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Investigation of Structural and Electronic Properties of $[Tris(Benzene-1,2-Dithiolato)M]^{3-}$ (M = V, Cr, Mn, Fe and Co) Complexes: A Spectroscopic and Density Functional Theoretical Study

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Abstract

In this study, the first raw transition metals from V to Co complexes with benzene-1,2-dithiolate (L^{2-}) ligand have been studied theoretically to elucidate the geometry, electronic structure and spectroscopic properties of the complexes. Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT) methods have been used. The ground state geometries, binding energies, spectral properties (UV-vis), frontier molecular orbitals (FMOs) analysis, charge analysis and natural bond orbital (NBO) have been investigated. The geometrical parameters are in good agreement with the available experimental data. The metal-ligand binding energies are 1 order of magnitude larger than the physisorption energy of a benzene-1, 2-dthiolate molecule on a metallic surface. The electronic structures of the first raw transition metal series from V to Co have been elucidated by UV-vis spectroscopic using DFT calculations. In accordance with experiment the calculated electronic spectra of these tris complexes show bands at 522, 565, 559, 546 and 863 nm for V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+} respectively which are mainly attributed to ligand to metal charge transfer (LMCT) transitions. The electronic properties analysis shows that the highest occupied molecular orbital (HOMO) is mainly centered on metal coordinated sulfur atoms whereas the lowest unoccupied molecular orbital (LUMO) is mainly located on the metal surface. From calculation of intramolecular interactions and electron delocalization by natural bond orbital (NBO) analysis, the stability of the complexes was estimated. The NBO results showed significant charge transfer from sulfur to central metal ions in the complexes, as well as to the benzene.

The calculated charges on metal ions are also reported at various charge schemes. The calculations show encouraging agreement with the available experimental data.

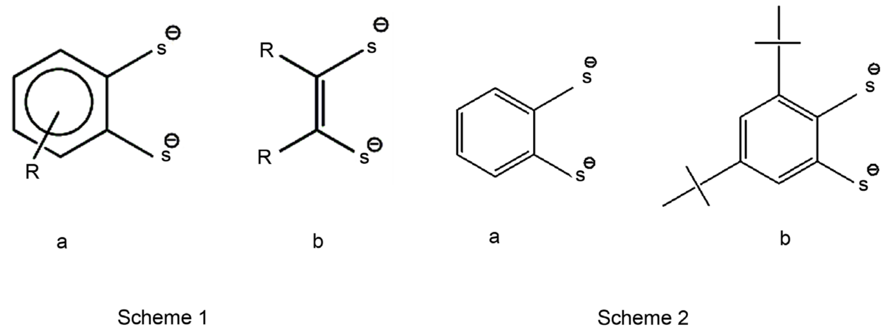
Keywords

Transition Metal, Time Dependent Density Functional Theory (TD-DFT), Binding Energy, Spectroscopy, Electronic Properties, Tris(Benzene-1,2-Dithiolato), Coordination Complex

1. Introduction

A metalloligand can be defined as a complex that contains several potential donor groups that enable coordination to a variety of metal ions. Among the well-established metalloligands, interest in the chemistry of dithiolene complexes has increased tremendously in the past five decades since their initial popularity in the 1960s [1]. Early interest focused primarily on the structural geometries [2], redox properties [3] [4] [5] and magnetic properties [6] of this class of complexes, which arise from the noninnocent property [7] [8] of dithiolenes. Ward and McCleverty [7] have pointed out that the term noninnocent is applied properly when it is referred to a particular combination of the metal and the ligand rather than to redox-active ligands only.

