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Synthesis, structural and spectroscopic properties of Tris (morpholinylthiocarbamate) Arsenic (III)

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ABSTRACT

Tris(morpholinylthiocarbamate)arsenic(III) were synthesized successfully and characterized by FTIR. The experimental results were compared with computational methods based on quantum chemical calculation. They are in good agreement with both of them. Structural, optical, vibrational properties also discussed.

Keywords: morpholinylthiocarbamate, FTIR, quantum chemical calculation.

INTRODUCTION

Arsenic is a very widespread element and all human beings are exposed to low doses of arsenic through food. Lower amounts are also consumed from drinking water and air. During the past 50 years inorganic pentavalent (arsenic +5) arsenical compounds of various formulations have been used in considerable quantities for the production of wood preservatives. According to the U.S. Bureau of Mines, the demand for arsenic for the production of wood preservatives has increased from 970 metric tons in 1971 to 14300 metric tons in 1991 (Loebenster, 1992). The most common arsenic based wood preservative is chromated copper arsenate type. Other arsenic based preservatives are ammoniacal copper arsenate, fluor chrome arsenate phenol, ammoniacal copper zinc arsenate and chromated copper arsenate. There are over 336 million cubic feet of treated wood in the United States. The largest proportion of this production (67%) is wood treated with arsenic based preservatives (Barnes and Nicholas, 1992).

Inarida.M[1] has reported the electronic spectra of diethyl dithiocarbamate complexes of central atoms with S^2 electron configuration.

Preparation and study of some arsenic trisdithiocarbamates have reported by A.I.Saklaetal[2]. Five coordinate Bromobis (dibutyl)dtc complex of As was reported by G.E.Monovshakisetal[3]. S.Eskeraretal [4] have reported the syntheses and spectroscopic study of a new series of mixed ligand complex of As(III) with dithioligands. So far organometallic complex of arsenic is an important in the current scenario.

Dithio ligands complexes may find applications in the detection of metal ions in natural waters [5]. Rivers waters [6]. Coastal sea waters, in lubricating oil compositions especially suitable for automobile engines giving low friction coefficient under low temperature and low rotation driving condition. Used as the antioxidant [7]. Stabilization of harmful metals from industrial wastes [8]. in hetero-junction devices as UV(blue) and UV (green) laser diodes and

as IR detectors[9].and separating metal ions from waste streams such as existing and abandoned mines, contaminated ground water, standing contaminated water, low level radioactive waste water[10]. Hence, the preparation and characterization by FTIR and UV spectra of these complexes are more important.

MATERIALS AND METHODS

Experimental:

Arsenic oxide is dissolved in water using sodium hydroxide pellets and neutralised with hydrochloric acid. It is slowly added to the aqueous solution of sodium morpholinyldithiocarbamate. White precipitate obtained, is filtered, dried and recrystallised from chloroform. Arsenic oxide and sodium morpholinyldithiocarbamate are taken in 1:1 molar proportion.

Computational Method:

For supportive evidence to the experimental observations, the quantum computations were performed with the aid of GAUSSIAN 09W software package [11]with internally stored HF/sto-3g* basis set methods.

RESULTS AND DISCUSSION

Molecular geometry

The optimized structure of Tris(morpholinyldithiocarbamato)arsenic(III) complex are shown in the following figure1. The corresponding minimum energy obtained by HF/STO-3G* method were fall on -5526.9763571. From the optimized geometry the optimized structural parameters are tabulated on table 1 and 2.

