

Synthesis, Characterization, and Computational Studies of Metal(II) Complexes Derived from β -diketone and Para-aminobenzoic Acid

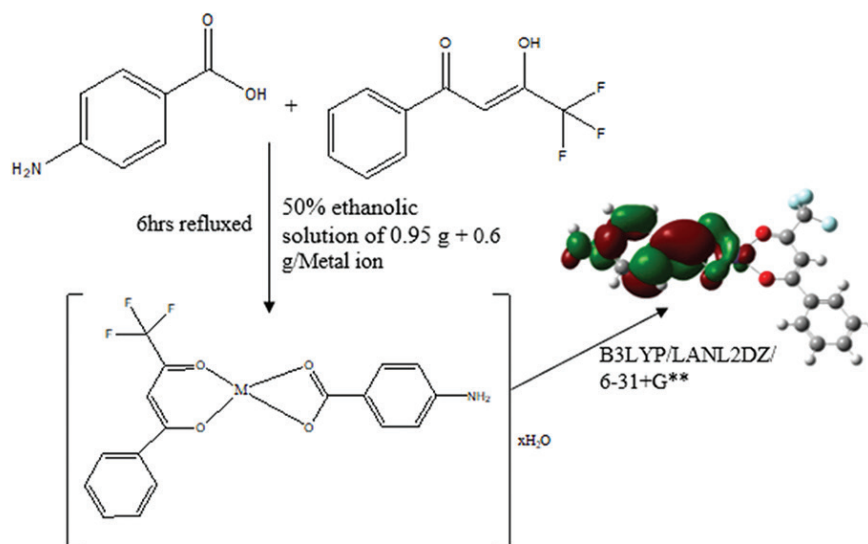
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ABSTRACT Some metal(II) mixed-ligand complexes of Mn, Fe, Co, Ni, Cu, and Zn, derived from 4,4,4-trifluoro-1-phenyl-1,3-butanedione (Tf) and para-aminobenzoic acid (Pa) were synthesized. Spectroscopic characterization was carried which includes infrared (IR) and electronic spectra (solid reflectance) measurements. Melting points, magnetic moments at room temperature, solubility, conductivity and percentage metal were also determined. The infrared spectra measurements suggest that the metal atoms coordinated to both ligands, Tf and Pa through the O₄ chromophores. The magnetic moments, percentage metal analysis, and electronic spectra measurements were used to confirm the octahedral geometry of Co(II), Ni(II) and the four-coordinate (tetrahedral/square-planar) complexes (Mn(II), Fe(II), and Cu(II)). The non-electrolytic nature of all the synthesized complexes was shown by conductivity measurements. The density functional theory calculations for all the metal complexes also support experimental results. Mn(II) and Fe(II) complexes had lower energy gaps, indicating higher reactivity compared to others.



KEYWORDS Metal-complexes, Density functional theory, Magnetic moments, Non-electrolyte, Electronic spectra.

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INTRODUCTION

The study of coordination compounds has been one of the focus for the inorganic chemist. This is because interesting, unexpected or undesirable properties, as well as reaction routes, may sometimes be discovered. Mixed ligand complexes of transition metals have been studied by many researchers.^[1-5] Moreover, it has been reported that they possess: Antitumor,^[6] antioxidant,^[4] anticancer, imaging agent,^[7] and antimicrobial activity against pathogenic microorganisms.^[7] They play a major role in biological developments such as metals activation of enzymes,^[8] storage and active transport of substances through membranes,^[9] and models for biochemical reactions.^[10]

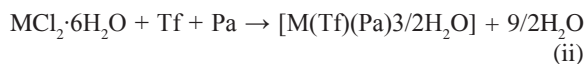
β -diketones or 1,3-diketones is one of the most widely used ligands in coordination chemistry.^[11] These have been found to be important intermediates and components for the synthesis of essential heterocyclic compounds such as isoxazole, triazole, and pyrazole which have provided a platform for the fast exchange of research in the areas of organic, bioinorganic, analytical, pharmaceutical, and medicinal chemistry.^[12-15] The wide application of these 1,3-diketones is easily explored because of their existence in solid form as “keto” and in solution as “enol” tautomers, which enable them to form a stable six-membered chelate ring on their own and by the replacement of a labile hydrogen with a metal cation.^[11,16,17] It was revealed by the spectroscopic analysis that these keto–enol tautomers exist in a state of reversible chemical reaction with each other^[18,19] equilibrium *in situ*. Numerous biological properties possessed by β -diketones and their metal complexes have also been published.^[20-24]

Thus, this study was aimed to synthesize new metal(II) mixed ligands complexes of 4,4,4-trifluoro-1-phenyl-1,3-butanedione (Tf) and para-aminobenzoic acid (Pa) with good structural diversity, reactivity, and stability.

RESULTS AND DISCUSSION

Analytical data

The complex formation of M(II) sulfates (M = Mn, Fe, Cu, and Zn) and chlorides (M = Co and Ni) with ligand followed equations (i) and (ii).



The ligands, (Tf) and (Pa) melted at 39–40°C and 188–190°C, respectively; whereas Mn(II), Fe(II), and Co(II) complexes melted in the range 128–164°C; while Ni(II), Cu(II), and Zn(II) complexes decomposed in the range 202–260°C, signifying coordination. Colored metal complexes were formed with the exception of white Zn (II) complex which might be due to *d-d* transitions^[25]. This is expected of Zn(II) complex due to its fully filled *d*-configuration (*d*¹⁰). The percentage metal analysis values

for experimental and theoretical were very close, which is indicative of the proposed masses. However, the formation of these mixed ligand complexes with their proposed structures was established by the melting and decomposition temperatures, percentage metal, room temperature magnetic measurements, electronic and infrared spectroscopies, and density functional theory calculations. These were done since attempts to grow suitable crystals for X-ray diffraction measurements were not successful. The analytical data for the ligands and the mixed-ligands metal complexes are presented in **Table 1**.

