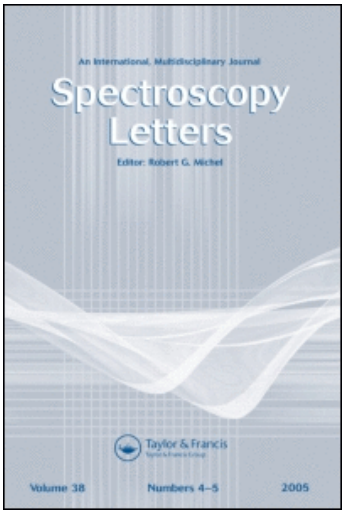

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STUDIES ON SOME THIAZOLYLAZO COMPOUNDS AND THEIR COBALT, NICKEL, AND COPPER COMPLEXES

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STUDIES ON SOME THIAZOLYLAZO COMPOUNDS AND THEIR COBALT, NICKEL, AND COPPER COMPLEXES

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ABSTRACT

The thiazolylazo compounds and their $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes of barbituric acid, uracil, thiouracil, citrazinic acid, chromotropic acid, gallic acid, pyrogallol and salicylic acid were prepared and characterized by ^1H NMR, IR and the effect of pH on the electronic absorption spectra. The mode of ionization, the electronic transitions and the dissociation constants were discussed. The stoichiometries of the complexes were of 1:1, 2:1 and 3:2 (M:L). The copper complexes are of isotropic ESR spectra (except that of gallic acid which

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showed a complicated one) and are of magnetically diluted behaviour with orbital contribution. Detailed DTA data were obtained and discussed.

Key Words: Thiazolylazo compounds; $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes; Barbituric acid; Uracil; Thiouracil; Citrazinic acid; Chromotropic acid; Gallic acid; Pyrogallol, Salicylic acid; ^1H NMR; IR

INTRODUCTION

The pyrimidine compounds are one of the most important classes from different views especially applied chemistry[1,2] and biological activity.[3,4] In our laboratory, Masoud et al.[5–45] published a series of papers to throw light on the chemistry of pyrimidine compounds and their complexes. The thiolylazo compounds and their $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes of barbituric acid, uracil, thiouracil, citrazinic acid, chromotropic acid, gallic acid, pyrogallol and salicylic acid are the selected compounds for studies through this paper by ^1H NMR, IR, ESR spectra and the effect of pH on the electronic absorption spectra. The thermal behaviour is also studied to give more spot light on the structural chemistry of these compounds.

EXPERIMENTAL

General Method of Preparation of the Free Azo Compounds

2-Amino thiazole (0.1 mole) was dissolved in HCl (0.2 mole/25 mL distilled water). The hydrochloride compounds were diazotized below 5°C with a solution of $NaNO_2$ (0.1 mole/30 mL distilled water). The diazonium chloride[46] was coupled with an alkaline solution (0.1 mole) of each of the following compounds; barbituric acid, uracil, thiouracil, citrazinic acid, chromotropic acid, salicylic acid, gallic acid and pyrogallol.

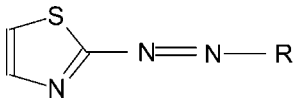
The crude dyes were collected by filtration and were crystallized from methanol,[47] then dried in a vacuum desiccator over anhydrous $CaCl_2$. The C, H, N and S contents were analyzed at the micro analytical unit, Chemistry Department, Faculty of Science, Cairo University, Table 1.

The possible structure is assumed to be as follows:

Table 1. Analytical Data and Some Properties of the Organic Compounds

Compound	m.p. °C	Colour	% Calc./(% Found) C	H	N	S
3-(2-thiazolylazo) citrazinic acid	>300	Brown	40.6	2.3	21.1	12.1
			(40.6)	(2.3)	(21.1)	(12.1)
5-(2-thiazolylazo) 2-thiouracil	262	Brown	35.2	2.1	29.3	26.8
			(35.5)	(2.1)	(29.5)	(20.1)
5-(2-thiazolylazo) uracil	>300	Brown	37.7	2.3	31.4	14.4
			(37.7)	(2.5)	(31.4)	(14.5)
5-(2-thiazolylazo) barbituric acid	172	Yellowish brown	35.2	2.1	29.3	13.4
			(37.7)	(2.1)	(29.5)	(13.5)
4-(2-thiazolylazo) disodium chromotropate	>300	Pink	32.8	1.5	8.8	20.3
			(32.8)	(2.0)	(8.9)	(20.5)
4-(2-thiazolylazo) pyrogallol	>300	Brown	45.6	3.0	17.7	13.5
			(46.0)	(3.2)	(18.1)	(13.9)
4-(2-thiazolylazo) salicylic acid	192	Yellowish green	48.2	2.8	16.9	12.8
			(48.2)	(3.1)	(17.1)	(12.1)
2-(2-thiazolylazo) gallic acid	>300	Brown	42.7	2.5	14.9	11.4
			(42.9)	(2.6)	(15.2)	(11.6)

R: Barbituric acid
: Uracil
: Thiouracil
: Citrazinic acid
: Chromotropic acid
: Gallic acid
: Pyrogallol
: Salicylic acid



Synthesis of Complexes

An ammoniacal solution of 0.01 mole of the metal (II) chloride {M = Co, Ni and Cu} was mixed with an ammoniacal solution of 0.01 mole of the organic compound. The reaction mixture was refluxed (2–3 h), left overnight where the complexes were precipitated, filtered, washed by ethanol and dried in a desiccator over anhydrous $CaCl_2$. Table 2 collects the analytical data for the prepared complexes, where the metal contents were determined

Table 2. Colours and Analytical Data of the Complexes

Complex	Colour	% Calc./(% Found) M	N	S	Cl
4-(2-thiazolylazo) pyrogallol (H_3L)					
$Co(HL)\cdot 4H_2O$	Black	16.1 (15.6)	11.5 (11.3)	8.8 (8.4)	– (–)
$Ni(HL)\cdot 4H_2O$	Black	16.0 (15.9)	11.5 (11.2)	8.8 (8.5)	– (–)
$Cu_2(H_3L)Cl_4\cdot 4H_2O$	Black	23.4 (23.9)	7.7 (7.5)	5.9 (6.2)	26.2 (26.1)
5-(2-Thiazolylazo) salicylic acid (H_2L)					
$Co(HL)OH\cdot H_2O$	Brown	17.3 (17.9)	12.3 (12.7)	9.4 (6.5)	– (–)
$Ni(H_2L)Cl_2$	Chocolate	15.6 (15.4)	11.1 (10.9)	8.5 (8.4)	18.8 (18.5)
$Cu_2LCl\cdot 3H_2O$	Black	27.4 (27.7)	9.1 (9.2)	6.9 (7.1)	7.6 (7.6)
3-(2-thiazolylazo) citrazinic acid (H_3L)					
$Co(HL)\cdot 3H_2O$	Brown	15.5 (15.3)	14.8 (–)	8.5 (8.5)	– (–)
$Ni(HL)\cdot H_2O$	Brown	17.3 (17.5)	16.5 (–)	9.4 (9.5)	– (–)
$Cu(H_2L)Cl$	Brown	17.5 (17.3)	15.4 (–)	8.8 (8.7)	9.8 (10.1)
5-(2-thiazolylazo)-2-thiouracil (H_2L)					
$Co_3L(H_2L)Cl_4$	Brown	22.1 (21.9)	17.6 (17.6)	16.1 (16.1)	17.9 (17.9)
$Ni_3L_2(OH)_2\cdot H_2O$	Pale yellow	25.1 (25.7)	19.9 (19.6)	18.2 (–)	– (–)
$Cu_3L_2(OH)_2\cdot H_2O$	Grey	26.5 (26.8)	19.5 (20.0)	17.9 (17.5)	– (–)
2-(2-Thiazolylazo) gallic acid (H_4L)					
$Co_3(HL)(H_2L)(OH)\cdot 7H_2O$	Black	20.1 (19.9)	9.5 (9.6)	7.3 (7.3)	– (–)
$[Ni_2(H_4L)Cl_4(H_2O)_5]3H_2O$	Black	17.1 (16.9)	6.1 (6.1)	4.7 (4.7)	20.7 (20.9)
$Cu_3(H_2L)_2Cl_2\cdot 8H_2O$	Black	19.7 (19.8)	8.7 (–)	6.6 (–)	7.4 (7.7)

All the prepared complexes have melting points >300°C.

by the usual complexmetric titration methods after decomposition with aquaregia.[48] The halogen content was determined by Mohr's method.[49]

Instruments and Working Procedure

I) Electronic absorption spectra in the visible and ultraviolet regions were made with Pye-Unicam SP 1800 spectrophotometer.

II) Infra red spectra were made using Pye-Unicam SP-1025 and SP 3-100 spectrophotometer equipped with NaCl-Prism over the frequency range 200–400° cm^{-1}.

III) Nuclear magnetic resonance were recorded in ^{6}d-dimethyl sulphoxide and ^{6}d-acetone using an EM-390, 90 MHz-NMR spectrophotometer. The magnetic susceptibilities of powdered samples were measured at Institutefur Physikaische und Theoretische Chemie Technische UniverSitat Graz, Austeria in the temperature range 300–77° (K at four different field strengths (1.32, 1.02, 0.71 and 0.42 {T}) using a modified Faraday balance (SUS-10, manufactured by A. Paar KG, Graz). The equipment was calibrated with freshly prepared $HgCo(NCS)_4$.[50]

IV) Thermal analysis (DTA) Performed on a Du Pont 9900 computerized thermal analyzer. The heating rate used was 10 degree/min. 60 mg sample was placed in a platinum crucible. Dry nitrogen was flowed over the sample at a rate 10 mL/min and a chamber cooling water flow rate was 10 e/h. The speed was 5 mm/min.

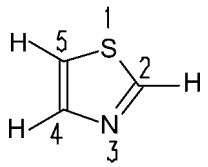
V) Electron spin resonance spectra were recorded at 100 KHz modulation and 10 CH_2 modulation amplitude on JES-200 spectrometer. 10 mV incident power was used and resonance conditions were at Ca 9.75 GHZ (X-band) at room temperature. Spectra were obtained with an air products LTD-3-110 Heli-Tran liquid helium transfer refrigerator. The field was calibrated with a powder sample of DPPH ($g = 2.0037$).

RESULTS AND DISCUSSION

^{1}H-NMR

Free thiazole[51] gave three ^{1}H-NMR peaks at $\delta = 7.41$, 7.18 and 8.88 ppm due to the oliphenic hydrogens at C(5), C(4) and C(2), respectively.

The higher deshielded proton is that at C(2) due to its location in the middle between nitrogen and sulphur atoms. However, the C(4) protons are higher deshielded than the C(5) proton, due to the effect of the neighbouring atoms.



The compounds under investigation could be classified into two categories:

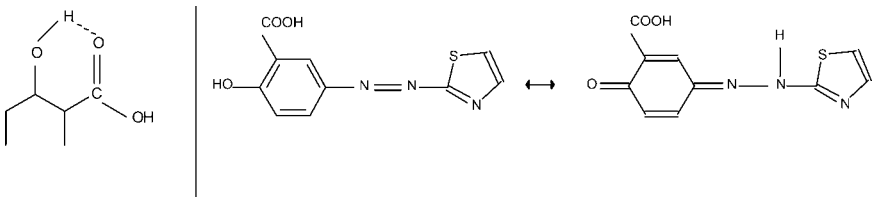
A) Those of the phenolic type:	B) Those of the pyrimidine series:
I) 5-(2-thiazolylazo) salicylic acid.	I) 5-(2-thiazolylazo) barbituric acid.
II) 4-(2-thiazolylazo) pyrogallol.	II) 5-(2-thiazolylazo) uracil.
	III) 5-(2-thiazolylazo)-2-thiouracil.

