

# Vibrational Analysis and NLO Impact of Coordinate Covalent Bond on Bis (Thiourea) Cadmium Bromide: A Comparative Computational Study

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## Abstract

In the present research work, the thorough experimental and theoretical investigation is made on the crystal compound; Bis (thiourea) Cadmium Bromide (BTCB) by recording FT-IR, FT-Raman and UV Visible spectra. The computational calculations are carried out by HF, CAM-B3LYP, DFT (B3LYP and B3PW91) and LSDA methods with 3-21 G (d, p) basis sets and the corresponding results were tabulated. The compound belongs to orthorhombic crystal class with space group of Pn2<sub>1</sub>a and point group of symmetry C<sub>2v</sub>. The NLO properties have been studied by calculating average Polarizability and diagonal hyperpolarizability. The physical and chemical properties of the coordination complex due to the Vander Waals link are found to be enriched. The thermodynamical parameters of TGA and DSC are compared with calculated values obtained from NIST thermodynamical program. The variation of specific heat capacity, entropy and enthalpy with respect to different temperature are displayed in the graph and are discussed.

**Keywords:** Bis(thiourea) cadmium bromide; BTCB; NLO; Polarizability; Diagonal hyperpolarizability; NIST; TGA-DSC

## Introduction

Now a day, the production of NLO crystal materials using organic compounds with the addition of metal oxides has much attention due to its tremendous electronic and optical applications. Generally, the crystals made up of organic amine derivatives have rich NLO properties. The high symmetry organic amine derivatives; Thiourea has high NLO coefficients with stable physical and chemical properties. Generally, the metal oxide materials are able to have rich semiconducting properties and optical activities. When such metal oxides are coupled with thiourea, the physiochemical, electrical and optical properties are enriched. Due to the symmetrical presence of S and N donors in thiourea, the metal oxides are connected through coordinate covalent bonds strongly. It is a new attempt to fabricate metal organic compound; Bis(thiourea) Cadmium Bromide (BTCB). After careful screening the literature, it is found that no quantum chemical computational work has been made on Bis (thiourea) Cadmium Bromide (BTCB) so far. In this present work, the structural properties, vibrational study, frontier molecular analysis, NMR, UV-Visible spectral investigations have been carried out. The electrical, optical and chemical parameters have been calculated by using HF, CAM, DFT and LSDA method with 3-21 G (d, p) basis set. The optical activity and NLO property analysis have been performed using appropriate quantum computational tools. Other industrial uses of thiourea include the production of flame retardant resins and vulcanization accelerators. Thiourea is used as an auxiliary agent in light-sensitive photocopy paper and almost all other types of copy paper.

## Specification on Recording of Spectra

- The FT-IR and FT-Raman spectra are recorded in Bruker IFS 66V spectrometer in the range of 4000-100 cm<sup>-1</sup> with the spectral resolution is  $\pm 2$  cm<sup>-1</sup>.
- The Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) curves for BTCB are obtained using Simultaneous Thermo gravimetric Analyzer (STA) 409C (NETZSCH) at a heating rate of 10°C/min in nitrogen.
- The absorption spectrum of BTCB is recorded using Varion Cary

5E UV-Vis-NIR spectrophotometer in the range 200-700 nm with high resolution.

## Computational Details

In this research work, the most fascinating level of theories RHF and DFT (LSDA, B3LYP and B3PW91) were carried out using the basis sets 3-21G (d, p). All these calculations were performed using GAUSSIAN 09W [1] program. In DFT methods, Becke's three parameter hybrid function combined with the Lee-Yang-Parr correlation function (B3LYP) [2,3], Becke's three parameter exact exchange function (B3) [4] combined with gradient-corrected correlation function of Lee, Yang and Parr (LYP) [5,6] and Perdew and Wang (PW91) [6,7] predict the best results for molecular geometry and vibrational frequencies for moderately larger molecules. The calculated frequencies are scaled down to yield the coherent with the observed frequencies. The scaling factors for scaling the harmonic frequencies are 0.864, 0.874, 0.90 and 0.934 for HF/3-21G (d, p) method. For DFT (B3LYP)/3-21G (d, p) basis set, the scaling factors are 0.92, 0.934, 0.96 and 0.98. For DFT (B3PW91)/3-21G (d, p) basis set, the scaling factors are 0.912, 0.92 and 0.93. For CAM (B3LYP)/3-21 G (d, p) basis set, the scaling factors are 0.91, 0.92, 0.93 and 0.96. For LSDA/3-21 G (d, p) level of basis set, the scaling factors such as 0.93, 0.94, 0.96, 0.97 and 0.98 are used. The observed (FT-IR and FT-Raman) and calculated vibrational frequencies with assignments are submitted in Table 1. Experimental and simulated spectra of IR and Raman are displayed in the Figures 1 and 2 respectively.

