

## Thiazolylazo 화합물의 분광학적, 자기적, 그리고 열적성질

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## Spectral, Magnetic, and Thermal Properties of Some Thiazolylazo Complexes

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**요 약.** Thiazolylazo 화합물과 barbituric산, uracil, thiouracil, citrazinic산, chromotropic산, gallic산, pyrogallol 그리고 salicylic산의 Co(II), Ni(II) 그리고 Cu(II) 착화합물을 제조하였고, <sup>1</sup>H NMR, IR, 그리고 전기 흡수 스펙트럼에 대한 pH영향에 의하여 규명하였다. 이온화형태, 전기적 전이 그리고 해리상수에 대하여 설명하였다. 구리 착화합물은 등방형 ESR스펙트럼이었으며 자기적으로 케토 기어를 갖는 묽은 성질이였다. 상세한 DTA 데이터 얻었고, 그 결과를 토론하였다.

**주제어:** 티아졸릴아조 화합물, (2-티아졸릴아조)살리실산 화합물, (2-티아졸릴아조)바비부릭산 화합물

**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 <sup>1</sup>H 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 showed a complicated one) and are of magnetically diluted behaviour with orbital contribution. Detailed DTA data were obtained and discussed.

**Keywords:** thiazolylazo compound, (2-thiazolylazo)salicylic acid, (2-thiazolylazo)barbituric acid

### INTRODUCTION

The pyrimidine compounds are one of the most important classes from different views especially applied chemistry<sup>1,2</sup> and biological activity.<sup>3,4</sup> In our

laboratory, Masoud *et al.*<sup>5-15</sup> published a series of papers to throw light on the chemistry of pyrimidine compounds and their complexes. The thiazolylazo compounds and their Co(II), Ni(II) and Cu(II) complexes of barbituric acid, uracil, thiouracil, citra-

zinc acid, chromotropic acid, gallic acid, pyrogallol and salicylic acid are the selected compounds for studies through this paper by  $^1\text{H}$  NMR, IR, ESR spectra and the effect of pH on the electronic absorption spectra. The thermal behaviour is also studied to give more spotlights on the structural chemistry of these compounds.

## EXPERIMENTAL

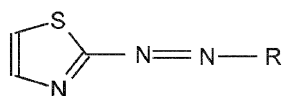
### General methods of preparation of the free azo compounds

2-Amino thiazole (0.1 mole) was dissolved in HCl (0.2 mole/25 ml distilled water). The hydrochloride compounds were diazotized below  $5^\circ\text{C}$  with a solution of  $\text{NaNO}_2$  (0.1 mole/30 ml distilled water). The diazonium chloride<sup>46</sup> 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<sup>47</sup>, and then dried in a vacuum desiccator over anhydrous  $\text{CaCl}_2$ . 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

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 a metal(II) chloride ( $\text{M}=\text{Co}$ ,  $\text{Ni}$  and  $\text{Cu}$ ) 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  $\text{CaCl}_2$ . *Table 2* collects the analytical data for the prepared complexes, where the metal contents were determined by the usual complexometric titration methods after decomposition with aquaregia.<sup>48</sup> The halogen content was determined by Mohr's method.<sup>49</sup>

### Instruments and working procedure

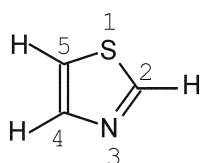
Electronic absorption spectra in the visible and ultraviolet regions were measured with a Pye-Unicam SP 1800 spectrophotometer. Infrared spectra were measured with Pye-Unicam SP - 1025 and SP 3-100 spectrophotometer equipped with NaCl-Prism over the frequency range  $200\text{-}4000\text{ cm}^{-1}$ . NMR spectra were recorded in dimethyl sulphoxide- $d_6$  and acetone- $d_6$  with 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  $300\text{-}77\text{ K}$  at four different fields (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  $\text{HgCo}(\text{NCS})_4$ <sup>50</sup>. 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 L/min and a chamber cooling water flow rate was 10 e/h. The speed was 5 mm/min. Electron spin resonance spectra were recorded at 100 KHz modulation and 10  $\text{CH}_2$  modulation amplitude on JES - 200 spectrometer. 10 mV incident power was used and resonance conditions were at around 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

### $^1\text{H-NMR}$ .

Free thiazole<sup>51</sup> gave three  $^1\text{H-NMR}$  peaks at  $\delta=7.41$ , 7.18 and 8.88 ppm due to the olefinic hydro-

gens 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.



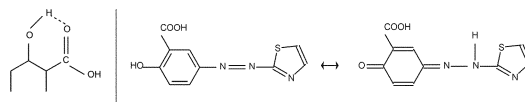
The data of the A series were recorded in acetone- $d_6$ , whereas those of the B series were obtained in the presence of DMSO- $d_6$  because of solubility problems.

5-(2-Thiazolyazo) salicylic acid gave quarter signals at  $\delta=6.6-7.0$  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  $\delta=7.16$  and 7.75 ppm, respectively (i.e., at a lower  $\delta$ -value with respect to the thiazole itself), may be attributed 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  $\delta$ -value than the other protons in phenyl ring). This is related to its existence, at the middle, between two withdrawing groups.

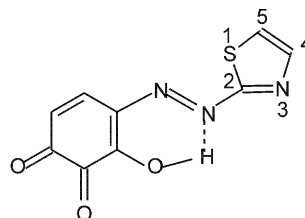
The absence of the carboxylic proton signal could be attributed to the rapid resonating nature of the acidic hydrogen between the two oxygen atoms of the acidic hydrogen between the two oxygen atoms of the carboxylic group.<sup>52</sup>



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



4-(2-thiazolyazo) pyrogallol shows a multiplet 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 of the azo group in conjugation with the thiazolyl moiety. The singlet band at  $\delta=14.9$  ppm indicates a hydroxyl proton of the pyrogallol moiety involved in strong intermolecular hydrogen bonding. This peak corresponds to one proton due to possible quinone formation.



5-(2-thiazolyazo) barbituric acid shows 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  $\delta$  value compared to the thiazole itself is probably due to the presence of the azo group in conjugation with the thiazole moiety. However, the latter band may be attributed to the C(5) proton of the barbituric acid moiety

The compounds under investigation could be classified into two categories

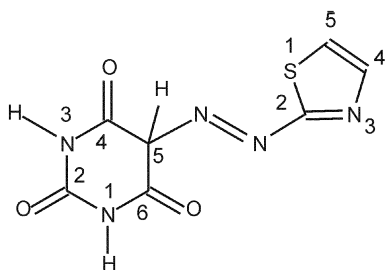
A) Those of the phenolic type:

- I) 5-(2-thiazolyazo) salicylic acid.
- II) 4-(2-thiazolyazo) pyrogallol.

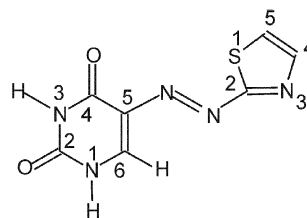
B) Those of the pyrimidine series :

- I) 5-(2-thiazolyazo) barbituric acid.
- II) 5-(2-thiazolyazo) uracil .
- III) 5-(2-thiazolyazo)-2-thiouracil.

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 N1, N3 protons of the 5-(2-thiazolylazo) barbituric acid may be attributed to the strong solvent - solute interaction, because the DMSO is hydrogen bonded to the NH group.<sup>52</sup>



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 of 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 were interpreted the presence of the keto form with the syn conformation<sup>46</sup> and the dilactam tautomeric structure in its ground state<sup>53</sup> 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.<sup>54</sup> 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...O bonding with the O atom of the DMSO solvent.<sup>55</sup> The data 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 to be more deshielded than that of the uracil itself, due to the effect of the azo group property.



5-(2-thiazolylazo)-2-thiouracil shows two doublets at  $\delta$ -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 because of 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-H and N<sup>3</sup>-H of the thiouracil moiety, the N<sup>3</sup>-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 DMSO-d<sub>6</sub> and the C(6) proton. 2-Thiouracil does 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.

