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ORIGINAL ARTICLE

Synthesis, characterization and biological properties of Co(II), Ni(II), Cu(II) and Zn(II) complexes with an SNO functionalized ligand

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Abstract Some new metal(II) complexes, ML_2 [M = Co, Ni, Cu and Zn], of 2-acetylthiophene benzoylhydrazone ligand (HL) containing a trifunctional SNO-donor system have been synthesized and characterized on the basis of physicochemical data by elemental analysis, magnetic moment, molar conductance, thermogravimetric and spectroscopic (electronic, IR, ^1H NMR and ^{13}C NMR) data. The ligand functions as monobasic SNO tridentates where the deprotonated enolic form is preferred in the coordination producing distorted octahedral complexes.

1. Introduction

Schiff base ligands are considered as "privileged ligands" (Singh et al., 2010) because they are easily prepared by condensation between aldehydes and primary amines. These ligands are able to coordinate many different metals and to stabilize them in various oxidation states (Abdel-Latif et al., 2007). The chemistry of transition metal complexes with Schiff bases has played an important role in the development of coordination chemistry as a whole. Multidentate Schiff bases have been widely used as ligands, because they can be easily attached to metal ions due to the formation of highly stable coordination compounds. These complexes show a large variety of catalytic (Youssef et al., 2009), biological (Patil et al., 2010), antifungal (Devi et al., 2004), anti tumor and anti HIV activities (Sheng et al., 2008). Furthermore, Schiff bases are utilized as starting material in the synthesis of industrial (Ando et al., 2004) and biological compounds such as β-lactams (Taggi et al., 2002). Furthermore, these compounds have been recently used in construction of poly vinyl chloride powder (PVC)-based membrane selective sensors (Mashhadizadeh et al., 2004) and as ionophore in metal ion-selective electrodes (Abu-Shawish et al., 2007). Metal complexes of S-, N-, and O-chelating ligands have attracted considerable attention because of their interesting physico-chemical properties, pronounced biological activities and their use as models for metalloenzyme active sites (Abu-Shawish et al., 2009). These results motivated making the present study that deals with the preparation and characterization of complexes of 2-acetylthiophene

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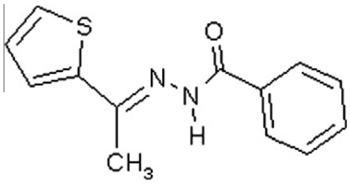

Figure 1 Proposed structure of 2-acetylthiophene benzoyl hydrazone.

benzoylhydrazone (Fig. 1) containing an SNO donor system with some divalent metal ions, namely Co(II), Ni(II), Cu(II) and Zn(II) as well as their biological activity due to their potentially useful properties. The solid complexes have been synthesized and characterized by elemental analysis, conductivity, thermo gravimetric analysis (TG), IR, NMR and electronic spectra. These complexes were found to have similar properties to those found with an analogous NNO functionalized ligand (Patil et al., 2010) and an SNO donor ligand (Jang et al., 2005; Chohan, 2001).

2. Experimental

2.1. Material and methods

2-Thiophenecarboxaldehyde and benzoylhydrazine were obtained from Merck. Reagent grade salts of all cations were purchased from Aldrich and used as received. Commercially available solvents were used as received. The infra red spectra for the materials were recorded on a Perkin–Elmer FT-IR spectrometer using KBr disc in the range of 4000–400 cm^{-1}. Melting points were recorded on a Gallenkamp apparatus and are uncorrected. UV–Vis spectra of methanolic solutions of the complexes were recorded on a SHIMADZU UV–Vis spectrophotometer (UV-1601). Conductivity measurements were made on a PHYWE conductivity meter. The metal content of the complexes was determined using a Perkin–Elmer A Analyst-100. The complexes were decomposed and digested in concentrated sulfuric and/or nitric acid before determination of the metal ions in their aqueous solutions (by atomic absorption, spectrophotometric or titrimetric method) (Vogel, 1987). Microanalysis of C, H, N and S was performed at the Microanalytical Center – Cairo University – Egypt. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 250-MHz spectrometer in DMSO-d_6. Chemical shifts are in ppm relative to internal Me_4Si. Magnetic measurements were done on the solid complexes using the Gouy method.

