

## Vibrational spectra and theoretical calculations of thiocyanatobi(piperidinyldithiocarbamate)antimony(III)

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### ABSTRACT

The FTIR and FT-Raman spectra of thiocyanatobi(piperidinyldithiocarbamate)antimony(III) have been recorded in the region 4000–400  $\text{cm}^{-1}$ . Utilizing the observed FTIR and FT-Raman data, a whole vibrational assignment and analysis of necessary modes of the compounds were carried out. The optimized molecular geometries, vibrational frequencies were calculated by using Hartree-Fock method with HF/3-21G basis set. The calculated HOMO and LUMO energies show that charge transfer occurs within the molecules. Also, several thermodynamic properties, Mullikan's population analysis, first order hyperpolarizability, several thermodynamic properties and molecular electrostatic potential were done by the HF method.

**Keywords:** Thiocyanatebi(piperidinyldithiocarbamate)antimony(III), FTIR, FT-Raman, HOMO, LUMO.

### INTRODUCTION

Dithiocarbamates, a set of small organic molecules with a strong chelating ability en route for inorganic species have widely been used in the agricultural industry for more than 80 years. Nowadays their applications have not only become apparent as pesticides and fungicides, but also widely used as vulcanization accelerators in the rubber industry. Besides, dithiocarbamates are also of biological significance due to their antibacterial, antituberculosis and antifungal properties. Their anti-oxidant properties make them even more valuable compounds [1, 2]. So many papers on dithiocarbamate complexes of fifth group elements (periodic table) have been available [3]. But, slight consideration has been recompense to the influence of heterocyclic amine (piperidine) of dithiocarbamates on the C-N and C-S bonds and consequently on the electronic structure of these complexes. In piperidine (-NR<sub>2</sub>) plays an important role in the behaviour of dithiocarbamates as ligands [4]. This paper discuss with the synthesis and spectroscopic studies of (SCN) Sb

[SC(S)NC<sub>5</sub>H<sub>10</sub>]<sub>2</sub>, thiocyanatobi (piperidinyldithiocarbamate)antimony(III).

### MATERIALS AND METHODS

#### EXPERIMENTAL

The Iodobi(piperidinyldithiocarbamate)antimony(III) were prepared by the literature method [5, 6]. All the materials are of analytical grade and hence all of them have been used as without further purification. The purity of these compounds was checked by TLC and melting point determination. The FT-IR spectrum was recorded in the range 4000–400  $\text{cm}^{-1}$  and Raman spectra is scanned in the range of 200–350  $\text{cm}^{-1}$ . The UV-visible absorption spectra of title complex have been examined in the range 200–500 nm.

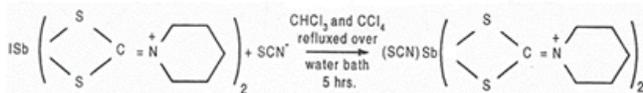
#### COMPUTATIONAL

Density functional theory scheming are carried out for title complex, Hartree-Fock (HF) and DFT calculations using GAUSSIAN 09W program package [7]. Initial geometry generated from the standard geometrical parameters was decreased without any constraint on the potential energy surface at Hartree-Fock level assuming the standard 32-1G basis set.

#### PREPARATION OF COMPLEX

##### Preparation of thiocyanatobi (piperidinyldithiocarbamate)antimony(III):

5.0 mmol of ISb[SC(S)NC<sub>5</sub>H<sub>10</sub>]<sub>2</sub> complex dissolved in 80 ml CHCl<sub>3</sub> and 2.5 mmol of CH<sub>4</sub>N<sub>2</sub>S is dissolved in 25 ml CCl<sub>4</sub> were employed. These two solutions are mixed and heated over water bath for 5 hours. It is allowed to settle, the precipitate is washed with water several times to remove excess of CNS<sup>-</sup> and then dried under vacuum. The sample is recrystallised from CHCl<sub>3</sub>.



## RESULT AND DISCUSSION

The synthesized complex has stable to the atmosphere, brown colour and melting point is 204°C via melting point analysis. Then the Thin layer chromatogram (TLC) is developed with a mobile phase of 6:1  $\text{CCl}_4$  and  $\text{CHCl}_3$  respectively and stationary phase of silica Gel-G for the complex. Separate peaks have been obtained on spraying dilute copper sulphate solution and the synthesized complex have the  $R_f$  value 51.3. In the elemental analysis showed that, 7.42 (7.20) % N, 30.95 (31.21) % C and 3.98 (4.0) % H respectively (figures in parentheses are the calculated values).

