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Article

Tetrazine bridging ligand in spin-only magnetic coupling in complex dimers

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Abstract

This study focuses on examining the unconventional magnetic coupling between two metal centers in dimers bridged by a tetrazine ring. Computational analysis was conducted to understand the impact of radical perturbation in the bridging ligand on the magnetic properties of previously synthesized three compound of nickel (Ni) dimers. To achieve this, broken-symmetry density functional theory (BS-DFT) functionals were applied to explore the magnetic interactions in greater depth. This approach provided an accurate quantitative representation of the coupling nature between the metal centers. To investigate the effect of the radical, the dimers were analyzed in two different oxidation states of the bridging tetrazine: the neutral state and the radical state were selected to explore the effectiveness of incorporating radical bridges into the architecture of single-molecule magnets. Initially, these complexes were studied in their neutral forms, prior to one-electron reduction. Magnetic coupling between the two nickel centers revealed antiferromagnetic interactions across all three models (Noodleman, Bencini, and Yamaguchi), as determined using broken-symmetry density functional theory (BS-DFT) calculations.

However, the addition of one electron to the bridging ligands induced a notable shift in the magnetic behavior. The magnetic moment curves indicated a preference for ferromagnetic coupling upon cooling, consistent with experimental observations. A series of DFT calculations was conducted to further investigate the influence of Hartree–Fock exchange (HF%) in hybrid functionals. The study highlights the critical importance of functional dependency in interpreting magnetic coupling and emphasizes the need for careful selection of functionals before drawing definitive conclusions.

Keywords: Dft ,coupling Dimers,Computational chemistry

Introduction

Over the past two decades, significant advancements have been made in the development of coordination compounds[1], ranging from mononuclear and multinuclear metal complexes to extended solid materials[2-4], which have demonstrated magnetic bistability. These molecular magnets are designed through the careful selection of bridging ligands and paramagnetic metal ions, allowing for precise structural control and the optimization of their magnetic properties at the molecular level.

In addition to their structural advantages, molecular magnetic materials have attracted considerable interest due to their potential applications in high-density information storage, permanent magnet design, magnetic sensing, and gas separation[4-6]. This interest is largely driven by their small size, low density, and chemical tunability.

To ensure the effectiveness of these applications under ambient conditions, it is essential to develop magnetic materials that exhibit stable magnetic ordering or slow magnetic relaxation at higher temperatures. Achieving this requires strengthening magnetic exchange interactions, which play a crucial role in determining the critical temperature of two- and three-dimensional magnets, the thermal relaxation barrier of single-chain magnets[8], and the stabilization of the spin ground state in single-molecule magnets[9].

Despite the critical importance of magnetic exchange strength, most molecular magnets consist of paramagnetic metal ions connected through diamagnetic ligands. In such cases, magnetic exchange occurs via an indirect superexchange mechanism through the ligand, leading to relatively weak magnetic coupling, particularly when multi-atom bridging ligands are involved. However, certain single- or two-atom

bridging ligands, such as oxo and cyano ligands, can mediate sufficiently strong superexchange interactions, enabling the development of magnetic materials with enhanced thermal stability[7] Three-dimensional magnets that operate at high temperatures face limitations in structural diversity and ligand functionalization. As an alternative approach, incorporating a paramagnetic bridging ligand can significantly enhance magnetic.

exchange strength due to the direct overlap of orbitals containing unpaired electrons[10]. This strategy has been fundamental in achieving the first room-temperature molecular magnet, enabling the first experimental observation of slow magnetic dynamics in one-dimensional systems and leading to the highest recorded magnetic blocking temperature for a single-molecule magnet[11].

In the pursuit of strong magnetic exchange interactions between metal ions and paramagnetic ligands, quinonoid-type ligands provide an ideal platform for developing molecular magnets[11]. Their ability to undergo redox reactions allows them to stabilize both diamagnetic and paramagnetic redox isomers. Studies have shown that dinuclear complexes bridged by tetraoxolene radicals exhibit strong metal–ligand interactions[12], with even greater magnetic exchange strength observed when nitrogen donors replace oxygen donors[13] due to their more diffuse orbitals, which enhance magnetic exchange.