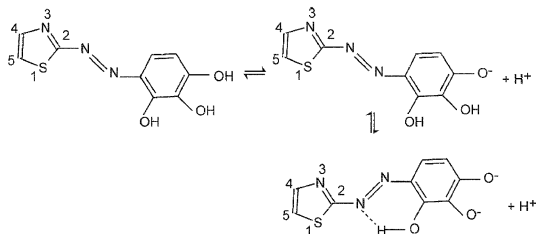
#### Effect of pH on the electronic absorption spectra of the organic compounds

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

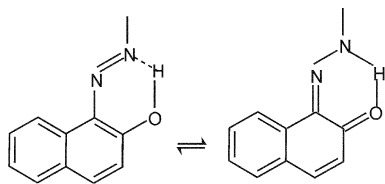
The electronic absorption spectra of  $1 \times 10^{-4}$  M 4-(2-thiazolylazo) pyrogallol shows two characteristic bands at 211 and 318 nm due to the  $\pi$ - $\pi^*$  transition. The intensity of the first band increases steadily in the pH range 2.4-8, followed by a stepwise decrease in the intensity with the increase of pH's (>8). The second band decreases in intensity 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 <sup>1</sup>H-NMR. Such a structure is protonated in an acidic medium giving the phenolic structure. Pyrogallol gave a well-defined band at  $\lambda_{max}$ -345 nm with an isobestic point at 355 nm in 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 at  $pK_1=4.8$  and  $pK_2=8.5$ .

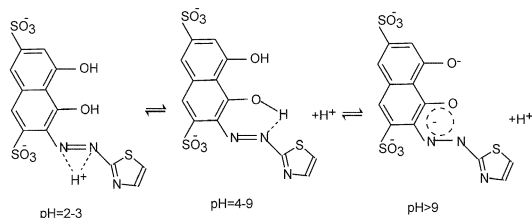
From all the previous discussions, the following ionization scheme for 4-(2-thiazolylazo) pyrogallol is postulated:



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 chromotrope could be seen at three well - defined bands at 237, 353, and 500 nm. A remarkable feature is that the positions of these bands is pH - independent, while their intensities are affected by the pH. The first two bands are sharp, whereas the last one is broad. The first band is due to the  $\pi-\pi^*$  transition of the phenolic ring, and the other two band assigned the  $\pi-\pi^*$  transition of the azo linkage overlapped with an intramolecular charge transfer effect.



So, the following mode of ionization might be postulated:



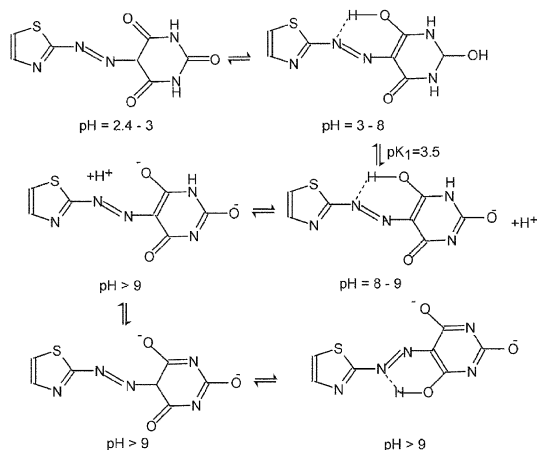
Two  $pK$  values were deduced:  $pK_1=3.5$  and  $pK_2=8.15$ .

The effect of pH on the electronic absorption spectra of  $1 \times 10^{-4}$  M 5-(2-thiazolylazo) barbituric acid appears at 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  $\pi$ -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 nonbonding electron pairs of the oxygen atoms. Both bands are red shifted as the pH increases. The modified limiting absorption plot gave  $pK_1$  and  $pK_2$  to be 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 pairs of electrons.

Thus, other  $n \rightarrow \pi^*$  transitions can be expected to take place from these nonbonding orbitals to different  $\pi^*$  molecular orbitals extending over such a large molecule. Also, most of azo compounds prefer their existence in the *trans*-azo isomer, 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  $1 \times 10^{-4}$  M 5-(2-thiazolylazo) uracil showed two characteristic bands; one is sharp at 209-214 nm and the

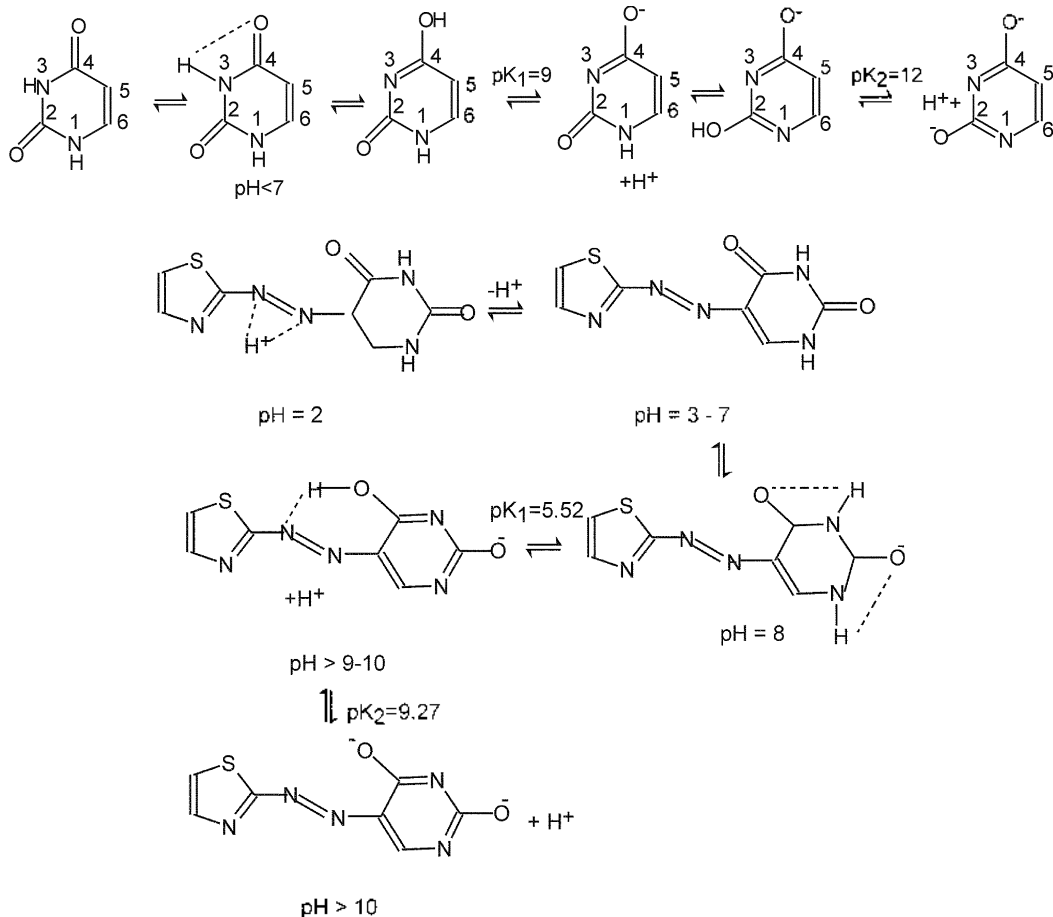
other is a shoulder at 250-264 nm. On increasing the pH, the intensity of the first band increased with a slight blue shift ( $\approx 5$  nm), while the second band remains unchanged. The first band may be due to the  $\pi-\pi^*$  of the two  $sp^2$ -hybridized carbons of the exocyclic band in heterocyclic ring, as uracil. The second band can be assigned to  $\pi\rightarrow\pi^*$  transition of the two carbonyl groups in b-positions as reported for uracil.

