Research Article

Synthesis, Characterization, and Magnetic and Thermal Studies on Some Metal(II) Thiophenyl Schiff Base Complexes

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4-(Thiophen-3-yl)-aniline undergoes condensation with \( o \)-vanillin to form an ONS donor Schiff base, 2-methoxy-6-[(4-thiophene-3-yl-phenylimino)-methyl]-phenol, which forms complexes of the type \([ML_2] \times H_2O\) where \( M = Mn, Co, Ni, Cu, Zn, Pd\). These complexes are characterized by elemental analysis, \(^1\)H nmr, electronic, mass, and IR spectroscopies and conductance measurements. The electronic, IR and CHN data are supportive of a 4-coordinate tetrahedral geometry for Mn(II), Co(II), Ni(II), and Zn(II) complexes and square-planar geometry for Cu(II) and Pd(II) complexes, with the chromophores \( N_2O_2 \). The magnetic data reveals that the complexes are magnetically dilute and mononuclear with exception of the Cu(II) complex, which exhibits some anti-ferromagnetisms. The complexes are air-stable solids, and none is an electrolyte in nitro methane.

1. Introduction

My group has in the last five years been actively involved in the synthesis, characterization, and thermal and biological properties of various Schiff bases and their M(II) chelates (\( M = VO, Mn, Co, Ni, Cu, Zn, Pd\)), with the objectives of deriving Schiff base chelates which can be used as precursors in metal-organic chemical vapor depositions (MOCVD) and those with good in vitro antimicrobial activities as surface cleaning agents [1–5]. Thiophenyl Schiff bases are particularly interesting because of their wide range of activities such as anticancer activity as shown by benzyl-N-[1-(thiophenyl-3-yl)ethylidene] hydrazine carbodithioate [6], antibacterial and antifungal activities typified by thiophenyl-azetidinones, -cephalexins and -vinyl anilines [7–16] as well as optical exhibited by thiophene-2-aldazine [17]. Other activities include structural activity exemplified by the hexacarbonyldiiron complex of N-(2-thienylmethylidene)aniline, which is composed of two thienyl moieties derived from the original thienyl imine and coupled together by a C–C bond [18]. Furthermore, Palladium imine complexes of 2-thiophenecarboxaldehyde are used as catalysts in the Suzuki cross-coupling of aryl bromides with phenyl boric acid [19]. Extensive literature reviews show that no studies are reported on the Schiff base derived from \( o \)-vanillin and 4-(thiophene-3-yl)-aniline and its metal(II) chelates [6–19]. Thus, the objective of this work is to synthesize, characterize, and investigate the magnetic and thermal properties of the Schiff base, 2-methoxy-6-[(4-thiophene-3-yl-phenylimino)-methyl]-phenol and its Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes. These metal complexes and its ligands are new, being reported here for the first time.

2. Experimental Details

2.1. Materials and Physical Measurements. Reagent grade \( o \)-vanillin, 4-(thiophene-3-yl)-aniline, manganese(II) nitrate dehydrate, cobalt(II) nitrate hexahydrate, nickel(II) nitrate hexahydrate, copper(II) nitrate hexahydrate, zinc(II) nitrate hexahydrate, and palladium(II) chloride are purchased from BDH and Aldrich chemicals and are used as received. Solvents are dried and distilled before use according to standard procedures. Melting points (uncorrected) are determined using the Stuart scientific melting point SMP1 machine, and conductivities of \( 10^{-3} \) M solutions of the complexes are measured in nitromethane at 25°C using a MC-1, Mark V conductivity meter with a cell constant of 1.0. The solid
reflectance spectra are recorded on a Perkin-Elmer λ20 spectrophotometer while infrared spectra are measured as KBr discs on a Perkin-Elmer FTIR paragon 1000 spectrometer in the range 4000–400 cm$^{-1}$. The elemental analyses C, H, and N are recorded on GmbH VarioEl analyser, and cobalt, nickel, copper, zinc, and palladium are determined titrimetrically and by atomic absorption spectroscopy [20]. The $^{1}$H nmr spectra are recorded on a 300 MHz Oxford Varian NMR instrument in CDCl$_3$ at 295 K. $^{1}$H chemical shifts are referenced to the residual signals of the protons of CDCl$_3$ and are quoted in ppm. Magnetic susceptibilities are measured on Johnson Matthey magnetic susceptibility balance, and diamagnetic corrections are calculated using Pascal’s constants [21]. Thermogravimetric analyses are done in static air, using a T6 Lineis thermal analyser with a heating rate of 10°C/min in the range 30–700°C. The MALDI-TOF mass and atomic absorption spectra are obtained using a Bruker Daltonic Reflex TOF spectrometer with graphite as matrix and Perkin Elmer Analyst 200 coupled to Winlab 32 software assembly, respectively.  