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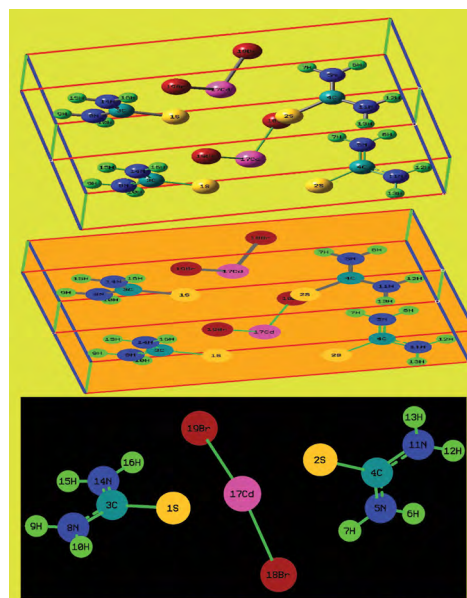
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Geometrical Parameters	Methods				
	HF	B3LYP	B3PW91	CAM – B3LYP	LSDA
	3-21G	3-21G	3-21G	3-21G	3-21G
<b>Bond length(Å)</b>					
(S1-C3)	1.783	1.778	1.770	1.769	1.764
(S1--Cd17)	2.755	2.703	2.679	2.665	2.580
(S2-C4)	1.782	1.778	1.770	1.769	1.764
(S2--Cd17)	2.755	2.703	2.679	2.665	2.580
(C3-N8)	1.326	1.346	1.344	1.339	1.338
(C3-N14)	1.312	1.329	1.327	1.322	1.323
(C4-N5)	1.312	1.329	1.327	1.322	1.323
(C4-N11)	1.326	1.346	1.344	1.339	1.338
(N5-H6)	1.000	1.017	1.016	1.015	1.026
(N5-H7)	1.008	1.035	1.037	1.033	1.061
(N8-H9)	0.999	1.015	1.014	1.013	1.024
(N8-H10)	0.998	1.013	1.013	1.012	1.023
(N11-H12)	0.999	1.015	1.014	1.013	1.024
(N11-H13)	0.998	1.013	1.013	1.012	1.023
(N14-H15)	1.000	1.017	1.016	1.015	1.026
(N14-H16)	1.008	1.035	1.037	1.033	1.061
(Cd17-Br18)	2.662	2.655	2.642	2.628	2.604
(Cd17-Br19)	2.662	2.655	2.642	2.628	2.604
<b>Bond angle(°)</b>					
(C3-S1--Cd17)	110.075	106.708	106.107	106.980	96.468
(C4-S2--Cd17)	110.081	106.744	106.124	106.979	96.446
(S1-C3-N8)	117.151	116.711	116.682	116.737	116.481
(S1-C3-N14)	123.523	123.717	123.570	123.675	122.999
(N8-C3-N14)	119.319	119.565	119.740	119.581	120.513
(S2-C4-N5)	123.525	123.711	123.570	123.678	123.001
(S2-C4-N11)	117.150	116.710	116.684	116.736	116.485
(N5-C4-N11)	119.318	119.572	119.739	119.578	120.507
(C4-N5-H6)	121.774	121.48	121.650	121.517	121.490
(C4-N5-H7)	121.625	121.548	121.328	121.545	121.323
(H6-N5-H7)	116.595	116.956	117.002	116.929	117.008
(C3-N8-H9)	122.596	122.604	122.665	122.593	122.652
(C3-N8-H10)	119.155	118.627	118.536	118.628	118.070
(H9-N8-H10)	118.248	118.765	118.793	118.777	119.276
(C4-N11-H12)	122.597	122.608	122.667	122.594	122.647
(C4-N11-H13)	119.155	118.631	118.535	118.628	118.075
(H12-N11-H13)	118.247	118.758	118.792	118.776	119.276
(C3-N14-H15)	121.775	121.476	121.652	121.515	121.486
(C3-N14-H16)	121.621	121.550	121.325	121.542	121.327
(H15-N14-H16)	116.597	116.956	117.003	116.934	117.008
(S1--Cd17--S2)	96.218	98.064	98.935	98.401	111.363
(S1--Cd17-Br18)	114.660	114.380	114.439	114.556	112.572
(S1--Cd17-Br19)	103.479	104.607	104.446	104.700	103.722
(S2--Cd17-Br18)	103.487	104.602	104.452	104.705	103.728
(S2--Cd17-Br19)	114.664	114.474	114.434	114.549	112.571
(Br18-Cd17-Br19)	121.704	118.981	118.636	118.379	113.151
<b>Dihedral angles(°)</b>					
(Cd17--S1-C3-N8)	157.572	157.873	156.581	157.768	145.295
(Cd17--S1-C3-N14)	-23.297	-23.022	-24.347	-23.101	-35.547
(C3-S1--Cd17--S2)	148.123	152.518	155.168	152.923	178.510
(C3-S1--Cd17-Br18)	-103.927	-97.373	-94.406	-96.613	-65.476
(C3-S1--Cd17-Br19)	30.878	34.527	36.944	34.697	57.193
(Cd17--S2-C4-N5)	-23.266	-22.940	-24.300	-23.081	-35.541
(Cd17--S2-C4-N11)	157.604	157.961	156.623	157.783	145.299
(C4-S2--Cd17--S1)	148.059	152.297	155.120	152.924	178.547
(C4-S2--Cd17-Br18)	30.816	34.408	36.889	34.688	57.225
(C4-S2--Cd17-Br19)	-103.998	-97.559	-94.464	-96.620	-65.447

(S1-C3-N8-H9)	178.030	176.100	175.740	176.662	173.723
(S1-C3-N8-H10)	-1.9	-3.261	-3.506	-2.989	-6.129
(N14-C3-N8-H9)	-1.137	-3.043	-3.368	-2.504	-5.456
(N14-C3-N8-H10)	178.931	177.594	177.384	177.843	174.691
(S1-C3-N14-H15)	179.438	177.664	177.421	178.147	172.891
(S1-C3-N14-H16)	0.266	-0.821	-0.982	-0.786	-2.125
(N8-C3-N14-H15)	-1.449	-3.255	-3.534	-2.746	-7.983
(N8-C3-N14-H16)	179.378	178.259	178.062	178.319	176.998
(S2-C4-N5-H6)	179.461	177.827	177.384	178.136	172.849
(S2-C4-N5-H7)	0.288	-0.721	-1.000	-0.803	-2.154
(N11-C4-N5-H6)	-1.426	-3.098	-3.566	-2.751	-8.024
(N11-C4-N5-H7)	179.400	178.351	178.048	178.308	176.971
(S2-C4-N11-H12)	178.050	176.238	175.734	176.642	173.661
(S2-C4-N11-H13)	-1.884	-3.250	-3.504	-3.013	-6.134
(N5-C4-N11-H12)	-1.116	-2.898	-3.379	-2.530	-5.519
(N5-C4-N11-H13)	178.948	177.611	177.381	177.813	174.684

**Table 1:** Optimized geometrical parameters for Bis (thiourea) Cadmium Bromide (BTCB) computed at HF, DFT (B3LYP& B3PW91), CAM – B3LYP and LSDA with 3-21G (d, p) basis sets.



**Figure 1:** Crystal view and structure of BTCB.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR isotropic chemical shifts are calculated (Gas, DMSO, Chloroform and  $\text{CCl}_4$ ) by the GIAO method with IEFPCM model [8-18] using B3LYP/6-311++G (d, p) level. The electronic properties; HOMO-LUMO energies, absorption wavelengths and oscillator strengths are calculated using B3LYP method of the time-dependent DFT (TD-DFT) [19-21], basing on the optimized structure in gas phase and solvent [DMSO, Chloroform and  $\text{CCl}_4$ ] mixed phase. Thermodynamic properties have been calculated from 100-1000°C in gas phase using B3LYP/6-311++G (d, p) method. Moreover, the dipole moment, nonlinear optical (NLO) properties, linear polarizabilities and first order hyperpolarizabilities and chemical hardness have also been studied.

## Results and Discussion

### Molecular geometry deformational analysis

From the crystal studies, it is observed that, the BTCB belongs to orthorhombic crystal class with space group of  $\text{Pn}2_1\text{a}$  and point

group of symmetry  $C_{2v}$ . The compound possesses the symmetrical geometry in which Cd ion is at the tetrahedral coordination site with two  $Br_2$  atoms and two  $NH_2$  atoms at its top end. This gives rise to a three dimensional bonding network. All thiourea molecules are planar and are equidistant from the central cadmium atom. This structure gives a polymeric character to BTCB molecule with asymmetric units contributing additively to the effective nonlinearity. The molecular structure is optimized by Berny's optimization algorithm using Gauss view program and is shown in Figure 3. The comparative optimized structural parameters such as bond length, bond angle and dihedral angle are presented in Table 2. The present compound contains cadmium metal atom, bromide atoms and four amino groups.

