

## SPECTRAL PROPERTIES AND CHARACTERIZATION OF SOME PYRIMIDINE AND PURINE COMPLEXES

Dr. M. S. Masoud<sup>a\*</sup>, M. Sh. Ramadan<sup>a</sup>, A. M. Sweyllam<sup>b</sup> and M. H. Al-Saify<sup>c</sup>

<sup>a</sup>Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

<sup>b</sup>Physics Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

<sup>c</sup>Sidi Kerir Petrochemicals Company, Alexandria, Egypt.

\*Corresponding Author: Dr. M. S. Masoud

Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

Article Received on 23/04/2020

Article Revised on 13/05/2020

Article Accepted on 03/06/2020

### ABSTRACT

The metal complexes of ligands Adenine, Adenine-Cytosine, Barbituric acid, Thiobarbituric acid and 2-Thiouracil were synthesized. The infrared spectral measurements assigned the characteristic bands and mode of bonding. The electronic absorption spectra and magnetic properties of the complexes revealed the tetrahedral, square pyramidal and octahedral geometries. The Mössbauer spectra for Fe(Adenine)<sub>3</sub> complex proved a high spin Fe<sup>III</sup> complex.

**KEYWORDS:** Ligands; Complexes; Infrared spectra; Electronic absorption spectra; Magnetic properties and Mössbauer spectra.

### INTRODUCTION

Molecular biology is an important in understanding the interactions between the various systems of a cell, including the interactions between deoxyribonucleic acid and ribonucleic acid, DNA and RNA, respectively and protein biosynthesis, (Figure 1).

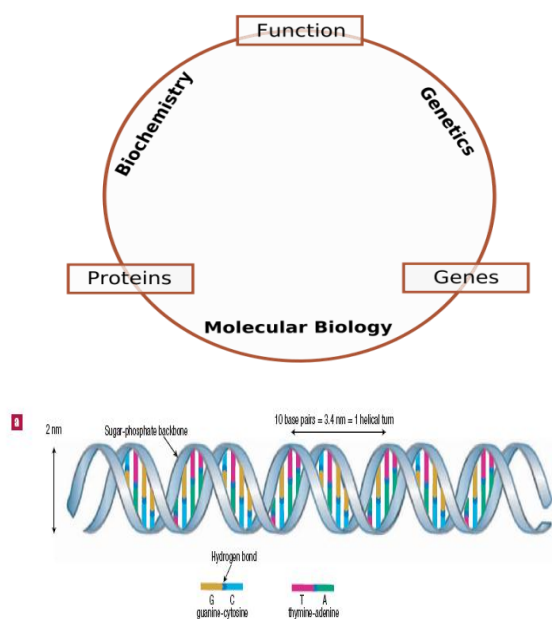


Figure (1): Schematic relationship between biochemistry, genetics and molecular biology with a double-helical DNA representation.

Bioinformatics or computational biology, is the interdisciplinary research field integrating biology with informatics, and is expected to a huge impact on the bioscientific, bioengineering and medical fields. There are many techniques in bioinformatics for DNA microarray data; however, these are mainly divided into fold-change analysis, clustering, classification, genetic network analysis, and simulation.<sup>[1,3]</sup>

The introduction of <sup>2</sup>H-, <sup>13</sup>C-, and <sup>15</sup>N-labeled oligonucleotide building blocks became paramount for structure elucidation of RNA and DNA molecules.<sup>[4-8]</sup>

The pyrimidines (1) and purines (2) are of great importance<sup>[9,16]</sup> where in our laboratory, numerous papers have been published from the structural and coordination chemistry views.<sup>[17,87]</sup> (Figure 2).

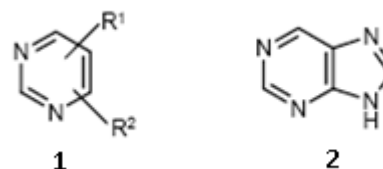


Figure (2): Pyrimidine and purine nuclei.

The pyrimidine nucleus is embedded in a large number of alkaloids, drugs, antibiotics, agrochemicals, and antimicrobial agents<sup>[88]</sup> Many simple fused pyrimidine such as purines and pteridines are biologically active by themselves, or are essential components of very important naturally occurring substances (*i.e.*, nucleic

acids). Some pteridine derivatives are also used as anti-leukemic drugs<sup>[89]</sup> or potassium-conserving diuretics. Some fused thieno[3,2-*d*] pyrimidines serve as anti-allergy drugs, some act as fungicides. A very important biologically active pteridine system (fused pyrazino[2,3-

*d*] pyrimidine) is present in folic acid (3) and several antibiotics. Pteridine was also found in riboflavin (6,7-(dimethyl-9-(D-1-ribyl) isoalloxazine, vitamin B2(4), a growth-regulator for microbes and animals,(Figure 3).

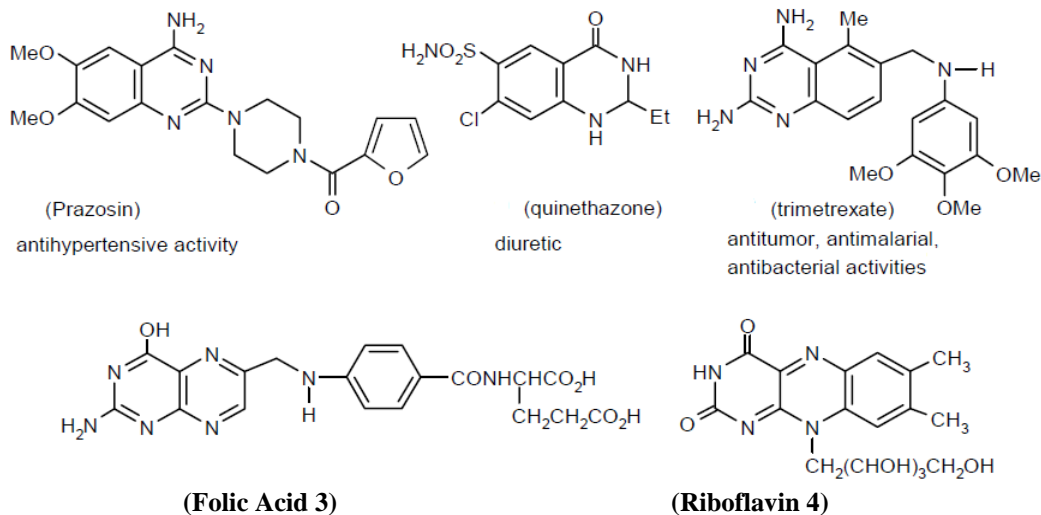
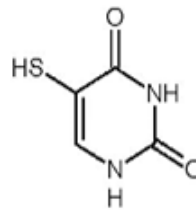
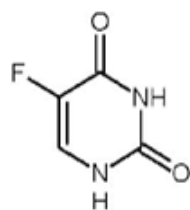
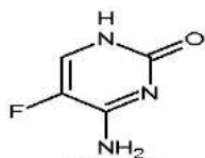


Figure (3): Some biologically active pyrimidine derivatives.

## Biological importance of pyrimidine

### 1-Antimicrobial activity

Microbes cause various types of disease like pneumonia, amoebiasis, typhoid, malaria, cough and cold infections and some severe diseases like tuberculosis, influenza, syphilis, and AIDS as well. Flucytosine is a fluorinated pyrimidine used as nucleosidalanti- fungal agent for the treatment of serious systemic infections caused by susceptible strains of candida and Cryptococcus.<sup>[90]</sup>



5-Fluorouracil(5-FU) 5-Thiouracil

Antineoplastic compounds possessing guanine nucleus like azathioprine<sup>[93]</sup> mercaptopurine<sup>[94]</sup> thioguanine<sup>[95]</sup> and tegafur<sup>[96]</sup> have been discovered. These drugs stop the use of regular cellular metabolites. Several anti-metabolites like mopidamol<sup>[97]</sup> nimustine<sup>[98]</sup> raltitrexed<sup>[99]</sup> uramustine<sup>[100]</sup> and trimetrexate<sup>[101]</sup> have been studied. A pyrimidine antimetabolite gemcitabine has antitumor activity against murine solid tumor.<sup>[102]</sup>

### 2-Anti-inflammatory activity

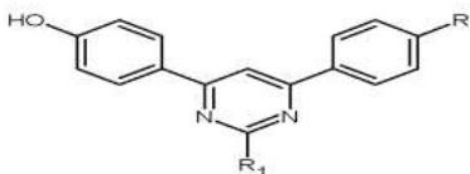
Anti-inflammatory refers to the property of a substance or treatment that reduces inflammation. Due to remarkable pharmacological efficiency of pyrimidine derivatives, anextensive research has been focused on anti-inflammatory activity of pyrimidine nucleus.

### 3-Anticancer activity

Cancer is an idiopathic disease and doctors and scientists are constantly trying to evolve new effective drugs for its treatment. There is no other disease which parallels cancer indiversity of its origin, nature and treatments. One of the early metabolites prepared for cancer treatment was 5-fluorouracil(5-FU)<sup>[91]</sup> a pyrimidine derivative. 5-Thiouracil also exhibits some useful antineoplastic activities.<sup>[92]</sup>

### 4-Antitubercular activity

Tri-substituted pyrimidines have their in vitro anti-malarial activity against Plasmodium falciparum in the range of 0.25- 2 $\mu$ g/ml and anti-tubercular activity against Mycobacterium tuberculosis at a concentration of 12.5  $\mu$ g/ml.<sup>[103]</sup>

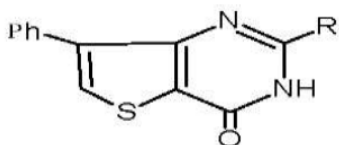


### 5-Central Nervous System(CNS) Activity (Sedative /hypnotic)

A wide variety of barbiturates are used as sedative, hypnotics and classified as drugs having short, intermediate and long duration of action.<sup>[104]</sup> Allobarbital, aprobarbital, phenobarbital, secobarbital, and pentobarbital are frequently used hypnotic barbiturates.<sup>[105]</sup> Hexobarbital, cyclobarbital and propallylonal are used sedatives hypnotics.<sup>[106]</sup>

### 6-Antihyperlipidemic activity

2-substituted-6-phenyl and 7-phenyl thieno[3,2-*d*]pyrimidin-4-ones are synthesized.<sup>[107]</sup> through cyclocondensation of the corresponding thiophenoaminoesters with a variety of nitriles in the presence of dry hydrogen chloride gas. Antihyperlipidemic activity has been reported in a few thienopyrimidines.



## Experimental

### A- Synthesis of metal complexes in the solid state

These were prepared by mixing metal chloride and acetylacetonate(acac) solutions with ligand solutions,

Table(1), hence they were refluxed, filtered and dried for the separated products. The metal ions were determined by atomic absorption techniques and complexometric titrations using published procedures.<sup>[108]</sup> The complexes were digested by aqua regia several times to complete decomposition for the organic ligand compounds.

## B- Instruments and working procedures

### i. Infrared spectrophotometer

The spectra of ligands and their complexes were recorded using SHIMADZU FTIR spectrophotometer.

### ii. UV-vis spectrophotometer and molar magnetic susceptibilities

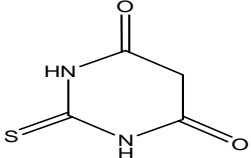
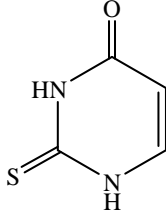
The nujol mull electronic absorption spectra of complexes were recorded using Halios  $\alpha$  instrument Molar magnetic susceptibilities, corrected for diamagnetism using Pascal's constants, were determined at room temperature (298 °K) using Faraday's method. The apparatus was calibrated with Hg[Co(SCN)<sub>4</sub>].

### iii. Mössbauer spectra

The Mössbauer spectrum for iron adenine complex was given. The measurements were performed by constant acceleration method at room temperature, with a source of colt-57(20 mCi) diffused into a Rh matrix. The data have been analyzed by means of least square fitting using the Mössfit computer program.

**Table (1): Names, abbreviations, melting points and structures of the ligands are given.**

Compound	Abbreviation	melting points °C	Structures
Adenine	(AD)	360-365	
Cytosine	(CY)	320-325	
Barbituric acid	(BA)	248	

Thiobarbituric acid (TBA)		245	
2-Thiouracil (TU)		340	

## Results and discussion

### A. Infrared spectra and mode of bonding

The five possible nitrogen binding sites of adenine are the pyrimidine N(1) and N(3), the imidazole N(7) and N(9) ring nitrogen, and the N(6) nitrogen of the exocyclic NH<sub>2</sub> group.