## MOLECULAR GEOMETRY

The optimized molecular structure of title complex beside with numbering of atoms is shown in Fig. 1. The corresponding global minimum energy -8927.5367169 is obtained by HF functional with the standard 3-21G basis set and the molecule belongs to  $C_1$  point group symmetry. The calculated optimized geometrical parameters are presented in Tables 1 and 2, respectively.

## FTIR SPECTRA OF THIOCYANATO BIS (PIPERIDINYL DITHIOCARBAMATO) ANTIMONY(III)

The electron donating capacity of the  $-\text{NR}_2$  group in dithiocarbamates affects the electronic structure of the complexes and it appears to play an important role in the preference of one form over the others. Since increasing the electron releasing ability of  $-\text{NR}_2$  group intensifies more electron density on to the sulfur atom, via the  $\pi$  system and, therefore, to the ion of Sb, it causes greater double bond character in  $\text{C}=\text{N}$  bond. This and, therefore, the contribution to one of the resonance forms is reflected in the shifting of  $\text{C}=\text{N}$  to higher frequencies. The FTIR spectrum of title complex is scanned in the range of 400 to 4000  $\text{cm}^{-1}$  and the fig.2 shows the experimental FTIR spectrum which falls between the stretching frequencies of  $\text{C}-\text{N}$  single bonds (1210, 1248.3 and 1248.3  $\text{cm}^{-1}$ ) and  $\text{C}=\text{N}$  bonds (1533.3 and 1500  $\text{cm}^{-1}$ ) and can be assigned to  $\text{C}=\text{N}$ . These frequencies are a characteristic of the dithiocarbamates and they seem to be sensitive to the substituents of Sb atoms. A shift to the higher frequency positions is anticipated to correspond to the electron releasing ability of the  $-\text{NR}_2$  group, but the observed shifts do not follow this order. This irregular behaviour may be due to a hindrance effect, since it is known that the frequency of absorption is influenced by the stereochemistry of the complex. It is clear from the literature, the increased double bond character of  $\text{C}=\text{N}$  bond is associated with decreased double bond character of  $\text{C}=\text{S}$  bond [8-10]. The  $\text{CH}_2$  bending modes are observed at (1453-1447.6  $\text{cm}^{-1}$ ). Among this,  $\text{C}=\text{N}$  stretching,  $\text{CH}_2$  bending and  $\text{C}-\text{N}$  single bond stretching vibrations are more intense and broad than any of the  $\text{C}=\text{S}$  stretching vibrations suggesting only these groups are contributing more to packing of complex molecules in the crystal lattice. Supportively, theoretical FTIR frequency bands are compared with the experimental frequency bands and the assignments mentioned in the Table 1.

## RAMAN SPECTRA OF THIOCYANATO BIS(PIPERIDINYLDITHIOCARBAMATO) ANTIMONY(III)

Raman spectra of thiocyanato bis(piperidinyldithiocarbamate) antimony (III) is shown in fig.3. The spectral characteristics are nearly superimposable to the FTIR spectrum. The vibrations, characteristics of  $\text{C}=\text{N}$  stretching vibrations (1504.2  $\text{cm}^{-1}$ ),  $\text{CH}_2$  bending modes (1441.7, 1344.5  $\text{cm}^{-1}$ ),  $\text{C}-\text{N}$  single bond stretching mode (1258.9  $\text{cm}^{-1}$ ) and  $\text{C}=\text{S}$  stretching modes (between 800 and 1200  $\text{cm}^{-1}$ ), are clearly evident. As there are several peaks due to  $\text{C}=\text{S}$  stretching vibrations, it could be concluded that the groups are proved to be non-equitant. It is also confirmed by its electronic spectrum where in the  $\pi-\pi^*$  transition of  $\text{C}=\text{S}$  groups is intense and gets overlapped with  $\pi-\pi^*$  transition of  $\text{S}=\text{C}=\text{S}$  group.

