Electronic, Chemical, Thermodynamics Properties Screening of $[M(SDPH)(VDPH)(X)a(Y)b)]^n$ (M = Cr, Mn, Fe, Co, Ni; X = NH_3; Y: H_2O; a = 0 or 1; b = 1 or 2; n = 0 or 1) Metal Complexes with an Extended Tight Binding Quantum Chemical Method

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Abstract. The capability of the Schiff's base complex from the *hydrazine* group, which has *azomethine* (-NHN=CH-) as the main group, has been studied for its potential in the medical field, such as anticancer, antioxidant, and antibacterial. The synthesis method and its reaction condition for coordinating the first-row transition complex compound with base Schiff's ligands SDPH (Salicylaldehyde-2,4-Dinitrophenylhydrazine) and VDPH (Vanillin-Dinitrophenylhydrazine) were still challenging to be applied as not all reaction conditions can succeed in the synthesis experiment. To determine the potential of first-row transition metal ions coordinating with SDPH and VDPH ligands, this research studies computationally the Extended Tight Binding Quantum Chemical method, called GFN2-xTB. Variations of the octahedral complex molecular formula used in computational calculations are $[M(L)_2X_aY_b]$ and $[M(L)_2X_aY_b]^+$ with M = (Cr, Mn, Fe, Co, Ni); L = SDPH and VDPH; X = NH_3 (a = 0 or 1); and Y = H_2O (b = 1 or 2). In addition, these complex compounds, which have metal ions with electron configuration d^4-d^7, were studied for their stability under high and low spin conditions. The data indicate the presence of stable complexes with more negative ΔG values were generally found in: (i) complexes with VDPH ligands, (ii) complexes containing the NH_3 ligand, (iii) complexes with metal ions M^{+3}, (iv) complexes having low spin magnetic properties. These results were also supported by the characteristics of global reactive descriptors, including a global electrophilicity index, electronegativity, chemical potential, chemical hardness, and chemical softness. It also included studies related to the HOMO-LUMO electronic energy to determine the reactivity and stability of the studied complex compounds.

Keywords: SDPH and VDPH complexes · First-row transition metals · GFN2-xTB

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1 Introduction

The coordination functionality of the central atom and the ligand is still one of the interesting issues that are currently being developed. One of the ligands that have various applications in the field of chemistry is Schiff's base ligand. The coordination of a Schiff's base ligand with a transition metal has received much more attention because it has many medical, pharmacology, and biological studies applications [1]. In addition, this research is supported by several studies reporting that Schiff's base has broad biological activities, especially as an antibacterial, antifungal antiviral and anti-inflammatory agent [2, 3] which are closely related to the characteristics of the ligand properties and the functionality of a complex [4]. Therefore, it is important to understand the character of the ligand and the central atom to be able to make coordination of complex compounds that are useful for life, especially in the biomedical field. Schiff base group hydrazone is a compound produced from the reaction of aldehydes with hydrazine. These hydrazone compounds can act as multidentate ligands with transition metals and show development in biological applications. [5, 6] Hydrazone in a Schiff's base compound with the main group of azomethine is (C=N), which is a substantial part for biological application [7–9]. This was stated in a study saying that Schiff's base complex with transition metals Fe(III), Cu(II), Zn(II) has been synthesized and produced complexes that are useful in the field of antimicrobials [10]. A group of Schiff's base derived from salicylaldehyde can provide a medium for producing valuable compounds with desirable certain biological and industrial attributes [11–13]. One of the Schiff base groups derived from salicylaldehyde is SDPH or (S*alicylaldehyde-2,4-dinitrophenyl hydrazin*e) which has successfully demonstrated in the presence of antioxidants activity when coordinated with Co(II) to form complex compounds [Co(II)(SDPH)] [14].

Modification of the hydrazone-derived ligand group with the main compounds salicylaldehyde vanillin, and hydrazine is a modification of the complex formula of the Schiff base, especially the SDPH and VDPH ligands which have not been widely synthesized yet. Consequently, this study was conducted to analyze the stability of a complex when formed and its characteristics, including reactivity and chemical stability.

Through the use of computational calculation methods, it is easier to identify possible non-covalent interactions of a compound that will be synthesized since this non-covalent interaction can increase the potential for biological activity for bioactive compounds [15]. One of the computational study is the semi-empirical quantum chemical, especially GFNn-xTB method. The GFNn-XTB method is a method that is popularly being developed. It has also a good performance in terms of of organic chemistry and several organometallic [16]. This is one of the reasons for using the GFN2-xTB method in this research. As it is known that this method is not yet commonly used, it will be a special appeal to develop it. In addition, it can help the calculation of complex compounds and transition metals which have hundreds or thousands of atoms. Besides, this is supported by a higher speed on GFNn-xTB than the DFT method. Therefore, this study focuses on the identification and screening of the Schiff's base complexes, especially the complex compound SDPH (*Salicylaldehyde-2,4-Dinitrophenylhydrazine*) and VDPH (*Vanillin-Dinitrophenylhydrazine*) with any transition metals first row using the GFN2-xTB method.

2 Computational Study

The methodology used in this study is the GFN2-xTB method, where extended tight binding is the scope of the atomistic-based semi-empirical method or SQM method which is usually used for atomistic modelling, biochemical and organometallic applications [17]. XTB comes from the expansion of density functional disturbances or DFT from electron density in a fluctuating to several massages alike as a broader or extended functional density binding model known as "xTB" [18]. The GFNn-xTB energy expressions are represented as a robust electronic structure scheme for the calculation of harmonic frequencies used in a calculated free energy, especially GFN2-xTB which is highly advised on a vibrational big scale frequency [19]. Another advantage of choosing GFN2-xTB method is more efficient, reasonable cost accuracy ratio, and high resistance [20]. Recently, the GFN2-xTB method has been developed to optimize the complex structure, such as optimization of the structure of La(III) complex compounds [21]. Complex compounds consisting of tens or even hundreds of atoms in a computational chemistry study require special methods because they are often limited to chemical compounds that have a simple number of atoms. This GFN2-xTB has been a thorough development and evaluation of a semi-empirical quantum chemical method. The common method used in the semi-empirical quantum chemical is the DFT which is usually used for complex compounds. The advantage of using the DFT method is that it has a fairly good level of accuracy, but it has the disadvantage of a fairly long calculation process so over time, quantum chemical methods were found that provide the right calculation process, one of which is GFN2-xTB. The GFN2-xtb method was developed because it has good geometry optimization results and is full of simple compounds to complex compounds [22]. Furthermore, GFN2-xtb methods can test benchmark sets regarding reaction energies on organometallic reactions. The GFNn-xTB method has calculation results which are shown by the success of the simulation of mass spectrum electron ionization, conformer-rotamer in organic chemistry, and optimization of lanthanoid complexes [22]. GFNn-xTB is also used in calculating the pKa of a reaction [23].

