

SPECTRAL PROPERTIES AND CHARACTERIZATION OF SOME PYRIMIDINE AND PURINE COMPLEXES

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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)₃ complex proved a high spin Fe^{III} 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).

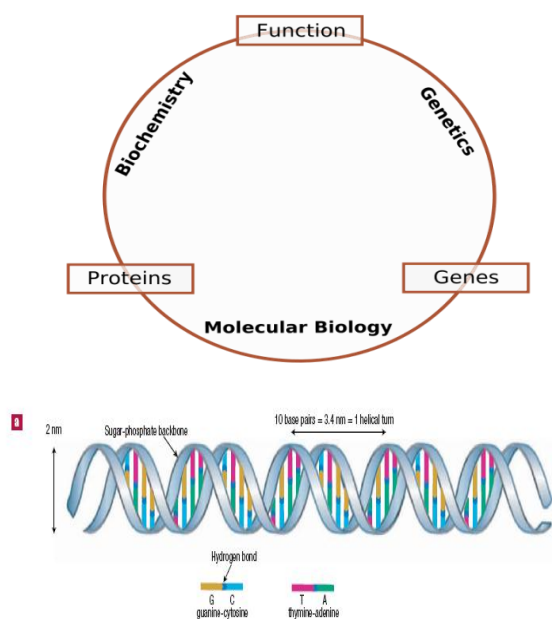


Figure (1): Schematic relationship between biochemistry, genetics and molecular biology with a double-helical DNA representation.

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.^[1,3]

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

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

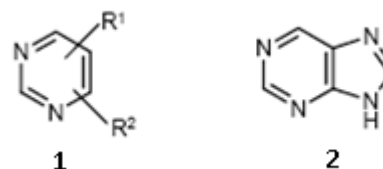


Figure (2): Pyrimidine and purine nuclei.

The pyrimidine nucleus is embedded in a large number of alkaloids, drugs, antibiotics, agrochemicals, and antimicrobial agents^[88] 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^[89] 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).

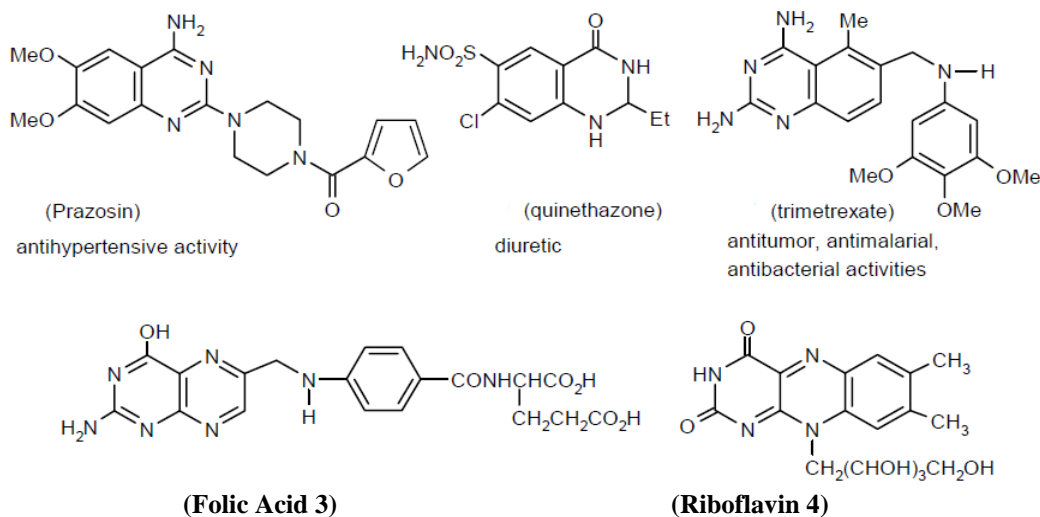
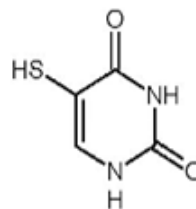
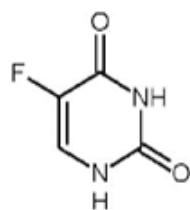
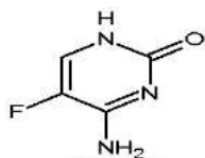


Figure (3): Some biologically active pyrimidine derivatives.

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.^[90]



5-Fluorouracil(5-FU) 5-Thiouracil

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

2-Anti-inflammatory activity

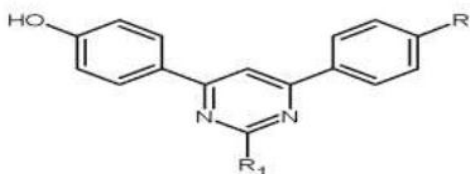
Anti-inflammatory refers to the property of a substance or treatment that reduces inflammation. Due to remarkable pharmacological efficiency of pyrimidine derivatives, anextensive research has been focused on anti-inflammatory activity of pyrimidine nucleus.

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)^[91] a pyrimidine derivative. 5-Thiouracil also exhibits some useful antineoplastic activities.^[92]

4-Antitubercular activity

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

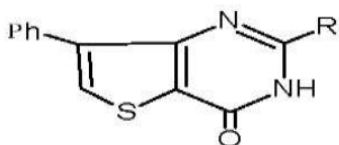


5-Central Nervous System(CNS) Activity (Sedative /hypnotic)

A wide variety of barbiturates are used as sedative, hypnotics and classified as drugs having short, intermediate and long duration of action.^[104] Allobarbitol, aprobarbitol, phenobarbitol, secobarbitol, and pentobarbitol are frequently used hypnotic barbiturates.^[105] Hexobarbitol, cyclobarbitol and propallylonal are used sedatives hypnotics.^[106]

6-Antihyperlipidemic activity

2-substituted-6-phenyl and 7-phenyl thieno[3,2-*d*]pyrimidin-4-ones are synthesized.^[107] 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.^[108] 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 α 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)₄].

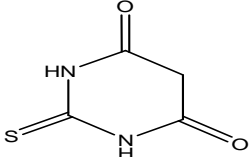
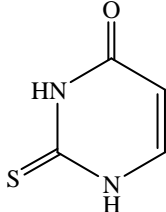
iii. Mössbauer spectra

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 | |

Cont.

| | | | |
|---------------------|-------|-----|---|
| 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_2 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 $3000\text{--}3600\text{ cm}^{-1}$ may be attributed to NH and OH stretching modes.^[109,110] 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.^[59,111,117] The 1242 cm^{-1} of adenine due to $\nu_{(\text{N7-C8})}$ is shifted to lower frequency upon complexation indicating the binding of adenine is through ring nitrogen.^[109] The $\nu_{(\text{C4=N3})}$ band of cytosine at 1550 cm^{-1} is shifted to lower frequencies upon complexation which gives indication for cytosine N(3) contribution in complex formation.

