrical parameters like bond lengths and angles of the $[tris(bdt)M]^{3-}$ (M= Cr^{3+}, Mn^{3+} and Fe^{3+}) complexes were calculated. The calculated geometrical parameters are depicted in Figure 2 and Table 1.

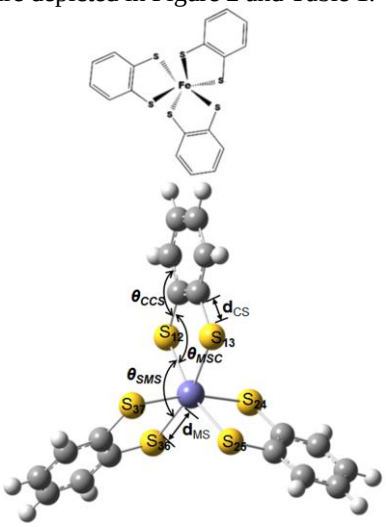

Fig. 2. The optimized geometry of the metal ligand binding complex $[Fe(bdt)_3]^{3-}$.

The metal and the sulfur atoms are 2.48 Å apart for Cr, 2.55 Å for Mn and 2.54 Å for Fe. The DFT and X-ray analysis of the tris-dithiolate complexes reported for chromium-sulphur (Cr-S) distances were 2.385 Å and 2.299 Å respectively.[17] The experimentally measured Cr-S distance in the monoanion of the tris complexes is 2.299 ±0.003 Å, shorter by 0.086 Å than the calculated one. The experimental average Cr-S distance in monoanion of the tris complex is 0.175 Å shorter than that for our DFT calculation of the $[tris(bdt)Cr]^{3-}$ complex. The Mn-S distances are 2.383 Å and 2.347 Å respectively in the $[Mn^{IV}(Cl_2\text{-}bdt)_3][Net_4]_2.CH_2Cl_2$ complex and 2.331 Å for the $[Mn(bdt)_3]^{2-}$ complex.[14] The DFT calculated $[tris(bdt)Mn]^{3-}$ complex is 2.55(±0.17) and 0.17 Å higher than experiment one.[14] The calculated Fe-S bond distance of the tris complex is 2.54 Å which is 0.29 Å higher than the experimental value of the complex of $[Fe^{III}(cyclam)(tdt)](PF_6)$ where the Fe-S distance is 2.25 Å.[22] The calculated values deviate from the experimental ones due to presence of bulky substituent group cyclam in the experimental study.

Table 1. Geometric parameters of the tris(benzene-1,2-dithiolato) complexes of Cr^{3+}, Mn^{3+} and Fe^{3+} transition metal ions. The average values with standard deviations are listed.

M^{3+}	d_{MS} (Å)	d_{CS} (Å)	θ_{SMS} (°)	θ_{CCS} (°)	θ_{MSC} (°)
Cr^{3+}	2.48 (±0.00)	1.77 (±0.00)	90.80 (±4.68)	119.7 (±0.00)	106.10 (±0.00)
Mn^{3+}	2.55 (±0.17)	1.77 (±0.01)	90.30 (±6.66)	119.3 (±1.20)	106.10 (±3.10)
Fe^{3+}	2.54 (±0.00)	1.76 (±0.00)	90.47 (±7.58)	119.6 (±0.00)	107.00 (±0.00)

The present S-M-S angles were significantly larger than the previous X-ray crystal structures. The average angle is nearly octahedral (90°). The angles formed by the metal ion and the two sulfur atoms of the dithiolate ligands are within 90.30° to 90.80° on an average indicating almost octahedral geometry in the coordination. The average S-Cr-S angle of the complex $[N(n\text{-}Bu)_4][Cr^{III}(^{3,5}L_{S,S})_2(^{3,5}L_{S,S})]$ is 84.22°[17] whereas theoretically calculated value of the present tris complex of $[Cr(bdt)_3]^{3-}$ is 90.80°.The experimental S-Mn-S angles of the $[Mn^{IV}(Cl_2\text{-}bdt)_3][NEt_4]_2.CH_2Cl_2$ and $[Mn(S,S\text{-}C_6H_4)_3]^{2-}$ complexes was 85.2° and 92.28° respectively.[21] The present DFT calculation estimates 90.30°(±6.66) which are within the experimental range. The theoretical S-Fe-S angles in our calculation was 90.47°, in good agreement with experimentally measured value (90.72°) in the $[(n\text{-}Bu)_4N]_2[Fe(bdt)_2]^2$ complex.[28] Figure 2 shows the average M-S bond distance's d_{MS}'s and the angles of S-M-S triplets, θ_{SMS}'s. The fluctuation of bond length in d_{MS} was significant. All the bond angles θ_{SMS}'s however fluctuate significantly from their average values.