The data of the A series, were recorded in ^{6}d-acetone while those of the B series were obtained in presence of ^{6}d-DMSO due to solubility properties.

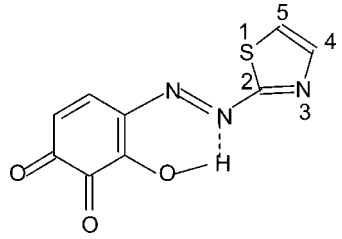
5-(2-Thiazolylazo) salicylic acid, gave quarted signals at $\lambda = 6.6$–7.0 ppm due to the C(5) and C(6) protons of the phenyl ring. The doublet appearance of the C(5) and C(4) protons of the thiazole ring at $\lambda = 7.16$ and 7.75 ppm, respectively, (i.e., at a lower δ-value with respect to the thiazole itself), may be argued to the presence of the azo group in conjugation to the diene system of the thiazole moiety. The triplet peak appeared at $\delta = 7.25$–7.60 ppm is due to the C(3) proton of the phenyl ring, (i.e., with a higher δ-value than the other protons in phenyl ring). This is related to its existence, at the middle, between two withdrawing groups.

The absence of the carboxylic proton signal could be argued to the fast resonating nature of the acidic hydrogen between the two oxygen atoms of the acidic hydrogen between the two oxygen atoms of the carboxylic group.[52]

The absence of the hydroxyl proton signal arised from the existence of: i) strong hydrogen bonding with the carboxy group and/or ii) the azo-hydrazo tautomerism.

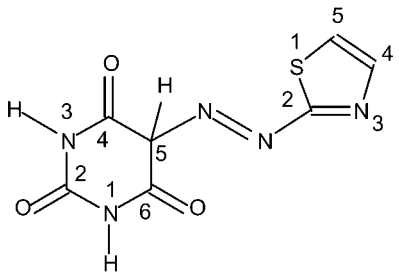


4-(2-thiazolylazo) pyrogallol showed a mulitiplet band at $\delta = 6.1$–7.7 ppm, due to four protons of the C(5) and C(6) of the phenyl ring diffused with the C(5) and C(4) protons of the thiazolyl moiety. The thiazolyl hydrogen becomes more shielded than the thiazole itself as a result to the presence of the azo group in conjugation with the thiazolyl moiety. The singlet band at $\delta = 14.9$ ppm represents a hydroxyl proton of the pyrogallol moiety involved in strong intermolecular hydrogen bonding. This peak represents one proton due to possible quinone formation.

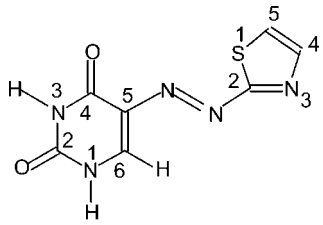


5-(2-thiazolylazo) barbituric acid showed two doublet bands at $\delta = 6.3$–6.5 and 6.6–6.8 ppm and a multiplet band at $\delta = 7.1$–7.5 ppm. The former bands are due to the C(5) and C(4) protons of the thiazolyl ring. The decrease in the δ-value compared to the thiazole itself is probably due to presence of the azo group in conjugation with the thiazole moiety. However, the latter band may be argued to the C(5) proton of the barbituric acid moiety.

The C(5) proton of the 5-(2-thiazolylazo) barbituric acid is more deshielded than the C(5) proton of the barbituric acid, probably due to the withdrawing property of the azo group. The absence of the N_1, N_3 protons of the 5-(2-thiazolylazo) barbituric acid may be argued to the strong solvent-solute interaction, since the DMSO is hydrogen banded to the NH group.[52]



The 5-(2-thiazolylazo) uracil compound, showed two doublet bands at $\delta = 5.4$–5.6 and 7.2–7.4 ppm due to the C(5) and C(4) protons of the thiazolyl ring, respectively. The high shielding property than thiazole itself is due to the presence of the azo group. The broad bands at $\lambda = 10.6$–11.1 and 7.5–8.0 ppm are due to the NH and the C(6) proton of the uracil moiety, respectively. The reported data for uracil assigned the presence of the keto from with the syn conformation[46] and the dilactam tautomeric structure in its ground state[53] where the C(4) rather than the C(2) carbonyl group is used as a proton acceptor in dimer formation. The DMSO solvent interaction with the solute stabilized the NH group,[54] to explain the doublet nature of the band at 6.2–7.4 ppm, probably due to the quasi-aromatic property of uracil ring, with the C(6) H $\cdots$ O bonding with the O atom of the DMSO solvent.[55] The date of 5-(2-thiazolylazo) uracil, suggest its existence in the keto form. The C(6) proton of the uracil moiety in 5-(2-thiazolylazo) uracil appeared more deshielded than that of the uracil itself, due to the effect of the azo group property.



5-(2-thiazolylazo)-2-thiouracil, showed two doublets at $\lambda = 5.6$–5.9 and 7.1–7.4 ppm due to the C(5) and C(4) hydrogens of the thiazolyl moiety, respectively. Both are more shielded than the thiazole itself due to the presence of the azo group in conjugation with the thiazole group. The doublet interfered band at 11.5–12.6 ppm, due to the S-Hand N^3-H of the thiouracil moiety, the N3-H is more deshielded than the S-H due to the high electronegativity of the nitrogen relative to the sulphur. The disappearance of the C(6) proton of the thiouracil moiety is probably due to the strong interference between the ^{6}d-DMSO and the C(6) proton. 2-thiouracil dose

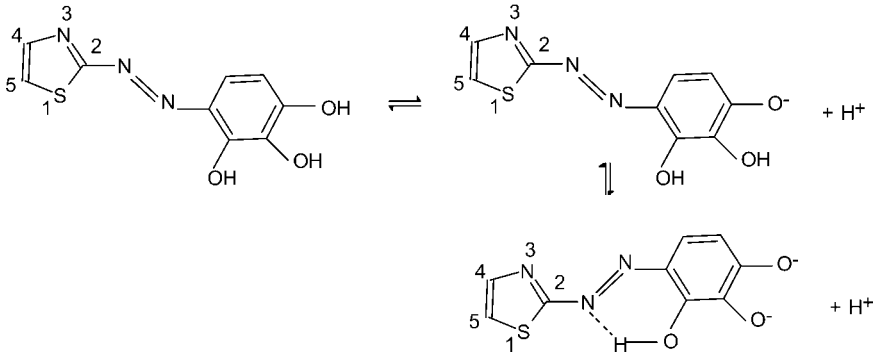
not show separate N-H and S-H proton peaks with no coupling between the C(6) and the amide proton but with possible coupling between C(6) and C(5) protons.

Effect of pH on the Electronic Absorption Spectra of the Organic Compounds

The electronic absorption spectra of the compounds under investigation are studied and pK values are evaluated based on both protonation.

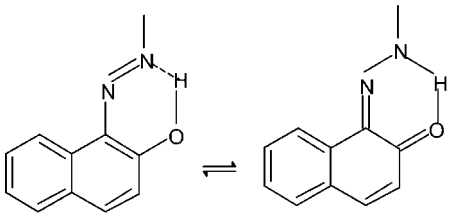
The electronic absorption spectra of 1×10^{-4} M 4-(2-thiazolylazo) pyrogallol showed two characteristic bands at 211 and 318 nm due to $\pi - \pi^*$ transition. The intensity of the first band increases successively in the pH range 2.4–8, followed by a stepwise decrease in the intensity with the increase of pH's (>8). The second band decreases in intesity as the pH increases. The proton of the hydroxyl group in ortho-position to the azo group is stabilized by the hydrogen bonding. The partial quinones structure is previously proved by ^{1}H-NMR Such structure is protonated in acidic medium giving the phenolic structure. Pyrogallol gave a well defined band at λ_{max} 345 nm with the detection of an isobestic point at 355 nm covering the pH range 4–7 due to the mono-ionized and the doubly ionized species. The triply ionized form is difficult to be formed even in strongly alkaline medium. Two pK values were deduced for pyrogallol, $pK_1 = 4.8$ and $pK_2 = 8.5$.

From all the previous discussions, the following ionization scheme for 4-(2-thiazolylazo) pyrogallol is postulated:

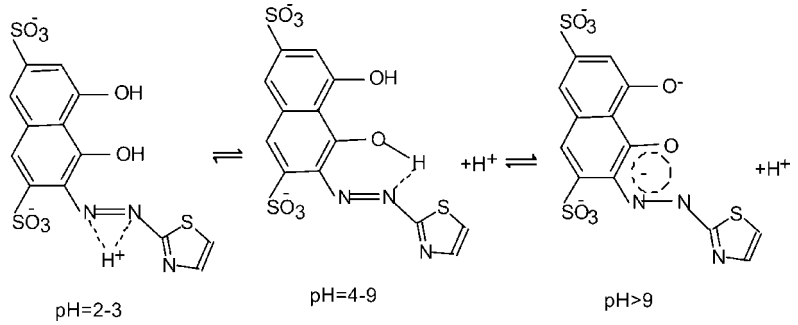


Two pK values were deduced ($pK_1 = 7.05$ and $pK_2 = 10.1$). The effect of pH on the electronic absorption spectra of 4-(2-thiazolylazo) disodium chromotropate, gave three well defined bands at 237, 353 and 500 nm. A remarkable feature is given where the positions of these bands is pH

independent, while their intensities are affected by the pH. The first two bands are sharp, while the latter one is broad. The first band is due to the $\pi-\pi^*$ transition of the phenolic ring, and the other two's assigned the $\pi-\pi^*$ transition of the azo linkage overlapped with an intramolecular CT effect.



So, the following mode of ionization is postulated:



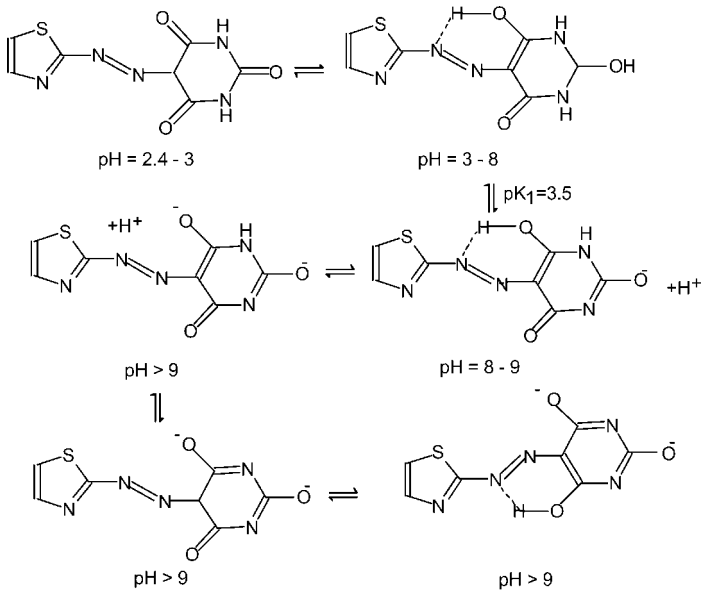
Two pK values were deduced: $pK = 3.5$ and $pK_2 = 8.15$.