By taking into account the dithiolene ligands, two main classes of molecules can be distinguished. Such as the non-benzenoid dithiolenes, where the p-delocalization is confined in the dithiolene core [9] and benzenoid systems, where the p-delocalization is extended to the aromatic ring [10]. Dithiolene ligands often are referred to as noninnocent when coordinated to transition metals [11] [12]. Let us turn our attention to the chemistry of tris (benzene-1,2-dithiolato) complexes. In contrast to their well-studied redox behavior, bond-making and bond-breaking reactivities of tris(benzene-1,2-dithiolato) complexes have been paid less attention [4]. The term "dithiolene" (L) will be used for two classes of ligands as shown in scheme 1(a) and 1(b) of **Figure 1** [13], irrespective of their "true" oxidation level as monoanionic radical $(L\bullet)^{1-}$, or as dianionic, closed-shell $(L^{Red})^{2-}$ ligand or as neutral 1,2-dithioketone $(L^{Ox})^0$ [14]. Previously, Sproules *et al.* have calculated the geometry and electronic structures of the $[V(L)_3]^z$ (z = 1+, 0, 1-, 2-, 3-, 4-) series by using density functional theory (DFT) and explored the stability of a trigonal prismatic structure over an octahedral one [15] [16]. No dianion containing ligand as shown in scheme 2(a) [13] in **Figure 1** has been isolated previously. The most reduced, trianionic $[Cr(dithiolene)_3]^{3-}$ form with an S = 3/2 ground state has been isolated only as $[PPh_4]_3$ $[Cr(mnt)_3]$ salt [17] [18] (as shown in scheme 2(b) [13] in **Figure 1**). Wieghardt *et al.* and others have successfully elucidated the electronic structures for the $[Cr(L)_3]^z$ (z = 0, 1-, 2-, 3-) [19] [20] electron transfer series and found a Werner-type compound with dithiolates. The following dianionic manganese



Scheme 1 Scheme 2

Figure 1. Binding schemes of metals coordination complexes [13].

(IV) complexes have also been isolated: $[PPh_4]_2$ $[Mn(mnt)_3]$ and $[N(nBu)_4]_2$ $[Mn(Cl_4\text{-}bdt)_3]$ both of which possess an $S = 3/2$ ground state [13] [18] [21] and only very recently $(PNP)_2$ $[Mn(bdt)_3]$ (PNP^+ = bis(triphenylphosphine)iminium) became the first structurally characterized tris(dithiolene)manganese compound [22]. They are isoelectronic with the corresponding trianions $[Cr(dithiolene)_3]^{3-}$. The corresponding tris(benzo-1,2-dithiolato)chromium complex $[N(n\text{-}Bu)_4]$ $[Cr^{III}(^{3,5}L^{\bullet}_{S,S})_2(^{3,5}L_{S,S})](S)_{1/2})$ has also been isolated: $(^{3,5}L_{S,S})^{2-}$ represents the closed-shell dianion 3,5-di-tert-butylbenzene-1,2-dithiolate(2-), and $(^{3,5}L^{\bullet}_{S,S})^{1-}$ is its monoanionic ∂ radical complex. Milsmann *et al.* reported on a similar series of iron(III) complexes, where a redox-innocent, closed-shell cyclam ligand (1,4,8,11-tetraazacyclotetradecane) and a potentially redox-noninnocent dithiolene ligand such as toluene-3,4-dithiolate or maleonitrile dithiolate are coordinated to a low-spin ferric ion, affording the octahedral monocations [23] [24]. Only a few such complexes containing a cis-$[Fe^{III}N_4S_2]$ core structure have been reported previously: $[Fe^{III}(L\text{-}N_4Me_2)\text{-}(bdt)]^+$($L\text{-}N_4Me_2$ = N,N_0-dimethyl-2,11-diaza [3.3]-(2,6)pyridinophane) [25], $[Fe^{III}(tripod)(bdt)]^+$ tripod = tris [(2-pyridyl)methyl]amine, and bis [(2-pyridyl)methyl] [(1-methylimidazole-2-yl)-methyl]amine [26] [$(bdt)^{2-}$ is unsubstituted benzene-1,2-dithiolate(2-)]. The former low-spin ferric compound exhibits an unusual thermal spin transition from an $S = 1/2$ low-spin ground state to an $S = 3/2$ intermediate-spin excited state [25]. $[Co^{III}(trien)(3,5\text{-}DTBsq\bullet)]Cl_2$ ($S = 1/2$) is one of the earliest examples (1976) [27], whereas $[Cr^{III}(tren)\text{-}(3,6\text{-}DTB_{sq}\bullet)](PF6)_2$ is probably the most thoroughly studied [28] [29]. Milsmann *et al.* employed the DFT to establish the presence of an S,S_0-coordinated benzene-1,2-dithiolate(1-) π radical in the two species $[Co^{III}(tren)(tmsdt\bullet)]^{2+}$ and $[Cr^{III}(tren)(tmsdt\bullet)]^{2+}$ [30].

