

Research Article

Synthesis and Characterization of Bioactive Acylpyrazolone Sulfanilamides and Their Transition Metal Complexes: Single Crystal Structure of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one Sulfanilamide

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Two Schiff base ligands Ampp-Sn 1 and Bmpp-Sn 2, afforded by a condensation reaction between sulfanilamide and the respective acylpyrazolone carbonyl precursors, their Mn(II), Co(II), Ni(II), and Cu(II) complexes prepared by the reaction of ligands and corresponding metal salts in aqueous solutions, were synthesized and then characterized by both analytical and spectroscopic methods, in a view to developing new improved bioactive materials with novel properties. On the basis of elemental analysis, spectroscopic and TGA results, transition metal complexes, with octahedral geometry having two molecules of the bidentate keto-imine ligand each, have been proposed. The single crystal structure of Bmpp-Sn according to X-ray crystallography showed a keto-imine tautomer type of Schiff base, having three intramolecular bonds, one short N2...H2...O3 hydrogen bond of 1.90 Å and two long C13...H13...O2 and C32...H32...O3 hydrogen bonds of 2.48 Å. A moderate to low biological activities have been exhibited by synthesized compounds when compared with standard antimicrobial agents on screening the synthesized compounds against *Staphylococcus aureus*, *Bacillus pumilus*, *Proteus vulgaris*, and *Aeromonas hydrophila* for antibacterial activity and against free radical 1, 1-diphenyl-2-picryl-hydrazyl (DPPH) for antioxidant activity.

1. Introduction

The electrophilic carbonyl carbon in aldehydes and ketones is a target site for nucleophilic primary amines to form an interesting group of ligands known as Schiff bases *via* a condensation reaction. Schiff bases possess remarkable reactivity and properties which have been observed to be more efficient when in coordination with transition metals, hence their diverse applications [1–8]. Acylpyrazolones are a series of heterocyclic diketones that have attracted a lot of research attention because of their chemistry and strong chelating properties especially towards transition metal ions [9] and numerous uses [10]. Knorr first synthesized pyrazolone derivatives

by reacting phenyl hydrazine with ethylacetoacetate to form a novel 1-phenyl-3-methyl-5-pyrazolone in 1883 and studies on this group of compounds have been on since then [11]. They have the ability to exist either in an enol or keto tautomer forms, which gives them the potential to form different types of interesting coordination compounds [12, 13]. Sulfanilamides are the simplest of the family of sulfa drugs. They act as metabolites capable of obstructing folic acid synthesis in bacteria, thereby causing cell death, the reason for their strong antibacterial activity [14]. There has been hypothesis that some metal complexes of sulphur containing ligands have shown more potency in their anticancer properties [15, 16]. Coombs and coworkers synthesized Schiff bases of

sulfanilamide with salicylaldehyde and their palladium complexes [14]. The single crystal structure of another salicylaldehyde Schiff base, N, N'-(*p*-phenyl sulfanilamide)-5,6-dimethoxypyrimidine-(2-hydroxyl benzene) methylenide, with excellent fluorescent properties has also been resolved [17]. We have reported the X-ray crystal and molecular structures of 4-benzoyl derivatives Schiff bases, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one phenylhydrazone [18] and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one-2,4-dinitrophenylhydrazone [19]. In continuation of our probe on new Schiff bases and taking the advantage of possible synergistic properties from the combination of acylpyrazolone and sulfanilamide, presented herein are the synthesis, characterization, antibacterial and antioxidant studies of 4-acylpyrazolone with 4-aminobenzenesulfonamide Schiff bases and their Mn(II), Co(II), Ni(II), and Cu(II) complexes.

2. Experimental

2.1. Materials and Methods. Melting point was determined using the Gallenkamp melting point apparatus. CHN elemental analyses were carried out on a LECO.TRUSpec Micro CHNS analyzer. FTIR spectra were measured as KBr Pellets (4000–370 cm^{-1}) on a Perkin-Elmer Model System 2000 FTIR spectrophotometer. Electronic spectra of metal complexes were recorded on a Perkin-Elmer Lambda 25 spectrophotometer and a Sherwood Scientific magnetic susceptibility balance was used for magnetic moments with powder samples of complexes at room temperature. Diamagnetism corrections were estimated from Pascal's constants. ^1H and ^{13}C NMR spectra in deuterated DMSO were recorded on a Bruker 600 MHz Avance II NMR spectrophotometer using trimethylsilane TMS, as internal standard. Chemical shifts are given in ppm (δ scale). Thermal analyses were done on a NETZSCH STA 449 C instrument at a temperature range of 20–900°C with a heating rate of 20°C min^{-1} in nitrogen gas. Mass spectra of ligands were determined by the Bruker micrOTOF-Q II 10390 mass spectrometer. They were analyzed with ACPI using a direct insertion probe (DIP). An external calibration with sodium formate was performed to attain the correct accurate mass. Single crystal X-ray diffraction studies were performed at 200 K using a Bruker Kappa Apex II diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All reagents, Manganese(II) chloride tetrahydrate $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, Cobalt(II) chloride hexahydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Nickel(II) chloride hexahydrate $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Copper(II) acetate monohydrate $(\text{CH}_3\text{COO})_2\text{Cu} \cdot \text{H}_2\text{O}$, sulfanilamide, and 3-methyl-1-phenyl-2-pyrazolin-5-one, and solvents were of analytical grade as supplied by Aldrich. Schiff base precursors 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one derivatives were synthesized and purified as reported earlier [20].

2.2. General Procedure for the Synthesis of Acylpyrazolone Schiff Bases. To a solution of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (2.0 mmol, 0.56 g) and 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one (2.0 mmol, 0.43 g) in methanol (40 mL) each in a separate round bottom flask sulfanilamide

was added in drops (2.0 mmol, 0.34 g) in hot methanol while stirring; Bmpp-Sn and Amp-Sn were precipitated, respectively, after 4 h of reflux. The resulting yellow (Bmpp-Sn) and pale-yellow (Amp-Sn) solids were filtered, washed with methanol, and dried at room temperature. They were recrystallized from methanol and stored over fused CaCl_2 . Suitable thread-like yellow single crystals of Bmpp-Sn for X-ray diffraction were grown at room temperature from slow evaporation of methanol solution after seven days.

2.2.1. 4-Acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one Sulfanilamide: Amp-Sn (1). Pale yellow solid, yield 74%, mp 232–234°C; IR KBr (ν_{max} , cm^{-1}): 3496 (N–H), 2954 (C–H), 1633 (C=N), 1503 (C=O). ^1H NMR (600 MHz, DMSO): δ (ppm) 13.1 (s, 1H, –NH), 8.0 (s, 1H, C=N–H), 7.9–7.2 (m, 9H, aromatic–H), 2.4 (s, 3H, CH_3). ^{13}C NMR (600 MHz, DMSO): δ (ppm) 165.4 (s, C=O), 164.5 (s, C=N), 148.2 (s, C–S) 142.8–116.6 (s, aromatic carbons), 17.6 (s, pyrazolone CH_3), 17.5 (s, acetyl CH_3); APCI-MS: m/z 371.11 ($[\text{M} + \text{H}]^+$, 100%). Anal. Calcd. $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_3\text{S}$ (370.11): C, 58.36; H, 4.90; N, 15.13%. Found: C, 58.42; H, 4.88; N, 15.18%.

2.2.2. 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one Sulfanilamide: Bmpp-Sn (2). Yellow solid, yield 69%, mp 102–104°C; IR KBr (ν_{max} , cm^{-1}): 3497 (N–H), 2927 (C–H), 1639 (C=N), 1504 (C=O). ^1H NMR (600 MHz, DMSO): δ (ppm) 12.8 (br, 1H, –NH), 8.0 (s, 1H, C=N–H), 7.8–7.1 (m, 14H, aromatic–H), 2.2 (s, 3H, CH_3). ^{13}C NMR (600 MHz, DMSO): δ (ppm) 190.5 (s, C=O), 139.3 (s, C=N), 148.2 (s, C–S) 132.2–110.7 (s, aromatic carbons), 16.5 (s, pyrazolone CH_3); APCI-MS: m/z 433.13 ($[\text{M} + \text{H}]^+$, 100%). Anal. Calcd. $\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_3\text{S}$ (432.13): C, 63.87; H, 4.66; N, 12.96%. Found: C, 63.84; H, 4.67; N, 12.79%.