The effect of pH on the electronic absorption spectra of 1×10^{-4} M 5-(2-thiazolylazo) barbituric acid, showed two bands at 212–215 and 254–259 nm in the pH range 2.4–11.8. The first band is due to the $\pi-\pi^*$ electronic transition of the conjugated π-system (i.e., the azo group and the diene system of the thiazole ring). The second band is attributed to the $n-\pi^*$ electronic transition of the n-electron pairs of the oxygen atoms. Both bands are red shifted as the pH increases. The modified limiting absorption plot gave pK_1 and pK_2 amounts 3.5 and 8.9, respectively.

However, the two lone pairs of electrons of the azo group are not the only interacting non-bonding electrons, since the barbituric acid part of the molecule contains nitrogen and oxygen atoms as extra sources of lone-pair of electrons.

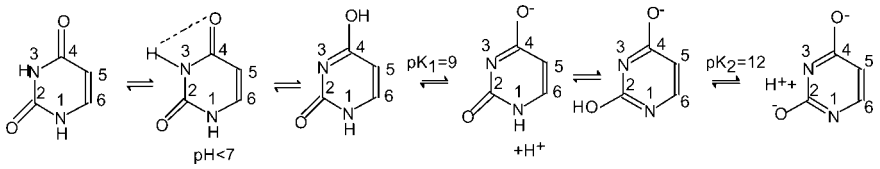
Thus, other $n \rightarrow \pi^*$ transitions are expected to take place from these non bonding orbitals to different π^* molecular orbitals extending over such a large molecule.[6] Also, most of azo compounds prefer their existence in the trans-azo isomer,[6] which possesses a lower steric instability than the cis-isomer.

The mechanism of ionization for 5-(2-thiazolylazo) barbituric acid is postulated:



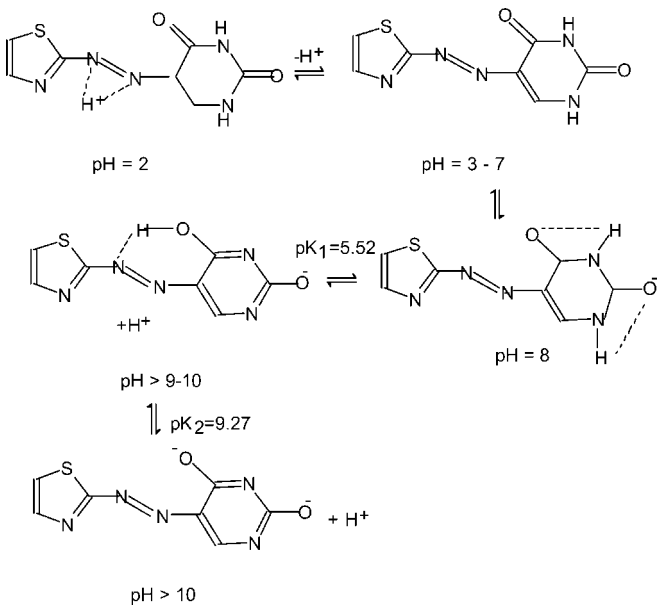
The effect of pH on the electronic spectra of 1×10^{-4} M 5-(2-thiazolylazo) uracil, showed two characteristic bands, one is sharp at 209–214 nm and the other is a shoulder at 250–264 nm. On increasing the pH, the intensity of the first band increased with a slight blue shift (=5 nm), while the second band remains unchanged. The first band may argue to the $\pi-\pi^*$ of the two sp^2 hybridized carbons of the exocyclic band in heterocyclic ring, as uracil. The second band is assigned to $\pi-\pi^*$ transition of the two carbonyl groups in β-positions as reported for uracil.

As the pH increased the two bands are red shifted and become more intense, where the compound is subjected to tautomerization with the presence of auxochromic groups.[56] The scheme of ionization is postulated as follow:



However, the lower pK values of the azo compound than the uracil may argued to the withdrawing property of the azo group.

From all the previous discussion, the following ionization scheme for 5-(2-thiazolylazo) uracil is postulated:

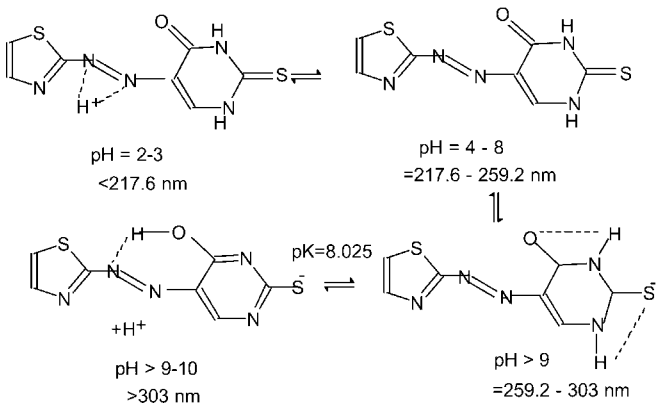


The electronic absorption spectra of 1×10^{-4} M 5-(2-thiazolylazo)-2-thiouracil gave two maximal bands at 213 and 272 nm in the pH range 2.4–8.0, where the intensity of both bands is decreased with the increase of pH accompanied with a slight blue shift ($\approx$13 nm for the second bands). However, at pH $\geq$9, four bands appeared at 210, 228, 258 and 310 nm. The first band is due to the $\pi-\pi^*$ of the two sp^2 hybridized carbons of the exocyclic band in heterocyclic ring. In alkaline medium, the blue shift of the second band is assigned to the formation of the -OH and -SH auxo-chromophore groups. The observed K-band at 310 nm assumes the phenomena of tautomerism between the thione and the thiol structures. The formation of the isobestic points at 217.6, 259.2 and 303.0 nm, assigned the presence of different absorbing species in equilibrium to each other: protonated, neutral and deprotonated forms. All the three-isobestic points covered all the pH-ranges (2.4–11.8). The data gave a pK value of 8.03. Thiouracil gave two bands at 210 and 270 nm in the pH range 2–7 due to the $\pi-\pi^*$ of two sp^2 hybridized carbons and the

coupled $\pi-\pi^*$ of the two carbonyl and thiocarbonyl groups in β-position, respectively. In the pH range 9.2–12.1, a band at 255 nm appeared while the former two's are red shifted due to successive ionization. Three isobestic points at 222, 254 and 302 nm are assigned, the presence of different absorbing species in equilibrium to each other: protonated, neutral and deprotonated forms. The 302 nm band is due intramolecular hydrogen bonded between N(3)-H with C=O and N(1)-H with C=S. The band at 222 nm is accompanied by a hypochromic shift, to increase of the aromatic character of the thiouracil ring. In alkaline solution (pH > 9) most of the bands are red shifted and become intense, due to tautomerization with the presence of auxochromic groups. Two modes of ionization could be presented:

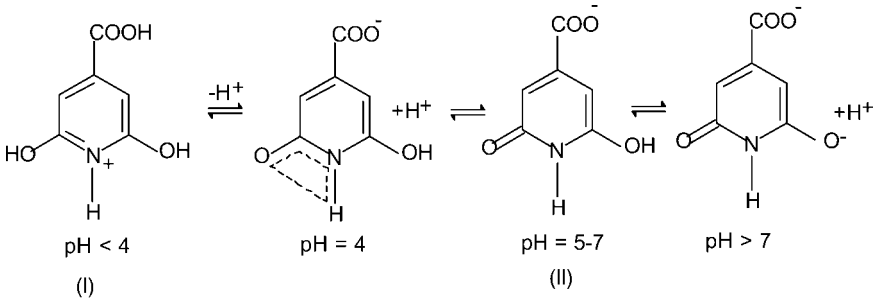
$$\text{I) HN-C=S}\longrightarrow\text{-N=C-SH;} \qquad \text{II) HN-C=O}\longrightarrow\text{-N=C-O-H}$$

The negative $FeCl_3$ test rest reaction for phenolic-OH and the lower pK value than of the reported phenolic compounds to suggest that the mode of ionization (I) is more acceptable than (II). The following scheme of ionization of 5-(2-thiazolylazo)-2-thiouracil is postulated:



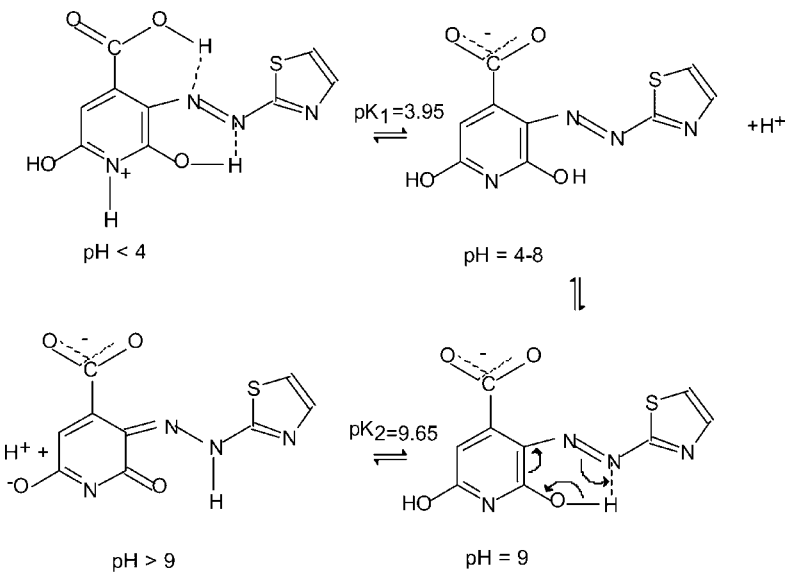
The electronic absorption spectra of 3-(-2-thiazolylazo) citrazinic acid, showed three characteristic regions in the wave length ranges: 209–216, 243–252 and 334–337 nm appeared in the pH range 2.4–11.8, except the second band disappeared in solutions with pH $\geq$10. The first and the second regions are both of the $\pi-\pi^*$ electronic transitions, the first of the aromatic π-system of the pyridine ring and the second is due to the carboxy group. The third band is of $n-\pi^*$ electronic transition of

the n-electrons of the oxygen atoms. As the pH increases the first and the third bands become more intense, meanwhile all bends are red shifted. However, the electronic absorption spectra of citrazinic acid at differet pH's, gave four regions 205–215, 228–233, 326–332 and 341–345 nm. The first region decreased in intensity with the increase of pH (2–4) followed by constant absorbance in pH range (5–12), accompanied by a regular red shift due to ionization with the formation of the keto isomer (structure II). Such data favour the $\pi-\pi^*$ electronic transition of the aromatic π-system of the pyridine ring (structure I). In acidic media (pH's 2, 3), the shoulder at 228 nm is due to $\pi-\pi^*$ transition of the carboxy group, becomes more intense with the increase of absorbance in solutions up to $pH = 4$. In pH range 5–12 the absorbance is pH independent, probably due to the overlapping between two $\pi-\pi^*$ electronic transition of both the carbonyl of the carboxylate group and the new carbonyl group of the keto isomer. Meanwhile, the π-band of the carboxylate anion is probably involved. Extra $n-\pi^*$ transition band appeared in solutions with pH (4–7), due to the carbonyl group of the keto form. The absence of this band in solutions of $pH > 7$ is probably due to the stabilization of the n-electrons of the keto group formed through ionization. The $n \longrightarrow \pi^*$ transition of the carbonyl group appeared in the wave length range 344–347 nm while the shoulder at 328 nm is due to the transition of the N-hetero atom of the pyridine ring at $pH = 2$, with successive increase in absorbance as the pH increases up to $pH = 4$. At $pH > 7$ such band is completely disappeared. The mode of ionization is explained as follows:



For the 3-(-2-thiazolylazo) citrazinic acid, the modified limiting absorption plot and the pH-As plot gave pK_1 and pK_2 values equal 3.95 and 9.65 respectively. The pK-values of the thiazolylazo citrazinic acid is smaller than that of citrazinic acid itself, due to the presence of the azo group that enhance the deprotonation process, where the mode of ionization

is given as follow:



Stereochemistry and Mode of Bonding of the Complexes

The IR spectra of 2-(2-thiazolylazo) disodium chromotropate, gave a characteristic broad band at 3433 cm^{-1} due to intermolecular hydrogen bonding resulting from the C_8-OH group in two different molecules to favour the associated structure. The bands at 1621, 1510 and 1400 cm^{-1} are due to $\nu_{C=N}$ and the stretching modes of the azo group in its asymmetric and symmetric states. The band at 1211 cm^{-1} is due to $\nu_{C\text{-}O}$, while that at 1050 cm^{-1} may assigned to $\nu_{C=N}$ and/ or ν_{S-O} of the sulphonic group. The γ_{OH} mode of vibration is assigned at 643 cm^{-1}.

