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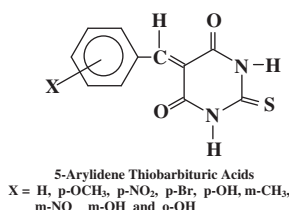
Spectral, coordination and thermal properties of 5-arylidene thiobarbituric acids

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HIGHLIGHTS

- 5-Arylidene thiobarbituric acids and their complexes were synthesized.
- The stereochemistry and mode of bonding were investigated.
- The ligands were of bidentate and tridentate nature.
- The complexes were of octahedral configuration with certain thermal stability.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthesis of 5-arylidene thiobarbituric acids containing different functional groups with variable electronic characters were described and their Co²⁺, Ni²⁺ and Cu²⁺ complexes. The stereochemistry and mode of bonding of 5-(substituted benzylidene)-2-TBA complexes were achieved based on elemental analysis, spectral (UV–VIS, IR, ¹H NMR, MS), magnetic susceptibility and conductivity measurements. The ligands were of bidentate and tridentate bonding through S, N and O of pyrimidine nucleolus. All complexes were of octahedral configuration. The thermal data of the complexes pointed to their stability. The mechanism of the thermal decomposition is discussed. The thermodynamic parameters of the dissociation steps were evaluated and discussed.

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Introduction

Pyrimidines are one of the most important compounds due to their biological activity and are involved in the structure of nucleic acid in living systems. The nucleic acid is related to antimetabolites used in anticarcinogenic chemotherapy. Barbiturates and thiobarbiturates are used as hypnotic drugs and produce depressive effect on central nervous system [1,2]. Most of the pyrimidines are with antimicrobial, anti-inflammatory, and anti-tumor activities properties [2]. Serum lipid peroxidation was measured by thiobarbituric acid reactive material method during physical exercise of different duration [3]. In our laboratory, a series of papers were appeared concerning the structural chemistry of biologically active

barbiturate compounds using different instruments of investigations [4–30].

In this paper, we prepare some substituted 5-(arylidene) thiobarbituric acids and their complexes. The mode of investigation is based on elemental analysis, magnetic moment, spectral methods (UV–VIS, IR), mass spectra, NMR and thermal analysis were recorded and the thermodynamic parameters were evaluated and discussed.

Experimental

Synthesis of the ligands

5-Arylidene thiobarbituric acids were prepared by condensation of thiobarbituric acid (0.1 mol) with the selected aromatic aldehydes (0.1 mol). Both were purchased from BDH Company and were used without further purification. The condensation was car-

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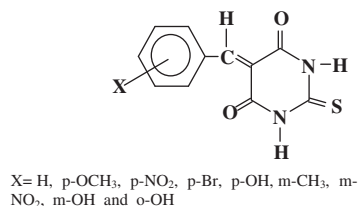


Fig. 1. A general skeleton of the 5-arylidene thiobarbituric acid.

ried out in EtOH. The obtained compounds were filtered off and crystallized in 75% (v/v) EtOH, then dried in a vacuum desiccator over (P₄O₁₀).

The elemental analysis of the compounds (C, H, N) were carried out at the central micro-analytical laboratory, Faculty of Science, Cairo University. A general skeleton of the prepared compounds is given in Fig. 1.

The molecular structure of the investigated compounds was optimized with PM3 semi-empirical method implemented in Gaussian 03W package. The corresponding geometry was optimized without any geometry constraints for full geometry optimization. Frequency calculation was executed simultaneously, and no imaginary frequency was found, indicating minimal energy structures. The quantum chemical parameters such as the highest occupied molecular orbital energy (*E*_{HOMO}), the lowest unoccupied molecular orbital energy (*E*_{LUMO}), energy gap (ΔE), total energy (TE), dipole moment (μ), electronegativity (χ), chemical potential

Table 3
The bond distances for the optimized compounds using PM3 method.

Bond	Compound, X=					
	H	m-CH ₃	m-NO ₂	m-OH	o-OH	p-Br
R(1,2)	1.221	1.242	1.222	1.220	1.221	1.221
R(1,3)	1.434	1.406	1.430	1.434	1.434	1.433
R(1,9)	1.473	1.477	1.475	1.474	1.472	1.474
R(2,12)	2.761	2.756	2.745	2.758	2.743	2.754
R(3,4)	1.408	1.393	1.411	1.408	1.408	1.409
R(4,5)	1.636	1.601	1.632	1.635	1.637	1.634
R(4,6)	1.406	1.395	1.407	1.406	1.405	1.406
R(6,7)	1.432	1.400	1.431	1.432	1.434	1.431
R(7,8)	1.220	1.244	1.219	1.219	1.219	1.219
R(7,9)	1.485	1.488	1.487	1.485	1.484	1.486
R(9,10)	1.355	1.354	1.352	1.354	1.355	1.354
R(10,11)	1.452	1.449	1.456	1.455	1.451	1.454
R(11,12)	1.397	1.400	1.397	1.396	1.400	1.398
R(11,16)	1.407	1.407	1.403	1.404	1.416	1.409
R(12,13)	1.392	1.395	1.391	1.392	1.388	1.393
R(13,14)	1.389	1.392	1.387	1.387	1.391	1.378
R(14,15)	1.394	1.402	1.402	1.404	1.388	1.383
R(14,17)						1.866
R(15,16)	1.386	1.395	1.396	1.397	1.402	1.388
R(15,17)		1.481	1.501	1.369		
R(16,17)					1.365	
R(17,18)			1.214			
R(17,19)			1.215			

(Pi), were calculated, Tables 1–3. The optimized structures for the studied compounds are represented in Fig. 2.