2.2. Thermal analysis

The thermogravimetric analysis of the solid complexes was carried out from room temperature to 800 °C using a Shimadzu-50 thermal analyzer (Sheb, 2009).

2.3. Synthesis of the Schiff base ligand

2-Acetylthiophene benzoylhydrazone: The ligand was prepared from 2-acetyl thiophene and benzoylhydrazine similar to that described in the literature (Pelagatti et al., 2003). The product was characterized by its infrared and its ^{1}H and ^{13}C NMR spectra. HL $C_{13}H_{12}N_2OS$, IR (cm^{-1}): 3245 (s, NH), 1705 (m, NH + CN), 1635 (s, CH=N), 1020 (s, N–N) and 752–687 (C–S–C) where s: sharp; m: medium; br: broad. Anal. Calcd. C, 63.91; H, 4.9 5; N, 11.47, and S, 13.12%. Found: C, 63.59, H, 5.02; N, 13.15; S, 13.69, yield 84%, ^{1}H NMR (DMSO-d_6) spectra 10.6 (s, ^{1}H, NH), 6.5–8.2 (m, 8H, Ar–H), 1.92 (s, 3H, CH_3), ^{13}C NMR: 187.2 (C=O), 152.1 (C=N), 139.2, 129.5, 127.0, 125.2, 123.6, 121.4, 112.7, 104.9 (Ar–C), 15.6 (CH_3).

2.4. Preparation of metal complexes

To a well-stirred suspension of 2-acetylthiophene benzoylhydrazone (1.0 mmol, 0.244 g) in methanol (25 mL) was added the metal acetate, namely $Co(OAc)_2{\cdot}4H_2O$, $Ni(OAc)_2{\cdot}4H_2O$, copper$(OAc)_2{\cdot}H_2O$ and $Zn(OAc)_2{\cdot}2H_2O$, (0.5 mmol) solid. The resulting mixture was stirred for 24 h during which a solid complex appeared. The solid was collected by filtration, washed with methanol, diethyl ether and dried in vacuo (Jang et al., 2005).

[CoL_2] (**1**): tan solid. Yield: 0.178 g (65%). mp. 180–182 °C. Anal. Calcd. for **$C_{26}H_{22}N_4O_2S_2Co$**: C, 56.62; H, 5.12; N, 10.18, S, 11.63. Found: C, 56.45; H, 5.07; N, 10.09; S: 11.69, Λ_M ($\text{Mho cm}^2\,\text{mol}^{-1}$): 0.23, and for chloroform solvent 0.36. UV–Vis. (nm, log ε): shoulder at 580 nm (3.48), 354 (4.34) and 260 (4.48). Significant infrared bands (cm^{-1}): 1575, 1500, 1365, 1148, 1065, 1018, 894, 710, 527.

[NiL2] (**2**): green solid. Yield: 0.192 g (69%). mp. > 320 °C (dec.). Anal. Calcd. for **$C_{26}H_{22}N_4O_2S_2Ni$**: C, 56.64; H, 5.10; N, 10.10; S, 11.60. Found: C, 56.75; H, 5.13; N, 10.18; S, 11.56. Λ_M ($\text{Mho cm}^2\,\text{mol}^{-1}$): 2.1, 7.26 and for DMF solvent 12.48, UV–Vis (nm, log ε): 400 (3.49), 318 (4.00) 254 (4.38). Significant infrared bands (cm^{-1}): 1591, 1510, 1477, 1370, 1294, 1182, 1078, 1014, 904, 796, 752, 694, 457.

