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SYNTHESIS AND CHARACTERIZATION OF NEW AZOPYRIMIDINE COMPLEXES

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New azo compounds containing barbituric acid, thiobarbituric acid or thiouracil, together with their complexes, were prepared. All the complexes are tetrahedral. Axial ESR spectra were observed for the complexes with a d_{x2-y2} ground state with small $g_{||}$ values indicating strong interaction between the ligands and their metal ions. Conductivity measurements proved semiconducting properties for the ligands and their complexes. Energies of activation (ΔE_a) and order of the thermal reactions (n) were calculated by DTA.

INTRODUCTION

Biological activities and industrial achievements of azo containing compounds stirred great interest. The azo moieties have antifungal and antibacterial activities [1] and are used in the determination of trace metals in food and drinking water [2]. Pyrimidine compounds are also used as hypnotic drugs for the nervous system [3], in detecting cancer [4] as chemotherapeutic agents and are involved in the structure of nucleic acids in living cells [5].
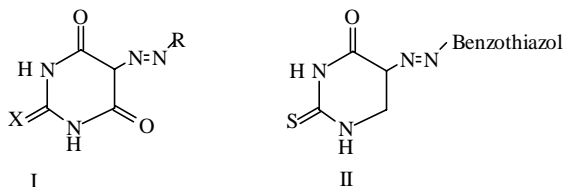
This article is part of a continuing investigation of transition metal complexes of azo compounds containing pyrimidine moieties in the laboratory of Masoud *et al*. [6–12].

EXPERIMENTAL

The ligands were prepared by the usual diazotization process [6] for barbituric and thiobarbituric acids with 2-aminopyrimidine, 2-aminopyrazine, 2-aminobenzothiazole, and 5-amino-l,3,4-thiadiazol-2-thione, I. Thiouracil is also diazotized with

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2-aminobenzothiazole to obtain ligand II. The crude products were crystallized using ethanol as a solvent followed by drying in a vacuum desiccator over P_4O_{10}.

I
X: O, S
R: Pyrimidine
  : Pyrazine
  : 1,3,4-Thiadiazol-2-thiol
X: S
R: Benzothiazol

II

The elemental analyses of the free ligands are in Table I. The transition metal complexes derived from cobalt(II), nickel(II), and copper(II), chloride salts were synthesized by refluxing (10 mmol) of an ammonia solution of the metal(II) chloride (Co, Ni, and Cu) with an ammonia solution of the organic compounds (10 mmol) for 1/2 h. The formed complexes were filtered, washed with ethanol, and dried in vacuum over P_4O_{10}. The melting points for all the complexes were over 300°C. The metal ions were determined by the usual complexmetric titration methods [13] and by atomic absorption techniques, Table II.

Electronic absorption spectra were measured using a PYE-Unicam spectrophotometer model 1750 covering the wavelengths from 190 to 900 nm. The spectra of the complexes were measured in DMSO. Infrared spectra were recorded using a Perkin Elmer spectrophotometer model 1430 covering the frequency range 200–4000 cm^{-1}.

TABLE I   Color and elemental analysis of organic compounds

Compound	Formula	Color	Calculated/(Found) %		
			C	H	N
5-[2-pyrimidineazo]barbituric acid	$C_8H_6N_6O_3$	Light violet	41.03 (40.82)	2.58 (2.43)	35.90 (36.2)
5-[2-pyrimidineazo]thiobarbituric acid	$C_8H_6N_6O_2S$	Brown	38.40 (37.8)	2.42 (2.30)	33.60 (33.95)
5-[pyrimidineazo]barbituric acid	$C_8H_6N_6O_3$	Brown	41.03 (41.13)	2.56 (2.41)	35.90 (34.2)
5-[2-pyrimidineazo]thiobarbituric acid	$C_8H_6N_6O_2S$	Black	38.40 (38.1)	2.42 (2.30)	33.60 (32.7)
5-[2-pyrimidineazo]barbituric acid	$C_9H_6N_8O_3$	Reddish Brown	39.42 (38.9)	2.20 (2.3)	40.88 (41.2)
5-[2-pyrimidineazo]thiobarbituric acid	$C_9H_6N_8O_2S$	Brown	37.24 (37.00)	2.08 (1.9)	38.62 (39.2)
5-[5′-1,3,4-thiadiazol-2-thiolazo]-thiobarbituric acid	$C_6H_4N_6O_3S_2$	Pale Yellow	26.44 (26.0)	1.48 (1.3)	30.85 (31.3)
5-[5′-1,3,4-thiadiazol-2-thiolazo]-thiobarbituric acid	$C_6H_4N_6O_2S_3$	Buff	24.98 (25.1)	1.40 (1.5)	29.15 (28.9)
5-[2-benzothiazolazo]thiobarbituric acid	$C_{11}H_7N_5O_2S_2$	Brown	34.23 (42.8)	2.31 (2.2)	22.92 (22.5)
5-[2-benzothiazolazo]thiouracil	$C_{11}H_7N_5OS_2$	Yellow	45.6 (44.9)	2.44 (2.3)	24.19 (24.0)

