

Electronic Structure, Reactivity, And Some Magnetic Properties of Paramagnetic Tetrahedral Di Nuclear Cobaltous Complexes. (Theoretical Study)

Ali K. Almansori 1 and Falah S. Abd-Suhail 2

1Department of chemistry, College of sciences, University of Kufa, Najaf,

2College of pharmacy, The Islamic University, Najaf.

alialmansori.aa@gmail.com

Abstract:

The tetrahedral paramagnetic di-cobaltous complex is an important class of coordination compounds that have many applications in various fields such as catalysis, single molecular magnet SMM, and spintronics[1], using BP86 functional[24] with def2-TZVP[25], basis set, while the broken symmetry theoretical method was conducted by B3LYP functional, the reactivity of the synthesized paramagnetic di cobaltous $[\text{Co}_2\text{LI}_2\text{OH}]^+$ complex[2] can be enhanced by the lowering HOMO-LUMO gap effect of oxo bridging ligand instead hydroxo ligand, also from the different theoretical approaches for calculating the exchange coupling constant to tetrahedral paramagnetic di-cobaltous complex, we found that the best approach was achieved by Noodlman treatment[3], also for such chemical environments the best calculated spin population was generated by Mulliken spin analysis.

Introduction:

Paramagnetic complexes are important systems in coordination chemistry, which exhibit unpaired electrons in their electronic configuration[4]. The presence of these unpaired electrons results in distinct magnetic properties, such as a high magnetic moment, which can be probed experimentally by various magnetic spectroscopic techniques[5], [6]. In addition, theoretical calculations provide a powerful tool for the analysis and understanding of the electronic structure and properties of these systems. One of the most important parameters in these calculations is the energy gap between the highest

occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This energy gap is a key determinant of the electronic properties of the system and plays a crucial role in determining its reactivity[7]. In addition, theoretical calculations provide a powerful tool for the analysis and understanding of the electronic structure and properties of these systems. One of the most important parameters in these calculations is the electron population, which can be described using various schemes, such as the Mulliken, Loewdin, and Mayer populations[8], [9]. These population analysis methods provide an efficient way of characterizing the distribution of electrons in a molecule, and are widely used in the study of paramagnetic complexes.

HOMO-LUMO gap:

The HOMO-LUMO energy gap in paramagnetic complexes is of particular interest due to its relation to the magnetic properties of the system. The size of the HOMO-LUMO gap can be used to predict the magnetic susceptibility of the complex, with larger gaps corresponding to higher susceptibilities. In addition, the HOMO-LUMO gap can be used to predict the redox behavior of the complex, as well as its ability to accept or donate electrons. These factors are critical in determining the catalytic activity and electronic properties of paramagnetic complexes, making the HOMO-LUMO gap a valuable parameter to study[1], [2].

The HOMO-LUMO gap in paramagnetic complexes can be calculated using a variety of theoretical methods, including density functional theory (DFT), time-dependent DFT (TD-DFT), and various ab initio methods. The accuracy of these calculations is dependent on a number of factors, including the basis set used, the level of theory employed, and the nature of the system being studied. Despite these challenges, the HOMO-LUMO gap remains a valuable parameter for characterizing the electronic properties of paramagnetic complexes[9].

Noodlman, Bincini, and Yamaguchi approaches in calculating J constant:

The coupling constants in paramagnetic complexes provide essential information regarding the electronic structure and properties of these compounds. These coupling constants are characterized by the strength and sign of the interaction between two magnetic nuclei, and are typically measured using various spectroscopic techniques. However, the interpretation of these coupling constants can be complex, and their calculation often requires advanced computational methods. One of the most commonly

used methods for calculating the coupling constants in paramagnetic complexes is the Noodlman approach[3], [10], and has been successfully applied to a wide range of di nuclear transition metal clusters.

Another popular approach is the Bincini method. which has provided valuable insights into the electronic structure of these compounds. A third method for calculating coupling constants in paramagnetic complexes is the Yamaguchi approach[11], [12]. which particularly useful for the calculation of coupling constants in lanthanide and actinide compounds, where relativistic effects can play a significant role in determining the electronic structure.