[CuL2] (**3**): olive green solid. Yield: 0.150 g (54%). mp. 295–297 °C (dec.). Anal. Calcd. for **$C_{26}H_{22}N_4O_2S_2Cu$**: C, 56.15; H, 5.07; N, 10.07; S, 11.53. Found: C, 56.01; H, 5.06; N, 10.12; S, 11.58. Λ_M ($\text{Mho cm}^2\,\text{mol}^{-1}$): 0.38. UV–Vis (nm, log ε): 370 (3.34), 354 (3.32) 260 (3.37). Significant infrared bands (cm^{-1}): 1586, 1519,1378, 1301, 1171, 1067, 1019, 904, 792, 703, 435.

[ZnL_2] (**4**): yellow solid. Yield: 0.168 g (60%). mp. 270–272 °C. Anal. Calcd. for **$C_{26}H_{22}N_4O_2S_2Zn$**: C, 55.96; H, 5.06; N, 10.04; S, 11.49. Found: C, 56.11; H, 5.07; N, 10.16; S, 11.52. Λ_M ($\text{Mho cm}^2\,\text{mol}^{-1}$): 6.78. UV–Vis (nm, log ε): 328 (3.34) and 268.5 (3.15). Significant infrared bands (cm^{-1}): 1581, 1491, 1425, 1372, 1305, 1167, 1068, 710, 454. ^{1}H NMR (in $CDCl_3$, ppm): 7.18–8.36 (br, 8H, ArH), 2.84 (s, 3H, CH_3). NMR spectral data of ZnL_2 ^{1}H NMR (ppm), 7.2–8.3 (br, ArH), 2.86 (s, 3H, CH_3), ^{13}C NMR: 169.14, 150.65, 136.0, 134.78, 134.29, 131.49, 130.23, 127.98, 125.8, 120.58, 40.33, 40.06, 39.77, 39.5, 39.22, 38.94, 38.67, 37.51, 37.2, 21.67.

2.5. Antibacterial studies

The newly synthesized complexes were tested for their antibacterial ad antifungal activity in vitro against bacterial strains such as *Escherichia coli, Staphylococcus aureus* and *Pseudomonas* employing the nutrient agar disc diffusion method at 1–10 mg/mL in *N*,*N*-dimethylformamide (DMF) by measuring the inhibition zone in millimeters (mm) (Saadeh et al., 2009).

3. Results and discussion

The reactions of appropriate metal(II) acetate with the Schiff base ligand derived from 2-acetylthiophene and benzoylhydrazone acting as tridentate ligand in methanol solution gave monomeric transition–metal(II) complexes, of $M^{II}L_2$ type (M = Co, Ni, Cu, Zn and L = 2-acetylthiophene benzoylhydrazone), respectively. The formulations were in accordance with the data of elemental analysis and physicochemical measurements. The molar conductance of the complexes determined at a concentration of ca. 1×10^{-3} M in chloroform for cobalt and nickel complexes and in DMSO for copper and zinc complexes show small values in the range 1.0–6.78 Mho cm^2 mol^{-1}, respectively, indicating that the complexes are non-electrolytes. The complexes are soluble in chloroform or in dimethyl formamide, and dimethyl sulfoxide, but are not soluble in common organic solvents.

3.1. Spectral properties

The IR spectrum of the ligand has several prominent bands appearing at 3245, 1705 and 1635 cm^{-1} due to $\nu_{N\text{–}H}$ and C=O stretching modes, respectively. Comparison of the IR spectra of the Schiff base and its metal complexes, such as Fig. 2 the infrared spectrum of the zinc complex, indicates that the Schiff base is coordinated to the metal atom by three sites, thus suggesting that the ligand acts as a tridentate ligand. The band due to ν(C=O) is completely missing in the spectra of the complexes, suggesting (Patil et al., 1982) enolization of the Schiff base on complexation. This is also supported by the fact that no band for ν(OH) in the spectra of the ligand and also in the complexes is observed. Instead, a band due to ν(C–O) at about 1245 cm^{-1} was observed for all the complexes, which supports the observation of their enolization during coordination. This fact suggests that the Schiff base remains in the keto form in the solid state, but in solution both the keto and enol forms remain in equilibrium (Dey and Bandyopadhyay, 1991). Deprotonation occurs from the enol form on complexation.

