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Article

Magnetism of Dinuclear Co (II) complexes, theoretical investigation of Single-Molecule Magnet

Haneen, K. Al-hasany[1*] and Karrar Al-Ameed[2]

1 Department of chemistry, College of sciences, University of Kufa, Najaf.
2 Department of chemistry, College of sciences, University of Kufa, Najaf.
1* haneenk.alsaabarawi@student.uokufa.edu.iq
2karrar.alameed@uokufa.edu.iq

Abstract

One of the most complicated chemical environments, when two metallic paramagnetic centers are magnetically interacted via in between magnetic ligand, and such a four di-cobalt coordination compounds, synthesized and published systems was chosen in this work to deduce problematic magnetic properties, and according to HOMO-LUMO gaps being investigated theoretically our second tetrazine ligand di-cobalt was the most chemically reactive and has most magnetic interactions among its sites, also Magnetic Coupling Constant (J) Analysis have been conducted via Noodleman, Bencini, and Yamaguchi Approaches for all our studied systems, and Noodleman's method was the most successful predominantly with exception to Albold system, finally Spin Density Analysis performed between Mulliken, and Loewdin methodologies for all systems, and Mulliken population densities have more accuracy, and relevance.

Introduction

Magnetic coupling constants J have a crucial role in explaining the magnetic interactions between unpaired electrons in dimeric transition metal complexes. These constants quantify the strength and nature of the exchange interactions between magnetic centers, which can be ferromagnetic (positive J) or antiferromagnetic (negative J).

Accurate calculation of *J* is essential for predicting and interpreting the magnetic properties of these complexes, which have applications in molecular magnetism, catalysis, and materials science.

We have chosen four dimeric cobalt complexes with problematic magnetic properties due to the presence of radical bridging ligands between the paramagnetic d^7 cobalt centers

In dimeric transition metal complexes, each metal center typically hosts one or more unpaired electrons. The interaction between these unpaired electrons leads to multiple possible spin states, including high-spin (ferromagnetic) and low-spin (antiferromagnetic) configurations. Traditional electronic structure methods, such as Hartree-Fock or standard Density Functional Theory (DFT), struggle to accurately describe these spin states due to the complex nature of the electron correlation effects and the near-degeneracy of the spin configurations (Neese, 2021).

One of the primary challenges is the presence of strong electron correlation in transition metal complexes, where the magnetic coupling arises from the overlap of atomic orbitals and the exchange interaction between unpaired electrons. Conventional methods often fail to capture the correct balance between the competing spin states, leading to inaccurate predictions of *J*. This inadequacy stems from the inability of these methods to describe the mixed-spin nature of the true ground state of the system, which is a superposition of different spin configurations (Pederson et al., 2020).

The broken-symmetry (BS) approach, introduced by Louis Noodleman in 1981, provides a practical solution to this problem within the framework of DFT (Noodleman, 1981). The BS approach involves explicitly breaking the spin symmetry of the system to construct an approximate low-spin (antiferromagnetic) state. In this method, the total spin symmetry of the wavefunction is intentionally violated to allow for a mixing of different spin states, resulting in a state that approximates the true ground state of the system.

By calculating the energies of both the high-spin (HS) and broken-symmetry (BS) states, the magnetic coupling constant *J* can be estimated using the following relationship:

$$J = \frac{E_{\mathrm{BS}} - E_{\mathrm{HS}}}{\langle S^2_{\mathrm{HS}} \rangle - \langle S^2_{\mathrm{BS}} \rangle}$$

where E_{BS} and E_{HS} are the energies of the broken-symmetry and high-spin states, respectively, and S^2 denotes the expectation value of the total spin squared.

Spin Density Analysis: Mulliken vs. Loewdin Approaches

In computational chemistry, the analysis of spin density is crucial for understanding the electronic structure of molecules, particularly in systems with unpaired electrons such as radicals, transition metal complexes, and magnetic materials. Spin density refers to the difference in the electron density of α-spin (spin-up) and β-spin (spin-down) electrons at a given point in space. Two widely used methods for the partitioning of spin density are the Mulliken and Loewdin population analyses.