The results of the optimization of the structure of organometallic complex compounds studied produced an excellent structure and the GFNn-xTB method is considered to have excellent performance in optimizing the structure of complex compounds. xTB [16]. The advantages of GFNn-xTB compared to DFT are efficiency and speed in the performance of calculations carried out especially in complex compounds [17]. This is evidenced by optimization of the geometric structure with all SQM methods in all finite elements $Z = 86$ including lanthanoids. This of course can also open up opportunities for finding conformational searches for systems with transition metals bonded to other compounds for optimizing their use in the chemical field. Optimizing the accuracy of the geometric structure produced by the GFNn-xTB method can be used as an alternative to the theory of the DFT method. The DFT method fails to describe a system that occurs in transition metals such as breaking chemical bonds and characterizing the correlation of static theory. This is due to the difficulty in describing the interactions of the degenerated states [24]. This tight bind extended method is designed not only for the calculation of the structure but also the energy of non-covalent interactions in a system with large molecules and atomic numbers such as complex compounds. The

advantages of good computational efficiency compared to its predecessor methods make the GFNn-xTB method considered appropriate for exploring the conformational space of molecular systems [25].

The study carried out is the optimization of molecular orbital geometry where there are a dozens of complex structure variations as well as major ligands, which include SDPH (*Salicylldehyde-2,4-Dinitrophenylhydrazine*) and VDPH (*Vanillin-dinitrophenylhydrazine*) ligands and L = SDPH and VDPH X = NH_3 and Y = H_2O, which reviewed based on electronic, chemical, and thermodynamic properties pada temperature standard 298K and the pressure constant which mean 1 atm. For the preparation of optimization of molecular structures of complex compound, we used Avogadro software to input geometry of the complexes. All calculations were executed with ORCA 4.2.0 software. The calculation of electronic properties is through the highest occupied molecular orbital- the lowest unoccupied molecular orbital (HOMO-LUMO) energy analysis. While the thermodynamic properties are based on changes in the resulting Gibbs free energy, while global reactivity descriptors are calculated for the stability and reactivity of complex compounds, including Softness (S), Electronegativity (χ), Electrophilicity index (ω), global electrophilicity, frontier molecular orbitals (FMO), Chemical Potential (μ) and Hardness (η).

3 Results and Discussion

3.1 Stabilization of Complex Compounds with Variation of First-Row Transition Metal Ions

The transition metal is an essential parameter in a complex compound playing a pivotal role in addition to ligands. In this study, the nature of each transition metal, especially the central first-row metals: [M: Cr, Mn, Fe, Co, Ni], was studied to determine the effect of variations in metal ion charge or oxidation number on the overall stability of the SDPH and VDPH complex compounds.

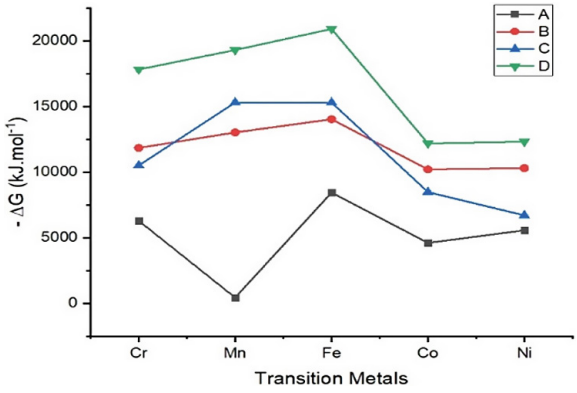


Fig. 1. ΔG energy any complexes with molecular formula: $[M(II)(L)_2(Y)]^n$ with (n = 0 or 1) and Y = H_2O. The complexes consist of, (A) $[M(II)(SDPH)_2(H_2O)_2]$; (B) $[M(II)(VDPH)_2(H_2O)_2]$; (C) $[M(III)(SDPH)_2(H_2O)_2]^+$; (D) $[M(III)(VDPH)_2(H_2O)_2]^+$

According to Fig. 1 in a complex compound, the total change in Gibbs free energy produced by each complex with variations in the charge of metal ions 2+ and 3+, and also from variations in the molecular formula of different complex compounds can produce the most negative total Gibbs free energy is D $[M(III)(VDPH)_2(H_2O)_2]^+$ complex. This indicates that complex compounds with a charge of 3+ and with variations in VDPH ligands have the highest negative energy. The value is -20909 kJ.mol^{-1}, followed by complex compounds C $[M(III)(SDPH)_2(H_2O)_2]^+$ and complex B:$[M(II)(VDPH)_2(H_2O)_2]$, while the lowest negative value is A $[M(II)(SDPH)_2(H_2O)_2]$. As a result, the change in Gibbs free energy from the most negative value is D (-20909 kJ.mol^{-1}) > C ($-15306{,}2$ kJ.mol^{-1}) > B ($-14029{,}7$ kJ.mol^{-1}) > A (-8443 kJ.mol^{-1}). The negative value of the change in Gibbs free energy occurring in the several complex compounds indicates that these are more thermodynamically stable than complex compounds with other types of metal ions. According to Fig. 1, complex compound with the molecular formula $[M(III)(SDPH)_2(H_2O)_2]^+$ has a more negative value since the central metal ion with a 3+ charge is more acidic than the metal ion with a 2+ charge. The more acidic the metal center, the easier the complex formation and the more stable complex compounds.

3.2 Effect of NH_3 Ligand on the Stability of Complex Compounds

This study carried out calculations on various types of complex compounds with different molecular formulas. The aim is to analyze the presence of NH_3 ligand effect on complex compounds for in terms of its stability.

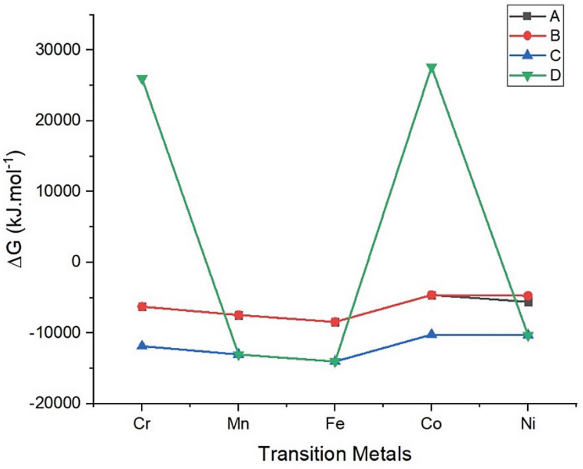


Fig. 2. ΔG energy any complexes with molecular formula $[M(II)(L)_2X(Y)]$ with X = NH_3 and Y = H_2O. The complexes consist of (A) $[M(II)(SDPH)_2(H_2O)_2]$; (B) $[M(II)(SDPH)_2(NH_3)(H_2O)]$; (C) $[M(II)(VDPH)_2(H_2O)_2]$; (D) $[M(II)(VDPH)_2(NH_3)(H_2O)]$

Figure 2 depicts a plot energy of total Gibbs free energy change for each complex compound. D $[M(II)(VDPH)_2(NH_3)(H_2O)]$ compound has the most negative energy at -14029.7 kJ.mol^{-1}.This value is slightly different compared to C $[M(II)(VDPH)_2$