Solubility and molar conductance measurements

The complexes are insoluble in water, sparingly soluble in dichloromethane and were most soluble in methanol and dimethyl sulfoxide (DMSO). Based on this the molar conductivities were measured in DMSO in the range 10.40–21.90/ohm cm²/mol. These values are below 60/ohm cm²/mol, indicating covalent character and because of values in the range 60–90/ohm/cm/mol as anticipated for 1:1 electrolyte.^[26,27] The values for each metal complex are presented in **Table 1**.

Electronic spectra and magnetic moments

The ligand bands were observed at 32.89 kK and 28.32–29.24 kK [**Table 2**] and were assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The Mn(II) complex displayed single absorption band at 15.53 kK, consistent with a four-coordinate, tetrahedral geometry and was assigned to ⁶A₁ → ⁴E₁ transition. The high spin Mn(II) complexes are associated with effective magnetic moment near to the spin-only value of 5.90 B.M; meanwhile, the ground term is ⁶A₁ and hence, there is no orbital contribution.^[28] Based on this, a room temperature moment of 4.90 B.M for this Mn(II) complex could confirm its tetrahedral geometry.

Fe(II) complex revealed two absorption bands at 15.50 kK and 18.52 kK. The term symbol for the ground state of Fe(II) ions in a *d*⁶ configuration, is ⁵D, which splits in tetrahedral crystal field with ⁵E → ⁵T₂ transition and with a spin-forbidden transition suggestive of a square planar complex. A moment of 3.4 B.M and 5.0 B.M are usually expected for square planar and tetrahedral Fe(II) complexes, respectively.^[29] A moment of 4.22 B.M was observed, which was suggestive of equilibrium between square planar and tetrahedral geometry.^[29] However, DFT calculation revealed that it has a tetrahedral geometry. Furthermore, two absorption bands at 17.86 kK and 21.51 kK were exhibited by Co(II) complex which is characteristic of six-coordinate high spin octahedral geometry; given to ⁴T_{1g}(F) → ⁴T_{2g} and ⁴T_{1g}(F) → ⁴A_{2g} transitions. Moments in the range 4.70–5.2 B.M are expected for high spin octahedral Co(II) complex. The Co(II) complex gave a moment of 6.02 B.M, suggestive of a high spin octahedral geometry.^[30]

Ni(II) displayed two absorption bands at 15.48 kK and 21.98 kK typical of 6-coordinate high spin and low spins octahedral geometry and assigned as ³A_{2g} → ³T_{1g} and ¹B_{1g} → ¹A_{1g} transitions, respectively. Magnetic moment of range 2.8–3.3 B.M were reported with high spin octahedral

Table 1: Analytical data of the ligands and their metal (II) complexes

Compounds	Form mass	% yield	Color	M.Pt./ D.T.(°C)	% Metal Theo.(Exp.)	Λ_M	Meff (B.M)	Geometry
Pa	137.14		Off-white	188-190	- (-)	-	-	-
Tf	216.16		Cream	39-40	- (-)	-	-	-
[Mn(Pa)(Tf)].1/2H ₂ O	415.25	42	Yellow	142-144	13.23 (13.19)	12.54	4.89	Tetrahedral
[Fe(Pa)(Tf)].2H ₂ O	443.19	72	Ruby red	128-130	12.60 (12.51)	20.36	4.23	Tetrahedral/ square planar
[Co(Pa)(Tf)]3/2H ₂ O	437.26	48	Orange	162-164	13.48 (13.20)	10.40	6.02	Octahedral
[Ni(Pa)(Tf)]3/2H ₂ O	437.04	56	Lime green	202*	13.45 (13.15)	18.20	2.51	Octahedral
[Cu(Pa)(Tf)].2H ₂ O	450.91	91	Pale blue	230*	14.09 (14.23)	21.90	1.86	Square planar
[Zn(Pa)(Tf)].2H ₂ O	452.71	66	White	260*	14.44 (14.64)	14.60	D	Tetrahedral

Pa: Para-aminobenzoic acid, Tf: 4,4,4-trifluoro-1-phenyl-1,3-butanedione, Form.: Formula, M.Pt.: Melting point, D.T*: Decomposition temperature, °C: Degree centigrade, %: Percentage, Theo.: Theoretical, Exp.: Experimental, Λ_M : Molar conductance (ohm⁻¹ cm² mol⁻¹), D: Diamagnetic, μ_{eff} : Effective magnetic moments, B.M: Bohr Magnetron

Table 2: Infrared and electronic spectra of the ligands and their complexes

Complexes	$\nu(\text{OH})$	$\nu(\text{NH}_2)$	$\nu(\text{C=O})$	$\nu(\text{C=C})$	$\nu(\text{C-O})$	$\nu(\text{M-O})$	Electronic spectra (KK)
(Pa)	3360m	3457s 3376m	1657s 1623s	1597s	1280s	-	29.24, 32.89
(Tf)	-	-	1599s	1491s 1467s	1254s 1200s	-	28.32
[Mn(Pa)(Tf)].1/2H ₂ O	3380b	3380b	1663s 1611m	1576s 1534s	1286m 1254s	457s	15.53
[Fe(Pa)(Tf)].2H ₂ O	3428b	3428b	1692s 1594s	1568s 1537s	1252s	484s 445m	18.52, 15.50
[Co(Pa)(Tf)]3/2H ₂ O	3305b	3305b	1664sh 1614m	1574s 1537s	1254s	398s	21.51, 17.86
[Ni(Pa)(Tf)] 3/2H ₂ O	3373b	3373b	1614m 1575s	1575s 1537s	1287m	413s	21.98, 15.48
[Cu(Pa)(Tf)].2H ₂ O	3439b	3439b 3289s	1694s 1607s	1574s 1546s	1253s 1220s	456s 431s	19.34, 14.56
[Zn(Pa)(Tf)].2H ₂ O	3416b	3416b 3295m	1689s 1664sh 1611s	1536s	1289s 1255s	491s	20.75

Pa: Para-aminobenzoic acid, Tf: 4,4,4-trifluoro-1-phenyl-1,3-butanedione, b: Broad, m: Medium, s: Sharp, sh: Shoulder, w: Weak, 1 kK: 1000/cm

Ni(II) while low spin octahedral Ni(II) complexes were diamagnetic. The Ni(II) complex showed a moment of 2.51 B.M corroborating spin equilibrium between the high spin and low spin octahedral geometry.^[31]

Furthermore, Cu(II) complex had two absorption bands at 14.56 kK and 19.34 kK assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_{1g}$ transitions of four-coordinate, square planar geometry.^[32] A moment of 1.9–2.2 B.M is usually observed for mononuclear copper(II) complexes, regardless of stereochemistry, expectedly higher than the spin-only moment of 1.73 B.M, due to orbital contribution and spin-orbit coupling.^[33] This Cu(II) complex displayed a magnetic moment of 1.86 B.M corroborating its mononuclear nature.