Overall, the Noodlman, Bincini, and Yamaguchi methods represent powerful tools for the calculation and interpretation of coupling constants in paramagnetic complexes. These methods have been applied to a wide range of compounds and have provided valuable insights into the electronic structure and properties of these materials. As such, they represent important contributions to the field of paramagnetic spectroscopy and are likely to continue to be important tools for many years to come.

Computational details:

The ORCA package[13], version 4.1.2, was used to run all the calculations in this study.[23] All optimized geometries were obtained using BP86 functional[14] with def2-TZVP basis sets for all atoms, in combination with the auxiliary basis sets of Weigend (def2/J). Subsequently, single point calculations were performed with various functionals to calculate exchange coupling constants using Noodleman formula. Convergence to the desired broken-symmetry states was confirmed by inspection of orbitals and spin populations. The broken symmetry approach is a computational method that involves modeling a molecule with broken spin symmetry. In other words, the method assumes that the molecule has two or more distinct spin states, each with a different electronic configuration. This approach is particularly useful for molecules with unpaired electrons, such as radicals, which exhibit spin-dependent interactions. By breaking the spin symmetry, the approach allows for a more accurate description of the coupling constants in these systems.

Results and discussion:

HOMO-LUMO gap related reactivities:

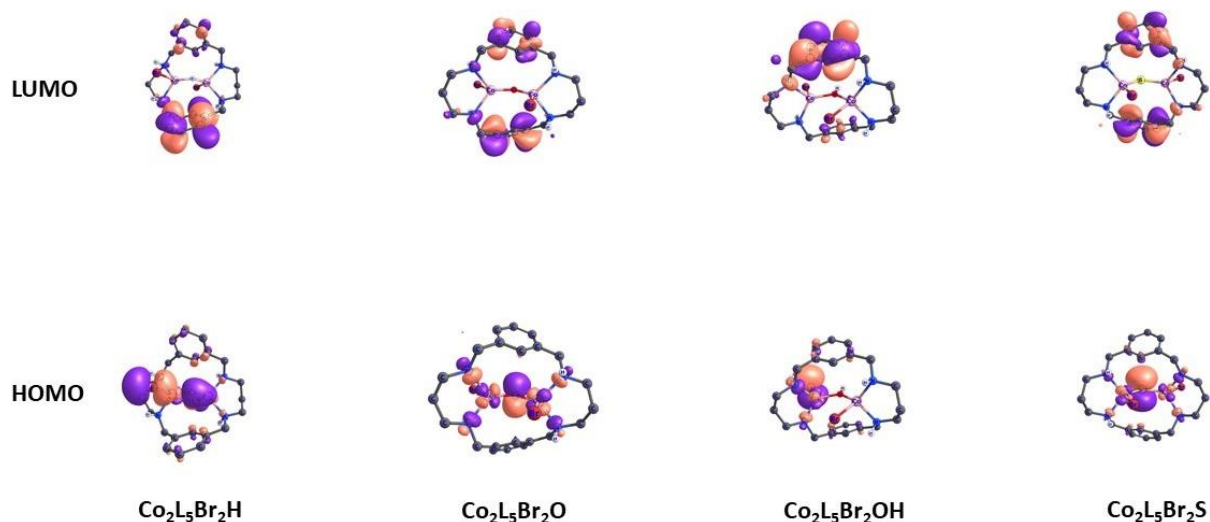


Figure 0.1: HOMO-LUMO orbitals for $\text{Co}_2\text{L}_2\text{Br}_2\text{X}$ complexes, L: tetraaza *m*-xylyl- ligand, X: H, O, OH, S bridging ligands.

As shown in Table 1 the high charge located at bridging ligands (O^{-2} , S^{-2}) lowers the studied gap in range (-4.49 and -3.94 eV) respectively, comparing to -1 charged ligands.