As the pH increases the two bands are red-shifted and become more intense, where the compound is subjected to tautomerization with the presence of auxochromic groups.<sup>5b</sup> The scheme of ionization is postulated as follow:

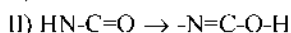
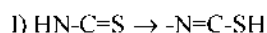
However, the lower pK values of the azo compound compared the uracil may be due to the withdrawing property of the azo group. From all of the

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

The electronic absorption spectra of  $1 \times 10^{-4}$  M 5-(2-thiazolylazo)-2-thiouracil give two maximal bands at 213 and 272 nm in the pH range 2.4-8.0, where the intensity of both bands is decreases with the increase in pH accompanied with a slight blue shift ( $\approx 13$  nm for the second bands) However, at  $\text{pH} \geq 9$ , four bands appear at 210, 228, 258, and 310 nm. The first band is due to the  $\pi-\pi^*$  transition 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 auxochromophore groups. The observed K-band at 310 nm assumes the tautomerism between the thione and the thiol structures. The formation of the isobestic points at 217.6, 259.2 and



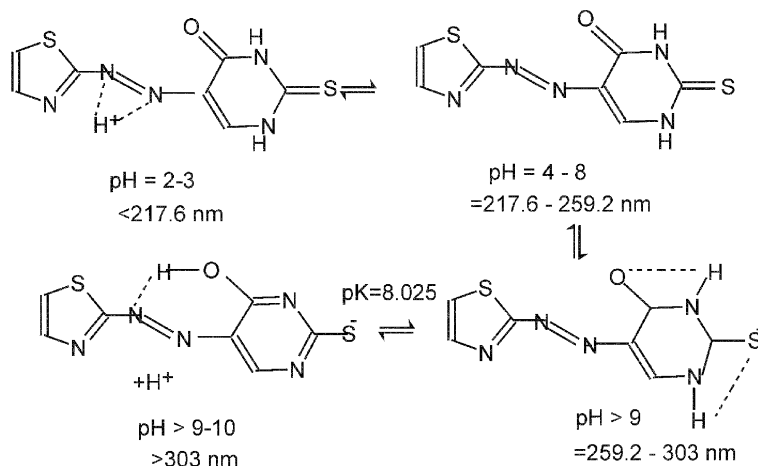
303.0 nm can be assigned the presence of different absorbing species in equilibrium to one another: protonated, neutral, and deprotonated forms. All of the three isobestic points cover all of the pH-ranges (2.4-11.8). The data gave a pK value of 8.03. Thio-uracil gives two bands at 210 and 270 nm in the pH range 2-7 due to the  $\pi-\pi^*$  of two  $sp^2$  hybridized carbons and gives the coupled  $\pi-\pi^*$  of the two carbonyl and thiocarbonyl groups in  $\beta$ -position, respectively. In the pH range 9.2-12.1, a band at 255 nm appears while the former two bands are red-shifted due to successive ionizations. Three isobestic points at 222, 254, and 302 nm are assigned to the presence of different absorbing species in equilibrium to each other: protonated, neutral, and deprotonated forms. The 302 nm band is due to the 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 the aromatic character of the thio-uracil ring. In the alkaline solution (pH >9), most of the bands are red-shifted and become intense, because of the tautomerization with the presence of auxochromic groups. Two modes of ionization could be presented:

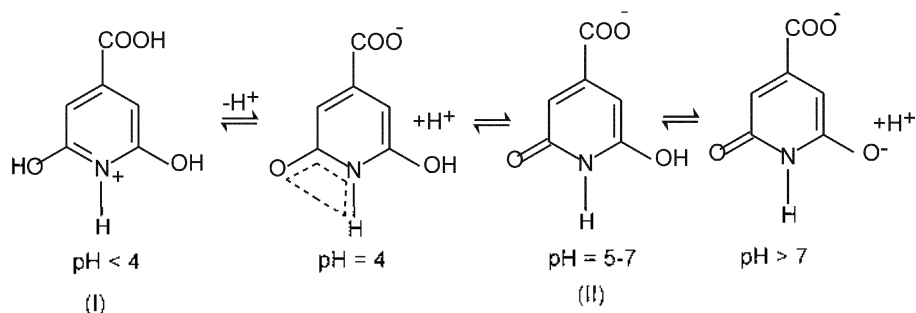


The negative FeCl<sub>3</sub> test reaction for phenolic-OH and the lower pK value than of the reported phe-

nolic compounds suggest that the mode of ionization (I) is more reasonable than (II). The following scheme of ionization of 5-(2-thiazolylazo)-2-thio-uracil is postulated:

The electronic absorption spectra of 3-(2-thiazolylazo) citrazinic acid show three characteristic bands 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 p-system of the pyridine ring and the second is due to the carboxyl 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, whereas all bands are red-shifted. However, the electronic absorption spectra of citrazinic acid at different pH gave four regions 205-215, 228-233, 326-332, and 341-345 nm. The first region decreased in intensity with the increase in 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  $p-\pi^*$  electronic transition of the aromatic p-system of the pyridine ring (structure I). In acidic media (pH's 2, 3), the shoulder at 228 nm is due to  $p\pi-\pi^*$  transition of the carboxy group and becomes more intense with the increase in absorbance in solutions up to pH=4. In the pH range 5-12 the absorbance is pH independent, probably due to



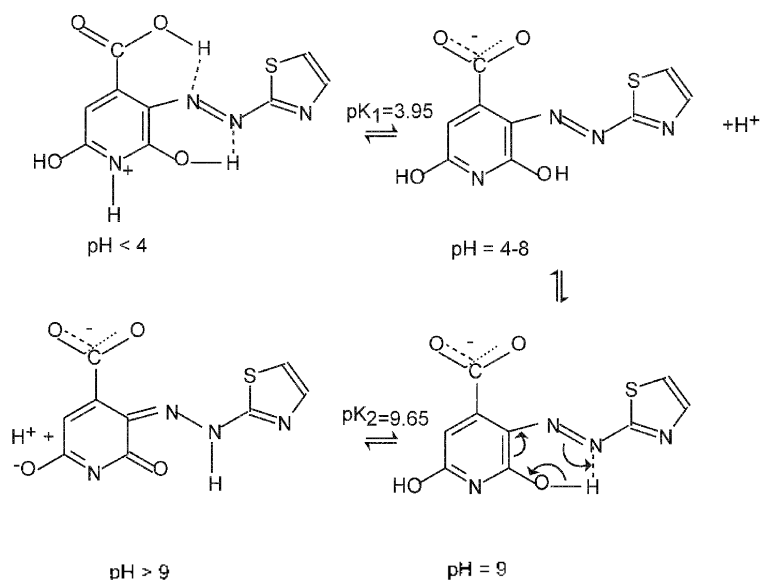


the overlapping between two  $\pi-\pi^*$  electronic transitions between the carbonyl of the carboxylate group and the new carbonyl group of the keto isomer. Meanwhile, the  $p$ -band of the carboxylate anion is probably involved. Extra  $n-\pi^*$  transition band appears in pH (4-7) because the carbonyl group of the keto form. The absence of this band in solutions of  $\text{pH} > 7$  is probably due to the stabilization of the  $n$ -electrons of the keto group formed through ionization. The  $n-\pi^*$  transition of the carbonyl group appears in 344-347 nm, while the shoulder at 328 nm is due to the transition of the N-hetero atom of the pyridine ring at  $\text{pH} = 2$ , with a successive increase in absorbance as the pH increases up to  $\text{pH} = 4$ . At  $\text{pH} > 7$  such a band completely disappears. The mode of ionization can be explained as follows:

For the 3-(2-thiazolylazo) citrazinic acid, the modified limiting absorption plot and the pH-As plot give  $\text{p}K_1$  and  $\text{p}K_2$  values are 3.95 and 9.65 respectively. The  $\text{p}K$ -values of the thiazolylazo citrazinic acid is lower than that of citrazinic acid because of 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 gives a characteristic broad band at  $3433 \text{ cm}^{-1}$  due to the intermolecular hydrogen bonding resulting from the  $\text{C}_8\text{-OH}$  group in two different molecules to favour the associated structure. The bands at  $1621$ ,  $1510$ , and  $1400 \text{ cm}^{-1}$  are due to





$\nu_{C=N}$  and the stretching modes of the azo group. The band at  $1211\text{ cm}^{-1}$  is due to  $\nu_{C=N}$  while that at  $1050\text{ cm}^{-1}$  may be assigned to  $\nu_{C-S}$  or  $\nu_{S-O}$  of the sulphonic group. The  $\gamma_{OH}$  mode of vibration is assigned at  $643\text{ cm}^{-1}$ .

Two regions in IR spectra of uracils were analyzed<sup>57</sup>: (a) the N-H stretching region in crystals and (b) the C=O stretching region in matrix-isolated monomers. The 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<sup>57</sup>. 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 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<sub>2</sub>O- or HCl-doped Ar matrixes to suggest the presence of open dimers in compounds.

