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Synthesis, characterization and biological activity of salen-mixed ligand complexes with nickel(II), copper(II) and cobalt(III)

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ABSTRACT

*The mixed Schiff base ligand, N,N'-o-phenylenebis(salicylideneimine) (H_2salen) with the ligands 4-aminoantipyrine (AAP) or ammonium pyrrolidinedithiocarbamate (APDC) were reacted with Ni(II), Cu(II) and Co(II) acetates. Four new different complexes were prepared and formulated as $[Ni_2(salen)(CH_3CO_2)_2(AAP)_2]$ (**1**), $[Ni_2(salen)(CH_3CO_2)_2(PDCH)_2]\cdot 2H_2O$ (**2**), $[Cu_2(salen)(CH_3CO_2)_2]\cdot 2H_2O$ (**3**) and $[Co(salen)(CH_3CO_2)]\cdot(H_2O)$ (**4**). The H_2salen ligand and its complexes were characterized by IR, UV-visible, TG, elemental analyses, and molar conductivities. The complexes were proposed to be distorted octahedral geometry with Ni(II) and Co(III) and distorted square planar geometry with Cu(II). Antibacterial activity of the complexes was tested against selected bacteria by agar well diffusion method.*

Keywords*:* Schiff base-mixed ligands; M(II/III) complexes; Spectroscopic, Thermal analysis; Antimicrobial activity.

INTRODUCTION

Interaction of Schiff base compounds with metal ions and their metal complexes have been extensively investigated due to their wide range of applications in medicine and engineering [1-8]. In recent years, there has been a considerable interest in the chemistry of antipyrine and its derivatives such as 4-aminoantipyrine (AAP, Fig. 1) or their metal complexes. These compounds are reported to exhibit a wide range of applications in various fields like biological properties as antifungal, antibacterial, analgesic, sedative, antipyretic, anti-inflammatory agents, analytical and therapeutical [9-18]. Pyrrolidinedithiocarbamates (PDC) which represent a class of antioxidants mediate a wide variety of effects in biological systems [19]. It is a multipotent synthetic compound well known for its metal chelation property [20]. Also, ammonium pyrrolidinedithiocarbamate (APDC, Fig.1) has been used recently in various preconcentration and separation techniques [21-25]. APDC is most widely used to determine the metal ions that form slightly soluble complexes in an aqueous solution [26].

The most motivating features of these ligands are the possibility of using them to synthesize complexes with different modes of bonding and their interesting biological activity. In recent years, there has been considerable interest in the complexes formed by H_2salen (Fig. 1), AAP, APDC and acetate ligands as they are common components of some biologically important molecules. As a part of our continued research work on synthesis, characterization and biological activity, the present paper describes the synthesis and characterization of new Ni(II), Cu(II) and Co(III) complexes with H_2salen mixed ligands. Thermal analysis is also helpful to study the chemical structure and thermal parameters of the complexes [27-29]. The study of the structural behavior of the complexes derived from the reaction of the metal ions, Ni(II), Cu(II) and Co(II) and with mixed H_2salen donor ligands is a matter of significant importance for the investigation of the geometries of the formed complexes during decomposition processes. The prepared metal complexes were screened for their *in vitro* antimicrobial activities

against four bacterial strains, *Bacillus subtillis* and *Staphylococcus aureus* as gram positive bacteria and *Escherichia coli* and *Pseudomonas aeroginosa* as gram negative bacteria by agar well diffusion method.

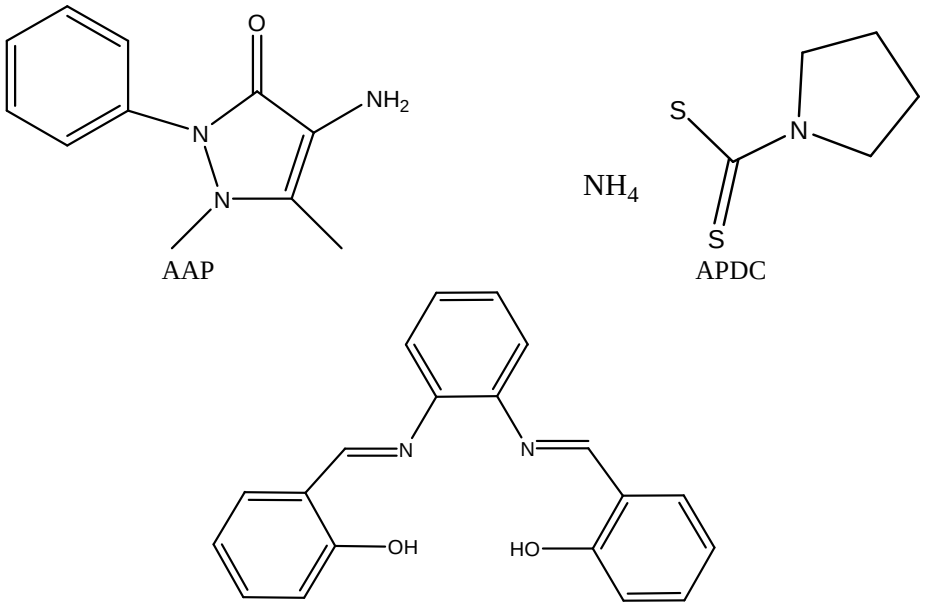


Fig.1. Structure of the ligands

EXPERIMENTAL SECTION

2.1. Materials and spectral measurements

All of the chemical used throughout this investigation were extra pure grade and used without further purification. Nickel(II) acetate, copper(II) acetate monohydrate and cobalt(II) acetate tetrahydrate were purchased from Merck Chemical Co., o-phenylenediamine, salicylaldehyde, 4-aminoantipyrine (AAP), ammonium pyrorolidinedithiocarbamate (APDC) were obtained from Aldrich.

The electronic absorption spectra were recorded in the region of 250–900 nm using UV-Vis. spectrophotometer model JASCO V-530 with quartz cell of 1.0 cm path length. The concentrations of measured solution in DMSO were fixed at 10^{-3} M.