2.2. Preparation of the Schiff Base (2-methoxy-6-[(4-thiophene-3-yl-phenylimino)-methyl]-phenol). A 20 mL solution of 8.71 mmol (1.33 g) o-vanillin in absolute ethanol is added dropwise to a stirring solution of 8.71 mmol (1.53 g) of 4-(thiophene-3-yl)-aniline in 30 mL of absolute ethanol. The resulting orange-colored solution is refluxed for 4 h after addition of 4 drops of acetic acid. The orange product formed on cooling to room temperature is filtered and washed with ethanol, and dried over anhydrous calcium chloride. The yields are 0.12 g (50%), 0.72 mmol (0.23 g) of the ligand in 30 mL of absolute ethanol, is added dropwise to a stirring solution of 0.36 mmol (0.064 g) of Pd(II) chloride, in 10 mL of absolute ethanol. The resulting solution is then buffered with 0.72 mmol (0.11 mL) of triethylamine and refluxed for 6 h during which the products formed. The precipitated solids are filtered, washed with ethanol, and dried over anhydrous calcium chloride. The yield is 0.18 g (70%).  

2.3. Preparation of the Metal(II) Complexes. The various complexes are prepared by gradual addition of 0.35 mmol (0.06–0.11 g) M(NO$_3$)$_2$·6H$_2$O (M = Mn, Co, Ni, Cu, Zn) neat to a stirring 0.7 mmol (0.22 g) of the ligand in 30 mL of absolute ethanol. The resulting solution are then buffered with 0.7 mmol (0.10 mL) of triethylamine and refluxed for 6 h during which the products formed. The precipitated solids are filtered, washed with ethanol, and dried over anhydrous calcium chloride. The yields are 0.12 g (50%), 0.17 g (70%), 0.17 g (70%), and 0.17 g (70%), and 0.14 g (60%), respectively.

The Pd(II) complex is prepared using a similar method. 0.36 mmol (0.064 g) of Pd(II) chloride, in 10 mL of absolute ethanol, is added dropwise to a stirring solution of 0.72 mmol (0.23 g) of the ligand in 30 mL of absolute ethanol. The resulting solution is then buffered with 0.72 mmol (0.11 mL) of triethylamine and refluxed for 6 h during which the product is formed. The product is filtered, washed with ethanol, and dried over anhydrous calcium chloride. The yield is 0.18 g (70%).  

Proton nmr measurements are done only for the diamagnetic Zn(II) and Pd(II) complexes. Zn(II) complex: $^{1}$H nmr (ppm) 8.70 (s, 1H, HCN), 8.34 (1H, s, C$_2$HS), 7.28–7.43 (m, 4H, C$_6$H$_4$); 6.88–6.98 (m, 2H, C$_2$H$_2$S); 3.94 (s, 3H, OCH$_3$).  

Pd(II) complex: $^{1}$H nmr (ppm) 8.67 (s, 1H, HCN), 8.30 (1H, s, C$_2$HS), 7.48–7.66 (m, 3H, C$_6$H$_3$); 7.00–7.47 (m, 4H, C$_6$H$_4$); 6.88–6.98 (m, 2H, C$_2$H$_2$S); 3.94 (s, 3H, OCH$_3$).  