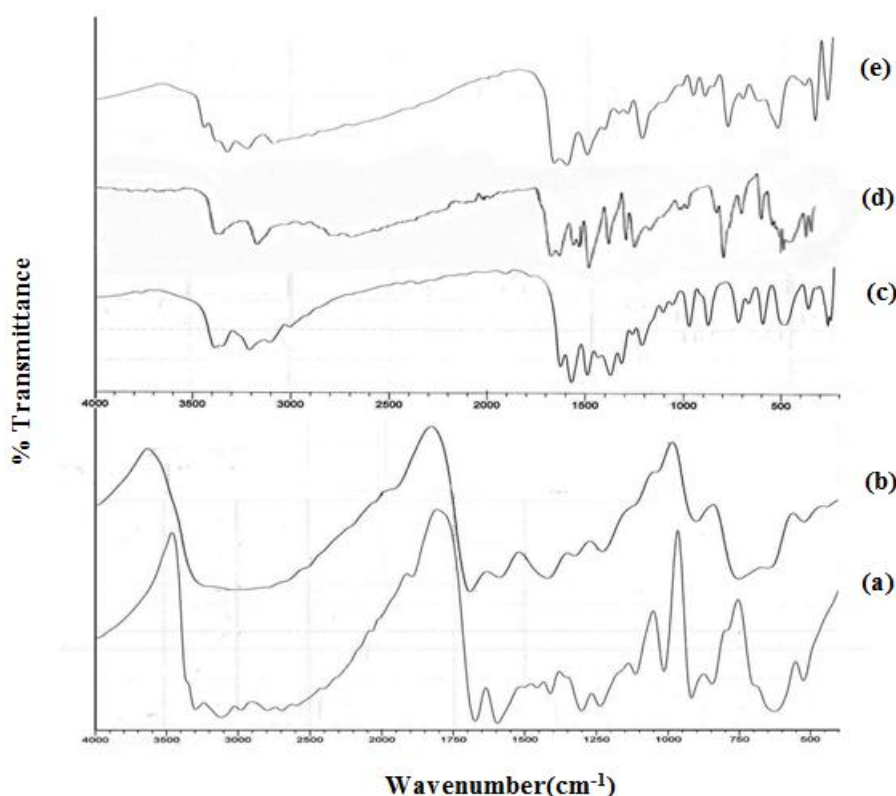


Figure (4): Infrared spectra of:

- (a) Adenine (b) $\text{Fe}(\text{Adenine})_3$
 (c) $\text{Co}(\text{acac})_2(\text{Adenine})$
 (d) Cytosine
 (e) $\text{Co}(\text{Adenine})(\text{Cytosine})(\text{OH})_2 \cdot 2\text{H}_2\text{O}$

Table (2): Fundamental infrared bands (cm^{-1}) of Adenine, Cytosine and their complexes.

| Adenine | Fe(Adenine) ₃ | Co(acac) ₂ (Adenine) | Assignments |
|---------|--------------------------|---------------------------------|---|
| 3286 | - | { 3371 } { 3335 } (sp) | $\nu_{(\text{OH})}$, $\nu_{(\text{NH}_2)}$ |
| 3111 | - | 3200 | $\nu_{(\text{NH}_2)}$, $2\delta_{(\text{NH}_2)}$ |
| 2970 | 3028 | 3099 | $\nu_{(\text{C}_8\text{-H})}$, $\nu_{(\text{C}_2\text{-H})}$, $\nu_{(\text{NH}_2)}$ |
| 1676 | 1684 | 1647 | $\delta_{(\text{NH}_2)}$ sym. in plane |
| - | - | 1591 | $\nu_{(\text{C}=\text{O})}$ |
| 1597 | 1589 | 1514 | $\nu_{(\text{C}_4\text{-C}_5)}$, $\nu_{(\text{C}_8\text{-N}_9)}$, $\delta_{(\text{C}_8\text{-H})}$ |
| 1504 | - | - | $\delta_{(\text{N}_1\text{-H})}$ |
| 1460 | - | - | $\delta_{(\text{C}_2\text{-H})}$, $\nu_{(\text{C}_8\text{-N}_9)}$, $\delta_{(\text{C}_8\text{-H})}$ |
| 1414 | 1421 | 1400 | $\nu_{(\text{N}_1\text{-C}_6\text{N}_6)}$ |
| 1358 | 1327 | 1346 | $\nu_{(\text{C}_5\text{-N}_7\text{-C}_8)}$ |
| 1306 | - | 1296 | $\nu_{(\text{N}_9\text{-C}_8)}$, $\nu_{(\text{N}_3\text{-C}_2)}$, $\delta_{(\text{C-H})}$ |
| 1242 | 1231 | 1246 | $\delta_{(\text{C}_8\text{-H})}$, $\nu_{(\text{N}_7\text{-C}_8)}$ |
| 1119 | - | 1146 | $\nu_{(\text{C}_2\text{-N}_3)}$ |
| 1020 | 1041 | 1014 | $\rho_{(\text{NH}_2)}$ |
| 926 | 901 | 920 | $\rho_{(\text{NH}_2)}$, $\nu_{(\text{N}_1\text{-C}_6)}$ |
| 854 | 752 | 768 | $\delta_{(\text{N}_1\text{-C}_2\text{-N}_3)}$, $\nu_{(\text{C}_5\text{-N}_7)}$, $\nu_{(\text{N}_9\text{-H})}$ |
| 636 | 652 | 646 | $\nu_{(\text{NH}_2)}$, ring deformation |
| 534 | 523 | - | $\omega_{(\text{NH}_2)}$, $\delta_{(\text{NH}_2)}$ |
| - | - | 532 | $\delta_{(\text{C}=\text{O})}$ |
| - | 444 | 417 | $\nu_{(\text{M-N})}$ |
| - | - | 316 | |