Table 1: HOMO-LUMO energy gap for eight di cobaltous systems in eV

System	HOMO-LUMO Gap(eV)
$\text{Co}_2\text{L}_5\text{Br}_2\text{H}$	-5.3
$\text{Co}_2\text{L}_5\text{Br}_2\text{O}$	-4.49
$\text{Co}_2\text{L}_5\text{Br}_2\text{OH}$	-5.64
$\text{Co}_2\text{L}_5\text{Br}_2\text{S}$	-3.94

$\text{Co}_2\text{L}_5\text{Br}_2\text{SH}$	-5.48
$\text{Co}_2\text{L}_5\text{Br}_2\text{Cl}$	-5.78
$\text{Co}_2\text{L}_5\text{Br}_2\text{Br}$	-5.75
$\text{Co}_2\text{L}_5\text{Br}_2\text{I}$	-5.62

The halogens show an increasing difference between highest occupied molecular orbital and lowest unoccupied molecular orbital from (-5.62, -5.75, reaching to -5.78 eV) as their covalent radii decreases.

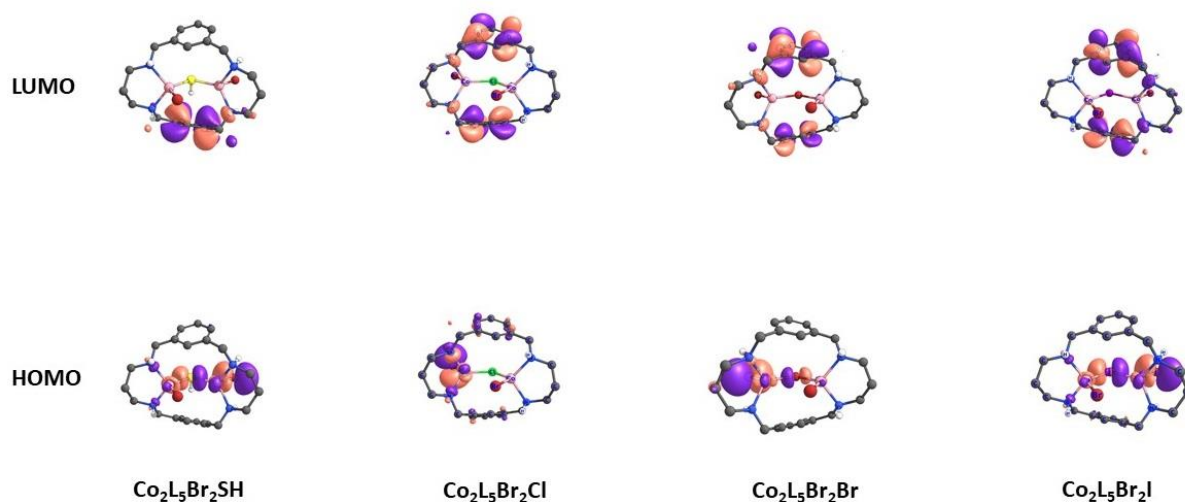


Figure 0.2: HOMO-LUMO orbitals for $\text{Co}_2\text{L}_5\text{Br}_2\text{X}$ complexes, L: tetraaza *m*-xylyl- ligand, X: SH, Cl, Br, I bridging ligands.

Hydroxo, and Thiol ligands exhibit the same HOMO-LUMO gap behavior but due to 3p orbital overlapping in S atom, the mentioned gap decreases by only 0.16 eV

Spin population analysis:

Mulliken population analysis[15] is one of the most widely used population analysis methods due to its simplicity and ease of implementation which can provide useful

insights into the electronic structure of molecules, including bond order and charge distribution, providing a straightforward way to analyze the electron density distribution within a molecule. On the other hand the Mulliken method can be sensitive to basis set choice and the accuracy of the computational method used, which can lead to overestimation of atomic charges and significant delocalization errors which can be seen from 0.02 – 0.04 higher spin populations. Or can result in non-integral charges, which may not be physically meaningful.