Table 1
The calculated quantum chemical parameters for the optimized compounds using PM3 method.

Compound, X=	Parameter								
	<i>E</i> _{HOMO} (eV)	<i>E</i> _{LUMO} (eV)	ΔE (eV)	μ (D)	Hardness (eV)	Softness (eV ^{−1})	Chem. pot. (eV)	X	Total energy
H	−9.305	−1.969	7.336	5.240	3.668	0.273	−5.637	5.637	−0.106
m-CH ₃	−9.240	−1.604	7.636	4.612	3.818	0.262	−5.422	5.422	−0.336
m-NO ₂	−9.560	−2.347	7.212	2.865	3.606	0.277	−5.953	5.953	−0.414
m-OH	−9.314	−1.976	7.338	5.601	3.669	0.273	−5.645	5.645	−2.037
o-OH	−9.226	−1.836	7.390	6.593	3.695	0.271	−5.531	5.531	−2.024
p-Br	−9.383	−2.092	7.291	4.046	3.646	0.274	−5.738	5.738	0.259
p-NO ₂	−9.602	−2.503	7.099	2.751	3.550	0.282	−6.053	6.053	−0.380
p-OCH ₃	−9.245	−1.919	7.327	6.606	3.663	0.273	−5.582	5.582	−1.788
p-OH	−9.268	−1.945	7.323	5.314	3.662	0.273	−5.607	5.607	−2.108

Table 2
The calculated Mulliken atomic charge densities for the optimized compounds using PM3 method.

Atom	Compound, X=									
	H	m-CH ₃	m-NO ₂	m-OH	o-OH	p-Br	p-NO ₂	p-OCH ₃	p-OH	
1 C	0.314	0.354	0.310	0.313	0.316	0.312	0.306	0.317	0.318	
2 O	−0.336	−0.316	−0.341	−0.333	−0.339	−0.335	−0.332	−0.341	−0.345	
3 N	0.049	−0.336	0.051	0.048	0.049	0.050	0.051	0.049	0.050	
4 C	−0.105	0.140	−0.110	−0.105	−0.103	−0.106	−0.110	−0.105	−0.105	
5 S	−0.234	−0.177	−0.211	−0.232	−0.241	−0.227	−0.207	−0.240	−0.239	
6 N	0.057	−0.331	0.059	0.056	0.056	0.057	0.058	0.058	0.059	
7 C	0.288	0.344	0.283	0.287	0.291	0.286	0.281	0.290	0.290	
8 O	−0.331	−0.326	−0.321	−0.328	−0.328	−0.328	−0.321	−0.336	−0.335	
9 C	−0.277	−0.237	−0.257	−0.271	−0.288	−0.269	−0.243	−0.289	−0.291	
10 C	0.146	0.084	0.127	0.140	0.163	0.137	0.111	0.157	0.159	
11 C	−0.128	−0.106	−0.138	−0.087	−0.165	−0.119	−0.059	−0.170	−0.174	
12 C	−0.074	−0.062	−0.027	−0.119	−0.045	−0.072	−0.109	−0.038	−0.026	
13 C	−0.110	−0.135	−0.126	−0.066	−0.149	−0.088	−0.009	−0.154	−0.212	
14 C	−0.059	−0.098	0.020	−0.155	−0.018	−0.084	−0.381	0.133	0.147	
15 C	−0.119	−0.078	−0.422	0.085	−0.217	−0.098	−0.025	−0.209	−0.164	
16 C	−0.060	−0.096	0.026	−0.110	0.146	−0.056	−0.091	−0.012	−0.017	
17 C,N,O and Br		−0.181	1.308	−0.224	−0.228	0.018	1.302	−0.182	−0.217	
18 O			−0.592				−0.593	0.044		
19 O			−0.597				−0.590	0.133		

