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Theoretical calculation of the exchange coupling constant in some polymeric nickel(II) complexes using range-separated functionals

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ABSTRACT

The magnetic parameters (J, g) of two nickel(II) 1D polymers (Ni(en)(ox) and Ni(ox)(ampy)$_2$; where en = ethylene diamine, ox = oxalate, ampy = 4-amino-pyridine) were calculated using 6-311+G* basis set and six range-separated DFT functionals (CAM-B3LYP, LC-BLYP, wB97, wB97X, wB97X-D3 and B2T-PLYP) together with the hybrid B3LYP method for sake of comparison. We found that the wB97, CAM-B3LYP and wB97X-D3 methods gave approximate value of J for compound **1** and the B2T-PLYP method was found to be the best method for compound **2**. The g values were calculated by the coupled perturbed approach. However, we assume that a higher approximation is needed in order to give satisfactory results for g. A new equation has been proposed to relate the experimental susceptibility to the J and g parameters. The Curie-Weiss law was included in this equation resulting in a good explanation of the steep part of the experimental curve below 20 K.

KEYWORDS
Curie-Weiss law
DFT calculations
Coupling constant
Magnetic parameters
Magnetic susceptibility
Exchange correlation functional

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1. Introduction

Measuring magnetic susceptibility (χ) of one dimensional Ni(II) complexes is an interesting subject. Many examples of these types of complexes can be found in the literature [1-9]. The value of the magnetic coupling constant (J) for these types of complexes are usually extracted from a plot of χ versus T. The values of the magnetic coupling constant obtained by this way are dependent on many factors. Some are related to the type of ligand involved, the angle of the bridge M-X-M [10] and to some extent on the Ni-Ni separation [8]. In addition, the polymer chain may show anti-ferromagnetic character for the investigated compound, but in a few cases, ferromagnetic behavior is also exhibited [11].

The problem is to fit the experimental curve (χ *vs* T) with an equation which gives the magnetic parameters (J, g), where g is the Landé splitting parameter, usually ~2. A nonlinear least square method is usually employed to make that fit. The analytical expression (Equation (1)) relating the susceptibility to the temperature for 1D Ni (II) polymers was first proposed by reference [2].

This is not the first time that two equations were used to fit the same experimental susceptibilities, by two different authors to give two different values of J [12]. Both values could be valid.

$$\chi = \frac{\left(2+0.0194X+0.777X^{2}\right)}{\left(3+4.346X+3.232X^{2}+5.834X^{3}\right)}\left(\mathrm{N}\beta^{2}g^{2}/\mathrm{kT}\right) \qquad (1)$$

where J is the nearest neighbor spin exchange coupling constant and $X = |J|/k\times T$.

Density functional theory (DFT) approach is a simple and quick method to calculate approximate values of the magnetic parameters. We assume that reliable values should be obtained from some multi-configurational, accurate theoretical approaches [13]. To do so, it requires greater computational resources, especially for large and moderately large molecules. Several attempts were done to estimate J in the literature [8,12,13]; some of them use simple DFT approach. In this study, we investigated the ability of some range-separated functionals hoping that they reproduce approximately experimental J and g values. Attempts to obtain values of J closer to the experimental values by employing range-separated functionals were performed before [14,15].

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Table 1. Theoretically calculated magnetic parameters.

Function	**Compound 1**		**Compound 2**	
	J (cm^{-1})	**g**	**J (cm^{-1})**	**g**
CAM-B3LYP	-14.43	2.11	-14.4	2.11
LC-BLYP	-25.78	2.10	-21.7	2.11
wB97	-19.56	2.11	-15.9	2.11
wB97X-D3	-17.86	2.12	-14.1	2.12
B2T-PLYP	-6.06	2.16	-7.00	2.19 [d]
B3LYP	-21.61	2.11	-21.7	2.11
If Equation (1) is applied	-29.90 [a], r = 0.9999	2.25 [a]	-24.40 [b], r = 0.999	2.20 [b]
If Equation (3) is applied	-12.8±0.11 [c], θ = 52.2±0.70, r = 0.9987	2.3±0.01[c]	-6.60±0.10 [c], θ = 65.5±1.0, r = 0.9937	2.33±0.005 [c]

[a] Data obtained from reference [1].

[b] Data obtained from reference [3].

[c] This work.

[d] Due to the large dimeric unit of compound **2** and the fact that B2T-PLYP involves energy calculations for g by high level MP2 method the basis set is reduced to 6-31G.