2.3. General Procedure for the Synthesis of Acylpyrazolone Schiff Bases Metal Complexes. To a solution of Bmpp-Sn (2 mmol, 0.87 g) and Amp-Sn (2 mmol, 0.74 g) in hot ethanol (40 mL) each in a separate round bottom flask aqueous solution of 2 mmol of corresponding metal salts was added in drops while stirring under reflux and followed by the addition of NaOH (2 mmol, 0.08 g) to precipitate the metal complex. After 4 h of reflux, the precipitates in different colours were filtered, washed with ethanol/water (1:1), dried at room temperature, and stored over fused CaCl_2 .

2.3.1. Bis(4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide)diaquamanganese(II) Monohydrate Mn(Amp-Sn) $_2$ (H $_2$ O) $_2$ ·H $_2$ O (1a). Yellow solid; yield 81%; mp 210–212°C; Molar cond. (10^{-3} M in DMF): 14.40 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$; μ_{eff} (B.M.): 5.61; UV-Vis (DMF) λ_{max} nm: 259 ($\pi \rightarrow \pi^*$), 377 ($n \rightarrow \pi^*$), 431 (d \rightarrow d); IR KBr (ν_{max} , cm^{-1}): 3484 (N–H), 3392 (O–H), 2920 (C–H), 1624 (C=N), 824 (H $_2$ O), 634 (M–N), 488 (M–O); Anal. Calcd. $\text{C}_{36}\text{H}_{40}\text{N}_8\text{O}_9\text{S}_2\text{Mn}$ (847.17): C 50.99, H 4.76, N 13.22%, Found: C 51.01, H 4.58, N 13.21%.

2.3.2. Bis(4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide)diaquacobalt(II) Co(Amp-Sn) $_2$ (H $_2$ O) $_2$ (1b). Yellow

solid; yield 82%; mp 150–151°C; Molar cond. (10^{-3} M in DMF): $11.22 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; μ_{eff} (B.M.): 4.43; UV-Vis (DMF) λ_{max} nm: 274 ($\pi \rightarrow \pi^*$), 377 ($n \rightarrow \pi^*$), 408, 632, 699 (d \rightarrow d); IR KBr (ν_{max} , cm^{-1}): 3491 (N–H), 3391 (O–H), 2923 (C–H), 1619 (C=N), 831 (H_2O), 631 (M–N), 486 (M–O); Anal. Calcd. $\text{C}_{36}\text{H}_{38}\text{N}_8\text{O}_8\text{S}_2\text{Co}$ (833.16): C 51.85, H 4.60, N 13.45%, Found: C 51.61, H 4.51, N 13.11%.

2.3.3. Bis(4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide)diaquanickel(II) Monohydrate Ni(Ampp-Sn) $_2$ (H $_2$ O) $_2$ ·H $_2$ O (1c). Yellow solid; yield 79%; mp 157–158°C; Molar cond. (10^{-3} M in DMF): $16.02 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; μ_{eff} (B.M.): 2.93; UV-Vis (DMF) λ_{max} nm: 257 ($\pi \rightarrow \pi^*$), 324 ($n \rightarrow \pi^*$), 596, 674 (d \rightarrow d); IR KBr (ν_{max} , cm^{-1}): 3488 (N–H), 3398 (O–H), 2934 (C–H), 1620 (C=N), 823 (H_2O), 622 (M–N), 488 (M–O); Anal. Calcd. $\text{C}_{36}\text{H}_{40}\text{N}_8\text{O}_9\text{S}_2\text{Ni}$ (850.93): C 50.77, H 4.74, N 13.16%, Found: C 50.65, H 4.71, N 13.30%.

2.3.4. Bis(4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide)diaquacopper(II) Monohydrate Cu(Ampp-Sn) $_2$ (H $_2$ O) $_2$ ·H $_2$ O (1d). Yellow solid; yield 83%; mp 298–299°C; Molar cond. (10^{-3} M in DMF): $7.04 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; μ_{eff} (B.M.): 1.90; UV-Vis (DMF) λ_{max} nm: 261 ($\pi \rightarrow \pi^*$), 365 ($n \rightarrow \pi^*$), 618, (d \rightarrow d); IR KBr (ν_{max} , cm^{-1}): 3482 (N–H), 3392 (O–H), 2922 (C–H), 1617 (C=N), 850 (H_2O), 628 (M–N), 498 (M–O); Anal. Calcd. $\text{C}_{36}\text{H}_{40}\text{N}_8\text{O}_9\text{S}_2\text{Cu}$ (855.78): C 50.48, H 4.71, N 13.09%, Found: C 50.44, H 4.59, N 13.21%.

2.3.5. Bis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide)diaquamanganese(II) Mn(Bmpp-Sn) $_2$ (H $_2$ O) $_2$ (2a). Pale yellow solid; yield 82%; mp 180–182°C; Molar cond. (10^{-3} M in DMF): $8.19 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; μ_{eff} (B.M.): 5.82; UV-Vis (DMF) λ_{max} nm: 277 ($\pi \rightarrow \pi^*$), 378 ($n \rightarrow \pi^*$), 424, 589 (d \rightarrow d); IR KBr (ν_{max} , cm^{-1}): 3483 (N–H), 3398 (O–H), 2938 (C–H), 1623 (C=N), 844 (H_2O), 619 (M–N), 470 (M–O); Anal. Calcd. $\text{C}_{46}\text{H}_{42}\text{N}_8\text{O}_8\text{S}_2\text{Mn}$ (953.19): C 57.91, H 4.44, N 11.75%, Found: C 57.72, H 4.14, N 11.22%.

2.3.6. Bis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide)diaquacobalt(II) Monohydrate Co(Bmpp-Sn) $_2$ (H $_2$ O) $_2$ ·H $_2$ O (2b). Pink solid; yield 89%; mp 144–146°C; Molar cond. (10^{-3} M in DMF): $10.30 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; μ_{eff} (B.M.): 4.46; UV-Vis (DMF) λ_{max} nm: 262 ($\pi \rightarrow \pi^*$), 376 ($n \rightarrow \pi^*$), 408, 540 (d \rightarrow d); IR KBr (ν_{max} , cm^{-1}): 3492 (N–H), 3398 (O–H), 2925 (C–H), 1618 (C=N), 849 (H_2O), 624 (M–N), 489 (M–O); Anal. Calcd. $\text{C}_{46}\text{H}_{44}\text{N}_8\text{O}_9\text{S}_2\text{Co}$ (975.20): C 56.60, H 4.55, N 11.49%, Found: C 56.33, H 4.92, N 11.16%.

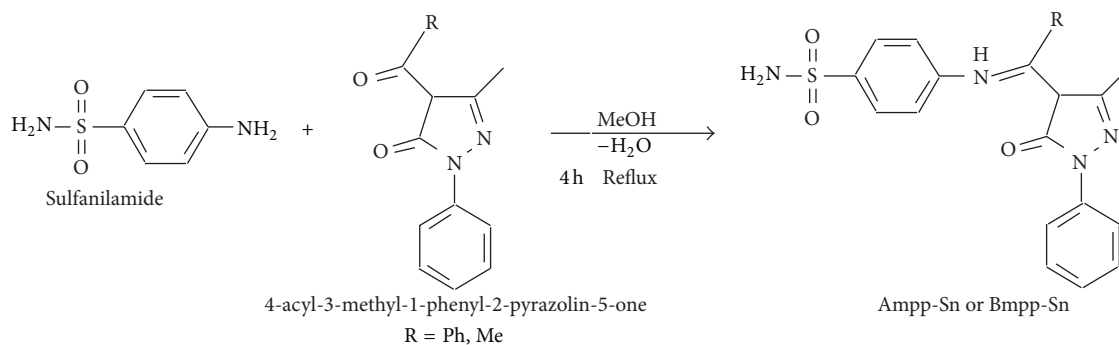
2.3.7. Bis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide)diaquanickel(II) Monohydrate Ni(Bmpp-Sn) $_2$ (H $_2$ O) $_2$ ·H $_2$ O (2c). Light green solid; yield 85%; mp 190–192°C; Molar cond. (10^{-3} M in DMF): $11.62 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; μ_{eff} (B.M.): 2.89; UV-Vis (DMF) λ_{max} nm: 278 ($\pi \rightarrow \pi^*$), 377 ($n \rightarrow \pi^*$), 410, 683 (d \rightarrow d); IR KBr (ν_{max} , cm^{-1}): 3489 (N–H), 3390 (O–H), 2935 (C–H), 1619 (C=N), 849 (H_2O), 625 (M–N), 486 (M–O); Anal. Calcd. $\text{C}_{46}\text{H}_{44}\text{N}_8\text{O}_9\text{S}_2\text{Ni}$ (974.96): C 56.62, H 4.55, N 11.49%, Found: C 57.01, H 4.29, N 11.30%.