Two regions in IR spectra of uracils were analyzed: [57] (a) the N-H stretching region in crystals and (b) the C=O stretching region in matrix-isolated monomers. The existed resonance leads to energy splitting and redistribution of intensities. These are: (a) a harmonic resonance between the N-H stretching in H-bonded groups and the C-H stretching, and (b) an inharmonic (Fermi) resonance between the C=O stretching and a combination band involving the N(3)-H and C=O bending vibrations.[57] Frequency shifts between the gaseous and solid phase were detected. The observed C=O band splitting in uracil supported a coupling between various C=O dipoles within the unit cell of uracil, leading to band–splitting

in the double bond region. The spectrum of the associated uracil species in matrixes suggests that it is a cyclic dimer, linked by C(2)...O...H-N(1) H-bonds. The FT-IR spectra of uracil were studied in pure Ar matrixes and H_2O or HCl doped Ar matrixes to suggest the presence of open dimers in associated compounds.

Transition moment directions for the double-bond region vibrations of uracil are calculated by using fixed partial charge model approximation. The coupling between the 2carbonyl bonds and the C-C double bond in uracil is sensitive to the choice of the corresponding stretching force constants.

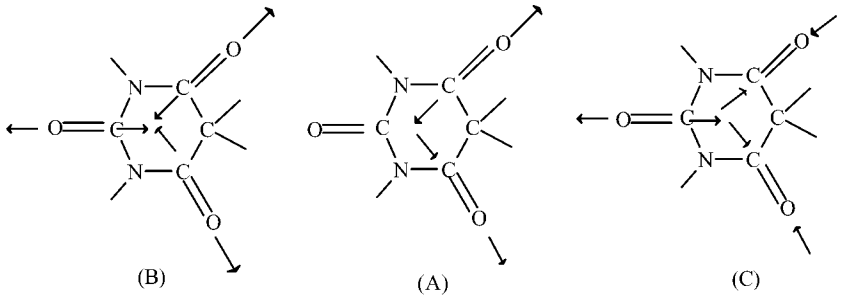
The external (lattice vibrations) spectrum is assigned on the basis of the normal mode calculations in the approximation of the rigid monomer. Vibrations of the double (N-H...O) H-bond are assigned. The spectral characteristics of uracil in autoassociates and hydrates were investigated using high – resolution IR spectroscopy in Ar matrixes. Shifts of vibration frequencies in simple complexes of 10–30 cm^{-1} in the 4000–400 cm^{-1} region were observed.

The monomeric molecules are in the 2,4-dioxo tautomeric form and are planar determined indirectly from the absence of band multiplicity.

The IR spectral data of 5-(2-thiazolylazo) uracil, showed a broad characteristic band the region 3200–3400 cm^{-1} assigned for the $\nu_{N\text{-}H}$, through hydrogen bond of the type N-H...O. The $\nu_{C\text{-}H}$ appeared at 2918 cm^{-1}. The bands at 1408 and 1486 cm^{-1} are assigned for ν_s and ν_{as} stretching vibrations of the azo group, respectively. These at 1660 and 1045 cm^{-1} are due to $\nu_{C=O}$ and $\nu_{C\text{-}N}$ from either the thiazolylazo linkage and/or those of the uracil moiety, to assist the existence of the keto structure. The of barbituric acid (BA) from the view of the fundamental groups C=O, N-H, and OH could explain the phenomena of keto-enol tautomerism, gave that the ring in BA is significantly distorted from planarity, in such a way that the methylene part of the ring has a boat configuration. Thus, the symmetry of the isolated molecule is C_5 of C_{2v}, the latter is not possible in the solid because of the manner in which the molecules are linked by hydrogen bonds.

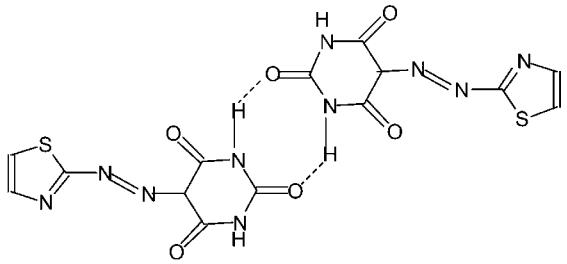
The spectra suggest the existence of a hydrogen bond, as evident form the presence of a well defined splitting sharp band in the frequency range 3050–3520 cm^{-1}. Such region is appeared at 3200–3400 cm^{-1} in a broad and splitted feature in the entitled compound. Such finding points to that solid BA and its thiazolylazo contains pairs of molecules linked through two hydrogen bonds, between the N-H groups in the 3 position and the carbonyls in the 2 position are in a ribbon structure through hydrogen bonds between the N-H groups in 1 position and carbonyls in the 4 position. The carbonyl in 6 position is not involved in the hydrogen bonding. BA gives ν_{NH} at 3200 cm^{-1} and ν_{CH2} at 2890 cm^{-1}. The latter becomes at 2950 cm^{-1} in the corresponding azo compound. The region 1800–1600 cm^{-1} is of

importance for BA data. A strong absorption at 1730 cm^{-1} and 1620 cm^{-1}, due to $\nu_{C=O}$ and $\nu_{C=N}$ stretching vibrations are appeared, respectively. Three carbonyl-stretching vibrations are expected to appear in this region. However, their assignments had been the subject of controversy. The study of BA showed that the highest frequency band is to the 4,6-carbonyl antisymmetric stretching mode (A), and the lower frequency band is due to the 2-carbonyl stretching mode (C). Others assigned the highest frequency band as the (C) mode beside the highest frequency and is assigned to the (B) mode and the middle band to the (C) mode while the lowest is to the (A) mode. This could be represented as follows:



Carbonyl stretchings of BA are: (A) 4,6-C=O antisymmetric stretch, (B) symmetric stretch, (C) 2-C=O stretch.

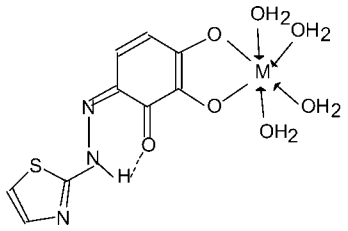
The C-N stretches appear at 1410, 1240 and 1195 cm^{-1} for BA, which has additionally two N-H in plane bending mode and CH_2. The CH_2 scissors are easily identified by the presence of two strong bands at 1360 and 1350 cm^{-1}. Two C-C stretching modes are expected to occur in this region by the presence of two bands at 1030 and 940 cm^{-1}. In the region 800–200 cm^{-1}, this is due to two N-H, six C=O and six ring modes. For the azo compound, intense bands at 1585 and 1451 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of the -N=N-group, respectively. That at 1684 cm^{-1} could be considered for overlapping of $\nu_{C=O}$ and $\nu_{C=N}$ modes. The band at 1070 cm^{-1} is assigned for $\nu_{C\text{-}N}$. The following structure is suggested:



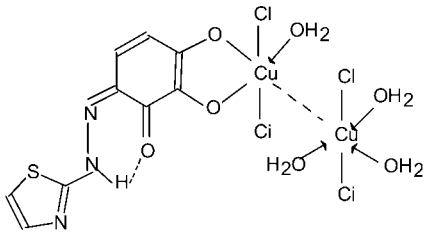
The IR spectral data of 4-(2-thiazolylazo) pyrogallol, H_3L, and its $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes gave the followings:

1) The ν_{OH} region in the free ligand is shifted towards lower frequency on complexation with all metals with the presence of broad shoulder at frequencies higher than 3600 cm^{-1}, to assign the existence of water molecules in the complexes.
2) The ν_{NH} (2830, 2930 cm^{-1}), $\nu_{C=O}$ (1664 cm^{-1}), $\nu_{C=N}$ (1612 cm^{-1}), ν_s (N=N) (1412 cm^{-1}), ν_{as} (N=N) (1503 cm^{-1}) and $\nu_{C\text{-}N}$ (1244 cm^{-1}) in the free ligand are nearly unaffected on complexation.
3) The $\nu_{C\text{-}O}$ band at 1377 cm^{-1} in the free ligand is shifted to lower frequency on complexation.
4) The bands at 593, 590 and 593 cm^{-1} in the $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes, respectively, are due to ν_{M-O}.
5) The nujol mull electronic absorption spectra of the Co (HL). $4H_2O$, Ni (HL). $4HO_2$ and Cu_2 (H_3L) $Cl_4 \cdot 4H_2O$ gave bands at 24,875, 18,656, 14,204; 2500, 17,482, 14,450 and 22,727, 17,857, 13,513 cm^{-1}, respectively. The first band is mainly of the C.T. type while the others are due to d-d transitions. In general the spectral pattern is due to Oh geometry.
6) The measured μ_{eff} values are 3.98, 3.35 and 2.17 BM, respectively, assign the octahedral geometry.