Magnetic Coupling Constant (J) Analysis: Noodleman, Bencini, and Yamaguchi Approaches

The Noodleman approach, introduced by Louis Noodleman in 1981, is based on the broken-symmetry (BS) method within the framework of Density Functional Theory (DFT) (Noodleman, 1981). This approach involves computing the energies of high-spin (HS) and broken-symmetry (BS) states. The HS state represents the ferromagnetic alignment of spins, while the BS state represents an approximate antiferromagnetic alignment. The magnetic coupling constant *J* is then derived from the energy difference between these states. Noodleman's approach is particularly advantageous for its simplicity and efficiency in handling large systems with multiple unpaired electrons.

Despite its popularity, the Noodleman method has limitations, particularly in the accuracy of the calculated *J* values. The BS state is an approximation and does not correspond to a true eigenstate of the system, which can lead to errors in the estimation of *J*. Moreover, the dependence on the choice of the DFT functional can significantly influence the results, requiring careful selection and validation for different types of magnetic systems (Gatteschi et al., 2021).

Andrea Bencini and Dante Gatteschi developed a method that extends the concepts of spin Hamiltonians and ligand field theory to calculate magnetic coupling constants (Bencini & Gatteschi, 1990). This approach involves fitting experimental magnetic susceptibility data to a theoretical model derived from the spin Hamiltonian, which includes the *J* parameter. The Bencini method is particularly effective for systems where detailed experimental magnetic data are available, providing an empirical way to determine *J* that can complement computational methods.

The primary advantage of the Bencini approach is its direct use of experimental data, which can yield highly accurate *J* values when the model fits well with the observed magnetic properties. However, this method requires high-quality experimental data and a good understanding of the underlying magnetic interactions to construct an accurate spin Hamiltonian model. Additionally, it is less straightforward to apply to large or complex systems where experimental data may be incomplete or difficult to interpret (Pederson et al., 2020).

The Yamaguchi approach, introduced by Kizashi Yamaguchi and co-workers, also utilizes the broken-symmetry DFT method but incorporates a spin-projection technique to improve the accuracy of *J* values (Yamaguchi et al., 1986). In this method, the spin contamination inherent in the BS state is corrected by projecting the BS wavefunction onto a pure spin state. This correction leads to more accurate estimations of the magnetic coupling constant compared to the conventional BS-DFT method.

The Yamaguchi approach has the advantage of providing more reliable *J* values for systems with significant spin contamination, making it particularly useful for complex magnetic systems where accurate spin-state descriptions are critical. However, the computational cost is higher than the conventional BS-DFT method, and the implementation of the spin-projection technique requires careful consideration of the spin states involved (Neese, 2021).

The Influence of HOMO and LUMO on Paramagnetic Dimer Complexes in Inorganic Compounds

The electronic structure of paramagnetic dimer complexes in inorganic chemistry is crucial for understanding their magnetic properties, reactivity, and stability. These complexes, which contain two metal centers with unpaired electrons, exhibit unique magnetic behaviors due to the interactions between the metal ions. The frontier molecular orbitals, specifically the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO), play a pivotal role in determining the electronic and magnetic properties of these complexes.

Influence on Magnetic Properties

The influence of HOMO and LUMO on the magnetic properties of paramagnetic dimer complexes is multifaceted, the relative energies and spatial distribution of the HOMO and LUMO can determine whether the magnetic interaction between the two metal centers is antiferromagnetic or ferromagnetic. When the HOMO of one metal center overlaps significantly with the LUMO of the other, it can lead to antiferromagnetic coupling due to the exchange interaction. Conversely, a symmetric overlap of HOMO-HOMO or LUMO-LUMO can promote ferromagnetic coupling (Gatteschi et al., 2021). This gab also also influences the degree of spin state mixing in the complex. Strong interactions between these orbitals can lead to significant mixing of spin states, affecting the overall magnetic moment and the thermal stability of the magnetic state (Liu et al., 2020).