2.3.8. Bis(4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide)diaquacopper(II) Cu(Bmpp-Sn) $_2$ (H $_2$ O) $_2$ (2d). Brown solid; yield 92%; mp 238–240°C; Molar cond. (10^{-3} M in DMF): $6.41 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$; μ_{eff} (B.M.): 1.93; UV-Vis (DMF) λ_{max} nm: 273 ($\pi \rightarrow \pi^*$), 378 ($n \rightarrow \pi^*$), 442, 751 (d \rightarrow d); IR KBr (ν_{max} , cm^{-1}): 3498 (N–H), 3399 (O–H), 2935 (C–H), 1617 (C=N), 840 (H_2O), 623 (M–N), 484 (M–O); Anal. Calcd. $\text{C}_{46}\text{H}_{42}\text{N}_8\text{O}_8\text{S}_2\text{Cu}$ (961.80): C 57.39, H 4.40, N 11.65%, Found: C 57.19, H 4.31, N 11.32%.

2.4. X-Ray Diffraction Study of Bmpp-Sn (2). Single crystal X-ray diffraction studies were performed at 200 K using a Bruker Kappa Apex II diffractometer with graphite monochromator, Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). APEXII was used for data collection and SAINT for cell refinement and data reduction. The structure was solved by direct methods using SHELXS-97 and refined by least-squares procedures using SHELXL-97 [21] with SHELXLE [22] as a graphical interface. Platon [23] and Ortep-3 [24] were used to prepare material and diagrams, respectively.

2.5. Antibacterial Studies. *In vitro* antibacterial activity of synthesized compounds was screened against Gram positive *Staphylococcus aureus* and *Bacillus pumilus* and Gram negative *Proteus vulgaris* and *Aeromonas hydrophila* bacterial isolates at 40 mg/mL in DMSO using the Kirby-Bauer disc diffusion technique based on the size of inhibition zone formed around the paper discs with some modifications [25]. Bacterial isolates were grown in freshly prepared nutrient broth growth media to obtain a minimum of 0.1 optical density OD of bacterial isolates suitable for screening. To a solidified about 20 mL Mueller-Hinton agar in Petri plates, 0.1 mL of test bacteria was spread over the medium using a sterilized spreader. Presterilized filter paper discs having a diameter of 6 mm which were impregnated into prepared solutions of synthesized ligands and complexes were placed in the inoculated Petri plates ensuring a reasonable equidistance from each other. Filter paper disc treated with DMSO was used as control while antibacterial chloramphenicol served as a standard drug and was used as a reference to evaluate the potency of the tested compounds under the same conditions. The Petri dishes were left for a few hours in the refrigerator for prediffusion and finally transferred to an incubator at 37°C for 24 h. This procedure was performed in triplicate. The bactericidal activities were determined by measuring the diameter of the zones showing complete inhibition of bacterial growth in millimeters and subtracting the diameter of the filter paper disc and finally dividing by 2 to obtain the exact zone of inhibition. The values were calculated as mean of triplicates.

2.6. Antioxidant (Free Radical Scavenging) Activity. Schiff base free radical scavenging activity and that of its metal complexes were tested against the stable free radical of 1, 1-diphenyl-2-picrylhydrazyl (DPPH), employing the method of Blois [26] with few modifications. A 0.1 mmol solution of the DPPH in methanol was prepared, and 1 mL of this solution was added to 3 mL prepared solutions of the test compounds in a mixture of DMSO and methanol in a mole



SCHEME 1: Synthesis of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one-sulfanilamide.

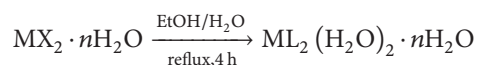
ratio of 1:9, respectively, at different concentrations (0.13, 0.25, and 0.50 mg/mL). The same procedure was carried out for standard drug, ascorbic acid, and an equal volume of dissolving solvents as control. The mixture was shaken vigorously and allowed to stand at room temperature in the dark for 30 min. With the use of a spectrophotometer at a wavelength of 517 nm the absorbance was measured. The capability of synthesized compounds to scavenge DPPH radical was calculated using the expression

$$\text{Scavenging activity (\%)} = \frac{A_0 - A_1}{A_0} \times 100, \quad (1)$$

where A_0 is the absorbance with control sample and A_1 is the absorbance with test samples including that of standard drug.

3. Results and Discussion

3.1. Synthesis. The acylpyrazolone Schiff base precursors, 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one, were synthesized using



$$\text{M} = \text{Mn}^{2+} \text{ (a)}, \text{Co}^{2+} \text{ (b)}, \text{Ni}^{2+} \text{ (c)}, \text{Cu}^{2+} \text{ (d)}; \text{X} = \text{Cl}^- \text{ or } \text{CH}_3\text{COO}^-; \text{L} = \text{Ampp-Sn (1)} \text{ or } \text{Bmpp-Sn (2)}.$$

The elemental percentage composition of **1**, **2**, **1a–d**, and **2a–d** found was in agreement with calculated values. Octahedral metal complexes with the corresponding Schiff base binding bidentately are proposed, having two molecules each of the Schiff base and two molecules of water to complete its octahedral geometry [28].

3.2. ^1H and ^{13}C NMR Spectroscopy. The ^1H NMR spectra of **2** showed a multiplet at 7.8–7.1 ppm due to the aromatic protons and a singlet each at 12.8 ppm and at 8.0 ppm, Figure 1, assigned, respectively, to the sulfanilamide NH_2 hydrogen $-\text{NH}$ and the azomethine nitrogen $\text{H}-\text{N}=\text{C}$ proton. The resonance peak due to methyl protons on the pyrazolone ring