3. Results and Discussion

The equations for the formation of the complexes are

\[ M(NO_3)_2 + 2HL \rightarrow [ML_2] + 2HNO_3 \]  

(1)

(Where M = Zn(II), Cu(II), Mn(II), Co(II), Ni(II))

\[ PdCl_2 + 2HL \rightarrow [PdL_2] + 2HCl. \]  

(2)

All complexes adopt [ML$_2$] stoichiometry, except Mn(II), Co(II) and Ni(II) complexes that form as [ML$_x$]$\cdot$xH$_2$O, where x = 1 and 0.5, respectively. Proposed structures for the ligand and the Cu(II) complex are shown in Figure 1. The formation of this ligand is confirmed by microanalysis and $^{1}$H nmr. The colors, melting points, and room temperature magnetic moments ($\mu_{et}$) of the compounds are presented in Table 1. Attempts to isolate suitable crystals for single X-ray structural determination have not been successful so far.

3.1. Infrared Spectra. The relevant infrared bands of the compounds are presented in Table 2. The broadband at 3360 cm$^{-1}$ in the ligand, which is conspicuously absent in the spectra of the metal(II) Schiff base complexes, is assigned as vOH stretching frequency, and it confirms involvement of the phenol O in chelation. It is broad due to intramolecular hydrogen bonding, usually very strong in Schiff bases [1]. The new broadband at 3500 cm$^{-1}$ in the spectra of Co(II), Ni(II), and Mn(II) complexes is assigned to the vOH frequency of crystallization H$_2$O. The coordinated C=N stretching vibrations are observed as three bands between 1614–1521 cm$^{-1}$ in the ligand [2–5] and 1639–1503 cm$^{-1}$ in the metal complexes with exceptions of the Cu(II) and Pd(II) complex which have two bands. The bathochromic/hypsochromic shifts of these bands in the complexes are attributed to the involvement of N atom of C=N in coordination to the metal ions. Moreover, it has been documented that square planar Pd(II) and Cu(II) Schiff base complexes do exhibit geometric isomerism [22], with the trans isomer showing two vC=N bands and the cis isomer a lone vC=N band. The spectra of the Cu(II) and Pd(II) complexes in this work show two vC=N bands and are consequently in the trans-isomeric form. The vPh/C–O and δC–H vibrations of the ligand are observed at 1461–1364 and 972 cm$^{-1}$, respectively. These suffer bathochromic shifts to 1298–1177 and 896–720 cm$^{-1}$ in the Schiff base complexes due to the coordination of the phenol oxygen atom and pseudoaromatic nature of the chelates [5, 6]. The observation of new bands at 480–405 and 581–542 cm$^{-1}$ due to v(M–O) and v(M–N) [11, 14, 22] is further evidence of coordination.

3.2. Electronic Spectra and Magnetic Moments. The electronic spectral data for the complexes are presented in Table 2.
The Mn(II) Schiff base complex shows two absorption bands at 15.00 and 23.11 kK, respectively, consistent with a four-coordinate, tetrahedral geometry and are assigned to $^6A_1 \rightarrow ^4E_1 (\nu_1)$ and $^6A_1 \rightarrow ^4A_1 (\nu_2)$ transitions [23]. A room temperature moment of 5.92 B.M is usually observed for the Mn(II) compounds, regardless of stereochemistry because the ground term is an $^6A_1$, and thus, orbital contribution is nil. This Mn(II) complex has a moment of 5.70 B.M. complementary of tetrahedral geometry [1].

The cobalt(II) Schiff base complex gives two absorption bands at 10.82 and 18.20 kK, respectively, typical of a four-coordinate tetrahedral geometry and is assigned to $^4A_2 \rightarrow ^4T_1(P) (\nu_2)$ and $^4A_2 \rightarrow ^4T_1(P) (\nu_3)$. The transition $^4A_2 \rightarrow ^4T_2 (\nu_1)$ in the range 5–7 kK is not observed as usual.