Molar conductances of a 10^{-3} M solution of the complexes were measured in DMSO at 25 ^{o}C using a 4310 Jenway model conductivity meter. The infrared spectra of the reactants and the obtained complexes were recorded using KBr discs on Perkin-Elmer 1430 ratio recording Infrared spectrometer. Elemental analyses were carried out in microanalysis unit of Cairo University, Egypt using CHNS-932 (LECO) and Vario EL elemental analysers. Thermal analyses (TG, DTG) were carried out using a Shimadzu TGA-50 H computerized thermal analysis system. The system includes program which process data from the thermal analyzer with the ChromotPac C-R3A. The rate of heating of the samples was kept at 10 ^{o}C/ min. Sample masses 1.440, 2.411, 3.053, 3.017, 3.285, 1.754, 1.964, 1.521 mg for nickel acetate tetrahydrate, H_2salen, AAP, APDC and complexes **(1,3, 3, 4)**, respectively were analyzed under N_2 flow at 20 ml/min. Cobalt, nickel and copper contents in the complex solutions were obtained using atomic absorption technique. An atomic absorption spectrometer model PYE-UNICAM SP 1900 and the corresponding lamp in each case were used for this purpose.

2.2. Preparations

H_2salen (sal-o-phdnH_2)

Schiff base ligand, *N,N′*-o-phenylenebis(salicylideneimine) (H_2salen) was prepared according to the known method [30] by reaction of o-phenylenediamine and salicylaldehyde (1:2 molar ratio) in ethanol. The mixture was heated and refluxed for 3 *h*. The formed bright yellow crystalline solid (salen) was collected by filtration and washed thoroughly with ethanol. yield (95%).

Anal. found (Calc. for $C_{20}H_{16}N_2O_2$ (316.36): C, 75.92 (75.93); H, 5.15 (5.10); N, 8.87 (8.85).

[Ni_2(salen)$(CH_3CO_2)_2$(AAP)$_2$] (**1**)

To a solution (20 mL) of nickel(II) acetate tetrahydrate, $Ni(CH_3CO_2)_2 \cdot 4H_2O$ (248.9 mg, 1.0 mmol) in ethanol, a solution of 4-aminoantipyrine (AAP) (406.48 mg, 2.0 mmol) in ethanol (30 mL) was added. The solution mixture

was stirred for about 5 *h* at *ca.* 50 °C. A hot solution of H_2salen (316.4 mg, 1.0 mmol) in ethanol (100 mL) was then added. The resulting clear mixture was refluxed for 2 *d* until the formation of reddish precipitate of complex **1** which was then separated, filtered off, washed several times with hot ethanol (5×2 mL), dried at 50 °C in an oven for 4 *h* and then in a desiccator in vacuo. Yield: 410.0 mg (42.9 %).

Anal. found (Calc. for $C_{46}H_{46}N_8Ni_2O_8$ (956.35): C, 57.54 (57.77); H, 4.96 (4.85); N, 11.69 (11.72); Ni, 12.13 (12.28).

$[Ni_2(salen)(CH_3CO_2)_2(PDCH)_2]\cdot 2H_2O$ (**2**)
To a solution (20 mL) of nickel(II) acetate tetrahydrate, $Ni(CH_3CO_2)_2\cdot 4H_2O$ (248.9 mg, 1.0 mmol) in ethanol, a solution of ammonium pyrrolidinedithiocarbamate (164.3 mg, 1.0 mmol) in ethanol (10 mL) was added. The turbid white mixture was stirred for about 5 *h* at *ca.* 50 °C and then, a hot solution of H_2salen (316.4 mg, 1.0 mmol) in ethanol (100 mL) was added. The resulting reddish mixture was refluxed for 1 *d* until formation of dark red precipitate of complex **2** which was then filtered off, washed several times with hot ethanol (5×2 mL), dried at 50 °C in an oven for 4 *h* and then in a desiccator in vacuo. Yield: 620.0 mg (70.4 %).

Anal. found (Calc. for $C_{34}H_{42}N_4Ni_2O_8S_4$ (880.41): C, 46.31 (46.39); H, 4.92 (4.81); N, 6.33 (6.36); Ni, 13.22 (13.34); S, 14.44 (14.57).

$[Cu_2(salen)(CH_3CO_2)_2]\cdot 2H_2O$ (**3**)
To a solution of copper acetate monohydrate, $Cu(CH_3CO_2)_2\cdot H_2O$ (199.7 mg, 1.0 mmol) in minimum amount of methanol, a solution of 4-aminoantipyrine (AAP) (203.24 mg, 1.0 mmol) in methanol (30 mL) was added. The clear green solution was stirred for about 6 *h* at *ca.* 50 °C. To the obtained green solution, a hot solution of H_2salen (316.4 mg, 1.0 mmol) in methanol (50 mL) was added. The resulting clear mixture was refluxed for 2 *d* until formation of precipitate of complex **3**. The volume of solution was reduced to half of its volume. The dark brown precipitate was filtered off, washed several times with hot methanol (5×2 mL), dried at 50 °C in an oven for 4 *h* and then in a desiccator in vacuo. Yield: 450.0 mg (75.6 %).

In a similar way that shown for the preparation of Ni(II) complexes **1** and **2**, the same experiment was repeated but using ammonium pyrrolidinedithiocarbamate instead of AAP (164.3 mg, 1.0 mmol) in methanol (10 mL) with stirring. The solution was stirred for about 6 *h* at *ca.* 25 °C until the formation of white turbid solution. A hot solution of H_2salen (316.4 mg, 1.0 mmol) in methanol (50 mL) was then added. The resulting mixture was refluxed for 1 *d* until the formation of precipitate of complex **3**. The volume of solution was reduced to half of its volume and the dark brown precipitate was filtered off, washed several times with hot methanol (5×2 mL), dried at 50 °C in an oven for 4 *h* and then in a desiccator in vacuo. Yield: 390.0 mg (65.5 %). The analysis results came in good consistence with the proposed formula as follows.

Anal. found (Calc. for $C_{24}H_{24}Cu_2N_2O_8$ (595.55): C, 48.43 (48.40); H, 4.14 (4.06); Cu, 21.45 (21.34); N, 4.73 (4.70).

$[Co(salen)(CH_3CO_2)]\cdot H_2O$ (**4**)
To a solution of cobalt acetate tetrahydrate, $Co(CH_3CO_2)_2\cdot 4H_2O$ (249.1 mg, 1.0 mmol) in methanol (20 mL), a solution of 4-aminoantipyrine (AAP) (406.5 mg, 2.0 mmol) in methanol (60 mL) was added. The resulting mixture was stirred for about 5 *h* at *ca.* 50 °C. A hot solution of H_2salen (316.4 mg, 1.0 mmol) in methanol (70 mL) was then added. The resulting mixture was refluxed for 2 *d* until formation of precipitate of complex **4**. The volume of solution was reduced to half of its volume. The dark greenish precipitate was filtered off, washed several times with hot methanol (5×2 mL), dried at 50 °C in an oven for 4 *h* and then in a desiccator in vacuo. Yield: 300.0 mg (66.6 %).