While the Loewdin population analysis[16] method has been shown to be less sensitive to basis set choice than the Mulliken method. Also, it can provide a more accurate description of charge distribution and delocalization in complex systems. And show lesser prone to producing non-integral charges. The computationally expense and the time consuming is considered to be a limitation, along with difficulty to interpret

From the table, the lowest electronegative bridging H atom makes highest electron population located at the two cobaltous centers with an average of 2.725, while only 2.62 population value is observed when highest electronegative oxo bridging ligand atom is presented.

Table 2: Mulliken, and Loewdin electronic population values for our eight di cobaltous complexes

System	Mulliken pop		Loewdin pop	
	CO1	CO2	CO1	CO2
Co₂L₅Br₂H	2.75	2.7	2.71	2.66
Co₂L₅Br₂O	2.64	2.6	2.61	2.58
Co₂L₅Br₂OH	2.7	2.7	2.67	2.67
Co₂L₅Br₂S	2.62	2.62	2.59	2.6
Co₂L₅Br₂SH	2.67	2.66	2.64	2.63
Co₂L₅Br₂Cl	2.67	2.68	2.64	2.65
Co₂L₅Br₂Br	2.67	2.68	2.64	2.65
Co₂L₅Br₂I	2.67	2.65	2.64	2.63

For Chloro, and Bromo with the same averaged electron populations values 2.675, can also be claimed to nearly the same E.N values 3.16 and 2.96 respectively according to the Pauling scale,

The same trend stands for another nearly similar electronegative values Sulfido, and Iodo with small difference of 0.08, the average populations are very close to show 2.62 and 2.66 respectively

Exchange coupling constant approaches:

While the dependence of J values on type of bridging ligands is well explained in our earlier paper still to be published, in this paper we will compare the certain differences, arises from different theoretical treatment by the three famous approaches, Noodlman, Bencini, and Yamaguchi treatments.

The Noodlman method shows the highest antiferromagnetic values because it involves a theoretical treatment of the magnetic anisotropy that arises from the coupling of the unpaired electrons with the nuclei of interest. The Noodlman method uses a combination of electronic structure calculations and experimental data to predict the coupling constants

Table 3: Noodlman, Bencini, Yamaguchi, coupling constants measured in cm-1

System	Noodlman	Bencini	Yamaguchi
Co₂L₅Br₂H	-101.05	-75.79	-100.28
Co₂L₅Br₂O	-119.84	-89.88	-118.65
Co₂L₅Br₂OH	-12.42	-9.31	-12.4
Co₂L₅Br₂S	-87.72	-65.79	-87.12
Co₂L₅Br₂SH	-25.91	-19.43	-25.86
Co₂L₅Br₂Cl	-10.99	-8.24	-10.98
Co₂L₅Br₂Br	-10.13	-7.6	-10.12
Co₂L₅Br₂I	-11.37	-8.53	-11.36

Bencini treatment generates the lowest AF values due to involving a quantum mechanical treatment of the coupling between the unpaired electron and the magnetic nuclei, which based on the application of perturbation theory

The Noodlman very close results generated by Yamaguchi method is mainly based on a relativistic treatment of the spin-orbit coupling that occurs in these compounds, and involves the use of density functional theory (DFT) calculations

Conclusion

lowering HOMO-LUMO gap can be achieved by replacement of hydroxo ligand by higher charge oxo, or sulfido bridging ligand, to increase reactivity of the synthesized paramagnetic di cobaltous $[\text{Co}_2\text{LI}_2\text{OH}]^+$ complex also from the three different theoretical approaches for calculating the exchange coupling constant to tetrahedral paramagnetic di-cobaltous complex, we found that the best approach was achieved by Noodleman treatment, also for such chemical environments the best calculated spin population was generated by Mulliken spin analysis. Finally, we recommend using CASSCF method to enhance our present results to higher level of accuracy.