The bis(dithiolate) metal and tris(dithiolate) metal complexes have been extensively studied [2] and only very recently, the spectroscopic methods like S K-edge X-ray absorption spectroscopy have been developed to the extent that the presence of a benezene-1,2-dithiolate(1-) π radical in a coordination compound can be established beyond doubt [31].

In the present study, we have performed systematically a theoretical investigation on the structures, binding energies, spectroscopic and electronic properties of $[M(bdt)_3]^{3-}$ (M = V, Cr, Mn , Fe and Co) which contains bdt^{2-} = benzene-1,2-dithiolate ligand (as shown in scheme 2(a) of **Figure 1**) in the gas phase using the first principles HF/DFT hybrid approach. The natural bond orbital (NBO) analysis on the tris complexes of benzene-1,2-ditholate (bdt^{2-}) complexes including V^{3+} to Co^{3+} is reported. These findings help us understand the thermodynamic behavior of each system as a function of the quantum chemistry descriptors.

2. Computational Details

We have studied the $[tris(bdt)M]^{3-}$ complexes where M = V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+} with the bdt^{2-} = benzene-1,2-dithiolate ligand (**Figure 2**). The dithiolene was taken to be oxidized (dithiolate). The compounds are theoretically examined by means of HF/DFT hybrid approach B3LYP [32] with the 6-311G(d,p) basis sets in gas phase. All the calculations were performed using Gaussian 09 program [33]. GaussView 5.0.8 was used for the visualization of the structures and simulated vibrational spectra. We have considered dithiolate as a weak-field ligand, the metal coordination complex was assumed to have high spin multiplicity. Geometry optimization was taken to be converged if the maximum atomic force was smaller than 0.00045 Hartree/Bohr and there was no imaginary frequency. No symmetry was imposed in all the calculations. After optimizing the geometry of the coordination complexes, the metal-ligand binding energies were calculated as [34] [35]

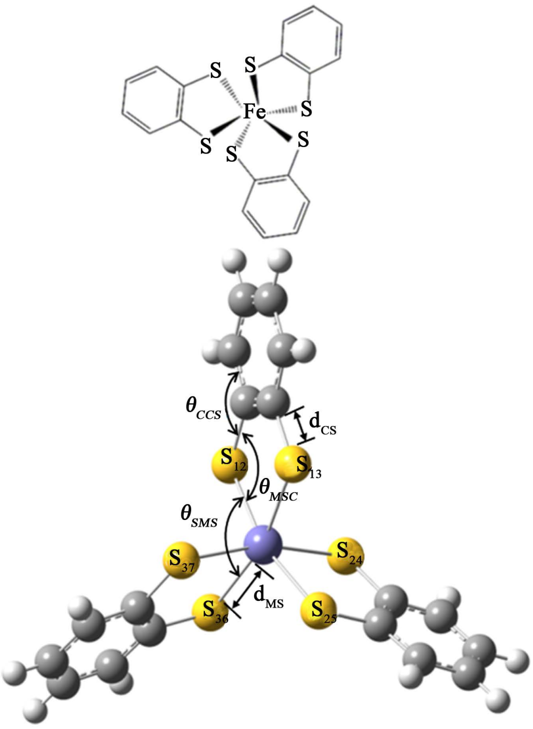


Figure 2. Metal binding to benzene-1,2-dithiolate, optimized geometry of the $[Fe(bdt)_3]^{3-}$ complex.

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

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, ΔE refers to the binding energy per ligand. The energy was calculated by optimizing the geometry of the complex and the ligand separately.

Electronically excited state calculation was carried out to compute the UV-Vis of the $[M(\text{dithiolate})_3]^{3-}$ complexes of V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+}. The vertical excitation energies were obtained using the time-dependent DFT at the level of CAM-B3LYP [36]/6-311 + G(d,p) after the ground state optimization.