$(H_2O)_2]$ compound value at -13025.4 kJ.mol^{-1}. According to this plot energy, the change of Gibbs free energy on the various complex compounds results not only a change of negative energy, but also a change of positive energy. This is proven by the number of total change in Gibbs free energy produced by complex compounds $[Cr(II)(VDPH)_2(NH_3)(H_2O)]$ and $[Co(II)(VDPH)_2(NH_3)(H_2O)]$ from molecular formula $[M(II)(VDPH)_2(NH_3)(H_2O)]$ at 25986 kJ.mol^{-1} and 27641 kJ.mol^{-1} respectively. Hence, not all complex compounds produce a negative total energy change. This negative energy value indicates that the complex is stable and occurs spontaneously. This is different from the results of several other complexes which are positive indicating a less stable complex. The complexes containing the NH3 ligan results more stable complexes compared to complexes without the NH3 ligan. This is because the NH_3 ligand is a ligand that has a better field strength than water although both are sigma donor ligands. Consequently, it has an implication for the formation of complexes that are easier and more stable. This occurs due to the character of the NH_3 ligand, apart from being a good base by being able to donate electrons to metal ions and being a suitable sigma donor ligand. Furthermore, the density of the electron environment around the complex becomes stable and makes the change in the Gibbs free energy bigger.

3.3 Effect of Electron Distribution on the Stability of Complex Compounds

The bar chart in Fig. 3 explains the effect of distributed electron of any complexes which results a total Gibbs free energy change. In this chart, the electron configurations d4-d7 of complexes with metal ions are Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}.

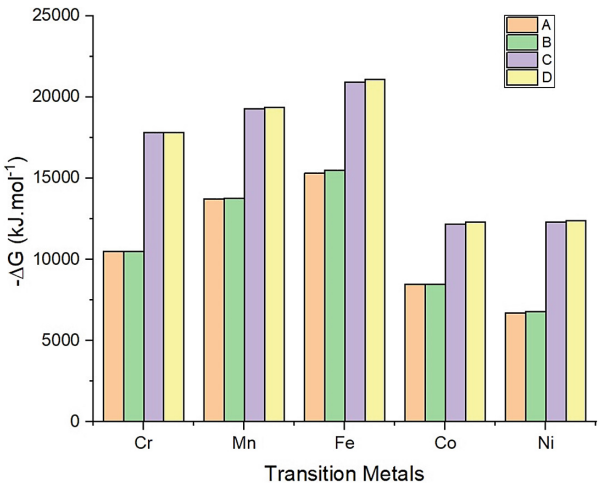


Fig. 3. ΔG energy any complexes with molecular formula $[M(II)(L)_2(Y)]$ with L = SDPH or VDPH, Y = H_2O. The complexes consist of (A) $[M(II)(SDPH)_2(H_2O)_2]$ HS; (B) $[M(II)(SDPH)_2(H_2O)_2]$ LS; (C) $[M(II)(VDPH)_2(H_2O)_2]$ HS; (D) $[M(II)(VDPH)_2(H_2O)_2]$ LS (with HS = High Spin) and LS = Low Spin)

Based on the results of the calculations, the results of the electron distribution of each complex were different. In this case, one representative of the calculation of complex compounds was taken with the molecular formula $[M(II)(L)_2(Y)_2]$ where L = SDPH or VDPH, and Y = H_2O) with spin variations, called high spin and low spin. The complex with a low spin state turned out to have the most negative Gibbs free energy change value. Although thermodynamically, the values for the high and low spin states were not much different for each complex. The value of the most negative Gibbs free energy change in the complex with the molecular formula $[M(II)(VDPH)_2(H_2O)_2]$ LS was -21087 kJ.mol^{-1}, whereas the smallest negative Gibbs free energy change value was the complex $[M(II)(SDPH)_2(H_2O)_2]$ HS at -6703 kJ.mol^{-1}. This indicates that the most stable complexes are found for complex compounds with variations in central metal and electron distribution, called complex compounds with the molecular formula $[M(II)(L)_2(Y)_2]$ with low spin.

3.4 Global Reactivity Descriptors

In the computational theory of quantum mechanics, where the global reactivity descriptor characteristic can explain the reactivity of a compound, in this study, the Schiff's base complex compound has been studied and can determine the chemical reactivity of a molecule, chemical stability, and polarization tendencies of the molecule [26]. In addition, this study related to the global quantum descriptor can also analyze a molecule selection [27].

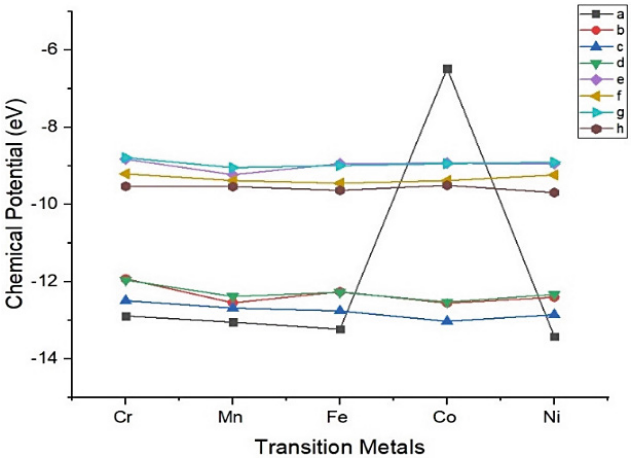


Fig. 4. Chemical Potential any complexes that consist of (a) $[M(III)(SDPH)_2(H_2O)_2]^+$; (b) $[M(III)(VDPH)_2(H_2O)_2]^+$ (c) $[M(III)(SDPH)_2(NH_3)(H_2O)]^+$; (d) $[M(III)(VDPH)_2(NH_3)(H_2O)]^+$; (e) $[M(II)(VDPH)_2(H_2O)_2]$; (f) $[M(II)(SDPH)_2(NH_3)(H_2O)]$; (g) $[M(II)(VDPH)_2(NH_3)(H_2O)]$; (h) $[M(II)(SDPH)_2(H_2O)_2]$

1) Chemical Potential (μ)

The chemical potential can describe the tendency of electrons to escape from equilibrium as the electronegativity of the molecule [27]. If the value of the chemical potential of the complex is greater than the others, the energy of the complex is more sensitive to the change of the electron's number [28]. The molecule's chemical potential indicates a tendency to donate or accept electrons. The lowest chemical potential shown in the complex compound is −6.477 eV for complex [M(II)(VDPH)2(H2O)2]. The lowest value indicates that the complex compound can stabilize a system with its electronic energy. In contrast, the highest value is −13.4208 eV in complex $[M(III)(SDPH)_2(H_2O)_2]^+$. This highest value of chemical potential indicates a lack of a complex compound with this structure in stabilizing the system (Fig. 4).