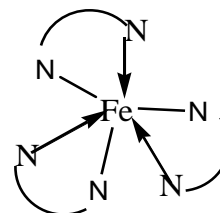
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| Cytosine | Co(Adenine)(Cytosine)(OH) ₂ .2H ₂ O | Assignments |
|----------|---|---|
| 3390 | 3313 | $\nu_{(\text{OH})}$, $\nu_{(\text{NH}_2)}$ |
| 3180 | 3211 | $\nu_{(\text{NH}_2)}$, $2\delta_{(\text{NH}_2)}$ |
| 3000 | 3078 | $\nu_{(\text{CH})}$ |
| 1660 | 1666 | $\nu_{(\text{C}=\text{O})}$ |
| 1610 | 1605 | |
| 1550 | 1502 | $\nu_{(\text{C}_4\text{-N}_3)}$ |
| - | 1418 | $\nu_{(\text{N}_1\text{-C}_6\text{N}_6)}$ |
| - | 1344 | $\nu_{(\text{C}_5\text{-N}_7\text{-C}_8)}$ |
| 1280 | 1302 | $\nu_{(\text{N}_9\text{-C}_8)}$, $\nu_{(\text{N}_3\text{-C}_2)}$, $\delta_{(\text{C-H})}$ |
| 1240 | 1227 | ν_{ring} , $\delta_{(\text{NH}_2)}$ asym.out of plane |
| 980 | 970 910 | $\rho_{(\text{NH}_2)}$, $\nu_{(\text{N}_1\text{-C}_6)}$ |
| 795 | 795 | |
| 565 | 540 | $\delta_{(\text{C}=\text{O})}$ |
| - | 403 | $\nu_{(\text{M-N})}$ |
| - | 351 | |

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

For Fe(adenine)₃ complex

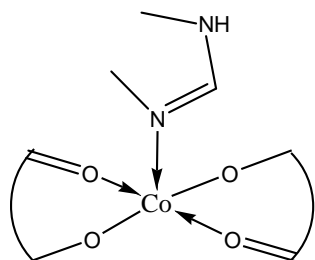
The $\nu_{(\text{C}_2\text{-N}_3)}$ band of adenine at 1119 cm^{-1} disappeared upon complexation with Fe(III), so the N(3) site is involved with N(9) in coordination as follows:



In case of Co(acac)₂(adenine) complex

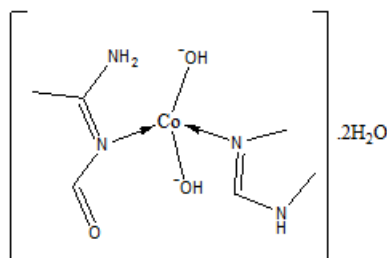
The presence of $\nu_{(\text{C}=\text{O})}$ at 1591 cm^{-1} of this complex spectrum proves that Co(II) is coordinated to

acetylacetonate anion which contributes with N(7) nitrogen of adenine to give the following structure.

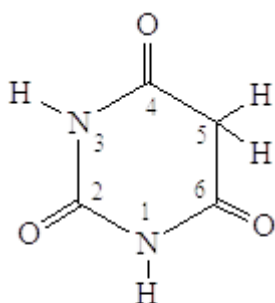


On the other hand, for Co(Adenine)(Cytosine)(OH)₂.2H₂O complex

The spectra of Adenine, Cytosine and their cobalt complex in the 3390-3286 cm⁻¹ region gave set of bands assigned to NH₂ and 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 $\nu_{(C=O)}$ (1660 and 1610 cm⁻¹), $\nu_{(C=N)}$ (1550 cm⁻¹), $\delta_{(C=O)}$ (565 cm⁻¹) and $\delta_{(N1-C6H)}$ (795 cm⁻¹), Table(2). Below 1600 cm⁻¹ the bands of Cytosine spectrum are mainly due to ring stretching and bending modes, beside CH and C-NH₂ bending modes.^[118] The $\nu_{(C5-N7-C8)}$ band of Adenine and $\nu_{(C4=N3)}$ 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 $\nu_{(M-N)}$ band at 351 and 403 cm⁻¹. The mode of bonding of this complex is given as follows:



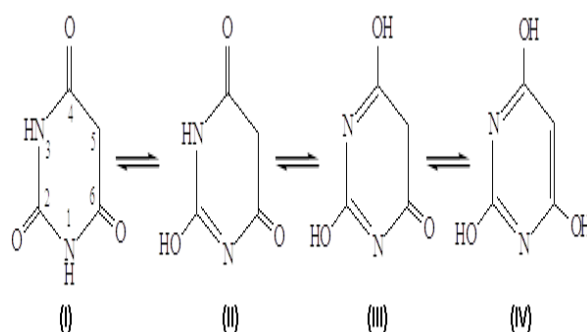
Mode of bonding of Barbituric acid and its complexes



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



d- The shifts or disappearance of both the ν_{NH} and $\nu_{C=O}$ 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 M-N bands or the free ligand may be subjected to half keto-half enol tautomerism and equilibria in the solid state^[58,124], i.e. conversion of -CNH to 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.^[124]

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

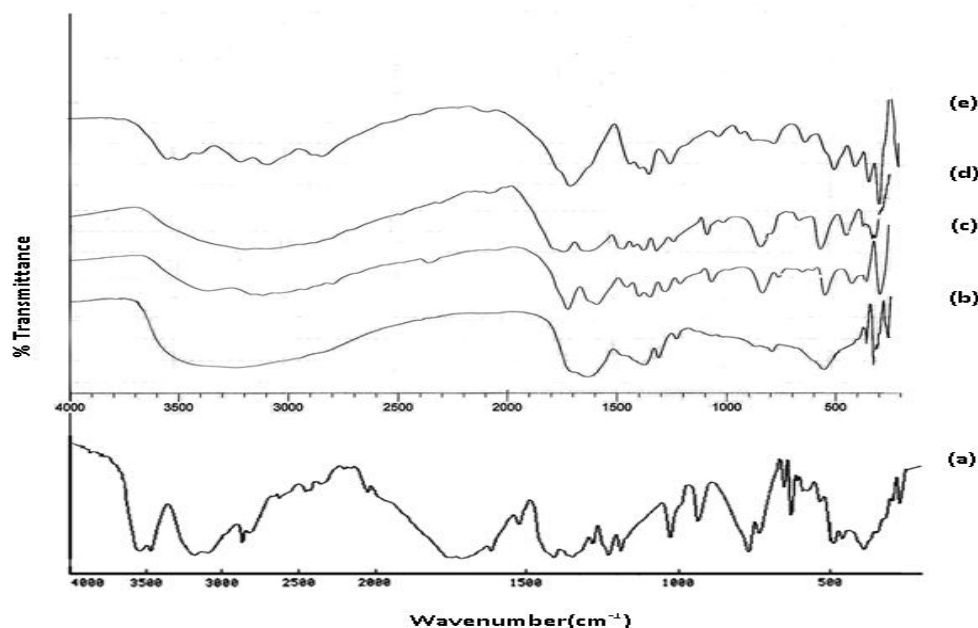


Figure (5): Infrared spectra of:

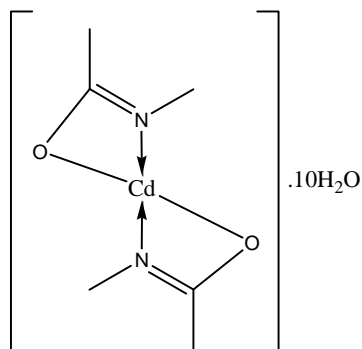
- (a) Barbituric acid
- (b) Cr(Barbituric acid)(OH).4H₂O
- (c) Zn(Barbituric acid)₂.3H₂O
- (d) Cd(Barbituric acid)₂.10H₂O
- (e) Hg(Barbituric acid)₂

Table (3): Fundamental infrared bands (cm⁻¹) of Barbituric acid and its complexes.