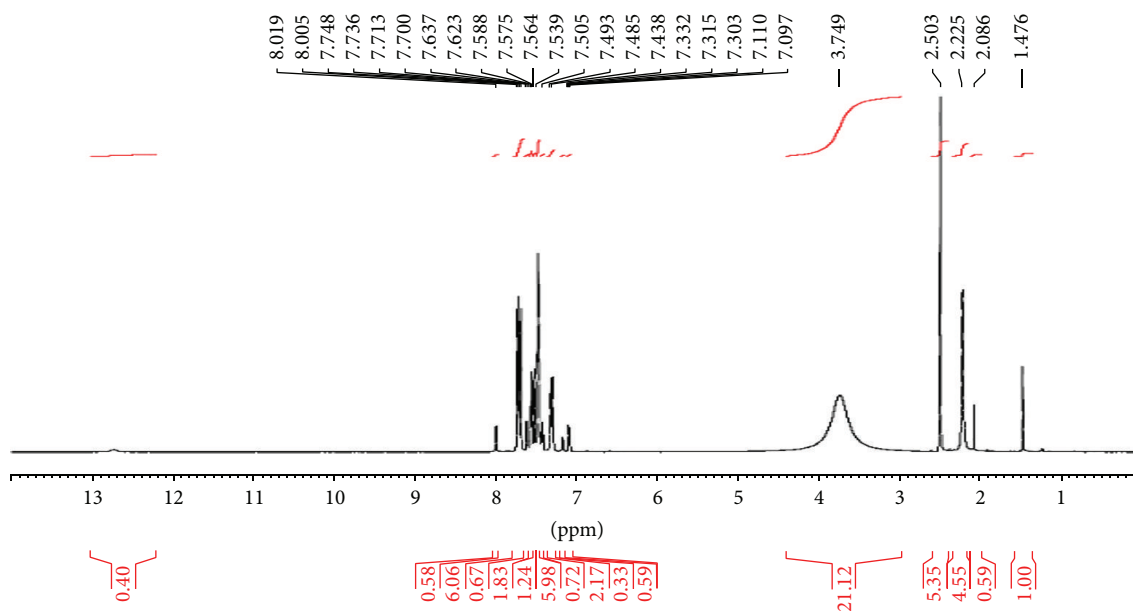
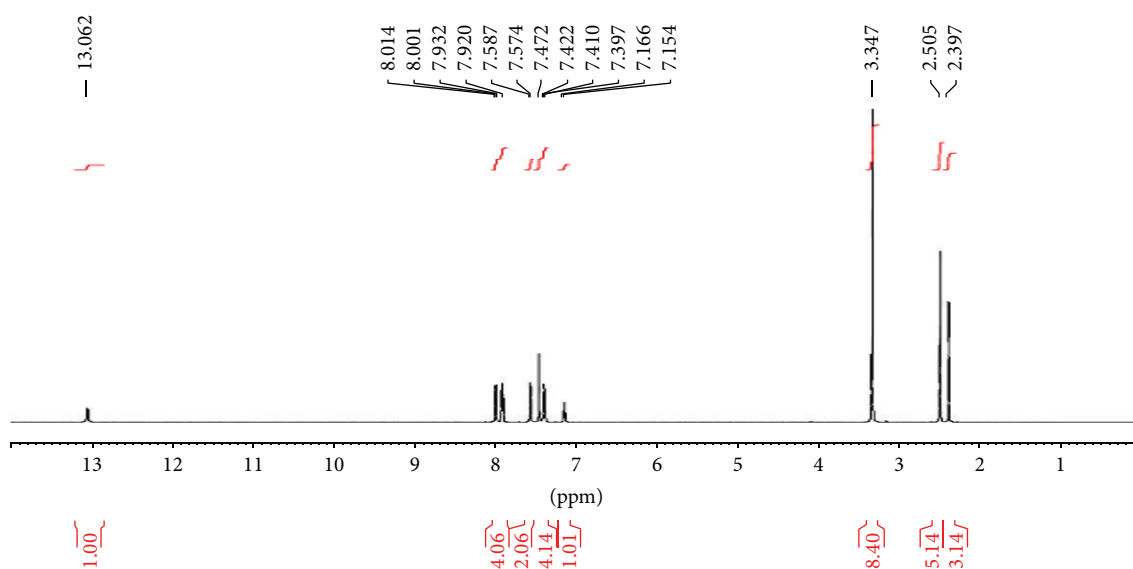
the reported method [20], while the Schiff base ligands 4-acetyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide (Ampp-Sn) **1** and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide (Bmpp-Sn) **2** were afforded by the condensation reaction of an aromatic amine 4-aminobenzenesulfonamide (sulfanilamide), with 4-acetyl or 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one in a 1:1 Molar ratio according to the synthetic Scheme 1.

They were obtained in more than 50% yield and recrystallized in methanol. Single threadlike crystal structure of **2** distorted with a water molecule was obtained from slow evaporation of a solution of methanol. Treatment of **1** or **2** with an appropriate metal salt afforded the metal complexes **1a–d** and **2a–d** having a general scheme presented in (2), which shows synthesis of 4-acyl-3-methyl-1-phenyl-2-pyrazolin-5-one-sulfanilamide transition metal complexes. Their Molar conductance values infer a nonelectrolyte behavior in DMF [27]:

is displayed upfield at 2.2 ppm integrating for an unequivalent number of hydrogen atoms.

^1H NMR spectrum of **1** was inconclusive as resonance peaks were not resolved enough to assign all necessary chemical shifts; however, the peak on the far downfield is due to sulfanilamide NH_2 hydrogen $-\text{NH}$ at 13.1 ppm integrated for one proton. The two sharp peaks observed at the far upfield are due to the methyl proton groups, pyrazolone methyl at 2.5 ppm, and the acetyl methyl at 2.4 ppm, although integrated for a higher proton value. The signals at 7.9–7.2 ppm are assigned to the aromatic protons while the peak at 8.0 ppm is due to azomethine hydrogen $\text{H}-\text{N}=\text{C}$, Figure 2.

The ^{13}C NMR spectra gave more information on the Schiff base ligands, Figures 3 and 4. A signal at 190.5 ppm in

FIGURE 1: ^1H NMR spectrum of Bmpp-Sn (**2**).FIGURE 2: ^1H NMR spectrum of Ampmp-Sn (**1**).

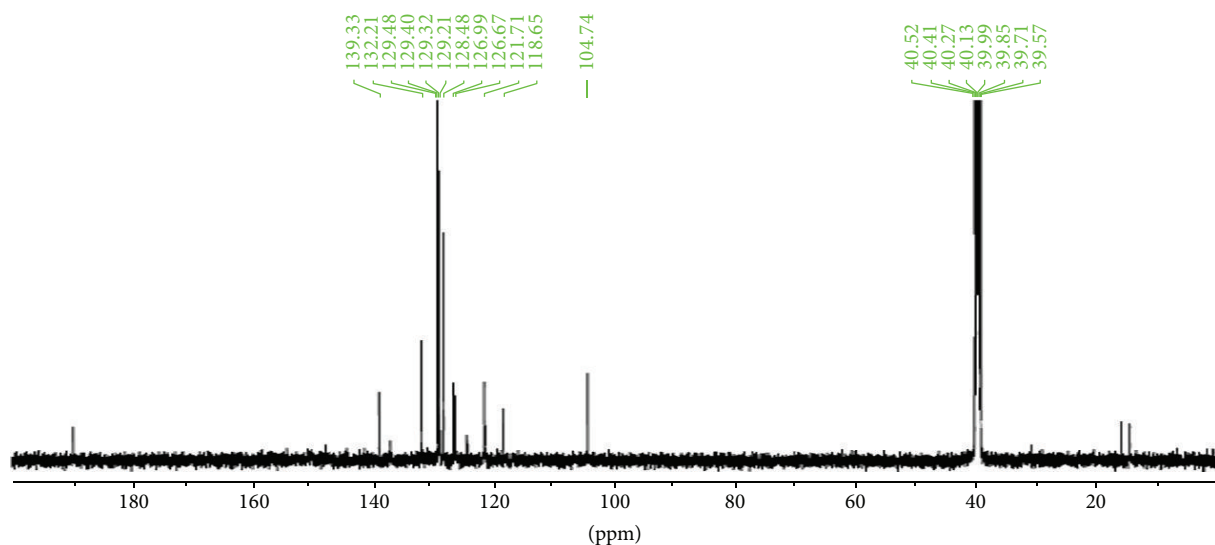
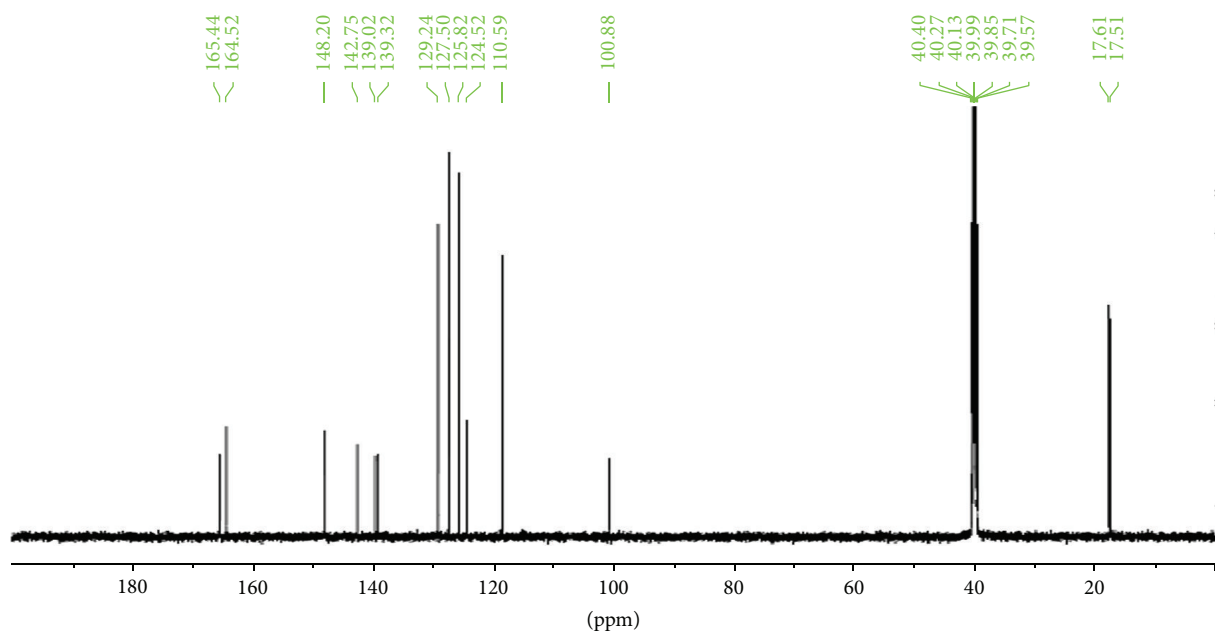
2 and that at 165.4 ppm in **1** may be assigned to the carbonyl carbon $\text{C}=\text{O}$. The azomethine carbon is observed at 139.3 ppm in the spectrum of **2** and at 164.5 ppm in **1** [29]. Signals due to aromatic carbon atoms are resonating at a chemical shift of 132.2–110.7 ppm in **2** and 142.8–116.6 ppm in **1**. Aliphatic methyl carbon may be assigned to a signal at around 16.5 ppm in **2** and the two methyl groups in **1** are assigned to the signals at 17.6 and 17.5 ppm.