3. Results and Discussion

3.1. Structural Analysis

After full optimization, the structural parameters such as bond distances and angles of the $[\text{tris(bdt)}M]^{3-}$ ($M = V^{3+}$, Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{3+}) complexes are calculated. The calculated geometrical parameters as depicted in **Figure 2** and **Table 1**. The metal and the sulfur atoms are 2.51 Å apart for V, 2.48 Å for Cr, 2.55 Å for Mn, 2.54 Å for Fe and 2.60 Å for Co. The DFT and X-ray analysis of the tris-dithiolate complexes reported V-S distances of 2.337 Å and 2.350 Å respectively [15], for Cr-S distances were 2.283 Å and 2.299 Å [19]. The experimental average Cr-S distance in the monoanion of the tris complexes at 2.299 ± 0.003 Å, is 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 $[\text{tris(bdt)}Cr]^{3-}$ 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 $[Mn(\text{bdt})_3]^{2-}$ complex [13]. The DFT calculated $[\text{tris(bdt)}Mn]^{3-}$ complex is 2.55 (±0.17) and 0.17 Å higher than experiment one [13]. 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 $[Fe^{III}(\text{cyclam})(\text{tdt})]$ (PF_6) where the Fe-S distance is 2.25Å [23]. The experimental value deviates due to present

Table 1. Geometric parameters of the tris(benzene-1,2-dithiolato) complexes of various transition metal ions. The metal-S bond lengths (d_{MS}'s), C-S bond lengths (d_{CS}'s) and the S-M-S bending angles (θ_{SMS}'s), the C-C-S bending angles (θ_{CCS}'s) and Metal-S-C bending angles (θ_{MSC}'s) are shown for trivalent metal ions ranging from V^{3+} to Co^{3+}. The average values are listed with the standard deviations in parentheses.

Metal	d_{MS} (Å)	d_{CS} (Å)	θ_{SMS} (˚)	θ_{CCS} (˚)	θ_{MSC} (˚)
V^{3+}	2.51 (±0.04)	1.76 (±0.00)	90.46 (±7.73)	119.93 (±0.26)	106.88 (±0.87)
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)
Co^{3+}	2.60 (±0.09)	1.75 (±0.01)	90.51 (±9.42)	119.14 (±0.15)	106.65 (±1.91)

bulky substitute group cyclam. The theoretically calculated average Co-S bond lengths is 2.60 Å for the tris complex whereas experimentally measured value was found 2.25 Å [30] of the complex $[Co^{III}(tren)(bdt)](PF_{6)1/2}(Cl)_{1/2}\cdot H_2O$. This deviation was due to present bulky groups tren and bdt in the complex $[Co^{III}(tren)(bdt)](PF_{6)1/2}(Cl)_{1/2}\cdot H_2O$.

The present S-M-S angles were significantly larger than the previous X-ray crystal structures. The average angle is nearly octahedral angle 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˚ [19] 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 $[Mn^{IV}(Cl_2\text{-}bdt)_3]$ $[NEt_4]_2\cdot CH_2Cl_2$ and $[Mn(S,S\text{-}C_6H_4)_3]^{2-}$ complexes was 85.2˚ and 92.28˚ respectively [13] 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 [37]. The DFT calculated average bond angle S-Co-S was found 90.51˚. 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 in d_{MS} was significant. All the, θ_{SMS}'s however fluctuate significantly from their average values.

3.2. Binding Energy

In this study we have investigated the metal-ligand binding energies, ΔE, of the trivalent metal ions considered and are presented in Figure 3 and Table 2. The ΔE values have greatly exceeded the physiorption energy of benzene-1,2-dithiol adsorbed on metallic surface. Lee *et al.* reported that a single benzene-1,2-dithiol molecule binds to a gold (111) surface with a binding energy of 6.0 kcal/mol [38]. A similar energy was reported in a DFT study of the adsorption of benzene-1, 2-dithiol to silver (111) surface (3.30 kcal/mol) [38]. The present ΔE