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

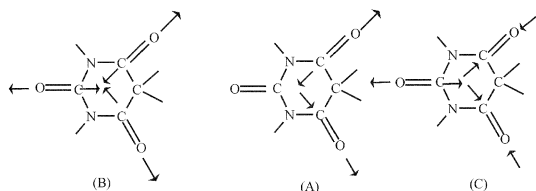
The external (lattice vibrations) spectrum is assigned on the basis of the normal mode calculations with the approximation of the rigid monomer. Vibrations of the double (N-H···O) H-bond are assigned. The spectral characteristics of uracil in autoassociates and hydrates were investigated using high-resolution IR spectroscopy in Ar matrixes. Shifts of vibration frequencies in simple complexes of  $10\text{--}30\text{ cm}^{-1}$  in the  $4000\text{--}400\text{ cm}^{-1}$  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-thi-azolylazo) uracil show a broad characteristic band at the region  $3200\text{--}3400\text{ cm}^{-1}$  assigned to the  $\nu_{N-H}$  through the hydro-

gen bond of the type N-H···O. The  $\nu_{C-H}$  appears at  $2918\text{ cm}^{-1}$ . The bands at  $1408$  and  $1486\text{ cm}^{-1}$  are assigned to  $\nu_s$  and  $\nu_{as}$  stretching vibrations of the azo group, respectively. Those at  $1660$  and  $1045\text{ cm}^{-1}$  are due to  $\nu_{C=O}$  and  $\nu_{C-N}$  from either the thiazolylazo linkage or the uracil moiety to suggest the existence of the keto structure. The of barbituric acid (BA) from the view of the fundamental groups C=O, N-H, and O-H could explain the phenomena of keto-enol tauto-merism, suggesting 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  $C_s$  or  $C_{2v}$ , the latter is not possible in the solid state because of the manner in which the molecules are linked by the hydrogen bonds.

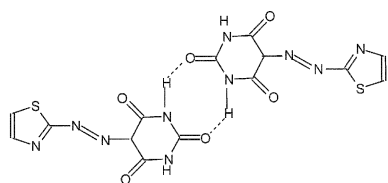
The spectra suggest the existence of a hydrogen bond, as evident from the presence of a well defined splitting sharp band in the frequency range  $3050\text{--}3520\text{ cm}^{-1}$ . Such region appears at  $3200\text{--}3400\text{ cm}^{-1}$  in a broad and splitted feature in the entitled compound. Such finding, points to the solid BA and thiazolylazo BA 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  $\nu_{NH}$  at  $3200\text{ cm}^{-1}$  and  $\nu_{CH2}$  at  $2890\text{ cm}^{-1}$ . The latter shifts to  $2950\text{ cm}^{-1}$  in the corresponding azo compound. The region  $1800\text{--}1600\text{ cm}^{-1}$  is of importance for BA data. Strong absorption at  $1730\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$  due to  $\nu_{C=O}$  and  $\nu_{C-N}$  stretching vibrations appear, 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 corresponds 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 anti-symmetric stretch, (B) symmetric stretch and (C) 2-C=O stretch.

The C-N stretches appear at 1410, 1240, and 1195  $\text{cm}^{-1}$  for BA, which has additionally two N-H in-plane bending modes and  $\text{CH}_2$ . The  $\text{CH}_2$  scissors are easily identified by the presence of two strong bands at 1360 and 1350  $\text{cm}^{-1}$ . Two C-C stretching modes are expected to occur in this region because of the presence of two bands at 1030 and 940  $\text{cm}^{-1}$ . In the region 800 - 200  $\text{cm}^{-1}$ , this is due to two N-H, six C=O and six ring modes. For the azo compound, intense bands at 1585 and 1451  $\text{cm}^{-1}$  are due to the asymmetric and symmetric stretching vibrations of the -N=N- group, respectively. That at 1684  $\text{cm}^{-1}$  could be considered for overlapping of  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=N}}$  modes. The band at 1070  $\text{cm}^{-1}$  is assigned to  $\nu_{\text{C-N}}$ . The following structure is suggested:



The IR spectral data of 4-(2-thiazolylazo) pyrogallol,  $\text{H}_3\text{L}$ , and its Co(II), Ni(II) and Cu(II) complexes gave the followings:

1. The  $\nu_{\text{OH}}$  region in the free ligand is shifted towards the lower frequency on complexation with all metals with the presence of a broad shoulder at frequencies higher than 3600  $\text{cm}^{-1}$ , suggesting the existence of water molecules in the complexes.

2. The  $\nu_{\text{NH}}$  (2830, 2930  $\text{cm}^{-1}$ ),  $\nu_{\text{C=O}}$  (1664  $\text{cm}^{-1}$ ),  $\nu_{\text{C=N}}$  (1612  $\text{cm}^{-1}$ ),  $\nu_{\text{N=N}}$  (1412  $\text{cm}^{-1}$ ),  $\nu_{\text{as}}$  (N=N) (1503  $\text{cm}^{-1}$ ) and  $\nu_{\text{C-N}}$  (1244  $\text{cm}^{-1}$ ) in the free ligand are nearly unaffected on complexation.

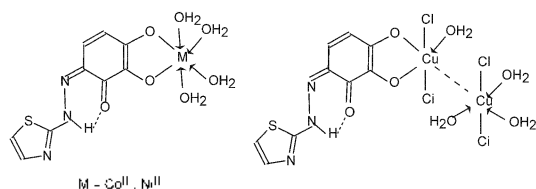
3. The  $\nu_{\text{C=O}}$  band at 1377  $\text{cm}^{-1}$  in the free ligand is shifted to lower frequency on complexation.

4. The bands at 593, 590 and 593  $\text{cm}^{-1}$  in the Co(II), Ni(II) and Cu(II) complexes, respectively, are due to  $\nu_{\text{NH}}$ .

5. The nujol-mull electronic absorption spectra of the Co(HL)4H<sub>2</sub>O, Ni(HL)4 HO<sub>2</sub> and Cu<sub>2</sub>(H<sub>3</sub>L)Cl<sub>4</sub> 4H<sub>2</sub>O gave bands at 24875, 18656, 14204; 2500, 17482, 14450 and 22727, 17857, and 13513  $\text{cm}^{-1}$ , respectively. The first band is mainly of the charge-transfer type while the others are due to d-d transitions. In general, the spectral pattern is poor due to O<sub>h</sub> geometry.

6. The measured  $\mu_{\text{eff}}$  values are 3.98, 3.35 and 2.17 BM, respectively, assign the octahedral geometry.

The structures of the complexes are suggested:



The IR spectra of 2-(2-thiazolylazo) gallic acid,  $\text{H}_2\text{L}$ , and its Co(II), Ni(II) and Cu(II) complexes, gave the followings:

1. The broad band at 3000-3450  $\text{cm}^{-1}$  and the shoulder at 3600  $\text{cm}^{-1}$  are due to the sharing -OH groups on complex formation through hydrogen bonding.

2. The doublet  $\nu_{\text{NH}}$  bands in the free ligand are not affected on complexation.

3. The band at 1690  $\text{cm}^{-1}$  that assigns the  $\nu_{\text{C=O}}$  in the free ligand becomes at 1680, 1683, and 1678  $\text{cm}^{-1}$  in Co(II), Ni(II) and Cu(II) complexes, respectively. The carbonyl group is involved in the structure of the complexes.

4. The  $\nu_{\text{C=N}}$  band in the free ligand (1625  $\text{cm}^{-1}$ ) appear at 1602, 1614, and 1607  $\text{cm}^{-1}$  in the Co(II), Ni(II) and Cu(II) complexes, respectively.

5. The carbonyl group identified at 1448 and 1517  $\text{cm}^{-1}$  in the free ligand ( $\nu_{\text{s}}$ ,  $\nu_{\text{as}}$  respectively) become at 1432, 1510; 1427, 1510, and 1407, 1530  $\text{cm}^{-1}$  Co(II), Ni(II) and Cu(II) complexes, respectively.

6. The azo group at 1464 and 1483  $\text{cm}^{-1}$  ( $\nu_{\text{s}}$ ,  $\nu_{\text{as}}$ ,

respectively) is nearly unaffected on complexation.

7. The band at 1550, 1381 and 1037  $\text{cm}^{-1}$  in the free ligand are due to  $\nu_{\text{C}=\text{O}}$ ,  $\nu_{\text{C}-\text{O}}$  and  $\nu_{\text{C}=\text{N}}$ , respectively. The bands at 1352, 1017; 1364, 1009 and 1347, 1022  $\text{cm}^{-1}$  in the Co(II), Ni(II), and Cu(II) complexes, respectively, assigned to  $\nu_{\text{C}-\text{O}}$  and  $\nu_{\text{C}=\text{N}}$ , respectively.