The resonance signal due to $\text{C}-\text{S}$ may be assigned to the signal at 148.2 ppm in **1**. Unfortunately, this particular signal could not be accounted for in **4** but its mass spectrum and crystal X-ray structure do confirm the proposed molecular structure.

3.3. Mass Spectroscopy. The molecular ion peak of the APCI source mass spectrum of **2** and **1** was observed at m/z 433 and m/z 371, respectively, and in agreement with the calculated theoretical Molar mass plus one hydrogen $[\text{M} + \text{H}]^+$, equivalent protonated ligands, Figures 5 and 6.

Also the protonated benzoyl Schiff base precursor fragmentation peak was observed at m/z 279, that is, $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_2$ in **2**, while that of acetyl Schiff base precursor $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_2$ was seen at m/z 216 in the spectrum of **1**.

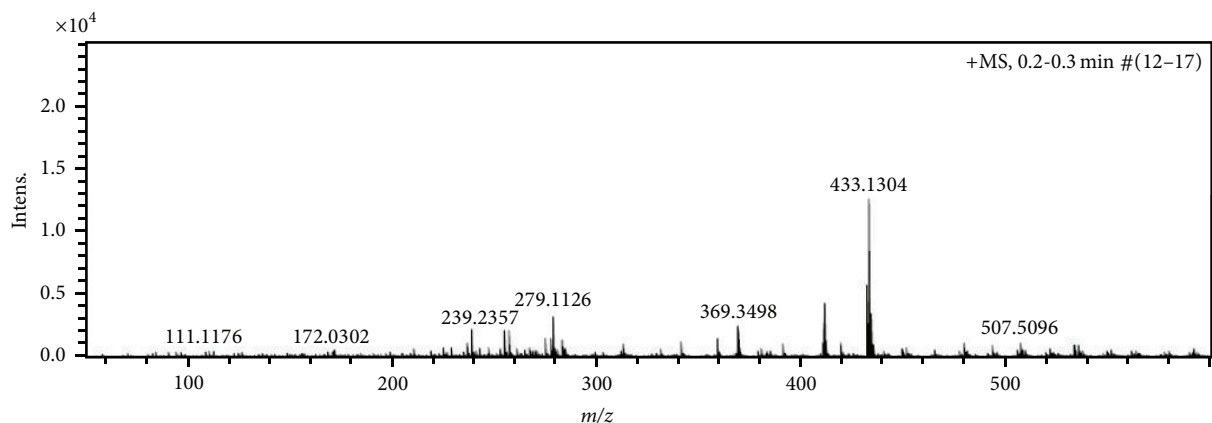
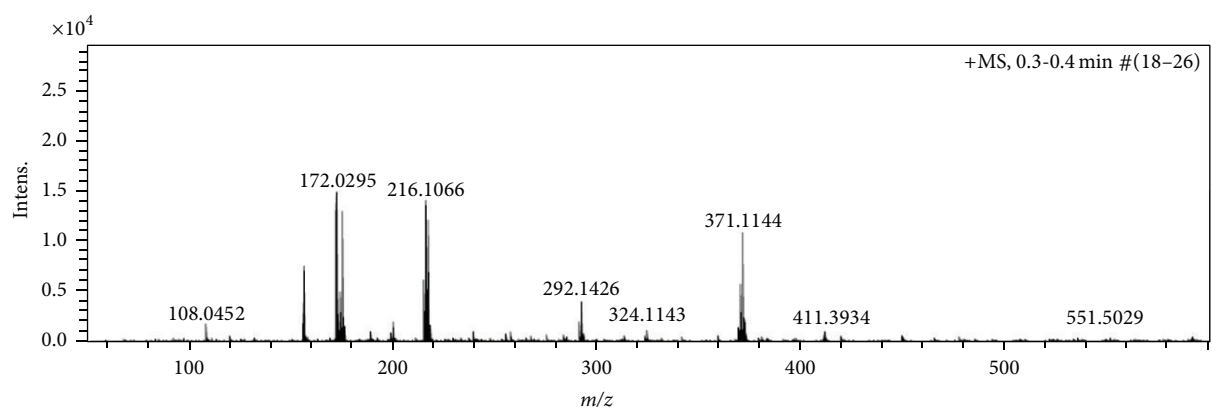
3.4. FT-IR Spectroscopy. The successful coordination of the sulfanilamide with acylpyrazolone to form the keto-imine tautomer Schiff bases was evident in the presence of

FIGURE 3: ^{13}C NMR spectrum of Bmpp-Sn (2).FIGURE 4: ^{13}C NMR spectrum of Ampp-Sn (1).

the azomethine ($\text{C}=\text{N}$) and ketone carbonyl ($\text{C}=\text{O}$) vibrating bands in their IR spectra. The ($\text{C}=\text{N}$) was observed at 1639 cm^{-1} in **2** and 1633 cm^{-1} in **1** which was modified and appeared at a lower wave number region of $1627\text{--}1617\text{ cm}^{-1}$ in the IR spectra of the metal complexes [30]. Ketone carbonyl group ($\text{C}=\text{O}$) was prominently observed at 1504 cm^{-1} in **2** and 1503 cm^{-1} in **1**, which were reduced in peak size or have disappeared in their corresponding metal complexes spectra showing a transformation of the double bond of carbonyl into a metal oxygen bond --C--O--M [31]. The octahedral Schiff base metal complexes were completed with two water molecules each and this bond can be seen from the formation of a vibrating band at around $850\text{--}823\text{ cm}^{-1}$ in addition to the broad

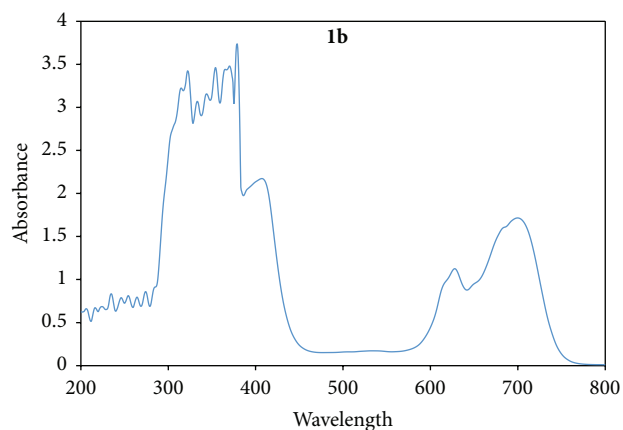
band at $3498\text{--}3390\text{ cm}^{-1}$ due to the --OH from the water molecules, which appeared originally at $3496\text{--}3497\text{ cm}^{-1}$ in **1** and **2** due to the --NH and --OH stretching frequencies [32]. The stretching bands that appeared at $634\text{--}619\text{ cm}^{-1}$ and $498\text{--}470\text{ cm}^{-1}$ are due to metal nitrogen bond M--N and that of metal oxygen M--O , respectively [33].