The amide-II band [ν(NH + CN)] was split, displaced to higher frequency and reduced in intensity. A shift to higher frequency (5–10 cm^{-1}) of the ν(N–N) band at about 1020 cm^{-1} and its splitting indicated (Yongxiang et al., 1989) coordination of the azomethine nitrogen. Moreover, the shift to lower frequency (5–10 cm^{-1}) of the band due to the azomethine ν(CH=H) linkage at about 1635 cm^{-1} also indicated involvement of azomethine group in coordination.

The ν(C–S–C) undergoes a negative shift in the complexes, indicating the coordination of the ring sulfur to the metal. The coordination through the azomethine nitrogen and sulfur is further supported by the occurrence on few bands at 460 and 360 cm^{-1} in the spectra of the complex, which may be assigned to $\nu(N \rightarrow M)$ and $\nu(S \rightarrow M)$ vibrations, respectively (Turan et al., 2010). However, the IR spectrum of the complex (M–S) bands could not be observed because the infrared spectra of the complexes were studied in the range 4000–400 cm^{-1}, which does not span the M–S stretching mode.

The NMR spectra of the free ligand and its zinc(II) complex (Fig. 3) have been recorded in DMSO-d_6. NMR spectra of the free ligand support the conclusions derived from the IR spectra. The ligand exhibits aromatic and heteroaromatic proton signals at δ 6.5–8.2 ppm. The signal for the NH proton appeared at δ 10.9 ppm (s, br) in the spectra of the free Schiff base ligand; this signal is absent in the spectrum of its zinc(II)