Binding Energy

In the present study we have examined the binding energies ΔE of metal-ligand for the considered trivalent metal ions and are presented in Table 2 and Figure 3.

The ΔE values have greatly exceeded the physiorption energy of 1,2-benzenedithiol adsorbed on metallic surface.

Lee et at. reported that a single 1,2-benzenedithiol molecule binds to a gold(111) surface and the binding energy was 6.0 kcal/mol.[29] A similar binding energy was reported in a DFT study of the adsorption of 1,2-benzenedithiol to silver(111) surface (3.30 kcal/mol).[30] The present ΔE values (476.58–486.36 kcal/mol) are one order of magnitude larger than these.

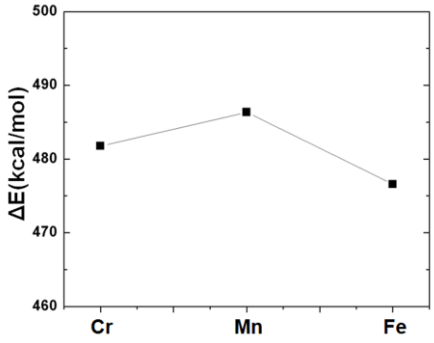

Fig. 3. Metal−ligand binding energies of the coordination complexes of tris $[M(bdt)_3]^{3-}$(M=Cr, Mn and Fe) complexes.

Interestingly, the previous DFT study of trivalent 1st row transition metal coordination with mussel adhesives proteins produced a one (1) order of magnitude increase in the cross-linking strength.[31] Figure 3 shows that the overall ΔE increases with increasing nuclear charge since the electrostatic interaction increased

Table 2. The calculated metal-ligand binding energies ΔE, zero point corrected binding energies ΔE_{ZPE}, thermal energies ΔE_{tots}, enthalpies ΔH_s and Gibbs free energies ΔG_s. The metal-ligand binding energies ΔE_s were corrected by using the thermodynamic conditions. All energies are of kcal/mol.

Metal	ΔE	ΔE_{ZPE}	ΔE_{tot}	ΔH	ΔG
Cr^{3+}	481.77	480.27	479.68	480.27	468.79
Mn^{3+}	486.36	485.04	484.31	484.90	474.08
Fe^{3+}	476.58	475.23	474.51	475.11	464.14

with increasing nuclear charge. The change in energy (ΔE) with the variation of Cr to Mn arises due to Jahn-Teller distortion. The dip in ΔE observed for Fe ion since Fe (III) has the d^5 electronic configuration. In this case, as all of the d orbitals are half filled occupied and the ligand-to-metal charge transfer is inefficient resulting in a reduced ΔE . The peak at Cr can be understood by noting that the ligand field stabilization should be largest for the d^3 configurations of a high-spin complex.

We have calculated the binding energies by including the zero-point energies (ZPEs), thermal energies, enthalpies and Gibbs free energies as summarized in Table 2. The vibrational, thermal, and entropic contributions to ΔE values turned out to be small, presumably due to the covalent nature of the metal ligand binding. The ZPE-, thermal-energy-, enthalpy-, Gibbs free energy corrected ΔE value was all within 6% of the uncorrected binding energies.

Spectroscopic Data

The TD-DFT calculations have been carried out to assign the electronic absorption bands on these complexes in gas phase optimized geometries using CAM-B3LYP/6-311+G(d,p)[27] level of theory. For studying excitation energies TD-DFT is a useful method. The electronic absorption spectra of complexes formed by Cr, Mn and Fe have been calculated and are presented in Figure 4. The metal complexes of transition metals normally show three different types of electronic excitation bands. The covered wavelength ranges are d-d transitions (300 - 1500 nm), metal-to-ligand charge-transfer (MLCT) and ligand-to-metal charge transfer (LMCT) transitions (200 - 500 nm).[32] The LMCT transitions known as intra-ligand charge transfer (ILCT) transitions are