TABLE II   Color and elemental analysis of the metal complexes

Complex	Color	Calculated/(found) %			
		C	H	N	M
Co[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	Red	31.09 (31.17)	1.96 (2.10)	27.19 (27.27)	19.07 (19.16)
Ni[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	Green	31.11 (31.21)	19.96 (1.85)	27.21 (27.31)	19.00 (19.22)
Cu$_3$[5-(2-pyrimidineazo)barbituric acid]$_2$·4H$_2$o	Black	26.51 (26.67)	195 (1.98)	23.18 (23.4)	26.20 (26.40)
Co[5-(2-pyrimidineazo)thiobarbituric acid]·H$_2$O	Brown	29.55 (29.65)	1.85 (1.95)	25.85 (25.40)	18.12 (18.00)
Ni$_3$[5-(2-pyrimidineazo)thiobarbituric acid]·H$_2$O	Brown	27.20 (27.10)	1.43 (1.48)	23.79 (23.91)	24.92 (24.82)
Cu$_3$[5-(2-pyrimidineazo)thiobarbituric acid]·H$_2$O	Black	26.65 (26.60)	1.40 (1.50)	23.31 (23.30)	26.44 (26.40)
Co$_3$[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	Brown	29.88 (29.80)	1.57 (1.50)	26.13 (26.21)	27.49 (27.51)
Ni[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	Brown	31.11 (30.90)	1.96 (1.81)	27.21 (27.21)	19.00 (18.59)
Cu[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	Brown	30.63 (30.51)	1.93 (1.90)	26.79 (26.82)	20.26 (20.10)
Co[5-(2-pyrimidineazo)thiobarbituric acid]·H$_2$O	Brown	29.55 (29.40)	1.86 (1.71)	25.85 (25.75)	18.12 (18.20)
Ni[5-(2-pyrimidineazo)thiobarbituric acid]·H$_2$O	Yellow-green	29.57 (29.50)	1.86 (1.80)	25.86 (26.5)	18.07 (18.10)
Cu[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	Black	29.13 (29.10)	1.83 (1.80)	25.48 (25.61)	19.27 (19.35)
Co$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo) barbituric acid]·2H$_2$O	Black	17.07 (17.10)	0.96 (0.70)	19.91 (19.80)	27.92 (28.01)
Ni$_3$[5-(5′-1,3,4-thiadiazol-2-thiolazo) barbituric acid]$_2$·6H$_2$O	Pale-green	17.52 (17.50)	1.70 (1.75)	20.44 (20.32)	21.42 (20.95)
Cu$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo) barbituric acid]·2H$_2$O	Green	16.71 (16.50)	0.93 (1.20)	19.48 (19.60)	29.46 (29.30)
Co$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo) thiobarbituric acid]·2H$_2$O	Brown	16.45 (16.46)	0.92 (1.10)	19.18 (19.25)	26.90 (26.80)
Ni$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo) thiobarbituric acid]$_2$·4H$_2$O	Yellow	15.21 (15.10)	1.70 (1.80)	17.74 (1.60)	24.78 (24.70)
Cu$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo) thiobarbituric acid]·2H$_2$O	Black	16.11 (16.10)	0.90 (1.05)	18.78 (18.80)	28.41 (28.50)
Co$_2$[5-(6-purineazo)barbituric acid]·2H$_2$O	Brown	25.49 (25.60)	1.43 (1.50)	26.42 (26.30)	27.79 (27.50)
Ni$_2$[5-(6-purineazo)barbituric acid]·2H$_2$O	Green	25.52 (25.51)	1.43 (1.40)	26.45 (26.55)	27.71 (27.70)
Cu$_2$[5-(6-purineazo)barbituric acid]·2H$_2$O	Green	24.95 (24.81)	1.40 (1.38)	25.86 (25.72)	29.33 (29.40)
Co$_2$[5-(6-purineazo) thiobarbituric acid]$_2$·H$_2$O	Brown	24.56 (24.41)	1.37 (1.43)	25.46 (25.30)	26.78 (26.58)
Ni$_3$[5-(6-purineazo) thiobarbituric acid]·6H$_2$O	Black	25.17 (25.10)	2.11 (2.00)	26.10 (26.10)	20.50 (20.40)
Cu$_2$[5-(6-purineazo) thiobarbituric acid]·2H$_2$O	Yellow-green	24.07 (24.10)	1.35 (1.40)	24.94 (24.80)	28.28 (28.30)
Co[5-(2-benzothiazolazo) thiobarbituric acid]·H$_2$O	Black	34.74 (24.56)	1.86 (1.90)	18.42 (18.32)	15.43 (15.41)
Ni$_3$[5-(2-benzothiazolazo) thiobarbituric acid]·2H$_2$O	Brown	29.73 (29.74)	2.25 (2.15)	15.76 (15.71)	19.83 (19.70)
Cu[5-(2-benzothiazolazo) thiobarbituric acid]·H$_2$O	Brown	34.33 (34.32)	1.83 (1.84)	18.20 (18.26)	16.51 (16.40)
Co[5-(2-benzothiazolazo) thiouracil]·H$_2$O	Brown	36.27 (36.30)	1.92 (1.90)	19.23 (19.20)	16.19 (16.12)
Ni[5-(2-benzothiazolazo) thiouracil]·H$_2$O	Buff	36.29 (36.32)	1.92 (1.85)	19.25 (19.35)	16.14 (16.30)
Cu[5-(2-benzothiazolazo) thiouracil]·H$_2$O	Pale-brown	35.82 (35.85)	1.90 (1.95)	18.99 (18.70)	17.24 (1730)

Electron spin resonance (ESR) spectra were recorded at 100 kHz modulation and 10 G modulation amplitude on a Varian E9 spectrometer; 10 mV incident power was used and resonance conditions were at 9.45 GHz (X-band) at room temperature. The field was calibrated with a powder sample of 2,2-diphenylpyridylhydrazone ($g = 2.0037$) [14].
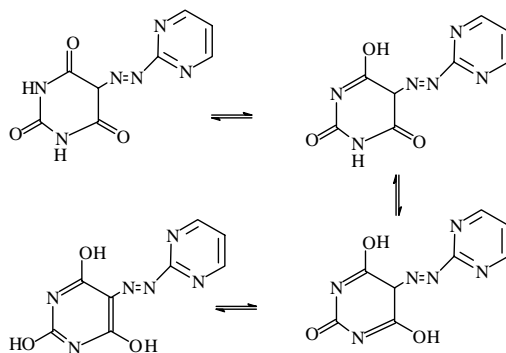
The electrical conductivity of the ligands and the complexes were measured in the temperature range 298–570 °K with a stability and accuracy of ±0.1°K. The measuring circuit consisted of an oscillator (10 Hz–10 MHz) BM 492 and a millivoltmeter (10 Hz–10 MHz) BM 494. The samples were prepared as tablets of thickness 0.1–0.3 cm at a pressure of about 5 ton/cm^2. The tablets were covered on both sides with silver paste to improve contact with the electrodes. The temperature was measured with a pre-calibrated Cu-constant thermocouple attached to the sample. The electrical conductivity was measured by applying a stabilized D.C. voltage across the potential difference. The conductivity of the sample was obtained during heating using the general equation:

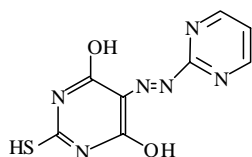$$\sigma = \frac{I}{V_c} \cdot \frac{d}{a}$$

where I is the current in amperes, V_c is the potential drop across the sample of cross sectional area a and thickness d. The differential thermal analysis (DTA) was carried out using a Shimadzu XD-30 thermal analyzer.

RESULTS AND DISCUSSION

The structure proposed for 5-[2-pyrimidinylazo]-barbituric acid based on its I.R. data is as follows:

The thiobarbituric acid derivative is represented as follows:

Shifts of the ν_{OH} band occur in the free ligands upon complexation, Table III, are due to the existence of a water molecule in these complexes [15] or due to hydrogen bond formation [16]. The shifts in the ν_{N-H} and $\nu_{C=O}$ bands, Table III, suggest that these groups are strongly involved in the structural chemistry of the complexes, either by the presence of M–N interactions or that the free ligands are subjected to tautomerism. The azo group is also affected upon complexation, from coordination to the metal ions, Table III. The change in positions of $\nu_{C=N}$ in the former ligand and thioamide bands in the latter indicates the presence of M–N and M–S bonds [17–19]. New IR bands appeared at 546 and 232 cm^{-1} assigned as ν_{M-O} and ν_{M-N} and 522 cm^{-1} (ν_{M-O}) for the cobalt(II) complexes, (536; 234 cm^{-1}) as ν_{M-O}; ν_{M-N} and 529 cm^{-1} (ν_{M-O}) for the nickel(II) complexes and (268; 235 cm^{-1}) as ν_{M-O}; ν_{M-N} for the copper(II) complex for the barbituric and thiobarbituric acid ligands, respectively.