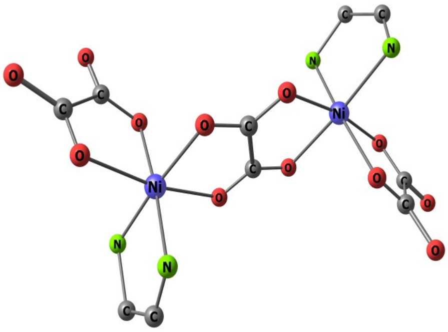

Figure 1. Molecular geometry of dimeric unit of charge = -2 used in the calculations, derived from the 1D zigzag polymer Ni(en)(ox). The environment around nickel atom is preserved. Hydrogen atoms are not shown for clarity. Drawn by Chemcraft software [16].

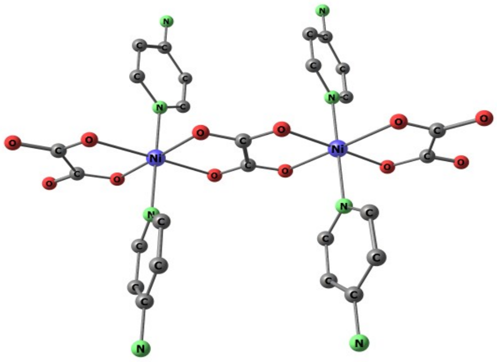

Figure 2. Molecular geometry of dimeric unit of charge = -2 used in the calculations, derived from the 1D polymer Ni(ox)(ampy)$_2$. The environment around nickel is preserved. Hydrogen atoms are not shown for clarity. Drawn by Chemcraft software [16].

In this work, we used a larger number of functionals and different basis set to calculate J values for Ni(en)(ox) and Ni(ox)(ampy)$_2$ compounds which have not been studied theoretically before.

2. Computational details

In order to estimate the theoretically J and g values of the both polymers, a dimeric unit was used in the calculations (Figures 1 and 2). The range-separated functionals (CAM-B3LYP [17], LC-BLYP [18], wB97 [19], wB97X [19], wB97X-D3 [20] and B2T-PLYP [21]) are used for the all calculations with 6-311+G* basis set. For comparison, the B3LYP hybrid functional [22] was also used for the calculation of the J and g values. We used ORCA 4.01 [23,24] program for the calculations. The advantage of range-separated functionals is to provide long range corrections. This property is absent in B3LYP and the other similar functionals. We used Equation (2) to calculate J values [25].

$$J = -(E[HS] - E[BS])/S_{max}^2 \tag{2}$$

where E[HS] and E[BS] are the total energies of the high spin and the broken symmetry wave functions, respectively, and S_{max}^2 is the maximal value of the spin squared of the system. In order to get good correlation of J with the geometry of the complexes, the coordinates of the atoms found by single crystal X-ray diffraction determinations [1,3] were used without further optimization.

3. Results and discussion

The magnetic properties (J, g) of compound **1** and **2** were calculated by ORCA 4.01 program using Equation (2) for J, and couple perturbed approach for g. Several range-separated functionals were utilized accounting for the long range interaction which is absent in Generalized Gradient Approximation (GGA) and hybrid types. These functionals are mentioned in the experimental section, and are illustrated in Table 1 together with their outcome. The experimental magnetic susceptibility (χ) values in the temperature range 5-320 K for compound **1** and 3.8-300 K for compound **2** are given in reference [1,3].

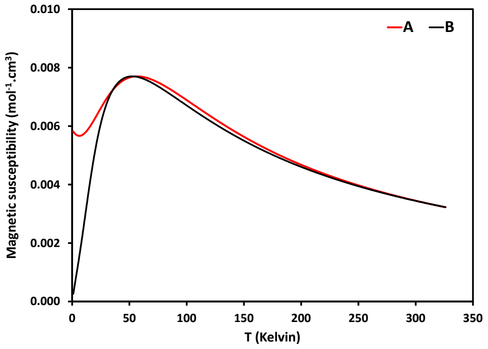

Figure 3. Magnetic susceptibility as a function of temperature. Red line represent the χ values calculated using Equation (1) and black line represent the χ values calculated using Equation (3) for compound **1** as a function of temperature.

