

Experimental and quantum chemical calculations of tris(morpholinylthiocarbamate)antimony (III)

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ABSTRACT

In this paper, vibrational analysis of tris(morpholinylthiocarbamate)antimony(III) were presented using experimental techniques and quantum chemical calculations. HOMO-LUMO properties and First hyperpolarizability also discussed.

Keywords: Tris(morpholinylthiocarbamate)antimony(III), HOMO-LUMO, NLO.

INTRODUCTION

Dithiocarbamate complexes are useful in water purification, metal ion detector in water, lubricating oil and potent antioxidant agent, IR spectral detector. So dithiocarbamate complexes are interested in the current research. Antimonydithiocarbamate complexes have potential applications in the field of medical, industrial and communication. Hence it is catalysed us to prepare arsenic dithiocarbamate complexes with simple synthesis route.

Synthesis and spectral study of new iodobis (dialkyldithiocarbamate) complex of antimony have been reported by R.R.Schanta et al.[1] and the computational study of Tris complex of dithiocarbamate of arsenic have been reported by P.S.Joseph et al.[2] The syntheses and spectroscopic study of a new series of mixed ligand complexes of antimony with dithioligands have been reported by S.Eskerar et al.[3]. FMN Khein et al. [4] have reported the indirect determination of antimony by molecular emission cavity and extraction as their diethyldithiocarbamate.

MATERIALS AND METHODS

Experimental Method

Antimony oxide is dissolved in concentrated hydrochloric acid. It is neutralized with sodium hydroxide solution. It is slowly added to the aqueous solution of sodium morpholinylthiocarbamate. Antimony oxide and sodium morpholinylthiocarbamate are taken in 1:1 molar proportion. White precipitate obtained, is filtered, dried and recrystallized from chloroform.

Computational Method

For supportive evidence to the experimental observations, the ab initio computations were performed with the aid of GAUSSIAN 09W[5] software package with internally stored HF/sto-3g* basis set methods. At first, the global minimum energy structure of the title molecule was optimized. Subsequently, the vibrational normal mode wavenumbers in association with the molecule were derived along with their IR intensity, Raman activity, HOMO-LUMO properties, thermo-dynamical properties also studied.

RESULTS AND DISCUSSION**Vibrational spectra**

The FTIR spectrum of Tris (morpholinyl)dithiocarbamate) antimony(III) is shown in Figure.1. this complex shows C = S stretching vibrations 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} .