The electronic absorption spectra showed characteristic bands at 640 and 520 nm indicating tetrahedral geometry with $^4A_2\,(F) \rightarrow {}^4T_1(P)$ [16,20–23] for the cobalt(II) complexes, 610 and 570 nm due to $^3T_1\,(F) \rightarrow {}^3T_1(P)$ [24] for the nickel(II) complexes and 610 and 580 nm due to $d_{x2-y2} \rightarrow d_{xy}$ transitions for the copper(II) complexes [25] for barbituric and thiobarbituric ligands, respectively. The room temperature magnetic moment values at 298 K for the cobalt(II), nickel(II), and copper(II) complexes with the barbituric acid ligand are 4.80, 3.70, and 1.50 B.M, whereas the values for the thiobarbituric acid analog are 4.90, 3.80, and 1.15 B.M. Thus the following structures are proposed for the complexes:
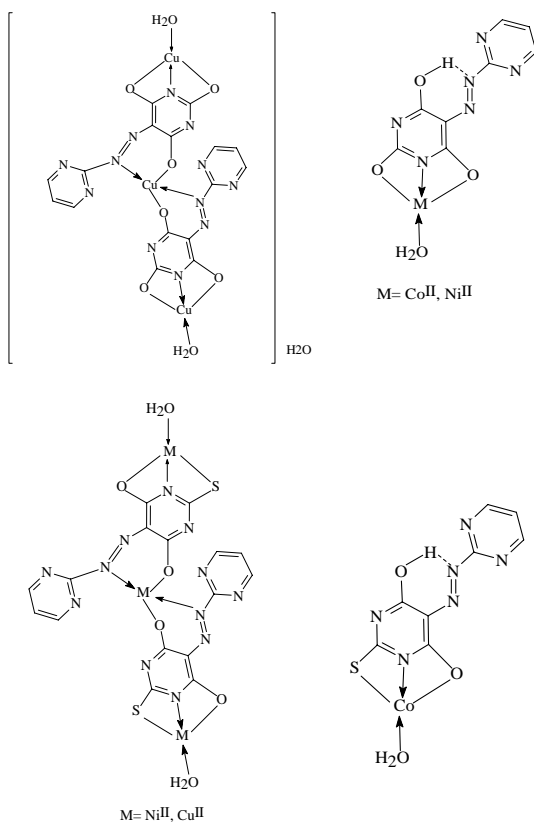
TABLE III Fundamental infrared bands (cm^{-1}) of the organic and their complexes
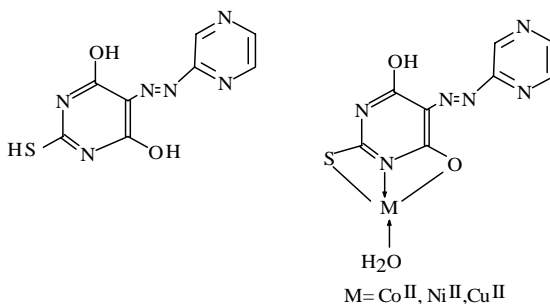
Compound	ν_{O-H}	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=N}$, (ν_{S-H})	$\nu_{N=N}$	Thioamide (I)	Thioamide (II)	Thioamide (III)	Thioamide (IV)	ν_{M-O}	ν_{M-N}	ν_{M-S}
5-[2-pyrimidineazo]-barbituric acid	3512	3266,3168, 3022	1715,1682	1640,1611, 1546	1454	—	—	—	—	—	—	—
—Co(II) complex	3375	3153,3046	1691	1523	1454	—	—	—	—	546	232	—
—Ni(II) complex	3397	—	—	1648,1546	1454	—	—	—	—	536	234	—
—Cu(II) complex	3313,3248		1693	1646,1582	1485	—	—	—	—	590,547	268,235	—
5-[2-pyrimidineazo]-thiobarbituric acid	3403	3250,3203 3137,3072	1669	*2587	1445	1621,1529, 1419	1354,129313	1078,1014, 9929	742	—	-	—
—Co(II) complex	3426	3287	—	—	1434	1620,1506	1382,1322	995	748	522	—	—
—Ni(II) complex	3339	—	—	—	1453	1637,1573	1392,1298	1005	738	529	—	—
—Cu(II) complex	3416	3190	—	—	—	1620,1523, 1477	1393,1319	994	745	—	—	—
5-[pytazineazo]-barbituric acid	3390	2972	1691	1602	1464	—	—	—	—	—	—	—
—Co(II) complex	3377	2971	1685	1521,1590	1448	—	—	—	—	234	434	—
—Ni(II) complex	3376	2971	—	1594	1496	—	—	—	—	234	390,369	—
—Cu(II) complex	3335	2971	—	1591	1486	—	—	—	—	233	434,390	—
5-[pytazineazo]-thiobarbituric acid	3419	3189,3106, 2882	1692	—	1440	1600,1526	1335	1188,1128, 1000	779	—	—	—
—Co(II) complex	3341	2970	—	—	1445	1529,1602	1318	1089,1098, 1003	—	590	232,267	389,368
—Ni(II) complex	3427	2918	1654	—	1445	1528,1602	1352	1198,1113	—	590	232,266	389,369
—Cu(II) complex	3368	2970	—	—	1444	1551,1621	1327	1088,1048	—	590	232,266	389,369
5-[5'-1,3,4-thiadiazol-2-thiolazo]barbituric acid	3388	3269,3088, 2918	1701	—	1433	1633,1596, 1534	1366,1330	1057	749	—	—	—
—Co(II) complex	3366	3117	—	—	—	1631,1596, 1498	1385,1408	1042,1133	—	409	—	369
—Ni(II) complex	3315	2970	—	—	—	1604,1525	1353,1397	1047	—	437,408	—	—
—Cu(II) complex	3282	3160	—	—	—	1600,1512	1337,1397	1047	—	407	—	369
5-[5-1,3,4-thiadiazol-2-thiolazo]thiobarbituric acid	3400	3258,3078	—	2881	1500	1621,1571	1387	1070,1041	769,744	—	—	—
—Co(II) complex	3342	—	—	—	1519	1609	1396	1049	786	—	—	389,341
—Ni(II) complex	3345	3161	—	—	1519	1604	1386	1048	779	—	231	341,339
—Cu(II) complex	3279	—	—	—	1511	1605	1395	1046	780	—	—	391,343

Compound												
5-[6-purineazo]-barbituric acid	3295,2999, 2839	—	1442, 1417, 1333	1594	1594	—	—	—	—	—	—	—
–Co(II) complex	3338	2772	1464, 1395, 1313	1549	1549	—	—	—	—	—	232,211	—
–Ni(II) complex	3453	2972	1466, 1386	1449	1449	—	—	—	—	591,457, 390	238,230	—
–Cu(II) complex	3574,3373	2971,2922	1464, 1400, 1306	1549	1549	—	—	—	—	593,445, 431	230,237	—
5-[6-purineazo]-barbituric acid	3414	2868	2607	1546	1546	1607	—	1156,1113	780,720	—	—	—
–Co(II) complex	3339	—	—	—	—	—	—	1144	794,730	—	228	441
–Ni(II) complex	3345	2975	—	—	—	1592	—	1133	736,653	—	231	440
–Cu(II) complex	3398	—	—	—	—	—	—	1145	647	558	—	—
5-[2-benzothiazoleazo]-thiobarbituric acid	3371	3138,2890	—	1462	1462	1614,1527	1145,1046	780,752	—	—	—	—
–Co(II) complex	3401	2966,2119	—	1445	1445	1620,1519	1153,1082	757,725	—	—	—	433,411
–Ni(II) complex	3352	2990,2920	—	1452	1452	1637,1578	1133,1088	739	—	—	—	433,411
–Cu(II) complex	3427	3054,2191	—	1446	1446	1519	1159,1080	753,723	—	—	—	—
5-[2-benzothiazoleazo]-thiobarbituric acid	3369	3185,3134, 3080	—	1445	1445	1622,1561	1213,1172	770,734	—	—	—	—
–Co(II) complex	3333	3044,2967, 2922,2916	—	1443	1443	1582,1521	1199,1033	753	—	—	317	455
–Ni(II) complex	3383	—	—	1446	1446	1590,1526	1014,1185	758,725	—	—	315,209	434
–Cu(II) complex	3314	—	—	1442	1442	1595,1530	1179,1041	730	570	—	315,209	—