## ELECTRONIC ABSORPTION SPECTRA

The electronic absorption spectra of the complex show three absorption bands. The absorption bands are attributed to the electronic transitions in the  $\text{NCS}_2$  groups of the parent ligands. The electronic spectrum of the title complex is shown in Fig.4. It shows broad absorption band with maximum 259.3 nm is assigned to an intramolecular charge transfer according to complex. This band to the inter ligand  $\pi-\pi^*$  transition located mainly in the  $\text{C}=\text{S}$  group [11, 12]. This is followed by less intense at 301 nm and 310 nm. Such absorption bands were also reported for iodo bis dialkyldithiocarbamate complex of antimony [13]. The bands due to second and third (301 nm and 310 nm) transitions might have overlapped with the absorption band due to  $\text{s}=\text{c}=\text{s}$  group. These bands depend on the basic character of the  $-\text{NR}_2$  group. As the basic character of piperidine (amine) is increased a slight shift to higher frequencies is observed. This phenomenon mirrors the polar character of the  $\text{C}=\text{N}$  bond.

The optical energy band gap of title complex is calculated by classical Tauc relation as given below  $ah\nu = [A(h\nu - E_g)]^n$  where  $E_g$  is the optical band gap. The optical band gap of the title complex is 4.7815 eV.

## HOMO – LUMO ANALYSIS

Molecular orbitals (HOMO and LUMO) and their properties such as energies are very useful for physicists and chemists and are very important parameters for quantum chemistry. This is also used by the frontier electron density for calculating the most reactive position in  $\pi$ -electron systems and also explains several types of reaction in conjugated system [14]. The conjugated molecules are branded by a small highest occupied molecular orbital – lowest unoccupied molecular orbital (HOMO-LUMO) parting, which is the result of a major degree of intramolecular charge located from the end-capping electron-donor groups to the efficient electron-acceptor groups through  $\pi$ -conjugated path [15].

This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly defined by one electron excitation from the highest occupied molecular orbital to the lowest unoccupied molecular orbital [16]. Recently, the energy gap between HOMO and LUMO has been used to prove the NLO, bioactivity [17, 18] from the inter ligand  $\pi-\pi^*$  transition. Figure 5 shows the HOMO – LUMO energy gap analysis.

HOMO energy = -3.2804 eV

LUMO energy = 0.5007 eV

HOMO—LUMO energy gap = 3.7811 eV

Moreover, the lowering in the HOMO and LUMO energy gap



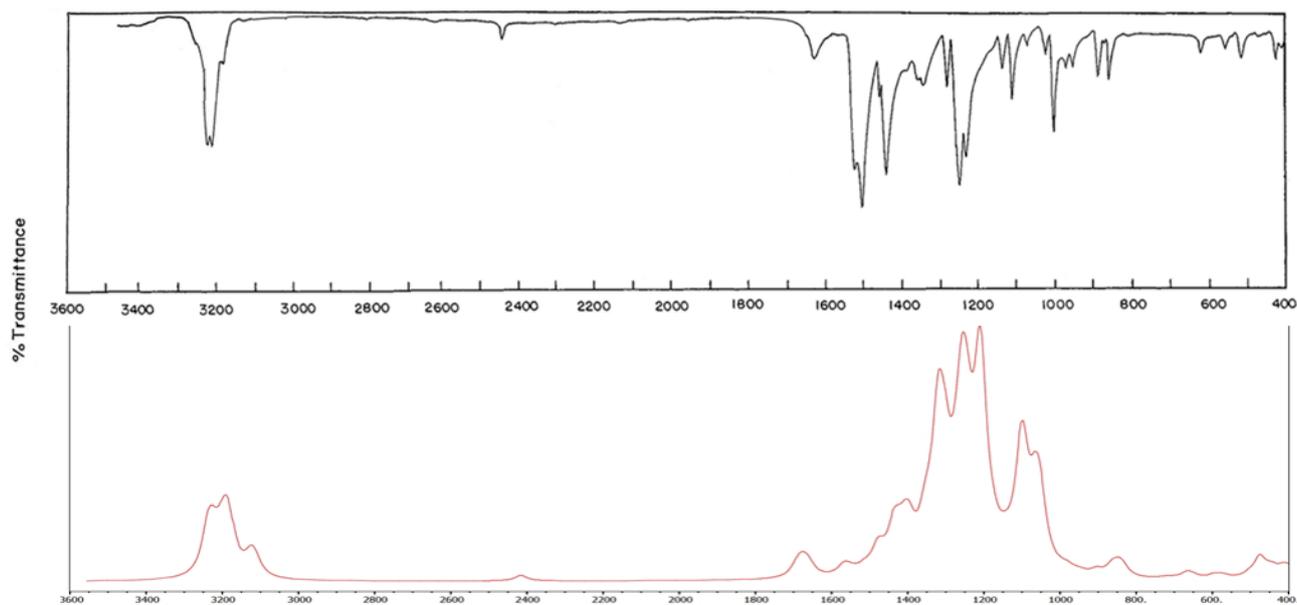


Fig.2 (a) Experimental and (b) Theoretical FTIR spectra of thiocyanatobi (piperidinyldithiocarbamate) antimony (III)