Computational details

Geometry optimizations were accomplished using, the [BP86] functional in conjnction with the [def2-TZVP] basis set for all atoms. The BP86 functional, which includes Becke's 1988 exchange functional with Perdew's 1986 correlation fnctional, is well-suited for gumetry optimizations due to its equilibrium of computational efficiency and accuracy in discribing transition metal complexs (Becke, 1988; Perdew, 1986). The def2-TZVP basis set provides a good compromis between computational, cost and the acuracy of the electronic structur, particularly for transition metals (Weigend & Ahlrichs, 2005).

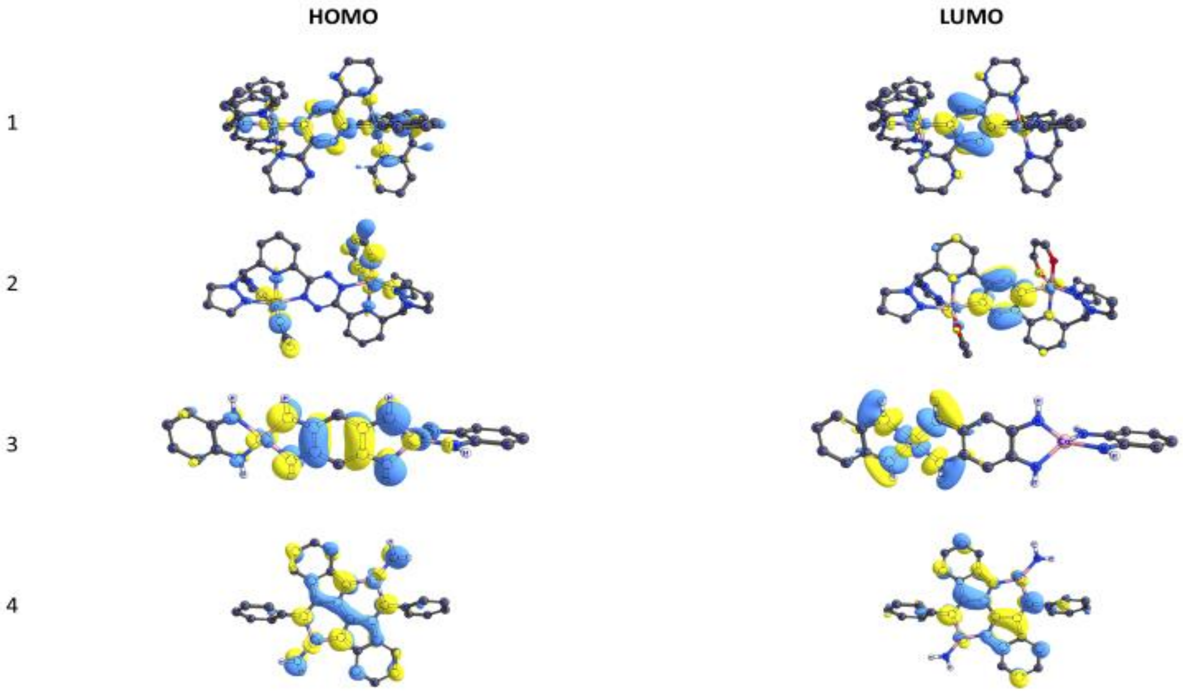
The optimized geometris were established to be local minima by, the absence of imaginary frequencies in subsquent vibrational, frequency calculations.