The same experiment was repeated but using ammonium pyrrolidinedithiocarbamate instead of AAP (328.6 mg, 2.0 mmol) in methanol (20 mL). Yield: 330.0 mg (73.3 %). The analysis results came in good consistence with the proposed formula as follows.

Anal. found (Calc. for $C_{22}H_{19}CoN_2O_5$ (450.33): C, 58.40 (58.68); H, 4.36 (4.25); Co, 12.92 (13.09); N, 6.31 (6.22).

2.3. Antibacterial activity
The *in vitro* antibacterial screening effects of the compounds were tested against four bacterial strains namely *Escherichia coli* and *Pseudomonas aeroginosa* (Gram negative bacteria) and *Bacillus subtillis* and *Staphylococcus aureus* (Gram positive bacteria) by agar well diffusion method using nutrient agar medium for antibacterial activity [31-33]. All bacteria were inoculated into Nutrient Broth and incubated for 24 *h* (1.0 ml of inocula were added to 50 ml of agar media (50 ºC) and mixed). The agar was poured into 120 mm petri dishes and allowed to cool to room

temperature. In the agar well diffusion method, the dilution plate method was used to enumerate microorganisms for 24 *h* [34, 35]. By using a sterilized cork borer (7 mm diameter), wells were dug in the culture plates. 0.1 mL of the compounds dissolved in DMSO (250 μmol/mL) were added to these wells. The petri dishes were left at 5 ºC for 2 *h* and then the plates were incubated at 35 ºC for bacteria (22–24 *h*). At the end of the period, inhibition zones formed on the medium were evaluated in milimeters (mm). DMSO was used as a control under similar conditions for comparison (0.1 mL). The zones of inhibition based upon zone size around the wells were measured and calculated as a mean of three replicates.

RESULTS AND DISCUSSION

The results of microanalysis of carbon, hydrogen and nitrogen in the investigated compounds are given in experimental part. The complexes were synthesized using M(II) actate, H_2salen ligand in a 1:1 mole ratio and (AAP or APDC). The results indicate the formation of different salen mixed ligand complexes with metal ions.

3.1. Electronic absorption spectra

The spectral data of the compounds are presented in Table 1. The electronic absorption spectrum of the synthesized H_2salen shows UV bands at 269, 295 and 330 nm. The bands at 269 and 295 nm are attributed to π→ π* transitions of the aromatic ring, 330 nm is assigned to n→ π* transition of azomethine group [36, 37].

In the complex **1** (Table 1), there are two absorption bands, assigned to π→π* transitions and one absorption band assigned to π*→*d* transitions. In the spectrum of complex **2**, there are four absorption bands, assigned to π→π*, *n*→π* and π*→*d* transitions. In the spectrum of complex **3**, there is one absorption band (305 nm) assigned to π→π* and one absorption band (416 nm) assigned to π*→*d* transitions. In the spectrum of complex **4**, one absorption band is observed at 316 nm assigned to *n*→π* and one absorption band at 346 nm assigned to π*→*d*. These transitions of the synthesized complexes are shifted towards lower and higher frequencies, depending on ligand structures.

Table 1. Electronic spectral data of the Schiff base and the metal complexes recorded in DMSO.

	λ_{max} (nm)									
compound	$\pi \rightarrow \pi^*$			$n \rightarrow \pi^*$	$\pi^* \rightarrow$ d		d → d* transition			
H_2salen	269	295		330						
1	286	302		--	351		470	741		907
2	291	--	315	329	373		470	741	808	907
3		305				416		741		907
4		--	316		346			741		907

In the VIS electronic absorption spectra, there are three absorption bands for complex **1**, four absorption for complex **2**, two absorption bands for complexes **3** and **4**. These bands could be assigned to a charge transfer transition, or even to *d*→*d** transition. The colour of complexes is probably due to these transitions. It is known that ligand splits *d*-orbitals of central ion in two groups. This splitting is weak and the excitation of electron between orbitals is always observed in visible electronic absorption spectra. The spectroscopic data of the nickel(II) ions in complexes **1** and **2** ($^3A_{2g} \rightarrow {}^3T_{1g}{}^{(P)}$, $^3A_{2g} \rightarrow {}^3T_{1g}{}^{(F)}$, $^3A_{2g} \rightarrow {}^3T_{2g}$) and cobalt(III) in complex **4** ($^1A_{1g} \rightarrow {}^1T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$) have a high-spin octahedral coordination environment [38] but complex **3** ($^2E_g \rightarrow {}^2T_{1g}$) show that the *d*→*d* transition is near to that of the square-planar complexes [39,40].

3.2. Conductance

The molar conductivity values of all complexes solutions (10^{-1} M) in DMSO at 25°C are in the range 1.98–4.97 $Ohm^{-1}\,cm^2\,mol^{-1}$, indicating that the complexes are non-electrolytes and suggesting that the ligands in the anionic form are coordinated to the metal ions [41, 42].

3.3. IR spectroscopy

The IR spectral data of the title compounds ($Ni(CH_3CO_2)_2{\cdot}4H_2O$, H_2salen, AAP, APDC) and complexes **1**, **2**, **3** and **4** are given in Table 2. The IR spectra of the complexes are compared with that of the free ligands to determine the changes that might have taken place during the complexation.

The IR spectrum of the H_2salen, exhibits a broad band centered at 3427 cm^{-1} due to the formation of strong intramolecular and intermolecular hydrogen bonding of phenolic –OH group. Two absorption are observed as very strong and medium bands at 1632 and 1592 cm^{-1} characteristic for ν(C=N) and ν(C=C), respectively. The C–C and C–O stretching vibrations are appeared as medium and strong bands at 1275 and 1190 cm^{-1} [43-47]. The band assigned to the azomethine group in the free Schiff base ligand was observed at 1632 cm^{-1} is shifted to lower

frequency in all metal complexes (21- 27 cm^{-1}). This indicates the participation of the nitrogen atom of the azomethine group in coordination [48-51].
The acetato group in complexes **1**, **2**, **3** and **4** were found to coordinate as a bidentate ligand. The $\nu_{as}(COO^{-})$ and $\nu_{s}(COO^{-})$ of the free acetate ion are *ca.* 1528 and 1414 cm^{-1}, respectively. In the bidentate complexes, the separation between ν(C–O) for complexes **1**, **2**, **3** and **4** (Δ =62, 64, 68, 53 cm^{-1}, respectively) are smaller than that of the free acetate ion (Δ =114 cm^{-1}) and confirmed the bidentate coordination mode in all complexes [45-47].