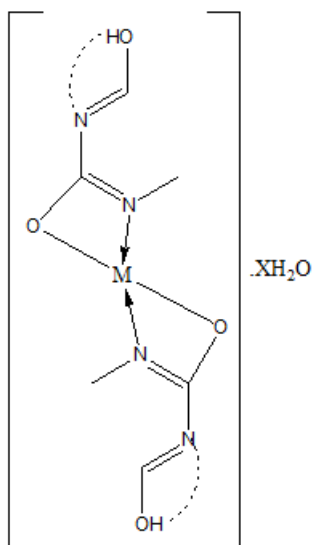
| Barbituric acid (BA) | Cr-BA | Zn-BA | Cd-BA | Hg-BA | Assignments |
|------------------------------------|--------------------------------|----------------------------------|----------------------------------|----------------------------------|--------------------------|
| 3552 3478 | 3211 | - 3356 | - - | {3531} {3477}(sp) | ν_{OH} |
| {3182} {3096}(sp) | - | {3153} {3105}(sp) | {3157} {3072}(sp) | {3196} {3076}(sp) | ν_{NH} |
| 2876 2830 | - - | - 2793 | 2899 2851 | 2872 2831 | ν_{CH} |
| {1744} {1718}(sp) | - | 1713 | 1705 | 1703 | $\nu_{C=O}$ |
| 1617 | 1612 | 1582 | 1597 | - | $\nu_{C=N}$ |
| 1410 | - | 1448 | 1435 | 1431 | δ_{NH} |
| 1366 1349 | 1356 - | 1391 1340 | 1387 1344 | 1387 1346 | ν_{C-O}, δ_{CH} |
| 1285 | 1292 | 1273 | 1285 | - | ν_{C-O}, δ_{OH} |
| 1232 1193 | - 1211 | - 1205 | - 1207 | 1252 - | ν_{C-N} |
| - | 1053 | 1063 | 1057 | 1034 | ν_{C-O}, ν_{C-N} |
| 1028 936 | 1005 - | 986 - | 986 - | - 933 | ν_{C-C} |
| - - 733 739 656 632 | - 852 775 - - - | - 829 756 - 646 - | - 808 764 - 635 - | 876 - 779 - 638 - | ρ_{CH}, ρ_{OH} |
| - | 536 | 538 | 534 | 503 | ν_{M-O} |
| - | 343 | 353 | 417 | 345 | ν_{M-N} |

SP: splitted

The mode of bonding for Cr(Barbituric acid)(OH⁻).4H₂O 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).



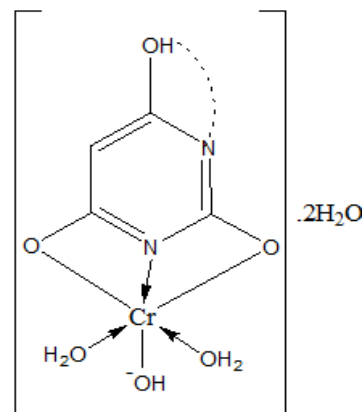
However, Zn(Barbituric acid)₂.3H₂O and Hg(Barbituric acid)₂ complexes pointed to that, the Barbituric acid is tautomerized to give bidentate centers for coordination. An intramolecular hydrogen bonding was remarked and accompanied by association through hydrogen bonding in Zn complex. The following structures are given:



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

The IR spectra of Thiobarbituric acid and Fe(Thiobarbituric acid)(OH).2H₂O complex are given in Figure (6) and Table (4). There is dynamic equilibria in solid state of TBA as the existence of ν_{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)₂.10H₂O, the presence of ν_{NH} band at 3157-3072 cm⁻¹ and $\nu_{C=O}$ band at 1705 cm⁻¹ upon complexation give bidentate donation as follows:



1. The spectra Fe(Thiobarbituric acid)(OH⁻).2H₂O complex exhibited a broad band at 3367 cm⁻¹, attributed to ν_{OH} , while that at 839-791 cm⁻¹ is assigned to coordinated water molecules.^[125]
2. The carbonyl absorption band $\nu_{C=O}$ of the ligand at 1674 cm⁻¹ was shifted to lower frequency upon Fe³⁺ complexation which indicated that at least one of the two carbonyl groups in the TBA is coordinated to metal ion.
3. The ν_{NH} band at 3231-3111 cm⁻¹ disappeared in the spectra of Fe³⁺ 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.^[126] 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 ν_{M-S} and ν_{M-N} bands is strong evidence for complexation.^[24,127,128]

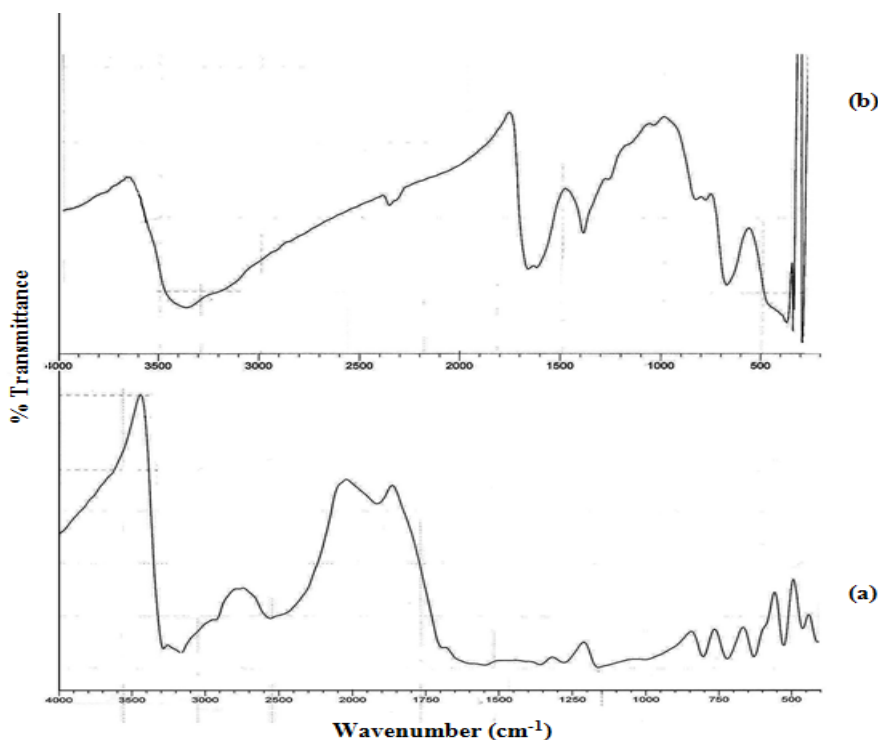


Figure (6): Infrared spectra of:

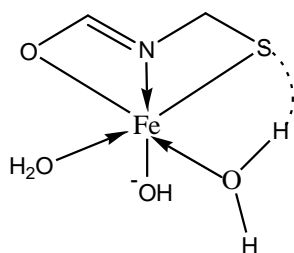
(a) Thiobarbituric acid (b) Fe(Thiobarbituric acid)(OH).2H₂O

Table (4): Fundamental infrared bands (cm⁻¹) of Thiobarbituric acid and its iron complex.

| Thiobarbituric acid | Fe(Thiobarbituric acid) | Assignments |
|--------------------------|-------------------------|------------------------|
| - | 3367 | ν_{OH} |
| {3231 3111}(sp) | - | ν_{NH} |
| 2876 2721 | - | ν_{CH} |
| 2511 1896 | 2362 - | ν_{SH} |
| 1674 | {1672 1628}(sp) | $\nu_{C=O}$ |
| 1533 | - | $\nu_{C=N}$ |
| 1344 | 1398 | ν_{C-O} |
| 1265 | 1277 | ν_{C-N} |
| 1150 | 1170 | ν_{C-C} |
| - | 1053 | ν_{C-S} |
| 993 797 714 623 | 839 791 | ρ_{CH}, ρ_{OH} |
| - | 683 | ν_{M-S} |
| - | 380 | ν_{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).2H₂O complex is given as follows:



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

The ν_{NH} band of 2-Thiouracil^[129] 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 H_2O .^[41,131] Bands assigned to $\nu_{(\text{M-O})}$, $\nu_{(\text{M-S})}$ and $\nu_{(\text{M-N})}$ are identified, Table(5).

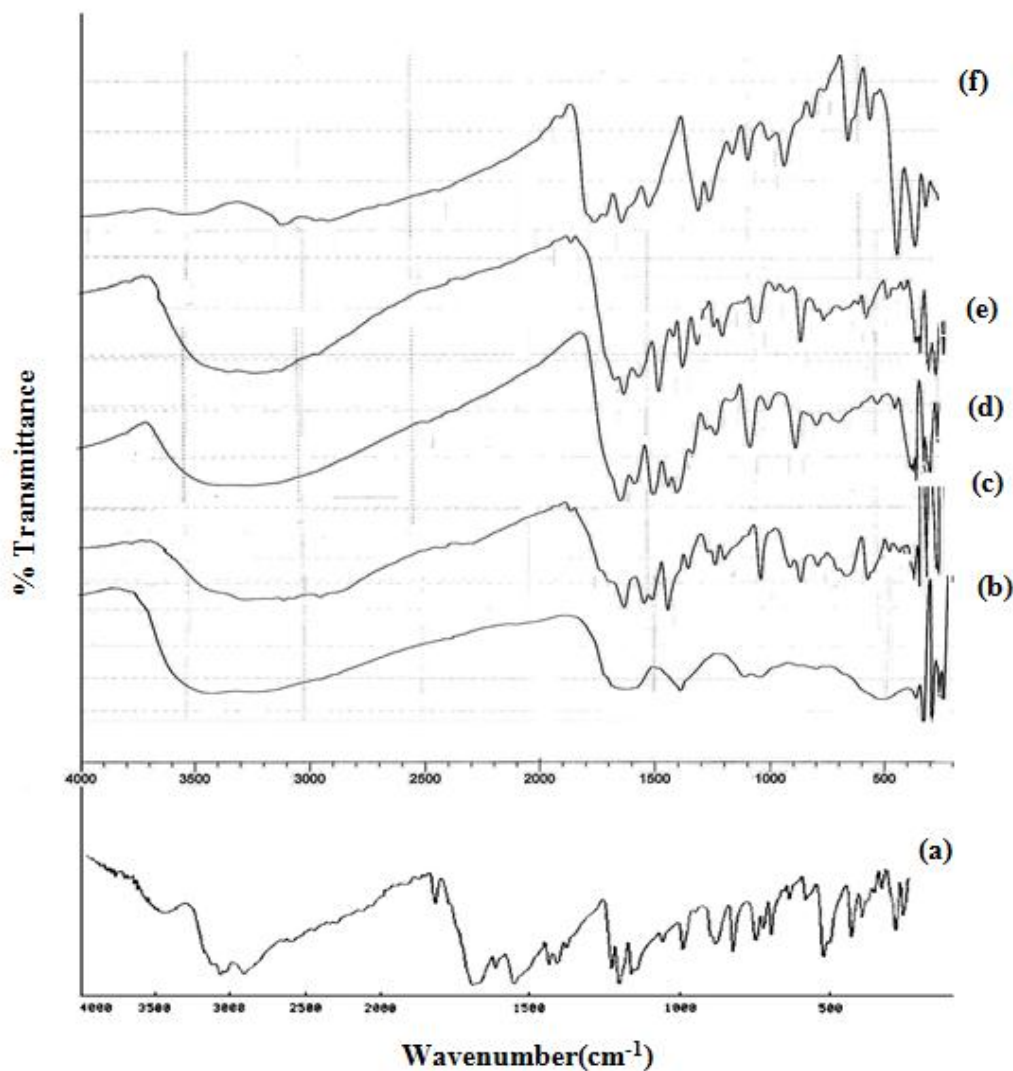


Figure (7): Infrared spectra of:

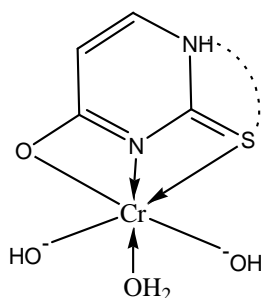
- (a) Thiouracil (b) $\text{Cr}(\text{Thiouracil})(\text{OH})_2 \cdot \text{H}_2\text{O}$
 (c) $\text{Mn}(\text{Thiouracil})_2 \cdot \text{H}_2\text{O}$ (d) $\text{Co-Ni}(\text{Thiouracil})_3 \cdot 4\text{H}_2\text{O}$
 (e) $\text{Ni-Cu}(\text{Thiouracil})_3 \cdot 4\text{H}_2\text{O}$ (f) $\text{Hg}(\text{Thiouracil})_2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