2) The Chemical Hardness (η) and Softness (S)

The Chemical hardness characteristics can describe a complex's hard or soft characteristics, while the hardness value can also be correlated with the obtained softness value like the concept of hard soft acid base. A large HOMO-LUMO gap can be found in a hard molecule. This molecule will be more stable if they have a large gap of HOMO-LUMO and also need much energy excitation to reach the manifold of excited states [28] (Fig. 5).

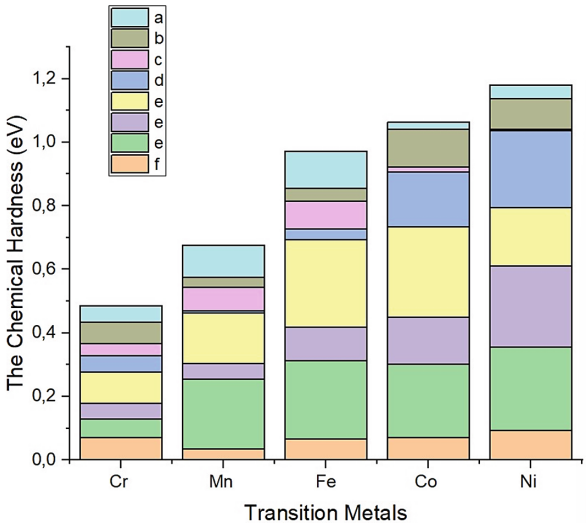


Fig. 5. The Hardness of complexes with any molecular formula, The complexes consist of: (a) $[M(II)(VDPH)_2(NH_3)(H_2O)]$; (b) $[M(II)(SDPH)_2(NH_3)(H_2O)]$; (c) $[M(II)(VDPH)_2(H_2O)_2]$; (d) $[M(II)(SDPH)_2(H_2O)_2]$; (e) $[M(III)(VDPH)_2(NH_3)(H_2O]^+$; (f) $[M(III)(SDPH)_2(NH_3)(H_2O)]^+$; (g) $[M(III)(VDPH)_2(H_2O)_2]^+$; (h) $[M(III)(SDPH)_2(H_2O)_2]^+$

The chemical hardness of each complex shown that the complex with the smallest hardness value is at $[M(II)(VDPH)_2(H_2O)_2]$ with a value of 0.0049 eV and the highest value of the hardness is to complex $[M(III)(VDPH)_2NH_3H_2O]^+$ with a value of

0.2836 eV. This hardness is also a measure of the molecule resistance which can be used to change its electronic structure. It can be shown that complex compounds with high hardness values have a tendency to stabilize the system [29]. Meanwhile, a low hardness value indicates that complex compounds tend to be less stable in stabilizing a system. Complex compounds that have high chemical hardness indicate a measure of the resistance system for changing its electronic structure. It is also in line with the principles of HSAB (Soft Hard Acids and Bases) [29] (Fig. 6).

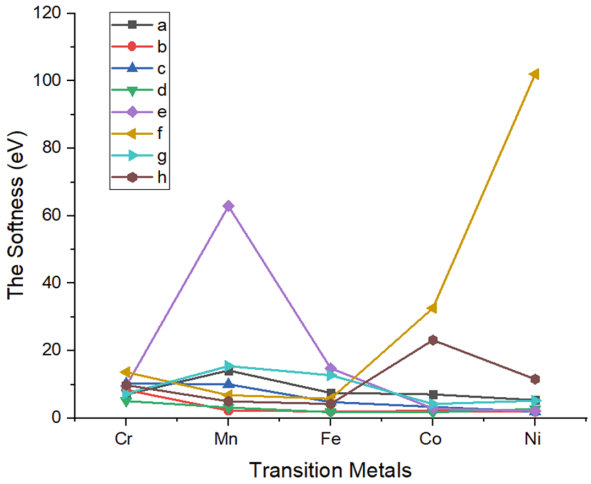


Fig. 6. The softness of any molecular complexes, the complexes consist of: (a) $[M(III)(SDPH)_2(H_2O)_2]^+$; (b) $[M(III)(VDPH)_2(H_2O)_2]^+$; (c) $[M(III)(SDPH)_2(NH_3)(H_2O)]^+$; (d) $[M(III)(VDPH)_2(NH_3)(H_2O)]^+$; (e) $[M(II)(SDPH)_2(H_2O)_2]^+$; (f) $[M(II)(SDPH)_2(H_2O)_2]$; (g) $[M(II)(SDPH)_2(NH_3)(H_2O)]$; (h) $[M(II)(VDPH)_2(NH_3)(H_2O)]$;

The softness is a measure of the ease of change transfer related to a high polarizability [30]. According to studied softness of various complex compounds, complex compounds with the highest softness value are complex compounds $[M(II)(VDPH)_2(H_2O)_2]$ with 102.0408 eV. In contrast, the lowest softness of complex compounds is $[M(III)(VDPH)_2NH_3H_2O]^+$ with the value of 1.763 eV. If the complex compound has the most significant softness, the stability of the complex compounds will decrease, while its reactivity will increase.

3) Electronegativity (χ)

The electronegativity value of various complex compounds, shown that the complex compounds which have a greater electronegativity than others are complex compounds with the molecular formula $[M(III)(SDPH)_2(H_2O)_2]^+$ with the central metal being Ni with the value of 13.4208 eV. While the lowest electronegativity value was obtained from $[M(III)(SDPH)_2(H_2O)_2]^+$ complex compounds with the same molecular formula but with different types of central metal, namely complex compounds with Co metal with a value of 6.477 eV (Fig. 7).

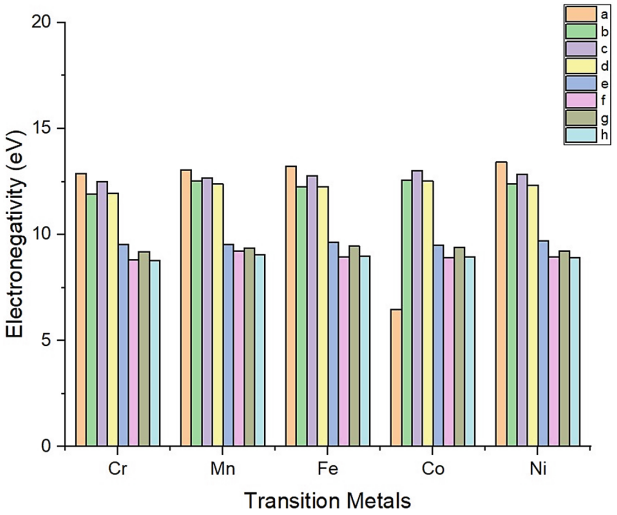


Fig. 7. Electronegativity of any molecular complexes. The complexes consist of: (a) $[M(III)(SDPH)_2(H_2O)2]^+$; (b) $[M(III)(VDPH)_2(H_2O)2]^+$; (c) $[M(III)(SDPH)_2\ (NH_3)(H_2O)]^+$; (d) $[M(II)(VDPH)_2(NH_3)(H_2O)]^+$; (e) $[M(II)(SDPH)_2(H_2O)2]$; (f) $[M(II)(VDPH)_2(H_2O)_2]$; (g) $[M(II)(SDPH)_2(NH_3)(H_2O)]$; (h) $[M(II)(VDPH)_2(NH_3)(H_2O)]$

