

## Study of Coordination Characteristics of Some Metal Complexes of 2-Thiouracil by Infrared Spectroscopy

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### ABSTRACT

The infrared spectra of 2-Thiouracil (Thu) have been recorded in the region 4000-400 cm<sup>-1</sup>. The assignments of fundamental frequencies have been proposed on the basis of assignments in related molecules. Correlation of vibrational assignments with those of related molecules have been pointed out.

The metal ion interactions of Thu with Cd (II), Hg (II), Cu (II), and Zn (II) bromides have been investigated by infrared spectroscopy. The results are consistent with the bonding of ligands through sulphur in all the complexes. The vibrational frequencies of metal complexes of 2-Thiouracil are correlated with the spectral data of other structurally related pyrimidine thione complexes.

### 1. INTRODUCTION

Coordination chemistry is undoubtedly the most active research area in inorganic chemistry. Several thousands of coordination complexes have been synthesized and investigated during the past few decades. Ever since the importance of coordination phenomenon in biological processes was realized, lot of metal containing macromolecules have been synthesized and studied to understand the role of these ligands in biological systems, and they also contribute to the development of new metal-based chemotherapeutic agents. These have resulted in the emergence of an important branch of inorganic chemistry viz. bioinorganic chemistry because in several cases, the metal chelates have been found to be more antimicrobial than the chelating agents themselves [1]. The importance of pyrimidine derivatives arises from their biological, medicinal and agricultural applications [2-4]. Metal complexes of pyrimidine have been extensively studied in recent years owing to their great variety of biological activity ranging from antimalarial, antibacterial, antitumor, antiviral activities etc. [5-6]. The use of Uracil, Thiouracil, and Pyrimidine thiones in the process of biochemical importance and providing bonding sites for metal ions has simulated much research [7]-[10]. Pyrimidine 2-thione is present in soluble ribonucleic acid [11], Pyrimidine 2-thione (pymt) and its derivatives find importance as antitumour and antithyroid agents [12]. Like the thiobases, 2-thiouracil, 4-thiouracil and 2-thiocytosine (whose molecular) structures are closely related to pyrimidine thiones (pymt) and 4, 6- Dimethyl Pyrimidine-2-thione (dimpymt), under certain conditions inhibit RNA synthesis leading to antitumour activity [13]. Numerous sulphur substituted pyrimidines have found applications as clinically useful drugs. It has been observed that 2-thiouracil inhibits biosynthesis of thyroid hormone. It is therefore considered interesting to study the infrared spectrum of the 2-Thiouracil and its donor characteristics with some transition metal ions. The selection of group IIB metal ions (Cd, Hg) is of special significance. They being toxic, pyrimidine thiones and Thiouracil have been found to have antitumour and antithyroid activity, it is considered

interesting to study their metal complexes. Also the selections of these metal ions were made by their known preference for sulphur donors. The interaction of metal ions with nucleobases is of great interest because of their relevance to the essential, medical or toxic bioactivity of metal, where nucleobases molecule can coordinate as exogenous ligands in metalloproteins, functions as cofactors in the enzymatic systems and construct important cell structures (RNA).

## 2. MATERIALS AND METHODOLOGY

### A. Preparative Procedures:

2-Thiouracil was from Aldrich chemical and used as such without any purification. The solvent ethanol was purified following the procedure of Vogel [14].

### B. Metal Salts:

CdBr<sub>2</sub>, CuBr<sub>2</sub>, HgBr<sub>2</sub>, and ZnBr<sub>2</sub> are all AR grade chemicals (E-merck).

### C. Metal Complexes:

Cadmium bromide (2 millimole) was treated with 2-Thiouracil in 1:2 molar proportion in hot ethanol with constant stirring and further refluxed for 1 hour, and cooled. The separated complex was filtered of under nitrogen, washed with ethanol and ether and dried in vacuum.

The copper, mercury and zinc complexes were obtained by the same procedure but using cold ethanol solution. Metal analysis for cadmium, mercury and copper were carried out following the procedure of Vogel [14].

Cadmium, Copper and Zinc: They were estimated by EDTA titration employing a few drops of xylenol orange indicator and hexamine as buffer.

Mercury: The solution was allowed to react with nitric acid to oxidize Hg (I) if any to Hg (II) state. The solution was then neutralized by sodium hydroxide and the metal estimated by EDTA titration using Eriochrome Black-T as an indicator.

### D. Spectral measurements:

A Bruker IFS-66V FT IR Spectrophotometer was employed to record the complexes of 2-Thiouracil in infrared spectrum (4000-400 cm<sup>-1</sup>) of the solid samples as KBr pellets available at Indian Institute of Technology, Madras.