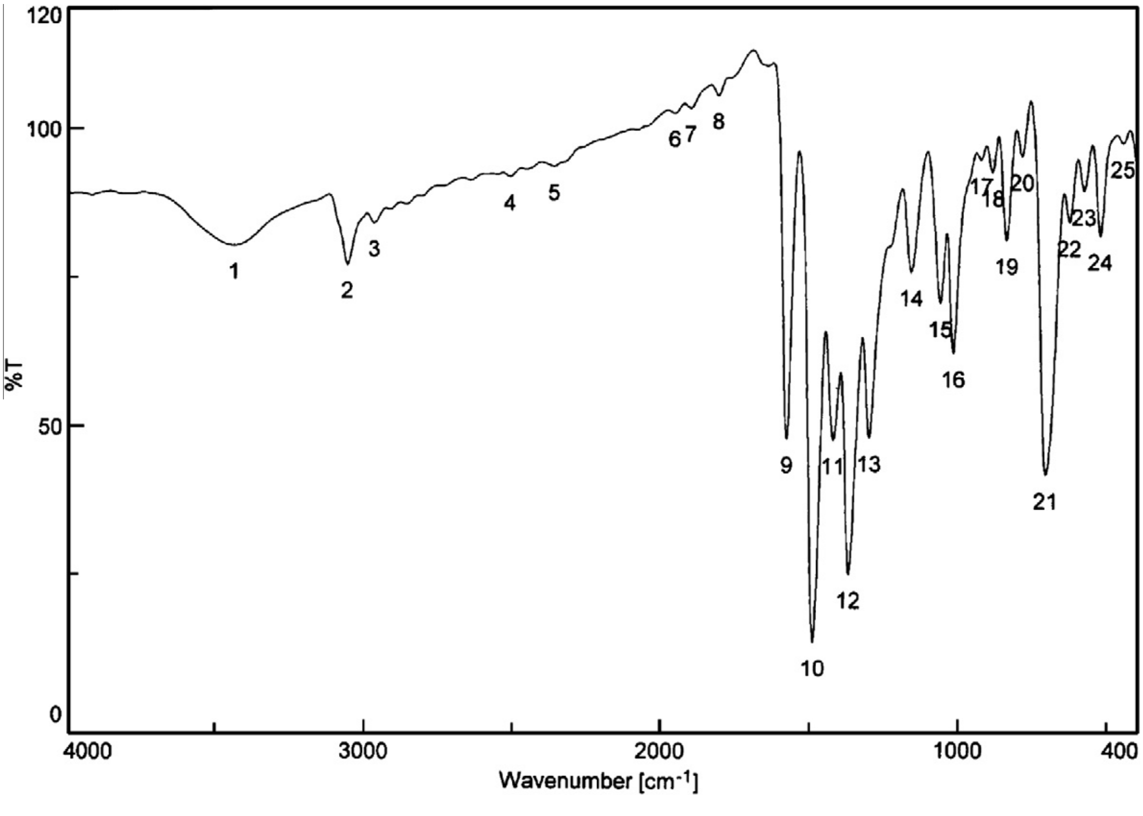

Figure 2 The infrared spectrum of the zinc(II) complex.

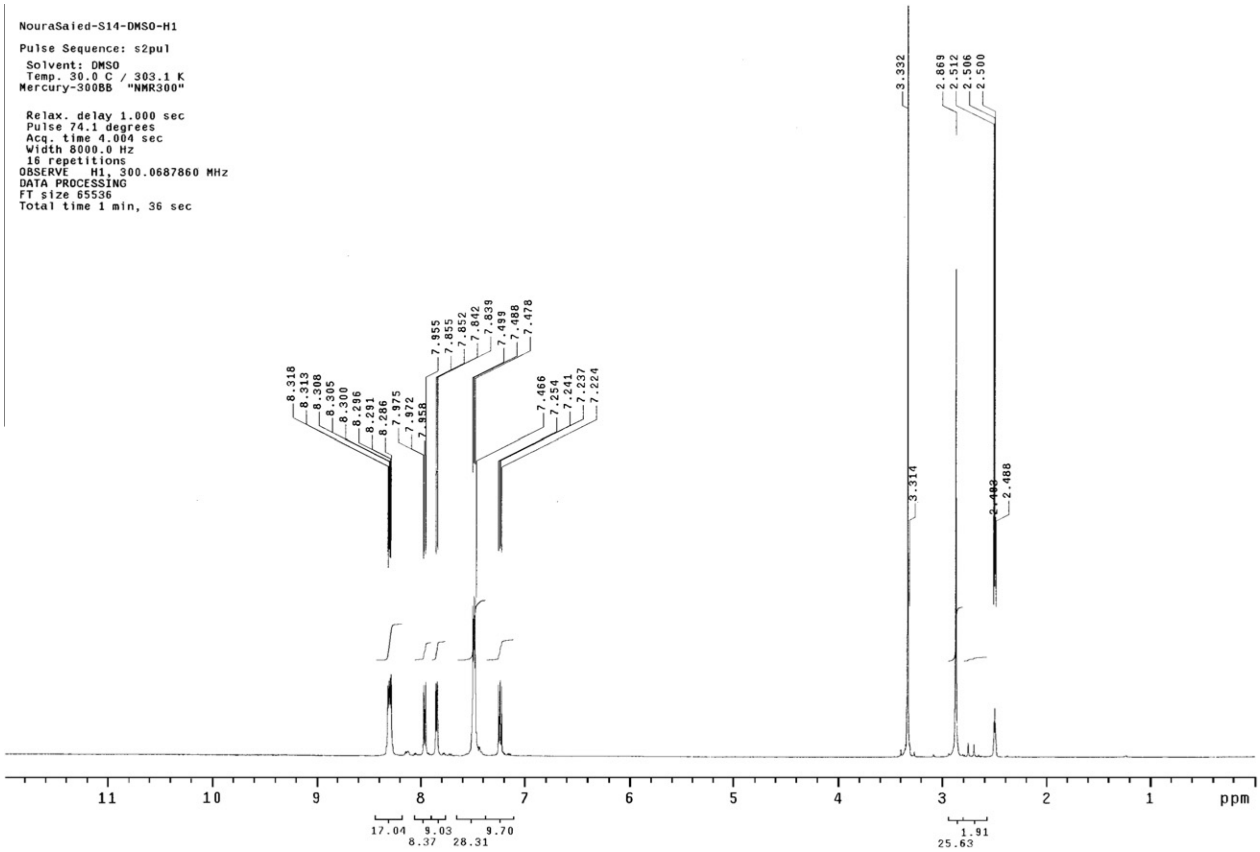

Figure 3 The ^{1}H-NMR spectrum of the zinc(II) complex.

complex. This indicated that the Schiff base is coordinated to the metal ions in the enolic form by deprotonation.