4) Global Electrophilicity (ω)

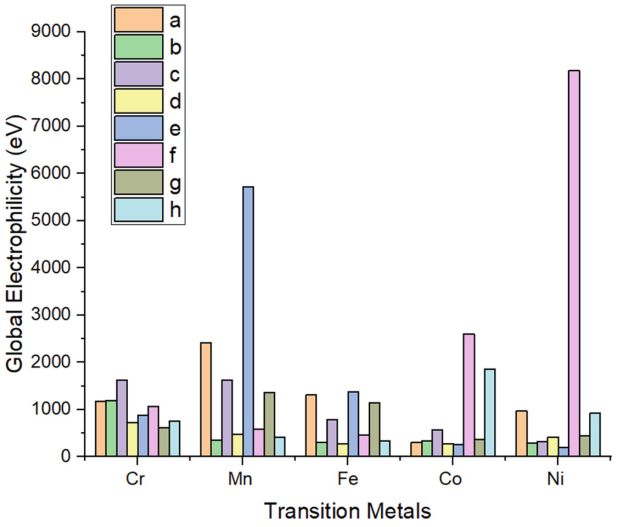


Fig. 8. Global Electrophilicity of any molecular complexes, the complexes consist of: (a) $[M(III)(SDPH)_2(H_2O)_2]^+$; (b) $[M(III)(VDPH)_2(H_2O)_2]^+$; (c) $[M(III)(SDPH)_2\ (NH_3)(H_2O)]^+$; (d) $[M(II)(VDPH)_2(NH_3)(H_2O)]^+$; (e) $[M(II)(SDPH)_2(H_2O)_2]$; (f) $[M(II)(VDPH)_2(H_2O)_2]$; (g) $[M(II)(SDPH)_2(NH_3)(H_2O)]$; (h) $[M(II)(VDPH)_2(NH_3)(H_2O)]$

Global Electrophilicity (ω) can show the species capability to accept electrons [31, 32]. The characteristics of various types of complex compounds indicated by the highest global electrophilicity value was found in complex compounds with the molecular formula $[M(II)(VDPH)_2(H_2O)_2]$ 8179.38772 eV, while the lowest global electrophilicity value was in complex compounds $[M(II)(SDPH)_2(H_2O)_2]$ 194.42736 eV. This shows that the electrophilicity index, when viewed in terms of thermodynamic properties, can measure the energy change when a chemical system becomes saturated while adding electrons. This global electrophilicity value that a large value indicates that the complex tends to have high electrophilic properties, while a low global electrophilicity value indicates that the complex tends to be more nucleophilic (Fig. 8).

3.5 Frontier Molecular Orbital

Frontier Molecular Orbital is popular to be used for HOMO and LUMO [33]. The HOMO is an electron donor depicting the ability to donate an electron, whereas the LUMO is an electron acceptor showing the ability to accept an electron [34, 35]. Frontier Molecular Orbitals analysis is one parameter that is quite important to be able to estimate and explain chemical reactivity, hardness, and softness of the compound such as complex compound. As is known, HOMO (π donor) [36] acts as a place to receive the highest electrons, while LUMO(π acceptor) [36] acts as an electron acceptor which acts to attract electrons, and the lowest energy orbital that can accept electrons [37]. FMO provides insight into the contribution of atoms to reactivity. HOMO-LUMO describes the basic fundamentals for examining chemical reactivity, compound stability, and compound stability.

The ability to accept electrons is attributed to the LUMO orbitals which are electronically vacant or unfilled orbitals. HOMO-LUMO energy difference. The highest HOMO-LUMO gap value indicates that the complex has high stability, but negligible or low reactivity of the compound. This is because a molecule with a small HOMO-LUMO gap (ΔE) explains that the molecule is more polarized and is generally related to high chemical reactivity. Furthermore, a low kinetic stability and HOMO-LUMO energy can show whether is it easy or not for a compound to accept electrons (Fig. 9).

The complex with the highest HOMO-LUMO gap value are complex with the molecular formula $[M(III)(VDPH)(NH_3)(H_2O)]^+$ 0.5672 eV, while complex compounds with the lowest HOMO-LUMO gap values are complex compounds with the molecular formula $[M(II)(SDPH)_2(H_2O)_2]$ 0.0159 eV. Complex that has highest HOMO-LUMO gap or ΔE indicated that more stable and less reactive and hard compound. Besides, the complex with the lowest HOMO-LUMO gap or ΔE are complex indicated less stable and more reactive and consist of soft compound (Table 1).

The highest H-L gap is NH_3 ligand which indicates that the NH_3 metal tends to have high stability and low chemical reactivity compared to other ligands [38]. While the lowest H-L gap is the VDPH ligand describing that the VDPH molecule without binding to other compounds has a high chemical reactivity and low stability. The order of the H-L gap from the highest is in the ligand $NH_3 > H_2O >$ SDPH > VDPH.

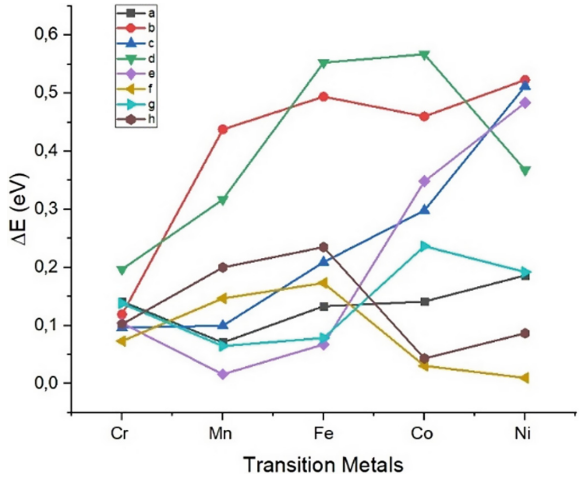


Fig. 9. ΔE (eV) energy of any molecular complex consist of: (a) $[M(III)(SDPH)_2(H_2O)_2]^+$; (b) $[M(III)(VDPH)_2(H_2O)_2]^+$; (c) $[M(III)(SDPH)_2\ (NH_3)(H_2O)]^+$; (d) $[M(II)(VDPH)_2(NH_3)(H_2O)]^+$; (e) $[M(II)(SDPH)_2(H_2O)_2]$; (f) $[M(II)(VDPH)_2(H_2O)_2]$; (g) $[M(II)(SDPH)_2(NH_3)(H_2O)]$; (h) $[M(II)(VDPH)_2(NH_3)(H_2O)]$