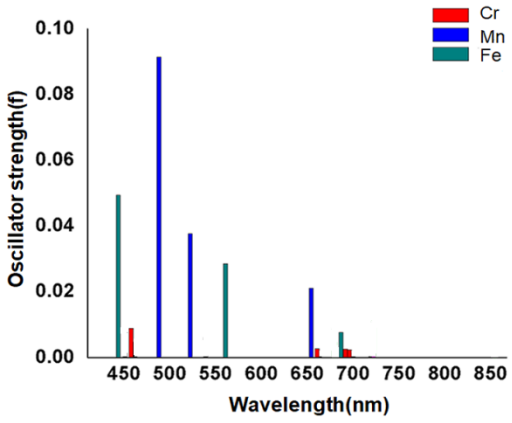

Fig. 4. UV−vis spectrum of the tris $[M(bdt)_3]^{3-}$(M=Cr, Mn and Fe) complexes obtained from the present calculation.

localized on the ligands, which occurs in the ultraviolet region. The n→ π and n → π* transitions (ILCT) are affected by the type of coordination. The calculated spectra of the model compound $[Cr(bdt)_3]^{3-}$ are 442 nm and two d-d transitions with comparatively low intensities in the visible region at 565 and 687 nm, in the octahedral chromium(III) complex. The $[Cr^{III}(^{3,5}L_{S,S})_3]^{3-}$ is the best described with a chromium(III) central ion (d^3, S=3/2) and three closed-shell dithiolate-(2-) ligands.[16] The calculated electronic spectra of the tris(dithiolene)chromium complex resemble closely to the corresponding tris(dioxolene)chromium complexes.[16]

For the trianion manganese $[tris(bdt)Mn]^{3-}$ complex, the absorption spectra were obtained at 453, 488 and 559 nm. These are in the range of experimentally measured absorption spectra (363, 508, 582 and 741 nm) of the $[Mn(S, S\text{-}C_6H_4)_3]^{2-}$ complex (where Mn is d^3) in CH_3CN solution.[20, 21] Our DFT calculated absorption spectra of the tris complex of iron

$[Fe(bdt)_3]^{3-}$ was found at 394, 546 and 650 nm respectively. The experimentally measured values of the complex of toluene-3,4-Dithiolate(tdt), $[Fe^{III}(cyclam)(tdt)](PF_6)$ complex, the monocation, shows absorption bands above 400 nm with maximum at 580 nm and 825 nm respectively.[22]

Electronic Properties

The electronic structure parameters are very important for understanding the molecular interactions with other species. In this study, we have calculated the electronic energy gap E_g, electron affinity A, electronegativity χ, chemical hardness η and chemical softness S for all the considered complexes. The results are presented in Table 3. The energetics of frontier molecular orbitals (FMOs), i.e., the HOMO and the LUMO energies are calculated. HOMO is considered as the outermost orbital containing electrons and acts as an electron donor. The electronic gap E_g considered the difference between HOMO and LUMO are depicted in Figure 5. Our investigation shows that E_g for the considered complexes gives the following trend: $Mn^{3+} < Cr^{3+} < Fe^{3+}$. The electron affinity and electronegativity values also follow the same trend (Table 3). From MOs plots (Figure 5), it can be concluded that the HOMO is mainly centered on metal coordinated sulfur atoms acts as a donor atoms whereas LUMO is on the metal surface. The energy gap E_g (between HOMO and LUMO) describes the molecular chemical properties. The energy gap also plays important role in predicting the polarizability of a molecule. The Smaller the energy gap, the more polarizable the molecule is.[24] The chemical stability of molecule can be also studied by the calculation of the chemical hardness η and chemical softness S as shown in Table 3.

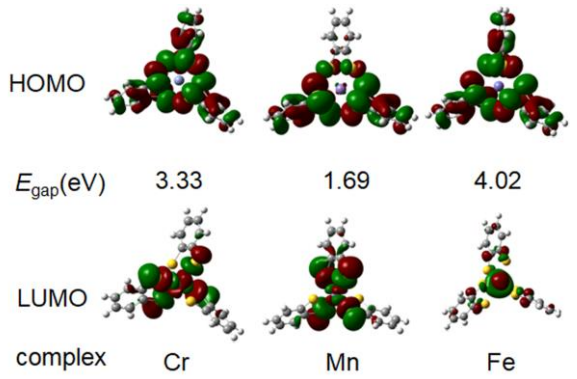

Fig. 5. Frontier MOs of the tris-complexes. The atoms H, C and S atoms are shown as white, gray, and yellow spheres, respectively. The orbital lobes shown in green and red represent the opposite phases.