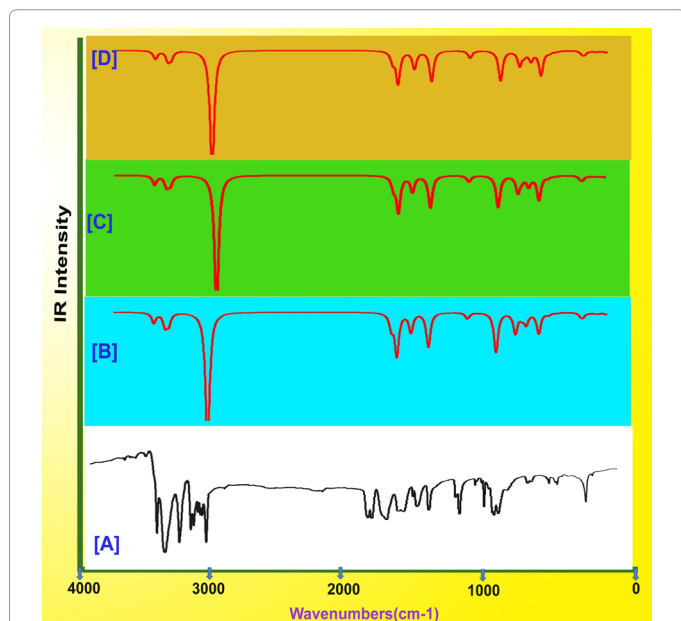


Figure 2: Experimental [A] and calculated [B, C and D] FT-IR spectra of Bisthiourea Cadmium Bromide (BTCB).

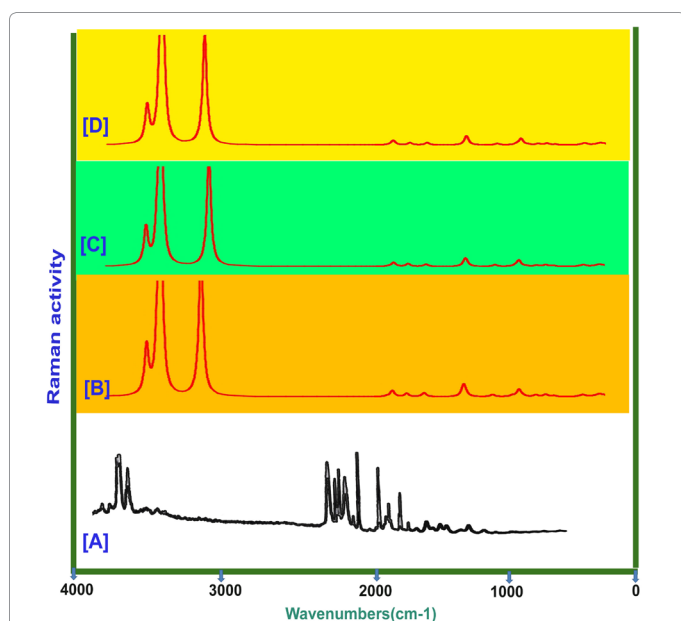


Figure 3: Experimental [A] and calculated [B, C and D] FT-Raman spectra of Bisthiourea Cadmium Bromide (BTCB).

S. No.	Symmetry Species $C_{2v}$	Observed Frequency (cm <sup>-1</sup> )		Methods					Vibrational Assignments
		FT-IR	FT-Raman	HF	B3LYP	B3PW91	CAM-B3LYP	LSDA	
				3-21G (d, p)	3-21G (d, p)	3-21G (d, p)	3-21G (d, p)	3-21G (d, p)	
1	A <sub>1</sub>	3350 s	3350 s	3346	3349	3349	3341	3348	(N-H) u
2	A <sub>1</sub>	3345 vs	3345 s	3345	3342	3342	3337	3344	(N-H) u
3	A <sub>1</sub>	3320 vs	3320 m	3321	3306	3321	3326	3319	(N-H) u
4	A <sub>1</sub>	3300 s	-	3283	3292	3296	3297	3298	(N-H) u
5	A <sub>1</sub>	3295 s	-	3279	3282	3293	3292	3292	(N-H) u
6	A <sub>1</sub>	3290 s	-	3279	3268	3257	3288	3288	(N-H) u
7	A <sub>1</sub>	3250 s	3250 w	3247	3248	3284	3249	3258	(N-H) u
8	A <sub>1</sub>	3245 vs	3245 w	3247	3245	3229	3233	3237	(N-H) u
9	A <sub>1</sub>	1610 s	1610 m	1622	1618	1608	1609	1607	(N-H) δ
10	A <sub>1</sub>	1600 m	1600 m	1621	1594	1590	1590	1588	(N-H) δ
11	A <sub>1</sub>	1590 s	-	1598	1577	1571	1584	1586	(N-H) δ
12	B <sub>2</sub>	1565 s	-	1580	1553	1554	1566	1569	(N-H) δ
13	B <sub>2</sub>	1540 w	1540 vs	1533	1526	1528	1526	1537	(N-H) δ
14	A <sub>1</sub>	1490 m	-	1476	1494	1480	1477	1489	(N-H) δ
15	A <sub>1</sub>	1470 s	-	1453	1452	1462	1453	1459	(N-H) δ
16	A <sub>1</sub>	1450 w	1450 s	1449	1448	1457	1449	1453	(N-H) δ
17	A <sub>1</sub>	1420 s	-	1408	1409	1419	1417	1413	(N-H) δ
18	A <sub>1</sub>	1380 s	-	1372	1376	1373	1372	1380	(C-N) u
19	B <sub>2</sub>	1310 s	1310 s	1316	1291	1326	1306	1302	(C-N) u
20	B <sub>2</sub>	1260 s	1260 m	1256	1258	1259	1251	1249	(C-N) u
21	B <sub>2</sub>	1240 m	1240 m	1208	1211	1233	1264	1239	(C-S) u
22	B <sub>2</sub>	1210 w	-	1207	1209	1232	1207	1208	(C-S) u
23	B <sub>2</sub>	1190 s	-	1189	1187	1186	1192	1185	(C-N) u
24	B <sub>2</sub>	990 m	990 w	984	995	1006	983	994	(N-H) γ
25	B <sub>1</sub>	860 m	-	859	857	825	858	856	(N-H) γ
26	B <sub>1</sub>	720 w	720 w	735	702	716	718	718	(N-H) γ
27	A <sub>2</sub>	690 w	-	709	688	694	684	684	(N-H) γ
28	A <sub>2</sub>	650 w	-	661	644	631	658	649	(N-H) γ
29	A <sub>2</sub>	600 w	-	602	598	602	594	594	(N-H) γ
30	A <sub>2</sub>	560 w	-	562	560	548	557	540	(N-H) γ
31	B <sub>2</sub>	510 w	-	534	535	509	513	519	(N-H) γ
32	B <sub>2</sub>	500 m	-	498	489	484	479	499	(Cd-Br) u
33	A <sub>1</sub>	480 m	480 w	495	479	474	457	472	(Cd-Br) u
34	A <sub>1</sub>	420 w	-	431	428	418	415	424	(Cd-S) u
35	A <sub>1</sub>	400 m	-	419	403	408	411	402	(Cd-S) u
36	B <sub>2</sub>	390 m	390 w	389	401	405	409	389	(C-N) δ
37	B <sub>2</sub>	380 w	380 w	379	360	365	374	376	(C-N) δ
38	A <sub>2</sub>	360 w	-	334	334	343	351	358	(C-S) δ
39	A <sub>2</sub>	310 m	310 w	309	314	326	313	305	(C-S) δ
40	A <sub>2</sub>	290 m	290 w	304	290	295	288	302	(Cd-Br) δ
41	B <sub>2</sub>	270 w	-	266	244	248	255	262	(Cd-Br) δ
42	B <sub>2</sub>	220 w	220 vw	229	241	246	236	228	(Cd-S) δ
43	B <sub>1</sub>	200 w	200 vw	194	196	198	202	206	(Cd-S) δ
44	B <sub>1</sub>	170 w	-	140	148	152	152	176	(C-N) γ
45	B <sub>1</sub>	165 w	-	138	140	142	142	158	(C-N) γ
46	B <sub>1</sub>	140 w	-	132	132	130	136	138	(C-S) γ
47	B <sub>1</sub>	130 w	-	126	124	124	130	128	(C-S) γ
48	B <sub>1</sub>	120 w	120 vw	102	106	106	108	112	(Cd-Br) γ
49	B <sub>1</sub>	110 w	110 vw	80	82	80	84	82	(Cd-Br) γ
50	B <sub>1</sub>	100 w	-	28	32	32	28	38	(Cd-S) γ
51	B <sub>1</sub>	90 w	-	18	24	24	22	26	(Cd-S) γ

