



Synthesis, spectroscopic characterization and coordination chemistry of novel chiral orthophthalaldehyde-derived schiff base ligands and their Mn (II) and Pd (II) complexes

Guguloth Veeranna¹, Ch VenkataRamanareddy², Vadde Ravinder³

¹ Department of Chemistry, JVR Government College Sathupally Khammam Telangana, India

² Professor, Department of Chemistry, Jawaharlal Nehru Technological University, Hyderabad, Telangana, India

³ Professor, Department of Chemistry, Kakatiya University Warangal, Telangana, India

Abstract

A novel series of chiral Schiff base ligands S1, S2, S3, S4, A1 and A2 was successfully designed and synthesized via the condensation of orthophthalaldehyde (OPA) with various chiral 1,2-diamines, amino acids, and ortho-aminobenzaldehyde under optimized reaction conditions. These ligands were engineered to function as multi-dentate donor frameworks, explicitly separating into N₄ tetradentate systems S1, S2, S3, S4 and N₂O₂ tetradentate systems A1, A2. The corresponding coordination complexes were subsequently synthesized by reacting these newly prepared ligands with divalent transition metal ions, specifically Manganese (II), and Palladium (II). Complete structural and physical characterization of both the free ligands and their metal complexes was systematically accomplished utilizing elemental (CHN) analysis, mass spectrometry, Fourier-transform infrared (FT-IR) spectroscopy, multinuclear NMR ¹H and ¹³C spectroscopy, electronic absorption spectroscopy, molar conductance measurements, magnetic susceptibility, electron spin resonance (ESR), and thermogravimetric analysis (TG-DTA). The experimental values obtained across all analytical techniques showed exceptional agreement with the proposed molecular formulas and tentative coordination structures. Molar conductance data revealed that the A₁ and A₂ coordination complexes exist as non-electrolytes across all metal systems due to internal charge neutralization via deprotonated phenolic or carboxylic groups. Conversely, the S1, S2, S3, and S4 complexes display non-electrolytic properties in Mn (II) frameworks where chlorides coordinate within the inner sphere, but transition into 1:2 electrolytic variants with Pd (II) matrices. Electronic absorption spectra combined with magnetic moment values validated high-spin octahedral environments for all Mn (II) systems, square planar geometries for the S-series Pd (II) systems. Thermal decomposition profiles substantiated the presence of coordinated and lattice water molecules uniquely within the A1 and A2 complexes, while indicating high thermal stability for the anhydrous S-series systems.

Keywords: Chiral schiff bases, orthophthalaldehyde, transition metal complexes, coordination geometry, spectral characterization, thermal analysis

Introduction

The fields of coordination chemistry and materials science remain profoundly dependent on the architectural versatility of Schiff base ligands. These ligands containing the characteristic azomethine (C=N) group are widely studied in coordination chemistry and materials science because of their structural flexibility, tunable electronic properties, and applications in catalysis, biomimetic chemistry, magnetochemistry, and optical materials (Bharati *et al.*, 2003; Shakir *et al.*, 1993) ^[1, 2]. Incorporating chirality into these ligands enhances their potential for asymmetric synthesis, enantioselective catalysis, and chiral molecular recognition (Jeewoth *et al.*, 1999) ^[3]. Tetradentate Schiff bases with N₄ and N₂O₂ donor sets form stable chelate complexes and influence the coordination geometry and electronic properties of transition metal ions (Colak *et al.*, 2000) ^[4].

Orthophthalaldehyde (OPA), containing two adjacent formyl groups on a rigid aromatic ring, is a valuable precursor for synthesizing open-chain and macrocyclic polydentate ligands. Its closely positioned aldehyde groups facilitate condensation with diamines and amino acids, producing rigid chiral frameworks with strong metal-binding capabilities (Shakir *et al.*, 2006; Chandra *et al.*, 2006) ^[5, 6]. Mn (II) (d⁵) and Pd (II) (d⁸) offer contrasting electronic and coordination properties: Mn (II) commonly

forms high-spin complexes, whereas Pd (II) generally favors low-spin square-planar geometry. These characteristics provide a useful basis for comparing the coordination behavior of new chiral Schiff base ligands (Carlin & Vandynevedt, 1997; Griffith, 2003) ^[7, 9].

The present study focuses on the synthesis of six novel chiral Schiff base ligands derived from OPA, including four N₄ tetradentate ligands (S1–S4) and two N₂O₂ tetradentate ligands (A1–A2), using chiral diamines, enantiopure amino acids, and ortho-aminobenzaldehyde. Their Mn (II) and Pd (II) complexes were prepared and systematically characterized through physical, spectroscopic, magnetic, and thermal analyses to investigate the relationships between ligand structure, donor atoms, and coordination geometry.