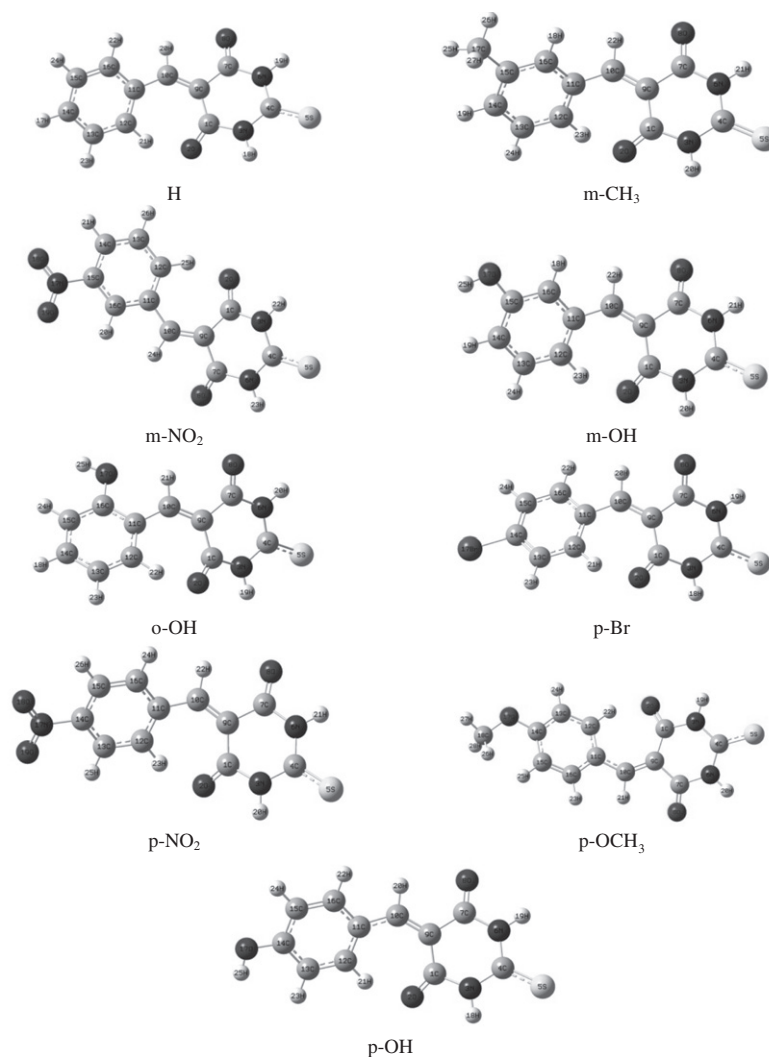


Fig. 2. The optimized structure for the compounds.

Table 4
Analytical data for the ligands.

Compound	Color	Formula	Melting point (°C)	% Calculated/(found)			
				C	H	N	S
5-Benzylidene thiobarbituric acid	Yellow	C ₁₁ H ₈ N ₂ O ₂ S	250	56.88 (56.60)	3.45 (3.60)	12.06 (12.10)	13.80 (13.75)
5-Salicylidene thiobarbituric acid	Pale yellow	C ₁₁ H ₈ N ₂ O ₃ S	300	53.22 (53.10)	3.25 (3.20)	11.28 (11.00)	12.91 (12.90)
5-(3-Hydroxybenzylidene) thiobarbituric acid	Orange	C ₁₁ H ₈ N ₂ O ₃ S	264	53.22 (53.50)	3.25 (3.35)	11.28 (11.10)	12.89 (12.91)
5-(3-Anisalidine) thiobarbituric acid	Yellow	C ₁₂ H ₁₀ N ₂ O ₃ S	238	54.65 (55.10)	3.84 (3.50)	10.68 (10.50)	12.22 (12.21)
5-(3-Nitrobenzylidene) thiobarbituric acid	Yellow	C ₁₁ H ₇ N ₃ O ₄ S	260	47.65 (47.90)	2.54 (2.30)	15.15 (15.10)	11.56 (11.54)
5-(4-Hydroxybenzylidene) thiobarbituric acid	Orange	C ₁₁ H ₈ N ₂ O ₃ S	>360	53.22 (52.90)	3.25 (3.10)	11.28 (11.40)	12.91 (12.85)
5-(4-Anisalidine) thiobarbituric acid	Orange	C ₁₂ H ₁₀ N ₂ O ₃ S	298	54.65 (54.30)	3.84 (3.70)	10.68 (10.30)	12.22 (12.19)
5-(4-Nitrobenzylidene) thiobarbituric acid	Yellowish white	C ₁₁ H ₇ N ₃ O ₄ S	217	47.65 (47.40)	2.54 (2.40)	15.15 (15.15)	11.56 (11.52)
5-(4-Bromobenzylidene) thiobarbituric acid	Canary yellow	C ₁₁ H ₇ N ₂ O ₂ SBr	>360	42.46 (42.30)	2.27 (2.30)	9.00 (9.00)	10.30 (10.26)

Synthesis of complexes

0.01 mol of each of cobalt(II), nickel(II), and copper(II) as chloride, were dissolved in mixed solvents of methanol and ammoniacal solution. These were mixed with methanolic solution of 0.02 mol of 5-arylidene-thio-barbituric acid. The reaction mixture was refluxed for 1 hr and left over night where the complexes were precipitated and separated by filtration and washed by methanol and dried in a vacuum desiccator over anhydrous CaCl₂. The formula, color and melting point of the ligands are given in Table 4.

Table 5 collects the analytical data for the prepared complexes, where the metal contents were determined by the usual complexometric titration methods [31], after decomposition with H₂O₂ and HNO₃.

Instruments and working procedures

Electronic absorption spectra

The spectrophotometric measurements of the ligands in the visible and ultraviolet regions in the wavelength range 190–600 nm

Table 5
Analytical data for Co(III), Ni(III) and Cu(III) 5-(o, m and p hydroxybenzylidene)-2-TBA complexes.

Complexes	Color	Formula	Conductance ¹	μ_{eff} 298 K	m.p (°C)	%Calculated/(found)		
						N	M	S
Co-I	Pale brown	Co (C ₂₂ H ₁₄ N ₄ O ₆ S ₂)·5H ₂ O	11	5.32	333	8.71 (8.74)	9.16 (8.217)	9.96 (9.58)
Ni-I	Pale brown	Ni (C ₂₂ H ₁₄ N ₄ O ₆ S ₂)·5H ₂ O·CH ₃ OH	7	3.10	338	8.64 (8.70)	8.69 (7.46)	9.49 (9.47)
Cu-I	Gray	Cu (C ₂₂ H ₁₄ N ₄ O ₆ S ₂)·4H ₂ O·Cl	41	2.10	285	8.41 (8.50)	9.53 (9.39)	9.62 (9.59)
Co-II	Pale brown	Co (C ₂₂ H ₁₄ N ₄ O ₆ S ₂)·4H ₂ O·CH ₃ OH	9	5.11	>360	8.52 (8.58)	8.97 (9.30)	9.99 (9.93)
Ni-II	Pale burble	Ni (C ₃₃ H ₂₂ N ₆ O ₉ S ₃)·4H ₂ O	11	3.07	>360	9.62 (9.50)	6.72 (7.45)	11.01 (11.00)
Cu-II	Pale gray	Cu (C ₂₂ H ₁₄ N ₄ O ₆ S ₂)·4H ₂ O·CH ₃ OH	5	2.07	>360	8.46 (8.50)	9.60 (9.26)	9.74 (9.69)
Co-III	Purple	Co (C ₂₂ H ₁₄ N ₄ O ₆ S ₂)·2H ₂ O·CH ₃ OH	11	5.28	300	9.02 (9.10)	9.49 (9.40)	10.32 (10.28)
Ni-III	Purple	Ni (C ₂₂ H ₁₄ N ₄ O ₆ S ₂)·4H ₂ O	4	3.01	300	8.96 (9.11)	9.39 (7.21)	10.26 (10.22)
Cu-III	Dark violet	Cu (C ₂₂ H ₁₄ N ₄ O ₆ S ₂)·4H ₂ O·CH ₃ OH	9	2.13	270	8.46 (8.50)	9.60 (9.39)	9.68 (9.43)