In a recent study, we designed a single-molecule magnet based on divalent iron (FeII), where an azophenine radical served as the bridging ligand. This system exhibited a well-isolated S = 7/2 spin ground state that remained stable even at 300 K, with an estimated magnetic exchange coupling constant of $J \approx 900\ cm^{-1}$.[14] These findings, along with the relative scarcity of radical-bridged molecular magnets with strong magnetic exchange, motivated us to extend our investigation to other transition metals. Our aim was to evaluate the generalizability of this approach and explore how structural factors influence metal–radical interactions.

In a complex dimer with a neutral tetrazine bridging ligand, the magnetic properties can be influenced by the nature of the metal centers and the ligand itself. When described as "spin-only magnetic," it suggests that the magnetic behavior arises purely from the unpaired electrons' spins in the metal centers, without significant contributions from orbital angular momentum. This typically occurs in transition

metal complexes where orbital contributions are quenched, and the magnetic moment can be calculated using the spin-only formula:

$\boldsymbol{\mu = \sqrt{n(n+2)}}$ Bohr magnetons where $\boldsymbol{n}$is the number of unpaired electrons.

The tetrazine ligand, being neutral, can facilitate electron delocalization between the metal centers, potentially affecting the overall magnetic interactions within the dimer. The specific magnetic properties would depend on the type of metal ions involved, their oxidation states, and the overall geometry of the complex.

Tetrazine bridging ligands play a crucial role in magnetic coupling in complex dimers. These nitrogen-rich ligands enable spin-only magnetic interactions between metal centers within a dimeric complex. The tetrazine bridge facilitates effective orbital overlap and electron exchange between the metal ions, resulting in different magnetic coupling behaviors like ferromagnetic or antiferromagnetic coupling, depending on the metal centers' specific characteristics and electronic configurations. Investigating these systems is vital for understanding and designing materials with particular magnetic properties, which have applications in molecular magnetism and spintronics.

The study of complex dimers with neutral tetrazine bridging ligands offers fascinating insights into the magnetic properties of transition metal complexes. These systems are particularly intriguing due to their "spin-only magnetic" behavior, where the magnetic characteristics arise predominantly from the spins of unpaired electrons in the metal centers, while contributions from orbital angular momentum are negligible. This phenomenon is commonly observed in transition metal complexes where orbital effects are effectively quenched.

A crucial aspect of understanding these complexes lies in calculating their magnetic moment using the spin-only formula, which depends on the number of unpaired electrons in the system. The magnetic behavior of these dimers is influenced by several factors, including the types of metal ions present, their oxidation states, and the overall geometry of the complex.

Tetrazine ligands, with their rich nitrogen composition, facilitate electron delocalization between metal centers. This delocalization is pivotal as it can determine the nature of magnetic interactions—ranging from ferromagnetic to

antiferromagnetic—within the dimer. Such interactions depend heavily on the electronic configurations and specific characteristics of the metal centers involved.

The ability to manipulate these magnetic properties is of significant interest in the design of materials with tailored magnetic characteristics, which have potential applications in molecular magnetism and spintronics. By exploring the interplay between tetrazine ligands and metal centers, researchers aim to develop advanced materials with customized magnetic behaviors, contributing to advancements in materials science and related fields.

The study of single molecule magnets (SMMs) based on transition metals is a crucial area of modern inorganic chemistry. Understanding the electronic structure and the nature of spin interactions between the paramagnetic sites in these complexes is essential for improving the molecular design of these magnets. SMMs have important applications in technology, including high-density data storage, quantum computing, spintronics, and MRI contrast agents[15-17]. A key focus in designing SMMs with specific.

properties is to enhance the magnetic coupling between the paramagnetic centers, which are typically metallic ions, within the molecules. This requires an in-depth understanding of the electronic structure at the molecular level, especially the factors that affect magnetic coupling interactions between metal centers[15,16,18-20].

The paramagnetic characteristics of transition metal complexes are generally due to unpaired electrons in their d-orbitals. Metals like iron, nickel, manganese, and cobalt are often used as paramagnetic centers in SMMs[17,21-23]. The unpaired electrons contribute to a magnetic moment, allowing the molecule to interact with an external magnetic field[24]. The energy barrier between different spin states arises from complex electronic and magnetic interactions within the molecule, exhibiting magnetic anisotropy. However, adding more paramagnetic metals does not necessarily improve magnetic properties. Instead, optimizing interactions between metal centers is vital for designing more effective molecular magnets. One successful strategy involves introducing a paramagnetic ligand between the metal centers, enhancing the coupling and often resulting in desired ferromagnetic behavior and increased magnetic anisotropy. A major goal in modern inorganic synthesis is to create SMMs with significant anisotropy by linking metals through radical-bridged ligands, such as N_2[25-26], azophenine[27], aminyl[24], p-semiquinone[28], and indigo[29]. Recent research has

focused on transition metal dimers coupled with organic radical bridges to design controlled SMMs[30].