Experimental

1. Materials and Reagents

All starting chemicals, including orthophthalaldehyde (OPA), chiral 1,2-diamines (such as chiral 1,2-diaminopropane and chiral 1,2-diaminocyclohexane derivatives), enantiopure amino acids (such as L-valine and L-leucine variants), ortho-aminobenzaldehyde, manganese (II) chloride tetrahydrate (MnCl₂·4H₂O), and palladium (II) chloride (PdCl₂), were obtained from commercial sources (Sigma-Aldrich, Alfa Aesar, and Merck) in highest

analytical purity and utilized without additional purification. Spectroscopic grade solvents including methanol, ethanol, acetonitrile, dichloromethane, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were dried and distilled according to standard chemical methods prior to use (Vogel, 2004)^[10].

2. Instrumentation and Physical Measurements

Elemental microanalyses for carbon, hydrogen, and nitrogen (% CHN) were executed utilizing a perkin-Elmer CHN analyzer. Metal contents were quantitatively determined via standard gravimetric methods or atomic absorption spectrophotometry following absolute decomposition of the organic fragments (Vogel, 2004)^[10]. Mass spectra were recorded on a high-resolution mass spectrometer utilizing electrospray ionization (ESI) or matrix-assisted laser desorption ionization (MALDI) techniques to confirm molecular ion peaks. Fourier-Transform Infrared (FT-IR) spectra were gathered in the solid state as KBr pellets within the 4000–400 cm^{-1} frequency range on a modern spectrometer, while far-infrared data were recorded utilizing specialized optics to observe metal-ligand vibrations. Multinuclear ^1H and ^{13}C Nuclear Magnetic Resonance (NMR) spectral lines were acquired at room temperature utilizing a 400 MHz spectrometer in appropriate deuterated solvents (CDCl_3) or ($\text{DMSO}-d_6$) with tetramethylsilane (TMS) acting as the internal reference marker.

Molar conductance values of the free ligands and corresponding complexes were measured at a concentration of 10^{-3} M in either dichloromethane or DMF using a calibrated digital conductivity bridge at ambient temperature (Geary, 1971)^[11]. Electronic absorption spectra were recorded in the 200–1000 nm region using a double-beam UV-Vis spectrophotometer. Magnetic susceptibility measurements were performed on finely ground solid samples at room temperature using a Gouy balance or an automated vibrating sample magnetometer (VSM), with calculations corrected for diamagnetic contributions using Pascal's constants (Carlin & Vandrynevedt, 1997)^[7]. Electron Spin Resonance (ESR) profiles for the copper complexes were gathered in the solid state at ambient temperature under X-band frequencies, with magnetic parameters calculated using the Kneubuhl approximation equations (Kneubuhl, 1960)^[12]. Thermogravimetric and Differential Thermal Analyses (TG-DTA) were conducted concurrently under a continuous nitrogen flow from 25 °C up to 800 °C at a steady heating ramp of 10 °C/min (Nikolaev *et al.*, 1969)^[13].

3. Synthesis of Chiral Schiff Base Ligands (S1–S4), (A1–A2)

The six chiral Schiff base ligands were prepared by condensing orthophthalaldehyde with the respective chiral amine-containing segments under precise stoichiometric controls:

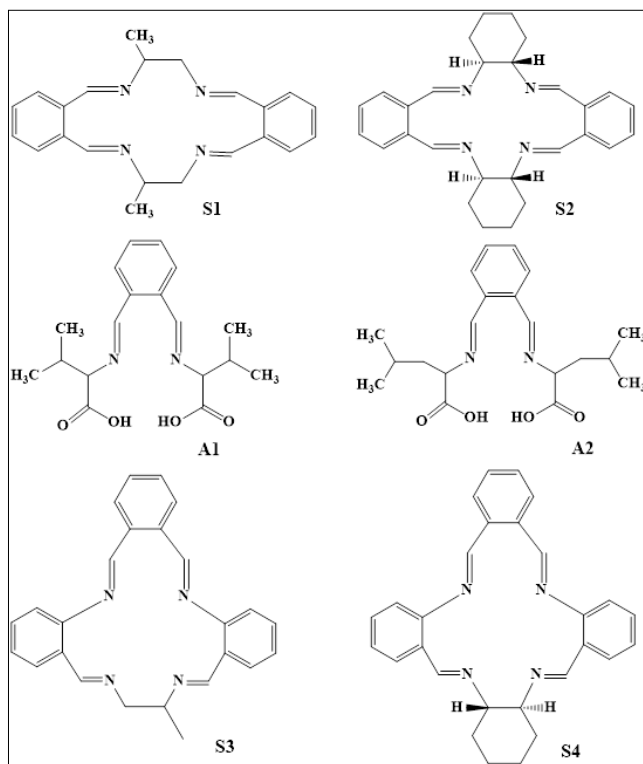
S1 and S2: Synthesized by reacting orthophthalaldehyde with the corresponding chiral 1,2-diamines in a 1:2 molar ratio in absolute ethanol under reflux for approximately 4–6 hours.