Table 3. The electronic parameters calculated for the tris(benzene-1,2-dithiolato) complexes.

Metal	Cr^{3+}	Mn^{3+}	Fe^{3+}
E_g(eV)	3.33	1.69	4.02
Electron affinity A (eV)	-7.53	-5.80	-8.02
Electronegativity χ (eV)	5.87	4.95	6.01
Chemical hardness η (eV)	1.66	0.85	2.01
Chemical Softness S (eV)	0.30	0.59	0.25

The molecule is considered to be hard for large energy gap and soft for small energy gap. Therefore, among the $[tris(bdt)M]^{3-}$ (M=Cr, Mn and Fe) complexes, the $[tris(benzene\text{-}1,2\text{-}dithiolato)Fe]^{3-}$ complex is the hardest, followed by those of Cr^{3+}, Mn^{3+} and Fe^{3+} respectively.

Atomic Charges

The atomic charge on the metal ion has been calculated and summarized in Table 4.

Table 4. The calculated metal atomic charges were obtained using various charge schemes, NPA, MK, CHelpG and CHelp.

Metal	Atomic charge on metal			
	[a]NPA	[b]MK	[c]CHelpG	[d]CHelp
Cr^{3+}	1.251	2.242	2.083	1.690
Mn^{3+}	1.408	2.247	1.927	1.746
Fe^{3+}	1.513	2.034	1.875	1.618

[a]Natural Population Analysis (NPA).[33]

[b]MK(Merz-Singh-Kollman).[34]

[c]CHelpG (CHarges from ELectrostatic Potentials using a Grid based method).[35]

[d]CHelp methods to fit the electrostatic potential method.[36]

Four different schemes were used to calculate the charges: Natural Population Analysis (NPA),[33] MK[34], CHelpG[34], and CHelp[35] methods. The atomic charges vary according to the schemes. For example, according to NPA method, the charge is 1.513 for Fe, but 2.038 if MK scheme was used. The atomic charge decreased with increasing nuclear charge. The present float of the atomic charge deviated considerably from a uniform decrease with increasing nuclear charge. The consistent decrease of metal charge was attributed to the increased covalent nature of the metal−sulfur bond (hence, the charge transfer increased from the ligand to metal). For the present metal complexes, Fe^{3+}, however, has the minimum charge, regardless of the charge scheme. The trends of charge decreasing were also noticed as the metal atom was changed from Cr to Mn and Fe, according to the MK, CHelpG and CHelp schemes.

Natural Bond Orbital (NBO) Analysis

The electronic wavefunction is explained the occupied and unoccupied Lewis localized orbitals by NBO[36] analysis. NBO analysis affords the most accurate possible "natural Lewis structure". The entire molecular system is considered to be stable by concerning the delocalization of electron density(ED) between occupied Lewis-type and unoccupied non-Lewis NBOs. The strength of donor-acceptor interactions, $F_{ij}^{(2)}$ are evaluated by second-order perturbation theory. The second-order perturbation energy or the stabilization energy, $F_{ij}^{(2)}$ associated with the

delocalization from $i \rightarrow j$ was estimated using Equation (2).

$$\Delta E_{ij}^{(2)} = -q\frac{\left(\hat{F}_{ij}\right)^2}{\varepsilon_j - \varepsilon_i} \quad (2)$$

Where q the donor orbital occupancy, ε_i and ε_j are diagonal elements and $\hat{F}_{ij}$ is the off-diagonal NBO Fock matrix element. The energy values are proportional to the intensities of NBO interactions. The $F_{ij}^{(2)}$ values depend on the donating tendency from donor to acceptor NBOs. Table 5 summarizes the $F_{ij}^{(2)}$ values of the tris(bdt)$_3$ complexes of trivalent Cr, Mn and Fe complexes in gas phase for the important NBO interactions.

Table 5. Considerable donor–acceptor interaction energies of [M(benzene-1,2-dithiolato)$_3$]$^{3-}$ (M=Cr^{3+}, Mn^{3+} and Fe^{3+}) complexes.