S.No	Experimental		Theoretical		Assignments
	FT-IR (cm <sup>-1</sup> )	Raman (cm <sup>-1</sup> )	FT-IR HF 3-21G (cm <sup>-1</sup> )	Raman HF 3-21G (cm <sup>-1</sup> )	
1	2416	--	2410	--	NCS stretching
2	1533	1504	1558	--	C = N stretching
3	1500	--	1474		
4	1445.1	--	1425	--	C=S strong
4	--	1441	1438		CH <sub>2</sub> bending modes
5	--	--	1434		
5	--	--	1424	--	
5	1360	--	1397		
8	1356	1344	1356		
9	1291	--	1313	1248	C–N single bonds
10	1248	1258	1260		
11	1210	--	1215		
12	1150	1200	--	1200	C=S weak
13	1108	1140	1100	1140	
14	1078	1050	1064	1105	
15	1025	1025	--	1025	
16	1000	100	885	1000	
		850		858	
17	--	415	391	385	Sb– SCN

Table 2. Important FT-IR spectral bands (cm<sup>-1</sup>) and their assignment of thiocyanatobi (piperidinyldithiocarbamate) antimony(III).

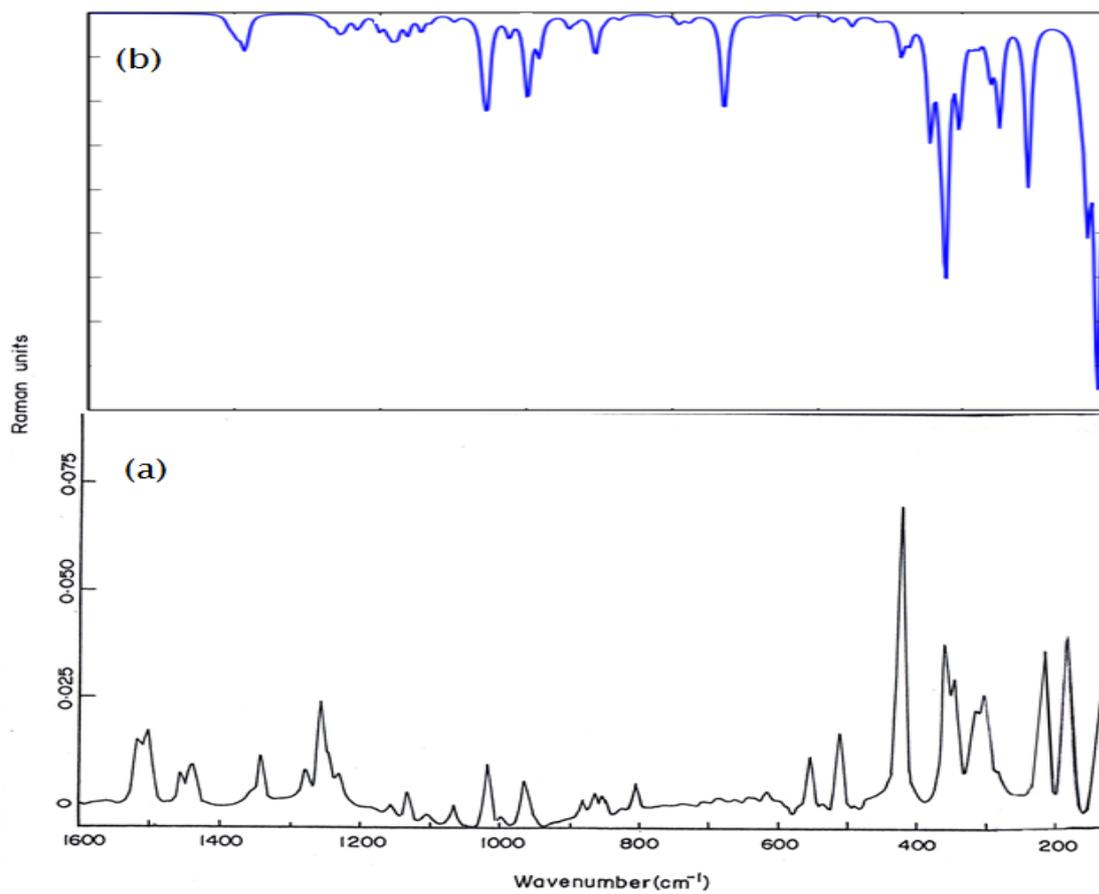


Fig.3 (a) Experimental and (b) Theoretical Raman spectra of thiocyanatobi (piperidinyldithiocarbamato) antimony (III)