A1 and A2: Prepared by mixing OPA with chosen enantiopure amino acids (L-valine and L-leucine derivatives) in a 1:2 molar ratio in a water-methanol mixture

containing a catalytic amount of sodium hydroxide to ensure deprotonation and solubility of the amino acid components.

S3 and S4: Prepared by a stepwise condensation routine involving OPA, the chosen chiral diamines, and ortho-aminobenzaldehyde to form the specific open-chain asymmetrical tetradentate N_4 systems.

In all cases, the target ligands precipitated as crystalline solids upon cooling, which were filtered, washed with ice-cold ethanol, recrystallized from hot acetonitrile or methanol, and dried in a vacuum desiccator over anhydrous calcium chloride.



Scheme 1: Structural topologies of the synthesized chiral Schiff base ligands

4. Synthesis of Mn (II) Complexes

The manganese (II) complexes were prepared by treating an ethanolic solution of the respective Schiff base ligand S1, S2, S3, S4, A1 and A2 1 mmol with a solution of manganese (II) chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) 1 mmol dissolved in the minimum volume of ethanol. The reaction mixture was stirred continuously and maintained under reflux conditions for 4 hours. For the A₁ and A₂ ligand systems, small quantities of sodium acetate were introduced to assist the deprotonation of the carboxylic acid residues. The resulting pale-colored precipitates were isolated by filtration, washed with cold ethanol followed by diethyl ether, and subsequently dried under vacuum.

5. Synthesis of Pd (II) Complexes

Palladium (II) complexes were generated by reacting palladium (II) chloride (PdCl_2), 1 mmol initially with lithium chloride in hot methanol to generate the soluble Li_2PdCl_4 intermediate in situ. This solution was filtered and added dropwise to a hot methanolic or acetonitrilic solution of the respective chiral ligand (1 mmol). The resulting mixture was stirred under reflux for 5 hours, leading to the precipitation of stable brown or yellow solids. The

precipitates were collected, washed thoroughly with water to eliminate residual salts, washed with cold ethanol, and dried under vacuum at 60 °C.

Results and Discussion

1. Characterization of Free Chiral Schiff Base Ligands

1.1 Elemental Analysis and Mass Spectrometry

The physical and analytical data compiled for the newly synthesized free ligands S1, S2, S3, S4, A1 and A2 are summarized in **Table 1**. The experimental percentage values found for carbon, hydrogen, and nitrogen match the calculated theoretical percentages, confirming the purity and proposed molecular formulas of the compounds.

Mass spectral data provided unambiguous validation of the ligand frameworks. The mass spectra of the N₄ donor ligands S1, S2, and S3 exhibited prominent sodium-adduct molecular ion peaks [M+Na]⁺ at m/z 367, 447, and 401, respectively. In contrast, the amino acid-derived N₂O₂ ligands A1 and A2, alongside the asymmetric N₄ ligand S₄, displayed protonated molecular ion peaks [M+1]⁺ at m/z 333, 361, and 419, respectively. These specific fragmentation and molecular mass distributions confirm that the condensation reactions between orthophthalaldehyde and the respective primary amine moieties proceeded via complete dual-formyl conversion without side-product generation.

Table 1: Physical and Analytical Data of Free Schiff Base Ligands

Ligand Code	Molecular Formula	Color	Yield (%)	Carbon % Found (Calc.)	Hydrogen % Found (Calc.)	Nitrogen % Found (Calc.)	Mass Peak (m/z)
S ₁	C ₂₂ H ₂₄ N ₄	Off-White	74	75.36 (76.71)	6.98 (7.02)	16.08 (16.27)	367 [M+Na] ⁺
S ₂	C ₂₈ H ₃₂ N ₄	Pale Yellow	78	78.69 (79.21)	7.54 (7.60)	12.89 (13.20)	447 [M+Na] ⁺
A ₁	C ₁₈ H ₂₄ N ₂ O ₄	White	82	64.58 (65.04)	7.12 (7.28)	8.36 (8.43)	333 [M+1] ⁺
A ₂	C ₂₀ H ₂₈ N ₂ O ₄	White	80	65.69 (66.64)	7.69 (7.83)	7.65 (7.77)	361 [M+1] ⁺
S ₃	C ₂₅ H ₂₂ N ₄	Yellow	71	78.67 (79.34)	5.74 (5.86)	14.35 (14.80)	401 [M+Na] ⁺
S ₄	C ₂₈ H ₂₆ N ₄	Deep Yellow	75	79.80 (80.35)	6.15 (6.26)	13.27 (13.39)	419 [M+1] ⁺
S ₁	C ₂₂ H ₂₄ N ₄	Off-White	74	75.36 (76.71)	6.98 (7.02)	16.08 (16.27)	367 [M+Na] ⁺

1.2 Infrared (IR) Spectroscopy

The characterization of the functional groups within the free ligands was initially evaluated via FT-IR spectroscopy (Table 2). All six ligands displayed a strong, sharp diagnostic absorption band positioned in the region of 1652–1631 cm⁻¹. This band is assigned to the azomethine stretching vibration, C=N, which establishes the complete conversion of the formyl groups of OPA into imine bonds (Wiles *et al.*, 1967)^[15].