¹ Conductance of 10–3 M in DMSO ($\mu\text{mho cm}^2 \text{mol}^{-1}$).**Table 6**
Assignment of electronic spectrum of Co(II), Ni(II) and Cu(II) complexes.^a

Complexes	Bands (cm ⁻¹)	Assignments
Co(II)-5-(salicylidine)-2-TBA	18,000	$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$
Ni(II)-5-(salicylidine)-2-TBA	15,455	$^3A_{2g} \rightarrow ^3T_{1g}(F)$
	1836	$^3A_{2g} \rightarrow ^3T_{1g}(P)$
Cu(II)-5-(salicylidine)-2-TBA	17,142	$^2T_{2g} \rightarrow ^2E_g$
Co(II)-5-(m-hydroxybenzylidene)-2-TBA	27,530	$^4T_{1g} \rightarrow ^4A_{2g}(F)$
	15,384	$^4T_{1g} \rightarrow ^4T_{1g}(P)$
Ni(II)-5-(m-hydroxybenzylidene)-2-TBA	19,565	$^3A_{2g} \rightarrow ^3T_{1g}(P)$
Cu(II)-5-(m-hydroxybenzylidene)-2-TBA	18,711	$^2T_{2g} \rightarrow ^2E_g$
Co(II)-5-(p-hydroxybenzylidene)-2-TBA	15,544	$^4T_{1g} \rightarrow ^4A_{2g}(F)$
	18,405	$^4T_{1g} \rightarrow ^4T_{1g}(P)$
Ni(II)-5-(p-hydroxybenzylidene)-2-TBA	17,006	$^3A_{2g} \rightarrow ^3T_{1g}(P)$
Cu(II)-5-(m-hydroxybenzylidene)-2-TBA	18,367	$^2T_{2g} \rightarrow ^2E_g$

^a The geometries of all complexes are of octahedral configuration.

were made with computerized UV–visible spectrophotometer (Shimadzu Corporation 1601 (PC).

Infrared spectra

Infrared spectra of the ligands and their complexes were recorded using Perkin–Elmer spectrophotometer model 1430 covering the frequency range 200–4000 cm⁻¹.

Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric measurements (TGA) were performed on a DII Pont 9900 computerized thermal analyzer at the Physics Department, Faculty of Science, El-Moenofia University. The heating rate used was 10°/min. 60 mg of the sample was placed in a platinum crucible. Dry nitrogen was flowed over the sample at a rate 10 cc/min and a chamber cooling water flow rate was 101/h. The speed was 5 mm/min.

Mass spectra

Mass spectra of the ligands were obtained using a mass spectrophotometer (EI) Q1MS LMR UP LR at the National Research Center, Cairo.

¹H NMR

¹H NMR was recorded out in Ottawa–Carleton Chemistry Institute, Carleton University, Canada.

Magnetic susceptibility measurements

Hg[Co(SCN)₄] complex was used for calibrating the Gouy tubes. Some of the complexes were measured using the Faraday method. Diamagnetic corrections were calculated from the data given by Figgis and Lewis [32].

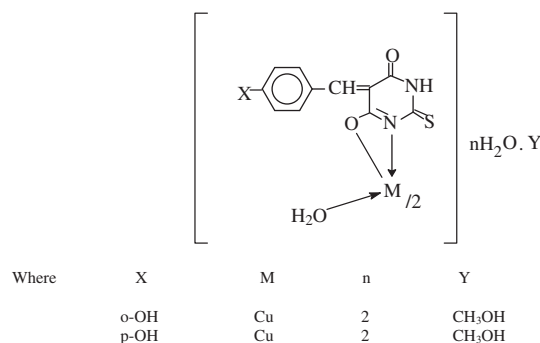
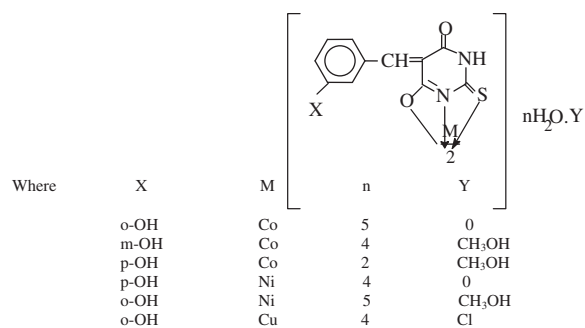
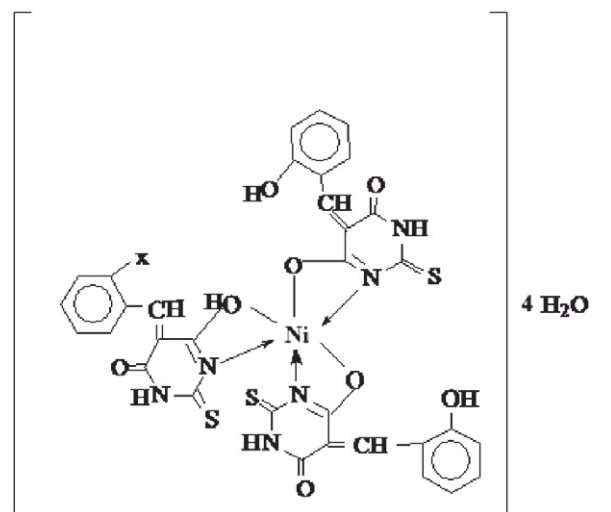
**Fig. 3.** Postulated structures of metal-5-(salicylidine)-2-thiobarbituric acid complexes.