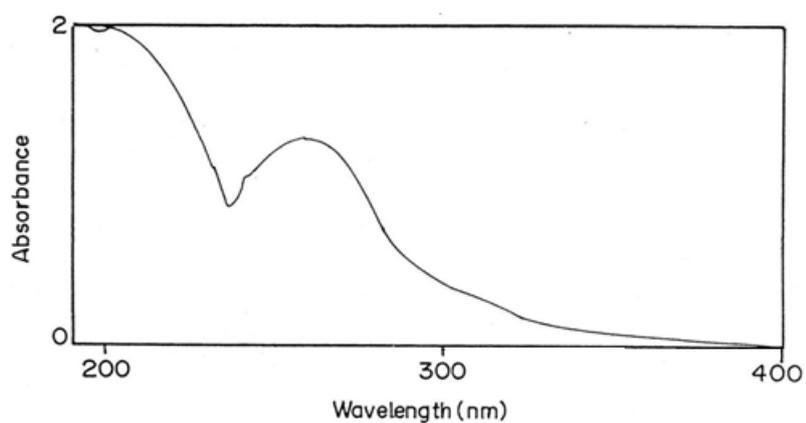


Fig.4 Absorption spectra of thiocyanatobi (piperidinyldithiocarbamato) antimony (III)

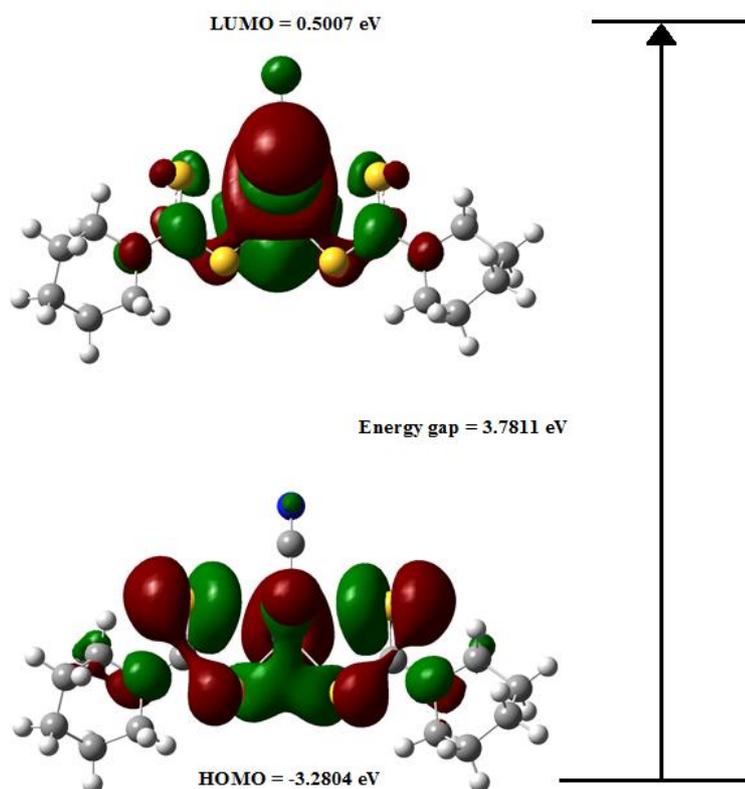


Fig.5 HOMO – LUMO energy gap analysis of thiocyanatobi (piperidinyldithiocarbamato) antimony (III)

$T$ (K)	$S$ (J/mol.K)[ $S^0_m$ ]	$C_p$ (J/mol.K)[ $C^0_{p,m}$ ]	$ddH$ (kJ/mol)[ $H^0_m$ ]
100.00	481.59	186.89	12.28
200.00	638.47	272.74	35.40
298.15	761.47	348.13	65.88
300.00	763.62	349.55	66.53
400.00	874.70	426.12	105.32
500.00	977.67	498.31	151.60
600.00	1074.29	561.92	204.69
700.00	1165.11	616.31	263.68
800.00	1250.51	662.61	327.69
900.00	1330.90	702.27	395.98
1000.00	1406.71	736.52	467.96

Table 3. Thermodynamic properties of thiocyanatobi (piperidinyldithiocarbamato) antimony(III)