In the Zn(II) complex, the aromatic and heteroaromatic proton signals appeared downfield, due to increased conjugation on coordination (Hong-Yun et al., 1992). ^{13}C NMR spectra likewise showed similar diagnostic features (Pasto and Johnson, 1969) for the free ligand as well as for its complexes. Thienyl carbons were found in the range 104.5–123.2 ppm, aromatic carbons at 124.8–137.3 ppm and the azomethine carbon signal was found at 150.65 ppm. Similarly, the presence of the C=O signal at about 187.4 ppm in the spectrum of the ligand and the absence of this signal in the spectrum of the complex and the appearance of a signal at a lower value supported the evidence that the ligands act in an enolized form. However, ^{1}H NMR spectrum for the complexes **1–3** was not helpful for identification of functional group due to paramagnetic electron configuration.

The cobalt(II) complex shows a magnetic moment value of 4.87 BM at room temperature. This high value of the magnetic moment and the stoichiometry suggest a coordination number of six for the central cobalt(II) ion and an octahedral geometry. The electronic spectrum of this complex is also consistent with its octahedral environment around the cobalt(II) ion. The spectra display two bands at 354 and 260 nm attributed to $^4T_{1g}$ (F) → $^4T_{2g}$ (F), $^4T_{1g}$ (F) → $^4A_{2g}$ (F) and $^4T_{1g}$ (F) → $^4T_{1g}$ (P) transitions, respectively, in a high-spin octahedral geometry (Chohan, 2001). The electronic spectra of the nickel(II) complex exhibit absorption bands at 400 and 318 and 254 nm, attributable to $^3A_{2g}$ → $^3T_{2g}$ (F), $^3A_{2g}$ → $^3T_{1g}$ (F) and $^3A_{2g}$ → $^3T_{1g}$ (P), transitions, respectively, in an octahedral geometry (Chandra, 1985). The calculated values of the ligand field parameters lie in the range reported for an octahedral structure. The value of the magnetic moment (3.2–3.7 BM) may be taken as additional evidence for its octahedral structure. The copper(II) complex exhibits magnetic moment of 1.71 BM, respectively, at room temperature. This value is quite close to the spin-allowed value expected for a $S = 1/2$ system and may be indicative of a distorted octahedral geometry around copper(II) ions. The copper(II) complex displays a broad band at 370 nm due to $^2B_{1g}$ → ^2E_g and two bands at 354 and 260 nm assigned to d–d transitions and a charge transfer band, respectively, of a distorted octahedral environment (Hong-Yun et al., 1992). The diamagnetic zinc(II) complex did not show any d–d bands and its spectrum is dominated only by a charge transfer band. The

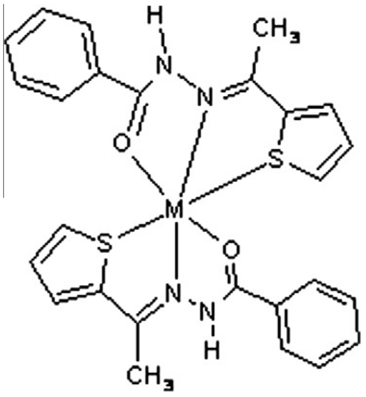

Figure 4 Proposed structure of the metal(II) complexes.

Table 1 Thermoanalytical results of the metal complexes.