### Table 1: Analytical data for the ligand and its complexes.

| Compound (empirical formula) | Formula mass | Color | m/z (100%) | $\mu_{eff}$ | % Yield | $\Lambda_m^*$ | M.p (°C) | Analysis (calculated) |
|-----------------------------|--------------|-------|------------|-------------|----------|------------|--------|-----------------------|
|                             |              |       |            |             |          |            |        | % C | % H | % N | % M |
| HL (C_{18}H_{15}NO_2S)      | 309.38       | Orange | 309        | —           | 80       | —          | 150–151| 69.82 | 4.53 | 4.35 | — |
| [MnL_2]H_2O                | 689.73       | Green  | 671        | 5.70        | 50       | 10.0       | 338–340| 62.54 | 4.32 | 4.02 | 8.02 |
| (MnC_{36}H_{30}N_2S_2O_5)  |              |        |            |             |          |            |        | (62.69) | (4.38) | (4.06) | (7.97) |
| [CoL_2]H_2O                | 693.71       | Brick Red | 675       | 4.33        | 70       | 20.0       | 290–292| 62.36 | 3.64 | 4.06 | 8.48 |
| (CoC_{36}H_{30}N_2S_2O_5)  |              |        |            |             |          |            |        | (62.33) | (4.36) | (4.04) | (8.50) |
| [NiL_2]1/2H_2O             | 684.48       | Yellow | 675        | 3.10        | 70       | 15.0       | 193–195| 63.07 | 3.86 | 4.17 | 8.55 |
| (NiC_{36}H_{30}N_2S_2O_4S) |              |        |            |             |          |            |        | (63.17) | (4.27) | (4.09) | (8.58) |
| [CuL_2]_2                | 680.31       | Brown  | 680        | 1.56        | 70       | 9.0        | 205–207| 64.14 | 4.06 | 4.01 | 9.35 |
| (Cu_2C_{17}H_{36}N_4S_2O_8)|              |        |            |             |          |            |        | (63.56) | (4.15) | (4.12) | (9.34) |
| [ZnL_2]                  | 681.76       | Yellow | 681        | D           | 60       | 17.0       | 316–318| 63.13 | 3.84 | 3.81 | 9.52 |
| (ZnC_{36}H_{30}N_2S_2O_4) |              |        |            |             |          |            |        | (63.42) | (4.14) | (4.11) | (9.53) |
| [PdL_2]                  | 723.18       | Green  | 720        | D           | 70       | 12.0       | 148–150| 60.37 | 3.42 | 3.86 | 14.70 |
| (PdC_{36}H_{30}N_2S_2O_4) |              |        |            |             |          |            |        | (59.79) | (3.90) | (3.87) | (14.72) |

* $\Omega^{-1}$ cm$^2$ mol$^{-1}$, D: diamagnetic.

Figure 1: Proposed structures for the ligand (a) and its Cu(II) complex (b).
since it lies in the infrared region [10]. This geometry is corroborated by a moment of 4.33 B.M [11].

Nickel(II) complexes are known to exhibit complicated equilibria between coordination numbers six (octahedral) to four (square planar/tetrahedral) [24]. The Ni(II) Schiff base complex exhibits two absorption bands at 14.29 and 20.21 kK typical of a 4-coordinate tetrahedral geometry, assigned to $^2T_1(F) \rightarrow ^2T_2$, ($\nu_2$) and $^2T_1(F) \rightarrow ^2A_2$, ($\nu_3$) transitions. Its moment of 3.10 B.M is complimentary of tetrahedral geometry, since moments of 3.1–3.5 B.M. are reported for distorted tetrahedral complexes [12].