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

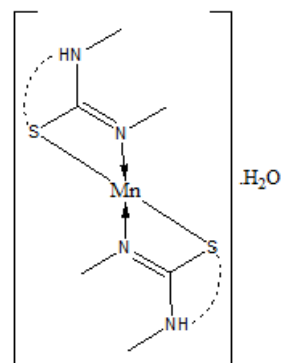
| 2-Thiouracil(TU) | Cr-TU | Mn-TU | Co-Ni-TU | Ni-Cu-TU | Hg-TU | Assignments |
|---|---------------------------------------|-------------------------------------|---------------------------------------|---|---|--------------------------------------|
| 3458 | 3396 | - | - | 3317 | 3508 | ν_{OH} |
| 3135 {3084} {3046}(sp) | 3223 - | 3249 - | 3286 - | 3200 - | 3072 - | ν_{NH} |
| 2926 | 2934 | 2928 | - | 2932 | 2920 | ν_{CH} |
| 2607 | 2378 | 2401 | 2434 | 2305 | 2611 | ν_{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 | δ_{NH} |
| 1390 | 1387 | 1416 | 1383 | 1385 | - | $\nu_{\text{C-O}}$ |
| 1239 1214 {1173} {1157}(sp) | - - 1115 | 1240 {1209} {1167}(sp) | 1275 {1211} {1173}(sp) | 1281 {1209} {1173}(sp) | - {1215} {1164}(sp) | $\nu_{\text{C-N}}$ |
| 1070 | 1049 | - | - | 1080 | 1063 | $\nu_{\text{C-C}}$ |
| 1001 | - | 1013 | 1024 | 1018 | 993 | $\nu_{\text{C-S}}$ |
| 960 892 835 759 734 707 647 | - 883 804 768 - - - | - 883 - 760 - - - | 943 - 825 - 731 - - | 943 891 829 - 729 - - | - 901 829 - - 704 648 | $\rho_{\text{CH}}, \rho_{\text{OH}}$ |
| - | 521 | 542 | 548 | 546 | 544 | $\nu_{\text{M-O}}, \nu_{\text{M-S}}$ |
| - | 374 | 446 | 461 | 447 | 444 | $\nu_{\text{M-N}}$ |

sp: splitted

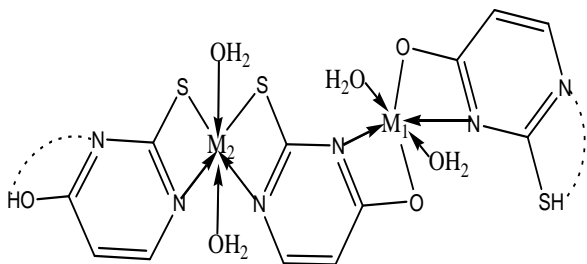
So, Thiouracil is tautomerized to give bidentate or tridentate centers for coordination, Figure (7) and Table (5). An intramolecular hydrogen bonding was observed, where the mode of bonding of $\text{Cr}(\text{Thiouracil})(\text{OH})_2 \cdot \text{H}_2\text{O}$ complex is given as follows:



The mode of bonding of $\text{Mn}(\text{Thiouracil})_2 \cdot \text{H}_2\text{O}$ is given, where tautomerization and association through hydrogen bonding occurred.

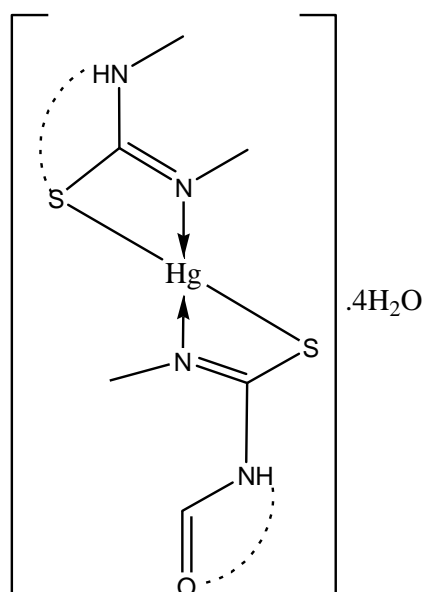


However, the disappearance of $\nu_{C=O}$ upon complexation of (Co-Ni, Ni-Cu) (Thiouracil)₃.4H₂O and the presence of ν_{C-O} , ν_{C-S} and $\nu_{C=N}$ suggest the bidentate tautomerization for coordination.^[54,61,67,81] The Thiouracil ν_{NH} band at 3135 cm⁻¹.^[131] is shifted to higher wave numbers 3286 and 3200 cm⁻¹ in the spectra of Co-Ni(Thiouracil)₃.4H₂O and Ni-Cu(Thiouracil)₃.4H₂O complexes, respectively confirming the participation of NH group in complexation. The appearance of new bands $\nu_{(M-O)}$, $\nu_{(M-S)}$ and $\nu_{(M-N)}$ verifying (M-O), (M-S) and (M-N) interactions.^[69,132,133] An intramolecular hydrogen bonding occurred according to the following structure:



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

For Hg(Thiouracil)₂.4H₂O complex, Thiouracil is tautomerized 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 Co(Adenine)(Cytosine) (OH)₂.2H₂O, Cr(Barbituric acid)(OH).4H₂O and Cr(Thiouracil) (OH)₂.H₂O complexes. The data for Zn(Barbituric acid)₂.3H₂O, Cd(Barbituric acid)₂.10H₂O and Hg(Barbituric acid)₂ complexes, Figure (9), Table (6), and the μ_{eff} value for

Hg(Thiouracil)₂.4H₂O complexes illustrates diamagnetic property and tetrahedral structures.

The Cr(Barbituric acid)(OH).4H₂O and Fe(Thiobarbituric acid)(OH).2H₂O 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.^[71]

However, Cr(Thiouracil)(OH)₂.H₂O complex, Table (6) gave three bands at 312 nm ($\pi-\pi^*$) electronic transition, 439 nm [CT($t_{2g}-\pi^*$)] and 600 nm [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.^[71]

The electronic absorption spectral band at 327 nm for Mn(Thiouracil)₂.H₂O complex is assigned to ${}^6A_1 \rightarrow {}^4T_{2g}$. Its magnetic moment is 5.11 B.M, typified the existence of T_d structure.^[71] The μ_{eff} values of Co-Ni(Thiouracil)₃.4H₂O and Ni-Cu(TU)₃.4H₂O complexes were 5.92 B.M and 3.95 B.M, respectively, which supports an overall O_h geometry.