Table 1. HOMO-LUMO energy of Ligands

Ligand	Energy of HOMO (eV)	Energy of LUMO (eV)	Energy of H-L Gap (eV)
SDPH	−9.8412	−9.0725	0.7687
VDPH	−9.4101	−9.2350	0.1751
NH_3	−10.6157	1.6655	14.1541
H_2O	−12.1657	1.9884	12.2812

4 Conclusions

The electronic, chemical, and thermodynamic properties of the SDPH and VDPH complexes with various types first -row transition metals have been thoroughly investigated and screened by extended tight binding or GFN2-xTB. Stabilization of the complexes with various molecular formula was examined systematically. The result reveals that SDPH and VDPH complexes with first-row transition metals tend to have stable and spontaneous conditions complex compounds. However, there are several complexes that also produce an unstable state proven by the total value of the positive Gibbs free energy change. The outcome depicts those complex compounds consisting of VDPH ligands tend to have a more negative total value of Gibbs free energy changes than complex compounds with SDPH ligands. The charge of 3+ complex compounds also tends to have more stable complex compounds. Furthermore, the influence of electron distribution at low spins results in a more negative Gibbs free energy change and makes the complex compound in a stable state. In this study, the NH_3 as a ligand gave the impact to stabilize

the complexes. It means NH3 has a good influence on the stability of the complex and makes the complexes more stable.

The acquired results are also supported by analysis of global reactivity descriptors consisting of a global electrophilicity index (ω), electronegativity (χ), chemical potential (μ), chemical hardness (η), and chemical softness (S) and frontier molecular orbitals. The results of any component of the global reactivity descriptors can support the previous results of thermodynamic (ΔG energy) which mean the complex compounds have high stability with low reactivity and the complex compounds with low stability with high reactivity are obtained which later are expected to be supporting data in the development of investigations on the conditions of synthesis of a complex compound with the main ligands SDPH and VDPH with experimentally.

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Appendixes

ΔG energy of any SDPH and VDPH Complexes

Complex	ΔG (kJ.mol^{-1})	Complex	ΔG (kJ.mol^{-1})
Co(II)(SDPH)$_2$(H$_2$O)$_2$ HS	−4610	Fe(II)(VDPH)$_2$(NH$_3$)(H$_2$O) LS	−14109.8
Co(II)(SDPH)$_2$(H$_2$O)$_2$ LS	−4699	Fe(III)(SDPH)$_2$(H$_2$O)$_2$ HS	−15306.2
Co(II)(VDPH)$_2$(H$_2$O)$_2$ HS	−10204	Fe(III)(SDPH)$_2$(H$_2$O)$_2$ LS	−15486.9
Co(II)(VDPH)$_2$(H2O)$_2$ LS	−10280	Fe(III)(VDPH)$_2$(H$_2$O)$_2$ HS	−20909
Co(II)(SDPH)$_2$(NH$_3$)(H$_2$O) HS	−6411	Fe(III)(VDPH)$_2$(H$_2$O)$_2$ LS	−21087
Co(II)(SDPH)$_2$(NH$_3$)(H$_2$O) LS	−6423	Fe(III)(SDPH)$_2$(NH$_3$)(H$_2$O) HS	−40205.6
Co(II)(VDPH)$_2$(NH$_3$)(H$_2$O) HS	27641	Fe(III)(SDPH)$_2$(NH$_3$)(H$_2$O) LS	−40366
Co(II)(VDPH)$_2$(NH$_3$)(H$_2$O) LS	27552	Fe(III)(VDPH)$_2$(NH$_3$)(H$_2$O) HS	−20903.8
Co(III)(SDPH)$_2$(H$_2$O)$_2$ HS	−8479	Fe(III)(VDPH)$_2$(NH$_3$)(H$_2$O) LS	−21078.8
Co(III)(SDPH)$_2$(H$_2$O)$_2$ LS	−8479	Mn(II)(SDPH)$_2$(H$_2$O)$_2$ HS	−7444.62
Co(III)(VDPH)$_2$(H$_2$O)$_2$ HS	−12187	Mn(II)(SDPH)$_2$(H$_2$O)$_2$ LS	−7554.65
Co(III)(VDPH)$_2$(H$_2$O)$_2$ LS	−12325	Mn(II)(VDPH)$_2$(H$_2$O)$_2$ HS	−13025.4
Co(III)(SDPH)$_2$(NH$_3$)(H$_2$O) HS	−8292	Mn(II)(VDPH)$_2$(H$_2$O)$_2$ LS	−13128.6
Co(III)(SDPH)$_2$(NH$_3$)(H$_2$O) LS	−8486	Mn(II)(SDPH)$_2$(NH$_3$)(H$_2$O) HS	−7446.41
Co(III)(VDPH)$_2$(NH$_3$)(H$_2$O) HS	25682	Mn(II)(SDPH)$_2$(NH$_3$)(H$_2$O) LS	−7561.83
Co(III)(VDPH)$_2$(NH$_3$)(H$_2$O) LS	27552	Mn(II)(VDPH)$_2$(NH$_3$)(H$_2$O) HS	−13028.8
Cr(II)(SDPH)$_2$(H$_2$O)$_2$ HS	−6295.86	Mn(II)(VDPH)$_2$(NH$_3$)(H$_2$O) LS	−13144.2
Cr(II)(SDPH)$_2$(H$_2$O)$_2$ LS	−6402.44	Mn(III)(SDPH)$_2$(H$_2$O)$_2$ HS	−13720.5

(*continued*)

(*continued*)