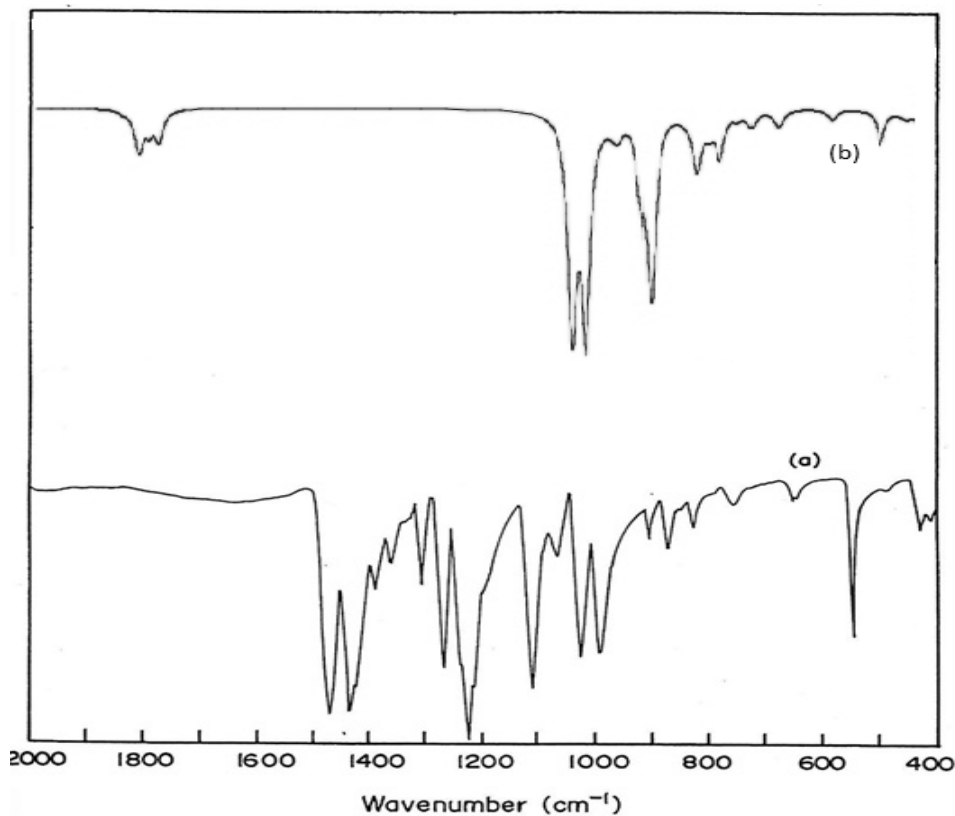


Figure 1. FTIR spectra of Tris(morpholinyl)dithiocarbamate)antimony(III) (a) Experimental (b) Computational

Table 1. Vibrational Frequency Assignments

Frequency	FT-IR HF/sto-3g*	Raman	Experiment value	Vibrational Assignment
386.4832	8.3658	44.0916		
413.8003	1.1862	4.7318		
416.1499	0.0002	35.6283		
438.9607	13.5387	2.2068		
460.3974	7.0701	1.4671		
462.1442	1.2831	7.0847		
519.9673	2.5819	0.3067		
539.0914	70.1804	4.1837		
541.2382	35.0197	10.0098		
615.8629	0.1265	0.5539		
617.6889	0.082	1.1605		
714.5842	17.0361	0.5267		
869.5614	0.0136	53.6635	800	
915.0384	26.8548	14.593		
925.0877	27.489	10.2767		
932.2754	0.1283	3.1643		
1016.1213	42.8773	15.5378		
1066.7285	11.4562	34.208		
1177.7545	37.857	0.2702		
1221.9929	138.4987	4.5284	1200	C=S sharp
1245.7404	3.7309	21.2959	1200	C-N
1245.757	5.8209	1.8304		
1275.7109	1.9735	1.7508	1356.0	CH ₂
1391.8648	395.3873	36.232	1300	C-N
1391.8788	395.1981	36.2313	1384.6	CH ₂
1397.3199	118.616	60.5346		
1426.6573	33.6688	1.2695		
1426.9997	79.7428	0.407		
1433.7944	51.8087	33.1457		
1434.7218	12.4828	19.0117	1435.2	CH ₂
1513.1392	11.9799	1.5136	1470.4	C=S
1528.579	26.6342	6.3904		
1561.5804	6.9135	15.2641		
1632.3754	431.2773	35.6297		
1685.7114	490.2738	8.3322		
1689.3919	75.6911	30.5251		
3213.6306	6.3781	13.7677		

HOMO-LUMO analysis

A deeper understanding of chemical reactive can be gained by this electronic absorption corresponds to the transition from the ground to the first excited state and it is mainly described by one electron excitation from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO)[6,7].

HOMO energy=-0.22844 au

LUMO energy= -0.09783 au

HOMO - LUMO energy gap= -0.13061 au

The HOMO is located over the antimony atom and corbamato groups attached to the morpholinylring. The HOMO→LUMO transition implies an electron density transfer from antimony atom to morpholinyl ring. Moreover, these orbital significantly overlap in their position for Tris(morpholinyl)dithiocarbamate) antimony(III) (Fig.3). The HOMO and LUMO energy gap explains the eventual charge transfer interactions takingplace within the molecule.

Molecular geometry

The optimized structure of Tris(morpholinyl)dithiocarbamate) antimony(III) complex are shown in the following fig(4). The corresponding minimum energy obtained by HF/3-21G*method were fall on -9624.1135476. From the optimized geometry the optimized structural parameters are tabulated on table (2a & 2b).