References:

- [1] E. Ruiz, P. Alemany, S. Alvarez, and J. Cano, "Structural modeling and magneto- structural correlations for hydroxo-bridged copper (II) binuclear complexes," *Inorg Chem*, vol. 36, no. 17, pp. 3683–3688, 1997.
- [2] A. A. Khandar *et al.*, "Synthesis, characterization and crystal structures of mono and dinuclear macrocyclic cobalt(II) complexes with a new tetraaza m-xylyl-based macrocyclic ligand," *New Journal of Chemistry*, vol. 39, no. 4, pp. 2822–2831, Apr. 2015, doi: 10.1039/c4nj01608d.
- [3] L. Noodleman, "Valence bond description of antiferromagnetic coupling in transition metal dimers," *J Chem Phys*, vol. 74, no. 10, pp. 5737–5743, 1981.
- [4] L. Mathivathanan *et al.*, "A trigonal prismatic Cu6-pyrazolato complex containing a μ_6 -F ligand," *Dalton Transactions*, vol. 44, no. 47, pp. 20685–20691, 2015, doi: 10.1039/c5dt03892h.
- [5] E. V. Govor *et al.*, "A Redox-Induced Spin-State Cascade in a Mixed-Valent Fe₃ (μ_3 -O) Triangle," *Angewandte Chemie*, vol. 129, no. 2, pp. 597–601, Jan. 2017, doi: 10.1002/ange.201610534.
- [6] A. N. Georgopoulou *et al.*, "Site preferences in hetero-metallic [Fe₉-: XNix] clusters: A combined crystallographic, spectroscopic and theoretical analysis," *Dalton Transactions*, vol. 46, no. 38, pp. 12835–12844, 2017, doi: 10.1039/c7dt02930f.
- [7] M. Mörtel, J. Oswald, A. Scheurer, T. Drewello, and M. M. Khusniyarov, "Molecular Valence Tautomeric Metal Complexes for Chemosensing," *Inorg Chem*, vol. 60, no. 18, pp. 14230–14237, Sep. 2021, doi: 10.1021/acs.inorgchem.1c01731.
- [8] F. A. Delesma, G. Geudtner, D. Mejía-Rodríguez, P. Calaminici, and A. M. Köster, "Range-Separated Hybrid Functionals with Variational Fitted Exact Exchange," *J Chem Theory Comput*, vol. 14, no. 11, pp. 5608–5616, Nov. 2018, doi: 10.1021/acs.jctc.8b00436.
- [9] S. F. Sousa, P. A. Fernandes, and M. J. Ramos, "General performance of density functionals," *Journal of Physical Chemistry A*, vol. 111, no. 42, pp. 10439–10452, Oct. 2007, doi: 10.1021/jp0734474.

- [10] L. Noodleman and E. R. Davidson, "Ligand spin polarization and antiferromagnetic coupling in transition metal dimers," *Chem Phys*, vol. 109, no. 1, pp. 131–143, 1986.
- [11] M. Nishino, S. Yamanaka, Y. Yoshioka, and K. Yamaguchi, "Theoretical approaches to direct exchange couplings between divalent chromium ions in naked dimers, tetramers, and clusters," *J Phys Chem A*, vol. 101, no. 4, pp. 705–712, 1997.
- [12] M. Shoji *et al.*, "A general algorithm for calculation of Heisenberg exchange integrals J in multispin systems," *Chem Phys Lett*, vol. 432, no. 1–3, pp. 343–347, 2006.
- [13] F. Neese, "Orca," *An ab initio, density functional and semiempirical program package version*, vol. 2, p. 19, 2009.
- [14] H. Hirao, "Which DFT functional performs well in the calculation of methylcobalamin? Comparison of the B3LYP and BP86 functionals and evaluation of the impact of empirical dispersion correction," *Journal of Physical Chemistry A*, vol. 115, no. 33, pp. 9308–9313, Aug. 2011, doi: 10.1021/jp2052807.
- [15] J. S. Gómez-Jeria, "An empirical way to correct some drawbacks of mulliken population analysis," *Journal of the Chilean Chemical Society*, vol. 54, no. 4, pp. 482–485, 2009.
- [16] G. Bruhn, E. R. Davidson, I. Mayer, and A. E. Clark, "Löwdin population analysis with and without rotational invariance," *Int J Quantum Chem*, vol. 106, no. 9, pp. 2065–2072, 2006.