Single-point broken-symmetry (BS) calculations were, then achieved on the optimized geometris to determine, the magnetic coupling constant J. These calculations employed a variety of fnctionals: B3LYP, BHLYP, M06, TPSS, TPSSh, and BP86. The B3LYP functional combins Becke's three-parameter exchang functional with the Lee-Yang-Parr corelation functional, providing, a good balance for a diversity of systems (Becke, 1993; Lee et al., 1988). BHLYP are a hybrid fnctional with a higher percentage, of Hartree-Fock exchang, which can provide, diffirent insights into magnetic interctions (Becke, 1993). The M06 functional, developed by Truhlar and co-workers, includes meta-GGA terms and is known for its acuracy in thermochemistry and kinetics (Zhao & Truhlar, 2008). TPSS is a meta-GGA fnctional developed by Tao, Perdew, Staroverov, and Scuseria, known for it accurate treatment of exchang-correlation energies (Tao et al., 2003). TPSSh is a hybrid type of TPSS that includes a portion, of Hartree-Fock exchange, ornamental its performance for several systems (Staroverov et al., 2003).

Results and discussion

In paramagnetic, cobalt dimer complexes, the HOMO and LUMO are particularliy important for some reasons, as an example when the magnetic interactions between the two metal centirs in a dimer complex are influenc by the overlap of there magnetic orbitals. The natur of the HOMO and LUMO can effect the extent of this overlape, thereby influencing the, magnetic coupling constant JJJ. A minor HOMO-LUMO gap can lead to stronger interctions and thus a more noticeable magnetic behavior (Pederson et al., 2020). On the other hand, the ease with which electrons can be relocated between the two metal centirs is influenc by the HOMO and LUMO energies. A smaller gap facilitates electron transfer, which can enhance the magnetic interactions and affect the overall magnetic properties of the complex (Neese, 2021), also The HOMO and LUMO levels dictate the chemical reactivity of the dimer complex. A higher HOMO energy indicates a greater tendency to donate electrons, while a lower LUMO energy suggests a greater ability to accept electrons. These properties can influence the interaction of the dimer with other molecules, affecting both its reactivity and its role as a catalyst in various reactions (Noodleman, 1981).

We refer to our investigated systems 1 as woods, 2 Yao, 3 Albold, and 4 as Fortier's regarding reactivity, HOMO and LUMO are calculated then visualized as shown in Figur.1



Figur.1: HOMO-LUMO for our systems 1 Woods, 2 Yao, 3 Albold. 4Fortier

By tracking the values in Table 1We can conclude that system 3 is most stable among the others, followed by 4, then 1, and finally the 2nd system is theoretically observed to be most reactive magnetic sound di-cobalt complex.

Table 1: HOMO-LUMO energy values calculated by B3LYP functional with TZVP basis set

system	HOMO	LUMO	Gab
1	-0.5259	-0.5038	0.0221
2	-0.3548	-0.3329	0.0219
3	0.0983	0.1303	0.032
4	-0.1589	-0.132	0.0269

In the study of magnetic properties of molecules, particularly those containing transition metals and organic radicals, the magnetic coupling constant *J* plays a pivotal role. This constant describes the strength and nature of the magnetic interaction between two or more unpaired electrons, which can be either ferromagnetic, or antiferromagnetic. Accurate determination of *J* is essential for understanding the magnetic behavior of materials and for designing novel magnetic compounds. Three prominent methods used for evaluating magnetic coupling constants are the Noodleman, Bencini, and Yamaguchi approaches, each with distinct methodologies and applications.

From Table 2 in system **1** were the cobalt-cobalt coupling interaction J value is -62 cm^{-1} we see that best results obtained with Noodleman approach, in the same level of performance Yamaguchi while Bencini comes last, noteworthy that all these data were conducted according to M06 functional, that resulted -13.2,

Table 2: coupling exchange values in (cm-1) calculated theoretically by different levels of DFT, by the three common approaches. For system *1*

FUNC	Noodleman	Bencini	Yamaguchi
BHLYP	1.1	0.8	1.1
M06	-13.2	-9.9	-13.3
B3LYP	3.5	2.6	3.5
TPSSH	6.1	4.6	6.1
TPSS	12.8	9.6	12.8
BP86	11.1	8.3	11.1