Recent research has highlighted significant progress in enhancing magnetic interactions through the use of radical bridges, such as nitrosyl nitroxide, which have proven effective in strengthening exchange coupling between metal centers, thereby improving magnetic stability. Additionally, compounds like H_4 tbca (1,2,4,5-benzenetetracarboxylic acid) and bpb (1,4-bis(4-pyridyl)benzene) have been explored as radical bridges linking cobalt centers, enabling control over magnetic anisotropy and extending the longevity of stable magnetic states[32-33].

Recently, dinuclear cobalt and nickel complexes with bipyridyl radical linkages have gained attention for their magnetic susceptibility and slow magnetic relaxation behavior[30]. These studies form the foundation for the development of single-molecule magnets (SMMs)[31-35,36] based on transition metals, essential for tuning magnetic properties[31].

In recent years, significant focus has been placed on the design of single-molecule magnets based on radical tetrazine rings[35-37]. These systems are characterized by the presence of a radical tetrazine six-membered ring. Several studies have successfully synthesized air-stable tetrazine-bridged Co_2 [38] and Ni_2 [39]dimers, as well as SMMs based on Dy_2 dimers using radical tetrazine bridges[40-41].

While these compounds are not entirely novel, earlier research in the 1980s[42] successfully synthesized similar copper-based compounds and compounds containing heavy metals[36]. However, the concept of single-molecule magnets (SMMs) was not established at that time, and the first SMM molecule was reported only in 1993[21].

Molecules containing tetrazine rings stand out due to their unique structural and electronic characteristics, making them some of the most intriguing bridging ligands in coordination chemistry. This has facilitated their application in a range of fields, including molecular magnetism[24], photocatalysis, energetic materials, and luminescence.

Tetrazine-based frameworks are nitrogen-rich compounds and are classified as redox non-innocent ligands, meaning they not only coordinate to metals but also influence the oxidation state[43] of the complexes. As illustrated in Figure 1, these molecules

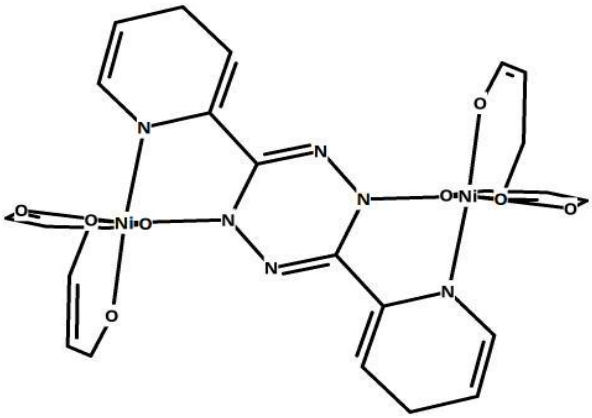
consist of a six-membered ring with four nitrogen atoms at positions 1, 2, 4, and 5, with substituents at positions 3 and 6.

Kaim and his colleagues have investigated the electrochemical properties of electron-rich metal complexes, demonstrating how these frameworks affect the electronic dynamics of the ligand-metal system.[42] They also made a significant contribution by identifying the first air-stable tetrazine radical complex, [(Ph_3 P)$_2$ Cu(Z_4 m,bptz__)Cu(PPh_3)$_2$] (BF_4), where bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, showing its potential in future molecular magnet applications The direct reduction of tetrazines was first demonstrated without intentionally adding a reducing agent. Later, Patra and colleagues showed the same tetrazine ring reduction in the compound [(p-cym) RuIICl_2 (m-bpytz)]+.[44] The magnetic properties of the first air-stable tetrazine-based radical-bridged complex, [Cp_2 Co[Dy(tmhd)$_3$]$_2$ (bptz)], and its neutral counterpart, [Dy(tmhd)$_3$]$_2$ (bptz)], were characterized by the Dunbar group.45 Both complexes exhibit single-molecule magnet (SMM) behavior in the absence of an applied field. Recently, the Dunbar group successfully isolated [Dy_3 (Hfac)$_6$ (bptz)$_3$], a novel radical-bridged lanthanide metallacycle46. The strength of the magnetic exchange coupling between the delocalized radical and Dy(III) was estimated to be J = 6.62 cm^{-1}.