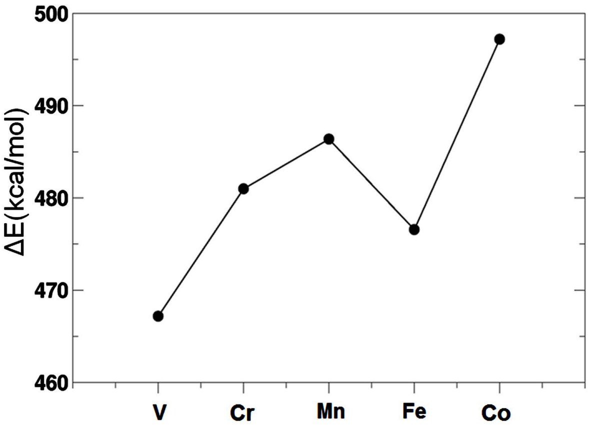


Figure 3. Metal-ligand binding energies of the coordination complexes of various metal ions for tris $[M(bdt)_3]^{3-}$ (M = V to Co) complexes.

Table 2. The calculated metal-ligand binding energies ΔE, zero point corrected binding energies, ΔE_{ZPEs}, thermal energies ΔE_{tots}, enthalpies ΔHs and Gibbs free energies ΔGs. The metal-ligand binding energies ΔEs were corrected by using the thermodynamic condition, 298.15 K and 1 atm. All energies are in units of kcal/mol.

Metal	ΔE (kcal·mol^{-1})	ΔE_{ZPE} (kcal·mol^{-1})	ΔE_{tot} (kcal·mol^{-1})	ΔH (kcal·mol^{-1})	ΔG (kcal·mol^{-1})
V^{3+}	467.19	465.74	465.10	467.19	436.90
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
Co^{3+}	497.20	537.56	495.24	495.83	485.76

values (467.19 - 497.20 kcal/mol) are an order of magnitude larger than these. Interestingly, the previous study also reported that trivalent 1st row transition metal coordination produced a 1 (one) order of magnitude increase in the cross-linking strength [39]. **Figure 3** shows that the overall ΔE increases with increasing nuclear charge due to the increased electrostatic interaction with increasing nuclear charge. The decreasing ΔE with changing Cr to Mn arises from the Jahn-Teller distortion of the metal complex. The dip in ΔE observed for Fe is ascribed to the d^5 configuration of Fe (III). In this case, as all of the d orbitals are occupied, 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. Regardless of the metal ion, the ZPE-, thermal-energy-, enthalpy-, Gibbs free energy corrected ΔE value were all within 6% of the uncorrected binding energies.

3.3. Spectroscopic Data

In order to assign the electronic absorption bands of the complexes, TD-DFT calculations have been carried out on these complexes in gas phase optimized geometries at the CAM-B3LYP [34]/6-311 + G(d,p) level of theory. TD-DFT is a useful method for studying excitation energies, and its application has increased in the recent years. The electronic absorption spectra of complexes formed by V, Cr, Mn, Fe and Co have been calculated. The calculated electronic absorption spectra of the tris complexes formed by V to Co are presented in **Figure 4** and **Table 3**. Transition metal complexes generally show three types of electronic excitation bands which cover a wide wavelength range: d-d (crystal-field) transitions (300 - 1500 nm); metal-to-ligand charge-transfer (MLCT) and ligand-to-metal charge transfer (LMCT) transitions (200 - 500 nm) [40]. The LMCT transitions localized on the ligands commonly known as intra-ligand charge transfer (ILCT) transitions, which regularly occur in the ultraviolet region. ILCT results

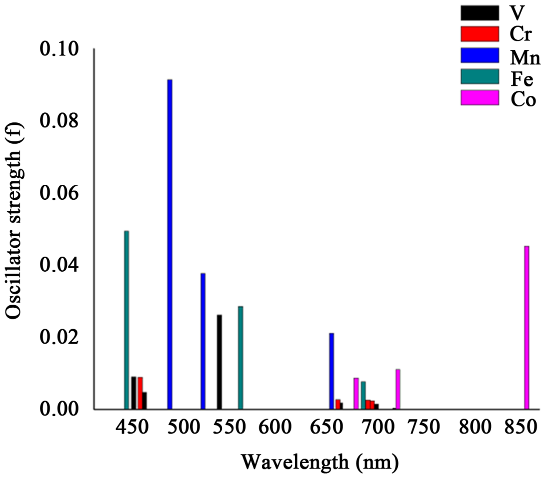


Figure 4. UV-vis spectrum of the tris $[M(bdt)_3]^{3-}$ (M = V to Co) complexes obtained from the present calculation.