The Zn (II) complex was expectedly diamagnetic with metal \rightarrow ligand charge transfer transition at 20.75 kK, as no d-d transition is expected since it has a fully filled 3d orbital

(d¹⁰) configuration, indicative of its diamagnetic nature and tetrahedral geometry.^[34]

The electronic spectra, as well as the room temperature magnetic moments in all cases of the metal complexes, suggest their mononuclear natures. The Mn(II), Fe(II), Cu(II), and Zn(II) complexes assumed four-coordinate (tetrahedral/square-planar) geometry while Co(II) and Ni(II) displayed six-coordinate (octahedral) geometry [Figure 1].

Infrared spectra

The relative infrared spectral data of the ligands and the metal complexes are presented in Table 2. The absorption bands are shown by the infrared spectra of Pa at 3457/cm and 3376/cm are due to $\nu(\text{NH}_2)_{\text{asym}}$ and $\nu(\text{NH}_2)_{\text{sym}}$, respectively. These bands overlapped with $\nu(\text{OH})$ bands in the metal complexes with little or no significant shift.



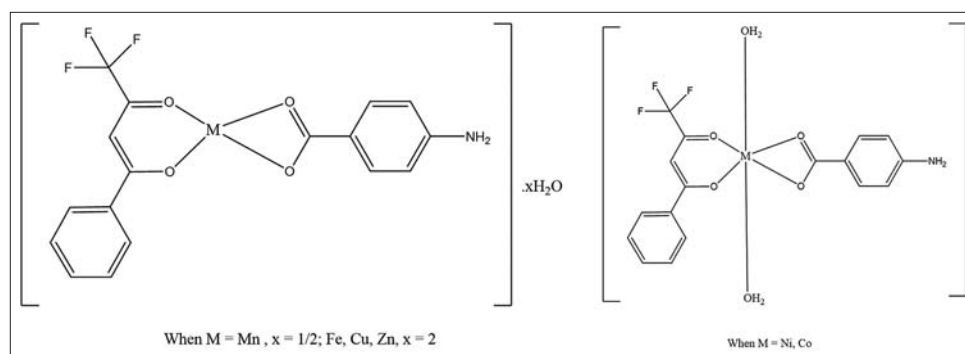


Figure 1: Proposed 2D structures for the mixed ligand metal(II) complexes

Table S1: Calculated Infrared and electronic spectra of the ligands and the complexes

Complexes	$\nu(\text{OH})$	$\nu(\text{NH}_2)$	νCH	$\nu\text{C}=\text{O}$	$\nu\text{C}=\text{C}$	νCOO^-	$\nu\text{M}-\text{O}$	Electronic spectra (KK)
Pa(p-aminobenzoic acid)	3430m	3535s	3040s	1710s	1523s	1230s	-	32.23
Tf(4,4,4- trifluoro-1-phenyl-1,3-butanedione)	-	-	3066m 3067s	1925s	1500s 1499s	1235s	-	20.7
[Mn(Pa)(Tf)].1/2H ₂ O	3978b	3482b	2994m	1848s	1626s 1523m	1232s 459s	459s	459s
[Fe(Pa)(Tf)].2H ₂ O	3779b	3339b	3033m 3000s	1684s 1599s	1584s 1548s	272s	492s 444m	18.62, 15.40
[Co(Pa)(Tf)].3/2H ₂ O	3420b	3305b	2710s	1724m	1588s	1287s	400s	22.01 17.40
[Ni(Pa)(Tf)].3/2H ₂ O	3381b	3373b	2710s	1614m 1575s	1662s 1534s	1341m	422s	21.93, 15.38
[Cu(Pa)(Tf)].2H ₂ O	3381b	3439b 3289s	3161m	1701s	1523s 1565s 1545s	1301s	466s 442s	19.25, 15.01
[Zn(Pa)(Tf)].2H ₂ O	3505b	3416b 3295m	2871w	16870s 1664s	1567s	1311s	489s	22.02

Pa: Para-aminobenzoic acid, Tf: 4,4,4-trifluoro-1-phenyl-1,3-butanedione, b: Broad, m: Medium, s: Sharp, sh: Shoulder, w: Weak, 1 kK: 1000/cm

However, the little shift was not due to coordination but hydrogen bonding.^[35] The (Pa) exhibited a medium band at 3360/cm assigned to $\nu(\text{OH})$, which was shifted in the metal complexes to 3305/cm–3439/cm due to coordination of the hydroxyl oxygen atom by deprotonation. The strong bands at 1657/cm, 1623/cm, and 1599/cm in (Pa) and Tf in the enol form were assigned as $\nu(\text{C}=\text{O})$ stretching vibrations. In these bands, there was a hypsochromic/bathochromic shift to 1575/cm–1694/cm in the metal(II) complexes due to coordination of the carbonyl oxygen atoms to the metal atoms.^[34] The strong bands exhibited by the ligands at 1200/cm, 1254/cm, and 1280/cm assigned to $\nu(\text{C}-\text{O})$ stretching vibrations, which was shifted in metal complexes to 1220/cm–1289/cm, also corroborated coordination. The new bands in the spectra of the metal complexes at the range 398/cm–491/cm were assigned as (M-O) vibrations, which were not present in the spectra of (Pa) and (Tf), an indication of coordination.