### Adenine and cytosine complexes

Some characteristic IR frequencies of the ligands and their complexes are given in Figure (4), Table (2). The bands in the region 3000-3600 cm<sup>-1</sup> may be attributed to NH and OH stretching modes.<sup>[109,110]</sup> The  $\nu_{(\text{NH}_2)}$  and

$\delta_{(\text{NH}_2)}$  bands of adenine are shifted to higher frequency regions after complexation. So, adenine coordinates through ring nitrogen with appreciable shifts of band frequencies and ring vibrations of the ligand.<sup>[59,111,117]</sup> The 1242 cm<sup>-1</sup> of adenine due to  $\nu_{(\text{N}_7-\text{C}_8)}$  is shifted to lower frequency upon complexation indicating the binding of adenine is through ring nitrogen.<sup>[109]</sup> The  $\nu_{(\text{C}_4=\text{N}_3)}$  band of cytosine at 1550 cm<sup>-1</sup> is shifted to lower frequencies upon complexation which gives indication for cytosine N(3) contribution in complex formation.

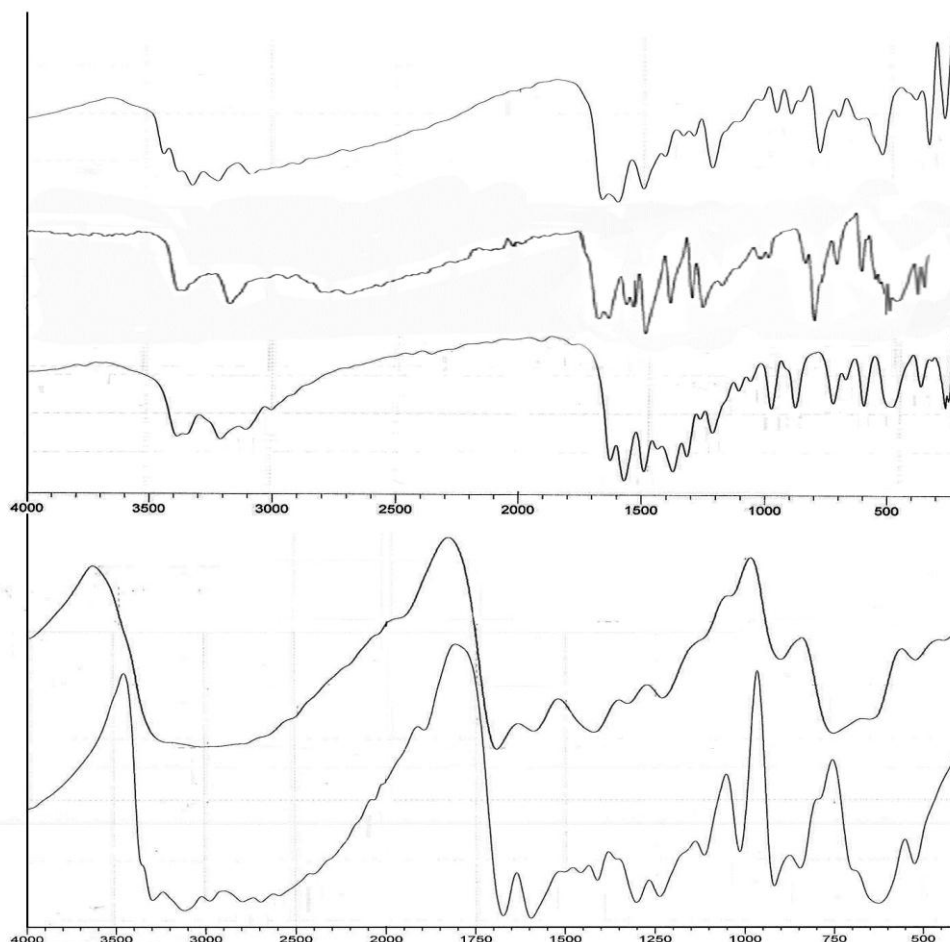


Figure (4): Infrared spectra of:

- (a) Adenine (b) Fe(Adenine)<sub>3</sub>  
 (c) Co(acac)<sub>2</sub>(Adenine)  
 (d) Cytosine  
 (e) Co(Adenine)(Cytosine)(OH)<sub>2</sub>.2H<sub>2</sub>O

Table (2): Fundamental infrared bands (cm<sup>-1</sup>) of Adenine, Cytosine and their complexes.

Adenine	Fe(Adenine) <sub>3</sub>	Co(acac) <sub>2</sub> (Adenine)	Assignments
3286	-	$\left\{ \begin{matrix} 3371 \\ 3335 \end{matrix} \right\}$ (sp)	$\nu_{(OH)}$ , $\nu_{(NH_2)}$
3111	-	3200	$\nu_{(NH_2)}$ , $2\delta_{(NH_2)}$
2970	3028	3099	$\nu_{(C_8-H)}$ , $\nu_{(C_2-H)}$ , $\nu_{(NH_2)}$
1676	1684	1647	$\delta_{(NH_2)}$ sym. in plane
-	-	1591	$\nu_{(C=O)}$
1597	1589	1514	$\nu_{(C_4-C_5)}$ , $\nu_{(C_8-N_9)}$ , $\delta_{(C_8-H)}$
1504	-	-	$\delta_{(N_1-H)}$
1460	-	-	$\delta_{(C_2-H)}$ , $\nu_{(C_8-N_9)}$ , $\delta_{(C_8-H)}$
1414	1421	1400	$\nu_{(N_1-C_6N_6)}$
1358	1327	1346	$\nu_{(C_5-N_7-C_8)}$
1306	-	1296	$\nu_{(N_9-C_8)}$ , $\nu_{(N_3-C_2)}$ , $\delta_{(C-H)}$
1242	1231	1246	$\delta_{(C_8-H)}$ , $\nu_{(N_7-C_8)}$
1119	-	1146	$\nu_{(C_2-N_3)}$
1020	1041	1014	$\rho_{(NH_2)}$
926	901	920	$\rho_{(NH_2)}$ , $\nu_{(N_1-C_6)}$
854	752	768	$\delta_{(N_1-C_2-N_3)}$ , $\nu_{(C_5-N_7)}$ , $\nu_{(N_9-H)}$
636	652	646	$\nu_{(NH_2)}$ , ring deformation
534	523	-	$\omega_{(NH_2)}$ , $\delta_{(NH_2)}$
-	-	532	$\delta_{(C=O)}$
-	444	417	$\nu_{(M-N)}$
-	-	316	

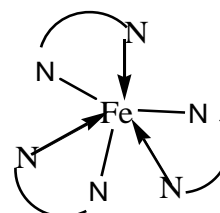
Sp: splittedCont.

Cytosine	Co(Adenine)(Cytosine)(OH) <sub>2</sub> .2H <sub>2</sub> O	Assignments
3390	3313	$\nu_{(OH)}$ , $\nu_{(NH_2)}$
3180	3211	$\nu_{(NH_2)}$ , $2\delta_{(NH_2)}$
3000	3078	$\nu_{(CH)}$
1660	1666	$\nu_{(C=O)}$
1610	1605	
1550	1502	$\nu_{(C_4=N_3)}$
-	1418	$\nu_{(N_1-C_6N_6)}$
-	1344	$\nu_{(C_5-N_7-C_8)}$
1280	1302	$\nu_{(N_9-C_8)}$ , $\nu_{(N_3-C_2)}$ , $\delta_{(C-H)}$
1240	1227	$\nu_{ring}$ , $\delta_{(NH_2)}$ asvm.out of plane
980	970	$\rho_{(NH_2)}$ , $\nu_{(N_1-C_6)}$
	910	
795	795	$\delta_{(N_1-C_6H)}$
565	540	$\delta_{(C=O)}$
-	403	$\nu_{(M-N)}$
-	351	

From the previous data Figure (4) and Table (2), the following modes of bonding are given.

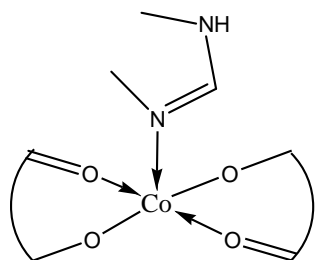
#### For Fe(adenine)<sub>3</sub> complex

The  $\nu_{(C_2-N_3)}$  band of adenine at 1119 cm<sup>-1</sup> disappeared upon complexation with Fe(III), so the N(3) site is involved with N(9) in coordination as follows:



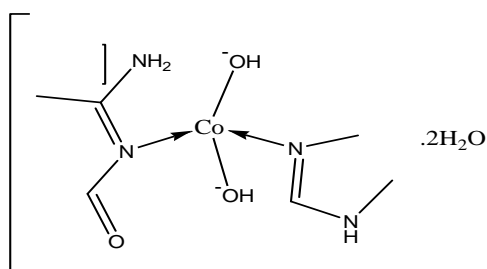
### In case of $\text{Co}(\text{acac})_2(\text{adenine})$ complex

The presence of  $\nu_{\text{C}=\text{O}}$  at  $1591\text{ cm}^{-1}$  of this complex spectrum proves that  $\text{Co}(\text{II})$  is coordinated to acetylacetonate anion which contributes with N(7) nitrogen of adenine to give the following structure.

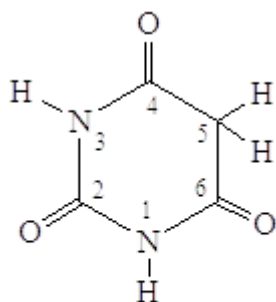


### On the other hand, for $\text{Co}(\text{Adenine})(\text{Cytosine})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ complex

The spectra of Adenine, Cytosine and their cobalt complex in the  $3390\text{--}3286\text{ cm}^{-1}$  region gave set of bands assigned to  $\text{NH}_2$  and  $\text{NH}$  vibrations. The bands of the complex were compared with that of Adenine and Cytosine, Table (2), subjected to changes on complexation. The characteristic bands of Cytosine are  $\nu_{\text{C}=\text{O}}$  ( $1660$  and  $1610\text{ cm}^{-1}$ ),  $\nu_{\text{C}=\text{N}_3}$  ( $1550\text{ cm}^{-1}$ ),  $\delta_{\text{C}=\text{O}}$  ( $565\text{ cm}^{-1}$ ) and  $\delta_{\text{N}_1\text{--C}_6\text{H}}$  ( $795\text{ cm}^{-1}$ ), Table(2). Below  $1600\text{ cm}^{-1}$  the bands of Cytosine spectrum are mainly due to ring stretching and bending modes, beside  $\text{CH}$  and  $\text{C--NH}_2$  bending modes.<sup>[118]</sup> The  $\nu_{\text{C}_5\text{--N}_7\text{--C}_8}$  band of Adenine and  $\nu_{\text{C}_4\text{--N}_3}$  band of Cytosine are shifted to lower frequencies upon complexation which give indication for Adenine N(7) and cytosine N(3) contributions in complex formation with appearance of  $\nu_{\text{M--N}}$  band at  $351$  and  $403\text{ cm}^{-1}$ . The mode of bonding of this complex is given as follows:



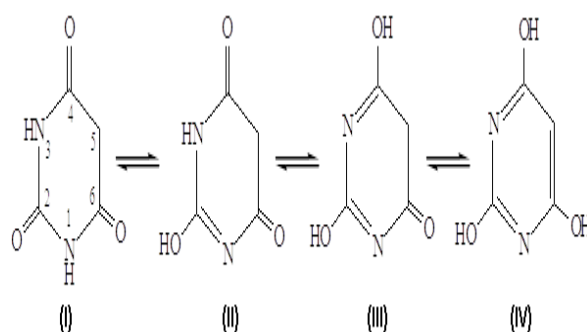
### Mode of bonding of Barbituric acid and its complexes



Barbituric acid

The fundamental bands of Barbituric acid and its complexes are given in Figure (5) and Table (3). The data of the entitled ligand and its complexes are studied as follows:

- The barbituric acid gave four IR bands.<sup>[119,120]</sup> at  $3552$ ,  $3478$ ,  $3182$  and  $3096\text{ cm}^{-1}$  due to  $\nu_{\text{OH}}$  and  $\nu_{\text{NH}}$ . The lower frequency of the  $\nu_{\text{NH}}$  band compared to its normal position ( $3460\text{--}3400\text{ cm}^{-1}$ ) points to the presence of an intramolecular hydrogen bonds of the type  $\text{OH}\cdots\text{N}$ .<sup>[121]</sup>
- Shifts of the  $\nu_{\text{OH}}$  band of the free ligand occur upon complexation, Figure (5) and Table (3), due to the existence of coordinated water molecules.<sup>[122]</sup> or  $\text{M--O}$  and hydrogen bond formations.<sup>[123]</sup>
- The band at  $2876\text{ cm}^{-1}$  in the free ligand is due to  $\nu_{\text{CH}}$



d- The shifts or disappearance of both the  $\nu_{\text{NH}}$  and  $\nu_{\text{C}=\text{O}}$  bands, Figure (5) and Table (3), suggest that these groups are strongly involved in the structural chemistry of the complexes. This is supported either by the probable existence of  $\text{M--N}$  bands or the free ligand may be subjected to half keto-half enol tautomerism and equilibria in the solid state<sup>[58,124]</sup>, i.e. conversion of  $\text{--CNH}$  to  $\text{C=N}$  occurred.