For the A1 and A2 ligand systems, additional prominent IR bands appeared as broad

envelopes centered at 2925 cm⁻¹ and 2943 cm⁻¹, corresponding to the stretching frequencies of the -OH group belonging to the carboxylic acid functions (Shakir *et al.*, 2006)^[5]. These two ligands also exhibited intense, broad bands at 1721 cm⁻¹ and 1710 cm⁻¹, which are assigned to the stretching modes of free carboxyl groups, ν C=O, originating from the amino acid building blocks. Aromatic -CH stretching frequencies and skeletal C=C vibrations were uniformly recorded for all systems in the standard baseline regions of 3062–3035 cm⁻¹ and 1525–1471 cm⁻¹, respectively.

Table 2: Diagnostic Infrared Vibrational Frequencies cm⁻¹ of Free Ligands

Ligand	ν C=N	ν OH	ν C=O	ν C-HAr, ν C=CAr
S ₁	1648	—	—	3039 / 1471
S ₂	1643	—	—	3052 / 1485
A ₁	1631	2925	1721	3035 / 1474
A ₂	1636	2943	1710	3062 / 1525
S ₃	1652	—	—	3054 / 1483
S ₄	1645	—	—	3058 / 1495

1.3 Multinuclear ¹H and ¹³C NMR Spectroscopy

The ¹H NMR spectra of the six ligands provided comprehensive confirmation of structural symmetry and proton environments. All ligands exhibited a clear singlet integration downfield in the range of δ 8.72–8.10 ppm, matching the azomethine protons -CH=N-, 2H. The successful condensation was further supported by the complete absence of any aldehydic proton signals near δ 9.98 ppm (Bharati *et al.*, 2003)^[1].

Interestingly, the ¹H NMR profiles of ligands S1 and S4 displayed two distinct peaks for the azomethine protons due to the chemically non-equivalent environments flanking the rigid aromatic core, whereas ligand S3 resolved into three distinct imine signals. For ligand S2, the aliphatic cyclohexane protons and chiral centers generated complex, well-defined multiplets within the δ 2.21–1.15 ppm and δ 5.24 ppm spans. Ligands A1 and A2 revealed a unique broad signal downfield at δ approx 11.0 ppm, confirming

the presence of the unreacted carboxylic -OH proton. Ligand S3 displayed a clear doublet at δ 1.42 ppm for its methyl groups, while its diastereotopic methylene protons appeared as a multiplet in the δ 4.25–3.90 ppm window. Aromatic protons for all six systems emerged as clear multiplets clustered across the δ 7.95–7.10 ppm region (Chandra *et al.*, 2006)^[6].

¹³C NMR spectra further verified the carbon skeletal configurations. Signal peaks recorded in the narrow δ 164.1–161.4 ppm interval was assigned to the azomethine carbons -C=N-, confirming successful OPA-amine condensation (Yang *et al.*, 2002)^[16]. The asymmetric or chiral carbons across all ligands generated signals bounded within the δ 74.2–58.7 ppm region. Ligands S1 and S3 exhibited a specific resonance at δ 62.3–60.2 ppm, validating the presence of an N-CH₂ methylene link (Chandra *et al.*, 2006)^[6]. Crucially, the ¹³C spectra of the A1 and A2 ligands displayed prominent signals downfield

near δ approx 175 ppm, confirming the free carboxyl carbon -COOH of the amino acid components (Wiles *et al.*, 1967)^[15]. Aryl carbon signals were distributed within the expected δ 142.5–120.6 ppm region.

Based on these combined analytical and spectroscopic investigations, the tentative structural geometries illustrated in Scheme 1 are assigned to the free ligands.

2. Characterization of Manganese (II) Complexes

Manganese represents a versatile transition metal with an [Ar] 3d⁵ 4s² valence configuration, predominantly

stabilizing into a +2 state via the loss of its 4s electrons to form a high-spin d⁵ configuration with one electron in each of the five 3d orbitals.

2.1 Elemental Analysis and Composition

The reaction of MnCl₂ · 4H₂O with individual ligands yielded stable mononuclear coordination complexes. The analytical data displayed in **Table 3** confirms a high degree of correlation between experimental values and theoretical calculations, establishing a 1:1 metal-to-ligand stoichiometry.