Computational results

TD-DFT has been used as powerful tools to model the spectroscopic properties of organic and inorganic complexes.^[36-38] Results revealed a decrease in π -electron delocalization in the conjugated system, and which led to a hypsochromic shift in its UV-Vis absorption spectra. [Fe

(Pa)(Tf)].2H₂O complex showed two absorption bands at 15.40, 18.62 kK which designates square planar geometry with a spin-forbidden transition. Mn(II) complex also gave a forbidden transition with a single band at 15.65 kK representative of a tetrahedral geometry. Ni(II) complex showed absorption bands of 21.93, 15.38kK also assigned to $n-\pi^*$ transition. The Co complex showed two bands between 17.40 and 22.01 kK which might be an indication of the octahedral geometry. Results agreed with experimental values, the slight difference might be attributed to the basis set and density functional used for computation.^[39] Cu(II) complex also revealed two bands at 19.25, 15.01 kK. Zn(II) complex gave one absorption band which is an indication of the tetrahedral geometry. According to DFT calculations, a medium ν -OH band of 3430/cm was found in the ligand, but in the metal complexes, a broadband and bathochromic shift which range from 3455 to 3987/cm were observed. This partially agrees with obtained experimental result [Table S1 in the supplementary]. $\nu\text{M}-\text{O}$ band was not found in the ligands but appeared in the complexes these might be due to coordination to the transition metal ions through the carboxylate oxygen. Results agree with experimental values, except for few metal complexes which might be due to the basis set applied and functional used for computation.

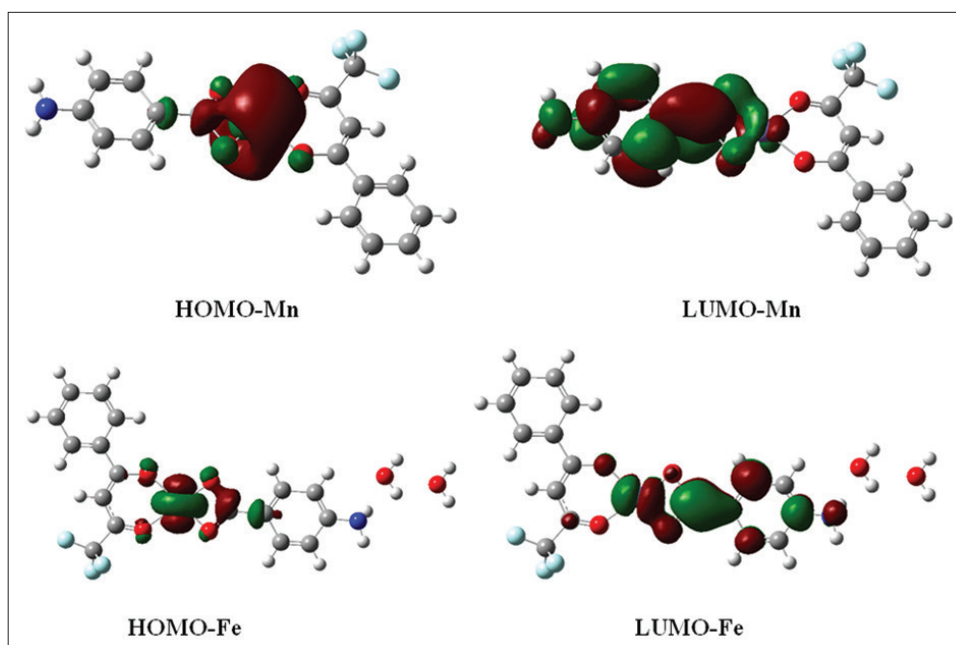


Figure 2: Frontier molecular orbitals of the metal complexes with the lowest energy gap. Other MO orbitals are presented in the supplementary data [Figure S1]

Table 3: Frontier molecular orbital energies, HOMO-LUMO energy gap and dipole moment of metal complexes obtained by B3LYP/6-31+G** (d,p) and LANL2DZ for metal ions

Complex	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Dipole moment (Debye)
[Co(Pa)(Tf)]3/2H ₂ O	-6.90	-6.26	0.64	12.60
[Cu(Pa)(Tf)].2H ₂ O	-4.52	-3.93	0.59	13.41
[Mn(Pa)(Tf)].1/2H ₂ O	-4.91	-4.83	0.08	16.32
[Fe(Pa)(Tf)].2H ₂ O	-5.51	-5.33	0.18	14.81
[Ni(Pa)(Tf) 3/2H ₂ O]	-5.11	-4.82	0.29	13.33
[Zn(Pa)(Tf)].2H ₂ O	-5.68	-5.47	0.21	15.88

HOMO: Highest occupied molecular orbital, LUMO: Lowest unoccupied molecular orbital