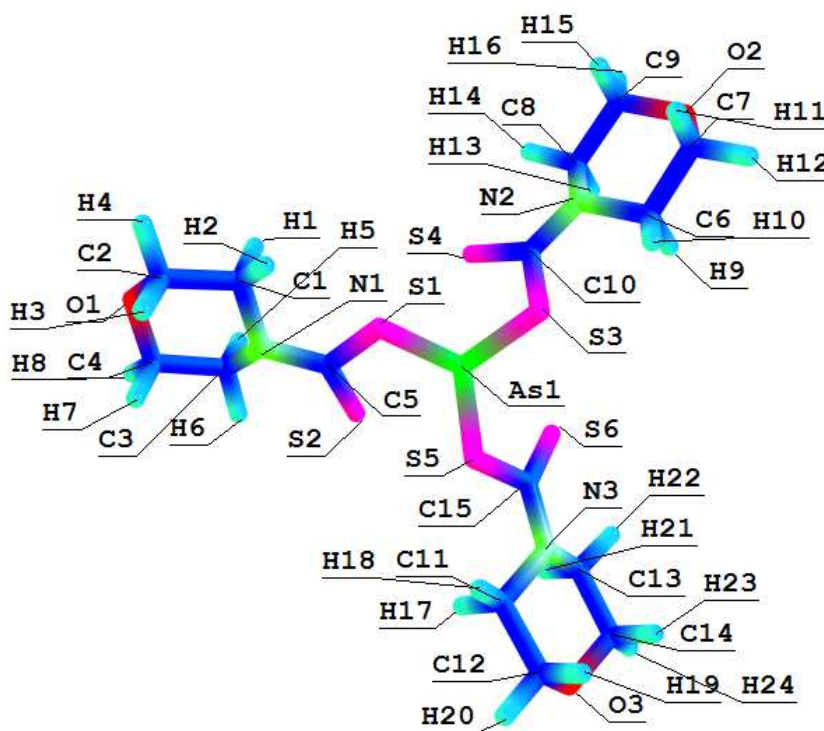


Figure 1: Optimized structure of Tris(morpholinyldithiocarbamato)arsenic III

Table 1: Bond Angle of Tris(morpholinyl)dithiocarbamate) arsenic(III)

Bond Angle			
A(C2-C1-N3)	109.5	A(N13-C15-H41)	110.9
A(C2-C1-H29)	109.3	A(N13-C15-H42)	108.5
A(C2-C1-H30)	109.1	A(N13-C17-S18)	115.7
A(C1-C2-O4)	112.2	A(N13-C17-S19)	124.4
A(C1-C2-H31)	109.0	A(O14-C16-C15)	111.9
A(C1-C2-H32)	109.3	A(O14-C16-H43)	110.9
A(N3-C1-H29)	111.0	A(O14-C16-H44)	107.0
A(N3-C1-H30)	109.8	A(C16-C15-H41)	109.4
A(C1-N3-C5)	112.8	A(C16-C15-H42)	110.3
A(C1-N3-C7)	122.5	A(C15-C16-H43)	109.2
A(H29-C1-H30)	108.1	A(C15-C16-H44)	109.5
A(O4-C2-H31)	111.0	A(H41-C15-H42)	108.2
A(O4-C2-H32)	107.0	A(H43-C16-H44)	108.3
A(C2-O4-C6)	108.3	A(S18-C17-S19)	119.9
A(H31-C2-H32)	108.3	A(C21-C20-N22)	109.5
A(C5-N3-C7)	118.9	A(C21-C20-H45)	109.3
A(N3-C5-C6)	109.4	A(C21-C20-H46)	109.1
A(N3-C5-H33)	110.9	A(C20-C21-O23)	112.1
A(N3-C5-H34)	108.5	A(C20-C21-H47)	109.0
A(N3-C7-S8)	116.1	A(C20-C21-H48)	109.4
A(N3-C7-S10)	124.8	A(N22-C20-H45)	111.1
A(O4-C6-C5)	111.9	A(N22-C20-H46)	109.8
A(O4-6-H35)	110.9	A(C20-N22-C24)	112.9
A(O4-C6-H36)	107.0	A(C20-N22-C26)	122.4
A(C6-C5-H33)	109.4	A(H45-C20-H46)	108.1
A(C6-C5-H34)	110.3	A(O23-C21-H47)	111.0
A(C5-C6-H35)	109.2	A(O23-C21-H48)	107.0
A(C5-C6-H36)	109.5	A(C21-O23-C25)	108.3
A(H33-C5-H34)	108.2	A(H47-C21-H48)	108.3
A(H35-C6-H36)	108.3	A(C24-N22-C26)	118.7
A(S8-C7-S10)	119.1	A(N22-C24-C25)	109.6
A(C7-S8-As9)	91.1	A(N22-C24-H49)	111.0
A(S8-As9-S18)	95.5	A(N22-C24-H50)	108.4
A(S8-As9-S27)	94.6	A(N22-C26-S27)	115.7
A(S18-As9-S27)	94.4	A(N22-C26-S28)	124.6
A(As9-S18-C17)	92.4	A(O23-C25-C24)	112.1
A(As9-S27-C26)	91.3	A(O23-C25-H51)	110.9
A(C12-C11-N13)	109.5	A(O23-C25-H52)	106.9
A(C12-C11-H37)	109.3	A(C25-C24-H49)	109.5
A(C12-C11-H38)	109.0	A(C25-C24-H50)	110.2
A(C11-C12-O14)	112.2	A(C24-C25-H51)	109.2
A(C11-C12-H39)	109.0	A(C24-C25-H52)	109.4
A(C11-C12-H40)	109.3	A(H49-C24-H50)	108.1
A(N13-C11-H37)	111.1	A(H51-C25-H52)	108.3
A(N13-C11-H38)	109.8	A(S27-C26-S28)	119.6
A(C11-N13-C15)	113.0	A(O14-C12-H40)	107.0
A(C11-N13-C17)	122.3	A(C12-O14-C16)	108.3
A(H37-C11-H38)	108.1	A(C15-N13-C17)	118.8
A(O14-C12-H39)	110.9	A(N13-C15-C16)	109.5