## 3. RESULTS AND DISCUSSIONS

The assignments given in the TABLE I were established after careful consideration of the assignments available for related molecules like Pyrimidine-2-thione [15],[22], 4,6-dimethyl pyrimidine-2-thione [15], 1,4,5,6-tetrahydropyrimidine-2-thione [15], 2-pyrimidone [16], 2-chloropyrimidine [17], pyrimidine [18], cytosine [19], thiocytosine and other related compounds. The general procedure followed for empirical assignments of thioureide frequencies are (i) N-deuteration studies (ii) S-methylation studies (iii) selenation technique (iv) study of polarization characteristics of infrared bands in the oriented crystalline samples [20].

### A. N-deuteration studies:

The thioureide N-H is replaced by heavier isotope deuterium. The infrared spectrum of n-deuteration labeled compound is compared with unlabeled N-H compound. The perturbation of frequencies consequent to N-deuteration is considered while making thioureide N-H assignments. Usually the N-H stretching modes are highly sensitive to deuterium labeling. They show pronounced lowering of frequencies.

### B. S-Methylation studies:

The thiocarbonyl group C=S is S-methylated. The infrared spectra of S-methylated compounds registers red shift of over 40 cm<sup>-1</sup> for C=S stretching mode, consequent to S-methylation due to decreased C=S bond order.

**TABLE 1.** SOME CHARACTERISTICS INFRARED FREQUENCIES ( $\text{cm}^{-1}$ ) OF 2-THIOURACIL

Thu frequencies	Main assignment
3084 vs	CH stretching
3050 w	
2922 w	NH stretching
2910 w	
1685 vs	C=O stretching+ ring stretching
1628s	Ring stretching (CN stretching )
1562 ms	
1450 ms	NH bending (in plane)
1421 ms	Ring stretching
1239 vs	
1213 vs	
1393 s	CH-bending
1175 s	C- H bending ring stretching
1070 s	Ring deformation
895 s	N-H bending (out of plane)
995 m	Ring breathing
760 ms	C=S stretching
648 s	C=O (in plane bending)
526 s	C=O (out of plane bending)
547 s	C=S (in plane bending)

### **C. Selenation technique:**

The sulphur atom is replaced by selenium and the infrared spectra of selenium with C=Se and compound with C=S are compared. Due to mass effect the C=Se stretching frequency is lowered compared to C=S. this selenation technique has been used to identity C=S and other thiouriede vibrations [21]-[22].

### **D. Polarization studies:**

Study of polarized infrared spectra of oriented crystalline samples is useful for making vibrational assignments in solids and in the factor group and site group analysis of crystals and also the polarization characteristics of C=S stretching frequencies of thiocarbonyl compounds. The use of Raman depolarization measurements in the classification of molecular vibrations is also known.

Using the above aids the vibrational spectra of pyrimidine-2-thione have been well studied by Shanmugam and Sathyanarayana [20]-[23].The problematic C=S stretching frequencies in these related molecules have been assigned. Using these data assignments of 2-Thiouracil is attempted here.

### **E. Comparison of the assignments:**

The assignments of 2-Thiouracil (Thu) (in TABLE I) are compared with those in related molecules such as pyrimidine, 2-pyrimidone, pyrimidine-2-thione, 4, 6-dimethyl pyrimidine-2-thione, 1, 4, 5, 6-tetrahydropyrimidine-2-thione in (TABLE II) to note the internal consistency in the assignments. The data generally appear to be a satisfactory representation. The assignments differ in some cases; however, salient features of the comparison are discussed below. The absence of band around  $2550 \text{ cm}^{-1}$  indicated the absence of S-H vibrations. Thus the thione tautomer of 2-Thiouracil (Thu) seems to be predominant in the solid state. It has been observed most of the thiopyrimidine derivatives exist in thione form in the solid state.

**F. N-H group frequencies:**

The N-H stretching frequency of 2-Thiouracil (Thu) assigned around  $2922\text{ cm}^{-1}$ , compatible in assignments made for Pyrimidine-2-thione (pymt) and 4,6-Dimethyl Pyrimidine-2-thione(dimpymt) around this region (TABLE II).