Structure (IV) represents Barbituric acid as 2,4,6-trihydroxypyrimidine. This structure has been proposed because of its acidic nature. X-ray analysis indicated that structure (I) is the predominant form in the solid state.<sup>[124]</sup>

e-New IR bands of the complexes appeared at ( $503\text{--}536\text{ cm}^{-1}$ ) and ( $343\text{--}417\text{ cm}^{-1}$ ) assigned as  $\nu_{\text{M--O}}$  and  $\nu_{\text{M--N}}$ , respectively. The  $\nu_{\text{OH}}$ ,  $\nu_{\text{C--N}}$  and  $\nu_{\text{C--O}}$  bands of Barbituric acid are shifted on complexation, indicating  $\text{M--O}$  interaction.

f- Barbituric acid is of bidentate or tridentate bonding. The bidentate chelation is suggested to be through N(1) and C(2)O while the tridentate interaction is via C(2)O, N(3) and C(4)O.

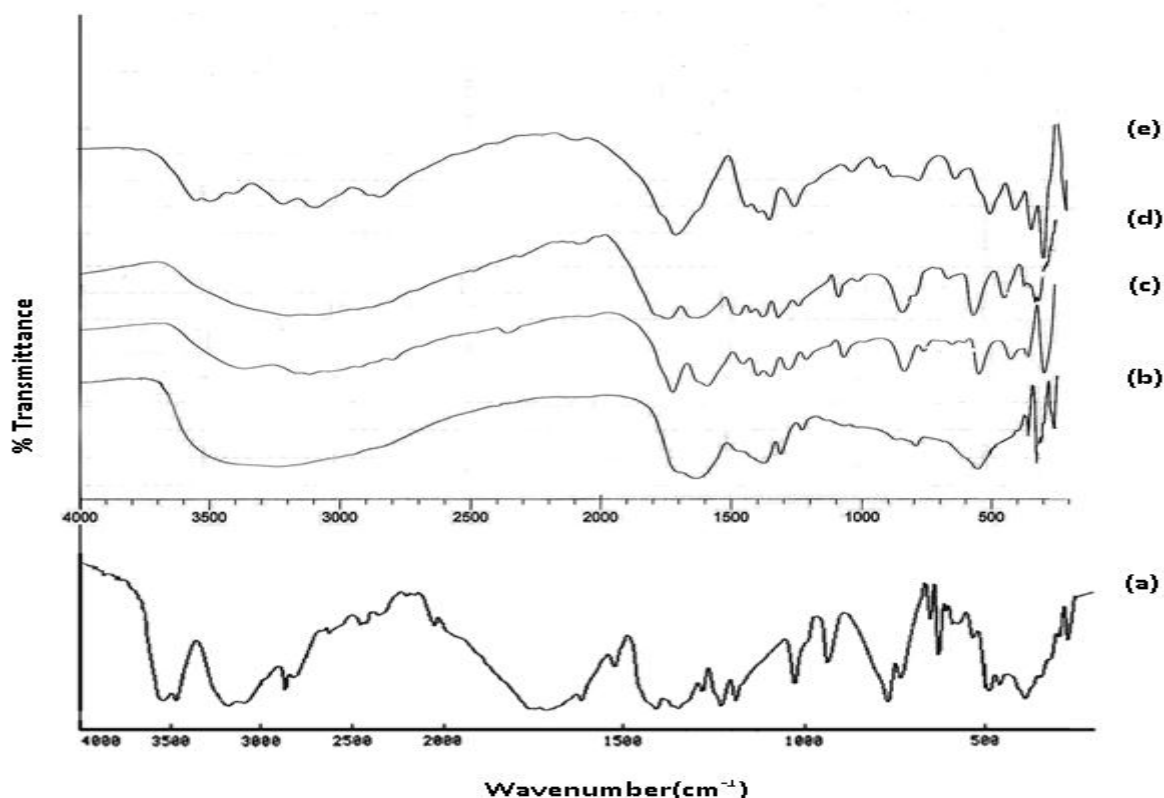


Figure (5): Infrared spectra of:

- (a) Barbituric acid (b) Cr(Barbituric acid)(OH)·4H<sub>2</sub>O
- (c) Zn(Barbituric acid)<sub>2</sub>·3H<sub>2</sub>O (d) Cd(Barbituric acid)<sub>2</sub>·10H<sub>2</sub>O
- (e) Hg(Barbituric acid)<sub>2</sub>

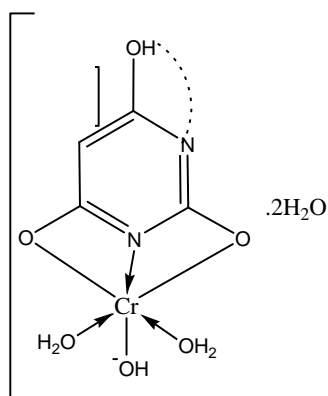
Table (3): Fundamental infrared bands (cm<sup>-1</sup>) of Barbituric acid and its complexes.

Barbituric acid (BA)	Cr-BA	Zn-BA	Cd-BA	Hg-BA	Assignments
3552	3211	-	-	3531	ν <sub>OH</sub>
3478		3356	-	3477 (sp)	
{ 3182 } { 3096 (sp) } { - }	-	{ 3153 } { 3105 (sp) } { - }	{ 3157 } { 3072 (sp) } { - }	{ 3196 } { 3076 (sp) } { - }	ν <sub>NH</sub>
2876	-	-	2899	2872	ν <sub>CH</sub>
2830	-	2793	2851	2831	
{ 1744 } { 1718 (sp) } { 1617 }	-	1713	1705	1703	ν <sub>C=O</sub>
	1612	1582	1597	-	ν <sub>C=N</sub>
1410	-	1448	1435	1431	δ <sub>NH</sub>
1366	1356	1391	1387	1387	ν <sub>C-O</sub> , δ <sub>CH</sub>
1349	-	1340	1344	1346	
1285	1292	1273	1285	-	ν <sub>C-O</sub> , δ <sub>OH</sub>
1232	-	-	-	1252	ν <sub>C-N</sub>
1193	1211	1205	1207	-	
-	1053	1063	1057	1034	ν <sub>C-O</sub> , ν <sub>C-N</sub>
1028	1005	986	986	-	ν <sub>C-C</sub>
936	-	-	-	933	
-	-	-	-	876	ρ <sub>CH</sub> , ρ <sub>OH</sub>
-	852	829	808	-	
733	775	756	764	779	

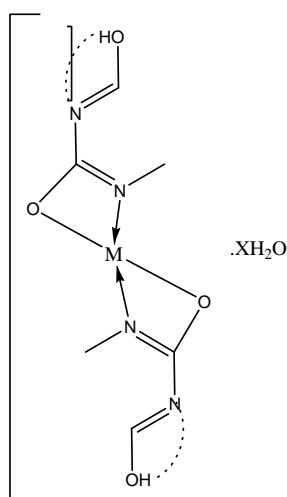
739	-	-	-	-	
656	-	646	635	638	
632	-	-	-	-	
-	536	538	534	503	$\nu_{M-O}$
-	343	353	417	345	$\nu_{M-N}$

**SP: splitted**

The mode of bonding for Cr(Barbituric acid)(OH<sup>-</sup>).4H<sub>2</sub>O complex is given as follows, where the Barbituric acid is tautomerized to give tridentate centers for coordination, as data is given, Figure (5) and Table (3).



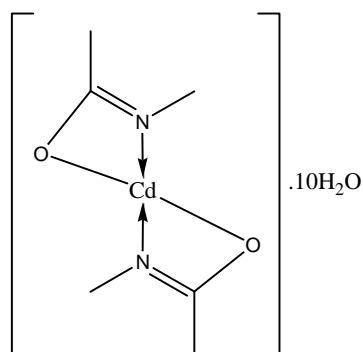
However, Zn(Barbituric acid)<sub>2</sub>.3H<sub>2</sub>O and Hg(Barbituric acid)<sub>2</sub> complexes pointed to that, the Barbituric acid is tautomerized to give bidentate centers for coordination. An intramolecular hydrogen bonding was remarked and accompanied by association through hydrogen bonding in Zn complex. The following structures are given:



M= Zn or Hg, X=3 or 0 respectively.

The IR spectra of Thiobarbituric acid and Fe(Thiobarbituric acid)(OH<sup>-</sup>).2H<sub>2</sub>O complex are given in Figure (6) and Table (4). There is dynamic equilibria in solid state of TBA as the existence of  $\nu_{SH}$  band in spectra. A comparison of the IR spectra of the ligand and the metal complex brings out the following facts to light:

Also, for Cd(Barbituric acid)<sub>2</sub>.10H<sub>2</sub>O, the presence of  $\nu_{NH}$  band at 3157-3072 cm<sup>-1</sup> and  $\nu_{C=O}$  band at 1705 cm<sup>-1</sup> upon complexation give bidentate donation as follows:



1. The spectra Fe(Thiobarbituric acid)(OH<sup>-</sup>).2H<sub>2</sub>O complex exhibited a broad band at 3367 cm<sup>-1</sup>, attributed to  $\nu_{OH}$ , while that at 839-791 cm<sup>-1</sup> is assigned to coordinated water molecules.<sup>[125]</sup>
2. The carbonyl absorption band  $\nu_{C=O}$  of the ligand at 1674 cm<sup>-1</sup> was shifted to lower frequency upon Fe<sup>3+</sup> complexation which indicated that at least one of the two carbonyl groups in the TBA is coordinated to metal ion.
3. The  $\nu_{NH}$  band at 3231-3111 cm<sup>-1</sup> disappeared in the spectra of Fe<sup>3+</sup> complex suggesting that the NH groups are either (i) participate in bond formation with the metal ion; or (ii) tautomerized with the adjacent groups to form the enol-thiol tautomer before complexation. It is reported that,<sup>[126]</sup> if Thiobarbituric acid doesn't allow the formation of en-thiol species, a complex formation between Thiobarbituric acid and the metal ion doesn't take place. The appearance of  $\nu_{M-S}$  and  $\nu_{M-N}$  bands is strong evidence for complexation.<sup>[24,127,128]</sup>