The structures of the complexes are suggested:



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



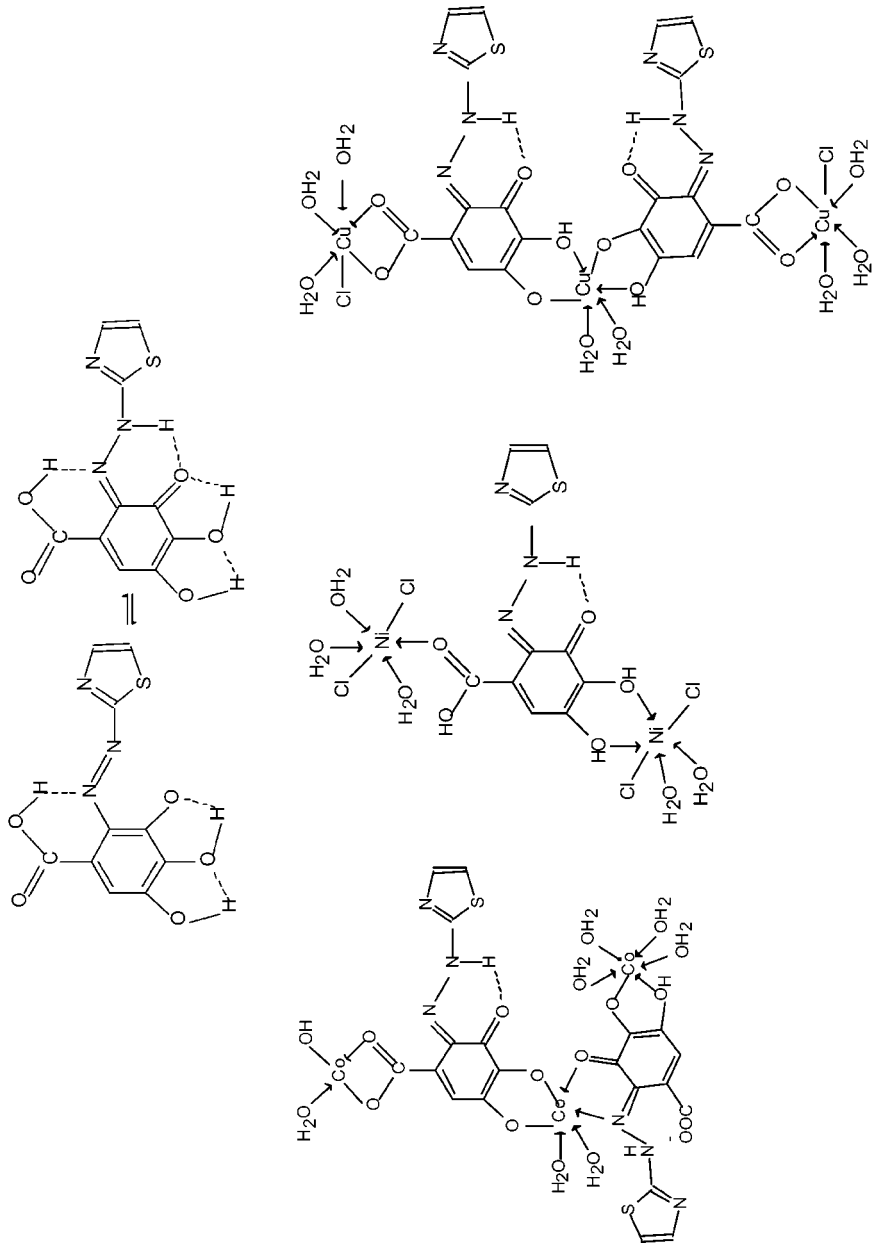
The IR spectra of 2-(2-thiazolylazo) gallic acid, HL, and its $Co^{(II)}$, $Ni^{(II)}$ and $Co^{(II)}$ complexes, gave the followings:

1. The board band at 3000–3450 cm^{-1} and the shoulder at 3600 cm^{-1} are due to the sharing-OH groups in complex formation through hydrogen bonding.
2. The doublet ν_{NH} bands in the free ligand are not affected on complexation.

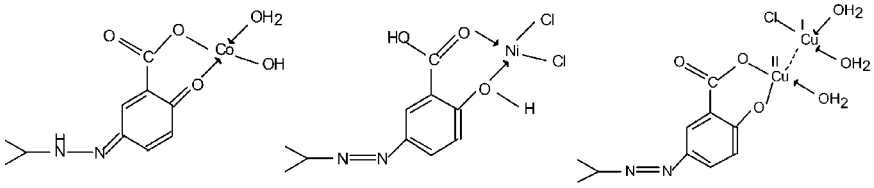
3. The band at 1690 cm^{-1} that assigns the $\nu_{C=O}$ in the free ligand becomes at 1680, 1683 and 1678 cm^{-1} in $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes, respectively. The carbonyl group is involved in the structure of the complexes.
4. The $\nu_{C=N}$ band in the free ligand (1625 cm^{-1}) appeared at 1602, 1614 and 1607 cm^{-1} in the $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$complexes, respectively.
5. The carbonyl group identified at 1448 and 1517 cm^{-1} in the free ligand (ν_s, ν_{as} respectively) became at 1432, 1510; 1427 and 1407, 1530 cm^{-1} Co^{II}, $Ni^{(II)}$ and Cu^{II} complexes, respectively.
6. The azo group at 1464, 1483 cm^{-1} (ν_s, ν_{as}, respectively) is nearly unaffected on complexation.
7. The band at 1550, 1381 and 1037 cm^{-1} in the free ligand are due to $\nu_{C=C}$, $\nu_{C\text{-}O}$ and $\nu_{C=N}$, respectively. The bands at 1352, 1017, 1364, 1009 and 1347, 1022 cm^{-1} in the $Co^{(II)}$, $Ni^{(II)}$, and $Cu^{(II)}$ complexes, respectively, assigned to $\nu_{C\text{-}O}$ and $\nu_{C\text{-}N}$, respectively.
8. The bands at 450; 593, 440, 588 and 412, 594 cm^{-1} in the $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes, respectively, assigned to $\nu_{M\text{-}N}$ and ν_{M-O}, respectively.
9. The nujol mull electronic absorption spectra of $Co_3(HL)_2 \cdot 8H_2O$, $[Ni_2(H_4L)Cl_4(H_2O)_5] \cdot 3H_2O$ and $[Cu_3(H2L)_2Cl_2] \cdot 8H_2O$ gave bands at 24,390, 18,867; 14,705, 24,752, 18,656, 14,084, and 26,315, 17,857, 13,513 cm^{-1}. The first bands are due to C.T. and the others are mainly of d-d transition with possible metal-metal interaction.
10. The measured μ_{eff} values for the Co(II), Ni(II) and Cu(II) complexes are 4.2, 3.8 and 4.4 BM, respectively, typified the octahedral geometry. The structures on page 396 are postulated for the free ligand the prepared complexes.

The I.R data for 5-(2-thiazolylazo) salicylic acid gave a broad band at 3230–3500 cm^{-1} due to ν_{OH} with hydrogen bonding. However, the doublet band at 2830–2980 cm^{-1} is assigned to the $\nu_{N\text{-}H}$. The bands at 1686 and 1637 cm^{-1} are due to $\nu_{C=O}$ and $\nu_{C=N}$, respectively. The azo position is carefully assigned by the presence of ν_s and ν_{as} at 1430 and 1546 cm^{-1}, respectively. However, the ν_s and ν_{as} of the carboxy group appeared at 1380 and 1492 cm^{-1}, respectively. The presence of ν_{NH} assists the creation of $\nu_{C=N}$, i.e., the hydrazo structure. The bands at 1260 and 1292 cm^{-1} are due to $\nu_{C\text{-}N}$ and $\nu_{C\text{-}O}$, respectively.

Comparing the IR spectral data of the ligand with that of its $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes the followings are given:

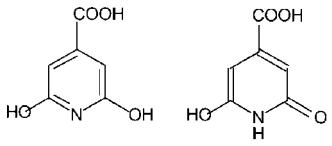


1. The doublet ν_{NH} band in the region 2850–2993 cm^{-1} appeared only in the $Co^{(II)}$ complex. However, all complexes gave a broad characteristic band in the range 3100–3500 cm^{-1} due to ν_{OH}.
2. The $\nu_{C=O}$ in the free ligand is absent in all complexes to assume its involving in the complexation process.
3. The $\nu_{C=N}$ and $\nu_{N=N}$ in the free ligand still remains in the same position in the corresponding complexes, i.e., both groups are not involved in the structural chemistry of these complexes.
4. The ν_{COOH} is affected on complexation as it shifted towards a higher frequency (=56 cm^{-1}). So the carboxyl group is involved in complexation.
5. The $\nu_{C\text{-}O}$ is also affected on complexation.
6. Generally, the ligand exists in the hydrazo structure in the $Co^{(II)}$ complex and in the azo form in both $Ni^{(II)}$ and $Cu^{(II)}$ complexes.
7. The bands at 591, 594 and 591 cm^{-1} in the $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes, respectively, are due to ν_{M-O}.
8. The nujol mull electronic absorption spectra of the Co(HL) $OH \cdot H_2O$, $Ni(H_2L)Cl_2$ and $Cu_2LCl \cdot 3H_2O$ gave bands at 24,390, 16,778, 30,864; 19,920; and 27,173, 19,417, 13,513 cm^{-1}, respectively. However, the first bands are of charge transfer nature beside the existence of Cu-Cu interaction. The other bands are mainly due to d-d transition of tetrahedral symmetry. So the following structures are suggested:



Citrazinic acid gave two infrared bands at 3110 and 2921 cm^{-1} due to $\nu_{N\text{-}H}$ and $\nu_{C\text{-}H}$, respectively. The broad nature of high frequency band indicates that the N-H group participates in a hydrogen bond structure. Other two strong IR bands at 1693 and 1604 cm^{-1} appeared due to $\nu_{C=O}$ of keto group and $\nu_{C=C}$, respectively. Also, the strong bands at 1308 and 1250 cm^{-1} are due to $\nu_{C\text{-}O}$ and $\nu_{C\text{-}N}$, respectively. These data indicated that citrazinic acid exists in the keto – imino form (II) rather than the dienol from (I). However, the two bands due to ν_{as} COOH and (ν_s COOH are assigned at 1529 and 1420 cm^{-1}, accompanied by the appearance of a splitted band at 1464 cm^{-1} due to the contributions of δ_{N-H} and $\nu_{C=N}$

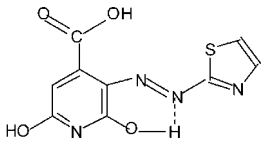
modes of vibrations. So, the following structures are proposed:



(I) (II)

The IR spectra of 3-(2-thiazolylazo) citrazinic acid, gave a broad characteristic band at 3150–3550 cm^{-1} due to stretching band of hydrogen bonded -OH group (ν_{OH}), followed by $\nu_{C\text{-}H}$ band 2990 cm^{-1}. The band at 1619 cm^{-1} is for $\nu_{C=C}$ and/or ν_{as} of the azo group. The ν_s of the azo group appeared at 1363 cm^{-1}.

The bands at 1530 and 1446 cm^{-1} are due to the ν_{as} COOH and ν_s COOH, respectively. The bands at 1293 and 1072 cm^{-1} are for the $\nu_{C\text{-}O}$ and $\nu_{C\text{-}N}$, respectively, i.e., the compound predominates in structure I in the azo dienol system.

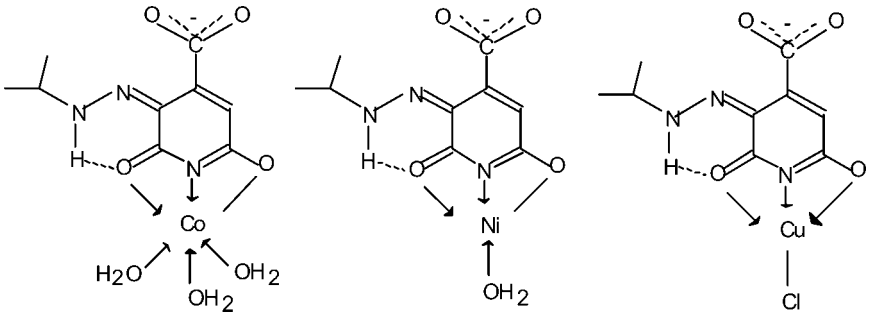


(I)

However the complexes derived from 3-(2-thiazolylazo) citrazinic acid, H_3L, with $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$, gave:

1. The ν_{OH} band of the free ligand became at 3314, 3329 and 3333 cm^{-1} in $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes, respectively. So, the-OH group is involved on complexation and/or the complexes are strongly associated with water molecules.
2. The sharp doublet bands at 2910 and 2940 cm^{-1} in the complexes, not detected in the free ligand, assigned the hydrazo formation through complexation.
3. The $\nu_{N=N}$ at 1619 and 1363 cm^{-1} for the free ligand disappeared on complexation.
4. The 1590 cm^{-1} broad band due to $\nu_{C=O}$ and $\nu_{C=N}$ for the complexes to assign the hydrazo formation.
5. The $\nu_{C\text{-}O}$ band at 1363 cm^{-1} in the free ligand is shifted towards lower frequency to confirm M-O interaction.
6. The position ν_{COOH} (symmetric and asymmetric) is nearly unchanged on complexation, i.e., the COOH group is not involved in complexation.