Donor-acceptor interaction	Cr^{3+}	Mn^{3+}	Fe^{3+}
$LP_{S12} \rightarrow LP^*_M$	23.92	32.52	23.94
$LP_{S13} \rightarrow LP^*_M$	24.22	32.52	23.95
$LP_{S24} \rightarrow LP^*_M$	24.03	14.92	23.95
$LP_{S25} \rightarrow LP^*_M$	24.23	30.71	23.95
$LP_{S36} \rightarrow LP^*_M$	24.12	30.71	23.91
$LP_{S37} \rightarrow LP^*_M$	24.26	14.94	23.98

The most important interaction energies arises due to interactions between the S lone pair electrons (LP_S) and antibonding orbital of the M^{3+}(LP_M^*)(M^{3+}=Cr, Mn and Fe). According to Table 5, $F_{ij}^{(2)}$ values decrease with a decrease in the ionic sizes. Therefore, the greatest donor–acceptor interaction energies values are in the tris(benzene-1,2-dithiol) complex of trivalent Cr and decrease gradually to Fe^{3+} ion with an exception for Mn^{3+}. The donor-acceptor interaction value of Mn complex is higher due to Jahn-Teller effect. The strongest interaction in Cr- , Mn- and Fe- complex is $LP_{S37} \rightarrow LP_{Cr}$, $LP_{S12} \rightarrow LP_{Mn}$ and $LP_{S37} \rightarrow LP_{Fe}$ respectively (as shown in Table 5). The results of NBO analysis is a sign of charge transfer from the lone pair orbitals located on the donor atoms (S) to the central metal ions.

IV. Conclusions

The structural, energetic, spectroscopic and electronic properties of [M(benzene-1,2-dithiolato)$_3$]$^{3-}$ (M=Cr^{3+}, Mn^{3+} and Fe^{3+}) complexes have been investigated theoretically using quantum chemical calculations based on HF/DFT hybrid approach. The calculated geometrical parameters of the tris (benzene-1,2-dithiolato) complexes are in good agreement with the experimentally measurement values. The binding energies of the tris complexes range from 476.58–486.36 kcal mol^{-1} which are one order higher than physically adsorbed on metallic surface. The electronic spectra of the Cr, Mn and Fe complexes have been successfully calculated using TD-DFT formalism and facilitated a transition assignment. Calculating the electronic spectra of this tris-complexes, we have begun to make meaningful comparisons to experimental spectra for study into many tris(dithiolato) complexes of early transition metals. The investigation of electronic parameters including frontier molecular orbital energies suggests that Fe containing complexes have the largest band gap and therefore being the hardest among all. The NBO results reproduce charge transfer from lone pair orbital's on the donor atoms to the central metal ions. The present calculated metal-ligand binding energies, geometries, stability and atomic charges of the metal-benzene-1,2-ditholato(bdt^{2-}) complexes will be used for such modeling using molecular dynamics or Monte Carlo simulations.

References

1. Nomura, M., T. Cauchy and M. Fourmigué, 2010. Radical Cpni(Dithiolene) and Cpni(Diselenolene) Complexes: Synthetic Routes and Molecular Properties, *Coord. Chem.Rev.*, **254**, 1406-1418.
2. Beswick, C.L., J. M. Schulman and E. I. Stiefel, 2004. Structures and Structural Trends in Homoleptic Dithiolene Complexes. In *Dithiolene Chemistry*, *Prog. Inorg. Chem*., 55-110.
3. Kirk, M. L., R. L. McNaughton and M. E. Helton, 2004. The Electronic Structure and Spectroscopy of Metallo-Dithiolene Complexes. In *Dithiolene Chemistry*, John Wiley & Sons, Inc. 111-212.
4. Wang, K, 2004. Electrochemical and Chemical Reactivity of Dithiolene Complexes. In *Dithiolene Chemistry*, John Wiley & Sons, Inc. 267-314.
5. Sellmann, D. and J. Sutter, 2004. Dithiolenes in More Complex Ligands. In *Dithiolene Chemistry*, *Prog.Inorg. Chem*. 585-681.
6. Cassoux, P., L. Valade, H. Kobayashi,A. Kobayashi,R. A. Clarkand A. E. Underhill, 1991.Molecular Metals and Superconductors Derived from Metal Complexes of 1,3-Dithiol-2-Thione-4,5-Dithiolate (Dmit), *Coord. Chem. Rev.*, **110,** 115-160.
7. Ward, M. D.and J. A. McCleverty, 2002. Non-Innocent Behaviour in Mononuclear and Polynuclear Complexes: Consequences for Redox and Electronic Spectroscopic Properties, *J. Chem. Soc. Dalton Trans.*, 275-288.
8. Jørgensen, C. K. 1966. Differences between the Four Halide Ligands, and Discussion Remarks on Trigonal-Bipyramidal Complexes, on Oxidation States, and on Diagonal Elements of One-Electron Energy, *Coord. Chem. Rev.*, **1**, 164-178.
9. Lim, B. S., D. V. Fomitchevand R. H. Holm, 2001. Nickel Dithiolenes Revisited: Structures and Electron Distribution from Density Functional Theory for the Three-Member Electron-Transfer Series [Ni(S2c2me2)2]$^{0,1-,2}$, *Inorg. Chem.*, **40**, 4257-4262.
10. Sellmann, D., H. Binder, D. Häußinger, F. W. Heinemannand J. Sutter, 2000.Transition Metal Complexes with Sulfur Ligands: Part Cxliv. Square Planar Nickel Complexes with Nis4 Cores in Three Different Oxidation States: Synthesis, X-