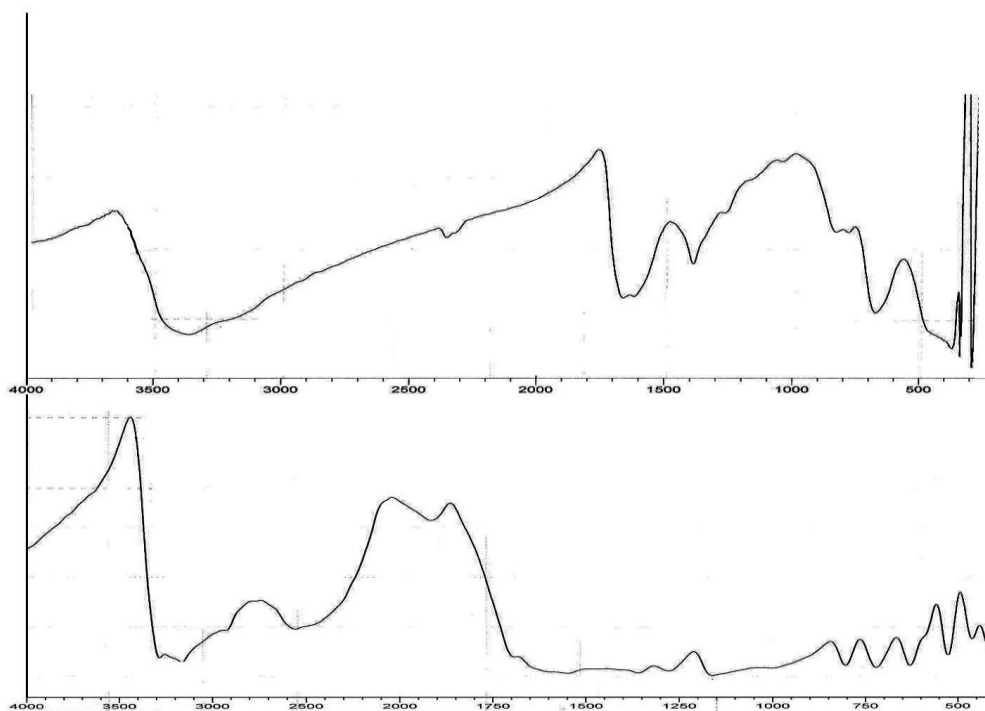


Figure (6): Infrared spectra of:

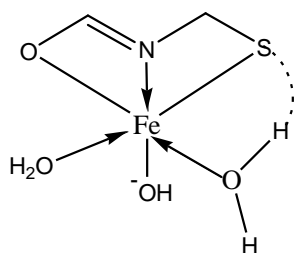
(a) Thiobarbituric acid (b) Fe(Thiobarbituric acid)(OH).2H<sub>2</sub>O

Table (4): Fundamental infrared bands (cm<sup>-1</sup>) of Thiobarbituric acid and its iron complex.

Thiobarbituric acid	Fe(Thiobarbituric acid)	Assignments
-	3367	$\nu_{\text{OH}}$
3231	-	$\nu_{\text{NH}}$
3111	-	$\nu_{\text{CH}}$
2876	-	$\nu_{\text{CH}}$
2721	-	$\nu_{\text{CH}}$
2511	2362	$\nu_{\text{SH}}$
1896	-	$\nu_{\text{C=O}}$
1674	1672	$\nu_{\text{C=O}}$
-	1628	$\nu_{\text{C=O}}$
1533	-	$\nu_{\text{C=N}}$
1344	1398	$\nu_{\text{C-O}}$
1265	1277	$\nu_{\text{C-N}}$
1150	1170	$\nu_{\text{C-C}}$
-	1053	$\nu_{\text{C-S}}$
993	839	$\rho_{\text{CH}}, \rho_{\text{OH}}$
797	791	
714	-	
623	-	
-	683	$\nu_{\text{M-S}}$
-	380	$\nu_{\text{M-N}}$

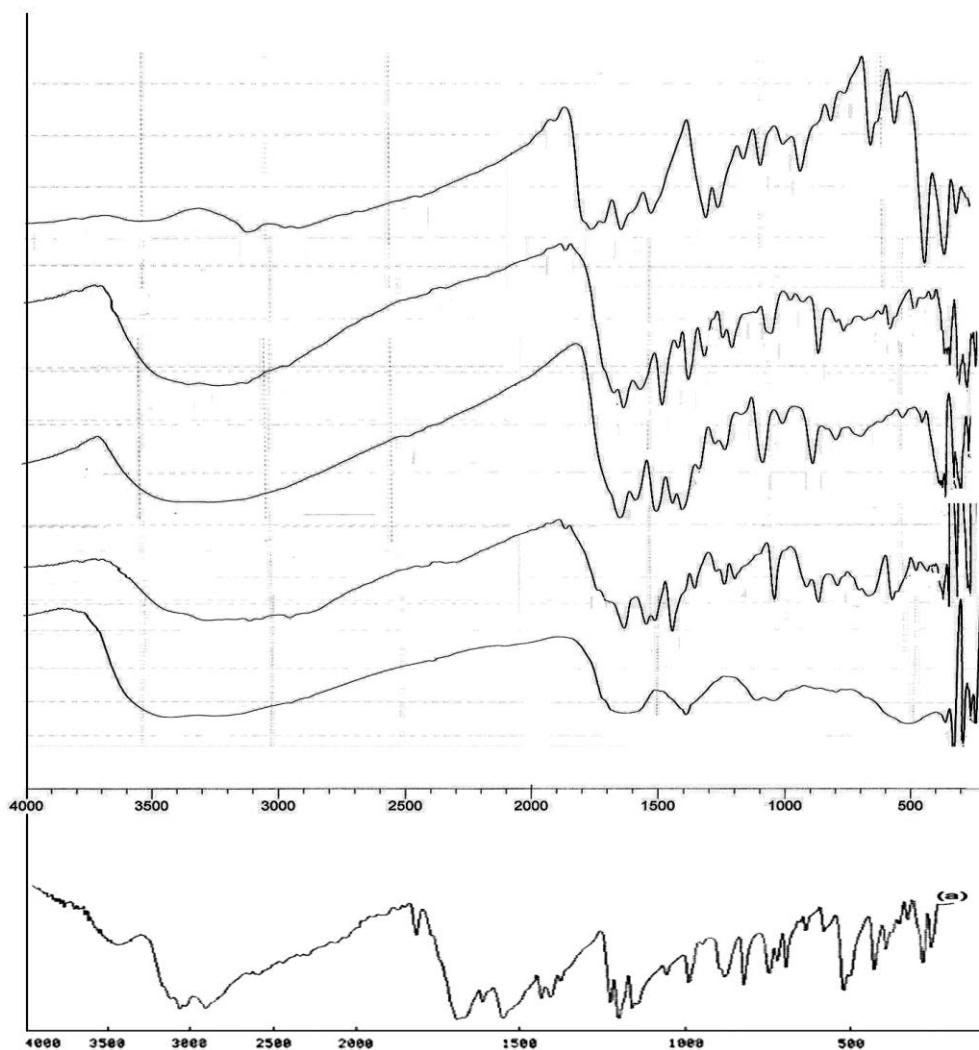
SP: splitted

According to data obtained from IR, Figure (6) and Table (4), Thiobarbituric acid is tautomerized to give tridentate centers for coordination. The mode of bonding for Fe(Thiobarbituric acid)(OH).2H<sub>2</sub>O complex is given as follows:



**Mode of bonding of Thiouracil and its complexes,**  
Figure(7) and Table(5).

The  $\nu_{\text{NH}}$  band of 2-Thiouracil<sup>[129]</sup> at  $3084\text{--}3046\text{ cm}^{-1}$  was completely absent on complexation, i.e. the NH group either participates in bond formation with the metal ion or tautomerised with the adjacent C=S and C=O groups to form the enol-thiol tautomer before chelation with the metal cation. The latter view is verified by the presence of  $\nu_{\text{C=N}}$ ,  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=S}}$  bands at  $1635\text{--}1589\text{ cm}^{-1}$ ,  $1416\text{--}1383\text{ cm}^{-1}$  and  $1024\text{--}993\text{ cm}^{-1}$ , respectively. The complexes show IR broad absorption band in the  $3508\text{--}3317\text{ cm}^{-1}$  region, suggesting the coordination of  $\text{H}_2\text{O}$ .<sup>[41,131]</sup> Bands assigned to  $\nu_{(\text{M-O})}$ ,  $\nu_{(\text{M-S})}$  and  $\nu_{(\text{M-N})}$  are identified, Table(5).



**Figure (7): Infrared spectra of:**

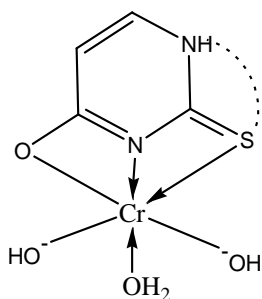
- (a) Thiouracil (b)  $\text{Cr}(\text{Thiouracil})(\text{OH})_2 \cdot \text{H}_2\text{O}$   
 (c)  $\text{Mn}(\text{Thiouracil})_2 \cdot \text{H}_2\text{O}$  (d)  $\text{Co-Ni}(\text{Thiouracil})_3 \cdot 4\text{H}_2\text{O}$   
 (e)  $\text{Ni-Cu}(\text{Thiouracil})_3 \cdot 4\text{H}_2\text{O}$  (f)  $\text{Hg}(\text{Thiouracil})_2 \cdot 4\text{H}_2\text{O}$

Table (5): Fundamental infrared bands ( $\text{cm}^{-1}$ ) of 2-Thiouracil and its complexes.

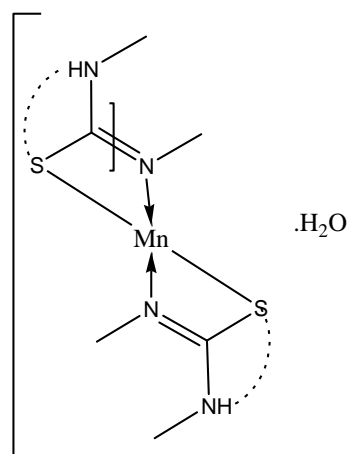
2-Thiouracil(TU)	Cr-TU	Mn-TU	Co-Ni-TU	Ni-Cu-TU	Hg-TU	Assignments
3458	3396	-	-	3317	3508	$\nu_{\text{OH}}$
3135	3223	3249	3286	3200	3072	$\nu_{\text{NH}}$
3084	-	-	-	-	-	
{ 3046 } { 2926 } (sp)						$\nu_{\text{CH}}$
2934	2928	-	2932	2920		
2607	2378	2401	2434	2305	2611	$\nu_{\text{SH}}$
1707	-	1707	-	-	1676	$\nu_{\text{C=O}}$
1626	1609	1605	1589	1635	1628	$\nu_{\text{C=N}}$
1562	1572	1518	1529	1531	1555	$\nu_{\text{C=C}}$
{ 1448 } { 1419 } (sp)	-	1485	1448	1445	1435	$\delta_{\text{NH}}$
{ 1390 }						
	1387	1416	1383	1385	-	$\nu_{\text{C-O}}$
1239	-	1240	1275	1281	-	$\nu_{\text{C-N}}$
1214	-	1209	1211	1209	1215	
{ 1173 } { 1157 } (sp)	1115	1167	1173	1173	1164	
{ 1070 }						
	1049	-	-	1080	1063	$\nu_{\text{C-C}}$
1001	-	1013	1024	1018	993	$\nu_{\text{C-S}}$
960	-	-	943	943		$\rho_{\text{CH}}, \rho_{\text{OH}}$
892	883	883	-	891	901	
835	804	-	825	829	829	
759	768	760	-	-		
734	-	-	731	729		
707	-	-	-	-	704	
647	-	636	631	646	648	
-	521	542	548	546	544	$\nu_{\text{M-O}}, \nu_{\text{M-S}}$
-	374	446	461	447	444	$\nu_{\text{M-N}}$

sp: splitted

So, Thiouracil is tautomerized to give bidentate or tridentate centers for coordination, Figure (7) and Table (5). An intramolecular hydrogen bonding was observed, where the mode of bonding of Cr(Thiouracil)(OH)<sub>2</sub>.H<sub>2</sub>O complex is given as follows:

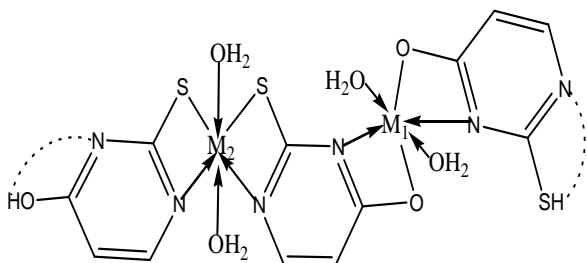


The mode of bonding of Mn(Thiouracil)<sub>2</sub>.H<sub>2</sub>O is given, where tautomerization and association through hydrogen bonding occurred.