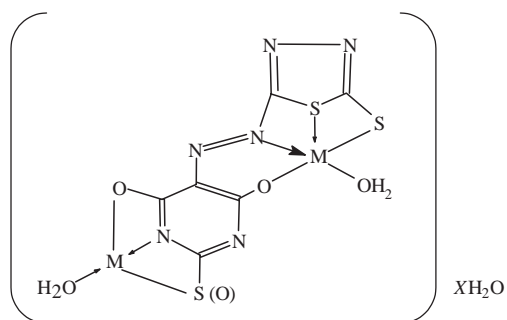TABLE IV Electronic absorption spectral bands and magnetic moment values of complexes

Complex	λ (nm)	μ (BM)
Co[5-(2-pyrimidineazo)barbituric acid]·H_2O	640	4.80
Ni[5-(2-pyrimidineazo)barbituric acid]·H_2O	610	3.70
Cu_3[5-(2-pyrimidineazo)barbituric acid]$_2$·$4H_2O$	610	1.50
Co[5-(2-pyrimidineazo)barbituric acid]·H_2O	520	490
Ni_3[5-(2-pyrimidineazo)barbituric acid]$_2$·H_2O	570	3.80
Cu_3[5-(2-pyrimidineazo)barbituric acid]$_2$·H_2O	580	1.15
Co_3[5-(pyrimidineazo)barbituric acid]$_2$·$2H_2O$	665,855	4.95
Ni[5-(pyrimidineazo)barbituric acid]·H_2O	660,760	3.82
Cu[5-(pyrimidineazo)barbituric acid]·H_2O	434,660	1.22
Co[5-(pyrimidineazo)thiobarbituric acid]·H_2O	670,885	4.85
Ni[5-(pyrimidineazo)thiobarbituric acid]·H_2O	710,805	3.65
Cu[5-(pyrimidineazo)thiobarbituric acid]·H_2O	670	1.22
Co_2[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]·$2H_2O$	650,840	4.90
Ni_3[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]$_2$·$6H_2O$	650,850	3.70
Cu_2[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]·$2H_2O$	580	1.25
Co_2[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]·$2H_2O$	670,850	4.97
Ni_2[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]$_2$·$4H_2O$	650,865	3.65
Cu_2[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]·$2H_2O$	650,760	1.18
Co_2[5-(6-purineazo)barbituric acid]·$2H_2O$	475,455,660	4.95
Ni_2[5-(6-purineazo)barbituric acid]·$2H_2O$	540,660,850	3.85
Cu_2[5-(6-purineazo)barbituric acid]·$2H_2O$	660,725	1.18
Co_2[5-(6-purineazo)thiobarbituric acid]·$2H_2O$	525,660	4.80
Ni_3[5-(6-purineazo)thiobarbituric acid]$_2$·$2H_2O$	660	3.80
Cu[5-(6-purineazo)thiobarbituric acid]·$2H_2O$	650	1.18
Co[5-(2-benzothiazoleazo)thiobarbituric acid]·H_2O	550	4.58
Ni_3[5-(2-benzothiazoleazo)thiobarbituric acid]$_2$·$2H_2O$	665,858	3.65
Cu[5-(2-benzothiazoleazo)thiobarbituric]·H_2O	660	1.27
Co[5-(2-benzothiazoleazo)thiobarbituric]·H_2O	655	4.75
Ni3[5-(2-benzothiazoleazo)thiobarbituric]·H_2O	650	3.62
Cu[5-(2-benzothiazoleazo)thiobarbituric]·H_2O	660	1.18

Similar results were obtained for the 5-pyrazine azo-barbituric acid ligand and its complexes indicating tetrahedral geometry as for the previous structures. The IR and electronic absorption spectra and room temperature magnetic moment values for 5-pyrazine-azo-thiobarbituric acid complexes, Table IV, support the following structure:
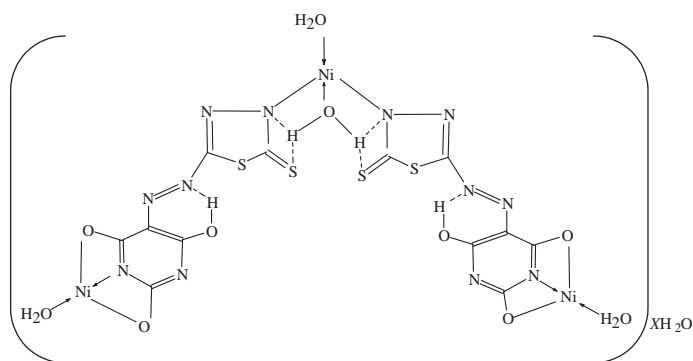

M= Co^{II}, Ni^{II},Cu^{II}

5-[5′-(1,3,4-thiadiazol-2-thiolazo] barbituric and thiobarbituric acids gave similar results where shifts occurred to the ν_{O-H} bands on complexation, probably due to the existence of water molecules [15] and/or hydrogen bond formation [16]. Also, the three ν_{N-H} bands in the free ligands, Table III, became only one band on complexation

indicating conversion of the –CNH group to C=N which is strongly involved in the structural chemistry of the complexes. The IR data also, indicated the involvement of the C=O and N=N groups on complexation. The four thioamide ligand bands are affected on complexation suggesting M–N and M–S bonding [17–19] together with the appearance of new bands due to $\nu_{M–O}$, $\nu_{M–S}$, and $\nu_{M–N}$, Table III. The electronic absorption spectra in DMSO showed bands characteristic for complexes in a tetrahedral or mixed tetrahedral-square-based pyramidal stereochemistry and from these data together with the room temperature magnetic moment data, Table IV, the following structure have been proposed for these complexes,
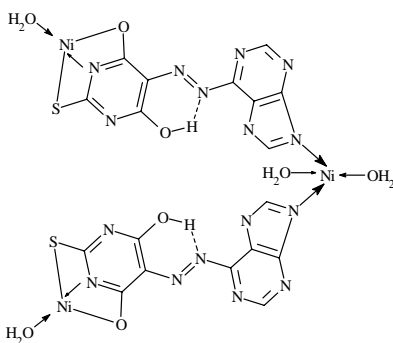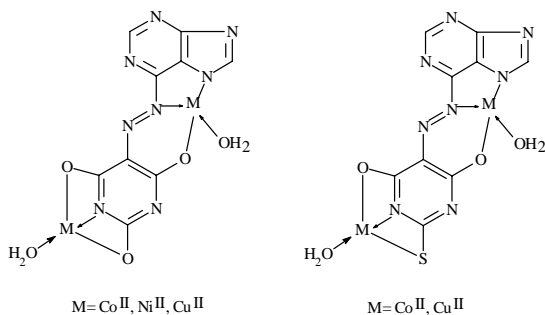