Table 7¹H NMR signals of 5-(substituted benzylidene) thiobarbituric acid in DMSO-d₆.

Compounds	δ (ppm) for free ligand	Assignments
5-(Salicylidene) thiobarbituric acid	13.3	O—H
	12.3	N—H
	7.1	C—H
	7.0, 7.25	C ₆ —H ₄
	5.0	Free O—H
	3.75–4.2 (br)	phenolic
	2.1	H-bond of O—H
5-(3-Hydroxybenzylidene) thiobarbituric acid	12.45	O—H
	12.3	N—H enol
	11.7	N—H keto
	8.1	C—H
	7.7, 7.4, 7, 6.5	C ₆ —H ₄
	5.9	OH phenolic
	2.0	SH
5-(4-Hydroxybenzylidene) thiobarbituric acid	12.35	O—H
	12.25	N—H enol
	11.6	N—H keto
	8.25	C—H
	8.4, 6.9	C ₆ —H ₄
	5.85	OH phenolic
	2.0	SH

Table 8a

Mass spectra for 5-(benzylidene)2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
C=S + NH	59	59.1
C=S + 2NH	76	76.1
2NH + C=O + C=S	102	102.1
Hetero ring – C=O	116	116.1
Hetero ring	144	144
Hetero ring + C ₂ H ₂ group	172	172
Base peak of ligand	232	232

Table 8b

Mass spectra for 5-(salicylidene)2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
C=S + NH	59	59
2NH + NH + C=O	87	88
Hetero ring – C=O	116	116
Hetero ring	144	143
Hetero ring + C ₂ H ₂ group	172	172.1
Ligand – H ₂ O group	230	230

Table 8c

Mass spectra for 5-(3-hydroxybenzylidene) 2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
C=S + NH	59	59
C=S + NH + C=O	87	89
Hetero ring – C=O	116	116.1
Hetero ring	144	144
Ligand – OH group	231	231
Base peak of ligand	248	248

Conductance measurements

The conductance measurements of 1×10^{-3} M solution of the compounds in DMSO were performed using a WTW model LF-42 Conductivity Bridge fitted with a LTA-100 conductivity cell.

Table 8d

Mass spectra for 5-(3-anisylidene)2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
SH + C=O	61	63
SH + C=O + NH	76	77.1
SH + C=O + NH + C=N	102	103
Hetero ring + CH	157	164.1
Hetero ring + C ₂ H ₂	170	172
Ligand – OCH ₃ Group	231	231
Base peak of ligand	262	262.1

Table 8e

Mass spectra for 5-(3-nitrobenzylidene)2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
C=S + NH	59	59
C=S + NH + OH	76	75
HO + C=S + NH + C=N	102	101.1
Hetero ring – C=O	116	116
Hetero ring	144	144.1
Ligand – NO ₂ group	231	230
Ligand – OH group	260	260.1
Base peak of ligand	278	277.1

Table 8f

Mass spectra for 5-(4-hydroxybenzylidene)2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
SH + C=O	61	63
C=O + NH + CSH	87	89.2
Hetero ring – C=O	116	118
Hetero ring – C	132	132.1
Hetero ring	144	150
Ligand – OH group	231	231.2
Base peak of ligand	248.27	248

Table 8g

Mass spectra for 5-(4-anisylidene) 2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
C=S + NH	59	59
C=S + NH + C=O	87	89
OH + C=S + NH + C=N	102	102
Hetero ring – C=O	116	117
Hetero ring	144	145
Hetero ring + C ₂ H ₂	170	172
Ligand – OCH ₃ group	231	230
Base peak of ligand	262	262

Table 8h

Mass spectra for 5-(4-nitrobenzylidene)2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
C=S + NH	59	59
C=S + NH + OH	76	75
OH + C=S + NH + C=N	102	101
Hetero ring – C=O	116	116
Hetero ring	144	149
Hetero ring + C ₂ H ₂	170	179
Ligand – NO ₂ group	231	230
Ligand – OH group	260	260
Base peak of ligand	277	277

Table 8i

Mass spectra for 5-(bromobenzylidene)2-thiobarbituric acid.

Assignments	M.Wt.	M/e peak
C=S + NH	59	59.1
C=S + 2NH	76	75.2
2NH + C=O + C=S	102	101
Hetero ring – C=O	144	153
Hetero ring	170	172
Hetero ring + C ₂ H ₂ group	231	231.1
Base peak of ligand	312	312

Results and discussions

Electrical conductivity

The molar conductance of the synthesized complexes in DMSO, Table 5, indicated non-electrolyte behavior except Cu-5-(salicylidine)2-TBA behaves as A[−]B⁺ electrolytes [33].