The Fe(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.^[71]

The band of Co(acac)₂(Adenine) at 410 nm is due to d-d transitions. However, its μ_{eff} value is 4.95 B.M, which supports square pyramidal geometry.^[71]

The Co(Adenine)(Cytosine)(OH)₂.2H₂O 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.^[71]

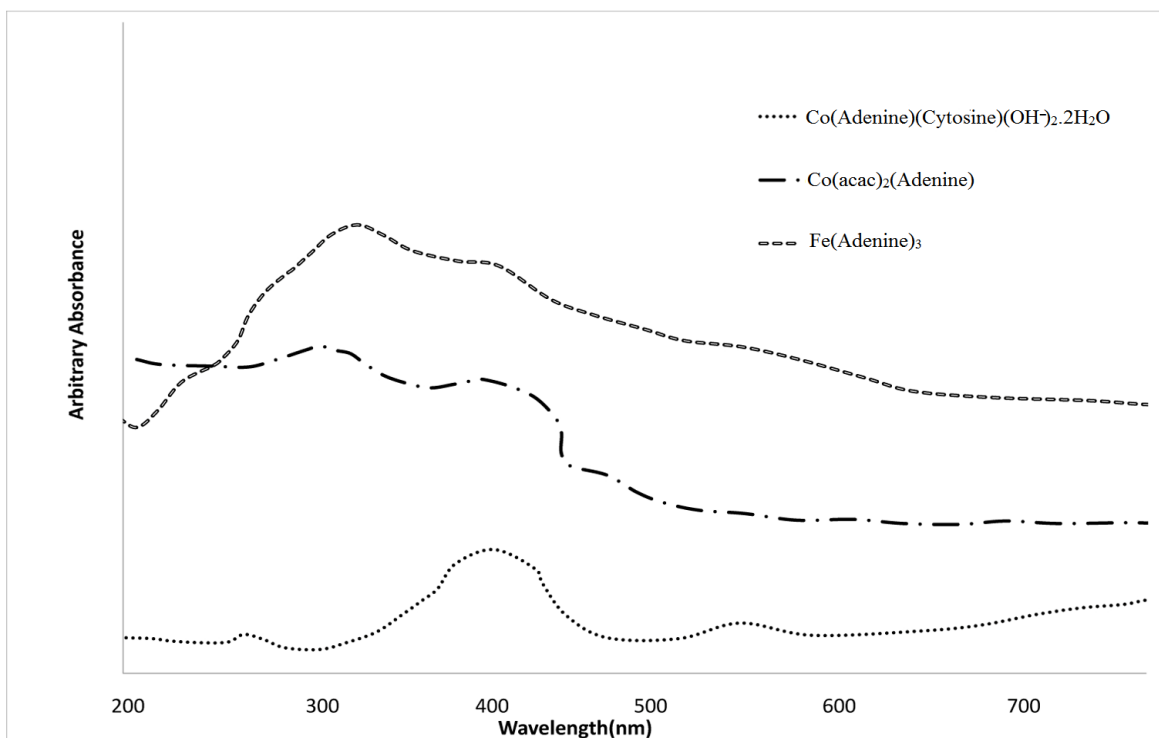


Figure (8): Nujol mull electronic absorption spectra of Fe(Adenine)_3 , $\text{Co(acac)}_2(\text{Adenine})$ and $\text{Co(Adenine)(Cytosine)(OH)}_2 \cdot 2\text{H}_2\text{O}$ complexes.

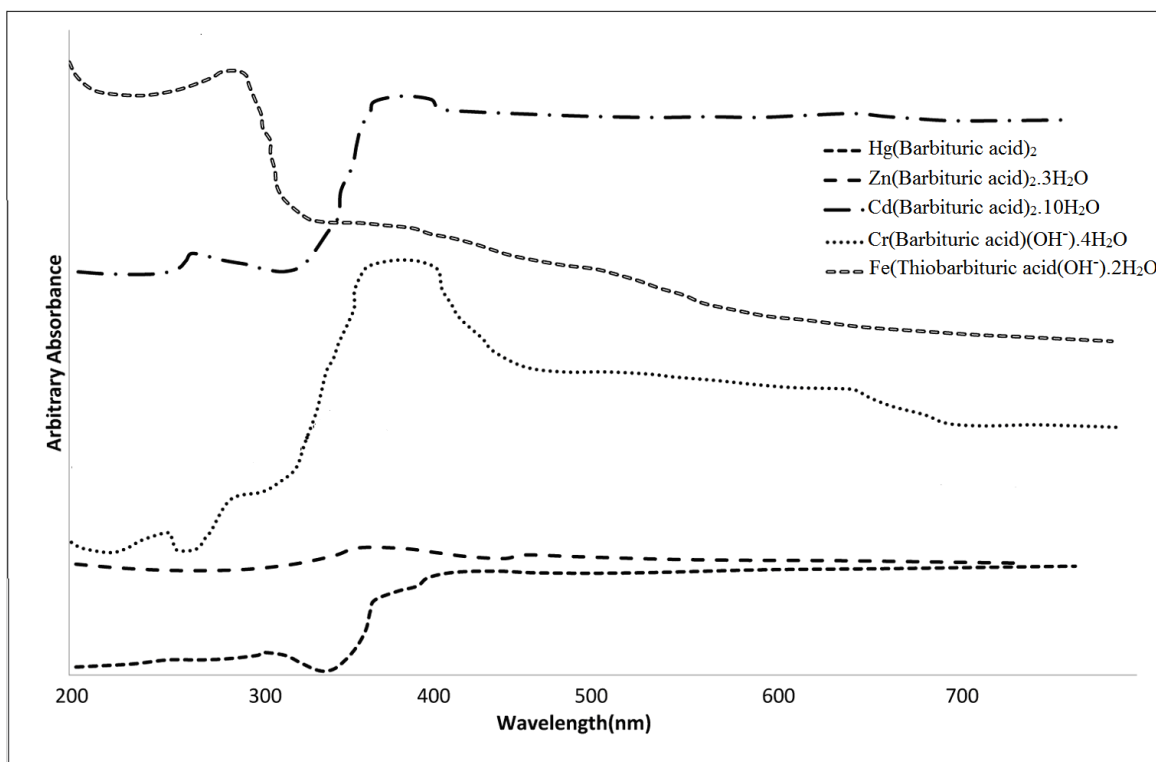


Figure (9): Nujol mull electronic absorption spectra of $\text{Cr(Barbituric acid)(OH)} \cdot 4\text{H}_2\text{O}$, $\text{Zn(Barbituric acid)}_2 \cdot 3\text{H}_2\text{O}$, $\text{Cd(Barbituric acid)}_2 \cdot 10\text{H}_2\text{O}$, $\text{Hg(Barbituric acid)}_2$ and $\text{Fe(Thiobarbituric acid)(OH)}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