where $X = 0$ in case of Co^{II} and Cu^{II} complexes for both barbituric and thiobarbituric ligands and $X = 2$ for Ni^{II}-5-[5′(1,3,4-thiadiazol-2-thiol)azo] thiobarbituric acid. Ni-5-[5′(1,3,4-thiadiazol-2-thiolazo] barbituric acid is proposed to have the following structure:
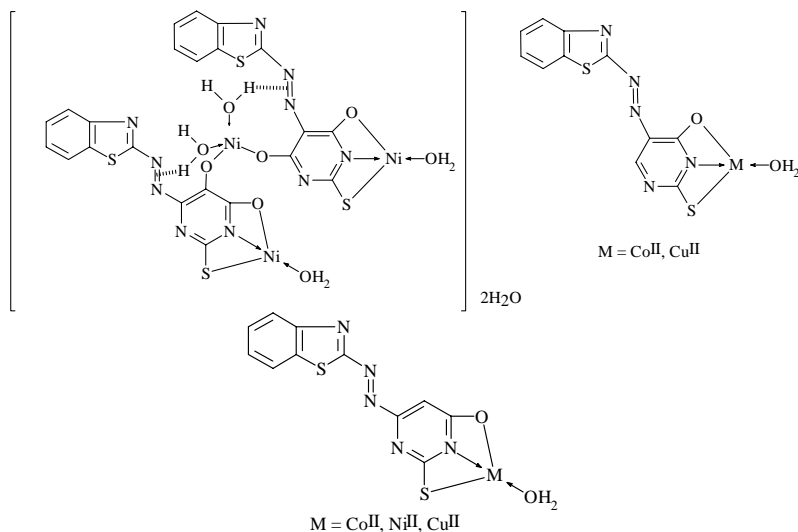

The IR spectral data of 5-[6-purine azo] barbituric and thiobarbituric acids and their complexes, Table III, showed shifts in the position of the NH bands suggesting M–N bonding. The $\nu_{O–H}$ band identified the presence of coordinated water molecules [15] or hydrogen bond formation [16]. The changes in ν_{SH}, $\nu_{C=N}$, and $\nu_{C=O}$ bands supported the M–S and M–O interactions. The shift or absence of $\nu_{N=N}$ in the complexes compared to the ligand suggests participation of the azo group in these complexes. New IR bands in the range 228–237 cm^{-1}, 370–593 cm^{-1}, and 440 cm^{-1} were observed due to $\nu_{M–N}$, $\nu_{M–O}$, and $\nu_{M–S}$, respectively.

The electronic absorption spectral properties and the room temperature magnetic values (Table IV) proved the tetrahedral configuration for these complexes:

M= Co^{II}, Ni^{II}, Cu^{II} M= Co^{II}, Cu^{II}

Similar spectral and magnetic moment values were obtained for 5-[2-benzothia-zoleazo]thiobarbituric acid and 5-(2-benzothiazoleazo] thiouracil and their complexes depicting the presence of these complexes in a tetrahedral geometry, Table IV.

M = Co^{II}, Cu^{II}

M = Co^{II}, Ni^{II}, Cu^{II}

A study of N–C$_{(8)}$ bond lengths in several metal [N, N′-bis (salicylidene) ethylene-diamine] complexes revealed two bond length categories [26]. The first range between 1.43 and 1.54 Å is due to conjugation between the π-orbitals of N with the π-orbitals of the aromatic ring. The second range ≥ 1.47 Å is observed when C$_{(8)}$ is part of a linear chain, a cyclohexyl group, ethylenediamine, tetramethylenediamine, or a cyclohexanediamine group. The coordination bond value in length (r) can be determined from the relation [27]:

$$\Delta v = \frac{32\pi\alpha}{a^2} \frac{v_{x=y} - v_{x-y}}{l} \exp. \left(-2\pi \frac{\sqrt{2r}}{a} \right)$$

where α = bond polarizability, Δv = shift in the oscillator frequency ($v_{\text{ligand}} - v_{\text{complex}}$), a = lattice constant of the metal salt ($a = 3.300$, 3.524, and 3.614 for cobalt, nickel, and copper, respectively [28]), v_{x-y} = frequency of an oscillator with a single bond, $v_{x=y}$ = frequency of an oscillator with a double bond, and l = length of the oscillator coordinated to the metal ion ($l = 1.950$, 1.905, and 1.993 for cobalt [29], nickel [26], and copper [26], respectively).

The α values are 48.61, 46.59, and 42.50 for cobalt, nickel, and copper, respectively [30]. From such data, the r-values were computed [31], Table V. It seems that copper

TABLE V   Coordination bond lengths of pyrimidine – metal complexes

Complex	r(Å)
Co[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	1.28
Ni[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	0.75
Cu$_3$ [5-(2-pyrimidineazo)barbituric acid]$_2$·4H$_2$O	0.53
Co[5-(2-pyrimidineazo)thiobarbituric acid]·H$_2$O	1.04
Ni$_3$[5-(2-pyrimidineazo)thiobarbituric acid]·H$_2$O	1.02
Cu$_3$[5-(2-pyrimidineazo)thiobarbituric acid]·H$_2$O	0.96
Co$_3$[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	0.26
Ni[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	0.18
Cu[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	0.14
Co[5-(2-pyrimidineazo)thiobarbituric acid]·H2O	0.79
Ni[5-(2-pyrimidineazo)thiobarbituric acid]·H2O	0.86
Cu[5-(2-pyrimidineazo)barbituric acid]·H$_2$O	0.59
Co$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]·2H$_2$O	2.85
Ni$_3$[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]$_2$·6H$_2$O	2.05
Cu$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]·2H$_2$O	1.90
Co$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]·2H$_2$O	3.72
Ni$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]$_2$·4H$_2$O	3.44
Cu$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]·2H$_2$O	3.43
Co$_2$[5-(6-purineazo)barbituric acid]·2H$_2$O	2.38
Ni$_2$[5-(6-purineazo)barbituric acid]·2H$_2$O	2.24
Cu$_2$[5-(6-purineazo)barbituric acid]·2H2O	1.51
Co$_2$[5-(6-purineazo)thiobarbituric acid]$_2$·H$_2$O	1.12
Ni$_3$[5-(6-purineazo)thiobarbituric acid]$_2$·6H$_2$O	3.12
Cu$_2$[5-(6-purineazo)thiobarbituric acid]·2H$_2$O	1.08
Co[5-(2-benzothiazole azo)thiobarbituric acid]·H$_2$O	1.75
Ni$_3$[5-(2-benzothiazole azo)thiobarbituric acid]$_2$·H$_2$O	2.48
Cu[5-(2-benzothiazole azo)thiobarbituric acid]·H$_2$O	1.66
Co[5-(2-benzothiazole azo)thiouracil]·H$_2$O	0.41
Ni[5-(2-benzothiazole azo))thiouracil]·H$_2$O	0.40
Cu[5-(2-benzothiazole azo)thiouracil]·H$_2$O	0.33