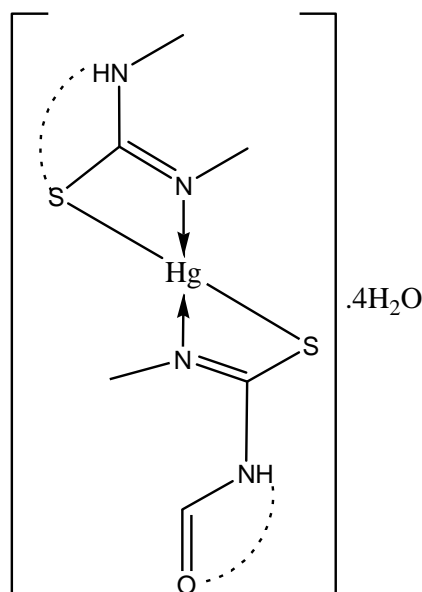
However, the disappearance of  $\nu_{\text{C=O}}$  upon complexation of (Co-Ni, Ni-Cu) (Thiouracil)<sub>3</sub>.4H<sub>2</sub>O and the presence of  $\nu_{\text{C-O}}$ ,  $\nu_{\text{C-S}}$  and  $\nu_{\text{C=N}}$  suggest the bidentate tautomerization for coordination.<sup>[54,61,67,81]</sup> The Thiouracil  $\nu_{\text{NH}}$  band at  $3135 \text{ cm}^{-1}$ .<sup>[131]</sup> is shifted to higher wave numbers 3286

and  $3200\text{ cm}^{-1}$  in the spectra of  $\text{Co-Ni}(\text{Thiouracil})_3 \cdot 4\text{H}_2\text{O}$  and  $\text{Ni-Cu}(\text{Thiouracil})_3 \cdot 4\text{H}_2\text{O}$  complexes, respectively confirming the participation of NH group in complexation. The appearance of new bands  $\nu_{(\text{M-O})}$ ,  $\nu_{(\text{M-S})}$  and  $\nu_{(\text{M-N})}$  verifying (M-O), (M-S) and (M-N) interactions.<sup>[69,132,133]</sup> An intramolecular hydrogen bonding occurred according to the following structure:



$M_1 = \text{Co}$  or  $\text{Ni}$ ,  $M_2 = \text{Ni}$  or  $\text{Cu}$ , respectively or  $M_1 = \text{Ni}$  or  $\text{Cu}$ ,  $M_2 = \text{Co}$  or  $\text{Ni}$ , respectively.

For  $\text{Hg}(\text{Thiouracil})_2 \cdot 4\text{H}_2\text{O}$  complex, Thiouracil is tautomeric to give bidentate centers for coordination as follows :



## B. Electronic absorption spectra and room temperature magnetic properties of the complexes

These are given in Figures (8-10), Table (6).

The most important bands are those in the visible region above 500 nm for  $\text{Co}(\text{Adenine})(\text{Cytosine})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cr}(\text{Barbituric acid})(\text{OH}) \cdot 4\text{H}_2\text{O}$  and  $\text{Cr}(\text{Thiouracil})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  complexes. The data for  $\text{Zn}(\text{Barbituric acid})_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cd}(\text{Barbituric acid})_2 \cdot 10\text{H}_2\text{O}$  and  $\text{Hg}(\text{Barbituric acid})_2$  complexes, Figure (9), Table (6), and the  $\mu_{\text{eff}}$  value for  $\text{Hg}(\text{Thiouracil})_2 \cdot 4\text{H}_2\text{O}$  complexes illustrates diamagnetic property and tetrahedral structures.

The  $\text{Cr}(\text{Barbituric acid})(\text{OH}) \cdot 4\text{H}_2\text{O}$  and  $\text{Fe}(\text{Thiobarbituric acid})(\text{OH}) \cdot 2\text{H}_2\text{O}$  complexes gave bands assigned to  $\pi-\pi^*$  and d-d electronic transitions, Table (6). However, these

complexes gave room temperature effective magnetic moment ( $\mu_{\text{eff}} = 4.96$  and  $5.92$  respectively) typified the existence of octahedral high spin states.<sup>[71]</sup>

However,  $\text{Cr}(\text{Thiouracil})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  complex, Table (6) gave three bands at 312 nm ( $\pi-\pi^*$ ) electronic transition, 439 nm [ $\text{CT}(t_{2g}-\pi^*)$ ] and 600 nm [ $\text{CT}(\pi-e_g)$ ]. The room temperature effective magnetic moment value  $\mu_{\text{eff}} = 4.96$  B.M (B.M: Bohr Magneton), is assigned to octahedral structure.<sup>[71]</sup>

The electronic absorption spectral band at 327 nm for  $\text{Mn}(\text{Thiouracil})_2 \cdot 2\text{H}_2\text{O}$  complex is assigned to  ${}^6A_1 \rightarrow {}^4T_{2g}$ . Its magnetic moment is 5.11 B.M, typified the existence of  $T_d$  structure.<sup>[71]</sup> The  $\mu_{\text{eff}}$  values of  $\text{Co-Ni}(\text{Thiouracil})_3 \cdot 4\text{H}_2\text{O}$  and  $\text{Ni-Cu}(\text{Thiouracil})_3 \cdot 4\text{H}_2\text{O}$  complexes were 5.92 B.M and 3.95 B.M, respectively, which supports an overall  $O_h$  geometry.

The  $\text{Fe}(\text{Adenine})_3$  complex gave four bands at 250, 279, 321 and 367 nm assigned to  $\pi-\pi^*$  transitions and  ${}^6A_1 \rightarrow {}^4T_{2g}$ . Its magnetic moment  $\mu_{\text{eff}} = 5.92$  B.M is very closely to octahedral geometry.<sup>[71]</sup>

The band of  $\text{Co}(\text{acac})_2(\text{Adenine})$  at 410 nm is due to d-d transitions. However, its  $\mu_{\text{eff}}$  value is 4.95 B.M, which supports square pyramidal geometry.<sup>[71]</sup>

The  $\text{Co}(\text{Adenine})(\text{Cytosine})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  complex gave three bands at 260, 400 and 548 nm where the first band is due to  $\pi-\pi^*$  transition while the others are for d-d transitions assigned to  ${}^6A_1 \rightarrow {}^4T_{2g}$ . Its magnetic moment is 5.31 B.M, typified the existence of tetrahedral structure.<sup>[71]</sup>

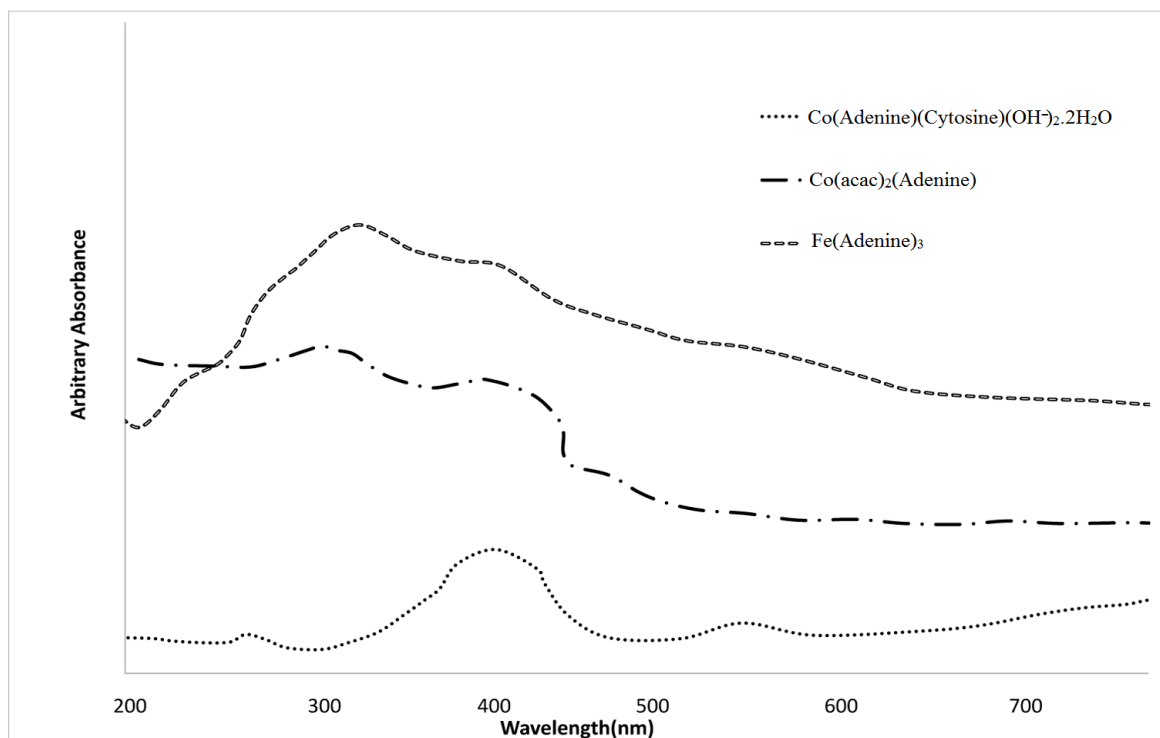


Figure (8): Nujol mull electronic absorption spectra of  $\text{Fe(Adenine)}_3$ ,  $\text{Co(acac)}_2(\text{Adenine})$  and  $\text{Co(Adenine)(Cytosine)(OH)}_2 \cdot 2\text{H}_2\text{O}$  complexes.

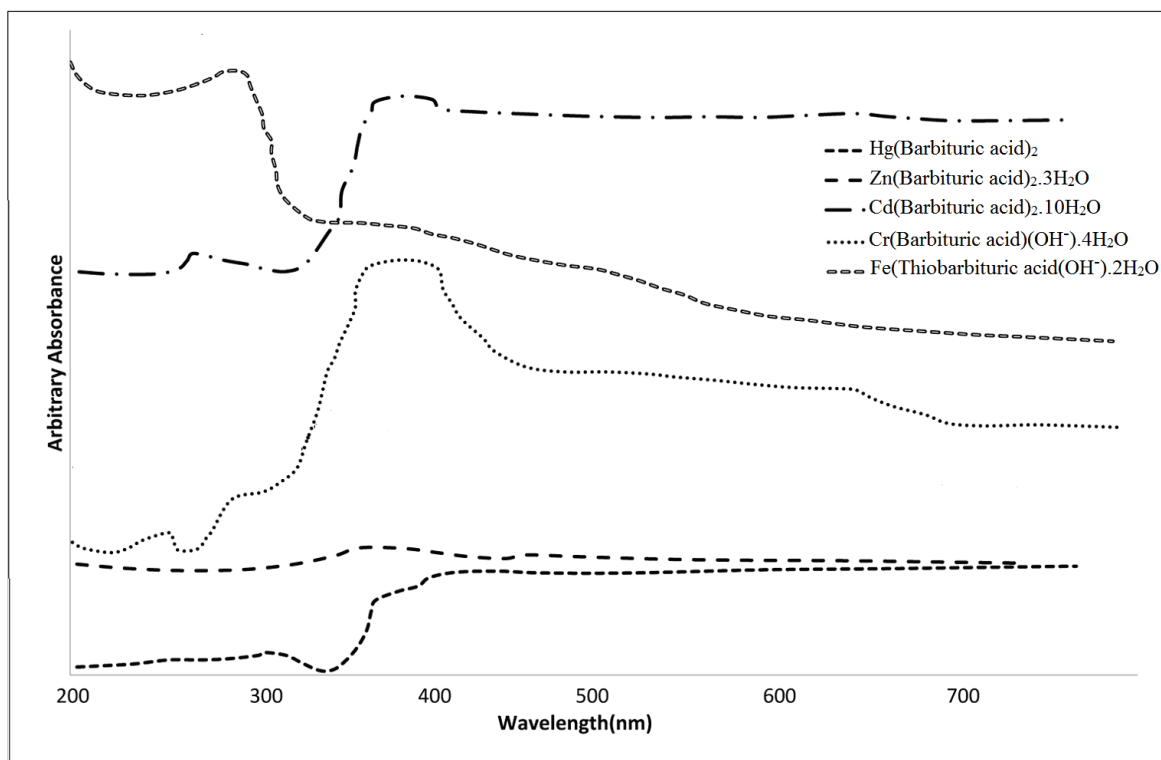


Figure (9): Nujol mull electronic absorption spectra of  $\text{Cr(Barbituric acid)(OH)} \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn(Barbituric acid)}_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cd(Barbituric acid)}_2 \cdot 10\text{H}_2\text{O}$ ,  $\text{Hg(Barbituric acid)}_2$  and  $\text{Fe(Thiobarbituric acid)(OH)} \cdot 2\text{H}_2\text{O}$  complexes.