The copper(II) complex displays two bands at 14.09 and 21.60 kK, assigned to $^2B_1g \rightarrow ^2A_1g$ and $^2B_1g \rightarrow ^2E_g$ transitions of 4-coordinate, square planar geometry [13]. A moment of 1.9–2.2 B.M is usually observed for mononuclear copper(II) complexes, regardless of stereochemistry [14]. A magnetic moment of 1.56 B.M is observed for this complex, indicative of the presence of some anti-ferromagnetic interactions, operating through Cu–Cu interactions [25]. However, this could not be probed further due to lack of facilities for variable temperature magnetic measurements and nonsuitable crystal for single X-ray diffraction measurement (Figure 1).

The Zn(II) complex expectedly shows only charge transfer transition from M → L and $\pi-\pi^*$ transitions, as no d-d transition is expected at 28.20, 35.00, and 42.00 kK, respectively. This complex is diamagnetic, confirming its tetrahedral geometry [12–14].

The Pd(II) complex shows absorption bands at 18.20 and 26.32 kK, typical of square planar geometry and is assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1E_{1g}$ transitions. This complex is expectedly diamagnetic [26].

### 3.3. $^1H$ nmr Spectra.

The ligand shows the phenolic proton as a singlet at $\delta$ 11.13 ppm (s, 1H, OH), the imine (s, 1H, HCN), and 2-thiophenyl (s, 1H, C$_2$HS) protons resonate as singlets at 9.93 and 8.70 ppm, respectively. The o-vanillin (m, 3H, C$_6$H$_3$) and phenyl (aniline) protons (m, 4H, C$_6$H$_4$) are both observed as multiplets at $\delta$ 7.35–7.43 and 7.00–7.47 ppm, respectively. The two protons of thiophenyl ring at 4 and 5 positions are seen as multiplets at $\delta$ 7.48–7.66, 7.00–7.47, and 6.88–6.98 ppm, respectively. The methoxy protons resonate as a singlet at 3.94 ppm (s, 3H, OCH$_3$).

In the Zn(II) complex spectrum, the phenolic proton disappears, an indication of coordination of the phenol oxygen to the Zn(II) ion, and other protons are all upfield shifted in comparison to the ligand. The imine hydrogen resonates as a singlet at 8.70 ppm (s, 1H, HCN) while the 2-thiophenyl proton is seen at 8.34 ppm as a singlet (s, 1H, HCN) and the methoxy protons are seen as multiplets at 3.94 ppm (s, 3H, OCH$_3$), and 3.93 ppm (s, 3H, OCH$_3$).

### 3.4. Mass Spectroscopy and Thermal Studies.

The mass spectra of the complexes showed peaks attributed to the molecular ions m/z at 809 [L]$^+$. In the Zn(II) complex spectrum, the phenolic proton disappears, an indication of coordination of the phenol oxygen to the Zn(II) ion, and other protons are all upfield shifted in comparison to the ligand. The imine hydrogen resonates as a singlet at 8.70 ppm (s, 1H, HCN) while the 2-thiophenyl proton is seen at 8.34 ppm as a singlet (s, 1H, HCN). The Pd(II) complex shows absorption bands at 18.20 and 26.32 kK, typical of square planar geometry and is assigned to $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1E_{1g}$ transitions. This complex is expectedly diamagnetic [26].