The IR spectrum of 4-aminoantipyrine exhibits bands between 3429 and 3038 cm^{-1} corresponding to vibrational motions of the aromatic C–H group. An intense band at 1647 cm^{-1} corresponding to C=O group is observed [52]. The IR-spectrum of the mixed 4-aminopyridine-salen complex, **1** show some characteristic bands at (2970, 2940 cm^{-1}) and 1645 cm^{-1}. The first two bands and second band are assigned to the coordinated NH_2 and C=O groups. This indicates that 4-aminopyridine acts as a neutral bidentate ligand.

The IR spectrum of the free APDC reveals that the ν(N–CSS) band defines a carbon–nitrogen bond order intermediate between a single bond (ν(1322–1245) cm^{-1}) and a double bond, ν(C=S) (1640 cm^{-1}) [53–55]. The band of 941 cm^{-1} is associated with ν(–C=S) vibrations. All of these bands are reflected in the spectrum of complex **2** with some expected shift in frequencies which can be attributed to the associated change in the electron density upon complexation. The absorption band in the 420–200 cm^{-1} region associated with ν(Ni–S) vibrations [56]. Also, there is no any absorption bands characteristic for the presence NH_4 group in complex **2**.

Bands in the region 550–400 are associated with M–O, M–N and M–S stretching vibrations [45-47].

Table 2. Characteristic infrared frequencies[*] (cm^{-1}) and tentative assignments[**] for title compounds, complexes 1, 2, 3 and 4

$Ni(CH_3CO_2)_2 \cdot 4H_2O$	H_2alen	AAP	APDC	Complex 1	Complex 2	Complex 3	Complex 4	Assignments[**]
3471 vs 3134 vs, br	3427 br 3386, s 3365, s 3295, s	3429, s 3323, s	3429, s, br	3431, s, br	3426 s, br	3417, s, br 3240, sh	3426, vs, br 3250, sh	ν(O–H); coordinated and uncoordinated H_2O; ν(N–H); intramolecular and intermolecular hydrogen bonding
	3045 w	3200, sh 3038, sh		3090, w 3025, w	3102, w 3077, w	3090, w 3025, w	3050, w	ν(C–H); aromatic
2930 s	2926 w 2856 w	2987, w 2906, w	2939, s 2866, s 2708,m,br 2522, m 2395,w	2970, w 2940, w	2963, w 2950, w	2935, w	2950, w	ν(C–H); aliphatic ν(N–H)
		1647, vs **1592, s**	1640, s	1645, s	1650, sh		1648, sh	ν(C=O); of AAP , ν(C=S) δ(H_2O) δ(NH)
	1632 vs 1592 m 1501 s			**1605, vs**	**1605, s**	**1609, vs**	**1611, vs**	ν(C=N) ν(C=C)
1528 vs **1414 vs**				**1506, m** **1444, vs**	**1510, vs** **1446, vs**	**1521, s** **1453, s**	**1505, sh** **1452, s**	**ν(C=O), $\nu_{as}(COO^{-})$; of acetato** **ν(C–O), $\nu_{s}(COO^{-})$; of acetato**
	1456 m 1401 w	1491, m 1443, m 1350, m 1273, m	1394, vs **1322**, s	1378, m 1335, w	1377, w **1332**, m	1382, m 1325, m	1400, m 1315, m	Phenyl breathing modes (quadrant vibrations) and C–H deformation **ν(N–CSS)**
	1275 m **1190** s 1154 vw	1232,w 1159,vw	1245, w 1156, s	1267, w **1193, m** 1139, m	1255, w **1188, m** 1139, m	1249, vw **1183, m** 1144, m	**1175, sh** 1140, m	ν(C–C), ν(C–N) and ν(C–O) chelating ring
1059 vw 1029 w 962 w **903 m**	1151 w 1059 vw 927 w 875 mw	1114, m	**996, m** **941, m** **818, w**	933, w 815, w	1044, w **939, w** **841, w**	1036, w 970, w 919, w 861, w	1050, w 950, w 850, w	Ring vibration, In plane CH-deformation **ν(C=S)**
818 w 747 m	**752 s**	**754, m**		**754, s**	**750, s**	**752, s**	**751, s**	
674 vs 626 m		662, m 570, m	688, w 567, w	628, w 577, w		611, w	695, w 640, w 600, w	In plane CH-quadrant deformations; phenyl Ring vibrations
548 s				546, m	536, w	530, w 511, w	547, w	ν(M–O)
				460, m	455, w	456, w	461, w	ν(M–O)
				435, w	414, w	430, w	425, w	ν(M–N) ν(M–S) in complex **2**

[*] *s, strong; m, medium; v, very; w, weak; br, broad.* [**] *ν, stretching; δ, deformation.*

3.4. Thermal analysis
The TG and DTG curves of the studied samples and complexes are shown in Fig. 2, the corresponding weight loss and assignment are listed in Table 3 to confirm the proposed structures for the complexes.

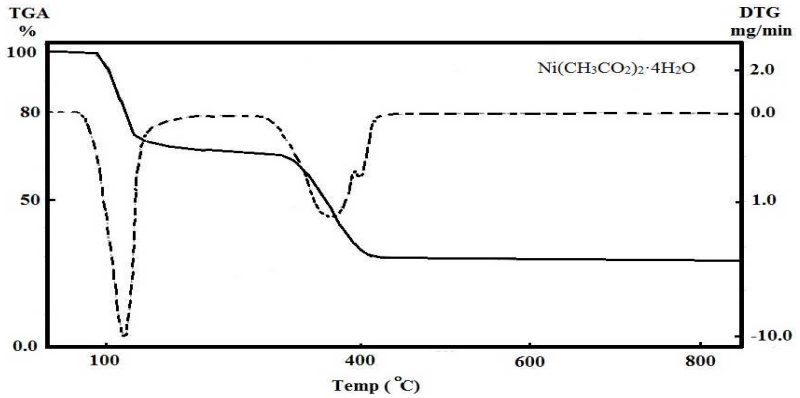
Thermograms of the free $Ni(CH_3CO_2)_2 \cdot 4H_2O$, H_2salen, AAP and APDC were measured separately for comparison with the corresponding coordinated units in complex molecules after reactions. The free $Ni(CH_3CO_2)_2 \cdot 4H_2O$ molecule decomposed in two steps. The first step of decomposition proceeds with a weight loss of 30.10% at 120 ^oC, associated with the loss of four water molecules (calculated 28.96%). The second step of decomposition proceeds with a weight loss of 39.90% (calculated 41.03%) at maximum temperature of 400 ^oC, attributed to the loss of $C_4H_6O_3$ of acetyl and acetate units. In a similar manner, Thermograms of the free H_2salen, AAP and APDC showed that decomposition reactions proceeded in two degradation steps for each compound at maximum temperatures of (266, 339 ^oC), (218, 317 ^oC) and (149, 195 ^oC), respectively.