3.5. UV-Visible Spectroscopy and Magnetic Moment. Bmpp-Sn and Ampp-Sn exhibited bands at the UV region due to charge transfer $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, which are usually intense as a result of the organic conjugate π bonds of the benzene ring [34]. Charge transfer transitions may interfere with each other, therefore preventing the expected

FIGURE 5: Mass spectrum of Bmpp-Sn (**2**).FIGURE 6: Mass spectrum of Ampp-Sn (**1**).

transitions in the visible region of the electronic spectra of compounds to be observed, as seen in the spectra of some of the metal complexes reported herein [35]. Absorption bands and wavelength values carefully assigned are presented in the experimental section. **2a** shows two bands in the visible region at 424 nm and 589 nm assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transitions, respectively, corresponding to a d^5 octahedral Mn(II) complex [36]. One band at 431 nm is assigned to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ in **1a**. The high spin d^5 octahedral manganese complexes were corroborated with the magnetic moment values of 5.82 and 5.61 BM for **2a** and **1a**, respectively [37]. **2b** displays two bands in the visible region at 408 nm and 540 nm corresponding to ν_1 (${}^4T_{2g} \rightarrow {}^4T_{1g}$) and (${}^4A_{2g} \rightarrow {}^4T_{1g}$) transitions, respectively. It similarly has a magnetic moment value of 4.46 BM, expected for an octahedral Co(II). Three bands were observed in the electronic spectra of **1b** with magnetic moment of 4.43 BM, at 408 nm, 632 nm, and 699 nm assigned as (${}^4T_{2g} \rightarrow {}^4T_{1g}$), (${}^4A_{2g} \rightarrow {}^4T_{1g}$), and (${}^4T_{1g(p)} \rightarrow {}^4T_{1g}$) transitions, respectively, peculiar to a d^7 octahedral geometry [38] (Figure 7).

The absorption bands at 410 nm and 683 nm were assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g(p)}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$, respectively, in **2c**. In **1c** the d-d bands at 596 nm and 674 nm are assigned

FIGURE 7: Electronic spectrum of Co(Ampp-Sn)₂(H₂O)₂ (**1b**).

to ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ and ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$ transitions, respectively. These transitions correspond to a d^8 Ni(II) with octahedral geometry. Their magnetic moment of 2.89 and 2.93 BM for **2c** and **1c**, respectively, further justifies the proposed geometries [39]. Two bands in the electronic spectra of **2d**, observed as a strong band at 442 nm and a broad band that

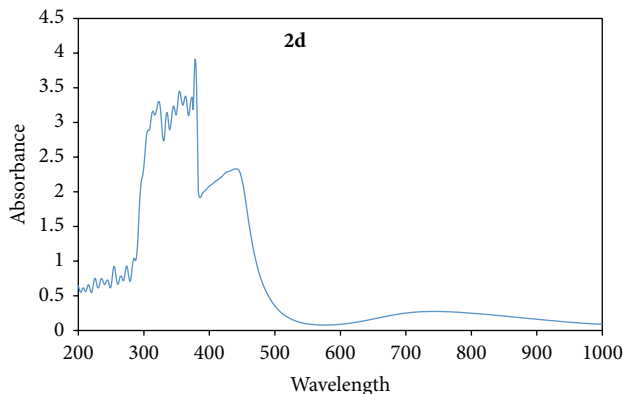


FIGURE 8: Electronic spectrum of $\text{Cu}(\text{Bmpp-Sn})_2(\text{H}_2\text{O})_2$ (**2d**).

peaks at 751 nm, were assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transitions, respectively (Figure 8), with a magnetic moment value of 1.93 BM. **1d** exhibited one single broad band characterized by a distorted octahedral $\text{Cu}(\text{II})$ at 618 nm which is assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition, with a magnetic moment value of 1.90 BM [38].

3.6. Thermogravimetric Analysis. TGA in collaboration with DTG results shows a multistep decomposition pattern in the thermograms of some of the metal complexes under investigation. Generally, relatively low thermal decomposition mass losses observed below 300°C are due to the removal of the coordinated and noncoordinated water molecules, although not so in some of the metal complexes with coordinated water molecule [40]. As they exhibited multiple decomposition steps, their assignments were not unequivocal. In **2a** the decomposition due to the removal of the four water molecules is observed at 220°C . The major decomposition at around 550°C with a mass loss of about 44% may be attributed to the removal of a molecule of **2** calculated as 45.3%. This decomposition was followed by a second, over a wide temperature range extending beyond 900°C , which may be attributed to the second Schiff base ligand, leaving a residue of manganese oxide. Schiff base ligands with more aromatic groups are generally more stable; hence the varying trends of decomposition are shown by **1a-d** as we proceed. The decomposition due to the elimination of the water molecules in **1a** is observed at 150 and 290°C . It was followed by a major decomposition at around 450°C attributed to the decomposition of a molecule of **1** with a mass loss of 40% and calculated as 43.7%. The final decomposition due to the second ligand extends beyond 900°C leaving the metal oxide. The removal of water molecules from **4b** was observed at around 100°C . The major decomposition at 400°C was attributed to the loss of **4** with a mass percentage of 45% which was calculated as 44.3%. The third decomposition over a wide temperature range was attributed to the second Schiff base ligand leaving a cobalt oxide residue behind with a percentage mass of 6.9% and calculated as 7.7% (Figure 9). The thermogram for **1b** exhibited multiple decompositions indicating about unequivocal assignments an evidence of its

low thermal stability. However, the water molecules elimination can be observed at 160°C .

Complex **2c** (Figure 10) exhibited decompositions due to water molecules at around 80 and 140°C . Its major decomposition occurred at 420°C associated with the removal of a molecule of **2** with an equivalent mass loss of 50% and calculated as 50.9%. The final decomposition at around 810°C was attributed to the removal of a total of four molecules of water and two molecules of the Schiff base leaving behind a nickel oxide residue with a percentage mass of 9% and calculated as 8.7%.

Another multistep decomposition trend was observed in **1c**. The elimination of the water molecules was evident from the decompositions at 170 and 280°C . A major decomposition due to the removal of a **1** molecule was observed at 440°C with a mass loss of 44% which is in agreement with the calculated mass loss of 43.5%. The final decomposition due to the removal of the second Schiff base extends beyond 900°C which was terminated with the left over nickel oxide. The thermal decomposition of **2d** showed an unexpected one decomposition step at 330°C which cannot be easily assigned. This observation may be due to the formation of gaseous reaction products. Also unexpectedly, the coordinated water molecule in **1d** cannot be accounted for in the TGA curve but a major decomposition at 440°C may be due to the elimination of one Schiff base ligand with a mass loss of 45%, calculated as 43.2% (Figure 11). This was followed by a second and final decomposition attributed to the fragmentation of the last **1** molecule, leaving behind a residue of the metal oxide with a remaining mass of around 11%, calculated as 8.8%.

On the basis of elemental analysis and spectroscopic and TGA results the proposed structures of metal complexes may be represented as seen in Figure 12.