Infrared spectra

It was necessary to investigate the infrared spectra of the prepared metal complexes compared with those of the free ligand to determine the mode of chelation [34]. The complexes may increase or decrease the vibrational frequency of coordinated functional groups depending on the strength of π -interaction occurring between the metal ion and π -electron of the functional group [16].

5-(Salicylidine)2-TBA complexes

- The broad bands appeared, at 3633–2722, 3633–2766 and 3633–2766 cm^{−1} for Co(II), Ni(II) and Cu(II) complexes, respectively, may be due to the possible existence of water molecule.
- The ν of O–H and N–H groups not detected in the formed complexes may be due to the involvement in the broad band of H₂O.
- The weak ν S–H appeared at 2633 cm^{−1} for 5-(salicylidine) TBA becomes more weaker for Co(II), Ni(II), and Cu(II) complexes, i.e. play some role in these complexes.
- The C=N and C=O groups appeared at the range 1544–1677 cm^{−1} for the ligand undergoes considerable shift to lower cm^{−1}, which indicated their entrance in the complexation process as a chelation site [35].
- The C=S group appeared at 1456 cm^{−1} for the free ligand subjected to positive shift to 1489 cm^{−1} for all complexes.
- New bands appeared at 597, 600, 600,594 and 592 cm^{−1} of very weak appearance for all complexes, respectively, may be due to the formation of M–O bond. Other medium new band appeared at 533 cm^{−1}, could be assigned as M–N band. The M–S band is not detected due to the weak bond formed and/or the hard-soft interaction behavior [36].

5-(*m*-Hydroxybenzylidene)2-TBA complexes

- Broad bands at 3656–2686, 3633–2766 and 3633–2766 cm^{−1} for Co(II), Ni(II) and Cu(II) complexes, respectively, could be due to H₂O moiety.
- The weak ν S–H, at 2633 cm^{−1} for the ligand is not changed in the formed complexes, and may be due to its stability in the ligand and the complexes.
- The ν of C=O and C=N appeared at 1644–1555 cm^{−1} for the ligand gave negative shift in the formed complexes may be due to the entrance of this group in the chelation processes.

- The ν C=S band appeared at 1444 cm^{−1} for the ligand is unchanged or weakly shifted on complexation, with one exception for Co(II) complex [32].
- Medium new bands in all complexes could be assigned as ν M–O (522–539 cm^{−1}) while the very weak one at (500–517 cm^{−1}) is assigned as ν M–N [36].

5-(*p*-Hydroxybenzylidene)2-TBA complexes

Nearly similar spectral bands were recorded as the previous complexes:

- Broad ν H₂O bands were given 3656–3–2655, 3677–2700 and 3666–2678 cm^{−1} for Co(II), Ni(II) and Cu(II) complexes, respectively.
- The weak ν S–H at 2611 cm^{−1} band for the ligand gives positive shift to 2633 cm^{−1} on complexation may be due to the increasing of nucleophilicity of the sulfur atom.
- The ν C=N and ν C=O appeared at 1683–1522 cm^{−1} for the ligand gives considerable change on complexation.
- The ν of C=S appeared at 1444 cm^{−1} for the ligand gives slightly change in the formed complexes of Ni(II) and Cu(II), meanwhile Co(II) complex remains unchanged.
- The ν of M–O appeared at 539 cm^{−1} as a weak appearance for Co(II), at 537 cm^{−1} as a medium band for Ni(II) and at 522 cm^{−1} as a medium band for Cu(II) complexes. The very weak band at 500–512 cm^{−1} could be assigned as ν M–N band [36].

Electronic spectroscopy and magnetic properties

The Nujol mull electronic absorption spectrum for the Co(II), Ni(II) and Cu(II) 5-(ortho, meta and para-hydroxybenzylidene)2-TBA complexes are collected in Table 6. The magnetic properties of the complexes proved the octahedral structures [37–41], Fig. 3 and Table 5.

Proton NMR spectroscopy and mass spectra

The signals of ¹H NMR spectrum of 5-(salicylidine)2-TBA ligand in (DMSO-d₆) are given in Table 7. The SH proton appeared at δ = 2.1 ppm. The broad band at δ = 3.75–4.2 ppm [42] is due to the proton of OH group of salicylidine. The singlet band for the proton of C–H group appeared at δ = 7.1 ppm, and those of the aromatic protons are detected at δ = 7.0–7.25 ppm [43]. Singlet N–H proton, at δ = 12.3 ppm, and also the proton of the OH group of TBA appeared at δ = 13.3 ppm, are due to denote keto-enol forms [44], (–C(O)–NH– ↔ C(OH)=N–). The position of S–H band not changed to indicate that S atom is not involved on complexation. The absence of the broad band of aromatic O–H group may be due to the breakdown of inter or intra hydrogen bond. Also the absence of the band of O–H of the TBA ring may be due to its involvement on complexation. Generally, all the chemical shifts (δ) of the hydrogen in the free ligand were shifted to higher value in the formed complex. The increasing (δ) of the ligand in the complex, pronounced the covalence nature of the complex and entrance some of electron pair inside the metal ion orbital by some extent, give de-shielding properties and hence increasing in chemical shift. The NH proton has chemical shift equals 10.7 ppm on complexation, relatively lower than the suggested value, probably due to breaking of intramolecular hydrogen bond gave decreasing in the chemical shift with broadening.

Similar conclusions are deduced for 5-(*m*-hydroxybenzylidene)2-TBA and 5-(*p*-hydroxybenzylidene)2-TBA. The signals of mass spectra for the all ligands are collected in Tables 8a–8i).