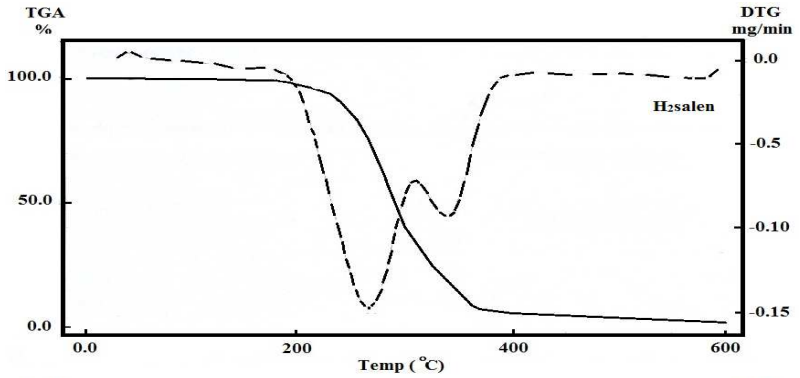
The decomposition reactions of $[Ni_2(salen)(CH_3CO_2)_2(AAP)_2]$ (**1**) occurred in three steps (Table 3 and Fig. 2). The first step of decomposition proceeds with a weight loss of 31.00% at 287 ^oC, associated with the loss of bridged salen (calculated 32.87%). The second step of decomposition proceeds at maximum temperature of 395 ^oC, attributed to the loss of $C_{22}H_{26}N_6O_2$ of two coordinated AAP molecules. The total weight loss associated with this step is 43.00% in good agreement with the calculated value of 42.50%. The third degradation step was observed as one decomposition peak at 508 ^oC with a calculated weight loss of 10.50 % and might be attributed to the loss of two acetyl units of the two chelated acetato ligands.

On the other hand, the decomposition of $[Ni_2(salen)(CH_3CO_2)_2(PDCH)_2] \cdot 2H_2O$ (**2**) occurs in five steps from 75 to 543 ^oC. The first step of decomposition proceeds with a weight loss of 5.00% at 75 ^oC, associated with the loss of two lattice water molecules (calculated 4.09%). The second and third steps of decomposition proceed at maximum temperatures of 216 and 323 ^oC, attributed to the loss of $C_{10}H_{18}N_2S_4$ of two coordinated molecules of PDCH (pyrrolidinedithiocarbamic acid). Similar to complex **1**, the third degradation step was observed as one decomposition peak at 543 ^oC with a weight loss of 9.50% (calculated weight loss 9.78%) and might be attributed to the loss of two acetyl units of the two chelated acetato ligands. The total weight loss associated with all steps (85.00%) is in agreement with the calculated value of 83.03%.

Table 3.The maximum temperature values for the decomposition along with the species lost in each step of the decomposition reactions of reactant compounds and complexes 1, 2, 3 and 4

Complex	Decomposition	T_{max}/ ^oC	Lost species	% Weight loss	
				Found	Calc.
$Ni(CH_3CO_2)_2 \cdot 4H_2O$	First step	120	$4H_2O$	30.10	28.96
	Second step	400	$C_4H_6O_3$	39.90	41.03
	Total loss		$C_4H_{14}O_7$	70.00	69.99
	Residue		NiO	30.00	30.01
H_2salen $C_{20}H_{16}N_2O_2$	First step	266	$C_{14}H_{12}O_2$	66.70	67.09
	Second step	339	$C_6H_4N_2$	33.30	32.91
	Total loss			99.09	100.00
	Residue			00.10	00.00
AAP $C_{11}H_{13}N_3O$	First step	218	C_6H_5	≅38.10	37.94
	Second step	317	$C_5H_8N_3O$	≅61.00	62.06
	Total loss			≅99.10	100.00
	Residue			≅00.90	00.00
APDC $C_5H_{12}N_2S_2$	First step	149	$C_5H_{12}N_2S$	81.82	80.61
	Second step	195		18.18	19.51
	Total loss			100.00	100.00
	Residue			00.00	00.00
$[Ni_2(salen)(CH_3CO_2)_2(AAP)_2]$ (**1**) $C_{46}H_{46}N_8Ni_2O_8$	First step	287	$C_{20}H_{14}N_2O_2$	31.00	32.87
	Second step	395	$C_{22}H_{26}N_6O_2$	43.00	42.504
	Third step	508	$2CH_3CO\ C_4H_6O_2$	10.50	9.002
	Total loss			84.50	84.376
	Residue		2NiO	15.50	15.624
$[Ni_2(salen)(CH_3CO_2)_2(PDCH)_2] \cdot 2H_2O$ (**2**) $C_{34}H_{42}N_4Ni_2O_8S_4$	First step	75	$2H_2O$	5.00	4.09
	Second step	216	$C_{10}H_{18}N_2S_4$	32.50	33.45
	Third step	323			
	Fourth step	404	$C_{20}H_{14}N_2O_2$	38.00	35.71
	Fifth step	543	$C_4H_6O_2$	9.50	9.78
	Total loss			85.00	83.03
	Residue		Ni_2O_2	15.00	16.97
$[Cu_2(salen)(CH_3CO_2)_2] \cdot 2H_2O$ (**3**) $C_{24}H_{24}Cu_2N_2O_8$	First step	103	$2H_2O$	6.41	6.05
	Second step	206, 235, 328	$C_{20}H_{14}N_2O_2$	52.04	52.78
	Third step	460, 556	$C_4H_6O_2$	15.33	14.46
	Total loss			73.78	73.29
	Residue		2CuO	26.22	26.71
$[Co(salen)(CH_3CO_2)] \cdot H_2O$ (**4**) $C_{22}H_{19}CoN_2O_5$	First step	143	H_2O	5.00	4.00
	Second step	218 281	$C_{20}H_{14}N_2O_{1.5}$	77.00	68.02
	Third step	525	CH_3CO		9.56
	Total loss			82.00	81.58
	Residue		$0.5\ Co_2O_3$	18.00	18.42