**Table 2.** COMPARISON OF THU INFRARED FREQUENCIES ( $\text{cm}^{-1}$ ) WITH RELATED MOLECULES

Pyrimidine	Pyrimidine-2-one	1,4,5,6-tetrahydro pyrimidine-2-thione	4,6-Dimethyl Pyrimidine-2-thione	Pyrimidine-2-thione	5,6-diamino-2-thiouracil	2-Thiouracil	Main Assignment
3095	3070	2960	2960	3080	–	3080	C-H stretching
3083	3019 2820	3160	3060	2960 3050	2979 2896	2922	N-H stretching
–	1540	1560	–	1565	1579	1562	C-N stretching
–	1648	–	–	–	1638	1685	C=O stretching
1146	1618	–	1620	1608	1638	1628	Ring stretching
1071	1230	1345	1590	1420	1456	1450	N-H bending
–	1350 1230	–	1330	1335	1376	1393	C-H bending
–	1198	–	1210	1210	1042	1070	Ring deforming +C-H bending+C-Xstretching
–	1160	–	1190	1182	–	1175	CH bending ring stretching
–	–	–	990	965	997	995	Ring breathing
–	952	635	590	965	892	895	N-H bending (out of plane)
–	636	–	–	–	649	648	C=O (inplane bending)
–	–	642	850	750	623	760	C=S stretching
–	–	340	520	470	551	547	C=S bending(inplane)
–	513	–	–	–	478	526	C=O (out of plane bending)

**G. C=S Vibrations:**

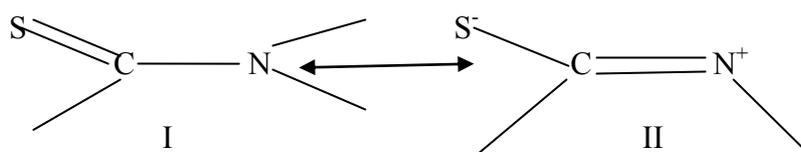
A band of interest in 2-Thiouracil is that arising from C=S stretching mode. A medium strong band around  $760\text{ cm}^{-1}$  may be attributed as arising predominantly from C=S stretching mode in 2-Thiouracil. A similar low frequency band has been assigned in the case of pyrimidine-2-thione ( $750\text{ cm}^{-1}$ ) [21]-[22]. The nature of C=S stretching mode of Thu is akin to that in alkyl thionamides [24]-[26]. It is found consistent with the corresponding frequency in thiones ( $720\text{ cm}^{-1}$ ) and that of tetrahydropyrimidine thione ( $642\text{ cm}^{-1}$ ) [21]-[22]. The C=S stretching mode is thus sensitive to molecular environment. Recently the vibrational spectra of 4, 6-diamino-2-thiouracil (DA2Thu) have been studied by Jeyanthi [27] and C=S stretching frequency assigned around  $623\text{ cm}^{-1}$ . The C=S bending fundamentals (in plane bending) may be assigned at  $547\text{ cm}^{-1}$  compatible with that of  $520\text{ cm}^{-1}$  of dimpymt.

### H. Metal Complexes:

The complexes have stoichiometry  $ML_2Br_2$  ( $M=Cd, Hg, Cu, Zn$ ). 2-Thiouracil (Thu) is a multisite ligand. Thiocarbonyl sulphur, pyrimidine ring nitrogens, carbonyl oxygen may have the possibility of coordinating with the metal ions. However the infrared spectral data indicate only the thiocarbonyl sulphur involves in coordination as discussed below.

### I. Infrared spectra of metal complexes:

Selected infrared frequencies of metal complexes of 2-Thiouracil (Thu) are assembled in TABLE I. The shifts in the infrared band positions of thiourea derivatives consequent to coordination have been discussed by Lane et al [28]. The free ligand may be considered to exist in two resonance forms as shown below.



Greater contribution from the polar form (II) is predicted. In the complexes of thiourea derivatives when coordinated through sulphur one looks for (i) a decrease in C=S stretching frequency and a concomitant increase in the C-N stretching frequency in the spectra of the metal complexes compared to that in the free ligand spectrum and (ii) appearance of new bands due to metal-sulphur stretching vibrations. The coordination of ligands through nitrogen atom would require a downward shift in the sensitive N-H stretching frequency by 200-300  $cm^{-1}$ . However in the spectra of complexes of Thu, there is no shift in the N-H frequencies. This suggests that the protonated nitrogen as the coordinating atom can be excluded in all the complexes discussed here. Also the carbonyl frequencies of the free ligand are not much affected in the infrared spectra of metal complexes investigated in the present work indicating their non-involvement in bonding with metal ions. In the spectra of Cadmium, Copper, Zinc and Mercury bromide complexes of Thu the stretching frequency assigned at 760  $cm^{-1}$  of the ligand shows a definite red shift of 20-25  $cm^{-1}$  due to decreased bond orders consequent to coordination with sulphur atom. The in plane bending C=S frequency assigned at 547  $cm^{-1}$  show marginal increase in the spectra of metal complexes as expected (TABLE III).