8. The bands at 450, 593; 440, 588 and 412, 594  $\text{cm}^{-1}$  in the Co(II), Ni(II) and Cu(II) complexes, respectively, are assigned to  $\nu_{\text{N}=\text{N}}$  and  $\nu_{\text{M}-\text{O}}$ , respectively.

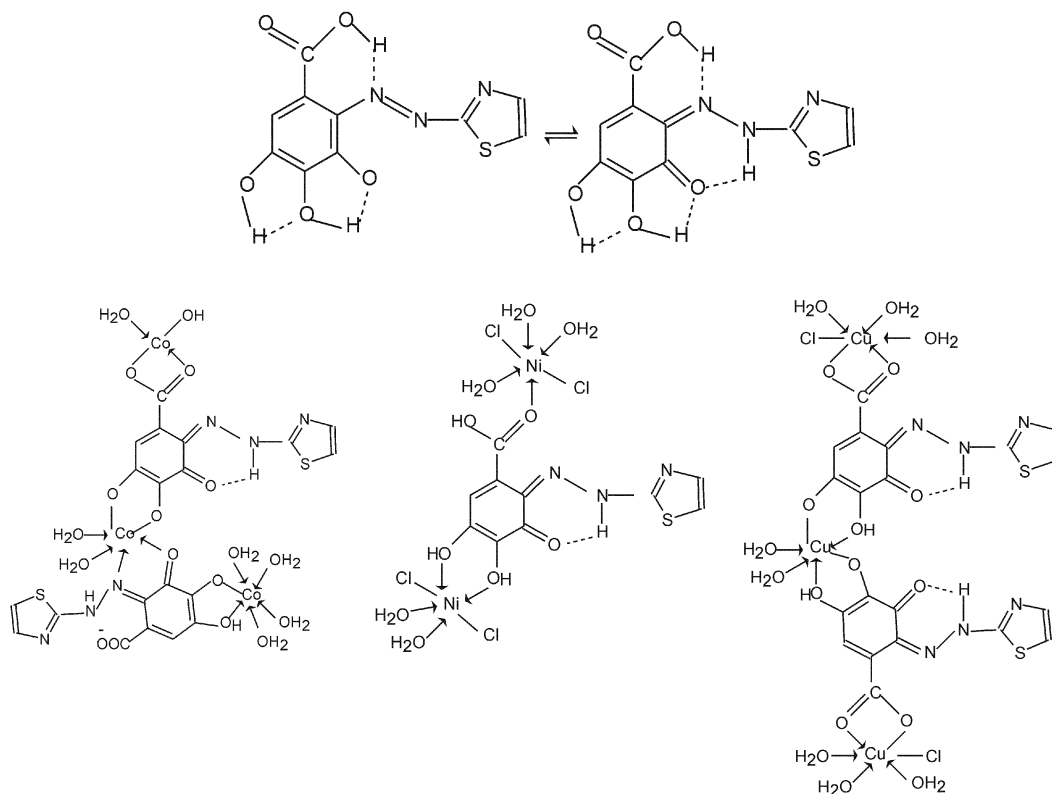
9. The nujol mull electronic absorption spectra of  $\text{Co}_3(\text{HL})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Ni}_2(\text{H}_4\text{L}) \text{Cl}_4(\text{H}_2\text{O})_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}_3(\text{H}_2\text{L})_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  give bands at 24390, 18867; 14705, 24752, 18656, 14084, and 26315, 17857, 13513  $\text{cm}^{-1}$ . The first bands are due to charge-transfer and the others are mainly due to d-d transition with possible metal-metal interaction.

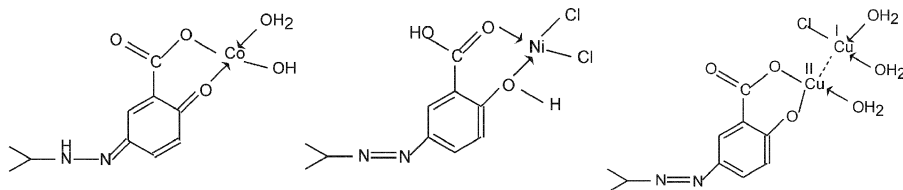
10. The measured  $\mu_{\text{eff}}$  values for the Co(II), Ni(II) and Cu(II) complexes are 4.2, 3.8 and 4.4 BM, respectively, typical of the octahedral geometry. The following structures are postulated for the free ligand the prepared complexes:

The IR data for 5-(2-thiazolylazo) salicylic acid give a broad band at 3230-3500  $\text{cm}^{-1}$  due to  $\nu_{\text{OH}}$  with hydrogen bonding. However, a doublet band at 2830-2980  $\text{cm}^{-1}$  is assigned to the  $\nu_{\text{N}=\text{H}}$ . The bands at 1686 and 1637  $\text{cm}^{-1}$  are due to  $\nu_{\text{C}=\text{O}}$  and  $\nu_{\text{C}=\text{N}}$ , respectively. The azo position is carefully assigned  $\nu_s$  and  $\nu_{\text{as}}$  at 1430 and 1546  $\text{cm}^{-1}$ , respectively. However, the  $\nu_s$  and  $\nu_{\text{as}}$  of the carboxy group to appear at 1380 and 1492  $\text{cm}^{-1}$ , respectively. The presence of  $\nu_{\text{NH}}$  seems to indicate  $\nu_{\text{C}=\text{N}}$ , i.e., the hydrazo structure. The bands at 1260 and 1292  $\text{cm}^{-1}$  are due to  $\nu_{\text{C}-\text{N}}$  and  $\nu_{\text{C}-\text{O}}$ , 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  $\nu_{\text{N}=\text{H}}$  band in the region 2850-2993  $\text{cm}^{-1}$  appears only in the Co(II) complex. However, all complexes gave a broad characteristic band in the range 3100-3500  $\text{cm}^{-1}$  due to  $\nu_{\text{OH}}$ .
2. The  $\nu_{\text{C}-\text{O}}$  in the free ligand is absent in all complexes to suggest 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  $\nu_{COOH}$  is shifted towards a higher frequency ( $56\text{ cm}^{-1}$ ). So, the carboxyl group is involved in complexation.

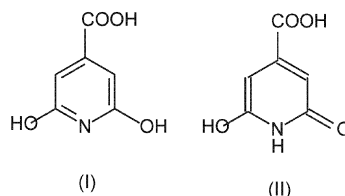
5. The  $\nu_{C=O}$  is also affected on complexation.

6. Generally, the ligand exists in the hydrazo form 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  $\text{cm}^{-1}$  in the Co(II), Ni(II) and Cu(II) complexes, respectively, are due to  $\nu_{N-O}$ .

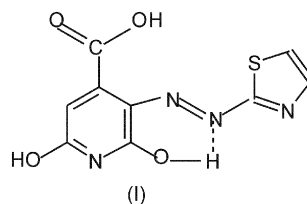
8. The nujol-mull electronic absorption spectra of the Co(HL)OH·H<sub>2</sub>O, Ni(H<sub>2</sub>L)Cl<sub>2</sub>, and Cu<sub>2</sub>LCl<sub>2</sub>·3H<sub>2</sub>O give bands at 24390, 16778; 30864, 19920 and 27173, 19417  $\text{cm}^{-1}$ , respectively. However, the first bands are of charge-transfer nature beside the existence of Cu-Cu interaction. The other bands are mainly due to d-d transition of T<sub>2g</sub> symmetry. So the following structures are suggested:

Citrazinic acid gives two IR bands at 3110 and 2921  $\text{cm}^{-1}$  due to  $\nu_{N-H}$  and  $\nu_{C-H}$ , 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  $\text{cm}^{-1}$  appear because of  $\nu_{C=O}$  of keto group and  $\nu_{C=C}$ , respectively. Also, the strong bands at 1308 and 1250  $\text{cm}^{-1}$  are due to  $\nu_{C-O}$  and  $\nu_{C-N}$ , respectively. These data indicated that citrazinic acid exists in the keto-imino form (II) rather than the dienol form (I). However, the two bands due to  $\nu_{as}$  COOH and  $\nu_s$  COOH appear at 1529 and 1420  $\text{cm}^{-1}$ , accompanied by the appearance of a splitted band at 1464  $\text{cm}^{-1}$  due to the contributions of  $\delta_{N-H}$  and  $\nu_{C-N}$  modes of vibrations. So, the following structures are proposed:



The IR spectra of 3-(2-thiazolyazo) citrazinic acid gives a broad characteristic band at 3150-3550  $\text{cm}^{-1}$  due to stretching band of the hydrogen bonded -OH group ( $\nu_{OH}$ ), followed by the  $\nu_{C-H}$  band 2990  $\text{cm}^{-1}$ . The band at 1619  $\text{cm}^{-1}$  is assigned to  $\nu_{C=C}$  or  $\nu_{as}$  of the azo group. The  $\nu_s$  of the azo group appears at 1363  $\text{cm}^{-1}$ .