| Compound | $\nu$(OH) | $\nu$(C=N) + $\nu$(C=C) | $\nu$(C–H) | $\delta$(M–N) | $\delta$(M–O) | Electronic transitions (kK) |
|----------|-----------|------------------------|-----------|-------------|-------------|---------------------------|
| HL       | 3360b     | 1614s $\rightarrow$ 1593s $\rightarrow$ 1521s | 1461s $\rightarrow$ 1364s | 972s         | —           | 33.50, 36.25, 40.20       |
| [MnL$_2$]H$_2$O | 3500b | 1612s $\rightarrow$ 1589s $\rightarrow$ 1551s | 1298s $\rightarrow$ 1194s | 848s 720s | 580m 561s | 450m 420s | 15.00, 23.11, 30.26, 33.45, 40.20 |
| [CoL$_2$]H$_2$O | 3500b | 1609s $\rightarrow$ 1575s $\rightarrow$ 1503s | 1231m $\rightarrow$ 1180m | 840s 777m | 575s 537m | 475m 415m | 10.82, 18.20, 32.0, 37.40, 41.0 |
| [NiL$_2$] | 3500b | 1599s $\rightarrow$ 1585s $\rightarrow$ 1537s | 1233s $\rightarrow$ 1192s | 853s 780m | 581s 564s | 460s 453s | 14.29, 20.21, 30.72, 36.25, 40.40 |
| [CuL$_2$] | — | 1587s $\rightarrow$ 1538s | 1237m $\rightarrow$ 1193m | 856s 795s | 573s 557s | 465s 410s | 14.09, 21.60, 30.92, 34.35, 41.20 |
| [ZnL$_2$] | — | 1609s $\rightarrow$ 1582s $\rightarrow$ 1504s | 1231m $\rightarrow$ 1197m | 896s 731m | 579s 562m | 480m 405m | 28.20, 35.00, 42.00 |
| [PdL$_2$] | — | 1592s $\rightarrow$ 1540s | 1240s $\rightarrow$ 1177s | 843m 783m | 562m 542m | 450m 420m | 18.20, 26.32, 30.25, 39.20, 43.00 |

Table 2: Relevant infrared and electronic spectral data of the ligand and its complexes.
Table 3: Thermal data for the ligand and its complexes.

| Compound                          | Temperature range (°C) | TG weight loss (%) | Assignments          |
|-----------------------------------|------------------------|--------------------|----------------------|
|                                  |                        | Calc. weight       | Found weight       |                      |
|                                  |                        | (%)                | (%)                 |                      |
| **HL** (C\(_{18}\)H\(_{15}\)NSO\(_2\))** | 30–220                 | 12.93              | 12.96               | C\(_2\)H\(_2\) + 0.5N\(_2\) |
|                                  | 220–420                | 65.94              | 66.32               | C\(_{11}\)H\(_{20}\)OS |
|                                  | 420–700                | 22.78              | 21.01               | C\(_3\)H\(_5\)        |
| **[MnL\(_2\)]H\(_2\)O** **(MnC\(_{36}\)H\(_{30}\)N\(_2\)S\(_2\)O\(_5\))**** | 30–200                 | 9.57               | 9.40                | H\(_2\)O + 1.5O\(_2\) |
|                                  | 210–450                | 44.07              | 44.45               | C\(_{20}\)H\(_{19}\)NS |
|                                  | 450–700                | 22.04              | 22.53               | C\(_{4}\)H\(_{10}\)OS |
|                                  |                        |                    |                     | Mn (residue)          |
| **[CoL\(_2\)]H\(_2\)O** **(CoC\(_{36}\)H\(_{30}\)N\(_2\)S\(_2\)O\(_5\))**** | 30–200                 | 4.90               | 4.77                | CH\(_4\) + H\(_2\)O  |
|                                  | 200–400                | 20.76              | 21.45               | C\(_{6}\)H\(_8\)S\(_2\) |
|                                  | 400–700                | 57.08              | 57.50               | C\(_{24}\)H\(_{16}\)O\(_4\)N\(_2\) |
| **[NiL\(_2\)]\(_1/2\)H\(_2\)O** **(NiC\(_{36}\)H\(_{30}\)N\(_2\)S\(_2\)O\(_4\)\(_{1.5}\))**** | 30–240                 | 10.67              | 10.56               | 0.5H\(_2\)O + SO\(_2\) |
|                                  | 240–420                | 23.08              | 22.73               | C\(_{10}\)H\(_{10}\)N\(_2\) |
|                                  | 420–700                | 55.81              | 55.51               | C\(_{23}\)H\(_{18}\)SO\(_2\) |
|                                  |                        |                    |                     | Ni (residue)          |
| **[CuL\(_2\)]** **(CuC\(_{36}\)H\(_{28}\)N\(_2\)S\(_2\)O\(_4\))** | 30–260                 | 17.93              | 17.86               | C\(_4\)H\(_2\)N\(_2\) |
|                                  | 260–440                | 33.81              | 33.63               | C\(_{13}\)H\(_{10}\)O\(_2\)S |
|                                  | 440–700                | 38.81              | 42.00               | C\(_{13}\)H\(_{10}\)NO\(_2\) |
|                                  |                        |                    |                     | Cu (residue)          |
| **[ZnL\(_2\)]** **(ZnC\(_{36}\)H\(_{28}\)N\(_2\)S\(_2\)O\(_4\))** | 30–260                 | 5.00               | 5.17                | H\(_2\)S              |
|                                  | 260–440                | 27.87              | 27.80               | C\(_{11}\)H\(_{10}\)OS |
|                                  | 440–700                | 52.22              | 52.21               | C\(_{22}\)H\(_{16}\)O\(_3\) |
|                                  |                        |                    |                     | Zn (residue)          |
| **[PdL\(_2\)]** **(PdC\(_{36}\)H\(_{28}\)N\(_2\)S\(_2\)O\(_4\))** | 30–210                 | 3.87               | 3.50                | C\(_{18}\)H\(_4\)     |
|                                  | 210–400                | 40.79              | 41.33               | C\(_{18}\)H\(_{13}\)SO |
|                                  | 400–700                | 33.32              | 33.42               | C\(_{13}\)H\(_{10}\)NO\(_2\) |
|                                  |                        |                    |                     | PdO (residue)         |