Table 3. Electronic spectra of $[tris(bdt)M]^{3-}$ (M = V, Cr, Mn, Fe and Co) complexes.

M	λ_{max} (nm)
V	431,448,522,691
Cr	442,565,687
Mn	453,488,559
Fe	394,546,656
Co	687,731,863

from n → π and n → π* transitions and is affected by the type of coordination. The calculated spectra of the model compound $[V(bdt)_3]^{3-}$ are 431, 448, 522 and 691 respectively whereas in $[PPh_4]_2$ $[V(bdt)_3]$ where vanadium has (IV) oxidation state showed the absorption maxima at 878, 681, 553, 426 and 327 respectively [15]. The calculated spectra of the model compound $[Cr(bdt)_3]^{3-}$ are 442 nm and two d-d transitions with relatively low intensities in the visible region at 565 and 687 nm, as typical for chromium (III) octahedral complex. The electronic structure of this complex is best described as $[Cr^{III}(^{3,5}L_{S,S})_3]^{3-}$ with a chromium (III) central ion (d^3, S = 3/2) and three closed-shell dithiolate-(2-) ligands [19]. The electronic spectra of these tris(dithiolene)chromium complexes resemble closely those reported previously for the corresponding tris(dioxolene) chromium complexes [19].

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 [22]. 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 [23]. The calculated absorption spectra of the Co tris complex $[tris(bdt)Co]^{3-}$ was found at 687, 731 and 863 nm which are overestimated compared to the measured spectra of the $[Co(III)(tren)(bdt)](PF_6)_{1/2}(Cl)_{1/2}\cdot H_2O$ complex at 463 nm and 646 nm respectively [30]. This discrepancies due to present bulky groups tren and bdt of the complex $[Co(III)(tren)(bdt)](PF_6)_{1/2}(Cl)_{1/2}\cdot H_2O$.

3.4. Electronic Properties

The electronic structure parameters are very important for understanding the molecular interactions with other species. We have calculated the electronic energy gap *Eg*, electron affinity *A*, electronegativity χ, chemical hardness η and chemical softness *S* for all the considered complexes. The results are presented in **Table 4**. The energetics of frontier molecular orbitals (FMOs), *i.e.*, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies are calculated. HOMO, which can be considered of as the outermost orbital containing electrons, tends to give these electrons and acts as an electron donor. On the other hand LUMO can be considered as the innermost orbital containing free places and accepts electrons. The difference between HOMO and LUMO provides the electronic gap Eg as depicted in **Figure 5**. Our investigation shows that Eg for the considered complexes increases in the following direction $Mn^{3+} > V^{3+} > Cr^{3+} > Co^{3+} > Fe^{3+}$. The electron affinity and electro negativity values also follow the same trend (**Table 4**). From MOs plots (**Figure 5**), it can be concluded that the HOMO is mainly centered on metal coordinated sulfur atoms (which acts as a donor atoms) whereas LUMO is mainly located on the metal surface.

The Energy gap characterizes the molecular chemical stability, and it is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The energy gap between HOMO and LUMO (E_g) also plays important role in predicting the polarizability of a molecule. Smaller the energy gap, the more polarizable the molecule is. 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 4**. Large energy gap is an indication of hard molecule and small energy gap is the sign of soft molecule. Therefore, among the $[tris(bdt)M]^{3-}$ (M = V, Cr, Mn, Fe and Co) complexes, the

Table 4. The electronic parameters calculated for the tris(benzene-1,2-dithiolato) complexes of considered transition metals.