Mulliken atomic charges:											
C <sub>1</sub>	-0.0066	C <sub>8</sub>	-0.1042	Sb <sub>15</sub>	0.44204	H <sub>22</sub>	0.06259	H <sub>29</sub>	0.06409	H <sub>36</sub>	0.05943
C <sub>2</sub>	-0.1051	N <sub>9</sub>	-0.2777	S <sub>16</sub>	-0.0278	H <sub>23</sub>	0.06077	H <sub>30</sub>	0.06239	H <sub>37</sub>	0.06297
N <sub>3</sub>	-0.2772	C <sub>10</sub>	-0.1004	C <sub>17</sub>	-0.0716	H <sub>24</sub>	0.06481	H <sub>31</sub>	0.06686	H <sub>38</sub>	0.08098
C <sub>4</sub>	-0.1029	C <sub>11</sub>	-0.0095	S <sub>18</sub>	-0.07	H <sub>25</sub>	0.05836	H <sub>32</sub>	0.07613	H <sub>39</sub>	0.05971
C <sub>5</sub>	-0.0084	C <sub>12</sub>	-0.1028	S <sub>19</sub>	-0.0314	H <sub>26</sub>	0.05935	H <sub>33</sub>	0.05727	H <sub>40</sub>	0.0616
C <sub>6</sub>	-0.1032	C <sub>13</sub>	-0.07	S <sub>20</sub>	0.07147	H <sub>27</sub>	0.06234	H <sub>34</sub>	0.06521	C <sub>41</sub>	-0.0679
C <sub>7</sub>	-0.0038	S <sub>14</sub>	-0.0736	H <sub>21</sub>	0.08753	H <sub>28</sub>	0.07571	H <sub>35</sub>	0.05973	N <sub>42</sub>	-0.2072

Table 4. Atomic charges of thiocyanatobi (piperidinyldithiocarbamato) antimony(III)

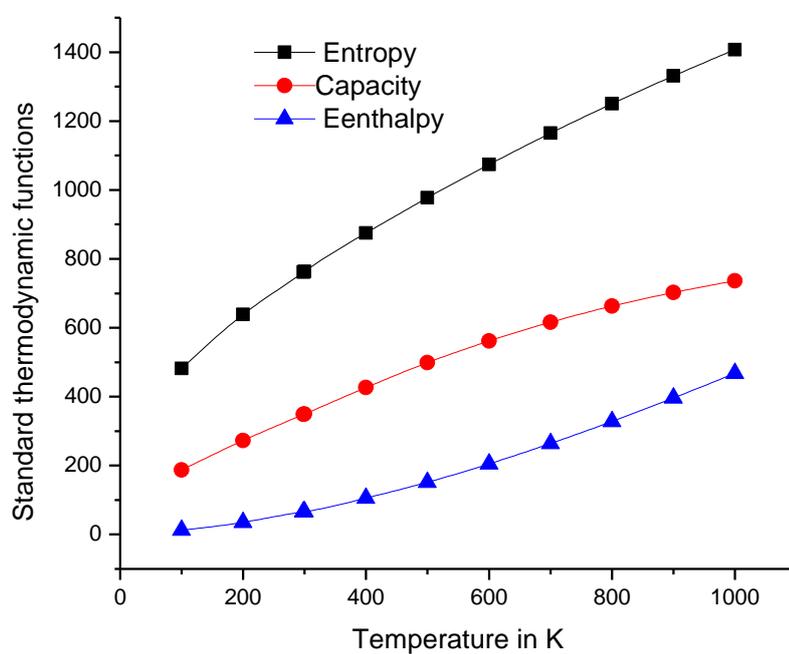


Fig.6 Thermodynamic properties of thiocyanatobi (piperidinyldithiocarbamato) antimony (III)