s – Strong; m- Medium; w – weak; as- Asymmetric; s – symmetric; u – stretching;

α – deformation, δ – In plane bending; γ – out plane bending; τ – Twisting;

Table 2: Observed and calculated vibrational frequencies of Bis (thiourea) Cadmium Bromide (BTCB) with HF, DFT (B3LYP& B3PW91), CAM – B3LYP and LSDA with 3-21G (d, p) basis sets.

The zero point vibrational energy of the compound in different level of calculations such as HF/LSDA/B3LYP/B3PW91/CAM-B3LYP with 3-21 G(d, p) basis set is 86.85, 78.35, 80.02, 80.55 and 81.43 Kcal/Mol, respectively. The calculated energy of HF is greater than DFT method since the assumed ground state energy in HF is greater than the true energy. Since the existence of coordinate covalent bond between organic element and metal, molecular structure belongs to multiple planes with respect to Cadmium bromide. The thiourea on both sides are somewhat tilted in order to sustain their equal distribution of charges of Br and H. Since the present compound is composed of metal atom and organic complex, the entire atoms are connected by covalent and co-ordination covalent bonds. Particularly, cadmium metal atom is connected with couple of thiourea by Vander walls bonds. The metal ions acted as a bridge for both thiourea. Normally, the metal ions make dative bond with organic atoms to form organo-metallic compound due to which the considerable amount of energy is released and make a crystal very strong.

In the experimental method, the bond lengths of C-S and C-N vibrations are 1.720 and 1.340 Å whereas in the calculation method, the corresponding bond lengths are 1.778 and 1.346 Å respectively. The internuclear distance of N5-H6=N14-H15 is 0.018 Å and this value is greater than that of N5-H7=N14-H16. This variation exists due to the attraction of Br and H atoms. Moreover, in this compound, both the amino groups are coupled with carbon atom in symmetrical manner. However, the bond distance of C-N is differed by 0.017 Å. This difference occurs between them is due to the attraction of H by Br. There exists a double bond between C and S atoms usually, but only one bond exists due to 2 lone pair of electrons which are transferred from the ligand (S) to the metal (Cd). The calculated bond length of Cd-S is 2.703 Å and this peculiar bond is called coordination covalent bond which has very high bond length when compared with others. It is concluded that from these calculated parameters, this organo-metallic compound is very strong due to the existence of complex bonds.

The coordination covalent bond is an anisotropic bond which is altered at any instant due to the relative orientation of the molecules. The induction and dispersion interactions are always attractive, irrespective of the orientation of the molecules, but the electrostatic interaction between the metal and organic atoms changes sign with respect to the charges of the atom. Thus, the electrostatic force of attraction depending on the charges of the molecule has restricted the bond length which is existed between the metal and organic atoms. Such a force of attraction between metal and organic atom also affect the surrounding atoms of opposite signs. The highly electronegative bromine atoms are attracted much more by the highly positive cadmium atoms.

**Mulliken charge analysis:** The Mulliken charge is used to understand the charge distribution on the chemical bonding because it facilitates positive and negative regions in the molecular space, at which the protons and electrons concentrate. Thus chemically significant regions; bonds can be identified; also gives the narration of the mechanism of electrophilic and nucleophilic substitutions. Normally, the charges are distributed evenly over the molecule which leads to be neutral. Whenever the substitutions are added to the molecule, the charge distribution is completely altered with respect to the substitution. Here, the negative charges are accumulated over the N atoms in thiourea even after the cadmium bromide is added. When the highly electronegative bromine atoms are coupled with positive cadmium atom, the high degree of Br-Cd-Br dipoles are formed. The remaining C and H of the molecule have positive space. Since

the addition of Cd-Br have been occurred in thiourea, the sulphur atoms become low order negative that is almost neutral. The Mulliken charges of each atom are presented in Table 3. Thus the entire charge levels of the molecule are altered on par with due to the substitution. Simultaneously, the chemical property has also changed for the same. The Mulliken charge analysis diagram is displayed in the Figure 4.