The C-N stretching frequency assigned at 1562  $cm^{-1}$  of the free ligand registers a marginal increase in the spectra of complexes. Thus, it may be concluded from the spectra that in these metal complexes the ligand coordinates through sulphur. However, the low frequency metal-ligand and metal bromide vibrations, usually observed below 400  $cm^{-1}$  could give much information regarding the coordination site.

### J. Structure of complexes:

Cadmium, Mercury, Copper and Zinc bromide complexes may be postulated to have tetrahedral geometry as predicted in the case of metal complexes of Pyrimidine-2-thione.

**TABLE 3.** SELECTED INFRARED BANDS ( $cm^{-1}$ ) OF THU-METAL BROMIDE COMPLEXES

Complex	N-H stretching	C-N str	C=O str	C=S str	C=O inplane bending	C=S inplane bending	C=O outplane bending
L-Thu	2910w	1562 ms	1685 ms	760s	648s	547 s	526 s
$CdL_2Br_2$	2924ms	1563 ms	1683 ms	735ms	647 ms	546 ms	526 s
$HgL_2Br_2$	2926m	1566 m	1683s	732ms	650 ms	547 s	525 s
$CuL_2Br_2$	2912m	1536 m	1685s	734ms	648 ssh	547 s	526 s
$ZnL_2Br_2$	2923m	1563 m	1682s	735ms	647 m	546 s	526 s

#### 4. CONCLUSION

It seemed appropriate to make a few remarks regarding the work described in the earlier. The vibrational spectra of several thiocarbonyl compounds have been supported with the aid of polarized infrared and Raman spectral data and normal coordinate calculations from time to time. Thus, in the present study, correlative criteria have been made use of in making vibrational assignments. Though the assignments proposed here are qualitative and empirical, the generally good agreement in the characteristics bands suggests that the proposed assignments are a satisfactory representation. The present work on corresponding bromo complexes should add to the spectral data earlier reported and should give further supportive evidence on the coordination characteristics of the ligand.

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#### References

- [1]. Srivastava, R. S. "Pseudotetrahedral Co (II), Ni (II) and Cu (II) complexes of N<sup>1</sup>-(O-chlorophenyl)-2-(2', 4'-dihydroxyphenyl)-2-benzylazomethine their fungicidal and herbicidal activity." *Inorganica Chimica Acta* 56, 1981, pp. L65-L67.
- [2]. Hung J, Werbel M." Investigations into the Synthesis of 6-Ethyl-5-(4-pyridinyl)-2,4-pyrimidine- diamine as a Potential Antimalarial Agent" *J Heterocycl Chem* 1984, pp. 21: 74.
- [3]. Rittich, Bohuslav, et al. "The antifungal activity of some aliphatic and aromatic acids." *Collection of Czechoslovak chemical communications* 57.5 (1992): pp, 1134-1142.
- [4]. Arfmann, Hans-Adolf, and Wolf-Rainer Abraham. "Microbial reduction of aromatic carboxylic acids." *ZEITSCHRIFT FUR NATURFORSCHUNG C* 48 (1993): pp. 52-52.
- [5]. Refat, Moamen S., Sabry A. El-Korashy, and Ahmed S. Ahmed. "A convenient method for the preparation of barbituric and thiobarbituric acid transition metal complexes." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 71.3 (2008): pp. 1084-1094.
- [6]. Casas J S, Castellans EE, Louce MD, Ellena J, Sanchez A, Sordo J, Taboada C. *J Inorg Biochem* 2006;1: pp. 1858–1860.
- [7]. Abbot, John, David ML Goodgame, and Ian Jeeves. "Complexes of pyrimidine-2-thione with some bivalent metal halides of the first transition series." *Journal of the Chemical Society, Dalton Transactions* 7 (1978): pp. 880-884.
- [8]. Battistuzzi, Raffaele, and Giorgio Peyronel. "Copper (I) complexes of neutral, deprotonated and protonated 4, 6-dimethylpyrimidine-2 (1H)-thione." *Transition Metal Chemistry* 3.1 (1978): pp. 345-351.
- [9]. Goodgame, D. M. L., and G. A. Leach. "Complexes of 1, 4, 6-trimethylpyrimidine-2-thione with some divalent metal halides." *Inorganica Chimica Acta* 32 (1979): pp. 69-73.
- [10]. Battistuzzi, R., and G. Peyronel. "Copper (I) and copper (II) complexes of 4, 6-dimethylpyrimidine-2 (1H)-one." *Spectrochimica Acta Part A: Molecular Spectroscopy* 36.6 (1980): pp. 511-515.
- [11]. Shefter, Eli, and Henry G. Mautner. "Acetylcholine and its thiolester and selenolester analogs: conformation, electron distribution, and biological activity." *Proceedings of the National Academy of Sciences* 63.4 (1969): pp. 1253-1260.