Table 3: Analytical Data of Mn (II) Complexes

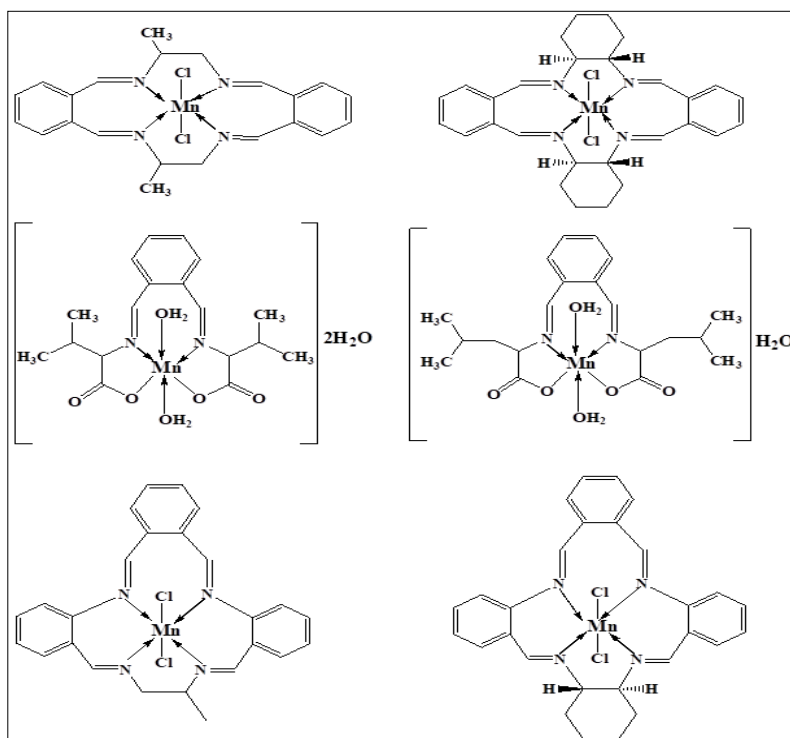
Complex Code	Proposed Formula	Color	Carbon % Found (Calc.)	Hydrogen % Found (Calc.)	Nitrogen % Found (Calc.)	Metal % Found (Calc.)
Complex 1.1	[Mn (S1) Cl ₂]	Pale Pink	55.94 (56.18)	5.10 (5.14)	11.84 (11.91)	11.62 (11.68)
Complex 1.2	[Mn (S2) Cl ₂]	Light Pink	61.34 (61.60)	5.81 (5.86)	10.15 (10.18)	9.69 (9.98)
Complex 1.3	[Mn (A1) (H ₂ O ₂)] · H ₂ O	Pinkish	47.27 (47.30)	6.61 (6.67)	6.12 (6.19)	12.01 (12.10)
Complex 1.4	[Mn (A2) (H ₂ O ₂)] · H ₂ O	Pinkish	51.35 (51.39)	6.88 (6.90)	5.96 (5.99)	11.65 (11.75)
Complex 1.5	[Mn (S3) Cl ₂]	Yellowish	59.60 (59.54)	4.58 (4.40)	11.37 (11.11)	11.01 (10.89)
Complex 1.6	[Mn (S4) Cl ₂]	Dark Pink	61.96 (61.78)	5.00 (4.81)	10.42 (10.29)	10.39 (10.09)

2.2 Mass Spectrometry and Molar Conductance

Mass spectra confirmed the proposed formulas. The complexes of ligands S1 and S4 exhibited clear mononuclear parent ion peaks at m/z 470 and 544, matching the fully coordinated species. The complexes derived from S2 and S3 revealed pseudomolecular peaks at m/z 551 and 505 representing [M+1]⁺, while the amino acid coordination derivatives 1.3 and 1.4 showed explicit sodium-adduct species corresponding to [M+Na]⁺ signatures.

Molar conductance values for all six Mn (II) complexes measured in dichloromethane were remarkably low, falling

into the 12.0–22.6 Ω^{-1} , cm², mol⁻¹ interval. This uniform behavior demonstrates that all the complexes behave as non-electrolytes in solution, confirming the absence of counterions or unbound ligands within an ionic outer sphere (Geary, 1971)^[11]. For complexes 1.1, 1.2, 1.5, and 1.6, this confirms that the chloride ions are directly coordinated to the manganese center within the coordination sphere. For complexes 1.3 and 1.4, it confirms that charge neutralization is achieved internally via covalent metal-oxygen bonds formed by the deprotonated carboxylate groups of the amino acids.



Scheme 2: Tentative structures of Schiff base Mn (II) complexes

2.3 Infrared Spectral Analysis

A comparative evaluation of the infrared spectra of the complexes against their corresponding free ligands provided

critical insights into structural connectivity. In the spectra of all six Mn (II) complexes, the characteristic azomethine stretching mode ν C=N shifted to lower frequencies by 30–

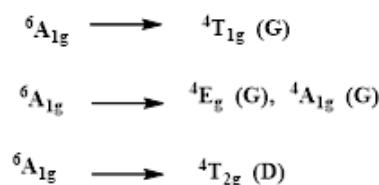
45 cm⁻¹, appearing in the 1625–1610 cm⁻¹ range. This negative shift indicates lone-pair donation from the azomethine nitrogen to the manganese center. This coordination behavior was further supported by the appearance of a new medium-intensity absorption band in the far-infrared region at 538–520 cm⁻¹, assigned to the ν Mn-N stretching vibration (Nikolaev *et al.*, 1969)^[13].