complexes have shorter coordination bond lengths than those of cobalt and nickel. This could be attributed to the increase in the strength of the electrostatic field of the copper ion as a result of the smaller ionic radius of copper(II) compared to that of nickel(II) or cobalt(II) ions. The room temperature X-band ESR of the $Cu_3[5$-(2-pyrimidineazo)barbituric$]_2 \cdot 4H_2O$ and $Cu_3[5$-(2-pyrimidineazo)thiobarbituric$]_2 \cdot 2H_2O$ complexes showed an axial ESR spectrum. The analysis of this spectrum according to Kneubuhl method [32] gave two *g*-values, $g_\parallel = 2.18$; $g_\perp = 2.08$ and $g_\parallel = 2.28$, $g_\perp = 2.02$ for the former and latter complexes. The small $g_\parallel$ values indicated strong interaction between the ligand and the metal ion. $g_\parallel > g_\perp$ suggests that a d_{x2-y2} ground state is present [33,34]. The calculated g_{av} from the relation $g_{av} = (g_\parallel + 2g_\perp)$ is 2.11 for both complexes. The deviation from that of the free electron value (2.0023) is due to covalence and provides further support for tetrahedral-distorted symmetry associated with d_{x2-y2} rather than d_{z2} state [35]. $A_\parallel > 100$, Table VI prohibits a *pseudo*-tetrahedral structure around copper [36,37]. As a measure of metal-ligand covalency, even for complexes not possessing D_{4h} symmetry [38–40], the coefficient α of the ground state d_{x2-y2} orbital has been calculated from the relation:

$$\alpha^2 = A_\parallel/0.036 + (g_\parallel - 2.0023) + 3/7(g_\perp - 2.0023) + 0.04$$

with $\alpha^2 = 0.771$ for $Cu_3[5$-(2-pyrimidineazo)barbituric acid$]_2 \cdot 4H_2O$ and 0.769 for its thiobarbituric acid analog, respectively, indicating that these complexes are not purely covalent in accord with the results obtained from IR and electronic spectral measurements. The contribution of 3d character in the copper 3d–4s ground state, is explained in another way [39].

$$\alpha^2 = 7/4[A_\parallel/P + |A|/P + 2/3g_\parallel - 5/21g_\perp - 6/7] \tag{a}$$

$$g = 1/3(g_\parallel + 2g_\perp)$$

$$A = 1/3(A_\parallel + 2A_\perp)$$

TABLE VI   ESR Data for copper(II) complexes at room temperature

Complex	$g_\parallel$	$g_\perp$	g_i	$\langle g \rangle$	G	$A_\parallel$	α^2	F^2	A_i	$g_\perp(M_5+2)$
Cu₃[5-(2-pyrimidineazo)barbituric acid]₂·4H₂O	2.18	–	–	2.11	2.25	184	0.771	0.938	–	–
Cu₃[5-(2-pyrimidineazo)thiobarbituric acid]₂·2H₂O	2.25	–	–	2.11	14.00	150	0.769	1.0197	–	–
Cu[5-(pyrazineazo)barbituric acid]·H₂O	–	2.09	2.09	–	–	–	–	–	120	–
Cu[5-(pyrazineazo)thiobarbituric acid]·H₂O	–	2.14	2.14	–	–	–	–	–	160	–
Cu₂[5-(5′-1,2,3 4- thiadiazol-2-thiolazo) barbituric acid]·2H₂O	2.25	–	–	2.15	5	100	0.600	0.962	–	4.15
Cu₂[5-(5′-1,2,3 4- thiadiazol-2-thiolazo) thiobarbituric acid]·2H₂O	2.48	–	–	2.20	8	171	1.092	1.018	–	4.2
Cu₂[5-(6-purineazo)barbituric acid]·2H₂O	2.35	–	–	2.13	35	135	0.802	1.042	–	–
Cu₂[5-(6-purineazo)thiobarbituric acid]·2H₂O	2.40	–	–	2.14	40	158	0.933	1.049	–	–
Cu[5-(2- benzothiazoleazo)thiobarbituric acid]·2H₂O	2.26	–	–	2.13	4.33	128	0.698	0.964	–	–
Cu[5-(2-benzothiazoleazo)thiouracil]·H₂O	2.46	–	–	2.21	5.11	200	0.173	0.997	–	4.18

Generally, $A_\perp$ is about 0.1 Å for copper(II) complexes [41], P is the free-ion dipole term proportional to $1/r^3$ and is given a value of $0.036\,\text{cm}^{-1}$. Estimates for this term in the literature vary over a range of approximately $\pm 0.005\,\text{cm}^{-1}$, K is the Fermi contact term and is usually given a value of 0.43 [39]. The corresponding equation for obtaining α^2 from the isotropic A value is:

$$\alpha^2 = |A|/PK + g - 2.0023/K \tag{b}$$

If the assumption that error on using Eq. (b) is due to a 4s contribution is correct, then Eqs. (a) and (b) can be written in the forms:

$$\alpha^2 F^2 = 7/4[|A_\parallel|/P - |A|/P + 2/3g_\parallel + 5/21g_\perp - 6/7]$$
$$\alpha^2 = |A|/PK + g - 2.0023/K + 1 - F^2/PK$$

Based on the preceding data, the F^2 value is 0.938 for Cu_3[5-(2-pyrimidineazo)barbituric acid]$_2$. $4H_2O$ and 1.0197 for Cu_3[5-(2-pyrimidineazo)thiobarbituric acid]$_2$. $2H_2O$. Equation (a) predicts a more covalent bond than predicted by Eq. (b). This discrepancy cannot be explained by a 4s contribution, but probably attributed to mixing the d_{z^2} and/or the 4p orbital into the d_{xy} ground state. The ESR spectra showed an isotropic nature, Table VI, with $g_\perp = 2.09$ and $A_\perp = 120$ for Cu[5-(pyrazineazo)barbituric acid]. H_2O and $g_\perp = 2.14$ and $A_\perp = 160$ for Cu[5-(pyrazineazo)thiobarbituric acid]. H_2O. Generally, copper(II) complexes having a symmetry lower than octahedral, undergo free rotation in the crystal lattice under fluid conditions [42] or give complexes containing grossly misaligned tetragonal axes [36,42]. The low $g_\perp$ and $A_\perp$ values indicated considerable π-bonding [32] with strong inplane bonding of the ligand. The powdered ESR spectrum of Cu_2[5'-1,3,4-thiadiazol-2-thiolazo)barbituric acid]. $2H_2O$ and Cu_2[5-(5'-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]. $2H_2O$ complex showed axial symmetry, Table VI, with $g_\parallel = 2.25$, $g_\perp = 2.05$, $A_\parallel = 100$, $g_\perp$ ($M_S \pm 2$) = 4.15 and $g_\parallel = 2.48$, $g_\perp = 2.06$, $A_\parallel = 171$ and $g_\perp$ ($M_S \pm 2$) = 4.2, respectively, suggesting a dimer or association between copper(II) atoms. The ESR spectral pattern of Cu_2[5-6-purineazo)barbituric acid]. $2H_2O$, Cu[5-(2-benzo-thiazoleazo)thiobarbituric acid]. H_2O, Cu_2[5-6-purineazo)thiobarbituric acid]. H_2O and Cu[5-(2-benzothiazoleazo)thiouracil]. H_2O showed axial symmetry with similar spectral patterns as discussed before.