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- [12]. Votruba, Ivan, Antonín Holý, and Karel Jošt. "Conversion of 2-mercaptopyrimidine into S-(pyrimidin-2-yl)-cysteine in growing *Escherichia coli* cells." *FEBS letters* 22.3 (1972): pp. 287-288.
- [13]. Holý, A., I. Votruba, and K. Jošt. "S-(Pyrimidin-2-yl)-L-cysteine: Chemical synthesis and biosynthesis in *Escherichia coli*." *Collection of Czechoslovak Chemical Communications* 39.2 (1974): pp. 634-646.
- [14]. A.I.Vogel, A text book of quantitative inorganic analysis, Fourth Edition (1978)
- [15]. S.Anusuya, M.Phil thesis, University of Madras. (1987) unpublished.
- [16]. R.Shanmugam and D.N Sathyanarayana, *Indian J.Pure and Applied Physics*.
- [17]. Picquenard, E., & Lautié, A. (1982) Etude par spectrométrie infrarouge et Raman de la pyrimidone-2 et de son chlorhydrate (chlorure d'oxo-2 pyrimidinium). 38 (6), pp. 641-648.
- [18]. Sarma, Y. Anantharama. "Planar vibrations of 2-chloropyrimidine." *Spectrochimica Acta Part A: Molecular Spectroscopy* 30.9 (1974): 1801-1806.
- [19]. Innes, K. K., J. P. Byrne, and I-G\_ Ross. "Electronic states of azabenzenes: A critical review." *Journal of Molecular Spectroscopy* 22.1 (1967): pp. 125-147
- [20]. Innes, K. K., J. P. Byrne, and I-G\_ Ross. "Electronic states of azabenzenes: A critical review." *Journal of Molecular Spectroscopy* 22.1 (1967): pp. 125-147.
- [21]. Susi, H., J. S. Ard, and J. M. Purcell. "Vibrational spectra of nucleic acid constituents—II: Planar vibrations of cytosine." *Spectrochimica Acta Part A: Molecular Spectroscopy* 29.4 (1973): pp. 725-733.
- [22]. Shunmugam, R., and D. N. Sathyanarayana. "Raman and polarized infrared spectra of pyridine-2-thione." *Spectrochimica Acta Part A: Molecular Spectroscopy* 40.8 (1984): pp. 757-761.
- [23]. Shunmugam, R., and D. N. Sathyanarayana. "Vibrational Spectra of 1, 4, 5, 6-Tetrahydropyrimidine-2-Thione and-2-One." *Bulletin des Sociétés Chimiques Belges* 92.11-12 (1983): pp. 943-950.
- [24]. Shunmugam, R., and D. N. Sathyanarayana. "Vibrational Spectra of Pyrimidine-2-Thione and Pyrimidine-2-Selone." *Bulletin des Sociétés Chimiques Belges* 93.2 (1984): pp. 121-127.
- [25]. Shunmugam, R., D. N. Sathyanarayana, and A. Anagnostopoulos. "Vibrational spectra of imidazoline-2-one and of imidazoline-2-thione and its N-methyl derivative." *Canadian journal of spectroscopy* 28.5 (1983): pp. 150-155.
- [26]. Devi, Kolar Ramakrishnaiaa Gayathri and Sathyanarayana, Dixit Narayanarao (1980) Assignment of fundamental vibrations of .N'-dimethylthiourea,. In: *Bulletin of the Chemical Society of Japan*, 53 (10). pp. 2990-2994.
- [27]. Desseyn, H. O., Aarts, A. J., Esmans, E., & Herman, M. A. (1979). The secondary thioamide function—I. The vibrational analysis of NN' dimethyl-dithiooxamide. *Spectrochimica Acta Part A: Molecular Spectroscopy*, 35(10), pp. 1203-1211.
- [28]. K.Jeyanthi, M.Phil thesis Bharathidasan university (2004). Unpublished.
- [29]. Lane, T. J., and A. Yamaguchi. "Quac hano, JV; Ryan, RA; Muzhushi, A." *Infrared Studies of Methylthiourea and its Metal Complexes J. Am. Chem. Soc* 81 (1959): pp. 38.