7. The bands at 449, 590, 442, 590 and 410, 591 cm^{-1} in the $Co^{(II)}$ and, $Ni^{(II)}$ and $Cu^{(II)}$complexes, are assigned for the $\nu_{M\text{-}N}$ and $\nu_{M\text{-}O}$, respectively.
8. The nujol mull electronic spectra $Co(H_2L) \cdot 3H_2O$, $Ni(H_2L) \cdot H_2O$ and $Cu(H_2L)Cl$ gave bands at 27,777, 19,083, 14,450; 27,765, 19,305, 14,184 and 28,901, 22,727, 15,384 cm^{-1}, respectively, with μ_{eff} equals 3.95, 2.95 and 1.59 BM at room temperature, respectively. The first band is of charge transfer nature, beside the existence of Cu-Cu interaction. The other bands are mainly due to d-d transition. The following structures are postulated:

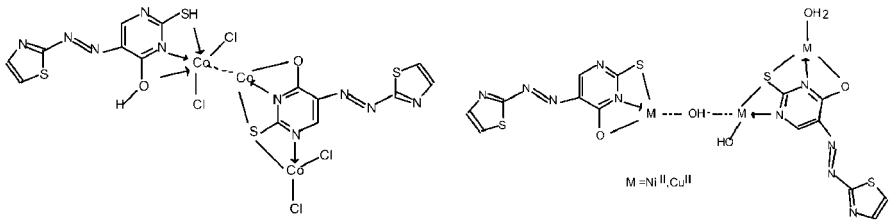


The IR spectrum of thiouracil compound showed ν_{NH} band at 3100 cm^{-1} which was completely disappeared on complexation, to suggest M-N bonding. The two $\nu_{C4=O}$ strong bands at 1720 and 1700 cm^{-1} in thiouracil ligand are almost absent on complexation to argue the presence of M-O bonding. The four thio-amide bands of thiouracil at 1580, 1245, 1160, and 790 cm^{-1}, are affected with different degrees during complexation to support M-S bonding, i.e., thiouracil is of tridentate attachment (N, O and S) on the reaction with the transition metal salts ($Co^{(II)}$, $Ni^{(II)}$, $Cu^{(II)}$). In the lower frequency region, some metal sensitive bands are observed, e.g., the nickel and the cobalt complexes showed $\nu_{M\text{-}S}$ bands at 360 and 305 cm^{-1}, respectively. The nujol mull electronic absorption spectra and the room temperature magnetic moment values of the thiouracil complexes of cobalt, nickel and copper gave Oh, Oh and square planar geometry, respectively.

The IR spectra of 5-(2-thiazolylazo)-2-thiouracil, H_2L, and its $Co^{(II)}$, $Ni^{(II)}$ and $Co^{(II)}$ complexes gave the followings:

1. The $\nu_{N\text{-}H}$ band at 3080 cm^{-1} in the free ligand becomes at 3395, 3375 and 3103 cm^{-1} in the corresponding $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes, respectively, due to complexation, so the N-H group is involved in complex formation confirming the M-N bonding.

2. The $V_{C4=O}$ in the free ligand at 1693 cm^{-1} is completely absent on complexation, confirming the M-O bonding.
3. The bands at 1442 and 1540 cm^{-1} in the free ligand are due to the symmetric and asymmetric stretching of the azo group, are nearly unaffected through complexation.
4. The $V_{C=O}$ bands at 894 and 1171 $cm^{-1}$are slightly affected to a lower wave number on complexation, indicating that the C=S group is involved in the complexation process.
5. The four thioamide bands of the free ligand at 780, 1174, 1234 and 1618 cm^{-1} are affected with different degrees during complexation to support M-S bonding.
6. The bands at 446, 550; 454, 555 and 430, 540 cm^{-1} for the $Co^{(II)}$, $Ni^{(II)}$ and $Cu^{(II)}$ complexes, respectively, are due to V_{M-N} and V_{M-O}, respectively.
7. The nujol mull electronic absorption spectra of $Co_3L(H_2L)\ Cl_4$, $Ni_3L_2\ (OH)_2 \cdot H_2O$ and $Cu_3L_2\ (OH)_2 \cdot H_2O$ gave bands at 26,315, 22,222, 15,384; 22,727, 16,129 and 27,322, 17,857 cm^{-1}, respectively, and their room temperature μ_{eff} values are 3.92, 3.01 and 1.67 BM. respectively. The first bands are mainly due to the charge transfer, beside the existence of M-M interaction. The other bands are mainly due to d-d transitions. The $Co^{(II)}$ complex exists in Oh environment, while the $Co^{(II)}$ and $Ni^{(II)}$ complexes are of square planar geometry. The following structures are postulated:



These complexes are of bi-and tri-metallic types, and exist in mixed four membered and six membered structures. The high melting point and the dissolution of these complexes suggest their higher stability.

Magnetic Properties at Different Temperatures

The results were measured down to the temperature of the liquid nitrogen around 78° K. By changing the field strength applied on measuring the magnetic susceptibility data, no critical changes were observed. So for clarity, the data are calculated at specified field strength (1.320 Tesla).

The magnetic susceptibility data for the tetrahedral copper, $Cu(H_2L)Cl$ complex, H_3L = 3-(2-thiazolylazo) citrazinic acid, showed a linear relationship between both $1/X_g$ or $1/X_m^-$ with T, Figs. 1 and 2, respectively.

The slope of the later plot ($1/X_m^-$ with T) is $1/c$ and the intercept is $-\phi/c$. So, both c and ϕ are obtained experimentally, where c equals to $0.362\,cm^3\ mol^{-1}$ and $\phi = -0.4706°K$, respectively. X_m^- is calculated from $X_{m(calc.)=c/(T-\phi)}$. The $\mu_{eff.}$ values were obtained from the relation:

$\mu_{eff} = 0.828[X_m(T-\phi)]^{1/2}$. The experimental and the calculated $\mu_{eff.}$ values are more or less the same. The determined magnetic moment values are slightly lower than that of the spin only predicted for a single electron (1.73 BM), indicating a weak antiferromagnetic behaviour. The non-zero value of ϕ indicated a very weak intermolecular interaction operative in the solid complex. The magnetic moment 1.594 BM at 297.8° K does not change appreciably down to 77.6° K (1.405 BM), such complex is of a magnetically diluted behaviour.

The X_g or X_m^-–T Plots, Figs. 3 and 4, show parabolic relations indicating a simple paremagnetic behaviour with X_{TIP} equals 1173.3×10^{-6} cgs. The octahedral copper, $Cu_2(H_3L)Cl_4 \cdot 4H_2O$ complex, H_3L = 3-(2-thiazolylazo) pyrogallol, showed a linear relationship between $1/X_g$ or $1/X_m^-$ with T, where C=O.605 $cm^3\,mol^{-1}$ and $\phi = 0.333°K$. Curie-Weiss law is obeyed. Nearly no differences were found between the calculated and the experimental μ_{eff} values. The observed magnetic moment values are higher than that of the spin of the free electron in all the temperature ranges for the

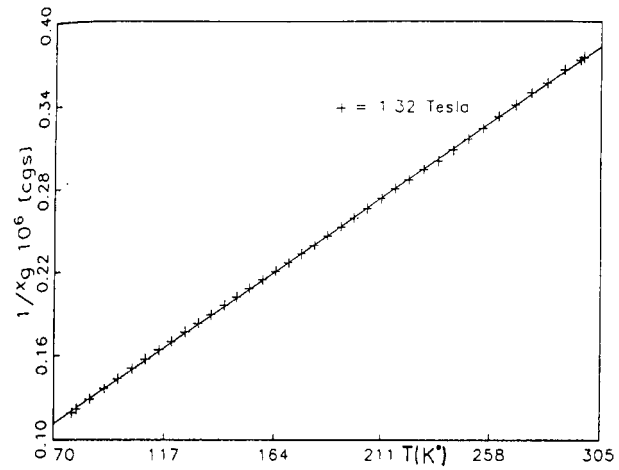


Figure 1.

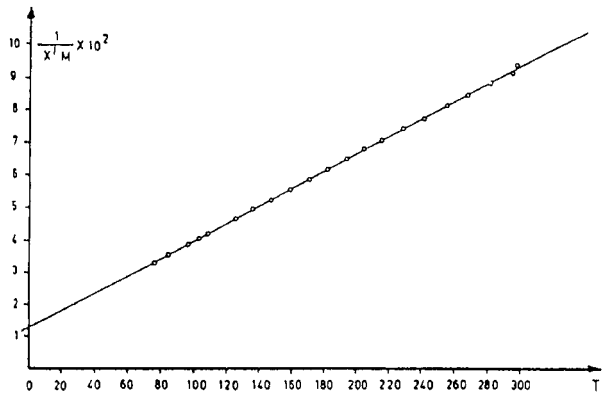


Figure 2.

studies indicating a ferromagnetic behaviour with ionic or rather weak covalent bonds. The magnetic moment of 2.165 BM at 296° K does not change markedly down to 77.90 K (1.9 BM), to indicate a magnetically diluted behaviour with small interaction between copper centers in this complex. The parabolic curves obtained on plotting X_g or X_m with T indicated a simple paramagnetism with X_{TIP} equals 2133×10^{-6} cgs.

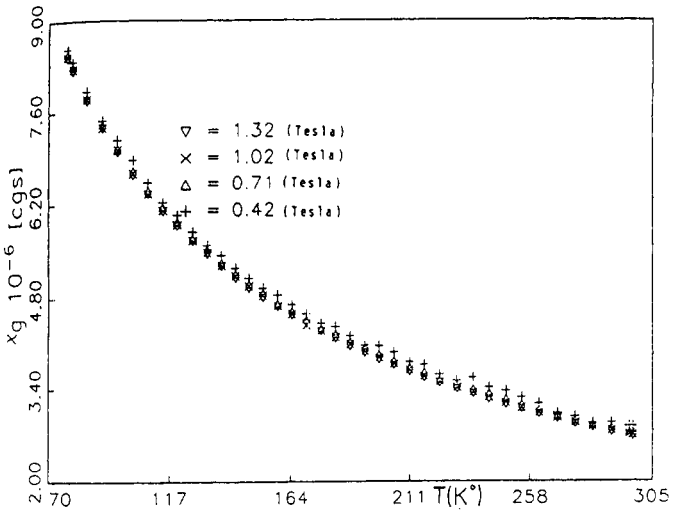


Figure 3.