Metal	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}
E_g(eV)	2.62	3.33	1.69	4.02	3.82
Electron affinity *A* (eV)	−6.97	−7.53	−5.80	−8.02	−7.88
Electronegativity χ (eV)	5.66	5.87	4.95	6.01	5.97
Chemical hardness (eV)	1.31	1.66	0.85	2.01	1.91
Chemical softness *S* (eV)	0.38	0.30	0.59	0.25	0.26

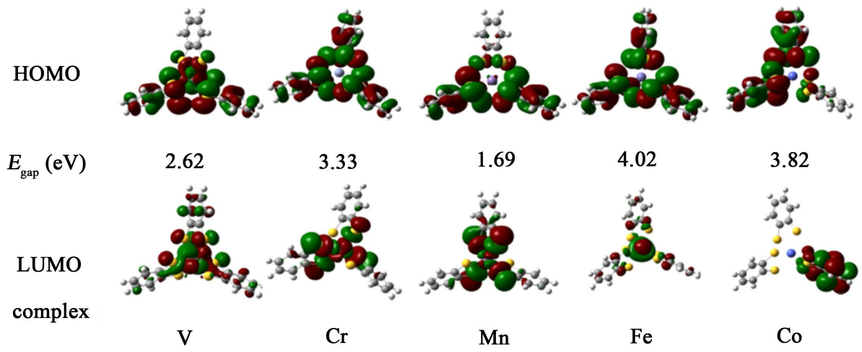


Figure 5. Frontier MOs of the tris(benzene-1,2-dithiolato) complexes. The H, C and S atoms are shown as white, gray, and yellow spheres, respectively. The orbital lobes shown in green and red represent the opposite phases.

[tris(benzene-1,2-dithiolato)Fe]$^{3-}$ complex is the hardest, followed by those of Co^{3+}, Cr^{3+}, V^{3+} and Mn^{3+} respectively. The soft molecules are more polarizable than the hard ones as they need small energy for excitation.

3.5. Atomic Charges

The atomic charge on the metal ion has been calculated and summarized in Table 5. Four different schemes were used to calculate the charges: Natural Population Analysis (NPA) [41], MK [42] (Merz-Singh-Kollman), CHelpG [43] (Charges from ELectrostatic Potentials using a Grid based method), and CHelp [44] methods. The atomic charges vary according to the schemes. For example, according to NPA method, the charge is 1.513 for Fe, but the charge is 2.038 if the MK scheme was used. The atomic charge decreased with increasing nuclear charge. The present drift of the atomic charge deviated considerably from a uniform decrease with increasing nuclear charge. The uniform decrease 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 complexes, however, the atomic charge was a minimum for Co^{3+}, regardless of the charge scheme. The charge also decreased as the metal atom was changed from Cr to Mn and Fe, according to the MK, CHelpG and CHelp schemes.

3.6. NBO Analysis

In the natural bond orbital (NBO) [45] analysis, electronic wave function is explained in terms of occupied Lewis and unoccupied Lewis localized orbitals. The delocalization of electron density(ED) between occupied Lewis-type and unoccupied non-Lewis NBOs correspond to stabilizing donor-acceptor interactions that contribute predominantly to the stabilization of the entire molecular system. The strength of donor-acceptor interactions, $E_{ij}^{(2)}$, are evaluated by second-order perturbation theory. For each donor (*i*) and acceptor (*j*) in the complexes, the stabilization energy or second-order perturbation energy, $E_{ij}^{(2)}$ associated with the delocalization from $i \rightarrow j$ was estimated using Equation (2).