### Vibrational assignments

The BTCB molecule has 19 atoms and 51 normal vibrational modes. The molecule possesses  $C_{2v}$  point group symmetry, which shows that all vibrational modes of BTCB molecule are both infrared (IR) and Raman active. In HF and DFT calculations, the calculated vibrational frequencies were scaled by scaling factors. The different calculated vibrational modes were scaled by different scaling factors for better agreement with the experimental values. On the basis of  $C_{2v}$  symmetry, the 51 fundamental vibrations of the molecule can be distributed as

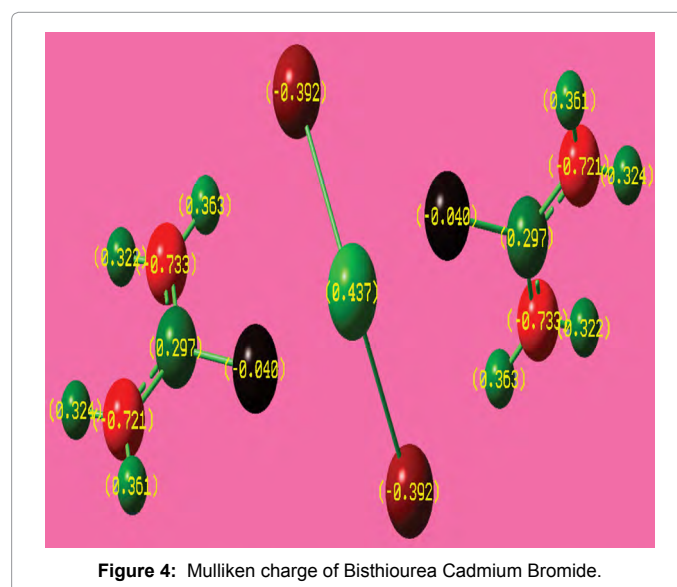


Figure 4: Mulliken charge of Bisthiourea Cadmium Bromide.

Atom	Mullikan Charges
S1	- 0.124
S2	- 0.124
C3	0.475
C4	0.475
N5	- 0.911
N8	- 0.891
N11	- 0.891
N14	- 0.911
H6	0.369
H7	0.434
H9	0.369
H10	0.410
H12	0.369
H13	0.410
H15	0.369
H16	0.434
Cd17	0.781
Br18	- 0.522
Br19	- 0.522

Table 3: Mulliken charges HF / 3-21G (d, p) level for Bis (thiourea) Cadmium Bromide (BTCB).

$$\Gamma \text{ Vib} = 19A_1 + 7A_2 + 11B_1 + 14B_2$$

$A_1$  and  $B_2$  irreducible representations correspond to stretching, ring deformation and in plane bending vibrations while  $A_2$  and  $B_1$  correspond to ring, torsion and out of plane bending vibrations. The harmonic vibrational frequencies (unscaled and scaled) are calculated at B3LYP and B3PW91 levels using the triple split valence basis set along with the diffuse and polarization functions; 3-21 G (d, p). The observed FT-IR and FT-Raman frequencies for various modes of vibrations have been presented in Tables 2 and 4 respectively. In this, the calculated frequencies are compared with the experimental values and this work reveals the over estimation of the calculated vibrational modes due to the neglect of a harmonicity and change of state of real system Table 5. Also, these computational calculations are carried out for frequency analysis to get the spectroscopic indication of the BTCB.

**Amino group vibrations:** The molecule is populated with couple of thiourea which contains bi  $NH_2$  groups. Generally, the amino group is a dominated ligand and make the impression strong in the vibrational pattern. As there are eight N-H bonds, eight vibrational bands of stretching modes are possible. Normally, the primary amines are recognized by strong absorption peaks in the regions of 3450-3100  $cm^{-1}$  and 3100-3300  $cm^{-1}$  due to the asymmetric and symmetric N-H stretching respectively [13,14]. Also the  $NH_2^+$  asymmetric and symmetric deformation wave numbers are expected to fall in the regions 1660-1610  $cm^{-1}$  and 1550-1485  $cm^{-1}$  respectively [15,16]. Also the observed N-H stretching frequencies are found at 3350, 3345, 3320, 3300, 3295, 3290, 3250 and 3245  $cm^{-1}$ . Out of these, the first three bands are assigned to asymmetric vibrations and the rest five bands are assigned to symmetric vibrations. Apart from these assignments, the last two vibrational bands are found to be moved down from the expected region. Due to the dominating character of the NH group, all the stretching vibrations should be observed within the expected region. But this is not so in this case. This is mainly due to the presence of sulphur with chain. The presence of N-H in plane bending vibrations (scissoring) are usually observed in the region 1610-1630  $cm^{-1}$ , rocking vibrations are assigned in the range 1100-1200  $cm^{-1}$  and the out of plane bending (wagging and twisting) vibrations are normally identified under the region 1150-900  $cm^{-1}$  [17-19]. In the present compound, the in-plane deformation vibrations are observed at 1610, 1600, 1590, 1565, 1540, 1490, 1470, 1450 and 1420  $cm^{-1}$ . The first two bands are moved up to the higher region and it is cleared that these vibrations are favoured and not affected by the sulphur. The out of plane bending vibrations are observed at 990, 860, 720, 690, 650, 600, 560 and 510  $cm^{-1}$ . Normally, whenever the metal atom coupled with the organic molecule, those normal vibrational modes of the same are suppressed much. The entire out of plane bending vibrations are found out of the expected region. This observation obviously shows that the N-H out of plane vibrations are hindering by metal complex vibrations. The entire out of plane vibrational modes are affected by other substitutions in the chain and this is observed from N-H vibrations.

**C-N vibrations:** The C-N stretching frequency is rather a tricky assignment since there exists problem in cascading of these frequencies with other vibrations [20]. According to the previous work [21], the C-N stretching vibrations were found in the region 1386-1266  $cm^{-1}$  for aromatic amines. In this present work, the C-N Stretching vibrations are observed at 1380, 1310, 1260 and 1190  $cm^{-1}$  which is making disagreement with the literature [22] due to the loading of sulphur and metal atoms with the molecule. The C-NH<sub>2</sub> in-plane and out-of-plane bending vibrations are appeared at 390 and 380  $cm^{-1}$  and 170 and 165  $cm^{-1}$  respectively. These two vibrations are affected much