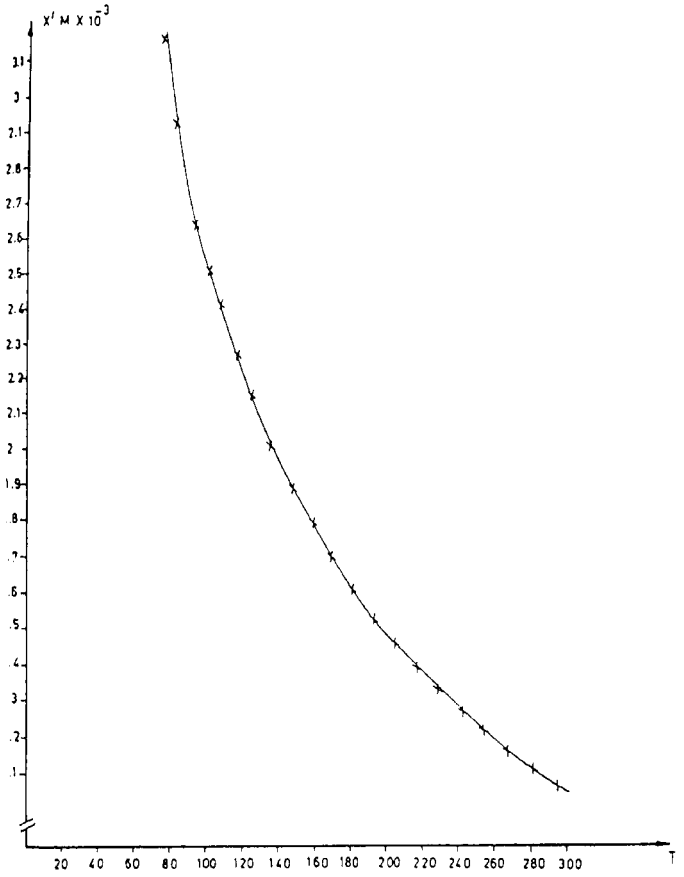


Figure 4.

The magnetic susceptibility measurements at different temperatures ranged from 297.7° K down to 77° K of the tetrahedral, $Cu_3L_2(OH)_2 \cdot H_2O$ complex, H_2L = 5-(2-thiazolylazo)-2-thiouracil, showed a linear relation between both $1/X_g$ or $1/X_m$ with T, with C=O.359 $cm^3\,mol^{-1}$ and $\phi = -0.1077$°K. A very small difference (0.01–0.03 BM) exists between the calculated and the measured magnetic moment values. The measured μ_{eff} is slightly less than the magnetic moment of the unpaired electron $\mu_{s.o}$ to indicate a weak antiferromagnetic behaviour, meanwhile the $\mu_{eff.}$ is 1.725 BM at 297.7° K and does not change down to 77° K (1.679° BM), indicating a magnetically diluted behaviour.[59] The super exchange through the bridging OH^- ions leads, also, to the lowering of the magnetic moment

value.[60] The plotting of X_g or X_m with T gave parabolic curves of a simple paramagnetic type with X_{TIP} equals 1352.36×10^{-6} cgs. The octahedral $Cu_3(H_2L)_2Cl_2 \cdot 8H_2O$ complex, $H_4L = 2$-(2-thiazolylazo) gallic acid, considered as a polymetallic system, showed a linear relationship between $1/X_g$ or $1/X_m$ with T with $c = 2.44\,cm^3\,mol^{-1}$and $\phi = 17.812°K$. The magnetic moment values ranged between 4.39 BM at 296.1° K and 4.42 BM at 76.6° K. The unexpected higher magnetic moment may be due to a very strong orbital angular momentum contribution, and the polymetallic nature of the system. The X_g or X_m^- vs. T gave parabolic curves to confirm the simple paramagnetic nature, and the temperature independent paramagnetic susceptibility X_{TIP} equals 3950.78×10^{-6} cgs.

Electron Spin Resonance of Copper Complexes

Figure 5 and Table 3 represent the room temperature X-band ESR spectra of $Cu_3(H_2L)_2Cl_2 \cdot 8H_2O$, H_4L is 2-(2-thiazolylazo) gallic acid where

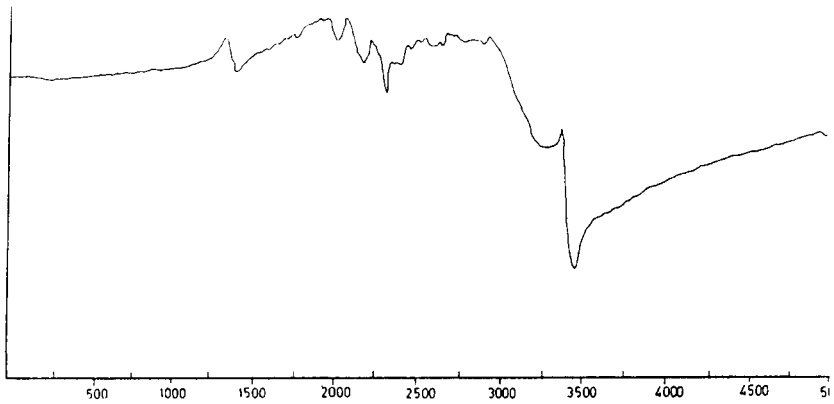


Figure 5. ESR spectra of Cu-thiazolylazo gallic acid.

Table 3. ESR Data for Some Copper Complexes

Complex	$g_\parallel$	$g_\perp$	$\langle g \rangle$	G	g_s	A
Thiazolylazo gallic acid	4.0652	3.871	3.94	1.1	1.986	62.5
Thiazolylazo thiouracil					2.007	175
Thiazolylazo salicylic acid					2.070	412.5
Thiazolylazo pyrogallol					2.085	243.75
Thiazolylazo citrazinic acid					2.085	337.5

a series of bands appeared, the copper hyperfine splitting is noticeable. The analysis of these bands gave a considerable interaction between the metal and the ligand in a strong association, as appeared from the calculated G value. For this complex $g_{//} > g_{\perp}$ to assign that the unpaired electron is in the $d_{x^2-y^2}$ orbital.

The room temperature polycrystalline X-band ESR spectral pattern of $Cu_3L_2(OH)_2 \cdot H_2O$, $H_2L = 5$-(2-thiazolylazo)-2-thiouracil; $Cu_2LCl \cdot 3H_2O$, $H_2L = 5$-(2-thiazolylazo) salicylic acid; $Cu_2(H_3L)Cl_4.4H_2O$, $H_3L = 3$-(2-thiazolylazo) pyrogallol; Cu (H_2L) Cl, $H_3L = 3$-(2-thiazolylazo) citrazinic acid, Fig. 6, Table 3, gave similar spectral trends. All are isotropic in nature with $g_s = 2.077$, 2.070, 2.085 and 2.085, respectively, with $A = 175.0$, 412.5, 243.75 and 337.5, respectively.

The data showed broad signals, which may be due to the polymeric nature of these complexes. Generally, $Cu^{(II)}$complexes having a lower symmetry than octahedral undergoes a free rotation or give complexes containing grossly misaligned tetragonal axes, i.e., such complexes are subjected to strong interaction to explain the isotropic spectra.

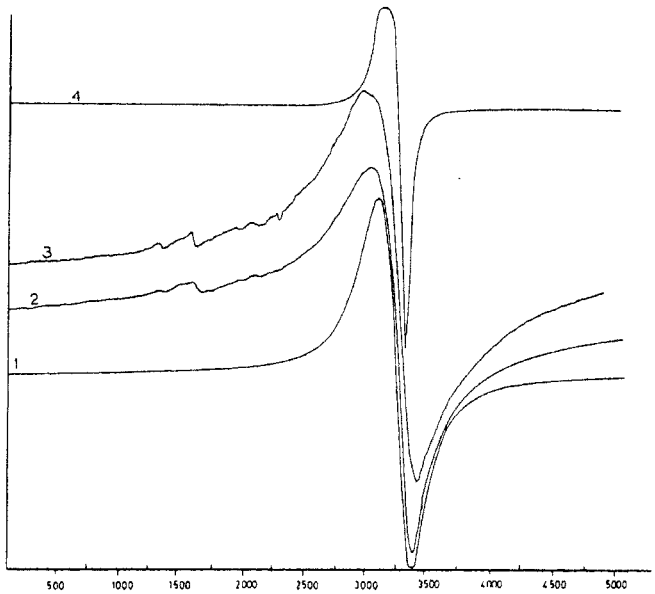


Figure 6. ESR spectral pattern of Cu-thiazolylazo: 1. pyrogallol, 2. salicylic acid, 3. citrazinic acid, 4. thiouracil.

Thermal Analysis

The DTA curves of 2-(2-thiazolylazo) disodium chromtropate, 5-(2-thiazolylazo) uracil and 5-(2-thiazolylazo) barbituric acid are represented in Fig. 7. All of them gave exothermic peaks.

The 2-(2-thiazolylazo) disodium chromotropate compound showed three peaks at 85.8, 406 and 551°C with activation energies 17.61, 100.1 and 149.7 kJ/mole, respectively, and an order of reactions 1.02, 0.526 and 1.998, respectively. The latter peak assigned the formation of Na_2O. The first peak is due to the dehydration reaction of probably adsorbed water. However, the 5-(2-thiazolylazo) uracil compound showed also, three peaks at 96.0, 372.0 and 548.0°C with activation energies 28.1, 815.6 and 17.05 kJ/mole, respectively, with an order 1.76, 0.996 and 1.16, respectively. The first peak is due to a dehydration reaction of probably adsorbed water, while the others may attributed to decomposition steps since both are at a higher temperature than the melting point.

The 5-(2-thiazolylazo) barbituric acid compound gave four DTA peaks at 83.8, 172, 365 and 506°C, with activation energies 29.05, 273.96, 285.17 and 195.97 kJ/mole and reaction orders 0.63, 1.69, 0.95 and 1.48. The first peak is due to a dehydration reaction of adsorbed water molecules, the others are due to the thermal agitation and decomposition reactions.

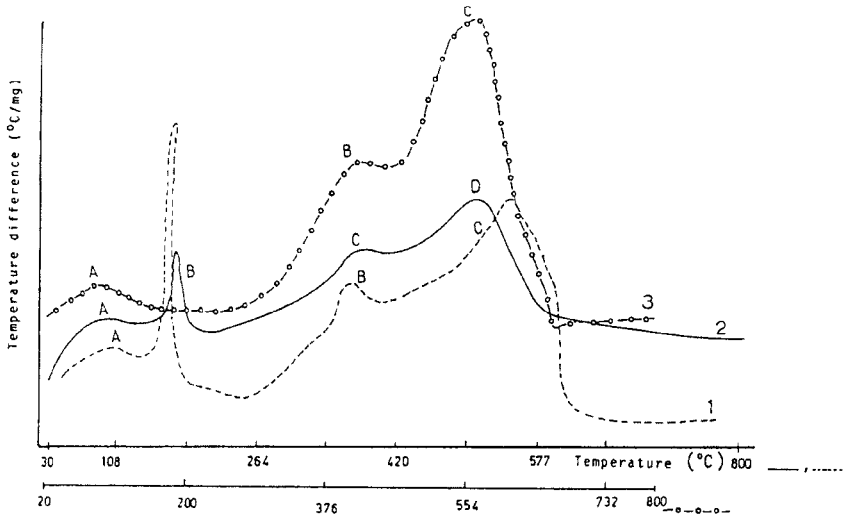


Figure 7. DTA Curves of (1) Thiazolylazo uracil, (2) Thiazolylazo barbituric acid, (3) Thiazolylazo chromatropate.