Table 2a. Bond length optimized for HF/STO-3G*

Bond Length			
R(1C-2C)	1.529	R(14O-16C)	1.440
R(1C-3N)	1.484	R(15C-16C)	1.528
R(1C-29H)	1.081	R(15C-41H)	1.082
R(1C-30H)	1.075	R(15C-42H)	1.074
R(2C-4O)	1.438	R(16C-43H)	1.084
R(2C-31H)	1.084	R(16C-44H)	1.079
R(2C-32H)	1.079	R(17C-18S)	1.820
R(3N-5C)	1.485	R(17C-19S)	1.763
R(3N-7C)	1.304	R(20C-21C)	1.529
R(4O-6C)	1.440	R(20C-22N)	1.484
R(5C-6C)	1.528	R(20C-45H)	1.081
R(5C-33H)	1.082	R(20C-46H)	1.075
R(5C-34H)	1.074	R(21C-23O)	1.438
R(6C-35H)	1.084	R(21C-47H)	1.084
R(6C-36H)	1.079	R(21C-48H)	1.079
R(7C-8S)	1.820	R(22N-24C)	1.485
R(7C-10S)	1.763	R(22N-26C)	1.304
R(11C-12C)	1.529	R(23O-25C)	1.440
R(11C-13N)	1.484	R(24C-25C)	1.528
R(11C-37H)	1.081	R(24C-49H)	1.082
R(11C-38H)	1.075	R(24C-50H)	1.074
R(12C-14O)	1.438	R(25C-51H)	1.084
R(12C-39H)	1.084	R(25C-52H)	1.079
R(12C-40H)	1.079	R(26C-27S)	1.820
R(13N-15C)	1.485	R(26C-28S)	1.763
R(13N-17C)	1.304		

Table 2b. Bond angle optimized for HF/STO-3G*

Bond Angle					
A(2C-1C-3N)	108.1	A(12C-11C-13N)	108.1	A(21C-20C-22N)	108.1
A(2C-1C-29H)	109.7	A(12C-11C-37H)	109.7	A(21C-20C-45H)	109.7
A(2C-1C-30H)	111.3	A(12C-11C-38H)	111.3	A(21C-20C-46H)	111.3
A(1C-2C-4O)	110.0	A(11C-12C-14O)	110.0	A(20C-21C-23O)	110.0
A(1C-2C-31H)	109.4	A(11C-12C-39H)	109.4	A(20C-21C-47H)	109.4
A(1C-2C-32H)	110.5	A(11C-12C-40H)	110.5	A(20C-21C-48H)	110.5
A(3N-1C-29H)	107.5	A(13N-11C-37H)	107.5	A(22N-20C-45H)	107.5
A(3N-1C-30H)	110.1	A(13N-11C-38H)	110.1	A(22N-20C-46H)	110.1
A(1C-3N-5C)	111.3	A(11C-13N-15C)	111.3	A(20C-22N-24C)	111.3
A(1C-3N-7C)	125.3	A(11C-13N-17C)	125.3	A(20C-22N-26C)	125.3
A(29H-1C-30H)	110.0	A(37H-11C-38H)	110.0	A(45H-20C-46H)	110.0
A(4O-2C-31H)	110.6	A(14O-12C-39H)	110.6	A(23O-21C-47H)	110.6
A(4O-2C-32H)	106.7	A(14O-12C-40H)	106.7	A(23O-21C-48H)	106.7
A(2C-4O-6C)	112.5	A(12C-14O-16C)	112.5	A(21C-23O-25C)	112.5
A(31H-2C-32H)	109.7	A(39H-12C-40H)	109.7	A(47H-21C-48H)	109.7
A(5C-3N-7C)	123.4	A(15C-13N-17C)	123.4	A(24C-22N-26C)	123.4
A(3N-5C-6C)	108.1	A(13N-15C-16C)	108.1	A(22N-24C-25C)	108.1
A(3N-5C-33H)	107.5	A(13N-15C-41H)	107.5	A(22N-24C-49H)	107.5
A(3N-5C-34H)	109.4	A(13N-15C-42H)	109.4	A(22N-24C-50H)	109.4
A(3N-7C-8S)	118.4	A(13N-17C-18S)	118.4	A(22N-26C-27S)	118.4
A(3N-7C-10S)	123.9	A(13N-17C-19S)	123.9	A(22N-26C-28S)	123.9
A(4O-6C-5C)	110.0	A(14O-16C-15C)	110.0	A(23O-25C-24C)	110.0
A(4O-6C-35H)	110.5	A(14O-16C-43H)	110.5	A(23O-25C-51H)	110.5
A(4O-6C-36H)	106.6	A(14O-16C-44H)	106.6	A(23O-25C-52H)	106.6
A(6C-5C-33H)	109.8	A(16C-15C-41H)	109.8	A(25C-24C-49H)	109.8
A(6C-5C-34H)	111.6	A(16C-15C-42H)	111.6	A(25C-24C-50H)	111.6
A(5C-6C-35H)	109.4	A(15C-16C-43H)	109.4	A(24C-25C-51H)	109.4
A(5C-6C-36H)	110.6	A(15C-16C-44H)	110.6	A(24C-25C-52H)	110.6
A(33H-5C-34H)	110.3	A(41H-15C-42H)	110.3	A(49H-24C-50H)	110.3
A(35H-6C-36H)	109.7	A(43H-16C-44H)	109.7	A(51H-25C-52H)	109.7
A(8S-7C-10S)	117.7	A(18S-17C-19S)	117.7	A(27S-26C-28S)	117.7