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



However the complexes derived from 3-(2-thiazolyazo) citrazinic acid, H<sub>3</sub>L, with Co(II), Ni(II) and Cu(II), gave:

1. The  $\nu_{OH}$  band of the free ligand appear at 3314, 3329 and 3333  $\text{cm}^{-1}$  in Co(II), Ni(II) and Cu(II) complexes, respectively. So, the -OH group is involved on complexation or the complexes are strongly associated with water molecules.

2. The sharp doublet bands at 2910 and 2940  $\text{cm}^{-1}$  in the complexes, not detected in the free ligand, assigned to the hydrazo formation through complexation.

3. The  $\nu_{N-N}$  at 1619 and 1363  $\text{cm}^{-1}$  for the free

ligand disappears on complexation.

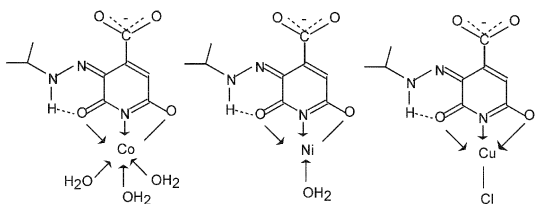
4. The  $1590\text{ cm}^{-1}$  broad band due to  $\nu_{\text{=O}}$  and  $\nu_{\text{C=N}}$  for the complexes suggests the hydrazo formation.

5. The  $\nu_{\text{C=O}}$  band at  $1363\text{ cm}^{-1}$  in the free ligand is shifted towards lower frequency to suggest M-O interaction.

6. The position of  $\nu_{\text{COOH}}$  (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  $\text{cm}^{-1}$  in the Co(II) and, Ni(II) and Cu(II) complexes, are assigned for the  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-O}}$ , respectively.

8. The nujol-mull electronic spectra Co(H<sub>2</sub>L)·3H<sub>2</sub>O, Ni(H<sub>2</sub>L)·H<sub>2</sub>O and Cu(H<sub>2</sub>L)Cl gave bands at 27777, 19083, 14450; 27765, 19305, 14184 and 28901, 22727, 15384  $\text{cm}^{-1}$ , respectively, and  $\mu_{\text{eff}}$  equals 3.95 2.95 and 1.59 BM at room temperature, respectively. The first band is of charge transfer nature. The other bands are mainly due to d-d transition. The following structures are postulated:



The IR spectrum of thiouracil compound shows  $\nu_{\text{NH}}$  band at  $3100\text{ cm}^{-1}$  which completely disappears on complexation, to suggest M-N bonding. The two  $\nu_{\text{C=N}}$  strong bands at  $1720$  and  $1700\text{ cm}^{-1}$  in thiouracil ligand disappear on complexation to suggest the presence of M-O bonding. The four thioamide bands of thiouracil at  $1580$ ,  $1245$ ,  $1160$ , and  $790\text{ cm}^{-1}$ , are affected to different extents 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), and Cu(II). In the lower frequency region, some metal-sensitive bands are observed; e.g., the nickel and the cobalt complexes show  $\nu_{\text{M-S}}$  bands at  $360$  and  $305\text{ cm}^{-1}$ , respectively. The nujol-mull electronic absorption spectra and the room temperature magnetic moment values of the thiouracil complexes of cobalt, nickel, and copper gave  $O_h$ ,  $O_h$  and

square-planar geometry, respectively.

The IR spectra of 5-(2-thiazolylazo)-2-thiouracil, H<sub>2</sub>L, and its Co(III), Ni(III) and Cu(III) complexes gave the followings:

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

2. The  $\nu_{\text{C=O}}$  in the free ligand at  $1693\text{ cm}^{-1}$  completely disappears on complexation, suggesting the M-O bonding.

3. The bands at  $1442$  and  $1540\text{ cm}^{-1}$  in the free ligand are due to the symmetric and asymmetric stretching of the azo group, and are nearly unaffected through complexation.

4. The  $\nu_{\text{C=S}}$  bands at  $894$  and  $1171\text{ cm}^{-1}$  are slightly affected to give 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  $1618\text{ cm}^{-1}$  are affected to different extents during complexation to support M-S bonding.

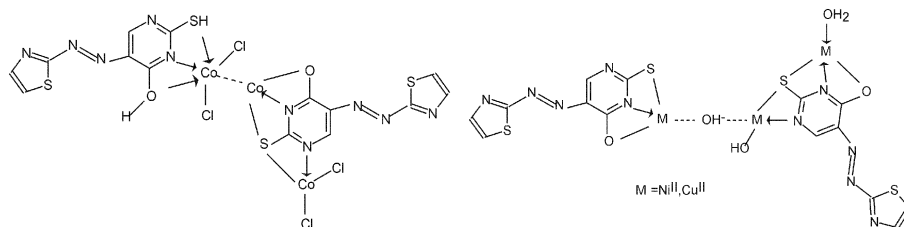
6. The bands at  $446$ ,  $550$ ;  $454$ ,  $555$ , and  $430$ ,  $540\text{ cm}^{-1}$  for the Co(II), Ni(II) and Cu(II) complexes are due to  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-O}}$ , respectively.

7. The nujol-mull electronic absorption spectra of Co<sub>3</sub>L(H<sub>2</sub>L)Cl<sub>4</sub>, Ni<sub>3</sub>L<sub>2</sub>(OH)<sub>2</sub>·H<sub>2</sub>O and Cu<sub>3</sub>L<sub>2</sub>(OH)<sub>2</sub>·H<sub>2</sub>O give bands at  $26315$ ,  $22222$ ,  $15384$ ;  $22727$ ,  $16129$  and  $27322$ ,  $17857\text{ cm}^{-1}$ , respectively, and their room temperature  $\mu_{\text{eff}}$  values are  $3.92$ ,  $3.01$  and  $1.67\text{ BM}$ , respectively. The first bands are mainly due to the charge transfer. The other bands are mainly due to d-d transitions. The Co(II) complex exists in  $O_h$  environment, while the Cu(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- 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 tempera-



ture 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 were calculated at specified field strength (1.320 Tesla).

The magnetic susceptibility data for the tetrahedral copper,  $\text{Cu}(\text{H}_2\text{L})\text{Cl}$  complex,  $\text{H}_2\text{L} = 3\text{-(2-thiazolylazo) citrazinic acid}$ , showed a linear relationship between both  $1/X_g$  or  $1/X_m$  with  $T$ .

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

$\mu_{\text{eff}} = 0.828 X_m (T - \phi)^{1/2}$ . The experimental and the calculated  $\mu_{\text{eff}}$  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  $\phi$  indicates a very weak intermolecular interaction operative in the solid complex. The magnetic moment 1.594 BM at 297.8 K does not vary 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 show parabolic relations indicating a simple paramagnetic behaviour with  $X_{\text{TP}}$  equals  $1173.3 \times 10^{-6}$  cgs. The octahedral copper,  $\text{Cu}_2(\text{H}_3\text{L})\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  complex,  $\text{H}_3\text{L} = 3\text{-(2-thiazolylazo) pyrogallol}$ , shows a linear relationship between  $1/X_g$  or  $1/X_m$  with  $T$ , where  $c = 0.605 \text{ cm}^3 \text{ mol}^{-1}$  and  $\phi = 0.333 \text{ K}$ . Curie-Weiss law is obeyed. Nearly no differences were found between the calculated and the experimental  $\mu_{\text{eff}}$  values. The observed magnetic moment values are higher than that of the spin of the free electron in all the temper-

ature ranges for the studies, indicating a ferromagnetic behaviour with ionic or rather weak covalent bonds. The magnetic moment of 2.165 BM at 296 K does not vary markedly down to 77.90 K (1.9 BM), indicating a magnetically diluted behaviour with small interactions between copper centers in this complex. The parabolic curves obtained on plotting  $X_g$  or  $X_m$  with  $T$  indicates a simple paramagnetism with  $X_{\text{TP}}$  equals  $2133 \times 10^{-6}$  cgs.