Ray Structural and Spectroscopic Studies, *Inorg. Chim. Acta.*, **300–302**, 829-836.

11. Eisenberg, R. and H. B. Gray, 2011. Noninnocence in Metal Complexes: A Dithiolene Dawn, *Inorg. Chem.*, **50,** 9741-9751.
12. Periyasamy, G., N. A. Burton, I. H. Hillier, M. A. Vincent, H. Disley, J. McMasterand C. D. Garner, 2007. The Dithiolene Ligand-'Innocent' or 'Non-Innocent'? A Theoretical and Experimental Study of Some Cobalt-Dithiolene Complexes, *Faraday Discuss*. **135**, 469-488.
13. McCleverty, J. A. 2007. Metal 1,2-Dithiolene and Related Complexes, In *Prog. Inorg. Chem.*, John Wiley & Sons, Inc. 49-221.
14. Banerjee, P., S. Sproules, T. Weyherm uller, S. G. DeBeerand K. Wieghardt, 2009. Electronic Structure of the [Tris(dithiolene)chromium]^{z} (z = 0, 1-, 2-, 3-) Electron Transfer Series and Their Manganese(IV) Analogues. An X-ray Absorption Spectroscopic and Density Functional Theoretical Study, *Inorg. Chem*., **48**, 5829–5847.
15. Davison, A., N. Edelstein, R. H. Holmand A. H. Maki, 1964. Synthetic and Electron Spin Resonance Studies of Six-Coordinate Complexes Related by Electron-Transfer Reactions, *J. Am. Chem. Soc.*, **86**, 2799-2805.
16. McCleverty, J. A., J. Locke, E. J. Wharton, and M. Gerloch, 1968. Transition-Metal Dithiolene Complexes. Part (IV). Trisdicyano-1,2-Dithiolene Complexes of First-Row Metals, and of Molybdenum and Tungsten, *J. Chem. Soc. A*, 816-823.
17. Kapre, R. R., E. Bothe, T. Weyhermüller, G. S. DeBeer,N. Muresan and K. Wieghardt, 2007. Electronic Structures of Tris(Dioxolene)Chromium and Tris(Dithiolene)Chromium Complexes of the Electron-Transfer Series [Cr(Dioxolene)$_3$]^{Z} and [Cr(Dithiolene)$_3$]^{Z} (Z = 0, 1−, 2−, 3−). A Combined Experimental and Density Functional Theoretical Study, *Inorg. Chem.*, **46**, 7827-7839.
18. Sproules, S., F. L. Benedito, E. Bill, T. Weyhermüller, G. S. DeBeerand K. Wieghardt, 2009. Characterization and Electronic Structures of Five Members of the Electron Transfer Series [Re (Benzene-1, 2-Dithiolato)$_3$]^{Z} (Z = 1+, 0, 1−, 2−, 3−): A Spectroscopic and Density Functional Theoretical Study, *Inorg. Chem.*, **48**, 10926-10941.
19. Wharton, E. J.and J. A. McCleverty, 1969. Transition-Metal Dithiolenes. Part Viii. Metal Complexes of Tris-Tetrachlorobenzene-1,2-Dithiol and Related Compounds, *J. Chem. Soc. A*, 2258-2266.
20. Stiefel, E. I., L. E. Bennett, Z. Dori , T. H. Crawford, C. Simoand H. B. Gray, 1970. Synthesis and Characterization of Tris(Maleonitriledithiolato)Metalates, *Inorg. Chem.*,**9**, 281-286.
21. Lin, C.-H., C.-G. Chen,M.-L.Tsai, G.-H.Leeand W.-F. Liaw, 2008.Monoanionic {Mn(NO)}$_5$ and Dianionic {Mn(NO)}$_6$ Thiolatonitrosylmanganese Complexes: [(NO)Mn(L)$_2$]− and [(NO)Mn(L)$_2$]$_2$− (Lh2 = 1,2-Benzenedithiol and Toluene-3,4-Dithiol), *Inorg. Chem.*, **47**, 11435-11443.