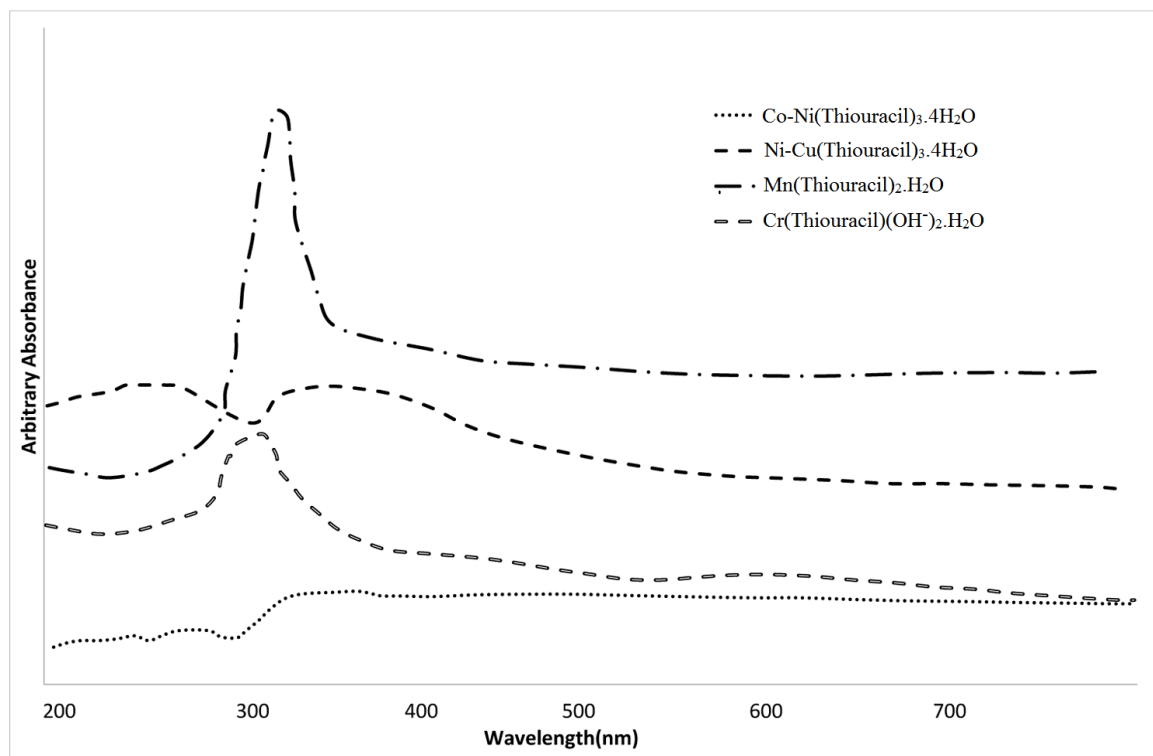


Figure (10): Nujol mull electronic absorption spectra of  $-\cdot-$  Cr(Thiouracil)(OH)<sub>2</sub>.H<sub>2</sub>O,  $- \cdot$  Mn (Thiouracil)<sub>2</sub>.H<sub>2</sub>O,  $\cdot \cdot \cdot \cdot$  Co-Ni (Thiouracil)<sub>3</sub>.4H<sub>2</sub>O and  $- -$  Ni-Cu(Thiouracil)<sub>3</sub>.4H<sub>2</sub>O complexes.

Table (6):  $\lambda_{\max}$  (nm) and room temperature effective magnetic moment values, 298 °K.

Complex	$\lambda_{\max}$ (nm)	$\mu_{\text{eff}}$ (B.M)*
Fe(Adenine) <sub>3</sub>	250, 279, 321, 367	5.92
Co(acac) <sub>2</sub> (Adenine)	300, 410	4.95
Co(Adenine)(Cytosine)(OH) <sub>2</sub> .2H <sub>2</sub> O	260, 400, 548	5.31
Cr(Barbituric acid)(OH) <sub>2</sub> .4H <sub>2</sub> O	238, 270, 325, 500, 621	4.96
Zn(Barbituric acid) <sub>2</sub> .3H <sub>2</sub> O	325	dia
Cd(Barbituric acid) <sub>2</sub> .10H <sub>2</sub> O	254, 325	dia
Hg(Barbituric acid) <sub>2</sub>	279, 318, 350	dia
Fe(Thiobarbituric acid)(OH) <sub>2</sub> .2H <sub>2</sub> O	291, 367, 500	5.92
Cr(Thiouracil)(OH) <sub>2</sub> .H <sub>2</sub> O	312, 439, 600	4.96
Mn(Thiouracil) <sub>2</sub> .H <sub>2</sub> O	327	5.11
Co-Ni(Thiouracil) <sub>3</sub> .4H <sub>2</sub> O	269, 327	5.92
Ni-Cu(Thiouracil) <sub>3</sub> .4H <sub>2</sub> O	265, 357	3.95

\* the  $\mu_{\text{eff}}$  value for Hg(Thiouracil)<sub>2</sub>.4H<sub>2</sub>O complex is dia.

### C. Mössbauer spectra

The nuclides which emit  $\gamma$ -rays are suitable to act as Mössbauer nuclides. Such nuclides should possess the following properties:

1. The energy of  $\gamma$ -radiations emitted should be in the range 10-200 keV.
2. The  $t_{1/2}$  of parent nuclide that generates the 1/2 emitter nuclide should be large (of the order of year).
3. The  $\gamma$ -emitter should have  $t_{1/2}$  ( $10^{-6}$ - $10^{-10}$  s).
4. The conversion factor should be low.
5. The absorber nuclide should be present in high isotopic abundance.

Standard reference absorber is essential as reference absorber for comparison of isomer shift (IS). The reference absorber should be stable (both physically and chemically) and must be resistant to radiations from the source.

The standard reference absorbers used are:

1. For Fe<sup>57</sup> source – A single crystal of sodium nitroprusside, Na<sub>2</sub>Fe(CN)<sub>5</sub>NO.2H<sub>2</sub>O.
2. For Sn<sup>119</sup> source – A crystal of barium stannate, BaSnO<sub>3</sub>.

The symmetry and the geometry of the molecules and their structures can be obtained from quadrupole splitting. Also, the isomer shift and curie point are of

great importance. Below curie point (i.e., the temperature below which a paramagnetic substance gets converted into ferromagnetic) the single Mössbauer line splits into six lines because of a sharp decrease in the electron density at the nucleus. Thus by mapping the Mössbauer spectrum over wide range of temperatures curie temperature can be found. The curie temperature of iron is 773°C that has been obtained by using this technique.

The correlation between the isomer shift( $\delta$ ) and the quadrupole splitting( $\Delta E_Q$ ) is of basic importance for electronic structure of complexes. The Mössbauer parameters, or possibly their temperature dependencies are used as the starting point in the quantum-chemical approach to the structure of complexes.

The Mössbauer spectrum may give information on:

1. The oxidation state of the Mössbauer atom.
2. The high-spin or low-spin nature of the electronic structure of the Mössbauer atom.
3. The covalency of the bonding involving the Mössbauer atom.
4. The symmetry of the immediate environment of the Mössbauer atom.
5. The rigidity of the crystal lattice containing the Mössbauer atom.
6. The magnetic interaction between the Mössbauer nuclei.
7. Compounds that contain Mössbauer atoms in different oxidation states within one molecule.

The qualitative evaluation of the Mössbauer spectra may be facilitated by the partial isomer shift (PIS).

$\delta$  is considered as an additive molecular parameter obtained by the addition of constant PIS values related to the ligands bound to the the Mössbauer atom, or related

to functional groups  $\delta = \sum_{i=1}^{i=N} (PIS)_i$ , where N is the coordination number of the Mössbauer atom.  $\delta$  is the

**The Mössbauer isomer shifts for different classes for iron compounds have been given as follows.**<sup>[134]</sup>

Oxidation state	Spin state	Isomer shift( $\delta$ , mm s <sup>-1</sup> )
Fe <sup>II</sup>	h.s	~ 1.3
Fe <sup>III</sup>	h.s	~ 0.5-0.7
Fe <sup>II</sup>	l.s	~ 0.1
Fe <sup>III</sup>	l.s	~ 0

From a chemical point of view, the s-electrons should give the constant contribution to the isomer shift, d- and p-electrons are to the quadrupole splitting. The isomer shift of the high spin complex is more positive than that of the low spin counter-part. This can be attributed to different symmetries of the d-electrons causing a change in the electric field gradient, i.e. decreasing s-electron density at the iron nucleus.

Fe<sup>III</sup> admixtures can be observed in Mössbauer experiments in concentrations at least higher than 5%. In

amount by which the spectrum shifted relative to a fixed emitted by his own source when at rest, but is better chosen as the center of absorption of a standard substance such as iron or sodium nitroprusside.

An increased electron density at the nucleus affects a negative isomer shift. The addition of an electron to Fe<sup>II</sup> increases the isomer shift to a positive side. PQS(partial quadrupole splitting) also contribute to the semi quantitative evaluation of Mössbauer spectra. Every ligand has a definite PQS contribution to the experimentally determined quadrupole splitting of the molecule.

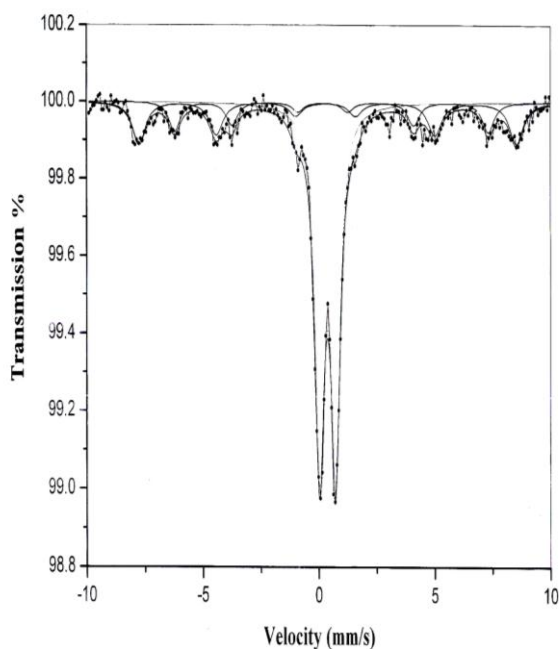
The PQS values of the individual ligands do not depend on the other ligands in the complex. The constancy of the PQS values assumes that the metal-ligand bond distance in a given system does not vary, or varies only slightly, or that the quadrupole splitting is not sensitive to any such variation. The PQS values of the ligands are also independent on the coordination number in the complex. The dependence of quadrupole splitting on chemical structure can be determined with the aid of the point charge model.

For high-spin iron(II) complexes, the electron transfer results in an increase in the symmetry of the d-shell, because the d<sup>6</sup> electron structure of the central iron(II) atom (t<sub>2g</sub>)<sup>4</sup>(e<sub>g</sub>)<sup>2</sup> progressively approaches the spherically symmetric d<sup>3</sup> electron structure characteristic of the high-spin iron(III) atom (t<sub>2g</sub>)<sup>3</sup>(e<sub>g</sub>)<sup>2</sup>. Promotion of d-electron transfer by an increase in the covalency increases the symmetry of the charge distribution around the iron nucleus, decreases the electric field gradient at the position of the nucleus a manifested as a decrease in quadrupole splitting( $\Delta E_Q$ ) substituents caused relatively small changes in Mössbauer parameters for both low and high-spin iron(II) and iron(III) complexes.

addition, the range of isomer shift and quadrupole splitting in Fe<sup>II</sup> low spin is overlapping with Fe<sup>III</sup> high spin. Nevertheless, Fe<sup>III</sup> high spin can be determined, because it looks like a time dependent h.s/l.s ratio.

Moreover, the percentage of contribution of Fe<sup>II</sup> and Fe<sup>III</sup> in the same complex could be calculated from the Mössbauer spectrum. Such contribution of Fe<sup>II</sup> and Fe<sup>III</sup> is expressed as (Fe<sup>II</sup> / Fe<sup>III</sup>) ratio.

The Mössbauer spectrum of Fe(Adenine)<sub>3</sub> complex, Figure (11) illustrates a high-spin Fe<sup>III</sup> complex.<sup>[135]</sup> The data are collected in Table (7).