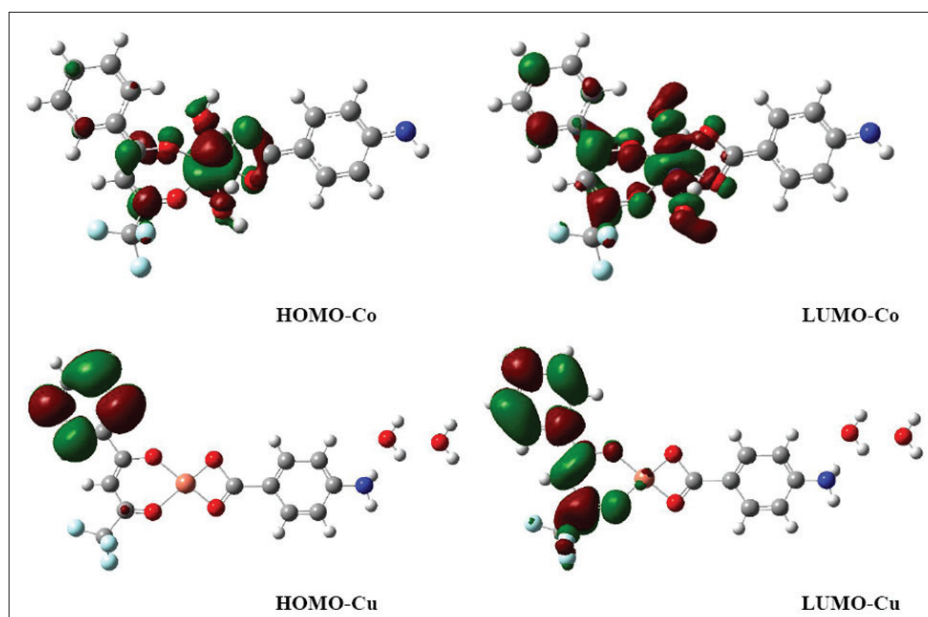


Figure S1: Frontier molecular orbitals of the other metal complexes

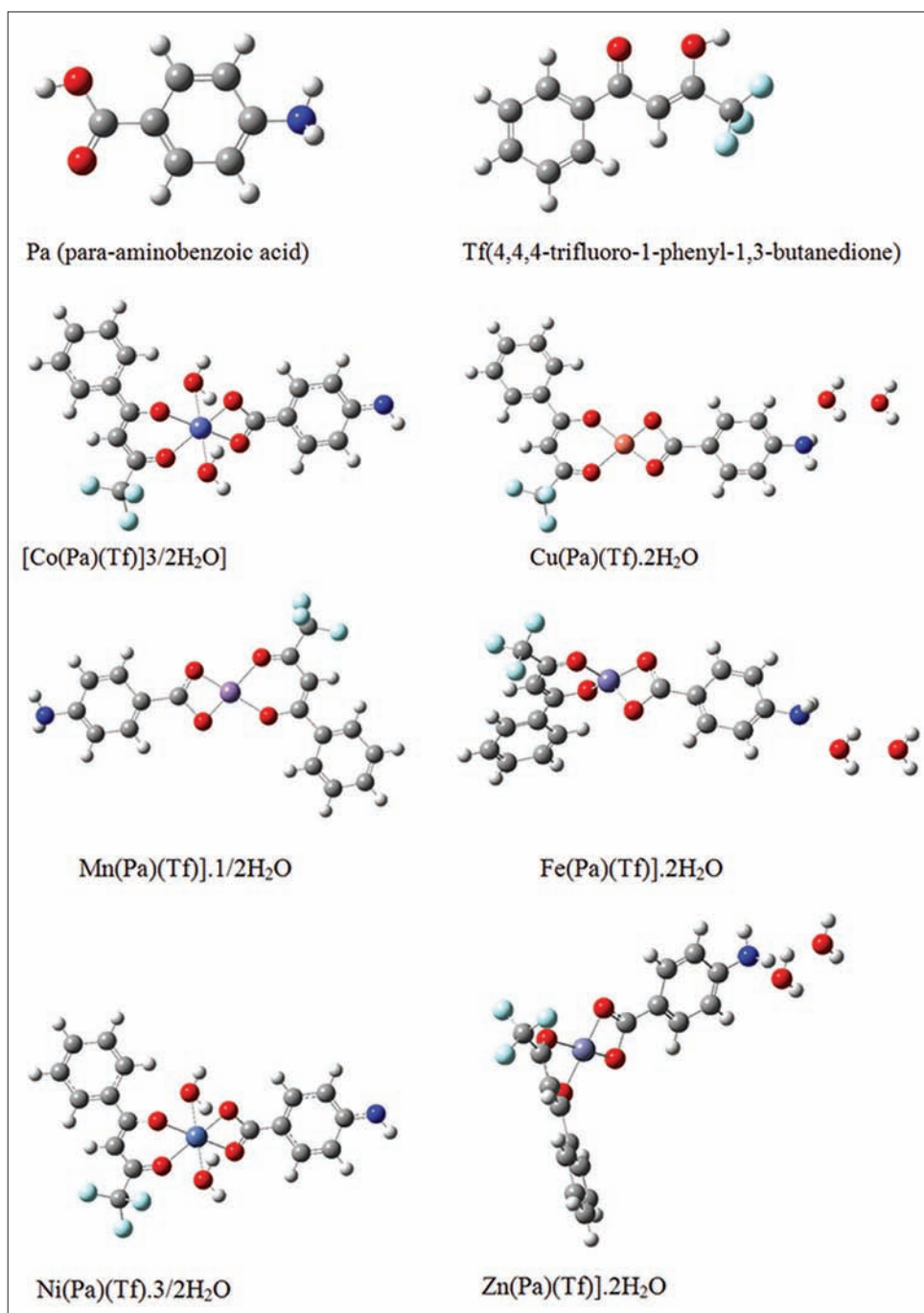


Figure 3: Optimized geometry of ligands and the metal(II) complexes obtained at B3LYP/LANL2DZ and 6-31+G** basis set

Molecular orbital analysis

Frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), are the key orbitals of compounds involved in reactions^[40] and explains the electron delocalization.^[41,42] The HOMO represents the ionization potential while the LUMO refers to the electron affinity. From **Figure 2**, the HOMO; of π -nature is delocalized over the C-C bonds of the ligands. A slight decrease of electron density was observed in the metal complexes, which further explains the hypsochromic shift in electronic transition. High HOMO delocalization was observed for Co complex,

which may be because of high electron cloud around the metal ion and the surrounding oxygen atom. The HOMO is located over the C=C bonds for both the ligands and metal complexes, which represents high ionization potential around the neighboring atoms [**Figure 2** and **Figure S1**]. All studied metal complexes especially Mn(II) complex have low energy gap indicating reactivity and stability.^[43,44] The increasing order of ΔE energies was Mn(II) < Zn (II) < Fe (II) < Ni < Cu (II) < Co. All studied metal complexes show high dipole moment with Mn(II) as the highest. This is an indication of the probable dipole-dipole interaction with systems like biological systems [**Table 3**].

EXPERIMENTAL SECTION

Materials and reagents

Reagent grade Tf, Pa, manganese(II) sulfate monohydrate, cobalt(II) chloride hexahydrate, iron(II) sulfate heptahydrate, nickel(II) chloride hexahydrate, copper(II) sulfate pentahydrate, and zinc(II) sulfate heptahydrate were obtained from Aldrich and BDH chemicals. Ethanol and DMSO were also used directly as supplied by BDH Chemicals Ltd., Poole, England.