Table 9

DTA and TGA analysis of Co(II), Ni(II) and Cu(II) complexes for 5-(salicylidine)2-thiobarbituric acid.

Complex	Type	T_m (K)	ΔE (kJ mol ⁻¹)	n	α_m	ΔS^* (kJ K ⁻¹ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	$10^{-3} Z$ (s ⁻¹)	Temp. TGA	Wt. loss %		Assignment
										Found	Calc	
Co(L) ₂ ·5H ₂ O									29–183 183.8– 500	14.78 31.22	13.94 30.68	Dehydration of 5H ₂ O elimination of 2(HC≡CNH ₂), CO ₂ and Benz.
	Endo Exo	334.97 751.02	0.046 0.210	0.37 0.39	2.05 2.31	–0.028 –0.021	–9.3950 –15.938	0.03 0.07	500– 1200	36.51	36.11	Elimination of 2(HC≡CNH ₂), CO and Benz. and formation of cobalt oxide
Ni(L) ₂ ·5H ₂ O·CH ₃ OH									25.29– 301.27	18.55	18.01	Dehydration of 5H ₂ O and elimination of CH ₃ OH
	Endo Endo	350.77 641.85	0.016 0.108	1.09 1.15	2.16 2.26	–0.036 –0.025	–12.905 –16.416	11.9 46.12	303.34– 443.34	21.30	21.26	Elimination of 2(HC≡CNH ₂) and SO ₂
	Endo	904.93	0.105	1.29	2.45	–0.027	–25.324	34.52	443.34– 984.56	47.38	47.84	Elimination of 2(HC≡CNH ₂), CO, SO ₂ and 2 Benz. and formation of nickel oxide
	Exo	1111.8	0.115	1.30	2.47	–0.028	–32.113	30.98				
Cu(L) ₂ ·4H ₂ O·Cl									20–206	10.97	10.77	Dehydration of 4H ₂ O
	Endo	341.58	0.0355	1.51	2.67	–0.0282	–9.645	33.48	208– 409	29.16	28.73	Elimination of HCl, Benz., CH ₄ and SO ₂
	Endo	691.94	0.0621	0.39	2.30	–0.0307	–21.253	24.86	409– 508	45.70	45.80	Elimination of 4(HC≡CH), 2NO, N ₂ and Benz. And formation of copper oxide
	Endo Endo	851.75 1067.7	0.3630 0.3750	3.37 2.18	3.37 3.08	–0.0140 –0.0169	–12.412 –18.080	173.28 130.38				

Table 10

DTA and TGA analysis of Co(II), Ni(II) and Cu(II) complexes for 5-(m-hydroxybenzylidene)2-thiobarbituric acid.

Complex	Type	T_m (K)	ΔE (kJ mol ⁻¹)	n	α_m	ΔS^* (kJ K ⁻¹ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	$10^{-3} Z$ (s ⁻¹)	Temp. TGA	Wt. Loss %		Assignment
										Found	Calc	
Co(L) ₂ ·H ₂ O·CH ₃ OH	Endo	339.89	0.0743	1.64	2.78	–0.0217	–7.3888	0.0732	16.12– 93.5	15.33	15.77	Dehydration of 4H ₂ O and elimination of CH ₃ OH
	Exo	689.72	0.2797	1.31	2.48	–0.0175	–12.109	0.1210	93.5– 406.4	32.97	32.61	Elimination of 2(HC≡CH), CO, 2NH ₂ OH and Benz.
	Exo	745.54	0.3647	1.59	2.74	–0.0151	–11.300	0.1615	406.4– 609.6	35.48	35.04	Elimination of 2(HC≡CNH ₂), CH ₄ , SO ₂ and Benz. and formation of cobalt oxide
Ni(L) ₃ ·4H ₂ O	Endo	355.00	0.0426	1.39	2.56	–0.027	–9.7300	37.004	20.45– 130.86	10.63	8.96	Dehydration of 4H ₂ O Elimination of C ₆ H ₆
									132.63– 291.03	8.93	9.20	Elimination of 2(HC≡CNH ₂), CO, SO ₂ and 2 Benz.
	Exo	692.80	0.0426	2.06	3.03	–0.031	–21.865	22.456	292.55– 430.52	39.96	40.07	
	Endo	976.27	0.4030	1.30	2.46	–0.017	–17.054	122.31				Elimination of 2(HC≡CH), CH ₄ , N ₂ and SO ₂ and formation of nickel oxide
Cu(L) ₂ ·4H ₂ O·CH ₃ OH									430.52– 550.58	18.26	17.71	
									31.02– 87	9.16	10.27	Dehydration of 2H ₂ O, elimination of CH ₃ OH
	Endo	349.52	0.0317	1.14	2.25	–0.0307	–10.759	24.657	87– 232.66	5.69	5.44	Dehydration of 2H ₂ O Elimination of C ₆ H ₆
	Endo	415.83	0.1370	1.07	2.13	–0.0204	–8.5234	84.970	234.29– 356.29	20.54	19.12	
	Endo	905.85	0.0360	0.75	1.35	–0.0418	–37.928	6.4990				Elimination of (H ₃ CC≡CNH ₂), H ₂ S and CO. Elimination of 2(HC≡CNH ₂), CO ₂ , SO ₂ and 2 Benz. and formation of copper oxide
	Endo	905.85	0.0405	1.57	2.72	–0.0350	–31.776	14.710	356.29– 631.11	50.67	50.74	

Thermal analysis

The DTA and TG data of 5-(salicylidine)2-TBA complexes, Table 9, gave strong endothermic peaks started at 20 °C, which could

be assigned to the liberation of water molecule and methanol moiety. However, the endothermic peaks for cobalt complexes at 29–183 °C are with weight loss 14.78% corresponding to liberation of 5H₂O. Meanwhile, the nickel complexes gave endothermic band

Table 11
DTA and TGA analysis of Co(II), Ni(II) and Cu(II) complexes for 5-(p-hydroxybenzylidene)2-thiobarbituric acid.