calc. = 65.94%) at 220–420°C. The final step is the loss of the fragment C\(_5\)H\(_5\), with mass losses of (obs. = 22.78%, calc. = 21.01%) at 420–700°C.

The Mn(II) complex decomposes in three phases. The first phase corresponds to the loss of 1.5 moles of O\(_2\) and H\(_2\)O between 30–200°C with mass losses of (obs. = 9.40%, calc. = 9.57%). The second phase is from 210 to 450°C and is attributed to the loss of the organic moiety C\(_{20}\)H\(_{19}\)NS with mass losses of (obs. = 44.37%, calc. = 44.07%). The final phase shows the loss of the organic moiety, C\(_8\)H\(_{10}\)OS, at 450–700°C with mass losses of (obs. = 22.53%, calc. = 22.33%) leaving Mn as the final product, and the fragment C\(_8\)N is lost as 8CO\(_2\) and 0.5N\(_2\).

The decomposition of the Co(II) complex also occurred in three steps. The first step is due to the loss of a mole of water and CH\(_4\) at 30–200°C, with mass losses of (obs. = 4.77%, calc. = 4.90%). The successive decomposition occurs within a temperature range of 200–400°C and is attributed to the loss of the organic moiety C\(_6\)H\(_8\)S\(_2\) with mass losses of (obs. = 22.53%, calc. = 22.33%) leaving Co as the final product, and the fragment CH is lost as CO\(_2\) + 0.5H\(_2\).

Cu(II) complex decomposes in three steps. The first step is attributed to the loss of the fragment C\(_8\)H\(_{12}\)N, with mass losses of (obs. = 17.86%, calc. = 17.89%) at 30–200°C. The second step ranges from 200 to 400°C and is attributed to the loss of the fragment C\(_{13}\)H\(_{10}\)O\(_2\)S with mass losses of (obs. = 22.73%, calc. = 23.08%). The final step is within a temperature range of 420–700°C and is attributed to the loss of the organic moiety C\(_{23}\)H\(_{18}\)SO\(_2\) (obs. = 55.51%, calc. = 55.81%). The remaining fraction is Ni residue, and the fragment CH is lost as CO\(_2\) + 0.5H\(_2\).