Atomic charges of Tris(morpholinyldithiocarbamato)antimony (III)

Table 6.4a Atomic charges of Tris (morpholinyldithiocarbamato)antimony(III)

Mulliken atomic charges:					
1	C	-0.227867	27	S	-0.133970
2	C	-0.078239	28	S	-0.126227
3	N	-0.760189	29	H	0.259685
4	O	-0.633703	30	H	0.298103
5	C	-0.223791	31	H	0.219197
6	C	-0.083049	32	H	0.238324
7	C	-0.211668	33	H	0.254941
8	S	-0.133976	34	H	0.305030
9	Sb	1.330315	35	H	0.220818
10	S	-0.126279	36	H	0.239171
11	C	-0.227882	37	H	0.259690
12	C	-0.078239	38	H	0.298127
13	N	-0.760192	39	H	0.219201
14	O	-0.633700	40	H	0.238330
15	C	-0.223784	41	H	0.254952
16	C	-0.083051	42	H	0.305008
17	C	-0.211700	43	H	0.220819
18	S	-0.133920	44	H	0.239177
19	S	-0.126210	45	H	0.259688
20	C	-0.227872	46	H	0.298114
21	C	-0.078243	47	H	0.219199
22	N	-0.760190	48	H	0.238329
23	O	-0.633702	49	H	0.254948
24	C	-0.223788	50	H	0.305013
25	C	-0.083048	51	H	0.220816
26	C	-0.211687	52	H	0.239174

The charge distribution of Tris(morpholinyldithiocarbamato)antimony (III) shows that the nitrogen and carbamato, oxygen atoms have negative charges whereas all the hydrogen atoms have positive charges. The maximum atomic charge is obtained for Sb when compared with other atoms. This is due to the attachment of negatively charged carbamato group. Various atomic charges tabulated in table (3).

Thermal 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[8] and are listed in Table (4). As observed from Table 4.7.1a, 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(4): Thermodynamic properties of Tris(morpholinyldithiocarbamate) Antimony(III)

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

Predication of first hyperpolarizability

The first hyperpolarizability (β_o) of the title complex and the related properties (β_o, α_o) were calculated using the HF/sto-3g* basis set, based on the finite field approach. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. Theoretically calculated values of hyperpolarizability are $2707.33895 \times 10^{-33}$ esu as shown in the table (5). We can conclude that the title complex is an attractive object for future studies of non-linear optical application.

Table (5) Polar and Hyper polar oordinates

Polar coordinate (au)	Polar coordinate $\times 10^{-33}$ (esu)	HyperPolar coordinate (au)	HyperPolar coordinate $\times 10^{-33}$ (esu)
α_{xx}	369.6313309	β_{xxx}	-220.2834646
α_{xy}	-0.0172152	β_{xxy}	1196.499614
α_{yy}	369.6229844	β_{yyv}	219.8911657
α_{xz}	0.0030315	β_{yyy}	-1191.632631
α_{yz}	0.6735184	β_{xzz}	-202.2232505
α_{zz}	254.1174061	β_{yyz}	1.3866725
Hyperpolarizability (β)		β_{yzz}	-216.0612651
		β_{zzz}	-0.0162837
		β_{zzz}	-3.0619563
		β_{zzz}	104.9151753
			313.374805 au
			2707.33895 esu

CONCLUSION

In this work, we have performed an experimental and quantum computational study on Tris (morpholinyl)dithiocarbamate) antimony (III) complex. Theoretical spectral frequencies FT-IR obtained. The theoretical data are in good agreement with experimental data of FT-IR. The HOMO and LUMO energy gape explains the charge transfer interactions taking place within the molecule. From the first hyperpolarizability calculation the title complex contains the NLO property.

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