Vibrational analysis

The FTIR spectrum of tris(morpholinyl)dithiocarbamate) arsenic(III) complex is shown in Figure 2, this complex shows C=S stretching vibration at lower wave number, 1470.4 cm^{-1} due to less nitrogen electron pair delocalization. The CH_2 bending modes are assigned to peaks at 1435.2, 1384.6 and 1356.0 cm^{-1} . The C-N single bond stretching vibrations are positioned between 1200 and 1300 cm^{-1} . The C=S stretching vibrations are intense and sharp between 800 and 1200 cm^{-1} . Above experimental data compared with computationally calculated data, they were good agreement with each other. Vibrational parameters are tabulated in table 3.

Table 2: Bond Length of Tris(morpholinyldithiocarbamate) arsenic(III)

Bond Length			
R(C1-C2)	1.553	R(N13-C15)	1.477
R(C1-N3)	1.480	R(N13-C17)	1.418
R(C1-H29)	1.094	R(O14-C16)	1.438
R(C1-H30)	1.086	R(C15-C16)	1.551
R(C2-O4)	1.437	R(C15-H41)	1.094
R(C2-H31)	1.095	R(C15-H42)	1.088
R(C2-H32)	1.092	R(C16-H43)	1.095
R(N3-C5)	1.477	R(C16-H44)	1.092
R(N3-C7)	1.417	R(C17-S18)	1.757
R(O4-C6)	1.438	R(C17-S19)	1.594
R(C5-C6)	1.551	R(C20-C21)	1.553
R(C5-H33)	1.094	R(C20-N22)	1.481
R(C5-H34)	1.088	R(C20-H45)	1.094
R(C6-H35)	1.095	R(C20-H46)	1.086
R(C6-H36)	1.092	R(C21-O23)	1.436
R(C7-S8)	1.756	R(C21-H47)	1.095
R(C7-S10)	1.595	R(C21-H48)	1.092
R(S8-As9)	2.181	R(N22-C24)	1.477
R(As9-S18)	2.184	R(N22-C26)	1.418
R(As9-S27)	2.187	R(O23-C25)	1.438
R(C11-C12)	1.553	R(C24-C25)	1.552
R(C11-N13)	1.480	R(C24-H49)	1.094
R(C11-H37)	1.094	R(C24-H50)	1.088
R(C11-H38)	1.086	R(C25-H51)	1.095
R(C12-O14)	1.437	R(C25-H52)	1.092
R(C12-H39)	1.095	R(C26-S27)	1.755
R(C12-H40)	1.092	R(C26-S28)	1.594

Table 3: vibrational parameters of Tris(morpholinyldithiocarbamate) arsenic(III)