In case of Yao, system **2** we observed from Table 3 that the best approach was under Noodleman method by BHLYP functional -2.6 cm^{-1} which decided after comparison with the measured J value -2.3 cm^{-1} in their published paper

Table 3: coupling exchange values in (cm-1) calculated theoretically by different levels of DFT, by the three common approaches. For system 2

FUNC	Noodleman	Bencini	Yamaguchi
BHLYP	-2.6	-1.9	-2.6
M06	-28.7	-21.5	-28.9
B3LYP	-9.7	-7.3	-9.7
TPSSH	-13.3	-10.0	-13.4
TPSS	-25.5	-19.1	-25.6
BP86	-44.2	-33.2	-44.6

In system **4**, according to the reported J value 14.5 cm^{-1} we can see that Bencini gives the best results -0.4 cm^{-1} while Noodleman, and Yamaguchi comes last, all these data were generated under BHLYP level of the theory according to Table 4.

Table 4: coupling exchange values in (cm-1) calculated theoretically by different levels of DFT, by the three common approaches. For system 3

FUNC	Noodleman	Bencini	Yamaguchi
BHLYP	-0.5	-0.4	-0.5
M06	-15.5	-11.6	-15.6
B3LYP	-12.8	-9.6	-12.8
TPSSH	-14.1	-10.6	-14.1
TPSS	-32.3	-24.2	-32.2
BP86	-62.9	-47.2	-62.5

Noteworthy that the system 3 published in [ref], no direct Co-Co exchange coupling value reported to compare with, but depending on the behavior of the used function Table 5 we recommend BHLYP to be -20 cm^{-1} according to Noodleman approach

Table 5: coupling exchange values in (cm-1) calculated theoretically by different levels of DFT, by the three common approaches. For system 4

FUNC	Noodleman	Bencini	Yamaguchi
BHLYP	-20.0	-15.0	-20.0
M06	-28.9	-21.7	-29.0
B3LYP	-43.8	-32.8	-43.8
TPSSH	-57.2	-42.9	-57.0
TPSS	-94.6	-70.9	-93.3
BP86	-115.7	-86.8	-113.4

Mulliken population analysis, introduced by Robert S. Mulliken, is one of the earliest and most commonly used methods for interpreting the results of quantum chemical calculations. This method partitions the electron density among atoms based on the contributions of atomic orbitals to molecular orbitals. In the context of spin density, Mulliken analysis provides a straightforward way to estimate the spin population on each atom by summing the contributions of spin-up and spin-down electrons localized on atomic orbitals (Mulliken, 1955; Zhang et al., 2021).

The straightforwardness of Mulliken analysis is one of its major rewards. It is easy to implement and computationally effectual, making it a popular choice for original qualitative insights. Mulliken analysis has noteworthy limitation. The results can be very basis-set dependent and may occasionally produce non-intuitive or non-physical spin population, particularly for diffuse or overlapping orbitals. This dependency arises because the technique does not account for, the orthogonality of the basis set (Yang et al., 2020).

Loewdin population analysis, proposed by Per-Olov Loewdin, addresses some of the limitations of the Mulliken method. The Loewdin method involves orthogonalizing the atomic orbitals before partitioning the electron density. This orthogonalization process reduces the dependence on the choice of the basis set and generally provides more stable and reliable results compared to Mulliken analysis (Loewdin, 1950; Liu et al., 2020).

In terms of spin density, the Loewdin method is known to yield more accurate and physically meaningful distributions of spin populations, especially in systems where the atomic orbitals have significant overlap. The orthogonalization ensures that the partitioning of electron density is more consistent with the true electronic structure of the molecule, making Loewdin spin densities preferable for quantitative studies and more accurate interpretations of magnetic properties (Cheng et al., 2021).