TGA
%
DTG
mg/min
100
80
50
0.0
2.0
0.0
1.0
-10.0
Ni(CH3CO2)2·4H2O
100
400
600
800
Temp (°C)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%
DTG
mg/min
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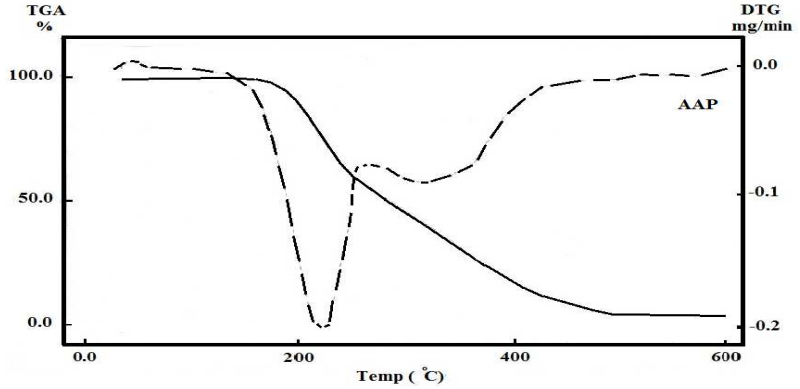
50.0
0.0
0.0
-0.5
-0.10
-0.15
H2salen
0.0
200
400
600
Temp (°C)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%
DTG
mg/min
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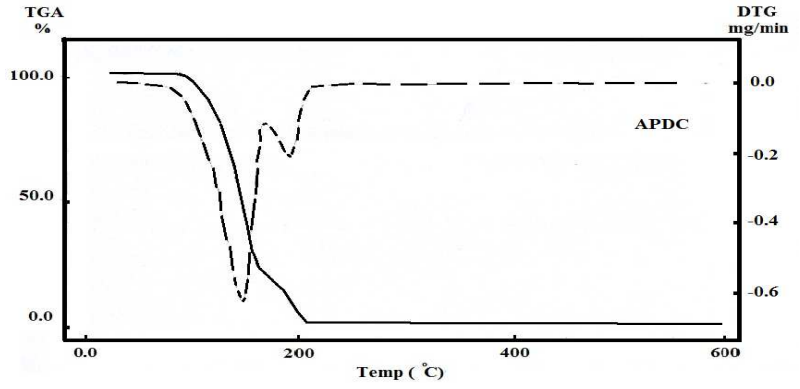
0.0
0.0
-0.1
-0.2
AAP
0.0
200
400
600
Temp (°C)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%
DTG
mg/min
100.0
50.0
0.0
0.0
-0.2
-0.4
-0.6
APDC
0.0
200
400
600
Temp (°C)

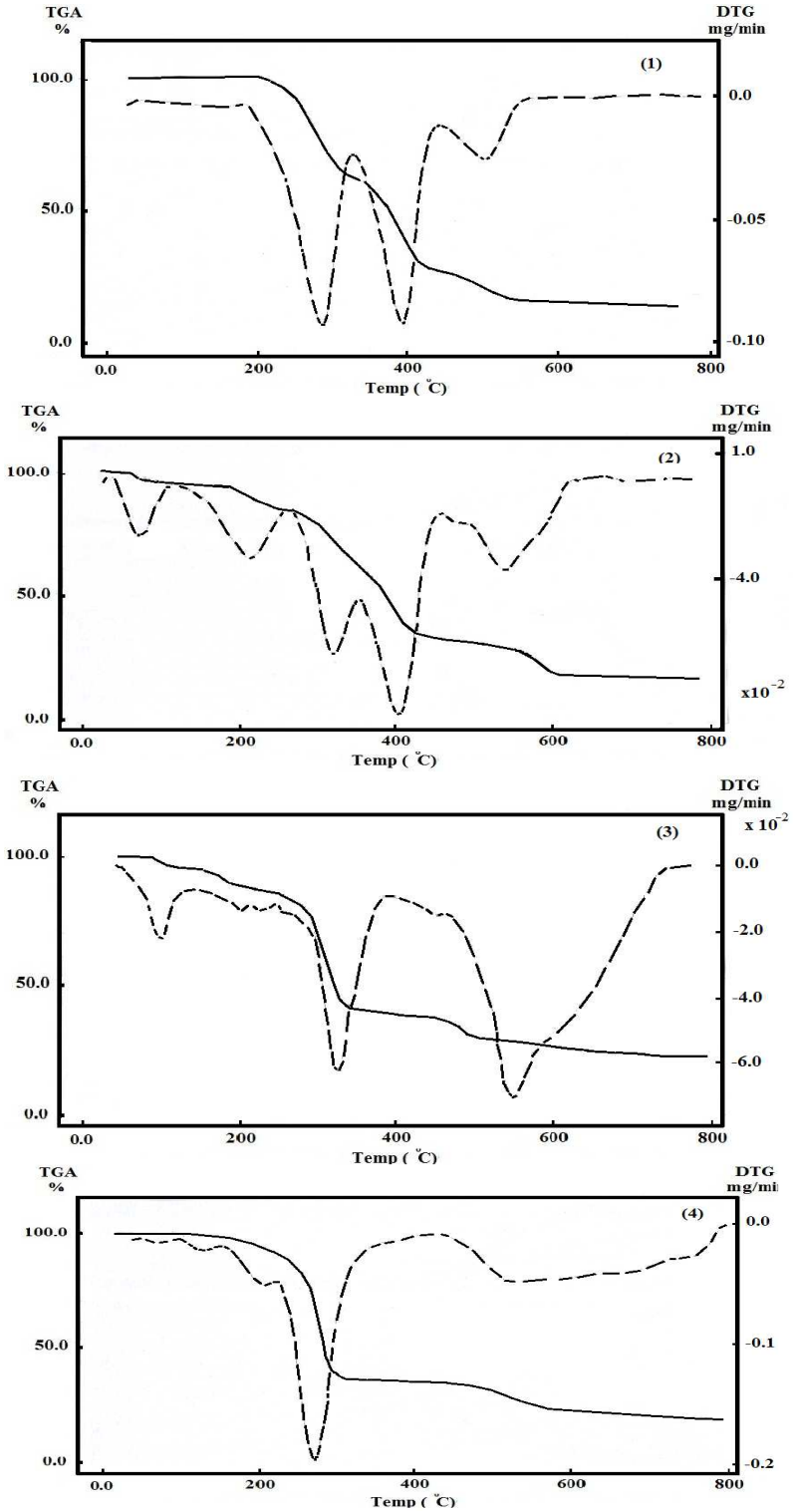

Fig. 2. Thermogravimeteric (TGA) and derivative (DTG) of Nickel(II) acetate, AAP, APDC, H_2salen and the prepared metal complexes (1, 2, 3, 4)