These studies have highlighted the significant potential of radical tetrazine-bridged complexes in the development of single-molecule magnets (SMMs). However, the exact mechanism by which a radical-bridged ring influences magnetic superexchange coupling is not yet fully understood, requiring further in-depth discussions to interpret the complex behavior of radical exchange coupling in such species. Notably, the same radical ring exhibits distinct coupling characteristics when bridging Ni_2 dimers as opposed to Co_2 dimers. While the former clearly demonstrates strong ferromagnetic coupling, the behavior of the cobalt species significantly deviates.

The puzzling nature of the magnetism observed in these tetrazine-bridged dimers remains unclear. More detailed investigations are essential to understand how the coupling mechanisms between the metal centers are influenced by the presence or absence of radical perturbations on the bridging tetrazine. In this study, we discuss the magnetic properties of tetrazine-bridged dimers, where the spin interactions between transition metal complexes predominantly govern the magnetic behavior. The magnetic exchange couplingconstant, J, is the key parameter we aim to investigate.

single-molecule magnets from tetrazine dimers, we engineered the addition of nonradicals by reducing the tetrazine ring, as suggested by Kaim et al. To study the influence of the radical systems on the exchange coupling mechanism, we calculated two different species for each dimer to highlight the main differences in their electronic structures. First, we determined the exchange coupling constants for the interaction between the two metals and then added a radical electron with spin = 1/2 as a perturbation to the system. This approach allowed us to calculate an additional J parameter resulting from the interaction of each metal with the radical tetrazine ring. Furthermore, we studied three different dimers based on Ni(II) . We will first present the Ni dimer, characterized by its unperturbed magnetism. These two compounds were synthesized experimentally, and their X-ray structures and magnetic data serve as references for our results.



Computaional datils

All calculations presented in this chapter were performed using Orca 4.2.1, an open-source software developed by Frank Neese's group at the Max Planck Institute[48]. This package employs Gaussian-type orbitals (GTOs) as the basis sets for atomic orbitals. Unlike Gaussian, Orca has been validated for accurately converging degenerate states, making it a powerful tool for computing the magnetic properties of paramagnetic transition metal complexes. Additionally, the(def2/J) auxiliary basis sets, developed by Weigend, were employed to accelerate the calculation of two-electron integrals.

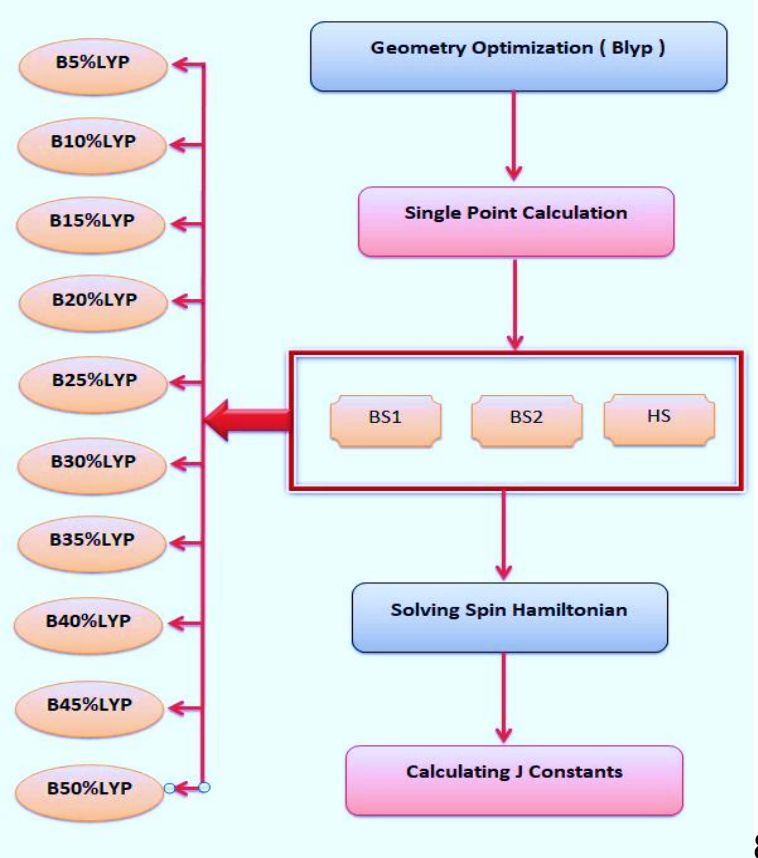
The study began with the crystal structure of the compounds, followed by Density Functional Theory (DFT) calculations to obtain the optimized geometries using the Generalized Gradient[49-50] Approximation (GGA) with the B3lyp functional[51] and the triple-zeta valence polarized basis set (def2-TZVP) [52]for all atoms in the studied compounds[53]. After ensuring that the vibrational modes of the converged geometries