Physical properties measurements

The solid reflectance spectra of studied metal complexes were recorded using a PC scanning spectrophotometer UV-1800/SHIMADZU machine in the range 190–900 nm and infrared spectra were recorded on KBr disc on an FTIR spectrum BX spectrophotometer (Perkin-Elmer) of range 4000–400 cm^{-1} . The magnetic moment susceptibilities measurement was determined using a Sherwood susceptibility balance MSB Mark 1 at 300 K, and diamagnetic corrections were calculated using Pascal's constant. The melting points and decomposition temperature were determined with Mel-Temp electrothermal machine, and molar conductivity measurements of 1×10^{-3} M solutions in DMSO were also measured using DDS-307A conductivity meter with a cell constant of 1.0 at 298 K, while percentage metal analysis was carried out by complexometric titration.

Synthesis

Preparation of metal complexes

The synthesis was carried out in accordance with a published procedure.^[45] To a stirring 10 mL of 50% ethanolic solution of 0.95 g (4.38×10^{-3} moles) of Tf, 0.6 g (4.38×10^{-3} moles) of Pa in 5 mL of 50% ethanol was added to give a clear solution. To the resultant stirring mixture at room temperature, 0.74–1.26 g (4.38×10^{-3} moles) of the hydrated M(II) sulfates (M = Mn, Fe, Cu, and Zn) and hydrated M(II) chlorides (M = Co and Ni) were added neatly and in bits. The result uncolored homogeneous solutions were refluxed for 6 h and the colored precipitates obtained were filtered, washed with ethanol, air-dried and finally kept in a desiccator over silica gel for further drying.

Computational details

A theoretical calculation based on quantum mechanics was applied to the ligands and the corresponding metal complexes. The geometry was optimized using Density Functional Theory (DFT/B3LYP)^[46,47] methods in conjunction with 6-31+G** basis set^[48,49] for N, F, C, and O atoms and LANL2DZ pseudopotential^[50-52] for Mn, Zn, Cu, Ni, Fe, and Co atoms. The combination of basis set has been successfully applied for metals based on correlation to experiment.^[51-54] The IR spectra were calculated with the same level of theory as an optimization. UV spectra were calculated using Time dependent-DFT (TD-DFT/B3LYP) methods in conjunction with 6-31G** basis set for N, F, C, and O atoms and LANL2DZ for Mn, Zn, Cu, Ni, Fe, and Co atoms. The TD-DFT calculation was done using Gaussian 09 [Figure 3].^[55]

CONCLUSION

In this study, it was observed that the ligands under study displayed functional characteristics as a bidentate ligand. They coordinated to the metal ions through the oxygen atoms of the carbonyl group in Tf and the carboxylate oxygen atoms of the Pa, respectively. The molar conductance measurements in DMSO suggest that the metal(II) complexes were covalent. Electronic spectra and room temperature magnetic moments supported a four-coordinate tetrahedral/square-planar geometry for Mn (II), Fe(II), Cu(II), and Zn(II) complexes; while Co(II) and Ni(II) assumed a six-coordinate octahedral geometry. Interestingly, some of these complexes exhibit special electronic properties such as spin-crossover and antiferromagnetism. Furthermore, the density functional theory calculation also suggested that studied metal(II) complexes, especially Mn(II) show good reactivity and stability. These properties might be significant in the development of drugs against pathogenic microorganisms.

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REFERENCES

- [1] Romerosa, A., Bergamini, P., Bertolasi, V., Canella, A., Cattabriga, M., Gavioli, R., Mañas, S. Biologically active platinum complexes containing 8-thiotheophylline and 8-(methylthio) theophylline, *Inorg. Chem.*, **2004**, *43*, 905–913.
- [2] Agarwal, R.K., Prasad, S. Synthesis, spectral and thermal investigations of some mixed ligand complexes of thorium (IV) derived from semicarbazones and diphenyl sulfoxide, *J. Iran Chem. Soc.*, **2005**, *2*, 168–175.
- [3] Mostafa, S.I., Hadjiliadis, N. New biologically active transition metal complexes of 2-mercapto-4, 6-diamino-5-hydroxypyrimidine, *Inorg. Chem. Indian J.*, **2007**, *2*, 2(3), 186–192.
- [4] Osowole, A.A., Agbaje, O.B., Ojo, B.O. Synthesis, characterization and antibacterial properties of some heteroleptic metal (II) complexes of paracetamol and vanillin. *Asian J. Pharm. Clin. Res.*, **2014**, *7*, 145–149.
- [5] Kleinhans, G., Guisado-Barrios, G., Peris, E., Bezuidenhout, D.I. Ruthenium (II) pincer complexes featuring an anionic CNC bis (1, 2, 3-triazol-5-ylidene) carbazolidine ligand coordinated in a meridional fashion, *Polyhedron*, **2017**, *143*, 43–48.
- [6] Galanski, M., Jakupec, M.A., Keppler, B.K. Update of the preclinical situation of anticancer platinum complexes: NOvel design strategies and innovative analytical approaches, *Curr. Med. Chem.*, **2005**, *12*, 2075–2094.
- [7] Orvig, C., Abrams, M.J. Medicinal inorganic chemistry: Introduction, *Chem. Rev.*, **1999**, *9*, 2201–2204.