S. No	Observed frequency	Calculated frequency				
		HF	B3LYP	B3PW91	CAM - B3LYP	LSDA
		3-21G	3-21G	3-21G	3-21G	3-21G
1	3350	3873	3641	3669	3668	3562
2	3345	3872	3641	3669	3668	3562
3	3320	3800	3540	3572	3577	3458
4	3300	3800	3540	3572	3577	3458
5	3295	3752	3514	3541	3548	3433
6	3290	3752	3514	3541	3548	3433
7	3250	3608	3185	3166	3233	2884
8	3245	3608	3185	3166	3233	2891
9	1610	1878	1734	1730	1749	1657
10	1600	1877	1733	1729	1748	1655
11	1590	1829	1690	1690	1704	1636
12	1565	1829	1689	1690	1703	1635
13	1540	1642	1558	1576	1590	1569
14	1490	1641	1557	1575	1589	1568
15	1470	1556	1424	1434	1453	1403
16	1450	1552	1420	1429	1449	1398
17	1420	1204	1110	1118	1134	1104
18	1380	1204	1110	1117	1134	1104
19	1310	1197	1104	1105	1117	1068
20	1260	1197	1104	1105	1117	1068
21	1240	967	865	881	903	905
22	1210	966	864	880	901	902
23	1190	820	711	719	745	710
24	990	820	711	719	745	710
25	860	735	675	689	692	685
26	720	735	675	688	691	684
27	690	709	620	631	658	622
28	650	708	620	631	658	622
29	600	602	539	548	556	540
30	560	602	539	548	557	540
31	510	534	471	476	480	472
32	500	534	470	475	479	471
33	480	495	428	431	457	425
34	420	494	428	431	457	424
35	400	419	403	408	411	402
36	390	417	401	405	409	402
37	380	218	212	215	220	235
38	360	192	197	202	207	224
39	310	178	185	192	196	218
40	290	175	171	174	180	189
41	270	133	144	146	150	164
42	220	132	142	145	148	163
43	200	97	98	99	101	103
44	170	70	74	76	76	88
45	165	69	70	71	71	79
46	140	66	66	65	68	69
47	130	63	62	62	65	64
48	120	51	53	53	54	56
49	110	40	41	40	42	41
50	100	14	16	16	14	19
51	90	9	12	12	11	13

**Table 4:** Calculated unscaled frequencies of Bis (thiourea) Cadmium Bromide (BTCB) computed at HF, DFT (B3LYP & B3PW91), CAM - B3LYP & LSDA with 3-21G (d, p) basis sets.

Energy levels	Energy in eV
H+8	6.903
H+7	6.684
H+6	6.575
H+5	6.258
H+4	6.147
H+3	6.027
H+2	5.971
H+1	5.838
H	5.751
L	1.734
L-1	1.583
L-2	0.858
L-3	0.446
L-4	0.036
L-5	0.121
L-6	0.420
L-7	0.931
L-8	1.033
L-9	1.414
L-10	1.449

**Table 5:** Frontier molecular orbitals with energy levels of Bis (thiourea) Cadmium Bromide (BTCB).

by other vibrations which make disagreement with literature values [23,24]. From these vibrations, it is observed that, the entire vibrations are altered with respect to the metal vibrations, even though the atom is bonded coordinate covalently. So this view ensures that, the metal is strongly bonded with thiourea and the crystal property of the thiourea is enriched by the addition of metal.

**C-S vibrations:** The rope connection of thio-cyanate complex is linked through the nitrogen atom or the sulphur atom. This bonding can be easily identified intensively by C-S stretching vibration which appeared in the region  $730-690\text{ cm}^{-1}$  [25-27]. In this present case, the C-S stretching vibrations are identified at  $1240\text{ cm}^{-1}$  (medium intensity) and  $1210\text{ cm}^{-1}$  (weak intensity) in IR spectrum. The observed bands are in agreement with the expected range and literature [28]. Usually, the C-S in-plane bending vibrations are observed in the region of  $440-410\text{ cm}^{-1}$  [28]. In this metal organic compound, the in-plane bending vibrations are found at  $360$  and  $310\text{ cm}^{-1}$  and the out-of-plane bending vibrations are found at  $140$  and  $130\text{ cm}^{-1}$ . These vibrational bands are pulled down to the lower region in the expected range and are due to the Vander Waals coupling of Cd ion.

**Cd-Br and Cd-S vibrations:** The BTCB molecule is a metal-organic crystal compound which comprises Cd metal ion linked with bromine atoms by forming coordinate covalent bond. Normally, in cadmium metal complex, the Cd-Br stretching is very important and is usually observed in the region  $315-120\text{ cm}^{-1}$  [29]. In this compound, the coordinate covalent bond stretching vibrations are identified at  $500$  and  $480\text{ cm}^{-1}$ . The Cd-Br in-plane bending vibrational peaks are appeared at  $290$  and  $270\text{ cm}^{-1}$  and out-of-plane bending vibrational peaks are appeared at  $120$  and  $110\text{ cm}^{-1}$ . It is concluded that, the Cd-Br vibrations are elevated to higher region. This observation clearly shows that the metal-organic inter nuclear distances are made up of coordinate covalent bond and are weak. Usually, these vibrations will not be affected in order to emphasize its uniqueness character.

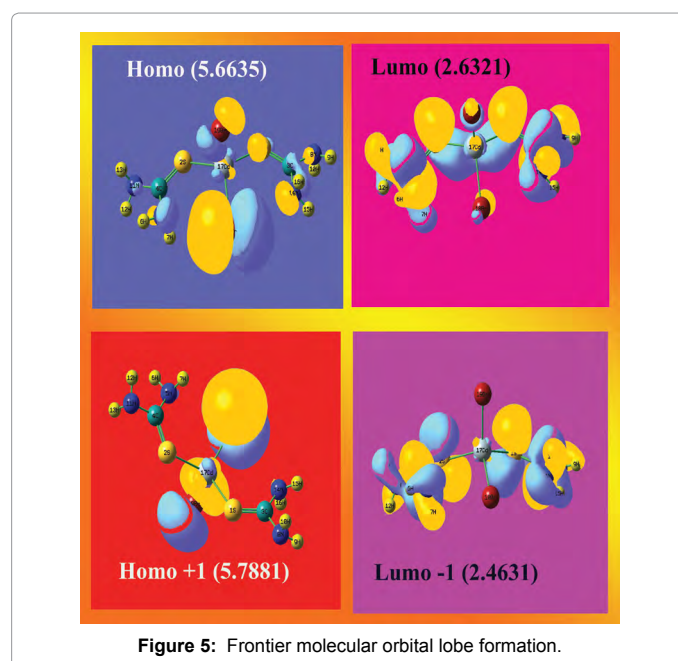
In BTCB molecule, the organic compound bithiourea is directly connected through sulphur atom with metal bromide by forming coordinate covalent bond as S-Cd-S. Due to the large force constants

and strong covalent bonds, generally, the Cd-S vibrations are pushed to the higher region by organic vibrations. The Cd-S bond is made up of coordinate covalent bond which is a very a weak bond and its vibrations fallback to the Cd-Br vibrations. In this present case, the Cd-S stretching vibrations are observed at  $420$  and  $400\text{ cm}^{-1}$ . The corresponding in-plane bending vibrations are found at  $220$  and  $200\text{ cm}^{-1}$  and out-of-plane bending vibrations are observed at  $100$  and  $90\text{ cm}^{-1}$ . The entire vibrations of Cd-S are observed in the lower region of the IR spectrum. This observation shows the weak attraction of the bond between the metal and organic compound. Although the bond observed in the present molecule is weak, its chemical properties are good and the present molecule possesses piezoelectric effect.