Complex	ΔG ($kJ.mol^{-1}$)	Complex	ΔG ($kJ.mol^{-1}$)
$Cr(II)(VDPH)_2(H_2O)_2$ HS	−11847.1	$Mn(III)(SDPH)_2(H_2O)_2$ LS	−13770.7
$Cr(II)(VDPH)_2(H_2O)_2$ LS	−11944	$Mn(III)(VDPH)_2(H_2O)_2$ HS	−19303.3
$Cr(II)(SDPH)_2(NH_3)(H_2O)$ HS	−6265.45	$Mn(III)(VDPH)_2(H_2O)_2$ LS	−19363
$Cr(II)(SDPH)_2(NH_3)(H_2O)$ LS	−6358.84	$Mn(III)(SDPH)_2(NH_3)(H_2O)$ HS	−13713.1
$Cr(II)(VDPH)_2(NH_3)(H_2O)$ HS	25986.1	$Mn(III)(SDPH)_2(NH_3)(H_2O)$ LS	−13781.3
$Cr(II)(VDPH)_2(NH_3)(H_2O)$ LS	25892.7	$Mn(III)(VDPH)_2(NH_3)(H_2O)$ HS	−367978
$Cr(III)(SDPH)_2(H_2O)_2$ HS	−10507	$Mn(III)(VDPH)_2(NH_3)(H_2O)$ LS	−368047
$Cr(III)(SDPH)_2(H_2O)_2$ LS	−10507	$Ni(II)(SDPH)_2(H_2O)_2$ HS	−5573
$Cr(III)(VDPH)_2(H_2O)_2$ HS	−15765.8	$Ni(II)(SDPH)_2(H_2O)_2$ LS	−5573
$Cr(III)(VDPH)_2(H_2O)_2$ LS	−16104	$Ni(II)(VDPH)_2(H_2O)_2$ HS	−10304
$Cr(III)(SDPH)_2(NH_3)(H_2O)$ HS	−10515.5	$Ni(II)(VDPH)_2(H_2O)_2$ LS	−10304
$Cr(III)(SDPH)_2(NH_3)(H_2O)$ LS	−10515.5	$Ni(II)(SDPH)_2(NH_3)(H_2O)$ HS	−4719
$Cr(III)(VDPH)_2(NH_3)(H_2O)$ HS	21567.5	$Ni(II)(SDPH)_2(NH_3)(H_2O)$ LS	−4719
Cr(III)(VDPH)2$(NH_3)(H_2O)$ LS	21567.5	$Ni(II)(VDPH)_2(NH_3)(H_2O)$ HS	−10302
$Fe(II)(SDPH)_2(H_2O)_2$ HS	−8442.99	$Ni(II)(VDPH)_2(NH_3)(H_2O)$ LS	−10302
$Fe(II)(SDPH)_2(H_2O)_2$ LS	−8540.33	$Ni(III)(SDPH)_2(H_2O)_2$ HS	−6703
$Fe(II)(VDPH)_2(H_2O)_2$ HS	−14029.7	$Ni(III)(SDPH)_2(H_2O)_2$ LS	−6800
$Fe(II)(VDPH)_2(H_2O)_2$ LS	−14119.9	$Ni(III)(VDPH)_2(H_2O)_2$ HS	−12319
$Fe(II)(SDPH)_2(NH_3)(H_2O)$ HS	−8427.06	$Ni(III)(VDPH)_2(H_2O)_2$ LS	−12409
$Fe(II)(SDPH)_2(NH_3)(H_2O)$ LS	−8529.86	$Ni(III)(SDPH)_2(NH_3)(H_2O)$ HS	−6709
$Fe(II)(VDPH)_2(NH_3)(H_2O)$ HS	−14015	$Ni(III)(SDPH)_2(NH_3)(H_2O)$ LS	−6801
		$Ni(III)(VDPH)_2(NH_3)(H_2O)$ HS	−12292
		$Ni(III)(VDPH)_2(NH_3)(H_2O)$ LS	−12376

The Global Reactive Descriptors

Complex	Chemical Potential (eV)	Chemical Hardness (eV)	The Softness (eV)	The Electronegativity (eV)	Global Electrophilicity (eV)	ΔE (eV)
$Co(II)(SDPH)_2(H_2O)_2$ HS	−9.238	0.043	11.682	9.238	996.88	9.195
$Co(II)(SDPH)_2(H_2O)_2$ LS	−9.503	0.174	2.873	9.503	259.45	9.329
$Cr(II)(SDPH)_2(H_2O)_2$ LS	−9.531	0.052	9.615	9.531	873.44	9.479
$Cr(II)(SDPH)_2(H_2O)_2$ HS	−9.331	0.032	15.699	9.331	1.366.94	9.300
$Fe(II)(SDPH)_2(H_2O)_2$ LS	−9.635	0.034	14.815	9.635	1.375.26	9.601
$Fe(II)(SDPH)_2(H_2O)_2$ HS	−9.181	0.055	9.017	9.181	760.07	9.126
$Ni(II)(SDPH)_2(H_2O)_2$ HS	−9.696	0.242	2.068	9.696	194.43	9.454
$Ni(II)(SDPH)_2(H_2O)_2$ LS	−9.696	0.242	2.068	9.696	194.43	9.454
$Mn(II)(SDPH)_2(H_2O)_2$ LS	−9.537	0.008	62.893	9.537	5.720.94	9.530
$Mn(II)(SDPH)_2(H_2O)_2$ HS	−9.216	0.035	14.368	9.216	1.220.33	9.181

(*continued*)

(*continued*)

Complex	Chemical Potential (eV)	Chemical Hardness (eV)	The Softness (eV)	The Electronegativity (eV)	Global Electrophilicity (eV)	ΔE (eV)
$Cr(II)(VDPH)_2(H_2O)_2$ LS	−8.829	0.037	13.643	8.829	1.063.44	8.792
$Cr(II)(VDPH)_2(H_2O)_2$ HS	−8.715	0.090	5.556	8.715	421.99	8.625
$Mn(II)(VDPH)_2(H_2O)_2$ HS	−8.862	0.026	19.120	8.862	1501.64	8.836
$Mn(II)(VDPH)_2(H_2O)_2$ LS	−9.231	0.073	6.817	9.231	580.84	9.158
$Fe(II)(VDPH)_2(H_2O)_2$ LS	−8.944	0.087	5.770	8.944	461.55	8.857
$Fe(II)(VDPH)_2(H_2O)_2$ HS	−8.609	0.068	7.310	8.609	541.76	8.541
$Co(II)(VDPH)_2(H_2O)_2$ LS	−8.931	0.015	32.680	8.931	2606.68	8.916
$Co(II)(VDPH)_2(H_2O)_2$ HS	−8.688	0.060	8.382	8.688	632.71	8.628
$Ni(II)(VDPH)_2(H_2O)_2$ HS	−8.953	0.005	102.041	8.953	8179.39	8.948
$Ni(II)(VDPH)_2(H_2O)_2$ LS	−8.953	0.005	102.041	8.953	8179.39	8.948
$Cr(III)(SDPH)_2(H_2O)_2$ HS	−12.889	0.071	7.062	12.889	1173.26	12.819
$Cr(III)(SDPH)_2(H_2O)_2$ LS	−12.889	0.071	7.062	12.889	1173.26	12.819
$Mn(III)(SDPH)_2(H_2O)_2$ LS	−13.051	0.035	14.144	13.051	2409.19	13.016
$Mn(III)(SDPH)_2(H_2O)_2$ HS	−12.709	0.326	1.532	12.709	247.40	12.383
$Fe(III)(SDPH)_2(H_2O)_2$ LS	−13.233	0.067	7.508	13.233	1314.60	13.166
$Fe(III)(SDPH)_2(H_2O)_2$ HS	−12.252	0.046	10.811	12.252	1622.95	12.206
$Co(III)(SDPH)_2(H_2O)_2$ LS	−6.477	0.071	7.072	6.477	296.69	6.406
$Co(III)(SDPH)_2(H_2O)_2$ HS	−6.276	0.069	7.210	6.276	283.99	6.207
$Ni(III)(SDPH)_2(H_2O)_2$ LS	−13.421	0.093	5.365	13.421	966.30	13.328
$Ni(III)(SDPH)_2(H_2O)_2$ HS	−12.671	0.521	0.959	12.671	154.00	12.150
$Cr(III)(VDPH)_2(H_2O)_2$ LS	−11.927	0.060	8.396	11.927	1194.35	11.867
$Cr(III)(VDPH)_2(H_2O)_2$ HS	−11.927	0.060	8.396	11.927	1194.35	11.867
$Mn(III)(VDPH)_2(H_2O)_2$ LS	−12.550	0.219	2.285	12.550	359.95	12.332
$Mn(III)(VDPH)_2(H_2O)_2$ HS	−12.158	0.166	3.008	12.158	444.67	11.991
$Fe(III)(VDPH)_2(H_2O)_2$ LS	−12.260	0.247	2.024	12.260	304.22	12.013
$Fe(III)(VDPH)_2(H_2O)_2$ HS	−11.308	0.083	6.013	11.308	768.91	11.225
$Co(III)(VDPH)_2(H_2O)_2$ LS	−12.559	0.230	2.174	12.559	342.88	12.329
$Co(III)(VDPH)_2(H_2O)_2$ HS	−11.397	0.075	6.631	11.397	861.38	11.322
$Ni(III)(VDPH)_2(H_2O)_2$ LS	−12.406	0.261	1.913	12.406	294.40	12.145
$Ni(III)(VDPH)_2(H_2O)_2$ HS	−11.843	0.027	18.727	11.843	2626.66	11.817
$Co(II)(SDPH)_2(NH_3)(H_2O)$ HS	−9.022	0.092	5.408	9.022	440.24	8.930
$Co(II)(SDPH)_2(NH_3)(H_2O)$ LS	−9.383	0.118	4.225	9.383	371.99	9.265
$Cr(II)(SDPH)_2(NH_3)(H_2O)$ LS	−9.208	0.069	7.252	9.208	614.91	9.140
$Cr(II)(SDPH)_2(NH_3)(H_2O)$ HS	−9.065	0.107	4.658	9.065	382.75	8.958
$Fe(II)(SDPH)_2(NH_3)(H_2O)$ LS	−9.451	0.039	12.739	9.451	1137.74	9.411
$Fe(II)(SDPH)_2(NH_3)(H_2O)$ HS	−8.944	0.086	5.794	8.944	463.44	8.857
$Ni(II)(SDPH)_2(NH_3)(H_2O)$ HS	−9.235	0.096	5.208	9.235	444.20	9.139
$Ni(II)(SDPH)_2(NH_3)(H_2O)$ LS	−9.235	0.096	5.208	9.235	444.20	9.139
$Mn(II)(SDPH)_2(NH_3)(H_2O)$ LS	−9.379	0.032	15.456	9.379	1359.64	9.347
$Mn(II)(SDPH)_2(NH_3)(H_2O)$ HS	−8.978	0.082	6.075	8.978	489.73	8.896
$Cr(II)(VDPH)_2(NH_3)(H_2O)$ LS	−8.788	0.051	9.804	8.788	757.22	8.737
$Cr(II)(VDPH)_2(NH_3)(H_2O)$ HS	−8.788	0.051	9.804	8.788	757.22	8.737