For complexes 1.3 and 1.4 (derived from ligands A1 and A2, the broad bands corresponding to the carboxylic ν OH mode (originally at 2943–2925 cm⁻¹) disappeared completely. Concurrently, the free carboxylate (ν C=O) bands were replaced by two distinct diagnostic bands situated at 1599–1588 cm⁻¹ and 1386–1365 cm⁻¹. These bands are assigned to the asymmetric ν COO⁻ and symmetric ν COO⁻ stretching vibrations of the carboxylate ion, respectively. This spectral profile confirms coordination via the carboxylate oxygen atom following deprotonation. The formation of this metal-oxygen bond was further validated by the appearance of a distinct vibrational mode in the 431–423 cm⁻¹ range, assigned to the ν Mn-O stretching frequency. Furthermore, these two complexes exhibited a broad band at 3400 cm⁻¹ and a distinct absorption at 754–739 cm⁻¹, corresponding to the rocking mode of coordinated water molecules (Wiles *et al.*, 1967)^[15].

In contrast, the infrared spectra of complexes 1.1, 1.2, 1.5, and 1.6 displayed a medium-intensity far-IR band in the 338–324 cm⁻¹ range. This band is assigned to the stretching mode of coordinated chlorine atoms, ν Mn-Cl, oriented in a trans configuration (Coltup *et al.*, 1964)^[17]. Aromatic ring frequencies showed no notable modifications across all coordination compounds.

2.4 Electronic Spectra and Magnetic Properties

Synthesis, spectroscopic characterization and coordination chemistry of novel chiral orthophthalaldehyde-derived schiff base ligands and their Mn (II) and Pd (II) complexes. The electronic absorption spectra of the Mn (II) complexes recorded in dichloromethane displayed very weak, low-intensity absorption bands located near 18,000 cm⁻¹ (550 nm), 25,000 cm⁻¹ (400 nm), and 29,000 cm⁻¹ (350 nm). These weak bands are assigned to the following electronic transitions, respectively:



These specific (d-d) transitions strongly support the assignment of an octahedral geometry around the central Mn (II) ion (Lever, 1968)^[18]. The bands are weak because the ground state of a high-spin (d⁵) system in a weak octahedral crystal field contains a single electron in each of the five (d)-orbitals, making all internal transitions spin-forbidden. The weak absorption bands observed arise from weak spin-orbit coupling interactions, which relax the selection rules slightly.

Magnetic susceptibility measurements at room temperature yielded magnetic moments μ_{eff} for the Mn (II) complexes in the 6.85–6.96 B.M. range. These values are higher than the theoretical spin-only value of 5.92 B.M., indicating significant orbital contributions to the total magnetic moment (Carlin & Vandrynevedt, 1997)^[7]. This magnetic data confirms a high-spin configuration for the central metal ion and supports the assignment of a mononuclear octahedral geometry for all six Mn (II) complexes.

3. Characterization of Palladium (II) Complexes

Palladium (II) possesses a d⁸ electronic configuration and typically exhibits a strong preference for low-spin, diamagnetic square planar coordination geometries.

3.1 Elemental Analysis and Mass Spectrometry

The analytical and physical data compiled for the palladium (II) complexes are presented in **Table 6**. The experimental percentages obtained for carbon, hydrogen, nitrogen, and palladium are in close agreement with the theoretical values calculated for the proposed molecular formulas.

Mass spectrometry confirmed the mononuclear nature of the complexes. Complexes 5.1 and 5.2 exhibited clear [M+1]⁺ pseudomolecular ion peaks at m/z 522 and 603, respectively. Complexes 5.3, 5.4, 5.5, and 5.6 displayed distinct molecular ion peaks [M]⁺ at m/z 436, 464, 555, and 595, respectively. These results confirm the successful formation of the target coordination complexes.

Table 4: Analytical Data of Pd (II) Complexes

Complex Code	Proposed Molecular Formula	Color	Carbon % Found (Calc.)	Hydrogen % Found (Calc.)	Nitrogen % Found (Calc.)	Palladium % Found (Calc.)
Complex 5.1	[Pd (S1)] Cl ₂	Brown	50.41 (50.64)	4.59 (4.64)	10.63 (10.74)	20.29 (20.40)
Complex 5.2	[Pd (S2)] Cl ₂	Yellowish	55.58 (55.87)	5.21 (5.36)	9.21 (9.31)	17.53 (17.68)
Complex 5.3	[Pd (A1)]	Brownish	48.97 (49.49)	5.37 (5.08)	6.29 (6.41)	24.05 (24.36)
Complex 5.4	[Pd (A2)]	Dark Yellow	50.98 (51.68)	6.01 (5.64)	5.97 (6.03)	22.47 (22.89)
Complex 5.5	[Pd (S3)] Cl ₂	Brown	54.02 (54.01)	3.99 (3.90)	10.08 (10.01)	19.15 (19.12)
Complex 5.6	[Pd (S4)] Cl ₂	Ochre Yellow	56.44 (56.39)	4.40 (4.25)	9.40 (9.30)	17.86 (17.82)