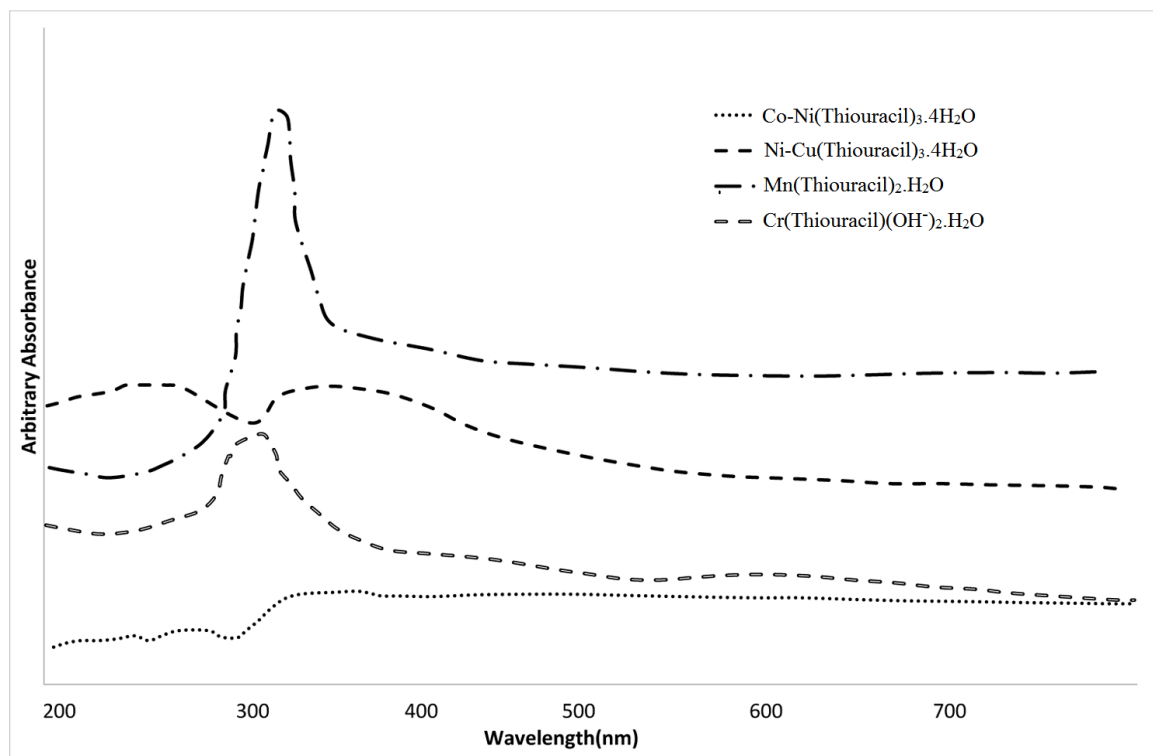


Figure (10): Nujol mull electronic absorption spectra of $\text{Cr(Thiouracil)(OH)}_2 \cdot \text{H}_2\text{O}$, $\text{Mn(Thiouracil)}_2 \cdot \text{H}_2\text{O}$, $\text{Co-Ni(Thiouracil)}_3 \cdot 4\text{H}_2\text{O}$ and $\text{Ni-Cu(Thiouracil)}_3 \cdot 4\text{H}_2\text{O}$ complexes.

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

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

* the μ_{eff} value for Hg(Thiouracil)₂·4H₂O complex is dia.

C. Mössbauer spectra

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

1. The energy of γ -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 γ -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 Fe⁵⁷ source – A single crystal of sodium nitroprusside, Na₂Fe(CN)₅NO·2H₂O.
2. For Sn¹¹⁹ source – A crystal of barium stannate, BaSnO₃.

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(δ) and the quadrupole splitting(ΔE_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).

δ 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. δ is the

The Mössbauer isomer shifts for different classes for iron compounds have been given as follows.^[134]

| Oxidation state | Spin state | Isomer shift(δ , mm s ⁻¹) |
|-------------------|------------|---|
| Fe ^{II} | h.s | ~ 1.3 |
| Fe ^{III} | h.s | ~ 0.5-0.7 |
| Fe ^{II} | l.s | ~ 0.1 |
| Fe ^{III} | 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^{III} 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^{II} 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 d⁶ electron structure of the central iron(II) atom (t_{2g})⁴(e_g)² progressively approaches the spherically symmetric d³ electron structure characteristic of the high-spin iron(III) atom (t_{2g})³(e_g)². 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(ΔE_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^{II} low spin is overlapping with Fe^{III} high spin. Nevertheless, Fe^{III} high spin can be determined, because it looks like a time dependent h.s/l.s ratio.

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

The Mössbauer spectrum of Fe(Adenine)₃ complex, Figure (11) illustrates a high-spin Fe^{III} complex.^[135] The data are collected in Table (7).

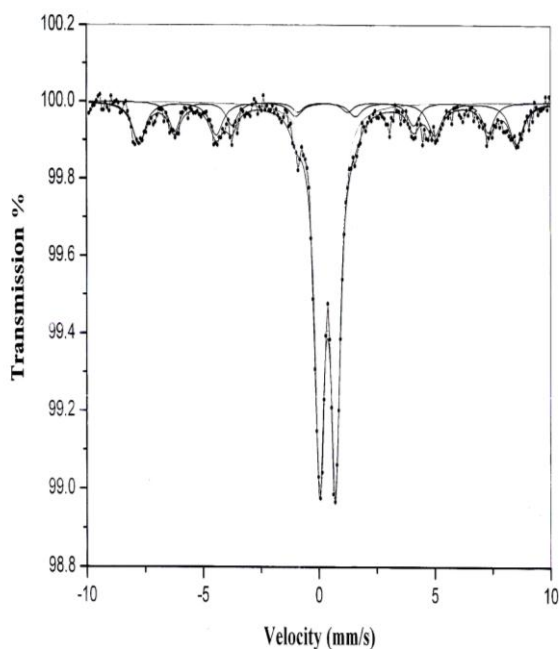


Figure (11): The Mössbauer spectrum of Fe(Adenine)₃ complex.

Table (7): The Mössbauer parameters of Fe(Adenine)₃ 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^{III} was also previously inferred from magnetic measurements and electronic spectroscopy. The data typified that the iron sample is mainly of high-spin octahedral Fe^{III} with minimum contribution of low-spin Fe^{II}.

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