- [8] Hughes, M. Coordination compounds in biology, *Compr. Coordin. Chem.*, **1987**, 6, 541.
- [9] Bouwman, E., Driessen, W., Reedijk, J. Model systems for Type I copper proteins: Structures of copper coordination compounds with thioether and azole-containing ligands. *Coord. Chem. Rev.*, **1990**, 104, 143–172.
- [10] Thakur, G.A., Athlekar, S.V., Dharwadkar, S.R., Shaikh, M.M. Synthesis and biological activity of mixed ligand dioxouranium (VI) and thorium (IV) complexes, *Acta Pol. Pharm.*, **2007**, 64, 9–15.
- [11] Maurya, R., Rajput, S. Oxovanadium (IV) complexes of bioinorganic and medicinal relevance: Synthesis, characterization, and 3D molecular modeling and analysis of some oxovanadium (IV) complexes involving O, O-donor environment, *J. Mol. Struct.*, **2004**, 687, 35–44.
- [12] Kel'in, A.V., Maioli, A. Recent advances in the chemistry of 1, 3-diketones: Structural modifications and synthetic applications, *Curr. Org. Chem.*, **2003**, 7, 1855–1886.
- [13] Lim, D., Fang, F., Zhou, G., Coltart, D.M. Direct carbon-carbon bond formation via soft enolization: A facile and efficient synthesis of 1, 3-diketones. *Org. Lett.*, **2007**, 9, 4139–4142.
- [14] Desai, K., Thaker, B. *Synthesis and Characterization of New Mixed Azomethyne Schiff-Base Complexes of Cobalt (ii), Nickel (ii) and Copper (ii) and Their Pyridine Adducts Involving Beta-Diketones as Ligands*, Indian Chemical SOC 92 Acharya Prafulla Chandra road ATTN: Dr indrajit kar/exec sec, Calcutta, India, **1990**, pp667–669.
- [15] Pradhan, J., Goyal, A. β -diketones: Important intermediates for drug synthesis. *Int. J. Pharm. Res. Allied Sci.*, **2015**, 4, 1–8.
- [16] Joshi, K.C., Pathak, V.N. Metal chelates of fluorinated 1, 3-diketones and related compounds, *Coordin. Chem. Rev.*, **1977**, 22, 37–122.
- [17] Mehrotra, R., Bohra, B., Gaur, D. *Metal β -Diketones and Allied Derivatives*, Academic Press, New York, 1978.
- [18] Allred, A.L., Thompson, D.W. Keto-enol equilibria in 2, 4-pentanedione and 3, 3-dideuterio-2, 4-pentanedione, *J. Phys. Chem.*, **1971**, 75, 433–435.
- [19] Bernal, A., Kuritka, I., Kasparkova, V., Saha, P. The effect of microwave irradiation on poly (vinyl alcohol) dissolved in ethylene glycol, *J. Appl. Polym. Sci.*, **2013**, 128, 175–180.
- [20] Agarwal, A., Goyal, A., Sharma, C. Synthesis And Spectral Studies of Mixed Ligand Complexes of Mn(III) With 2-Hydroxypropiophone And Substituted Salicylaldehyde or β -Diketones, *J. Appl. Chem.*, **2014**, 3, 1510–1516.
- [21] Sheikh, J., Juneja, H., Ingle, V., Ali, P., Hadda, T.B. Synthesis and *in vitro* biology of Co (II), Ni (II), Cu (II) and Zinc (II) complexes of functionalized β -diketone bearing energy buried potential antibacterial and antiviral O, O pharmacophore sites, *J. Saudi Chem. Soc.*, **2013**, 17, 269–276.
- [22] Sheikh, J., Parvez, A., Juneja, H., Ingle, V., Chohan, Z., Youssoufi, M., Hadda, T.B. Synthesis, biopharmaceutical characterization, antimicrobial and antioxidant activities of 1-(4'-O- β -d-glucopyranosyloxy-2'-hydroxyphenyl)-3-aryl-propane-1, 3-diones, *Eur. J. Med. Chem.*, **2011**, 46, 1390–1399.
- [23] Nishiyama, T., Shiotsu, S., Tsujita, H. Antioxidative activity and active site of 1, 3-indandiones with the β -diketone moiety. *Polym. Degrad. Stab.*, **2002**, 76, 435–439.
- [24] Kemp, K.C., Fourie, E., Conradie, J., Swarts, J.C. Ruthenocene-containing β -diketones: Synthesis, p K a' values, keto-enol isomerization kinetics, and electrochemical aspects. *Organometallics*, **2008**, 27, 353–362.
- [25] Osunlaja, A., Ndahi, N., Ameh, J., Adetoro, A. Synthesis, physico-chemical and antimicrobial properties of Co (II), Ni (II), and Cu (II) mixed-ligand complexes of dimethylglyoxime. *RJSET*, **2011**, 3, 1233–1238.
- [26] Liu, J., Wu, B.W., Zhang, B., Liu, Y. Synthesis and characterization of metal complexes of Cu (II), Ni (II), Zn (II), Co (II), Mn (II) and Cd (II) with tetradentate schiff bases, *Turk. J. Chem.*, **2006**, 30, 41–48.
- [27] Raja, I., Christudhas, M., Raj, G.A.G. Synthesis, characterization, metal ion intake and antibacterial activity of cardanol based polymeric Schiff base transition metal complexes using ethylenediamine, *J. Chem. Pharm. Res.*, **2011**, 3, 127–135.
- [28] Osowole, A., Kolawole, G., Kempe, R., Fagade, O. Spectroscopic, magnetic and biological studies on some metal (II) complexes of 3-(4, 6-dimethyl-2-pyrimidinylamino)-1-phenyl-2-butanone and the mixed complexes with 2, 2'-bipyridine and 1, 10-phenanthroline, *Synth. React. Inorg.*, **2009**, 39, 165–174.
- [29] Hawrelak, E.J., Bernskoetter, W.H., Lobkovsky, E., Yee, G.T., Bill, E., Chirik, P.J. Square planar vs tetrahedral geometry in four coordinate iron (II) complexes. *Inorg. Chem.*, **2005**, 44, 3103–3111.
- [30] Sun, B.W., Zhao, Q.H., Liao, D.Z., Jiang, Z.H., Yan, S.P., Wang, G.L., Yao, X.K. Crystal structure and ferromagnetic behavior of a cis-Co (II) complex with nitronyl nitroxide, *Can. J. Chem.*, **2000**, 78, 322–327.
- [31] Ohtsu, H., Tanaka, K. Equilibrium of low- and high-spin states of Ni (II) complexes controlled by the donor ability of the bidentate ligands, *Inorg. Chem.*, **2004**, 43, 3024–3030.
- [32] Chohan, Z.H., Pervez, H., Rauf, A., Scozzafava, A., Supuran, C.T. Antibacterial Co (II), Cu (II), Ni (II) and Zn (II) complexes of thiazazole derived furanyl, thiophenyl and pyrrolyl Schiff bases, *J. Enzym. Inhib. Med. Chem.*, **2002**, 17, 117–122.
- [33] Chohan, Z.H., Kausar, S. Synthesis, characterization and biological properties of tridentate NNO, NNS and NNN donor thiazole-derived furanyl, thiophenyl and pyrrolyl Schiff bases and their Co (II), Cu (II), Ni (II) and Zn (II) metal chelates, *Metal Based Drugs.*, **2000**, 7, 17–22.
- [34] Al-Saif, F.A., Refat, M.S. Ten metal complexes of vitamin B 3/niacin: Spectroscopic, thermal, antibacterial, antifungal, cytotoxicity and antitumor