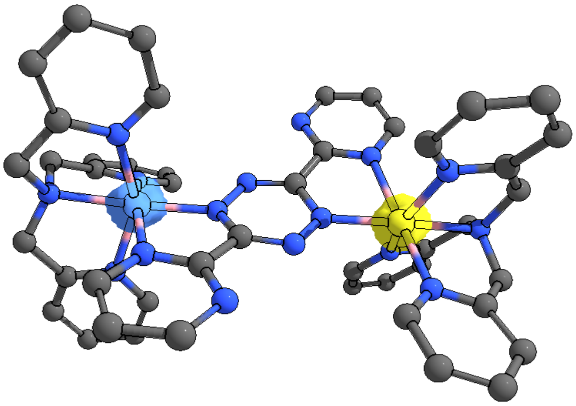
Among Mulliken and Loewdin spin densities in broken symmetry state mentioned in Table 6,

Table 6: Electron populations in broken symmetry spin state for 1st and 2nd cobalt centers, calculated by Mulliken, and Loewdin methods

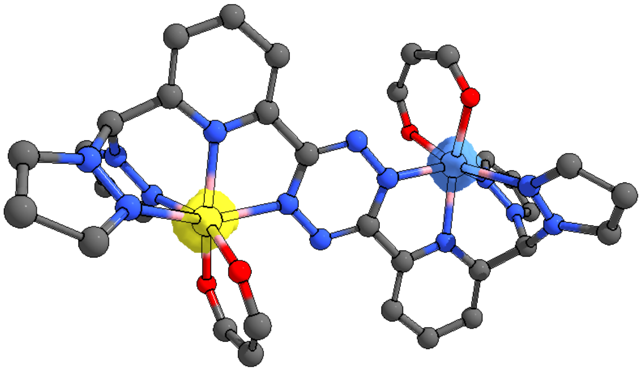
system	Mulliken		Loewdin	
	Co1	Co2	Co1	Co2
1	2.72	-2.7	2.71	-2.71
2	2.81	-2.81	2.79	-2.79
3	2.79	-2.79	2.76	-2.76
4	2.81	-2.81	2.77	-2.77

That densities generated by Mulliken method is more reliable in comparison with Lowden’s due to higher electron fragment localizations on cobalt centers Figure .2, resulted from considerations discussed earlier in introduction section

(1)



(2)



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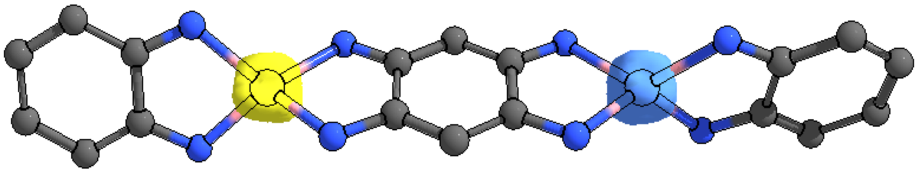

(4)

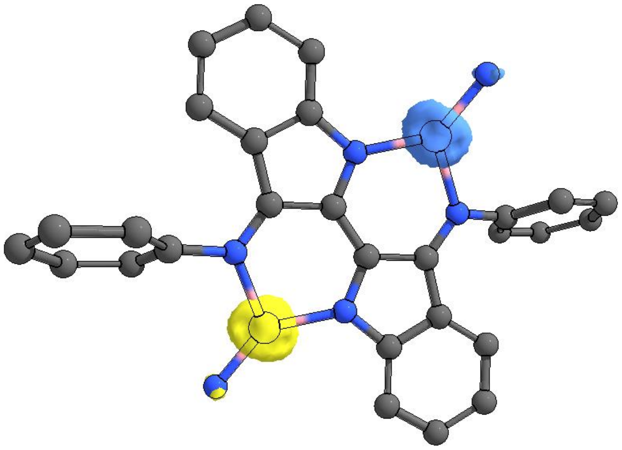

Figure .خطأ! لا يوجد نص من النمط المعين في المستند2: Visualized spin densities being calculated by DFT to four systems, showing broken symmetry spin state, yellow cloud resents up spin electrons, blue cloud represents down spin electrons

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