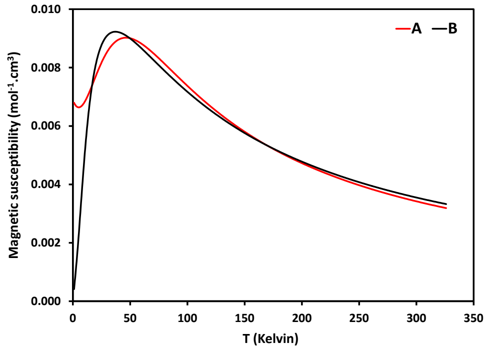

Figure 4. Magnetic susceptibility as a function of temperature. Red line represent the χ values calculated using Equation (1) and black line represent the χ values calculated using Equation (3) for compound **2** as a function of temperature.

In order to find the J and g values, they used a non-linear least square technique applied to the experimental data according to Equation (1) [2].

The curve of χ *vs* T calculated according to Equation (1) fit very well the experimental curve except a deviation was noticed below 20 K in the both complexes. A steep decrease of the experimental curve in the range < 20 K was observed, which is not accounted by Equation (1). They attributed this decrease as a result of what is called Haldane gap [26].

In this work, we propose another explanation of the steep part of the curve by applying the Curie-Weiss law to Equation (1) leading to Equation (3). This not the first time, the Weiss constant was used in a susceptibility-temperature relation [27].

$$\chi = \frac{\left(2 + 0.0194X + 0.777X^2\right)}{\left(3 + 4.346X + 3.232X^2 + 5.834X^3\right)}\left(\mathrm{N}\beta^2\mathrm{g}^2/\mathrm{k}(\mathrm{T}+\theta)\right) \qquad (3)$$

where θ is the Weiss constant.

The values of J and g parameters were already published in the references [1,3]. These values actually represent the experiment results due to the exact fit of Equation (1) in this temperature range. The numerical values of the experimental magnetic susceptibilities were reproduced here in the temperature range 20-350 K utilizing Equation (1).

The magnetic susceptibilities of compound **1** and **2** were calculated using Equation (1) (red curve in Figures 3 and 4), while the same susceptibilities were also calculated using Equation (3) (black curve in Figures 3 and 4). The curve in the range 1-20 K is an extrapolated values using Equation (3). The difference appears in the range ~1-20 K. Black curve (Equation (3)) accounts for the steep part found the experimental data of references [1,3], while Equation (1) (red curve failed to explain this range).

New values of the exchange coupling constants (J) which are obtained by the applying Equation (3) are different from those given by references [1,3] as illustrated in Figure 3 and 4. The calculated g values are nearly the same and/or lower than those given from Equations (1) or (3), Table 1. This may be attributed to the medium quality of the basis set used. As for J values according to Table 1, the range-separated functionals are on the average closer to the values deduced from Equation (3) involving Weiss constant especially CAM-B3LYP, wB97 and wB97X-D3 for the compound **1**. The range-separated functional LC-omega-PBE has given the better results than other functionals according to references [14,15]. We notice that compound **1** is a linear zigzag polymer while compound **2** is quite linear. This may explain the different values of J. The high values of θ here although it is rare but are known in literature [28,29]. The low values of J relative to θ can be explained to be due moderate and weak magnetic coupling. The effect of the quality of the basis function on the value of J is also studied at fixed functional for compound **1**. The results are shown in Table 2.

Table 2. Effect of basis set quality on the calculated magnetic coupling J at fixed functional (CAM-B3LYP) for compound **1**.

Basis set	J (cm^{-1})
SVP	-15.5
Def2-SVP	-14.7
TZVPP	-15.7
6-311+G*	-14.43
Def2-TZVPP	-15.4
QZVPP	-15.3

It is quite obvious that in our case, the quality of the basis set has little or no effect on the value of J. Also, the adding diffuse part to the basis set is ineffective. Although the difference in energy between the triplet wavefunction and the broken symmetry function is very small (few cm^{-1}), we think that this small amount should be affected by changing the quality of the basis set.

4. Conclusions

The purpose of this research is to calculate two magnetic parameters (J and g) for two nickel(II) polymers. We use different exchange correlation functionals under the DFT approximation. The calculated J due to some types of range-separated functionals using the ORCA program in most cases are approximately close to the values found by us applying Equation (3). The Weiss constant was added to Equation (1) to obtain Equation (3). The new equation was able to explain the steep part in the temperature range < 20 K of the experimental curve (χ *vs* T), which is not explainable by Equation (1). We recommend testing the CAM-B3LYP, wB97 and wB97X-D3 functionals for other system not studied in this work based on their roughly approximating the values of J. For compound **2**, we found that the best functional that reproduce J is B2T-PLYP. These results lead us to the conclusion that the best functional for calculating J is compound dependent.

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Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.

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