### Frontier molecular analysis

The probable transitions in electronic-vibrational energy levels of frontier molecular orbitals are used to identify the electro-optical properties of the organic compounds. The overlapping of molecular orbitals in bonding and antibonding is used in making the stabilization of orbital [30]. In molecular interaction, there are two important orbitals that involved in interacting with each other. They are HOMO and LUMO. HOMO is the highest energy occupied molecular orbital that represents the ability to donate an electron. LUMO is the lowest energy unoccupied molecular orbital that represents the ability to accept an electron. These orbitals are also called the frontier orbitals. The interaction between them is much stable and is called filled empty interaction. During the interaction, the electron density is generally occupied in the region between two nuclei. The energy of in-phase interaction is greater than the out-of-phase interaction and forms bonding and antibonding molecular orbital.

The 3D view of frontier orbitals in gas is shown in Figure 5. In the figure, the HOMO is mainly localized over the cadmium, Br, N atoms and C-S group in which the two sigma bond interactions are observed over the C-S of thiourea and one delta bond interaction found over cadmium bromide. The N and Br atoms of the molecule are connected by S orbital lobes. However, LUMO is characterized by a charge distribution that connects the cadmium-bromide atoms and C-S bonds in which there are two sigma and one delta bond



**Figure 5:** Frontier molecular orbital lobe formation.

interactions are identified. From this observation, it is inferred that, the in-phase and out-of-phase interactions are present in HOMO and LUMO respectively. The HOMO→LUMO transition implies that an electron density is transferred between cadmium bromide and thiourea separately. Thus, the obtained transitions in the electron clouds of thiourea and metal complex ensure the occurrence of incorporation of physical and chemical properties. The kubo gap energy of the present material is 4.02 eV, which shows moderate electrical activity and effective optical activity.

### NMR analysis

Usually, the NMR signals of the compounds explain the chemical environment of the carbons. In this case, the carbons are situated in different environment and proportionately, the chemical properties are obtained alternatively. The chemical shifts of the compound are reported in ppm relative to TMS for <sup>1</sup>H and <sup>13</sup>C NMR spectra and are presented in Table 6.

In the present compound, the metallo-organic compound has been taken for the study in which the molecule contains two carbons along with two amine groups. The <sup>13</sup>C NMR chemical shift of such two carbons is greater than 100 ppm, as in the expected regions.

In this case, the chemical shift of C3 is 166.03 ppm and that of C4 is 168.92 ppm. Since both the carbons C3 and C4 have similar groups, the chemical shift is same for both. Due to the migration of double bond from C-S to C-N, the chemical shift of both carbons is very high. The chemical shift of Br (2845.51) is finite and apparently high due to the random breaking of proton shield by the fusing of coordinate covalent bond with organic molecules. The chemical shift of H6, H7, H9, H10, H12, H13, H15 and H16 are calculated as 1.86, 2.32, 1.40, 1.60, 1.34, 1.68, 1.86 and 2.15 ppm respectively. From these result, it is observed that, the chemical shift of H7 and H16 are higher than the rest of other hydrogen atoms in the chain. This is purely due to the extended influence on hydrogen atom by nearby bromine atoms. Hence it is concluded that the chemical property of the metal is directly coupled with organic molecules and this shows that the present metal complex molecule have an additional chemical property.

### Optical property analysis

The UV and visible spectrum of the compound in gas and different solvents (DMSO, chloroform and CCl<sub>4</sub>) are calculated at B3LYP/3-21 G (d, p) level using the TD-DFT approach. The calculated excitation energies, oscillator strength (*f*), wavelength (*λ*) and spectral assignments are given in Table 7. The major contributions of the transitions are assigned according to the result of SWizard program [31].

According to TD-DFT calculations, the overall transitions belong to quartz UV region. In gas phase, the strong transition is observed at 654 nm and its oscillator strength is *f*=0.0061 with energy gap of 1.89 eV. Also in this phase, two more strong transitions are observed at 562 and 557 nm and their corresponding oscillator strengths are *f*= 0.0037 and 0.0046 with energy gap of 2.20 and 2.22 eV. These transitions are indicated as *n* → *σ*\* which belongs to the visible region. In this, the band is designated as R-band (German, Radikalartig) which is attributed to the above said transition of chain of chromophoric groups, such as Cadmium bromide group.

From TD-DFT calculations, the following features are inferred. Their molar absorptivities are low. They transferred from hypsochromic to bathochromic shift. In this case, the solvent effect is inactive. The simulated UV-Visible spectra in gas and solvent phase are shown in Figure 6.

Atom position	According to TMS B3LYP/ 6-311+G (2d, p) (ppm)			
	Gas	DMSO	Chloroform	CCl4
S1	187.89	256.32	240.74	221.88
S2	185.23	250.47	235.07	217.02
C3	166.03	175.80	173.48	170.91
C4	168.92	177.51	175.36	173.06
N5	94.17	93.89	94.49	94.59
N8	84.07	89.92	88.52	86.90
N11	85.31	91.17	89.70	88.08
N14	92.34	93.10	93.39	93.21
H6	1.86	2.68	2.47	2.25
H7	2.32	2.48	2.43	2.39
H9	1.40	2.40	2.14	1.86
H10	1.60	2.21	2.06	1.89
H12	1.34	2.40	2.11	1.81
H13	1.68	2.25	2.12	1.97
H15	1.86	2.67	2.45	2.23
H16	2.15	2.47	2.41	2.33
Cd17	3759.86	3807.27	3788.83	3776
Br18	2845.51	2885.67	2878.86	2870.03
Br19	2840.04	2945.81	2927.03	2903.36

Table 6: Calculated <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of Bis (thiourea) Cadmium Bromide (BTCB).