22. Milsmann, C., G. K. Patra, E. Bill, T. Weyhermüller, G. S. DeBeer and K. Wieghardt, 2009.Octahedral Monodithiolene Complexes of Iron: Characterization of S,S′-Coordinated Dithiolate(1−) II Radical Monoanions: A Spectroscopic and Density Functional Theoretical Investigation, *Inorg. Chem.*, **48**, 7430-7445.
23. Becke, A. D.1993. Density-Functional Thermochemistry. III. The Role of Exact Exchange, *J. Chem. Phys.*, **98**, 5648-5652.
24. Frisch M. J., G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrze. wski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J Fox, 2010. Gaussian 09, Revision B.01. Gaussian Inc., Wallingford.
25. Myradalyyev, S., T. Limpanuparb, X. Wangand H. Hirao, 2013. Comparative Computational Analysis of Binding Energies between Several Divalent First-Row Transition Metals (Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) and Ligands (Porphine, Corrin, and Tmc), *Polyhedron*, **52**, 96-101.
26. Matin, M. A., M. M. Islam, T. Bredow and M. A. Aziz, 2017. The Effects of Oxidation States, Spin States and Solvents on Molecular Structure, Stability and Spectroscopic Properties of Fe-Catechol Complexes: A Theoretical Study, *Advances in Chemical Engineering and Science*, **7**, 137-153.
27. Yanai, T., D. P. Tewand N. C. Handy, 2004. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (Cam-B3lyp), *Chem. Phys. Lett.*, **393,** 51-57.
28. Cerdeira, A. C., D. Simão, I. C. Santos, A. Machado, L. C. J. Pereira, J. C. Waerenborgh, R. T. Henriquesand M. Almeida, 2008. (N-Bu4n)[Fe(Cbdt)$_2$]: Synthesis, Crystal Structure and Magnetic Characterisation of a New Fe(III) Bisdithiolene Complex, *Inorg. Chimica Acta.*, **361**, 3836-3841.
29. Lee, Y. J., I. C. Jeon, W.-K. Paik and K. Kim, 1996. Self-Assembly of 1,2-Benzenedithiol on Gold and Silver: Fourier Transform Infrared Spectroscopy and Quartz Crystal Microbalance Study, *Langmuir*,**12**, 5830-5837.
30. Matin, M. A., R. K. Chitumalla, M. Lim, X. Gaoand J. K. Jang, 2015. Density Functional Theory Study on the Cross-Linking of Mussel Adhesive Proteins, *J. Phys. Chem. B,* **119,** 5496−5504.
31. Mohammed, L. S., I. S. Hamza, F. R. M. AL-Deen andB. R. J. Muhyedeen, 2014. DFT and MP2 Study of Pd(II) and Ni(II) PhCN, DMSO and Dithiooxamide Complexes—Part II: Theoretical, *J. Applicable Chem.*, **3**, 2102-2122.
32. Reed, A. E., R. B. Weinstockand F. Weinhold, 1985. Natural Population Analysis, *J. Chem. Phys.*, **83**, 735-746.
33. Singh, U. C. and P. A. Kollman, 1984. An Approach to Computing Electrostatic Charges for Molecules, *J. Comput. Chem.*, **5**, 129-145.
34. Breneman, C. M.and K. B. Wiberg, 1990.Determining Atom-Centered Monopoles from Molecular Electrostatic Potentials. The Need for High Sampling Density in Formamide Conformational Analysis, *J. Comput. Chem.*, **11**, 361-373.
35. Chirlian, L. E. and M. M. Francl, 1987. Atomic Charges Derived from Electrostatic Potentials: A Detailed Study, *J. Comput. Chem.*, **8**, 894-905.
36. Weinhold, F. and C. R. Landis, 2001. Natural Bond Orbitals and Extensions of Localized Bonding Concepts, *Chem. Edu. Res. Pract.*, **2**, 91-104.