Complex	Type	T_m (K)	ΔE (kJ mol ⁻¹)	n	α_m	ΔS^* (kJ K ⁻¹ mol ⁻¹)	ΔH^* (kJ mol ⁻¹)	$10^{-3} Z$ (s ⁻¹)	Temp. TGA	Wt. Loss %		Assignment
										Found	Calc	
Co(L) ₂ ·2H ₂ O·CH ₃ OH	Endo	336.18	0.0791	1.61	2.76	-0.0211	-7.1250	0.0781	19.35–133	10.67	10.9	Elimination of 2H ₂ O and CH ₃ OH
	Exo	700.93	0.32380	1.07	2.13	-0.0177	-12.411	0.1188	135–422.5	39.04	40.07	Elimination of 2(HC≡CNH ₂), CO, SO ₂ and Benz
	Exo	750.83	0.68060	1.47	2.64	-0.0103	-7.7581	0.2885	422.58–1200	31.54	31.97	Elimination of 2(HC≡CNH ₂), CO and Benz. and formation of cobalt oxide
Ni(L) ₂ ·4H ₂ O	Endo	348.59	0.050215	1.52	2.68	-0.0254	-8.8880	46.568	20.61–116.62	12.26	11.48	Dehydration of 4H ₂ O
	Endo	493.00	0.094900	1.30	2.46	-0.0237	-11.727	57.207				
	Endo	765.09	0.309100	0.84	1.64	-0.0210	-16.067	79.976				
	Endo	974.94	0.105200	1.13	2.23	-0.0294	-28.705	28.972	118.48–999.77	75.75	76.36	Elimination of 4(HC≡CNH ₂), CH ₄ , CO, 2SO ₂ and 2 Benz. and formation of nickel oxide
	Exo	1190.4	0.397000	2.31	2.31	-0.0197	-23.492	93.141				
Cu(L) ₂ ·4H ₂ O·CH ₃ OH	Endo	341.15	0.0562	1.86	2.92	-0.0236	-8.0680	58.155	28.58–122	10.27	10	Dehydration of 2H ₂ O and elimination of CH ₃ OH
									122–253.42	5.44	5.51	Dehydration of 2H ₂ O
	Endo	607.36	0.0370	0.88	1.73	-0.0362	-22.041	12.715	254.92–365.23	14.99	14.15	Elimination of CO, CH ₄ and HC≡CH, N ₂
									365.23–834.00	53.31	53.34	Elimination of 2(HC≡CNH ₂), 2CO, SO ₂ and 2 Benz. And formation of copper oxide
	Endo	1214.7	0.0298	1.51	1.95	-0.0200	-25.081	83.458				

at 25–301 °C and weight loss 18.55% corresponding to liberation of 5H₂O and CH₃OH molecules. Similarly an endothermic peak of copper (II) complexes at 20–206 °C assigned to the liberation of 4H₂O. The other stepwise decomposition of the complexes started at 184, 303 and 208 °C as endothermic peaks for Co(II), Ni(II) and Cu(II) complexes, respectively, with one exception where the last step of Ni complexes proceed with exothermic reaction.

The data for 5-(3-hydroxybenzylidene)2-TBA complexes, Table 10, gave endothermic peaks assigned to the liberation of water molecule and methanol moiety. The peak at 16–93 °C for the Co(II) complex with a weight loss 15.33% is due to liberation of 4H₂O and CH₃OH molecules. Nickel complexes gave a peak at 20–130 °C with a weight loss 10.63% corresponding to liberation of 4H₂O. Meanwhile copper complexes gave a peak at 31–87 °C with a weight loss 9.16% equivalent to liberation of 2H₂O and elimination of CH₃OH molecule. Other bands appeared at 87–232.66 °C due to liberation of other 2H₂O molecule. The other peaks attributed to the decomposition steps ended with the formation of metal oxides as a final residue. All peaks are endothermic except the last steps of Co(II) complex and the second step of Ni(II) complex proceeding with exothermic reactions.

In a similar way, the data of 5-(4-hydroxybenzylidene)2-TBA complexes, Table 11, gave an endothermic peaks for cobalt complexes at 19–133 °C with weight loss 10.67% corresponding to liberation of 2H₂O and CH₃OH molecules. Nickel complexes gave a peak at 20–116 °C with a weight loss 12.26% due to liberation of 4H₂O. Copper complexes gave an endothermic peak at 28–122 °C with a weight loss 10.27% due to liberation of 2H₂O and elimination of CH₃OH molecule. It gave also other band at 122–253.42 °C corresponding to liberation of 2H₂O. Other stepwise decomposition peaks of the complexes started at 135, 118 and 254 °C as endothermic peaks for Co(II), Ni(II) and Cu(II) complexes, respectively, with one exception the last steps of Co(II), Ni(II) complexes proceeding with exothermic reactions.

The mathematical analysis of data gave:

1. The negative values of ΔS indicated that the activated complex has a more ordered structure than the reaction.

2. The low values of Z (collision factor) indicated the slow nature of the reaction [45–50]. The degree of decomposition (α) was calculated and given in Tables 8a–11.

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