**Figure (11):** The Mössbauer spectrum of Fe(Adenine)<sub>3</sub> complex.

**Table (7):** The Mössbauer parameters of Fe(Adenine)<sub>3</sub> complex.

Magnetic	Mössbauer parameters			
	H	IS	QS	LW
Phase I	504	0.35	0.87	0.69
Phase II	419	0.37	0.37	0.59
Non-magnetic	-	0.37	0.69	0.47

The presence of a high-spin octahedral configuration for Fe<sup>III</sup> was also previously inferred from magnetic measurements and electronic spectroscopy. The data typified that the iron sample is mainly of high-spin octahedral Fe<sup>III</sup> with minimum contribution of low-spin Fe<sup>II</sup>.

## REFERENCES

1. M. Schena, D. Shalon, R. W. Davis and P. O. Brown, *Science*, 1995; 270: 467.
2. S. Yamakawa, K. Ando, A. Chisaka, K. Yashida, A. Shinmyo and T. Kohchi, *J. Biosci. Bioeng.*, 2004; 98: 140.
3. N. Mera, H. Aoyagi, S. Nakasona, K. Iwasaki, H. Saiki and H. Tanaka, *J. Biosci. Bioeng.*, 2004; 97: 169.
4. B. Goswami, B. L. Gaffney and R. A. Jones, *J. Am. Chem. Soc.*, 1993; 115: 3832.
5. C. Wang, H. Gao, B.L. Gaffney and R. A. Jones, *J. Am. Chem. Soc.*, 1991; 113: 5486.
6. B. L. Gaffney, C. Wang and R. A. Jones, *J. Am. Chem. Soc.*, 1992; 114: 4047.
7. Y. S. Rhee, C. Wang, B. L. Gaffney and R. A. Jones, *J. Am. Chem. Soc.*, 1993; 115: 12607.
8. X. Zhang, B. L. Gaffney and R. A. Jones, *J. Am. Chem. Soc.*, 1998; 120: 615.
9. W. L. F. Armarego, In "The Chemistry of Heterocyclic Compounds, Fused Pyrimidines", Part I: "Quinazolines", D.J. Brown, Ed.; Vol. 24/1, Interscience Publishers: New York- London - Sydney, 1967.
10. M. Legerverend, *Tetrahedron*, 2008; 64: 8585.
11. W. B. Parker, *Chem. Rev.*, 2009; 109(7): 2880.
12. S. Ostrowski, *Polish J. Chem.*, 75, 1661 (2001); *Jordan J. Chem.*, 2009; 4(1).
13. A. C. Tella and J. A. Obaleye, *Int. J. Chem. Sci.*, 2010; 8(3): 1675.
14. J. Cieplik, M. Stolarczyk, J. Pluta, O. Gubrynowicz, I. Bryndal, T. Lis and M. Mikulewicz, *Acta Poloniae Pharmaceutica, Drug Research*, 2011; 68(1): 57.
15. L. Zhuo, K. Kou, Y. Wang and H. Chen, *Designed monomers and polymers*, 2015; 18(1): 42.
16. Y. Liang and S. F. Wnuk, *Molecules*, 2015; 20: 4874.
17. M. S. Masoud, A. M. Heiba and F. M. Ashmawy, *Trans. Met. Chem.*, 1983; 8: 124.
18. M. S. Masoud, T. M. Salem and Z. Zaki, XXIII International Conference on Coordination Chemistry, p. 372, Colorado, USA, 29 July - 3 August, 1984.
19. A. A. Hasanein, M. S. Masoud and A. M. Heiba, *Current Science*, 54(2), 1165 (1985); *J. Chem. Soc. Pak.*, 1987; 9(2): 199.
20. M. S. Masoud and S. S. Haggag, 30<sup>th</sup> IUPAC Congress, Manchester 9-13 September (1985); 8<sup>th</sup> International symposium on solute-solute-solvent interaction, p. 210, p. 303, University of Regensburg, 9-10 August (1987); 3<sup>rd</sup> National Symposium on Crystallography, Cairo, Academy of Scientific Research and Technology, National Committee of Technology, 26-27 January (1988); 5<sup>th</sup> World Conference on Thermal Analysis, Corfu, Greece, May 16-17 (1988); 9<sup>th</sup> Arabian Chemistry Conference, Kuwait, 15-19 December (1990); *Thermochimica Acta*, 1992; 196: 221.
21. M. S. Masoud, N. A. Ibrahim, S. A. Abou Ali, G. Y. Ali and I. M. Abed, *Ind. J. Chem.*, 1986; 25A: 389.
22. M. S. Masoud, S. A. Abou Ali, G. Y. Ali and I. M. Abed, *Thermochim. Acta*, 1987; 122: 209.
23. M. S. Masoud, M. E. Kassem, Y. Abd El-Aziz and S. Massoud, X<sup>th</sup> Conference on Solid State Science and Applications, p. 46, Alex., 1987; 6-9.
24. M. A. El-Dessouky, M. S. Masoud, F. A. Ali and S. A. Abou El-Enein, *Affinidad*, 416, August 321 (1988); 2<sup>nd</sup> Chemistry Conference, Fac. of Sci., Alex. Univ. 28-30 June, 178, 196 (1988); *Trans. Met. Chem.*, 15, 443 XXVII Colloquium spectroscopicum international, Bergen, Norway, 1991; 9-14.
25. M. S. Masoud, M. Khater and N. El-Guindi, *J. Iraqi Chem. Soc.*, 1988; 13: 177.



26. M. S. Masoud, E. M. Soliman, A. E. El-Kholy and E. A. Khalil, *Thermochem. Acta*, 1988; 136: 1.
27. M. S. Masoud and Z. M. Zaki, *Trans. Met. Chem.*, 13, 321 (1988); *Bull. Fac., Sci., Mansoura Univ.*, 1990; 17(1): 71.
28. M. S. Masoud, E. M. Soliman and A. M. Heiba, *Trans. Met. Chem.*, 1989; 14: 175.
29. M. S. Masoud and S. Abou El-Enein, *Thermochim. Acta*, 1989; 140: 365.
30. M. S. Masoud, E. A. Khalil and A. R. Youssef, *Synth. React. Inorg. Met.-Org. Chem.*, 1990; 20(6): 793.
31. M. S. Masoud, S. S. Haggag, E. M. Soliman and M. El-Shabasy, *J. Mater. Sci.*, 1991; 26: 1109.
32. M. S. Masoud, S. A. Abou El-Enein and E. El-Shereafy, *J. Therm. Anal.*, 1991; 37: 365.
33. M. S. Masoud and E. A. Khalil, *Polish J. Chem.*, 1991; 65: 933.
34. M. S. Masoud, M. E. Kassem, Y. Abd El-Aziz and S. M. Khalil, *Bull. Fac. Sci., Mansoura University*, 1991; 18(1): 105.
35. M. S. Masoud, E. A. Khalil and S. S. Haggag, *Pak. J. Sci. Ind. Res.*, 35,480 (1992); *Nucleosides, Nucleotides and Nucleic Acids*, 2006; 25(1): 73.
36. M. S. Masoud, S. A. Abou El-Enein and O. F. Hafez, *J. Therm. Anal.*, 1992; 38: 1365.
37. M. S. Masoud, M. M. El-Essawi and A. M. Amr, *XXI Congress on Molecular Spectroscopy, EUCMOS XXI, Technical University of Vienna, Austria, 23-28 August (1992); Anal. Proc.*, 1992; 29: 370.
38. E. A. Khalil, M. S. Masoud and A. El-Marghany, *Pak. J. Sci. Ind. Res.*, 1993; 36: 68.
39. M. S. Masoud, E. El-Shereafy, E. A. Khalil and O. H. Abd El-Hamid, *Egypt J. Anal. Chem.*, 1993; 2(1): 95.
40. M. S. Masoud, Z. M. Zaki, F. M. Ismail and A. K. Mohamed, *Z. für Phys. Chem., Bd.*, 1994; 185: 223.
41. M. S. Masoud, O. H. El-Hamid and Z. M. Zaki, *Trans. Met. Chem.*, 1994; 19: 21.
42. M. S. Masoud, S. S. Haggag, Z. M. Zaki and M. El-Shabasy, *Spectrosc. Lett.*, 1994; 27(6): 775.
43. S. A. Abou El-Enein, M. S. Masoud, A. El-Khatib and S. Abd El-Aziz, *Alexandria Engineering J.*, 1994; 33(3): D103.
44. M. S. Masoud, O. F. Hafez and N. A. Obeid, *Pak. J. Sci. Ind. Res.*, 1994; 37(10): 421.
45. M. S. Masoud, H. M. El-Nahas and S. S. Haggag, *Pak. J. Sci. Ind. Res.*, 1995; 38(3-4): 108.
46. M. S. Masoud, S. S. Haggag and O. H. Abd El-Hamid, *Revue Roumaine De Chimie*, 1996; 41(1-2): 21-27.
47. M. S. Masoud, A. K. Ghonaim and A. A. Mahmoud, *1<sup>st</sup> International Conference on Basic Sciences and Advanced Technology, Faculty of Science, Assiut University, "A 5-1,AP8", "P. 24, 46", 10-11 Nov.(1996); 2<sup>nd</sup> Mediterranean Basic Conference on Analytical Chemistry 23-28 Nov., Robot (Morocco) (1997); 36<sup>th</sup> Annual Eastern Analytical Symposium & Exposition, Somerset, New Jersey, USA, 1997; 525: 27,16- 21.*
48. M. S. Masoud, M. M. Ghonaim and O. A. El-Wahab, *Egypt J. Appl. Sci.*, 1996; 11(8): 302.
49. M. S. Masoud, R. H. A. El-Sayed, A. H. Mostafa and N. H. Abd El Moneium, *The 5<sup>th</sup> International Conference of Chemistry and its Role in Development, Department of Chemistry, Faculty of Science, El Mansura University*, 1999; 19-22.
50. M. S. Masoud, S. A. Abou El- Enein and H. M. Kamel, *3<sup>rd</sup> International Scientific Conference (Science, Development and Environment), Faculty of Science, Al-Azhar University, p.72, 22- 25 March (1999); Ind. J. Chem.*, 2002; 41: 297.
51. M. S. Masoud, A. El Marghany, S. K. El Sadany and N. G. Ali, *The 5<sup>th</sup> International Conference of Chemistry and its Role in Development, Department of Chemistry, Faculty of Science, El Mansura University*, 1999; 19-22.
52. M. S. Masoud, A. A. Hasanein, A. K.Ghonaim, E. A. Khalil and A. A. Mahmoud, *Z. für Phy. Chem., Bd.*, 1999; 209: 223.
53. M. S. Masoud, A. M. Hindawy and R.H. Ahmed, *Pak. J. Sci. Ind. Res.*, 1999; 42(1): 11.
54. M. S. Masoud, E. A. Khalil, A. A. Ibrahim and A. El-Marghany, *Z. für Phys. Chem., Bd.*, 211S, 13 (1999); *Spectrochim. Acta*, 2007; 67A: 662.
55. M. S. Masoud, S. A. Abou El-Enein and N .A. Obeid, *Z. für Phys. Chem.*, 2001; 215(7): 867.
56. M. S. Masoud, A. K. Ghonaim, R. H. Ahmed, A. A. Mahmoud and A. E. Ali, *Z.für Phys. Chem.*, 2001; 215(4): 531.
57. M. S. Masoud, A. K. Ghonaim, R. H. Ahmed, S. A. Abou El-Enein and A. A. Mohmoud, *J. Coord. Chem.*, 2002; 55(1): 79.
58. M. S. Masoud, A. A.Soyed, A. E. Ali and O. K. Sharsherah, *J.Coord.Chem.*, 2003; 56(8): 725.
59. M. S. Masoud, A. A. Soayed and A. E. Ali, *Spectrochim. Acta*, 2004; 60A: 1907.
60. M. S. Masoud, S. A. Abou El-Enein, M. Ayad, and A. S. Goher, *Spectrochim. Acta*, 2004; 60A: 77.
61. M. S. Masoud, A. M. Hindawey, E. A. Khalil and A. M. Ramadan, *Bull. Fac. Sci., Assuit University*, 33(2B), 1-8 (2004); *Can. J. Anal. Sci. Spectrosc.*, 2005; 50(6): 297.
62. M. E. Mahmoud, M. S. Masoud and N. N. Maximous, *Mikrochim. Acta*, 2004; 147(1-2): 111.
63. M. S. Masoud, A. E. Ali, M. A. Shaker and M. Abdul Ghani, *Spectrochim. Acta*, 2004; 3155.
64. M.S. Masoud, E.A. Khalil, A.M. Hafez and A.F. El-Husseiny, *Spectrochim. Acta*, 2005; 989.
65. M. S. Masoud, E. A. Khalil, O. H. Abd El-Hamid and A. A. Soayed, *The Egyptian Science Magazine*, 2005; 2(2): 33.
66. M. S. Masoud, M. F. Amira, S. A. El-Moneim, G. M. Moghazy, A. A. Abou-Hagar and Gh. M. El-Ashry, *The Egyptian Science Magazine*, 2005; 2(4): 88.
67. M. S. Masoud, T. S. Kasem, M. A. Shaker and A. A. Ali, *J. Therm. Anal. Calorim.*, 2006; 84(3): 549.