Sample	Stage	DTA_{max} (K)	TGA temp. range	Mass loss (%)		Evolved moiety
				Exper.	Calcd.	
CoL_2	I	303.9	275–340	41.3	44.2	$C_{13}H_{12}N_2OS$
	II	424.4	340–480	42.7	44.2	$C_{13}H_{12}N_2OS$
NiL_2	I	351	280–380	44.5	44.1	$C_{13}H_{12}N_2OS$
	II	419	360–550	45.7	44.1	$C_{13}H_{12}N_2OS$
CuL_2	I	273	225–375	44.8	43.7	$C_{13}H_{12}N_2OS$
	II	443	375–500	42.5	43.7	$C_{13}H_{12}N_2OS$
ZnL_2	I	346	275–420	42.4	42.4	$C_{13}H_{12}N_2OS$
	II	507, 551	420–575	43.3	42.4	$C_{13}H_{12}N_2OS$

charge transfer band at 328 nm was assigned to the transition $^2E_g \rightarrow {}^2T_{2g}$, possibly in an octahedral environment (Chohan, 2001). The band at 268 nm is likely to be an intraligand transition for it is observed for the free ligand. On the basis of the above observations, it is tentatively suggested that all of the complexes show an octahedral geometry (Fig. 4) in which the two ligands act as tridentates. These possibly accommodate themselves around the metal atom in such a way that a stable chelate ring is formed giving, in turn, stability to the formed metal complexes.

The results obtained in this study justify the structure proposed to $M^{II}L_2$ complexes. These results are the same as those found for the crystallographically determined structure and spectroscopically confirmed by Jang et al. (2005).

The thermal behavior of Co(II), Ni(II), Cu(II) and Zn(II) complexes has been studied as a function of temperature. The thermal behavior of all the complexes is almost same. The thermal decomposition of $Co(C_{13}H_{11}N_2OS)_2$, $Ni(C_{13}H_{11}N_2OS)_2$, $Cu(C_{13}H_{11}N_2OS)_2$ and $Zn(C_{13}H_{11}N_2OS)_2$ takes place in two major steps as indicated by DTG peaks around 272–350 °C and 418–550 °C. These show the mass loss of the Schiff base moiety. That is the metal complexes decompose gradually with the formation of metal oxide above 600 °C. The nature of proposed chemical change with the temperature range and the percentage of metal oxide are presented in Table 1.

3.2. Antibacterial properties

The title Schiff bases and their metal(II) chelates were evaluated for their antibacterial activity against the standard bacterial strains of (a) *E. coli*, (b) *S. aureus* and (c) *Pseudomonas aeruginosa*. The compounds were tested at a concentration of 30 μg/0.01 mL in DMF solution, using the paper disc diffusion method as earlier reported (Chohan and Kausar, 2000). The inhibition zones are the clear ones around the discs, which were measured in mm.

The ligand and its M^{II} complexes are inactive on the standard bacterial strains used in this study. In contrast, *N*-(2-thienylbenzylmethyl) benzoylhydrazone and its metal(II) complexes showed marked antimicrobial activity (Chohan, 2001) despite the apparent similarity in these ligands and in their analogous complexes. This appears to be a case of the structure–function relationship commonly observed in biological effect of chemical compounds. The compounds presented herein contain a methyl group in place of hydrogen as compared to those reported (Chohan, 2001). This exchange apparently made these compounds inactive. The activity of any compound is a complex combination of steric, electronic and pharmacokinetic factors.

4. Conclusions

A number of new metal(II) complexes, $M^{II}L_2$ (M = Co, Ni, Cu and Zn) with the trifunctional SNO-donor atoms have been synthesized and characterized on the basis of elemental analysis, magnetic moments, molar conductances, thermogravimetric and spectroscopic (electronic, IR, ^{1}H NMR and ^{13}C NMR) data. The ligands behave as monobasic SNO tridentate, bonding to the metal(II) ion through the acetylthiophene ring sulfur, azomethine nitrogen, and benzoyl oxygen to form a distorted octahedral structure where the deprotonated form is preferred in the coordination. The resulting data indicate that the complexes are in accordance with the above formulation.

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