The TG curve of Cu(II) complex (**3**) showed three main decomposition stages at 103, (206, 235, 328) and (460, 556) ^{o}C. The first weight loss peak of 6.41% (calculated 6.05%) corresponds to the loss of the two hydrated water molecules from the complex. The second main stage of decomposition proceeds at three maximum temperatures with a total weight loss of 52.04% and might be attributed to the loss of organic salen molecule (calculated 52.78%). The third main step of decomposition proceeds at two maximum temperatures with a total weight loss of 15.33 % (calculated 14.46 %) and might be attributed to the loss of two acetyl units of the chelated acetato ligands. The total weight loss associated with these steps (73.78%) is in good agreement with the calculated value of 73.29%.

Decomposition of [Co(salen)(CH_3CO_2)]·H_2O (**4**) also, occurred in three main steps. Water is lost at 143 °C with 5.00% weight loss (calculated 4.00%). The second step of decomposition proceeded at two maximum temperatures (218, 281 °C) associated with a calculated weight loss of 68.02% and might be attributed to the loss of coordinated salen molecule. The third degradation step was observed as one decomposition peak at 525 °C with a calculated weight loss of weight 9.56 % and might be attributed to the loss of acetyl unit of the chelated acetato ligands. The total weight loss associated with the second and third steps (77.00%) is in good agreement with the calculated value of 77.58%.

3.5. Proposed structure of the complexes

The proposed structures of the complexes based on the analytical data are given in Figs. 3-6. As illustrated in the discussion, some differences have been observed and indicated due to the differences in the nature of metal ions and type of ligands used as well as the experimental conditions.

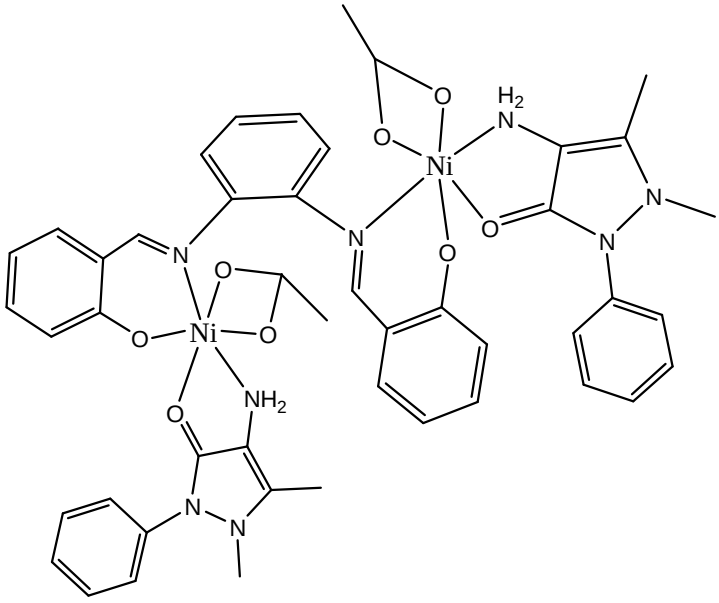

Fig. 3. Suggested structure of the distorted octahedral configuration of Ni(II)-mixed ligand complex (1) containing, salen, AAP and acetate

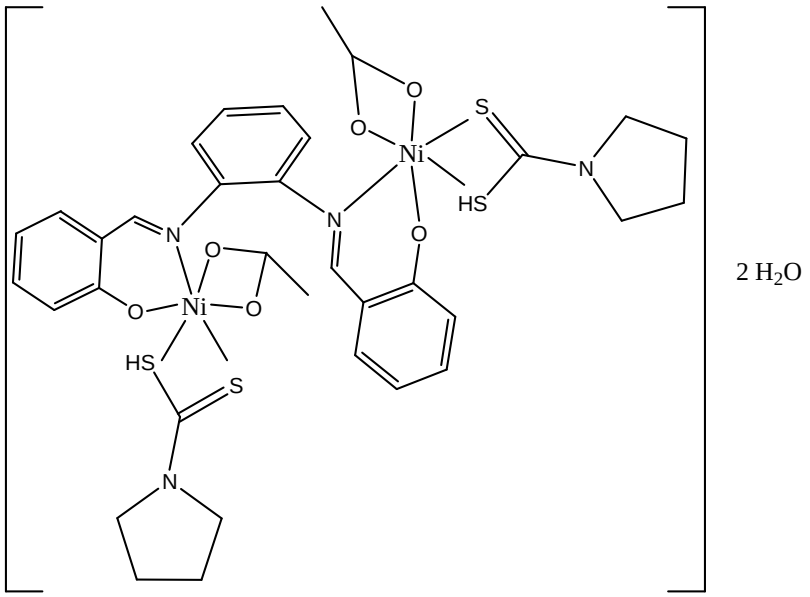

Fig. 4. Suggested structure of the distorted octahedral configuration of Ni(II)-mixed ligand complex (2) containing, salen, PDCH and acetate

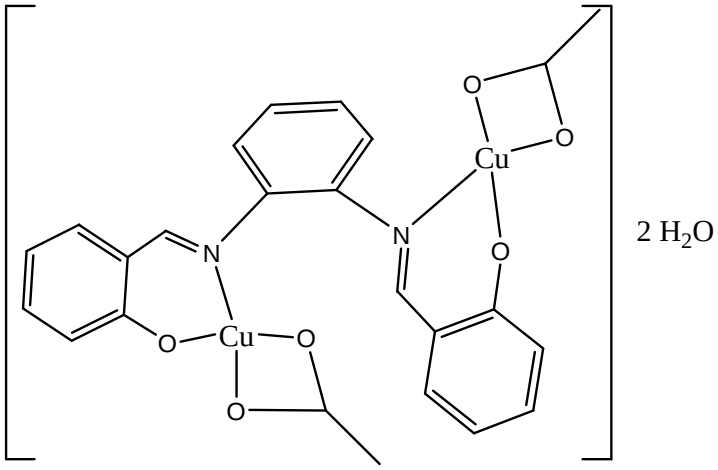

Fig. 5. Suggested structure of Cu(II)-mixed ligand complex (3) containing salen and acetate