The conductivity data of the ligands, Table VII, were measured over the temperature range 294–588 K. A discontinuity in the conductivity plots was observed for all the ligands, with different transition temperatures, resulting in more than one activation energy. It is apparent that the ΔE value is temperature dependent and that the conductivity of all the ligands increases with increasing temperature above 180°C. Thus, the complexes exhibit semiconducting properties above 180°C [43,44]. The phenomenon of discontinuity in the conductivity plots can be ascribed to a molecular rearrangement or a crystallographic transition [45]. The shallow behavior observed in most of the ligands can be attributed to enolketo tautomerism [46]. Therefore, the first step in the conduction process is delocalization of π-electrons while the second step involves excitation of an electron from the highest-filled π-molecular orbitals to the lowest unfilled ones [47]. The log σ values with low ΔE values obtained for the ligands can be ascribed to intermolecular hydrogen bond formation between the hydroxyl and

TABLE VII Electrical conductivity data of the ligands and their complexes

Compound	ΔE_1 (eV)	ΔE_2 (eV)	ΔE_3 (eV)	ΔE_4 (eV)	$-\log \sigma°$ at 40°C	Transition temp. (°C)
5-[2-pyrimidineazo]barbituric acid	0.21	0.43	—	—	6.63	60,160
Co[5-(2-pyrimidineazo)barbituric acid]·H₂O	0.71	—	—	—	5.56	140
Ni[5-(2-pyrimidineazo)barbituric acid]·H₂O	0.17	0.41	—	—	6.50	70,170
5-[2-pyrimidineazo]thiobarbituric acid	0.26	0.27	2.30	0.29	6.83	70,140,160,200
Co[5-(2-pyrimidineazo)thiobarbituric acid]·H₂O	0.37	1.65	—	—	6.32	90,140,190
Ni₃[5-(2-pyrimidineazo)thiobarbituric acid]·2H₂O	0.09	0.39	—	—	7.18	80,170
Cu₃[5-(2-pyrimidineazo)thiobarbituric acid]₂·2H₂O	0.10	1.58	0.77	—	4.34	60,90,160
5-[pyrimidineazo]barbituric acid	0.15	0.36	—	—	5.18	130,200
Co₃[5-(pyrimidineazo)barbituric acid]₂·2H₂O	0.14	0.17	—	—	3.95	90,140
Ni[5-(pyrimidineazo)barbituric acid]·H₂O	0.13	0.54	—	—	6.40	160,210
5-[pyrimidineazo)thiobarbituric acid	0.04	0.36	1.17	0.69	5.30	70,170,200
Co[5-(pyrimidineazo)thiobarbituric acid]·H₂O	0.21	0.54	0.69	—	6.88	80,190
Ni[5-(pyrimidineazo)thiobarbituric acid]·H₂O	0.23	0.25	—	—	3.80	50,170
Cu[5-(pyrimidineazo)thiobarbituric acid]·H₂O	0.98	—	—	—	5.90	90,140
5-[5′-1,3,4-thiadiazol-2-thiolazo]barbituric acid	0.17	0.29	2.74	—	6.30	50,140,210
Co₂[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]·2H₂O	0.81	0.29	—	—	4.50	180
Ni₃[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]·6H₂O	0.22	0.41	—	—	6.65	70,110,145
Cu₂[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]·2H₂O	0.15	0.10	0.56	—	5.25	160,210
5-[5′-1,3,4-thiadiazol-2-thiolazo]thiobarbituric acid	0.05	2.28	—	—	6.55	76,120,200
Co₂[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]·2H₂O	0.18	0.06	0.36	—	5.45	60,140
Ni₂[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituric acid]·4H₂O	0.04	0.31	0.43	—	6.85	100,140,170
5-[6-purineazo]barbituric acid	0.37	0.45	—	—	5.27	80,100,190
Co₂[5-(6-purineazo)barbituric acid]·2H₂O	0.23	0.14	0.54	0.72	5.96	80,170,190
Cu₂[5-(6-purineazo)barbituric acid]·2H₂O	0.24	0.08	0.49	—	7.26	90,160,170
5-[6-purineazo]thiobarbituric acid	0.12	0.19	0.38	—	4.86	110,190
Co₂[5-(6-purineazo]thiobarbituric acid]·2H₂O	0.80	0.95	—	—	3.98	90,140,180
Ni₃ [5-(6-purineazo]thiobarbituric acid]·6H₂O	0.08	0.36	0.36	—	5.47	45,110,125,140
Cu₃ [5-(6-purineazo]thiobarbituric acid]·2H₂O	0.10	0.23	—	—	5.38	60,105,160
5-[2-benzothiazoleazo]thiobarbituric acid	0.11	2.18	0.86	—	6.13	70,110,130
Co[5-[2-benzothiazoleazo]thiobarbituric acid]·H₂O	0.07	0.01	0.96	—	5.42	110,190,250
Ni₃[5-[2-benzothiazoleazo]thiobarbituric acid]·H₂O	0.24	0.38	0.82	0.25	4.42	50,75
Cu[5-[2-benzothiazoleazo]thiobarbituric acid]·H₂O	0.11	0.35	—	—	5.48	90,110,160
5-[2-benzothiazoleazo]thiobarbituric	0.11	0.17	0.05,0.29	0.80,1.25	4.02	140,160
Co[5-[2-benzothiazoleazo] thiobarbituric]·H₂O	0.19	0.16	0.71	—	6.60	55,95,190
Ni[5-[2-benzothiazoleazo thiobarbituric]·H₂O	0.15	0.36	—	—	6.40	80,125
Cu[5-[2-benzothiazoleazo] thiobarbituric]·H₂O	0.11	0.53	—	—	7.12	160

the azo groups [48]. The decrease in conductivity as the temperature is increased, observed in the conductivity plots, could be due to scattering of carriers by photons due to lattice vibrations within the temperature range studied [49], alternatively, it indicates the consumption of energy in the dissociation process rather than thermal agitation of electrons. All the complexes exhibit a similar discontinuity behavior in the temperature range 294–588 K. The behavior of all the complexes except Ni[5-pyrazineazo)thiobarbituric acid] $\cdot$ H$_2$O, Ni[5-2-benzothiazoleazo)thiobarbituric acid]$_2 \cdot$ 2H$_2$O and Cu[5-(2-benzothiazoleazo)thiouracil] $\cdot$ H$_2$O complexes gave good evidence for desolvation and *pseudo*-polymorphic transformation [49,50]. The complexes show slight semiconducting behavior with activation energies, Table VII, indicating that the electrons in the available orbitals of the complexes are not of high mobility [51]. Thus, the most realistic description of the complexes involves an interaction of the metal orbitals with ligands to give new molecular orbitals, which are delocalized over the whole molecular complex [52]. It is sufficient to consider quantitatively the behavior of the lowest unoccupied π MO of the ligands that interact with the appropriate metal orbitals. The relevant ligand orbitals transform as B_{1u} and B_{2g}, which may interact with $4p_z$ and $3d_{z2}$ orbitals, respectively. The B_{1u}-type MOs are sufficiently stabilized on interaction with the $4p_z$ orbital to become occupied, providing an explanation of the resonating structures [52]. The discontinuity in conduction curves of the complexes is due to different crystallographic or phase transitions [53].