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

In Equation (2), q is the donor orbital occupancy, ε_i and ε_j are diagonal elements (orbital energies) of donor and acceptor NBOs respectively and $\hat{F}_{ij}$ is the off-diagonal NBO Fock matrix element. Values of this energy are proportional to the intensities of NBO interactions or to the extent of intramolecular charge transfer (ICT) within a molecular entity. The greater the electron donating tendency from donor to acceptor NBOs is, the larger the $E_{ij}^{(2)}$ values and the more intense the interaction between the electron donors and the electron acceptors are. Table 6 summarizes the $E_{ij}^{(2)}$ values of the tris(benzene-1,2-dithiol) complexes of trivalent V, Cr, Mn, Fe and Co complexes in gas phase for the important NBO interactions. The most important interaction energies of these complexes are due to interactions between the lone pair electron of the S atom(LP_0) and antibonding orbital of the M^{3+}(LP_M^*) (M^{3+} = V, Cr, Mn, Fe and Co). According to Table 6, $E_{ij}^{(2)}$ values decrease with a decrease in the ionic sizes. Therefore, donor-acceptor interaction energies are the greatest values in the tris(benzene-1,2-dithiol) complex of trivalent V ion except Mn. The donor-acceptor interaction value of Mn complex is higher due to Jahn-Teller

Table 5. Atomic charges on the metal atoms obtained using various charge schemes, NPA, MK, CHelpG and CHelp schemes.

Metal	Atomic charge on metal			
	[a]NPA	[b]MK	[c]CHelpG	[d]CHelp
V^{3+}	1.224	1.914	1.846	1.796
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
Co^{3+}	1.362	1.944	1.636	1.598

[a]Natural Population Analysis (NPA) [41]. [b]MK(Merz-Singh-Kollman) [42]. [c]CHelpG (CHarges from ELectrostatic Potentials using a Grid based method) [43]. [d]CHelp methods to fit the electrostatic potential method [44].

Table 6. Significant donor-acceptor interaction energies of $[M(\text{benzene-1,2-dithiolato})_3]^{3-}$ ($M = V^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}$ and Co^{3+}) complexes.

Donor-acceptor interaction	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Co^{3+}
$LP_{S12} \rightarrow LP^*_M$	28.15	23.92	32.52	23.94	19.35
$LP_{S13} \rightarrow LP^*_M$	25.40	24.22	32.52	23.95	17.07
$LP_{S24} \rightarrow LP^*_M$	25.37	24.03	14.92	23.95	17.07
$LP_{S25} \rightarrow LP^*_M$	28.06	24.23	30.71	23.95	19.34
$LP_{S36} \rightarrow LP^*_M$	26.48	24.12	30.71	23.91	23.58
$LP_{S37} \rightarrow LP^*_M$	26.21	24.26	14.94	23.98	23.58

effect. The strongest interaction in V-complex is $LP_{S12} \rightarrow LP_{V,}$ in Cr-complex is $LP_{S37} \rightarrow LP_{Cr}$, in Mn-complex is $LP_{S12} \rightarrow LP_{Mn}$. In Fe-complex the strongest interaction is $LP_{S37} \rightarrow LP_{Fe}$ and in Co-complex is $LP_{S36} \rightarrow LP_{Co}$. The results of NBO analysis reflect generally charge transfer from lone pair orbitals located on the donor atoms S to the central metal ions. NBO analysis provides the most accurate possible "natural Lewis structure".

4. Conclusion

The structural, energetic, spectroscopic and electronic properties of $[M(\text{benzene-1,2-dithiolato})_3]^{3-}$ ($M = V^{3+}$, Cr^{3+}, Mn^{3+}, Fe^{3+} and Co^{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 experimental measurement values. The binding energies of the tris complexes range from 467.19 - 497.20 $kcal \cdot mol^{-1}$ which are 1 (one) order higher than physically adsorbed on metallic surface. TD-DFT calculations have been successively employed to simulate the electronic spectra of the V, Cr, Mn, Fe and Co complexes and facilitated a transition assignment. With the electronic structure of this tris-complexes, we have begun to make meaningful comparisons to experimental spectra for investigation into many tris(dithiolato) complexes of early transition metals. The investigation of electronic parameters including frontier molecular orbital energies suggests that Fe containing complexes should have the largest band gap and therefore being the hardest among all. The results of NBO analysis reflect charge transfer from lone pair orbitals located on the donor atoms to the central metal ions. The present metal-ligand binding energies, structures, stability and atomic charges of the metal-benzene-1,2-ditholato (bdt^{2-}) complexes will serve as a cornerstone for such modeling using molecular dynamics or Monte Carlo simulations.

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Conflicts of Interest

The authors declare no conflict of interest.

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