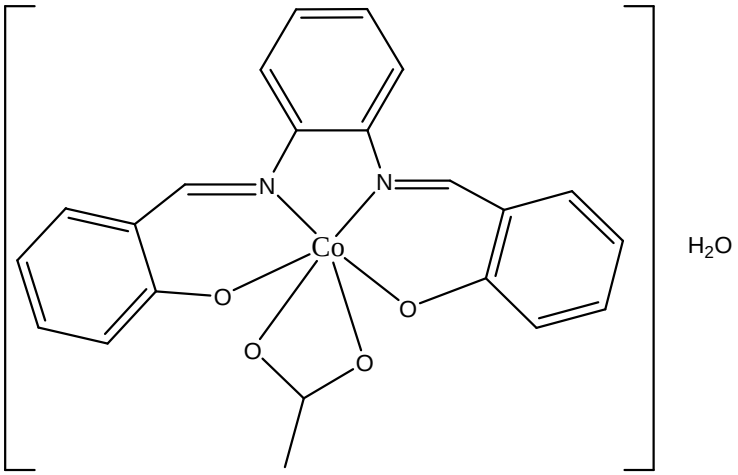

Fig. 6. Suggested structure of the distorted octahedral configuration of Co(III)-mixed ligand complex (4) containing salen and acetate

The Ni(II) ions in complexes **1** and **2** were proposed to have a distorted octahedral environment. The six coordination sites are distributed between salen ($^{-}$ONNO^{-}), acetato (O,O^{-}) and AAP (O of carbonyl groups, N of NH_2 group) in a neutral way as in complex **1** or PDCH (S,S) as in complex **2**, as shown in Figs. 3 and 4. According to the forgoing discussion, ammonium pyrrolidinedithiocarbamate (APDC) was converted in the reaction mixture into pyrrolidinedithiocarbamic acid (PDCH) and coordinated with Ni(II) via S of SH group and S of C=S group as a chelating ligand in complex **2**.

The neutral binuclear Cu(II) complex (**3**) is obtained with ionized OH groups of salen and acted as bridging ligand via O^{-} and N (imino) to two Cu(II) ions. In this complex, two molecules of acetato ligands are bounded to Cu(II) ions with a distorted square planar geometry, as shown in Fig. 5.

In Co(III) complex (**4**), salen coordinated with central ion in the $^{-}$ONNO^{-} manner. The remaining two sites were occupied with a chelating acetato group to produce a distorted octahedral geometry, Fig. 6.

3.6. Antimicrobial activity

The *in vitro* antibacterial activity of the title compounds were tested against four bacterial strains, *Bacillus subtillis* and *Staphylococcus aureus* as gram positive bacteria and *Escherichia coli* and *Pseudomonas aeroginosa* as gram negative bacteria by agar well diffusion method, Table 4. Complexes **1** and **2** did not show any activity against *Bacillus subtillis, Staphylococcus aureus and Pseudomonas aeroginosa* but showed moderate activity against *Escherichia Coli*. Complexes **3** and **4** showed an activity against *Bacillus subtillis* and *Staphylococcus aureus* and moderate activity against *Escherichia coli* and *Pseudomonas aeroginosa*. The remarkable activity of H_2salen and complexes may be due to the presence of the azomethine, hydroxyl groups and structural changes in the molecules. The antibacterial activities of Cu(II) and Co(II) complexes could be further studied for the treatment of infections caused by any of the above organisms.

Table 4. Antibacterial activity of H_2salen and its complexes

Compounds	Antibacterial activity (inhibition zone diameter in mm)			
	Bacteria			
	Bacillus subtillis, G^+	*Staphylococcus aureus*, G^+	*Esherichia. Coli*, G−	*Pseudomonas aeroginosa*, G−
H_2alen	6	5	-	-
$[Ni_2(salen)(CH_3CO_2)_2(AAP)_2]$ (**1**)	-	-	10	-
$[Ni_2(salen)(CH_3CO_2)_2(PDCH)_2]\cdot 2H_2O$ (**2**)	-	-	12	-
$[Cu_2(salen)(CH_3CO_2)_2]\cdot 2H_2O$ (**3**)	18	19	11	11
$[Co(salen)(CH_3CO_2)]\cdot H_2O$ (**4**)	16	18	12	12

CONCLUSION

H_2salen ligand and the formed complexes with metal acetates were synthesized and characterized by elemental analysis, conductivity measurements, IR and UV/VIS spectra as well as thermal analysis. Based on the obtained experimental data and literature indications, the structural formulae to these compounds were suggested and formulated as $[Ni_2(salen)(CH_3CO_2)_2(AAP)_2]$ (**1**), $[Ni_2(salen)(CH_3CO_2)_2(PDCH)_2]\cdot 2H_2O$ (**2**), $[Cu_2(salen)(CH_3CO_2)_2]\cdot 2H_2O$ (**3**), $[Co(salen)(CH_3CO_2)]\cdot(H_2O)$ (**4**),

According to the IR data of the compounds, the H_2salen Schiff base ligand behaves in the prepared mononuclear or binuclear mixed ligand complexes as a dianionic tetradentate $^-$ONNO$^-$ ligand. The four bonding sites are the oxygen atom of the ionized phenolic OH and the nitrogen atom of the azomethine C=N groups. H_2salen behaves as a bridging tetradentate ligand to two M(II) atoms in complexes **1**, **2** and **3**. The acetato ligands act as chelating ligands to all complexes.

In the mixed ligand complex **1**, AAP acts as a neutral bidentate ligand via N of the amino group and O atom of –C=O group. In the mixed ligand complex **2**, PDCH behaves as a neutral bidentate ligand with Ni(II) via S atoms of C=S and SH groups.

Thermal studies to the free ligands and the prepared complexes showed the mixed ligand complexes decomposed at higher temperatures in comparison with the free ligands.

The biological activity test results showed that the metal complexes have antibacterial activity against some bacterial strains except for Ni(II) complexes. The ligands and metal complexes (Cu(II) and Co(III)) might be effective as antimicrobial agents bacteria.

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