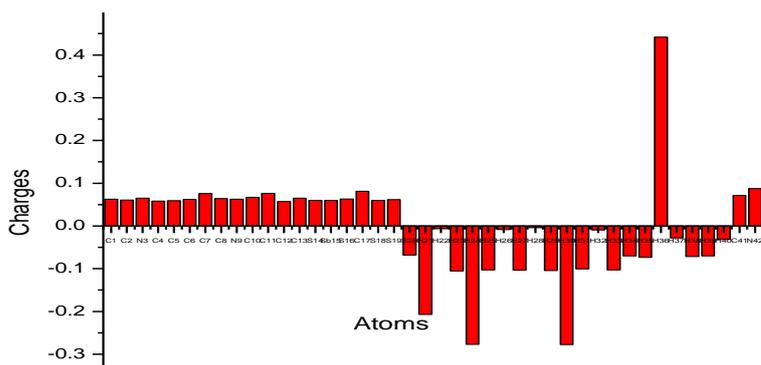


Fig.7 Plot of Mulliken's charges obtained by HF 3-21G method

Polar coordinate (au)		Polar coordinate $\times 10^{-33}$ (esu)	HyperPolar coordinate (au)		HyperPolar coordinate $\times 10^{-33}$ (esu)
$\alpha_{xx}$	226.8913347	33.6252958	$\beta_{xxx}$	15.4689174	133.6406181
$\alpha_{xy}$	-0.1793638	-0.026581715	$\beta_{xxy}$	377.8513606	3264.37126
$\alpha_{yy}$	176.91219	26.21838656	$\beta_{xyy}$	3.2509413	28.08585717
$\alpha_{xz}$	-2.1634314	-0.320620533	$\beta_{yyy}$	-2.2282017	-19.25010295
$\alpha_{yz}$	-0.0452116	-0.006700359	$\beta_{xxz}$	-3.8118087	-32.9313589
$\alpha_{zz}$	88.0022248	13.04192972	$\beta_{xyz}$	-2.401145	-20.744212
			$\beta_{yyz}$	-27.4084679	-236.7899767
			$\beta_{xzz}$	-3.0031839	-25.94540667
			$\beta_{yzz}$	-55.1766673	-476.6877818
			$\beta_{zzz}$	-14.054692	-121.4227006
Polarizabilities ( $\alpha$ )			163.9352 au		$0.024.2952 \times 10^{-30}$ esu
First hyperpolarizability ( $\beta_0$ )			320.6905 au		$2.770542 \times 10^{-30}$ esu
Anisotropy of the Polarizability ( $\Delta\alpha$ )			121.9044 au		$0.01806623 \times 10^{-30}$ esu

Table 5 Polar and Hyperpolar coordinates of thiocyanatobi (piperidinyldithiocarbamate) antimony(III)

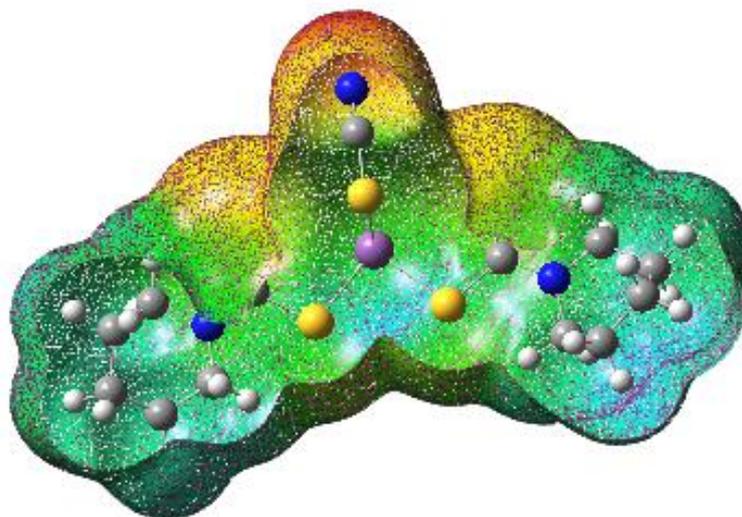


Fig.8 Molecular electrostatic potential of thiocyanato bis (piperidinyldithiocarbamato) antimony (III)

clarifies the eventual charge transfer interactions that take place within the molecule. From the fig.4, HOMO is located over the antimony atom and corbamato groups attached to the piperidiny ring. The HOMO→LUMO transition implies an electron density transfer from corbamato groups to thiocyanato group.

### THERMODYNAMIC PROPERTIES

On the basis of vibrational analyses, the standard thermodynamic functions: heat capacity ( $C_{p,m}^0$ ), entropy ( $S_m^0$ ) and enthalpy ( $H_m^0$ ) were calculated using Perl script THERMO.PL[19] and are listed in Table 3. Then the graph was drawn using temperature in X axis and standard thermodynamic functions in Y axis (fig.6) As observed from Table 3, the values of  $C_{p,m}^0$ ,  $S_m^0$  and  $H_m^0$  all increase with the increase of temperature from 100 to 1000 K, which is attributed to the increase of the molecular vibration as the temperature increases. Table 3. Thermodynamic properties of thiocyanatobi (piperidinyldithiocarbamato) antimony(III)

### MULLIKEN POPULATION ANALYSIS

Mulliken atomic charge calculation has a main role in the application of quantum chemical calculation to molecular system, because atomic charges affect dipole moment, polarizability, electronic structure of molecular systems. The charge distributions calculated by Mulliken method for the equilibrium geometry of title complex are listed in Table 4. The charge distribution on the molecule has an important influence on vibrational spectra. The resultant, Mulliken's plots are shown in Fig. 7.