68. M. S. Masoud, A. A. Soayed and A. S. El-Kholany, Proceeding of the 3<sup>rd</sup> international Chemical & Environmental Engineering Conference, 16-18 May (2006); *J. of Radioanalytical and Nuclear Chemistry*, 2011; 1-8.
69. M. S. Masoud, E. A. Khalil, A. M. Ramadan, Y. M. Gohar and A. Swayllam, *Spectrochim. Acta*, 2007; 67A: 669.
70. M. S. Masoud, M. Sh. Ramadan and M. H. Al-Saify, Chem-04, Faculty of Science, Cairo University, p.50, 5-8 March (2006); International conference on Science and Technology, Prague, Czech Republic, 2007; 5-6.
71. M. S. Masoud, M. F. Amira, A. M. Ramadan and Gh. M. El-Ashry, *Spectrochim. Acta*, 2008; 69A: 230.
72. H. H. Hammud, K. H. Bouhadir, M. S. Masoud, A. M. Ghannoum and S. A. Assi, *Journal of Solution Chemistry*, 2008; 37(7): 895.
73. M. S. Masoud, S. A. Abou El-Enein and A. M. Ramadan and A. S. Goher, *J. Anal. Appl. pyrolysis*, 2008; 81(1): 45.
74. M. S. Masoud, M. Sh. Ramadan, A. El-Samahy, I. Mahmoud and M. H. Al-Saify, Chem-05, Faculty of Science, Cairo University, 2008; 48: 3-5.
75. M. T. Zaworotko, H. H. Hammud, G. Mc- Manus, A. M. Ghannoum, A. Kabbani and M. S. Masoud, *J. Chem. Crystall.*, 2009; 39: 853.
76. M. S. Masoud, A. El-Merghany and M. Y. Abd El-Kaway, International Conference on Chemistry and its Role in Development, Department of Chemistry, Faculty of Science, University of Mansoura, (16-19) April (2007); *Synthesis and Reactivity in Inorganic and Metal-Organic and Nano-Metal Chemistry*, 2009; 39(9): 537.
77. M. S. Masoud, A. El-Merghany, A. M. Ramadan and M. Y. Abd El-Kaway, *J. Therm. Anal. Calorim.*, 2010; 101(3): 839.
78. M. S. Masoud, M. K. Awad, M. A. Shaker and M. M. T. El-Tahawy, *Corrosion Science*, 2010; 52(7): 2387.
79. M. S. Masoud, M. A. Shaker, A. E. Ali and G. S. Elsalala, Seventh International Scientific Conference, Environment, Development and Nanotechnology, Faculty of Science, Al-Azhar University, Cairo, Egypt, 170, 22-24 March (2010); *Spectrochim. Acta*, 2012; 90A: 93.
80. M. S. Masoud, A. M. Hindawy, A. A. Soayed and M. Y. Abd El-Kaway, *J. Fluid Phase Equilibria*, 312,37 (2011); Research Conference for Egyptian Faculties of Science, Alexandria University, Session 6, OR-11 (18-19) May (2011); *Spectrochim. Acta*, 2012; 92A: 256.
81. M. S. Masoud, A. A. Soayed and A. F. El-Husseiny, *Spectrochim. Acta*, 2012; 99A: 365.
82. N. Z. Shaban, M. S. Masoud, M. A. Mawlawi, D. Awad and O. M. Sadek, *J. Physiol. Biochem.*, 2012; 68(4): 475.
83. M. S. Masoud and M. Y. Abd El-Kaway, *Spectrochim. Acta*, 2012; 102A: 175.
84. M. S. Masoud, A. El-Marghany, A. Orabi, A. E. Ali and R. Sayed, *Spectrochim. Acta*, 2013; 107A: 179.
85. M. K. Awad, M. S. Masoud, M. A. Shaker, A. E. Ali and M. M. T. El-Tahawy, *Research on Chemical Intermediates*, 2013; 39(6): 2741.
86. M. S. Masoud, A. E. Ali and M. Y. Abd El-Kaway, *J. Therm. Anal. Calorim.*, 2014; 116(1): 183.
87. M. S. Masoud, M. F. El-Shahat and A. S. Elkholy, *Spectrochim. Acta*, 2014; 127A: 216.
88. D. J. Brown, In "The Chemistry of Heterocyclic Compounds, The Pyrimidines", Taylor, E.C., Ed.; Vol. 23, J. Wiley & Sons: New York – Chichester – Brisbane – Toronto – Singapore, 1994.
89. A. Albert, In "Selective Toxicity: The Physico-Chemical Basis of Therapy", 7<sup>th</sup> ed., N.B. Chapman ; J.E. Hall Eds.; London, 1985; 347.
90. A. Polak and H. J. Scholer, *Chemotherapy*, 1975; 21: 113.
91. R. A. Cox, *Quart. Rev.*, 1968; 22: 934.
92. O. N. Al Safarjalani, X. J. Zhou, R. H. Ras, J. Shi, R. F. Schinazi, F. N. Naguib and M. H. El Kouni, *Cancer Chemother. Pharmacol.*, 2005; 55: 541.
93. G. B. Elion, *Fed. Proc.*, 1967; 26: 898.
94. J. H. Burchenal, *Blood*, 1953; 8: 965.
95. B. D. Clarkson, *Cancer*, 1970 5: 227.
96. S. A. Giller, R. A. Zhuk and M. I. U. Lidak, *Dokl. Akad. Nauk. SSR*, 1967; 176: 332.
97. J. L. Ambrus, I. Stadler, M. Kulaylat, A. Koreshi and S. Akhtar, *J. Med. Chem.*, 1996; 27: 21.
98. M. Weller, B. Muller, R. Koch, M. Bamberg and P. Krauseneck, *J. Clin. Oncol.*, 2003; 21: 3276.
99. T. M. Horton, *Clin. Cancer Res.*, 2005; 11: 1884.
100. B. J. Kennedy, J. L. Torkelson and E. Torlakovic, *Cancer*, 1999; 85: 2265.
101. J. R. Bertino, *Biochem. Pharmacol.*, 1979; 28: 1983.
102. L. W. Hertel, G. B. Border, J. S. Kroin, S. M. Rinzel, G. A. Poore, G. C. Todd and G. B. Grindey, *Cancer Res.*, 1990; 50: 4417.
103. A. Agrawal, K. Srivastava and S. K. Puri, *Bio. Org. Med. Chem. Lett.*, 2005; 15: 5218.
104. T. C. Daniels and E. C. Jorgensen, "Central nervous system depressants in Wilson and Gisvoids Textbook of Organic medicinal and Pharmaceutical Chemistry", ed. R. F. Doerge, J. B. Lippen-Cott, Philadelphia, 1982; 33.
105. D. S. Threlkeld, *Facts and Comparisons*, 1998; 269.
106. J. Vida and J. Yevich, "Sedative hypnotics, In Burger's Medicinal Chemistry and Drug Discover" , 6<sup>th</sup>ed. D. J. Abraham, John Wiley, New Jersey, 2003; (6): 203.
107. C. J. Shishoo, U. S. Pathak, K. S. Jain, I. T. Devani and M. T. Chhabria, *Chem. Inform.*, 1994; 25(38): 436.
108. A. Vogel, "Textbook of Quantitative Chemical Analysis", 4<sup>th</sup> Indian Reprint, 2004.
109. I. Somasundaram and M. Palaniandavar, *Indian J. Chem.*, 1993; 32A: 495.
110. R. Singh, S. Tyagi, S. Singh, S. M. Singh and U. P. Singh, *Synth. React. Inorg. Met. Org. Chem.*, 2002; 32(5): 853.

- 111.S. Shirotake, Chem. Pharm. Bull., 1980; 28: 1673.
- 112.R. Savoic, J. Jutier, L. Prizant and A. Beauchamp, Spectrochim. Acta, 1982; 38: 561.
- 113.J. Brigando, D. Colitis and M. Morel, Bull. Soc. Chem. Fr., 1969; 3445: 3449.
- 114.T. Fujita and T. Sakaguchi, Chem. Pharm. Bull., 1977; 25: 1055.
- 115.A. Specca, C. Mikulshi, F. Iaconianni, L. Pytlewski and N. Karayannies, J. Inorg. Nucl. Chem., 1981; 43: 2771.
- 116.A. Specca, L. Pytlewski, C. Mikulshi and N. Karayannies, Inorg. Chim. Acta, 1982; 66: 153.
- 117.A. Lautie and A. Novak, J. Chem. Biol., 1968; 65: 1359.
- 118.L. Bancu, P. Bourosh, I. Jitaru, Y. Simonov and J. Lipkowski, Revue Roumaine de Chimie, 2006; 51(5): 397.
- 119.M. S. Masoud, G. B. Mohamed, Y. H. Abdul-Razek, A. E. Ali and F. N. Khairy, J. Kor. Chem. Soc., 46(2) 99(2002); Spectrosc. Lett., 2002; 35: 377.
- 120.W. Kemp, "Organic Spectroscopy", The Macmillan Press Ltd., London, 1982.
- 121.S. Pati, "The Chemistry of the Hydrazo, Azo and Azoxy Groups", Part 1, Wiley, New York, 1975.
- 122.K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", P. 156, John Wiley, New York, 1963.
- 123.M. S. Masoud, S. A. Abou El-Enein, I. M. Abed and A. E. Ali, J. Coord. Chem, 2002; 55(2): 153.
- 124.I. L. Finar "Organic Chemistry, Vol. 2: Stereochemistry and the Chemistry of Natural Products", 5<sup>th</sup> Ed., Pearson Education (Singapore) Pte. Ltd., Indian Branch, 482 F. I. E. Patparganj, Delhi 110 092, India, 2002.
- 125.S. L. Stefan, B. A. El-Shetary, W.G. Hanna and S. B. El-Maraphy, Microchem. J., 1987; 35: 51.
- 126.J. Morvay, G. Kozepesy and V. Nikolasev, Acta, Pharm. Hung, 1969; 39: 54.
- 127.K. C. Satpathy, A. K. Panda, R. Mishra, A. P. Chapdar and S. K. Pradhan, J. Indian Chem. Soc., 1994; 71: 593.
- 128.Z. M. Zaki and G. G. Mohamed, Spectrochim. Acta, 2000; 56A: 1245.
- 129.X. Huang and Z. Liu, J. Org. Chem., 2002; 67: 6731.
- 130.U. P. Singh, R. Ghose and A. K. Ghose. Trans. Met. Chem., 1988; 13: 50.
- 131.A. Odani, H. Kozlowski, J. Swiatek-Kozlowska, B. P. Operschall and H. Sigel, J. Inorg. Biochem., 2007; 101: 727.
- 132.M. M. S. Prakash and M. Adharvanachary, IJPSR, 2011; 22(11): 2947.
- 133.A. W. Addison, P. J. Burke, K. Henrich, T. N. Rao and E. Sinn, Inorg. Chem., 1983; 22(24): 3645.
- 134.N. N. Greenwood and T. C. Gibb, Mössbauer Spectroscopy, (Chapman and Hall, London), 1971.
- 135.E. J. Baran, R. C. Mercader, F. Hueso-Ureña, M. N. Moreno-Carretero, M. Quiros-Olozabal and J. M. Salas-Peregrin, Polyhedron, 1996; 15(10): 1717.