3.2 Molar Conductance and Magnetic Properties

Molar conductance measurements performed in dichloromethane at a concentration of 10⁻³ M revealed a clear correlation with the ligand framework:

Complexes 5.3 and 5.4 (derived from the (A1) and (A2) amino acid ligands) exhibited low conductance values in the 13.0–26.5 Ω^{-1} , cm², mol⁻¹ range, confirming that they behave as non-electrolytes.

In contrast, complexes 5.1, 5.2, 5.5, and 5.6 displayed high conductance values in the 48.5–60.5 Ω^{-1} , cm², mol⁻¹ range. This behavior confirms that they act as 1:2 electrolytes in solution, establishing that the two chloride ions are located outside the coordination sphere as counter-ions (Geary, 1971)^[11]. The presence of these ionic chlorides was further verified qualitatively via positive silver nitrate precipitation tests.

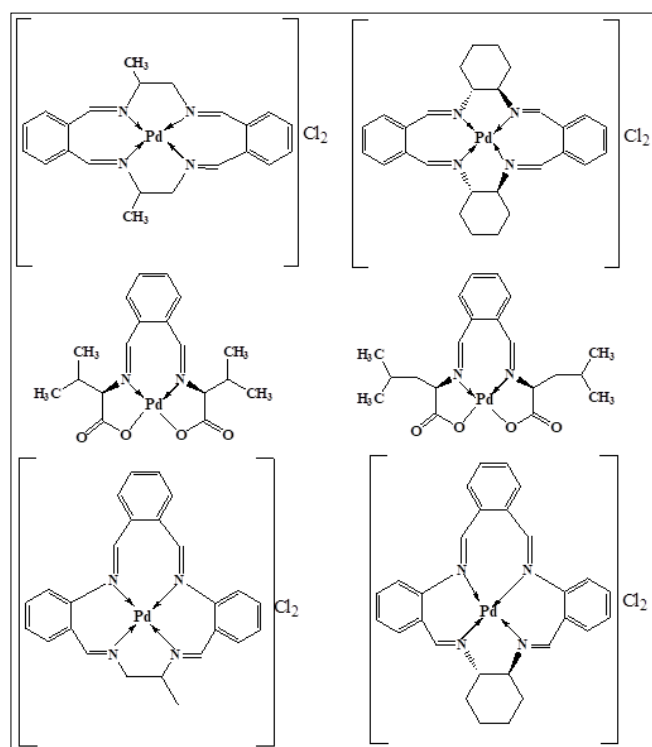
Magnetic susceptibility measurements confirmed that all six Pd (II) complexes are completely diamagnetic at room temperature. This confirms a low-spin d^8 electronic configuration, consistent with a square planar coordination geometry around the palladium center (Griffith, 2003)^[9].

3.3 Infrared and Electronic Absorption Spectroscopic Studies

The infrared spectra of the Pd (II) complexes exhibited a negative shift in the azomethine stretching frequency, ν C=N, by 25–40 cm^{-1} , appearing in the 1620–1610 cm^{-1} range. This shift confirms coordination through the imine nitrogen atoms, supported by the appearance of a far-IR band at 535–519 cm^{-1} assigned to the ν Pd-N stretching mode (Quagliano *et al.*, 1961)^[23].

For the amino acid derivatives 5.3 and 5.4, the asymmetric and symmetric stretching modes of the carboxylate groups appeared at 1598–1586 cm^{-1} and 1370–1356 cm^{-1} , respectively, confirming coordination via the deprotonated carboxylate oxygen atoms. This was further corroborated by a far-IR band at 438–426 cm^{-1} corresponding to the ν Pd-O stretching frequency (Ivanova *et al.*, 2005)^[24].

The electronic absorption spectra of the Pd (II) complexes recorded in DMF displayed a broad, low-intensity d-d transition band in the 22,450–20,460 cm^{-1} (445–488 nm) region. This band is assigned to the $^1B_{1g} \leftarrow ^1A_{1g}$ transition, characteristic of a square planar geometry (Lever, 1968)^[18]. Additionally, a strong absorption band appeared in the 34,540–31,260 cm^{-1} (289–319 nm) range, assigned to a ligand-to-metal charge transfer (LMCT) process.