3.7. Crystallographic Data. Slow evaporation of **2** in methanol afforded needle-like single crystals of Schiff base **2** with a water molecule distortion formulated as $\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_3\cdot\text{H}_2\text{O}$. A summary of crystal data is presented in Table 1.

Solid state molecular structure of $\text{Bmpp-Sn}\cdot\text{H}_2\text{O}$ as seen in Figure 13 is essentially planar with the plane of the methylpyrazolone group but with the phenyl groups turned out of the plane in accordance with reported crystal structures [18, 28]. The phenyl rings C11–C16, C21–C26, and C31–C36 make dihedral angles of $39.44(12)^\circ$, $66.26(13)^\circ$, and $34.38(13)^\circ$, respectively, with the methylpyrazolone group.

There are three intramolecular bonds: one short $\text{N2}\cdots\text{H2}\cdots\text{O3}$ hydrogen bond of 1.90 \AA and two long $\text{C13}\cdots\text{H13}\cdots\text{O2}$ and $\text{C32}\cdots\text{H32}\cdots\text{O3}$ hydrogen bonds of 2.48 \AA each (Figure 14).

Pairs of $\text{Bmpp-Sn}\cdot\text{H}_2\text{O}$ are alternatively stacked in the c-axis direction and connected with two $\text{C22}\cdots\text{H22}\cdots\text{O3}$ hydrogen bonds of 2.45 \AA , two $\text{C16}\cdots\text{H16}\cdots\text{C}$ (pyrazolone ring) π -ring interactions of 2.66 \AA , and two $\text{N1}\cdots\text{H1B}\cdots\text{C}$ (C31–C36 phenyl ring) π -ring interaction of 2.70 \AA . A water molecule connects adjacent $\text{Bmpp-Sn}\cdot\text{H}_2\text{O}$ in the b-axis direction with two hydrogen bonds $\text{N1}\cdots\text{H1A}\cdots\text{O4}\cdots\text{H4B}\cdots\text{N4}$ of length 1.74 and 2.13 \AA , respectively. Crystallographic data for the structural analysis have been deposited

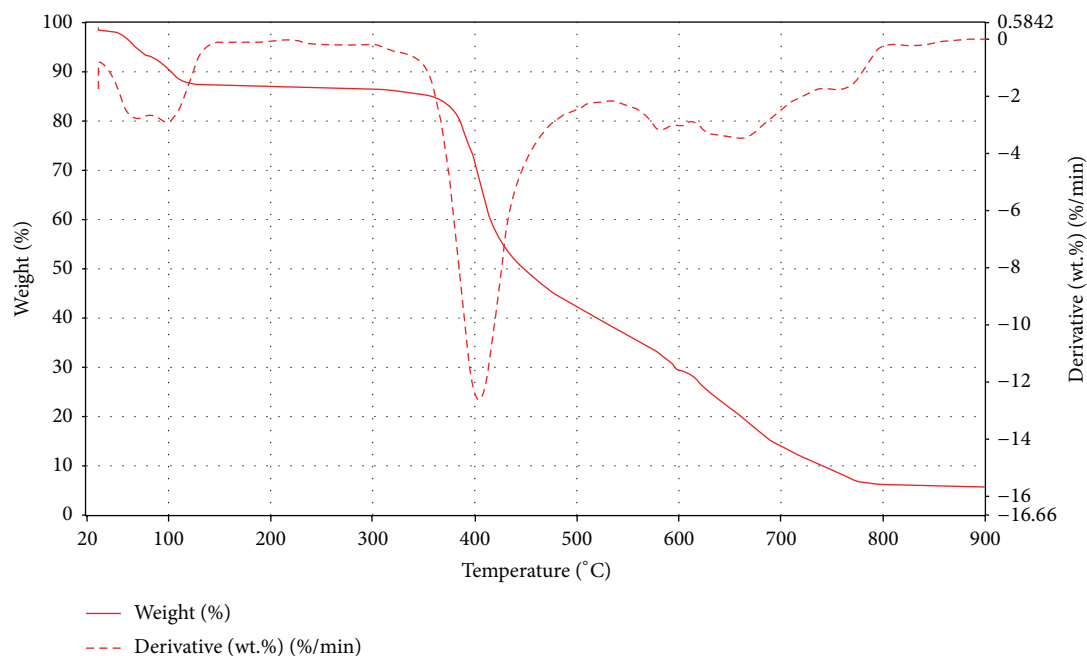


FIGURE 9: TGA and DTG curve of $\text{Co}(\text{Bmpp-Sn})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ (**2b**).

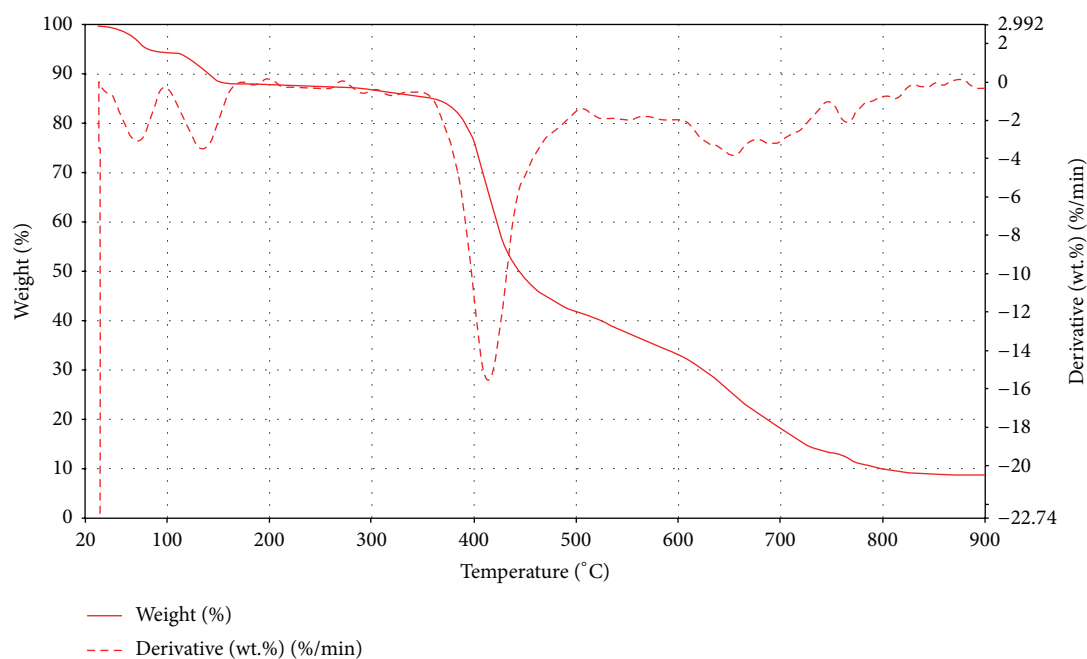


FIGURE 10: TGA and DTG curve of $\text{Ni}(\text{Bmpp-Sn})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ (**2c**).

with the Cambridge Crystallographic Data Centre, CCDC, number 923953.

3.8. Antibacterial Activity. A generally moderate to poor activity of reported compounds with some showing no activity at all is observed relative to the standard chloramphenicol drug, as seen from the mean values of bacterial growth

inhibition zones carried out in triplicate at 40 mg/mL concentration. **2** exhibited a broad spectrum activity (active against all selected bacterial isolates) and showed the highest zone of inhibition value of 24 mm against *Aeromonas hydrophila* (Table 2). **2b**, **2c**, **1c**, and **1** on the other hand exhibited activity against three of the selected bacterial isolates.