However the foundation of orders as 0.5 and 0.63 suggest that the reaction procedure in somehow complicated mechanisms.

The 5-(2-Thiazolylazo) thiouracil compound, H_2L, showed three peaks at 81.9, 267.3 and 577.1°C. The second one is of endothermic behaviour while the others are exothermic in nature. The calculated energies of activation are 30.23, 122.11 and 272.70 kJ/mol accompanied with order of reactions 1.01, 1.35 and 1.50, respectively. Its cobalt complex showed three exothermic reactions at 93.5, 369.5 and 414.3°C with activation energies 39.78, 149.6 and 70.29 kJ/mol and orders 0.86, 1.06 and 1.12, respectively. The nickel complex showed three exothermic peaks at 118.3, 362.5 and 488.3°C with activation energies 52.38, 459.35 and 623.55 kJ/mol with orders 1.13, 0.92 and 1.61, respectively. The following observations and conclusions are given:

1. All the first peaks are probably assigned to dehydration processes to favour the hygroscopic nature for these compounds.
2. The dehydration process has higher energy of activation in the complexes rather than the free ligand where the water molecules in the complexes are of stronger bonding.
3. The energy of activation for the different decomposition steps of the tetrahedral nickel complex is higher than that of octahedral cobalt complex. So, the octahedral cobalt complex is strongly subjected to distortion and the tetrahedral nickel is more stable, i.e., the former complex needs more energy for decomposition than the latter.
4. The second and third peaks are due to the thermal agitation with the major final formation of the oxides of cobalt and nickel.[61]
5. The appearance of fraction orders like 1.61 and 1.35 suggests that the reaction proceeds via complicated mechanism.

The 3-(2-thiazolylazo) citrazinic acid showed two, DTA exothermic peaks at 109.5 and 224.5°C with energies of activation 13.68 and 112.97 kJ/mol and orders of decomposition 1.156 and 1.408, respectively, (i.e., of the first order type). The cobalt complex showed three exothermic decomposition peaks at 118, 379.7 and 460.8°C with energies of activation 115.8, 337.45 and 239.27 kJ/mol and their order of decomposition are 1.86, 1.88 and 1.84, respectively (i.e., mostly of the second order type). The nickel complex showed four characteristic decomposition peaks at 98.4, 285.5, 339.4 and 432.98°C, with energies of activation 27.259, 255.157, 573.67 and 152.39 kJ/mol accompanied with the decomposition orders 2.01, 0.973, 0.758 and 1.98, respectively. The first decomposition step is due to dehydration process. Such step in the corresponding complexes is of higher activation energy than that of the free ligand. This is in harmony with that

the water molecules in the complexes are strongly bonded to the complexes. Meanwhile, the octahedral cobalt complex is of higher ΔE than that of the tetrahedral nickel complex. The other peaks are due to the thermal agitation the decomposition steps.

The 5-(2-thiazolylazo) salicylic acid, H_2L, showed two exothermic peaks at 97.3 and 287.9°C and their activation energies are 43.65 and 106.14 kJ/mol and their orders are 0.787 and 1.197. However the cobalt complex showed one broad characteristic exothermic thermal agitation peak at 483.1°C with activation energy 130.6 kJ/mol and an order of reaction 1.1. The nickel complex gave two exothermic peaks at 125.6 and 297.9°C, with activation energies 26.1 and 124.7 kJ/mol and orders of 1.22 and 1.92, respectively. The free ligand showed a dehydration step at 97.3°C. The water molecule exists in the cobalt complex in its coordination sphere. The second peak in the salicylic azo ligand is due to the formation of some decomposition products where it takes place at a temperature higher than its melting point. For the nickel complex, the observed two peaks may due to the thermal agitation and the decomposition steps ended with the formation of the metal oxides. Generally, two patterns of behaviour can be discerned,[52,53] one in which the chloro complex with the metal either decomposes directly to the oxide exothermically or decomposes endothermically to the metal chloride followed by an exothermic conversion to the oxide.

The DTA for 3-(2-thiazolylazo) pyrogallol, showed three exothermic peaks at 76, 240 and 452°C and their energies of activation are 41.04, 44.68 and 239.02 kJ/mol, their orders of reactions: 0.97, 1.09 and 1.15, respectively. The cobalt complex showed four well-defined peaks at 68.26, 149.12, 495.7 and 538.1°C with activation energies of 62.36, 117.07, 498.8 and 508.49 kJ/mol, respectively, and their reaction orders are 0.619, 1.126, 1–617 and 2.237, respectively. The nickel complex, gave two characteristic peaks at 63.3 and 296.7°C, with activation energies of 10.79 and 16.87 kJ/mol and their reaction orders are 1.68 and 1.34, respectively. Generally, the first peaks are due to the dehydration processes, and happened at higher temperature in the free ligand rather than its complexes. So, the mode of interaction between the water molecules with the free ligand is stronger than that in case metal complexes. However, in spite of the cobalt and nickel complexes has the same geometry, both decomposed in a different pattern as controlled from the variation in their DTA curves. This is probably related to the variation in the electronic configuration and the chemistry of both metals. The other bands in either the free ligand or the complexes are due to the thermal agitation and the formation of different decomposition products, with the formation of metal oxides a final product.

The 2-(2-thiazolylazo) gallic acid ligand, H_4L, showed two exothermic peaks, at 103.5 and 281.28°C with activation energies of 46.84 and

83.14 kJ/mol and the reaction orders 1.144 and 1.007, respectively. The cobalt complex showed two exothermic peaks at 178.7 and 334°C with activation energies of 83.14 and 273.17 kJ/mol and the orders are 1.139 and 1.03, respectively. The nickel complex gave two exothermic peaks at 60.5 and 546.5°C with activation energies 122.05 and 321 kJ/mol and reaction orders are 1.76 and 1.13, respectively.

The first peak in the free azo ligand is due to the dehydration process while the second is considered as a decomposition product. However the first peak in the cobalt complex is due to the thermal agitation, meanwhile this peak in the nickel complex is attributed to dehydration process of the three water molecules present in the outer sphere. The datum is in harmony with its occurrence at a relatively low temperature. The second very broad peaks in both cobalt and nickel complexes are due to the thermal decomposition. However, its occurrence at higher temperature in the nickel complex compared to the cobalt complex is due to the difference in the electronic structure of both metals.

The values of Z were obtained, Tables 4 and 5, based on of Horowitz-Metzger equation[63] by making use of the relation:

$$Z = E/RT_m\beta \exp(E/RT_m^2).$$

and the entropies of activation ($\Delta S^{\#}$) were obtained from the relation

$$Z = KT_m/h \exp(\Delta S^{\#}/R).$$

Table 4. Thermal Properties of Some Organic Azo Compounds

Compound	Peaks (°C)	E_a (kJ/mole)	Order	β	α	ΔS (J/k mole)	Z (s^{-1})
Thiazolylazo chromotropate	58.8	17.58	1.02	2.04	2.511	−97.91	12.4986
	406	100.11	0.526	0.198	2.941	−104.58	3.7289
	551	149.65	1.998	2.99	1.884	−94.72	69.4258
Thiazolylazo uracil	96	28.09	1.176	2.299	2.325	−95.93	22.2878
	372	815.6	0.996	1.99	2.251	−86.56	520.9100
	548	170.5	1.16	2.27	2.194	−95.19	60.8166
Thiazolylazo barbituric acid	83.8	29.05	0.63	0.83	2.771	−99.22	8.6584
	172	273.96	1.69	2.82	1.874	−87.14	306.3146
	365	286.17	0.95	1.89	2.315	−91.73	123.3675
	506	195.97	1.48	2.65	2.012	−93.68	87.6860

Table 5. Thermal Properties of Some Ligands and Their Metal Complexes

Compound	Peaks (°C)	E_a (kJ/mole)	Order	β	α	ΔS (J/k mole)	Z (s^{-1})
Thiazolylazo thiouracil	81.9	30.233	1.010	2.02	2.397	−95.81	22.1201
	267.3	122.110	1.350	2.52	2.081	−92.83	76.9164
	577.1	272.700	1.500	2.67	1.984	−93.04	114.3678
Cobalt complex	93.5	39.780	0.860	1.67	2.484	−95.69	23.6656
	369.5	149.600	1.060	2.11	2.254	−94.05	65.3311
	414.27	70.290	1.120	2.21	2.302	−97.31	28.3301
Nickel complex	118.3	52.380	1.130	2.23	2.257	−94.07	39.4727
	362.5	459.350	0.920	1.82	2.333	−89.68	216.8177
	488.3	623.550	1.610	2.75	1.900	−88.45	364.9578
Thiazolylazo citrazinic acid	109.5	13.680	1.156	2.27	2.563	−98.94	10.0211
	224.5	112.970	1.408	2.58	2.054	−92.39	79.9612
Cobalt complex	118.0	115.800	1.860	2.92	1.867	−89.82	128.2951
	379.7	337.450	1.880	2.94	1.819	−89.60	227.6704
	460.8	239.270	1.840	2.91	1.864	−92.07	129.0745
Nickel complex	98.4	27.259	2.010	3.00	2.087	−95.13	27.9736
	285.5	255.157	0.973	1.94	2.294	−90.95	133.7107
	339.4	573.670	0.758	1.36	2.516	−89.27	234.0672
	432.98	152.39	1.980	2.99	1.865	−93.46	84.4892
Thiazolylazo salicylic acid	97.300	43.65	0.787	1.46	2.548	−95.89	22.6080
	287.900	106.14	1.197	2.33	2.179	−93.97	58.2262
Cobalt complex	483.100	130.60	1.100	2.18	2.249	−95.73	48.2489
Nickel complex	125.600	26.10	1.220	2.36	2.340	−96.69	19.4520
	297.900	124.70	1.920	2.96	1.879	−92.61	86.4584
Thiazolylazo pyrogallol	76.000	41.04	0.970	1.94	2.381	−94.64	30.1232
	240.000	44.68	1.090	2.16	2.346	−96.89	23.7170
	452.000	239.02	1.150	2.26	2.169	−92.89	101.6459
Cobalt complex	68.261	62.36	0.619	0.77	2.757	−96.10	19.6294
	149.120	117.07	1.126	2.22	2.197	−91.42	88.8336
	495.700	498.80	1.617	2.76	1.903	−89.54	272.1451
	538.100	508.49	2.237	3.10	1.722	−89.51	289.5513
Nickel complex	63.300	10.79	1.680	2.81	2.508	−98.10	11.1344
	296.700	16.87	1.340	2.51	2.607	−100.74	9.0695
Thiazolylazo gallic acid	103.50	46.84	1.144	2.25	2.258	−94.18	36.8951
	281.28	83.14	1.007	2.01	2.329	−95.37	39.0855
Cobalt complex	178.70	83.14	1.139	2.24	2.219	−93.36	55.5149
	334.00	273.17	1.030	2.06	2.243	−91.17	136.9232
Nickel complex	60.50	122.05	1.760	2.86	1.881	−88.21	170.6029
	546.50	321.00	1.130	2.23	2.175	−92.73	119.9338

where, R represents molar gas constant, β rate of heating (KS^{-1}), K the Boltzman constant and h the Planck's constant.

It seems that Δs values are nearly of the same magnitude to suggest uniform decomposition pattern affected by stereochemistry of the metal complex and in some cases the electronic character of the substituents of the ligands.

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