The magnetic susceptibility measurements at different temperatures from 297.7 K down to 77 K of the tetrahedral,  $\text{Cu}_2\text{L}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$  complex,  $\text{H}_2\text{L} = 5\text{-(2-thiazolylazo)-2-thiouracil}$ , shows a linear relation between both  $1/X_g$  or  $1/X_m$  with  $T$ , with  $c = 0.359 \text{ cm}^3 \text{ mol}^{-1}$  and  $\phi = -0.1077 \text{ K}$ . A very small difference (0.01 - 0.03 BM) exists between the calculated and the measured magnetic moment values. The measured  $\mu_{\text{eff}}$  is slightly less than the magnetic moment of the unpaired electron  $\mu_{s,0}$  to indicate a weak antiferromagnetic behaviour, whereas the  $\mu_{\text{eff}}$  is 1.725 BM at 297.7 K and does not vary down to 77 K (1.679 BM), indicating a magnetically diluted behaviour<sup>58-59</sup>. The super exchange through the bridging  $\text{OH}^-$  ions leads, also, to the lowering of the magnetic moment value<sup>60-61</sup>. The plotting of  $X_g$  or  $X_m$  with  $T$  gave parabolic curves of a simple paramagnetic type with  $X_{\text{TP}}$  equals  $1352.36 \times 10^{-6}$  cgs. The octahedral  $\text{Cu}_2(\text{H}_2\text{L})_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$  complex,  $\text{H}_2\text{L} = 2\text{-(2-thiazolylazo) gallic acid}$  considered as a polymetallic system, shows a linear relationship between  $1/X_g$  or  $1/X_m$  with  $T$  with  $c = 2.44 \text{ cm}^3 \text{ mol}^{-1}$  and  $\phi = 17.812^\circ\text{K}$ . The magnetic moment values 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  $X_m$  versus  $T$

gives parabolic curves to confirm the simple paramagnetic nature, and the temperature independent paramagnetic susceptibility  $\chi_{\text{TP}}$  equals  $3950.78 \times 10^{-6}$  cgs.

#### Electron spin resonance of copper complexes

Table 3 represents the room-temperature X-band ESR spectra of  $\text{Cu}_2(\text{H}_2\text{L})_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ , where  $\text{H}_2\text{L}$  is 2-(2-thiazolylazo) gallic acid. gives a series of bands and the copper hyperfine splitting is noticeable. The analysis of these bands suggests a considerable interaction between the metal and the ligand in a strong association, as appeared from the calculated G value. For this complex  $g_{\parallel} > g_{\perp}$  suggests that the unpaired electron is in the  $d_{x^2-y^2}$  orbital.

The room-temperature polycrystalline X-band ESR spectral pattern of  $\text{Cu}_2\text{I}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ ;  $\text{H}_2\text{L}=5$  (2-thiazolylazo)-2-thiouracil,  $\text{Cu}_2\text{I}_2\text{Cl}_3 \cdot \text{H}_2\text{O}$ ;  $\text{H}_2\text{L}=5$  (2-thiazolylazo) salicylic acid,  $\text{Cu}_2(\text{H}_2\text{L})\text{Cl}_4 \cdot 4\text{H}_2\text{O}$ ;  $\text{H}_2\text{L}=3$ -(2-thiazolylazo) pyrogallol,  $\text{Cu}(\text{H}_2\text{L})\text{Cl}$ ;  $\text{H}_2\text{L}=3$ -(2-thiazolylazo) citrazinic acid, Table 3, exhibits similar spectral trends. All are isotropic in nature with  $g_{\parallel}=2.077, 2.070, 2.085$  and  $2.085$ , respectively, with  $\Lambda=175.0, 412.5, 243.75$ , and  $337.5$ , respectively.

The data show broad signals, which may be due to the polymeric nature of these complexes. Generally, Cu(II) complexes having a lower symmetry than octahedron undergo 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.

#### Thermal analysis

The DTA curves of 2-(2-thiazolylazo) disodium chromotropate, 5-(2-thiazolylazo) uracil and 5-(2-thiazolylazo) barbituric acid give 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 are assigned to the formation of  $\text{Na}_2\text{O}$ . The first peak is due to the dehydration reaction of probably adsorbed water. However, the 5-(2-thiazolyl-

azo) uracil compound shows also three peaks at 96.0 372.0 and 548.0 °C with activation energies of 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 the dehydration reaction of probably adsorbed water, while the others may be attributed to decomposition because both are placed at a higher temperature than the melting point.

The 5-(2-thiazolylazo) barbituric acid compound gives 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 also due to the dehydration and the others are due to the thermal decomposition. However, the orders baserved as 0.5 and 0.63 suggest that the reaction procedure throughly somehow complicated mechanisms.

The 5-(2-Thiazolylazo) thiouracil compound,  $\text{H}_2\text{L}$ , shows three peaks at 81.9, 267.3 and 577.1 °C. The second one is endothermic while the others are exothermic. 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 shows three exothermic peaks 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 shows 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 of the first peaks are probably assigned to dehydration to explain the hygroscopic nature of these compounds.

2. The dehydration process has a higher energy of activation in the complexes rather than the free ligand.

3. The energy of activation for the different decomposition steps of the tetrahedral nickel complex is higher than that of the 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 mechanisms.

The 3-(2-thiazolylazo) citrazinic acid shows 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 shows 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 consistent with the fact that the water molecules in the complexes are strongly bonded to the complexes. Meanwhile, the octahedral cobalt complex is of higher  $\Delta E$  than that of the tetrahedral nickel complex. The other peaks are due to the decomposition steps.

The 5-(2-thiazolylazo) salicylic acid, H<sub>2</sub>L, showed two exothermic peaks at 97.3 and 287.9°C, their activation energies are 43.65, and 106.14 kJ/mol and their orders are 0.787 and 1.197. However, the cobalt complex shows 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 gives 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 shows a dehydration step at 97.3°C, because of the water molecule in the cobalt complex. The second peak in the salicylic azo ligand is due to the formation of

some decomposition products. For the nickel complex, the observed two peaks may be due to the decomposition steps with the ultimate 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 shows 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 shows 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 gives 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 metal complexes. Although the cobalt and nickel complexes have the same geometry, both decompose in different patterns as seen 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 as a final product.

The 2-(2-thiazolylazo) gallic acid ligand, H<sub>4</sub>L, shows 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 shows 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 gives 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, 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 the dehydration process of the three water molecules present in the outer sphere. These data are consistent with the 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<sup>2,63</sup> by making use of the relation:  $Z = E/RT_m \beta \exp(E/RT_m^2)$  and the entropies of activation ( $\Delta S^\ddagger$ ), were obtained from the relation:  $Z = KTI_m/h \exp(\Delta S^\ddagger/R)$  where,  $R$  represents a molar gas constant,  $\beta$  rate of heating ( $Ks^{-1}$ ),  $K$  the Boltzman constant and  $h$  the Plancks constant.