### PREDICTION OF FIRST HYPERPOLRIZABILITY ( $\beta_0$ )

Analysis of organic metallic compounds having conjugated  $\pi$ -electron. Systems and large hyperpolarizability using IR and Raman spectroscopy has evolved as a subject of research. The potential application of the title complex in the field of non-linear optics demands the study of its structural and bonding features contributing to the hyperpolarizability increase by analysing the vibrational modes using IR and Raman spectroscopy. The HF 3-21G method has been used for the prediction of first hyperpolarizability. The tensor components of first hyperpolarizability ( $\beta_0$ ) were systematically calculated by using the same method as said above. From the computed tensorial components,  $\beta_0$  is the calculated for the title complex by taking into account the Kleimann symmetry relations and square norm of the Cartesian expression for the b tensor. The relevant expressions used for the calculation are shown below.

$$\beta_0 = [(\beta_x^2 + \beta_y^2 + \beta_z^2)]^{1/2}$$

where

$$\beta_x = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})$$

$$\beta_y = (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})$$

$$\beta_z = (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})$$

Theoretically calculated values of first hyperpolarizability and dipole moment are  $2.770542 \times 10^{-30}$  esu and 9.111D. The values of l and b for urea are 1.3732 D and  $0.37289 \times 10^{-30}$  esu respectively. According to the magnitude of the first hyperpolarizability the title complex will have a potential applicant in the development of NLO materials. Table 5 shows the polar and hyperpolar coordinates of title complex.

### MOLECULAR ELECTROSTATIC POTENTIAL (MEP)

MEP at a point in the space around a molecule gives a hint of the net electrostatic effect produced at that point by the total charge distribution (electron + nuclei) of the molecule and relates with the dipole moments, electronegativity, and partial charges chemical reactivity of the molecule. It provides a visual method to understand the relative polarity of the molecule. Thus MEP helps as a useful quantity to explain hydrogen bonding, reactivity and structure-activity relationship of molecule. Potential increases in the order red < orange < yellow < green < blue; red denotes regions of most negative electrostatic potential, which corresponds to an attraction of the proton by the concentrated electron density in the molecule; blue denotes regions of most positive electrostatic potential and green denotes regions of zero potential. Such electrostatic potential surfaces have been plotted for thiocyanato bis (piperidinyldithiocarbamato) in HF 3-21G. Projections of these surfaces along the molecular plane are depicted in Figs.8. It is clear from the figure that the atoms N42, C14, S20, S14 and S18 holds Most negative electrostatic charges and the piperidine ring holds most positive electrostatic charges. This figure provides a visual representation of the chemically active sites and comparative reactivity of atoms.

### CONCLUSION

The work embodied in this dissertation deals with the synthesis and characterization of thiocyanatobi (piperidinyldithiocarbamato) antimony(III) complex and adducts with the ligand piperidinyldithiocarbamato. Then melting point, TLC and elemental analysis was down and the results are given. In FT-IR spectral studies were used to investigate the mode of bonding of the ligands to the metal ion. The FT-IR and Raman spectra of adducts show vibrational frequencies in the region  $1533-1500\text{cm}^{-1}$ ,  $1445.1\text{cm}^{-1}$ ,  $1291-1210\text{cm}^{-1}$  and  $1150-1000\text{cm}^{-1}$  which can be attributed to C=N(stretching), C=S(strong), C-N(stretching), C=S(weak) respectively. These bands indicate that dithiocarbamate moiety is bonded to metal ion in a symmetrical bidentate fashion involving both the sulphur atoms of dithiocarbamate moiety. From the electronic spectra the absorption bands are attributed to the electronic transitions in the NCS<sub>2</sub> groups of the parent ligands is clearly evident. The HOMO-LUMO energy gap clarifies the eventual charge transfer interactions occur within the molecule. Furthermore, the thermodynamic, Mulliken population analysis, first-order hyperpolarizabilities and MEP properties of the molecule have been calculated in order to get vision into the complex.

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