were free from any imaginary frequencies, single-point calculations were performed to investigate three different spin states. For radical species, three spin configurations were examined: High-spin (HS) state, where the number of unpaired electrons is maximized.

Broken-symmetry state 1 (BS1), in which the radical electron on the tetrazine ring is flipped. Broken-symmetry state 2 (BS2), where the spin of one of the metallic centers is flipped from all-alpha to all-beta. The primary objective of these calculations was to determine the magnetic exchange interaction constant (J), which quantifies the strength of the magnetic coupling between spin centers. To achieve this, different mathematical approaches were employed to solve the linear equations derived from the Heisenberg-Dirac-van Vleck (HDVV) spin Hamiltonian. Here, the non-relativistic Kohn-Sham Hamiltonian eigenvalues were mapped onto the diagonal elements of the spin Hamiltonian, as represented in the following equation.

$$H_{\mathrm{HDvV}} = -J_{ij} \sum_{i>j} S_i . S_j \qquad 1$$

Noodleman's broken symmetry (BS) method was chosen to all extract all the exchange coupling constants of the compounds involved in this study[54,55-57] the summary of this process can be represented in the flow diagram:



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the structure and the electronic configuration of tetrazine-bridged dimer. Hydrogen atoms are omitted for clarity

Results and discussions

We conducted a series of calculations to compare three promising ligands introduced as radical bridges to enhance the magnetic properties of single-molecule magnets. Specifically, we investigate the effect of radical ligand perturbation on the magnetic properties by studying the dimers both before (neutral) and after (radical) the addition of an extra electron on the bridge. The three ligands examined are bipyridine , tetrazine , and tetraoxolene, all of which are redox-active species ,To analyze the effect of the radical tetrazine ring on the coupling interactions between the ligands, we studied the compounds in two different oxidation states: the oxidized (non-radical) form, where the tetrazine ring is neutral, and the reduced (radical) form, where an extra electron is added, as synthesized by Woods et al. and Yao et al. It can be observed that the coordination sites of nickel atoms are nearly octahedral in the divalent nickel charge state. The clear result is the degenerate state of the d8 configuration, which is not affected by Jahn-Teller distortion. Radicals derived from the compound 1,2,4,5-tetrazine (known as s-tetrazine) have attracted significant attention in the field of coordination chemistry due to their unique redox properties

and their ability to enhance magnetic interactions in metal complexes. The tetrazine ring is known for its electron-deficient nature, which enables it to accept electrons and form stable radical anions. These anions play a crucial role in strengthening magnetic coupling between metal centers—an important feature in the design of single-molecule magnets (SMMs) that rely on efficient magnetic communication. Studies have shown that incorporating s-tetrazine-based radical ligands into transition metal or lanthanide complexes significantly affects their magnetic properties, as the reduction of the tetrazine bridge to its radical anion form greatly enhances magnetic interactions between the metal centers.