Cu(II) complex decomposes in three steps. The first step is between 30–260°C, which indicates the loss of H\(_2\)S, with mass losses of (obs. = 5.17%, calc. = 5.00%). The second step involves the loss of the organic moiety C\(_{13}\)H\(_{10}\)OS, The TGA curve of the Ni(II) complex reveals a three-step decomposition. The first is the loss of 0.5 mole of water and SO\(_2\) at 30–240°C, with mass losses of (obs. = 10.56%, calc. = 10.67%). The second step ranges from 240 to 420°C and is assigned to the loss of the organic moiety, C\(_{10}\)H\(_{10}\)N\(_2\) with mass losses (obs. = 22.73%, calc. = 23.08%). The final step is within a temperature range of 420–700°C and is attributed to the loss of the organic moiety C\(_{23}\)H\(_{18}\)SO\(_2\) (obs. = 55.51%, calc. = 55.81%). The remaining fraction is Ni residue, and the fragment CH is lost as CO\(_2\) + 0.5H\(_2\).

Zn(II) complex decomposes in three steps. Step one is between 30–260°C, which indicates the loss of H\(_2\)S, with mass losses of (obs. = 33.63%, calc. = 33.74%). The final step is from 400 to 700°C corresponding to the loss of the organic moiety C\(_{13}\)H\(_{10}\)O\(_2\)NS, with mass losses of (obs. = 42.0%, calc. = 38.72%). The remaining residue is Cu.
from 260 to 440°C, with mass losses of (obs. = 27.80%, calc. = 27.87%). The final step is attributed to the loss of the organic moiety, C$_{22}$H$_{22}$N$_2$O$_3$, at 440–700°C, with mass losses of (obs. = 52.21%, calc. = 52.22%), leaving behind the Zn residue, and the C$_3$ fragment is lost as 3CO$_2$.

The Pd(II) complex also decomposes in three phases. The first phase is between 30–210°C and is attributed to loss of C$_{2}$H$_{4}$, with mass losses of (obs. = 3.50%, calc. = 3.87%). The second phase involves the loss of the organic moiety, C$_{13}$H$_{22}$N$_2$SO, at 210–400°C, with mass losses of (obs. = 41.33%, calc. = 40.79%) while the final stage involves the loss of the organic moiety, C$_{15}$H$_{2}$N$_2$SO, from 400 to 700°C, with mass losses of (obs. = 33.42%, calc. = 33.32%), leaving behind PdO residue, and the fragment C$_3$ is lost as CO$_2$.

In all cases with the exceptions of the ligand and the Cu(II) complex, the decomposition pattern showed the loss of carbon fragments which got oxidized to CO$_2$, and hydrogen or nitrogen which were lost as gases. Thus, the decomposition pattern corroborates the proposed formulation of the complex.

3.5. Conductance. The molar conductances of the complexes in nitromethane are below 20.0 ohm$^{-1}$ cm$^2$ mol$^{-1}$ confirming their covalent nature. A value in the range 75–90 ohm$^{-1}$ cm$^2$ mol$^{-1}$ is expected for a 1:1 electrolyte [12].

4. Conclusion

The Schiff-base ligand coordinates to the Mn(II), Ni(II), Co(II), Cu(II), Pd(II), and Zn(II) ions in a tetradentate manner using the N$_2$O$_2$ chromophores. The assignment of a 4-coordinate square-planar geometry to Cu(II) and Pd(II) complexes and tetrahedral geometry to Mn(II), Ni(II), Co(II), and Zn(II) complexes is corroborated by elemental analysis, thermal, magnetic, and electronic spectral measurements. The Cu(II) and Pd(II) complexes exhibit geometric isomerism and are in the trans-isomeric form as confirmed by their infrared spectra. Furthermore, the Cu(II) complex exhibits some anti-ferromagnetic interactions, operating through a dimeric structure while the other complexes are mononuclear.

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