(*continued*)

(*continued*)

Complex	Chemical Potential (eV)	Chemical Hardness (eV)	The Softness (eV)	The Electronegativity (eV)	Global Electrophilicity (eV)	ΔE (eV)
$Mn(II)(VDPH)_2(NH_3)(H_2O)$ HS	−8.819	0.078	6.443	8.819	501.17	8.742
$Mn(II)(VDPH)_2(NH_3)(H_2O)$ LS	−9.045	0.100	5.000	9.045	409.07	8.945
$Fe(II)(VDPH)_2(NH_3)(H_2O)$ LS	−8.993	0.118	4.255	8.993	344.16	8.876
$Fe(II)(VDPH)_2(NH_3)(H_2O)$ HS	−8.636	0.087	5.754	8.636	429.10	8.549
$Co(II)(VDPH)_2(NH_3)(H_2O)$ LS	−8.942	0.022	23.148	8.942	1850.70	8.920
$Co(II)(VDPH)_2(NH_3)(H_2O)$ HS	−8.673	0.101	4.941	8.673	371.64	8.572
$Ni(II)(VDPH)_2(NH_3)(H_2O)$ HS	−8.909	0.043	11.574	8.909	918.64	8.866
$Ni(II)(VDPH)_2(NH_3)(H_2O)$ LS	−8.909	0.043	11.574	8.909	918.64	8.866
$Cr(III)(SDPH)_2(NH_3)(H_2O)$ HS	−12.492	0.048	10.352	12.492	1615.53	12.444
$Cr(III)(SDPH)_2(NH_3)(H_2O)$ LS	−12.492	0.048	10.352	12.492	1615.53	12.444
$Mn(III)(SDPH)_2(NH_3)(H_2O)$ LS	−12.686	0.050	10.040	12.686	1615.73	12.636
$Mn(III)(SDPH)_2(NH_3)(H_2O)$ HS	−12.419	0.159	3.139	12.419	484.09	12.260
$Fe(III)(SDPH)_2(NH_3)(H_2O)$ LS	−12.759	0.104	4.787	12.759	779.23	12.654
$Fe(III)(SDPH)_2(NH_3)(H_2O)$ HS	−11.781	0.095	5.271	11.781	731.67	11.686
$Co(III)(SDPH)_2(NH_3)(H_2O)$ LS	−13.027	0.149	3.355	13.027	569.27	12.878
$Co(III)(SDPH)_2(NH_3)(H_2O)$ HS	−11.898	0.124	4.026	11.898	569.87	11.774
$Ni(III)(SDPH)_2(NH_3)(H_2O)$ LS	−12.854	0.256	1.952	12.854	322.59	12.598
$Ni(III)(SDPH)_2(NH_3)(H_2O)$ HS	−12.220	0.133	3.748	12.220	559.74	12.087
$Cr(III)(VDPH)_2(NH_3)(H_2O)$ LS	−11.960	0.098	5.079	11.960	726.52	11.862
$Cr(III)(VDPH)_2(NH_3)(H_2O)$ HS	−11.960	0.098	5.079	11.960	726.52	11.862
$Mn(III)(VDPH)_2(NH_3)(H_2O)$ LS	−12.387	0.159	3.154	12.387	483.85	12.228
$Mn(III)(VDPH)_2(NH_3)(H_2O)$ HS	−12.154	0.069	7.236	12.154	1068.92	12.085
$Fe(III)(VDPH)_2(NH_3)(H_2O)$ LS	−12.274	0.276	1.809	12.274	272.53	11.998
$Fe(III)(VDPH)_2(NH_3)(H_2O)$ HS	−11.337	0.127	3.953	11.337	507.98	11.210
$Co(III)(VDPH)_2(NH_3)(H_2O)$ LS	−12.530	0.284	1.763	12.530	276.79	12.246
$Co(III)(VDPH)_2(NH_3)(H_2O)$ HS	−11.438	0.165	3.024	11.438	395.58	11.272
$Ni(III)(VDPH)_2(NH_3)(H_2O)$ LS	−12.332	0.184	2.720	12.332	413.60	12.148
$Ni(III)(VDPH)_2(NH_3)(H_2O)$ HS	−11.814	0.021	23.529	11.814	3283.93	11.793

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