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

## REFERENCES

1. Yang, H.; Zhang, G.; Hu, Y.; Wang, Q.; Wang, Q. Lihua Jianyan. *Huaxue Fence* **1991**, *5*, 262.
2. Bartnik, R.; Strzyzewski, W. *Pol. J. Appl. Chem.* **1992**, *2*, 207.
3. Rittich, B.; Pirochtova, M.; Hrib, J.; Jurtikova, K.; Dolezal, P. *Collect. Czech. Chem. Commun.* **1992**, *5*, 1134.
4. Arfmann, H. A.; Abraham, W. R. *Z. Naturforsch. C: Biosci.* **1993**, *48*(1-2), 52.
5. Masoud, M. S.; Heiba, A. M.; Ashmawy, F. M. *Trans. Met. Chem.* **1983**, *8*, 124.
6. Masoud, M. S.; Hasanien, A. A.; Heiba, A. M. *Spectroscopy Lett.* **1984**, *8*, 441.
7. Masoud, M. S.; Heiba, A. M. *Current Science* **1985**, *2*, 1165.
8. Masoud, M. S.; Ibrahim, N. A.; Abou Ali, S. A.; Ali, G. Y.; Abed, I. M. *Ind. J. Chem.* **1986**, *25A*, 389.
9. Masoud, M. S.; Khalil, E. A.; Kassem, M. E. *Reactivity of Solids* **1986**, *2*, 269.
10. Hasanein, A. A.; Masoud, M. S.; Heiba, A. M. *The Indian Textile Journal* **1987**, *3*, 110.
11. Masoud, M. S.; Abou Ali, S. A.; Ali, G. Y.; Abed, I. M. *Thermochem. Acta* **1987**, *122*, 209.
12. Hasanein, A. A.; Masoud, M. S.; Heiba, A. M. *J. Chem. Soc. Pak.* **1987**, *2*, 199.
13. El-Dissouky, M. A.; Masoud, M. S.; Ali, F.; Abou El-Enein, S. *Affinidad* **1988**, *416*, 321.
14. Masoud, M. S.; Soliman, E. M.; El-Kholy, A. E.; Khalil, E. A. *Thermochem. Acta* **1988**, *136*, 1.
15. Masoud, M. S.; Zaki, Z. M. *Trans. Met. Chem.* **1988**, *13*, 321.
16. Masoud, M. S.; Soliman, E. M.; Heiba, A. M. *Trans. Met. Chem.* **1989**, *14*, 175.
17. Masoud, M. S.; Zaki, Z. M. *Bull. Fac. Sci., Mansoura Univ.* **1990**, *17*, 71.
18. Masoud, M. S.; El-Dessouky, M. A.; Aly, F. A.; Abou El-Enein, S. A. *Trans. Met. Chem.* **1990**, *15*, 443.
19. Masoud, M. S.; Khalil, E. A.; Youssef, A. R. *Synth. React. Inorg. & Met.-Org. Chem.* **1990**, *20*, 793.
20. Masoud, M. S.; Haggag, S. S.; Soliman, E. M.; El-Shabasy, M. *J. of Material Science*, **1990**, *26*, 1109.
21. Masoud, M. S.; Abou El-Enein, S. A.; El-Shereafy, E. *J. of Thermal Analysis* **1991**, *37*, 365.
22. Masoud, M. S.; Khalil, E. A. *Polish J. Chem.* **1991**, *65*, 933.
23. Masoud, M. S.; Kassem, M. E.; Abd El-Aziz, Y.; Khalil, S. M. *Bull. Fac. Sci. Mansoura Univ.* **1991**, *18*, 105.
24. Masoud, M. S.; Haggag, S. S. *Thermochem. Acta* **1992**, *196*, 221.
25. Masoud, M. S.; Khalil, E. A.; Haggag, S. S. *Pak. J. Sci. Ind. Res.* **1992**, *35*, 480.
26. Masoud, M. S.; Abou El-Enein, S. A.; Hafez, O. F. *J. of Thermal Analysis* **1992**, *38*, 1365.
27. Masoud, M. S.; El-Essawi, M. M.; Amr, A. M. *Anal. Proc.* **1992**, *29*, 370.
28. Masoud, M. S.; El-Shereafy, E.; Khalil, E. A.; Abd El-Hamid, O. H. *Egypt J. Anal. Chem.* **1993**, *2*, 95.
29. Masoud, M. S.; Haggag, S. S.; El-Nahas, H. M.; Abd El-Hi, N. *Acta Chim. Hung.* **1993**, *130*, 783.
30. Khalil, E. A.; Masoud, M. S.; El-Marghany, A. *Pak. J. Sci. Ind. Res.* **1993**, *36*, 68.
31. Masoud, M. S.; Zaki, Z. M.; Ismail, F. M.; Mohamed, A. K. *Z. Fir Phys. Chem.* **1994**, *185*, 223.
32. Masoud, M. S.; El-Hamid, O. H. A.; Zaki, Z. M. *Trans. Met. Chem.* **1994**, *19*, 21.

33. Masoud, M. S.; Haggag, S. S.; Zaki, Z. M.; El-Shabasy, M. *Spectroscopy Lett.* **1994**, *27*, 775.
34. Masoud, M. S.; El-Khatib, A.; Abd El-Aziz, S. *Alexandria Engineering J.* **1994**, *33*, D103.
35. Masoud, M. S.; Hafez, O. F.; Obeid, N. A. *Pak. J. Sci. Ind. Res.* **1994**, *37*, 421.
36. Masoud, M. S.; El-Nahas, H. M.; Haggag, S. S. *Pak. J. Sci. Ind. Res.* **1998**, *38*, 108.
37. Masoud, M. S.; Haggag, S. S.; Abd El-Hamid, O. H. *Revue Roumaine De Chimie* **1996**, *41*, 21.
38. Masoud, M. S.; Ghonaim, M. M.; Heiba, O. *Egypt J. Appl. Sci.* **1996**, *11*, 302.
39. Masoud, M. S.; Hasanein, A. A.; Ghonaim, A. K.; Khalil, E. A.; Mahmoud, A. A. *Z. Fur Phys. Chem.* **1999**, *209*, S. 223.
40. Masoud, M. S.; Hindawy, A. M.; Ahmed, R. H. *Pak. J. Sci. Ind. Res.* **1999**, *1*, 11.
41. Masoud, M. S.; Khalil, E. A.; Ibrahim, A. A.; Marghany, A. A. *Z. Fur Phys. Chem.* **1999**, *211*, 13.
42. Masoud, M. S.; Hammud, H. H. *Ultra Scientist for Physical Sciences* **2000**, *12*, 12.
43. Masoud, M. S.; Kh. Ghonaim, A.; Ahmad, R. H.; Abou El-Enein, S. A.; Mohamed, A. A. accepted for publication. *J. Coordination Chem.* **2002**, *55*, 1.
44. Masoud, M. S.; Kh. Ghonaim, A.; Ahmed, R. H.; Mahmoud, A. A.; Ali, A. E. accepted for publication. *Z. Fur Phys. Chem.* **2001**, *215*, 531.
45. Masoud, M. S.; Abou El-Enein, S. A.; Obeid, N. A. accepted for publication. *Z. Fur Phys. Chem.* **2001**, *215*, 867.
46. Vogel, A. I. *Practical Organic Chemistry*; Longmann: Third Edition; 1961.
47. Langova, H. M.; Sommer, L. *Talanta* **1969**, *16*, 681.
48. Schwarzenbach, G. *Complexometric Titration*. Translated by H. Irving Methuen Co.: London, 1957.
49. Vogel, A. I. *A Text - Book of Quantitative Inorganic Analysis*, 3<sup>rd</sup> Ed.; 1961; p. 512.
50. Bunzli, J. C. G. *Inorg. Chim. Acta* **1960**, *36*, I, 413.
51. Zimmer, H. *Strukturaufklarung Organischer Verbindungen*. Springer-Verlag, Berlin Heidelberg; New York, 1976.
52. Becker, D. E. *High Resolution NMR*, 2<sup>nd</sup> Ed. New York, 1980.
53. Subbarao, N. S.; Bray, J. P. *J. Chem. Phys.* **1977**, *3*, 1085.
54. Joesten, M. D.; Schaad, I. J. *Hydrogen Bonding*; Marcel Dekkers: New York, 1974.
55. Bruskov, I. V.; Buchnev, N. V.; Okon, S. M.; Shulyupina, V. N.; Boltov, I. V. *Biopolymers* **1989**, *2*, 259.
56. Wojcik, M. J.; Rostkowska, H.; Szczeniowski, K.; Person, W. B. *Spectrochim. Acta* **1989**, *4*, 499.
57. Real, J. A.; Munno, G. P.; Chiappetta, R.; Julve, M.; Lloret, F.; Jaumaux, Y.; Colin, J. C.; Blondin, G. *Angew. Chem. Int.* **1994**, *11*, 1184.
58. Kato, M.; Jonassen, H. B.; Fanning, J. C. *Chem. Rev.* **1964**, *99*.
59. Sletten, J.; Sorensen, A.; Julve, M.; Jaumaux, Y. *Inorg. Chem.* **1990**, *29*, 5054.
60. Gadalla, A. M.; Hsuan-Fu Yu. *J. Thermal Analysis* **1991**, *37*, 319.
61. Allan, J. R.; McCloy, B.; Paton, A. D. *Thermochim. Acta* **1993**, *214*, 211.
62. Dollimore, D. *Anal. Chem.* **1994**, *12*, 17R.
63. Horowitz, H.; Metzger, G. *Anal. Chem.* **1963**, *35*, 1464.