- studies of Mn (II), Fe (III), Co (II), Ni (II), Cu (II), Zn (II), Pd (II), Cd (II), Pt (IV) and Au (III) complexes, *J. Mol. Struct.*, **2012**, *1021*, 40–52.
- [35] Kovala-Demertzi, D., Tsangaris, J.M. Complexes of 2, 4-diamino-5 (3', 4', 5'-trimethoxy-benzyl) pyrimidine (trimethoprim) with palladium (II), *Inorg. Chim. Acta.*, **1986**, *125*, L31–L3.
- [36] Cave, R.J., Castner, E.W. Time-dependent density functional theory investigation of the ground and excited states of coumarins 102, 152, 153, and 343, *J. Phys. Chem., A.*, **2002**, *106*, 12117–12123.
- [37] Jacquemin, D., Perpète, E.A., Scuseria, G.E., Ciofini, I., Adamo, C. TD-DFT performance for the visible absorption spectra of organic dyes: Conventional versus long-range hybrids, *J. Chem. Theory Comput.*, **2008**, *4*, 123–135.
- [38] Jacquemin, D., Perpète, E.A., Ciofini, I., Adamo, C. Accurate simulation of optical properties in dyes, *Account. Chem. Res.*, **2008**, *42*, 326–334.
- [39] Liu, X., Cole, J.M., Low, K.S. Molecular origins of dye aggregation and complex formation effects in coumarin 343, *J. Phys. Chem. C.*, **2013**, *117*, 14723–14730.
- [40] Hirata, S., Zhan, C.G., Aprà, E., Windus, T.L., Dixon, D.A. A new, self-contained asymptotic correction scheme to exchange-correlation potentials for time-dependent density functional theory, *J. Phys. Chem. A.*, **2003**, *107*, 10154–10158.
- [41] Ariyageadsakul, P., Vchirawongkwin, V., Kritayakornupong, C. Determination of toxic carbonyl species including acetone, formaldehyde, and phosgene by polyaniline emeraldine gas sensor using DFT calculation, *Sensors Actual. B Chem.*, **2016**, *232*, 165–174.
- [42] Xie, F., Zhang, X.J., Yu, J.H., Xu, H., Chu, Y.F., Fan, Z.Q. Effects of stretching and compression on conducting properties of an Au-alkanedithiol-Au molecular junction, *Chem. Phys.*, **2016**, *467*, 21–25.
- [43] Ibeji, C.U., Adejoro, I.A., Adeleke, B.B. A benchmark study on the properties of unsubstituted and some substituted polypyrrroles, *J. Phys. Chem. Biophys.*, **2015**, *5*, 1–11.
- [44] Lawal, M.M., Govender, T., Maguire, G.E., Kruger, H.G., Honarparvar, B. DFT study of the acid-catalyzed esterification reaction mechanism of methanol with carboxylic acid and its halide derivatives, *Int. J. Quantum Chem.*, **2017**, *114*, 1–12.
- [45] Ekennia, A.C., Onwudiwe, D.C., Olasunkanmi, L.O., Osowole, A.A., Ebenso, E.E. Synthesis, DFT calculation, and antimicrobial studies of novel Zn (II), Co (II), Cu (II), and Mn (II) heteroleptic complexes containing benzoylacetone and dithiocarbamate, *Bioinorg. Chem. Appl.*, **2015**, *2015*, 1–12.
- [46] Lee, C., Yang, W., Parr, R.G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B.*, **1988**, *37*, 785.
- [47] Kohn, W., Becke, A.D., Parr, R.G. Density functional theory of electronic structure, *J. Phys. Chem.*, **1996**, *100*, 12974–12980.
- [48] Blanton, W.B., Gordon-Wylie, S.W., Clark, G.R., Jordan, K.D., Wood, J.T., Geiser, U., Collins, T.J. Synthesis and crystallographic characterization of an octameric water complex, (H₂O)₈, *J. Am. Chem. Soc.*, **1999**, *121*, 3551–3552.
- [49] Siless, G.E., Butler, M., Cabrera, G.M. Study of metal complexation of cardenolides with divalent metal ions by electrospray ionization mass spectrometry. *Int. J. Mass Spectrom.*, **2017**, *419*, 44–51.
- [50] Ren, F.Q., Zhang, F.Q., Li, Y.F., Lv, J., Ma, W.J. Density functional study of the structural, stability, magnetic properties and chirality of small-sized Al_xZr_y (x+y ≤ 9) alloy clusters, *J. Theor. Comput. Chem.*, **2017**, *16*, 1750058.
- [51] Mutter, S.T., Deeth, R.J., Turner, M., Platts, J.A. Benchmarking of copper (II) LFMM parameters for studying amyloid-β peptides, *J. Biomol. Struct. Dyn.*, **2018**, *36*, 1145–1153.
- [52] Hay, P.J., Wadt, W.R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, *J. Chem. Phys.*, **1985**, *82*, 299–310.
- [53] Chioma, F., Ekennia, A.C., Ibeji, C.U., Okafor, S.N., Onwudiwe, D.C., Osowole, A.A., Ujam, O.T. Synthesis, characterization, antimicrobial activity and DFT studies of 2-(pyrimidin-2-ylamino) naphthalene-1, 4-dione and its Mn (II), Co (II), Ni (II) and Zn (II) complexes, *J. Mol. Struct.*, **2018**, *1163*, 455–464.
- [54] Yang, Y., Weaver, M.N., Merz, K.M.Jr. Assessment of the “6-31+ G**+ LANL2DZ” mixed basis set coupled with density functional theory methods and the effective core potential: Prediction of heats of formation and ionization potentials for first-row-transition-metal complexes, *J. Phys. Chem. A.*, **2009**, *113*, 9843–9851.
- [55] Frisch, M., Trucks, G., Schlegel, H., Scuseria, G., Robb, M., Cheeseman, J. *09, Revision D09. 01*, Gaussian Software. Inc., Wallingford, CT, 2009.