Frequency	IR intensity	Raman activity	Experimental	Assignment
409.3413	0.0241	0.5302		
468.2124	6.9922	1.7589		
470.0085	0.0121	11.2782		
805.000	0.9292	-	800	C=S stretching
1185.8364	52.0989	0.7817		
1187.2931	7.9026	0.4355		
1201.00	54.703	-		C=S stretching
1216.0863	58.0543	38.8438		C-N stretching
1219.00	273.523	-		C-N stretching
1248.1102	0.5244	0.5166		
1248.1122	0.5232	0.516		
1248.1824	1.207	0.2818		
1287.8552	160.8457	4.6628		
1287.8604	160.84	4.6611		C-N stretching
1291.1226	0.0002	21.8747		
1320.2072	5.9997	23.0256		
1320.2176	6.0035	23.0158		
1324.459	34.5053	53.783		C-N stretching
1354.000	33.8365	-	1356.0	CH ₂ bending
1381.000	139.68865	-	1384.6	CH ₂ bending
1390.000	533.00622	-		CH ₂ bending
1393.921	106.5703	4.3499		
1393.9242	106.384	4.3477		
1395.1376	7.7228	17.2341		
1409.2481	475.0029	15.7479		CH ₂ bending
1409.2504	474.9575	15.7579		
1417.4534	30.207	30.8772		
1421.9971	29.002	3.9183		
1421.9993	28.9488	3.9091		
1423.645	73.4468	25.9539		
1435.0000	141.85542	-	1435.2	CH ₂ bending
1450.7325	7.8572	3.5106		

1450.7337	7.8429	3.5112		
1451.2846	0.0009	11.0406		
1471.000	27.52791	-	1470.4	C=S stretching weak
1517.5335	6.0708	3.654		
1518.5284	83.9229	6.7232		
1528.9666	29.593	29.025		
1529.9754	20.6553	4.6552		
1588.7754	261.9369	50.759		