On plotting ΔE against log σ° for the present complexes, best-fit straight lines were obtained. Therefore, the following empirical equations are deduced: for Co^{II} complexes: $\Delta E = 0.088 \log \sigma^\circ + 0.52$ based on ΔE_1 and $\Delta E = 0.085 \log \sigma^\circ + 0.54$ based on ΔE_2; for Ni^{II} complexes: $\Delta E = 0.024 \log \sigma^\circ + 0.26$ based on ΔE_1 and $\Delta E = 0.092 \log \sigma^\circ + 0.55$ based on ΔE_2; and for Cu^{II} complexes: $\Delta E = 0.020 \log \sigma^\circ + 0.22$ based on ΔE_1 and $\Delta E = 0.063 \log \sigma^\circ + 0.18$ based on ΔE_2.

The DTA curves of cobalt(II), nickel(II), and copper(II) complexes have exothermic peaks in the temperature range studied indicating decomposition of these complexes. The energies of activation (ΔE) for decomposition were evaluated based on the methods of Piloyan *et al.* methods [54], Table VIII. The order of chemical reactions (*n*) were calculated *via* the peak symmetry method [55], Table VIII. The following points are concluded:

1. The DTA curves showed exothermic peaks at temperatures higher than 250°C in all complexes indicating stability of these complexes up to 250°C and after which they are thermally decomposed [56].
2. The activation energy ΔE_a value for the Ni$_3$[5-(2-benzothiazoleazo)thiobarbituric acid]$_2$. 6H$_2$O complex (Ni$_3$L$_2 \cdot$ 6H$_2$O; $\Delta E_a = 2303.00$ kJ/mol) is very much higher than those of its cobalt (CoL $\cdot$ H$_2$O; $\Delta E_a = \Delta 76.74$ kJ/mol) and copper (CuL $\cdot$ H$_2$O; $\Delta E_a = 216.89$ kJ/mol) homologues, pointing to the existence of the nickel complex in an associated structure through intermolecular hydrogen bonding and/or intermolecular hydrogen bonding between the coordinated water and the host molecule [57].
3. In all the studied complexes, the ΔE_a values of the cobalt(II) complexes are higher than those of the copper(II) analogues, based on electronic configurations point of view Cu$^{(II)}$ (d^9) and Co$^{(II)}$ (d^7) with one and three unpaired electrons, respectively [57].

TABLE VIII DTA data of the complexes

Compound	ΔE_a KJ/mol	n	Z	ΔS^* KJ/mol	ΔH^* KJ/mol	T_m (°K)	S	α_m
Co[5-(2-pyrazineazo)thiobarbituric acid]·H_2O	443.41	2.39	20.63	−0.23	−162.80	717	3.61	0.46
Cu$_3$[5-(2-pyrimidineazo)thiobarbituric acid]$_2$·H_2O	147.10	1.26	6.42	−0.24	−168.76	713	1.00	0.59
Co[5-(pyrazineazo)thiobarbituric acid]·H_2O	1833.24	1.26	112.80	−0.21	−156.65	735	0.99	0.5
Ni[5-(pyrazineazo)thiobarbituric acid]·H_2O	489.84	1.13	21.83	−0.22	−173.04	762	0.80	0.62
Cu[5-(pyrazineazo)thiobarbituric acid]·H_2O	193.97	1.05	10.31	−0.23	−139.51	603	0.96	0.62
Ni$_3$[5-(5′-1,3,4-thadiazol-2-thiolozo)barbituric acid]$_2$·$6H_2O$	–	0.80	3.60	−0.24	−170.68	707	0.40	0.67
Cu$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid]·$2H_2O$	–	0.98	21.25	−0.23	−123.06	548	0.60	0.63
Ni$_2$[5-(5′-1,3,4-thiadiazol-2-thiolazo)thiobarbituricacid]·$4H_2O$	138	0.97	6.26	−0.24	−179.36	689	0.59	0.64
Cu$_2$[5-5′-1,3,4-thiadiazol-2-thiolozo)thiobarbituric acid]·$2H_2O$	120.51	0.90	4.90	−0.24	−181.50	758	0.51	0.65
Co$_2$[5-(6-purineazo)barbituric acid]·$2H_2O$	306.00	1.66	16.52	−0.23	−139.75	614	1.73	0.64
Cu$_2$[5-(6-purineazo)barbituric acid]·$2H_2O$	249.42	1.42	14.99	−0.23	−125.59	552	1.27	0.61
Co$_2$[5-(6-purineazo)thiobarbituric acid]$_2$·$2H_2O$	556.04	1.08	25.03	−0.22	−125.57	752	0.73	0.62
Ni$_3$[5-(6-purineazo)thiobarbituric acid]$_2$·$6H_2O$	116.40	1.45	4.09	−0.24	−178.80	746	1.32	0.56
Cu$_2$[5-(6-purineazo)thiobarbituric acid]$_2$·$6H_2O$	267.90	1.15	13.54	−0.23	−147.66	643	1.39	0.56
Ni$_3$[5-(2-benzothiazolazo)thiobarbituric acid]$_2$·$2H_2O$	2303.00	2.52	135.66	−0.21	−168.30	793	4.00	0.54
Cu[5-(2-benzothiazolazo)thiobarbituric acid]$_2$·$2H_2O$	216.89	1.51	12.00	−0.23	−134.70	586	1.43	0.55
Co[5-(2-benzothiazolazo)thiouracil]·H_2O	568.85	1.37	18.43	−0.23	−161.57	709	1.18	0.57
Ni[5-(2-benzothiazolazo)thiouracil]·H_2O	1408.76	2.36	93.94	−0.21	−141.73	663	3.51	0.46
Cu[5-(2-benzothiazolazo)thiouracil]·H_2O	122.26	1.08	6.13	−0.24	−147.00	623	0.73	6.13

4. In spite of the high molecular weight of the nickel complexes, $Ni_3L_2 \cdot 6H_2O$ with 5-[6-purineazo]thiobarbituric acid and 5-[5-1,3,4-thiadiazol-2-thiolazo]barbituric acid ligands, the ΔE_a values, 116.40 and 73.14 kJ/mol, respectively, are less than those of their copper(II) homologues $Cu_2L \cdot 2H_2O$ (267.90 and 338.29 kJ/mol, respectively). The ΔE_a value of the nickel complex cannot represent all the decomposition of the complex, but just decomposition of the N–Ni–N moiety.

5. Most of the thiobarbituric acid complexes exhibit higher ΔE_a values than those of the barbituric acid homologues due to the electronegativity difference between oxygen and sulfur. The thiobarbiturates are structurally more conjugated and more stable than the barbiturate complexes.

6. The metal complexes gave two types of decomposition reactions: (i) first-order reaction for all cobalt and copper complexes except that Co[5-(2-pyrimidineazo)thiobarbituric acid] $\cdot H_2O$ which was second-order. (ii) Ni_3[5-(5′-1,3,4-thiadiazol-2-thiolazo)barbituric acid] $\cdot 6H_2O$ and the thiobarbituric analog and Ni_3[5-(6-purineazo)thiobarbituric acid]$_2 \cdot 6H_2O$ proceed *via* first-order reactions, whereas Ni-5-[2-benzothiazoleazo]thiobarbituric acid and Ni-5-[2-benzothiazoleazo]thiouracil proceed *via* second-order reactions.

7. The change of entropy ΔS^* values for all complexes are given in Table VIII. The negative values of ΔS^* indicated that the activated complexes have a more ordered structure than the reactants [57]. The lower values of collision factor, Z, in most of the complexes indicated the slow nature of the reaction [58]. The degree of decomposition (α_m) was calculated and given in Table VIII.

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