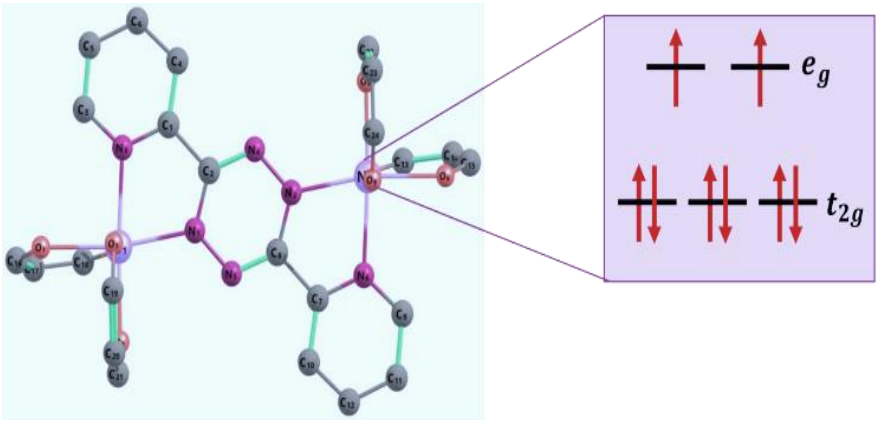

Figure 1.3 the structure and the electronic configuration of tetrazine-bridged dimer. Hydrogen atoms are omitted for clarity. This study presents key magnetic parameters for a tetrazine-bridged nickel dimer, focusing on how varying percentages of Hartree-Fock exchange (HFX) influence spin-state characteristics, energy splitting, and magnetic exchange interactions. The parameters evaluated include the expectation values of the total spin squared $\langle S^2 \rangle$ for both high-spin (HS) and broken-symmetry (BS) states, energy differences (ΔE) between these states, and exchange coupling constants calculated using three distinct theoretical models: Noodleman, Benicini, and Yamaguchi. Additionally, spin density (ρ) values on the two nickel centers (Ni_1 and Ni_2) were analyzed to assess magnetic delocalization.

A clear trend is observed in the $\langle S^2 \rangle$ values as HFX increases. For the HS state, the $\langle S^2 \rangle$ values remain close to the ideal value of S(S+1) for an S = 2 system, reflecting a well-described spin configuration. In contrast, the BS state shows significant spin contamination at lower HFX values, with $\langle S^2 \rangle$ near 2, deviating from the expected singlet. However, as HFX increases, this contamination diminishes, indicating an

improved representation of the spin states and a more accurate broken-symmetry description.

Energy splitting (ΔE) between the HS and BS states shows a pronounced decrease with increasing HFX. At low exchange contributions (5% HFX), ΔE is large (~33.5 cm^{-1}), but this value rapidly declines, approaching ~3 cm^{-1} at 30–40% HFX. This trend suggests a progressive weakening of the exchange interaction as Hartree-Fock exchange increases.

Exchange coupling constants derived from Noodleman's, Benicini's, and Yamaguchi's approaches all reflect a similar pattern: stronger antiferromagnetic coupling at low HFX that steadily weakens with increasing exchange, approaching negligible values beyond 30% HFX. This consistency across computational models supports the reliability of the observed Spin population analysis further reveals that as HFX increases, the spin densities on Ni_1 and Ni_2 grow in magnitude, indicating greater spin localization. This shift implies reduced magnetic delocalization and a clearer differentiation between the magnetic centers, further supporting the conclusion that higher HFX percentages enhance the definition of the broken-symmetry state and modulate magnetic exchange pathways within the dimer system.

.Table 1: list of spin contamination parameters $< S^2 >$ energies splitting between broken symmetry state and high spin state ($\Delta E\ cm^{-1}$), exchange coupling constant ($J\ cm^{-1}$) coupling and mulliken spin densities (ρ)parameters of tetrazine Ni dimer.

HFX%	HS $< S^2 >$	BS $< S^2 >$	ΔE	Noodle Man	Benicini	Yamaguchi	$\rho_{Ni_1}{}^1$	ρ_{Ni_2}
5%	6.0417	2.0468	33.52	-8.38	-5.59	-8.39	1.546914	-1.546873
10%	6.0237	2.0257	15.891	-3.97	-2.65	-3.97	1.587579	-1.587518
15%	6.0159	2.0167	8.142	-2.04	-1.36	-2.04	1.627645	-1.627635
20%	6.0125	2.0128	5.198	-1.3	-0.87	-1.3	1.664656	-1.664656
25%	6.0109	2.0111	3.354	-0.84	-0.56	-0.84	1.697447	-1.697451
30%	6.01	2.0102	3.263	-0.82	-0.54	-0.82	1.725961	-1.725969
35%	6.0095	2.0097	3.163	-0.79	-0.53	-0.79	1.750456	-1.750468
40%	6.0092	2.0095	3.143	-0.79	-0.52	-0.79	1.771477	-1.771489
45%	6.009	2.0095	3.667	-0.92	-0.61	-0.92	1.789407	-1.789418
50%	6.0089	2.0096	3.946	-0.99	-0.66	-0.99	1.804793	-1.804807

The figure1.4 illustrates the variation of the magnetic exchange coupling constant (in cm^{-1}) as a function of the Hartree-Fock (HF) exchange percentage for a Ni–Ni dimer bridged by a tetrazine radical ligand. The coupling constants are derived using three theoretical frameworks: Noodleman (blue), Bencini (orange), and Yamaguchi (green), offering a comparative perspective on computational treatment.