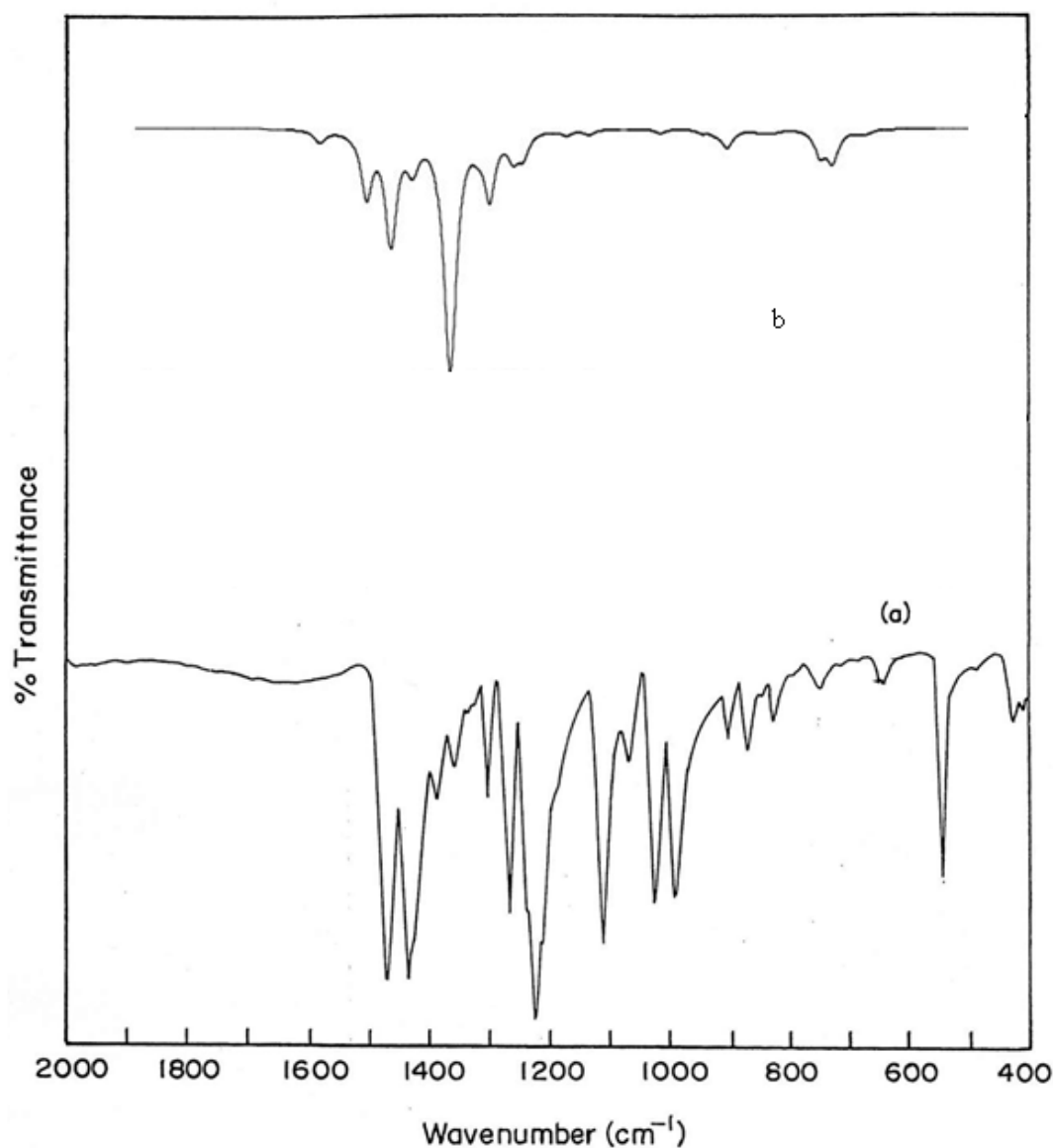


Figure 2 FTIR Experimental (a) and theoretical spectrum (b) of Tris(morpholinyldithiocarbamate) arsenic (III)

UV analysis

The UV theoretical spectrum of the title complex is shown in figure 3. The spectrum of the title complex gives an intense peak at 339.12 nm. This is followed by very less intense peaks with maximum at 335.93 nm and 332.76 nm. These result good agreement with computational calculation