Scheme 3: Tentative structures of Schiff base Pd (II) complexes

3.4 Multinuclear ^1H and ^{13}C NMR Profiling of Pd (II) Complexes

Because the Pd (II) complexes are diamagnetic, they could be comprehensively characterized via multinuclear NMR spectroscopy, allowing a direct comparison with the spectra of the free ligands. The ^1H NMR spectra of all six

complexes exhibited a notable downfield shift ($\delta = 0.15$ – 0.35 ppm) for the azomethine proton singlet $-\text{CH}=\text{N}-$ relative to the free ligands, appearing in the δ 8.55–7.25 ppm range. This downfield shift confirms the donation of lone-pair electron density from the imine nitrogen to the palladium center (Shakir *et al.*, 2006)^[5]. For complexes 5.3 and 5.4, the broad singlet corresponding to the carboxylic acid proton ($\delta \sim 11.0$ ppm) disappeared completely, confirming deprotonation and subsequent coordination of the carboxylate oxygen. Aliphatic and aromatic proton signals displayed minimal changes in their positions, confirming that they do not participate directly in coordination (Chohan & Praveen, 2001)^[25].

The ^{13}C NMR spectra of the complexes exhibited a notable downfield shift for the azomethine carbon signals $-\text{C}=\text{N}-$, appearing in the δ 155.3–151.5 ppm range compared to the δ 164.1–161.4 ppm range for the free ligands. This shift reflects the decrease in electron density at the imine carbon upon coordination of the adjacent nitrogen atom (Tzschach *et al.*, 1985)^[26]. Interestingly, the carboxyl carbon signals $-\text{CO}-$ in complexes 5.3 and 5.4 remained essentially unchanged at $\delta \sim 176$ ppm, indicating that the electronic environment of this carbon is relatively unaffected by coordination through the oxygen atom (Muralidhar Reddy *et al.*, 2007)^[27]. Aryl carbon resonances displayed minimal shifts, confirming the stability of the aromatic backbone. Based on these combined analytical and spectroscopic findings, the structures illustrated in Scheme 2 are assigned to the copper (II) and palladium (II) complexes.

3.5 Thermal Analysis (TG-DTA)

Thermogravimetric and differential thermal analyses (TG-DTA) provided a reliable method for evaluating the thermal stability of the complexes and determining the nature of any water molecules present (lattice or coordinated). Coordinated and lattice water molecules exhibit distinct thermal decomposition profiles due to differences in their binding modes within the crystal lattice: lattice water molecules are weakly bound and typically desorb in the 70–130 $^{\circ}\text{C}$ temperature range, whereas coordinated water molecules are directly bound to the metal center and require higher temperatures (140–220 $^{\circ}\text{C}$) for desorption (Allan & Veitch, 1983)^[28].

The thermal decomposition profiles of the complexes exhibited a clear dependence on the ligand framework:

The thermograms of complexes 1.1, 1.2, 1.5, and 1.6 (the Mn (II)S-series) and all the Pd (II) complexes displayed no weight loss or endothermic DTA peaks up to 220 $^{\circ}\text{C}$. This confirms the complete absence of either lattice or coordinated water molecules, establishing that these complexes exist in an anhydrous state (Allan & Veitch, 1983)^[28].

In contrast, complexes 1.3 and 1.4 (the Mn (II) A-series) exhibited a clear initial weight loss in the 75–120 $^{\circ}\text{C}$ range, accompanied by a distinct endothermic DTA peak. The observed weight loss corresponds to the desorption of two lattice water molecules for complex 1.3 and one lattice water molecule for complex 1.4. These complexes then exhibited a second well-defined weight loss phase in the 148–215 $^{\circ}\text{C}$ range, accompanied by an endothermic DTA peak. This phase corresponds to the loss of two coordinated water molecules, consistent with the elemental analysis data (Nikolaev *et al.*, 1969)^[13].

Conclusion

This study describes the successful design, synthesis, and characterization of six new chiral Schiff base ligands S1–S4, A1–A2 derived from orthophthalaldehyde, along with their mononuclear complexes with Manganese (II), and Palladium (II) ions. Analytical and spectroscopic characterization confirmed that the reactions proceeded with high purity and established a 1:1 metal-to-ligand stoichiometry for all complexes. Molar conductance measurements showed that the complexes function as non-electrolytes or 1:2 electrolytes depending on the specific ligand framework and metal center. Spectroscopic and magnetic data confirmed a high-spin octahedral geometry for all the Mn (II) complexes, where the S-series ligands coordinate via four imine nitrogens and two axial chlorides, while the A-series ligands coordinate via two imine nitrogens, two carboxylate oxygens, and two axial water molecules. The palladium (II) S-series complexes were shown to possess square planar geometries, with the chloride ions located outside the coordination sphere as counter-ions. Palladium (II) complexes retained a square planar configuration. Thermal analysis verified the presence and stoichiometry of lattice and coordinated water molecules within the amino acid-derived complexes, while confirming the high thermal stability of the anhydrous systems. These findings demonstrate the structural versatility of orthophthalaldehyde-derived chiral Schiff base ligands and highlight their utility for developing stable transition metal complexes with tailored coordination environments.

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