Across all levels of HF exchange, the values remain negative, indicating a consistently antiferromagnetic interaction between the two nickel centers. However, the absolute magnitude of is notably reduced relative to that observed in a previously studied neutral bipyridine-bridged dimer. This attenuation suggests that the tetrazine

radical bridge, despite its redox activity, does not facilitate magnetic communication as effectively as neutral bridging ligands.

At lower HF exchange percentages (5%–20%), the antiferromagnetic coupling is more pronounced, reflected by more negative values. This corresponds to a more delocalized electronic structure that enhances magnetic exchange. As the HF exchange percentage increases, steadily approaches zero, indicating a suppression of magnetic coupling, likely driven by increased electron localization associated with greater exact exchange contributions. This behavior is consistent with trends observed in the neutral dimer, reinforcing the idea that Hartree-Fock exchange influences the delocalization pathways critical for efficient magnetic interactions.

Among the computational methods, Yamaguchi consistently predicts the strongest exchange interactions at lower HF percentages, whereas Noodleman and Bencini yield slightly less negative values. At higher HF exchange levels, the results from all three methods converge, suggesting that method-dependent discrepancies diminish as exchange localization dominates.

Overall, the analysis underscores the key role of the tetrazine radical bridge in modulating exchange interactions, and highlights the sensitivity of computed values to the treatment of exact exchange. This emphasizes the importance of method selection when modeling radical-bridged magnetic systems, particularly in systems where subtle electronic effects govern magnetic behavior.

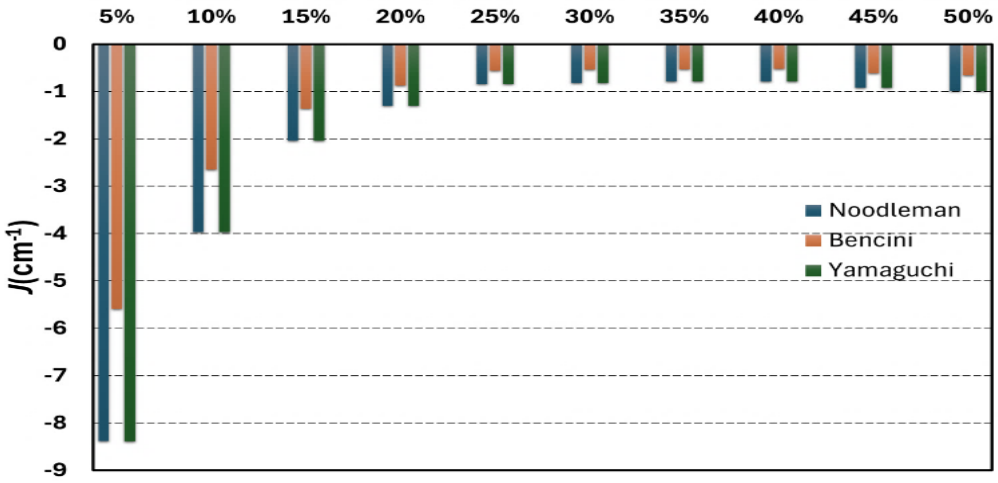

Figure 1.4 : the exchange coupling constants for Tetrazine bridged dimer

the study the efficiency of different organic ligands before the radical perturbation, we have studied the three different ligands before the one-electron reduction. The neutral ligands order will be discuss starting from the Bipyridne, tetrazine and finally

the tetraoxolene bridging ligands. In this form, two spin states are required to study the magnetic parameters that are represented by the exchange coupling constat (***J***). We have proved that the functional choice in the study of the magnetic coupling is very crucial, in particular, the exchange integral part of the Hamiltonian. Therefore, we have conducted series of Becke hybrid functionals with varies Hartree-Fock exchange (HFX) percentage (ranged from 5% to 50%).

computed using broken-symmetry density functional theory (BS-DFT) with varying percentages of Hartree-Fock exchange (HFX) in the B3LYP functional. The results provide insights into spin contamination, energy splitting between the high-spin (HS) and BS states, exchange coupling constants J computed using three magnetic behavior.

different models (Noodleman, Bencini, and Yamaguchi), and the spin density distribution on the Ni centers. A systematic trend in magnetic interactions is observed as the fraction of exact exchange increases, affecting both the coupling strength and spin localization.

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