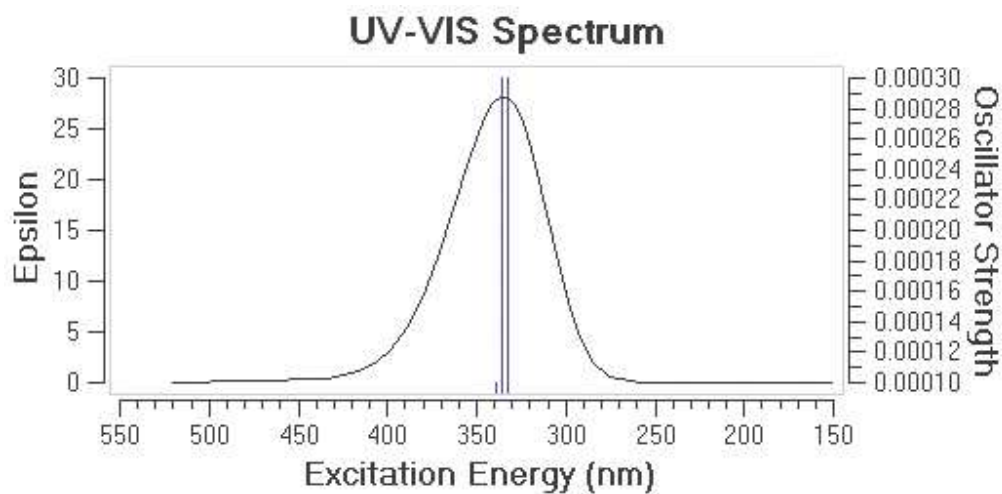


Figure 3: UV theoretical spectrum

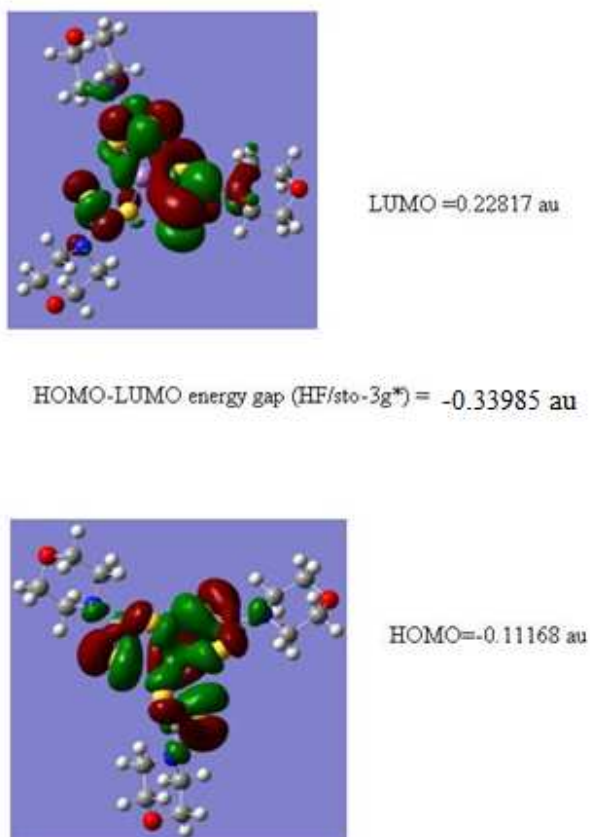


Figure 4: HOMO-LUMO image

HOMO-LUMO analysis

The energies of two important molecular orbital of the complex of arsenic III, the highest occupied molecules (HOMO) and the lowest unoccupied molecules (LUMO) were calculated and are presented in figure4. The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties [12] Molecular orbital (HOMO and LUMO) and their properties are very useful for molecular physics. The conjugated molecules are characterized by a small highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO-LUMO) separation, which is the result of a significant degree of intramolecular charge transfer from the electron-donor molecules to the efficient electron-acceptor molecules through π - conjugated path [13]. This electronic absorption leads to the transition of zero level energy to the first level excited energy state [14]

HOMO energy (HF/sto-3g*) = -0.11168 au

LUMO energy (HF/sto-3g*) = 0.22817 au

HOMO-LUMO energy gap (HF/sto-3g*) = -0.33985 au

The HOMO is located over the arsenic atom and carbamate groups attached to the morpholinyl ring. The HOMO→LUMO transition implies an electron density transfer from arsenic atom to morpholinyl ring. Moreover, these orbital significantly overlap in their position for Tris(morpholinyl)dithiocarbamate) arsenic(III) as shown in Figure 4. The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule.

Atomic charges:

Table 4: Atomic charges of tris(morpholinyl)dithiocarbamate) arsenic(III)

Mulliken atomic charges:					
1	C	-0.011976	27	S	0.109392
2	C	0.016990	28	S	-0.140082
3	N	-0.288462	29	H	0.064456
4	O	-0.259569	30	H	0.074095
5	C	-0.007317	31	H	0.054304
6	C	0.016576	32	H	0.070997
7	C	0.111707	33	H	0.063227
8	S	0.108663	34	H	0.088854
9	As	-0.263395	35	H	0.054620
10	S	-0.141574	36	H	0.070630
11	C	-0.012183	37	H	0.064474
12	C	0.016839	38	H	0.073513
13	N	-0.288436	39	H	0.054608
14	O	-0.258903	40	H	0.071235
15	C	-0.007002	41	H	0.063513
16	C	0.016632	42	H	0.088150
17	C	0.113040	43	H	0.054897
18	S	0.109191	44	H	0.070957
19	S	-0.140911	45	H	0.064403
20	C	-0.011744	46	H	0.073981
21	C	0.017333	47	H	0.054477
22	N	-0.288644	48	H	0.070902
23	O	-0.259668	49	H	0.062922
24	C	-0.007197	50	H	0.088274
25	C	0.016607	51	H	0.054309
26	C	0.111355	52	H	0.070937

The charge distribution of Tris(morpholinyl)dithiocarbamate)arsenic(III) shows that the arsenic and carbamate, oxygen atoms have negative charges whereas all the hydrogen atoms have positive charges. The maximum atomic charge is obtained for S and C when compared with other atoms. This is due to the attachment of negatively charged carbamate group. Various atomic charges tabulated in table 4.

Thermodynamic properties

On the basis of vibrational analyses and statistical thermodynamics, 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 [15] and are listed

in Table (5). As observed from Table 8, 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 enhancement of the molecular vibration as the temperature increases.

Table 5: Thermodynamic properties

T (K)	S (J/mol.K) [S_m^0]	Cp (J/mol.K) [$C_{p,m}^0$]	ddH (kJ/mol) [H_m^0]
100.00	494.04	204.99	12.64
200.00	674.28	323.24	39.33
298.15	821.88	422.04	75.93
300.00	824.50	423.89	76.71
400.00	960.17	523.90	124.11
500.00	1087.38	618.11	181.29
600.00	1207.56	700.63	247.34
700.00	1320.97	770.57	321.00
800.00	1427.83	829.57	401.09
900.00	1528.51	879.66	486.62
1000.00	1623.47	922.57	576.78

CONCLUSION

In this study, we have performed an experimental and quantum computational study on Tris (morpholinyl)dithiocarbamate arsenic (III) complex. Theoretical spectral frequencies FT-IR and UV are obtained. The theoretical data are in good agreement with experimental data of FT-IR. The charge transfer from lone pair of atom to its anti-bonding orbital is more. The HOMO LUMO energy strongly supports the presence of intramolecular energy transfer with the molecule.

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