Although it is expected that chelation of metal ion to Schiff base does increase the possibility of microbial growth

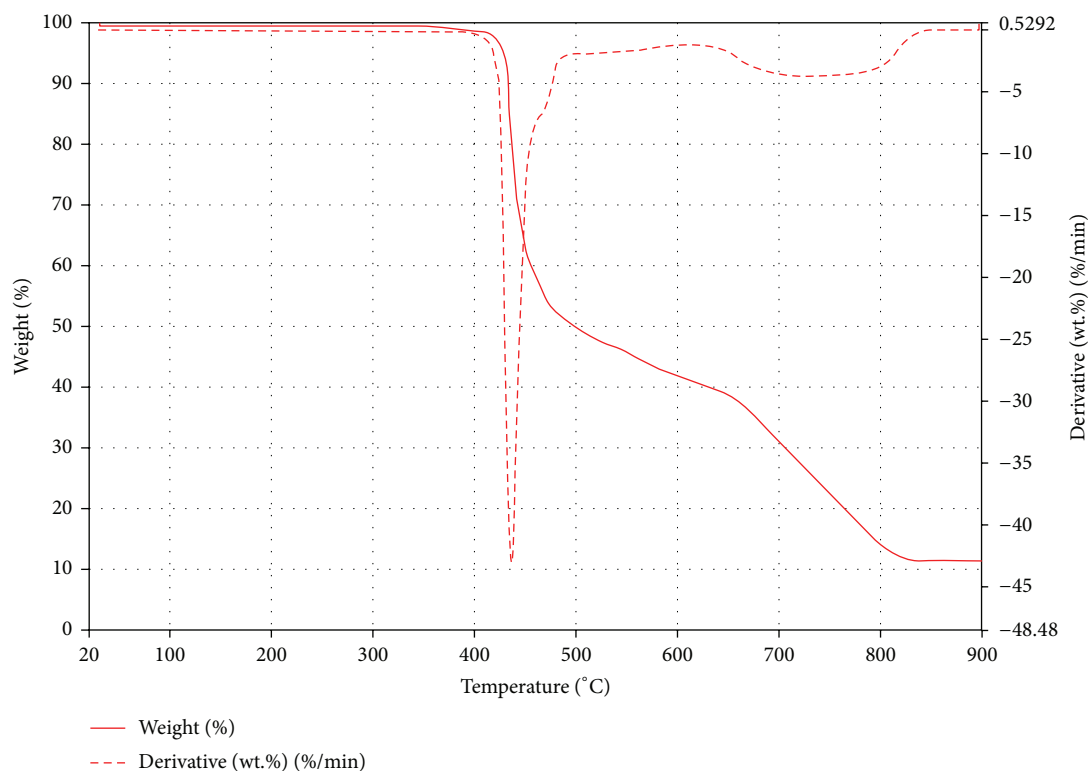


FIGURE 11: TGA and DTG curve of $\text{Cu}(\text{Ampp-Sn})_2(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ (**1d**).

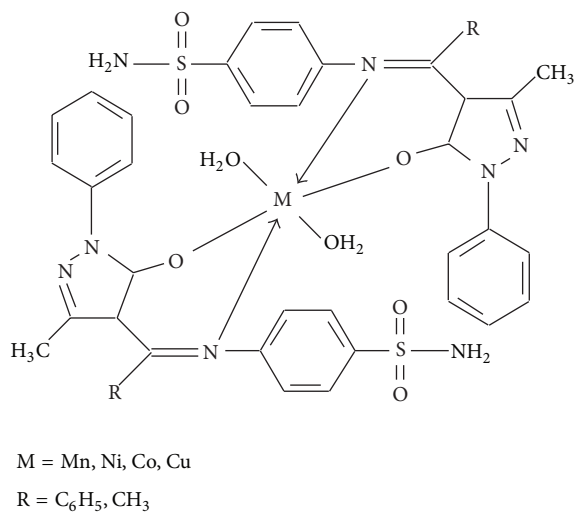


FIGURE 12: Proposed structural scheme for metal complexes.

inhibition [41], the observed variation herein may be as a result of impermeability of bacterial isolates cell wall or the nature of their ribosomes [42].

3.9. Antioxidant (Free Radical Scavenging) Activity. The reduction/scavenging capability is taken as the decrease in absorbance at a constant wavelength relative to the control sample which is made possible by antioxidant properties [43]. It is evident that the potential antioxidant properties of some

TABLE 1: Crystal data for **2**.

Compound	Bmpp-Sn
Formula	$\text{C}_{23}\text{H}_{20}\text{N}_4\text{O}_3\text{S} \cdot \text{H}_2\text{O}$
Crystal colour and form	Orange/block
Formula weight	450.52
Crystal system	Monoclinic
Space group	$\text{C}2/c$
a	23.3366 (4) (\AA)
b	14.7706 (3) (\AA)
c	12.5787 (2) (\AA)
α	$90 (2)^\circ$
β	$100.727 (2)^\circ$
V	4257.21 (13) (\AA^3)
Z	8
$D_{(\text{calc})}$	1.406 (Mg cm^{-3})
$F(000)$	1888
θ range	2.2–28.3 ($^\circ$)
Crystal size	$0.24 \times 0.38 \times 0.56$ (mm)
Reflections measured	19945
Independent/observed	5285/4408
$\mu(\text{MoK}\alpha)$	0.71073 ($/\text{mm}$)
Temperature	296 (K)
Parameters	108

naturally occurring ingredients from plants and synthetic analogs are as a result of having electron-donating groups [44] and as such the inductive effects of the sulfur and

TABLE 2: Zone of growth inhibition exhibited by sulfanilamide Schiff bases and metal complexes at 40 mg/mL (mm).

Ligand and complexes	<i>Staphylococcus aureus</i>	<i>Bacillus pumilus</i>	<i>Proteus vulgaris</i>	<i>Aeromonas hydrophila</i>
2	12.5	7.5	10.3	24.0
1	NI	5.0	8.5	4.0
2a	8.5	NI	NI	8.0
2b	13.3	16.0	NI	15.0
2c	8.0	NI	11.5	21.0
2d	NI	10.3	NI	8.0
1a	NI	NI	NI	8.5
1b	NI	9.0	NI	NI
1c	4.5	6.0	NI	6.0
1d	NI	NI	8.5	15.0
Chloramphenicol	30.0	20.0	42.0	40.0
DMSO	NI	NI	NI	NI

NI = no inhibition.

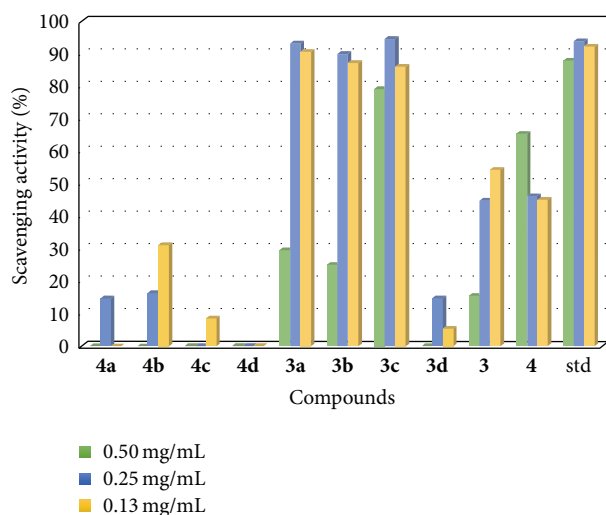


FIGURE 15: Chart showing the scavenging activity.

into consideration, synthesized compounds may be useful antitumour candidates.

Additional Information

Crystallographic data for 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide reported herein has been deposited with the Cambridge Crystallographic Data Centre (CCDC) number 923953. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: +44 1223 336 033], or deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

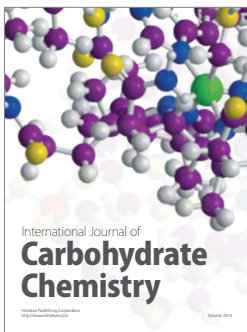
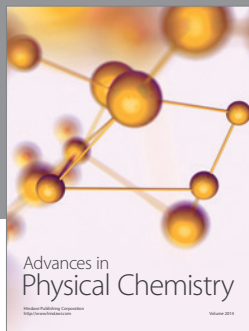
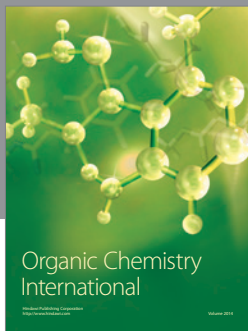
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