λ (nm)	E (eV)	( f )	Major contribution	Assignment	Region	Bands
<b>Gas</b>						
654.03	1.8957	0.0061	H→L	n→σ*	Visible	R-band (German, radikalartig)
562.82	2.2029	0.0037	H→L	n→π*	Visible	
557.12	2.2254	0.0046	H→L	n→π*	Visible	
<b>DMSO</b>						
426.60	2.9064	0.0084	H→L	n→π*	Visible	R-band (German, radikalartig)
393.90	3.1476	0.0045	H→L	n→π*	UV	
380.92	3.2549	0.0055	H→L	n→π*	UV	
<b>Chloroform</b>						
472.61	2.6234	0.0082	H→L	n→π*	Visible	R-band (German, radikalartig)
439.56	2.8206	0.0032	H→L	n→π*	Visible	
401.88	3.0851	0.0044	H→L	n→π*	Visible	
<b>CCl<sub>4</sub></b>						
528.11	2.3477	0.0082	H→L	n→π*	Visible	R-band (German, radikalartig)
493.37	2.5130	0.0033	H→L	n→π*	Visible	
445.78	2.7813	0.0053	H→L	n→π*	Visible	

Table 7: Theoretical electronic absorption spectra of Bis (thiourea) Cadmium Bromide (BTCB) (absorption wavelength λ (nm), excitation energies E (eV) and oscillator strengths (*f*) using TD-DFT/B3LYP/3-21G (d, p) method.

In the case of DMSO solvent, the calculated absorption spectrum indicates that, the maximum absorption wavelength corresponds to the electronic transition and it undergoes from the HOMO+1 to LUMO-1 with maximum contribution. The Frontier molecular orbital diagram is presented in the Figure 7. Here, the chromophores are cadmium bromide group, the crystal properties are increased in the present compound. In the case of DMSO solvent, strong transitions are observed at 426, 393 and 380 nm and their corresponding oscillator strengths are *f*=0.0084, 0.0045 and 0.0055 with maximum energy gap 3.25 eV. They are denoted as *n* → *π*\* transition and belongs to the visible region. One of the electronic transitions is observed at IR region. Hence from gas to solvent, the electronic transitions retained at the visible

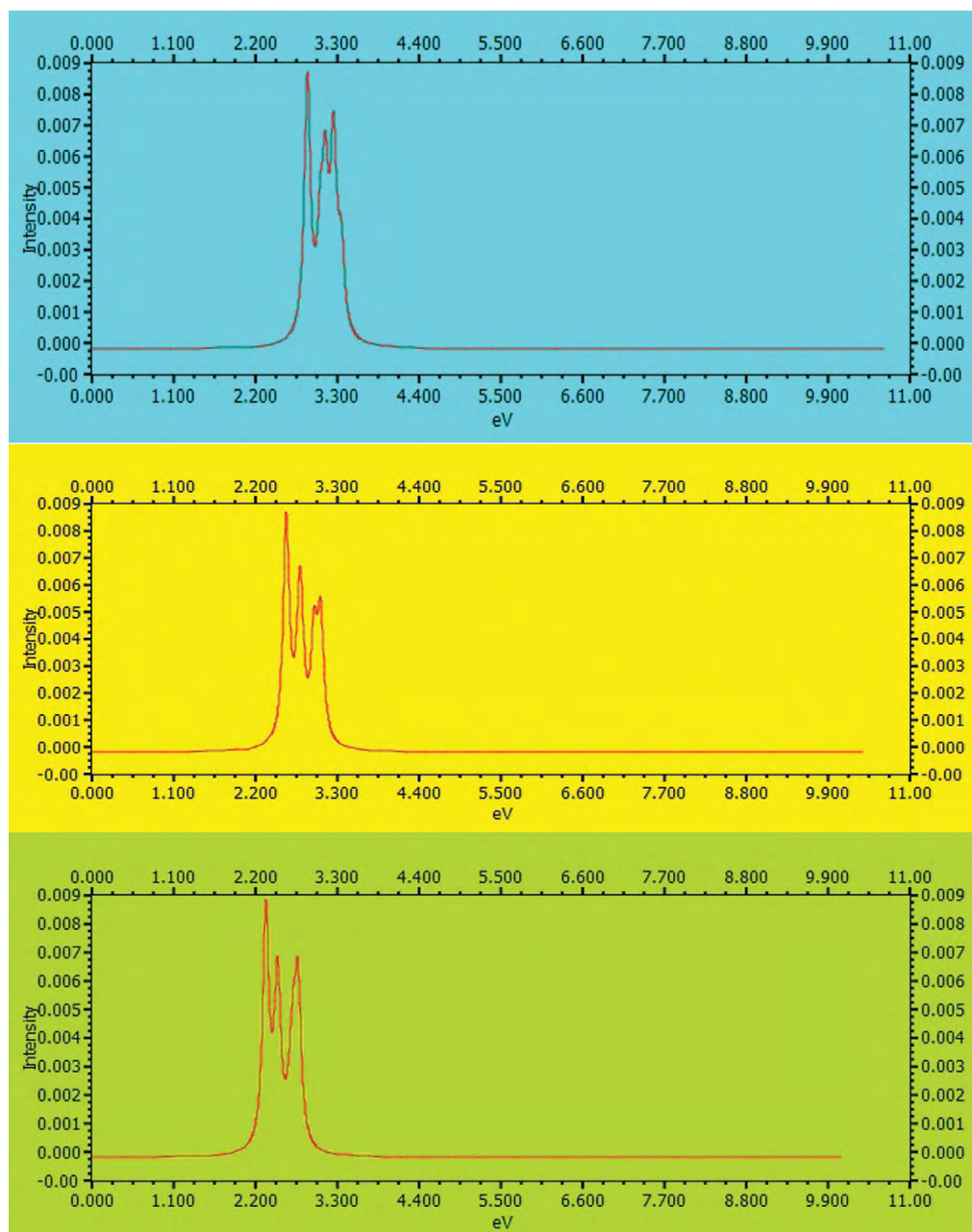


Figure 6: Simulated UV-Visible spectra of BTCB.

region. This observation clearly indicates that, the present molecule has visible active and it has very high optical properties. Moreover, the optical band gap is calculated as 3.25 eV and this view clearly ensure that the present compound BTCB possess LO as well as NLO properties.

The chemical hardness and potential, electro negativity and Electrophilicity index are calculated and their values are shown in Table 8. The chemical hardness is a property which has good chemical stability. For the present compound BTCB, the chemical hardness is calculated as 2.00 and so it has high chemical stability. The chemical stability and metal character of the compound is enhanced by substituting the Cd-Br group.

Also, the electro negativity of the compound is calculated as

3.74 and this property shows that the chemical bonds in the present molecule will be changed from covalent to ionic. The bonding nature of the present compound is rehabilitated to rich ionic property and this is due to the addition of Cd atom.

Electrophilicity index is a factor which is used to measure the energy lowering due to maximal electron flow between donor [HOMO] and acceptor [LUMO]. From the Table 8, it is found that the Electrophilicity index is 3.48 which is high and this value ensures that the strong energy transformation is taking place between HOMO+1 and LUMO-1. One more important electronic property of the molecule is its dipole moment. Whenever the molecules possess large dipole moment, the intermolecular interactions are very strong. The dipole moment value



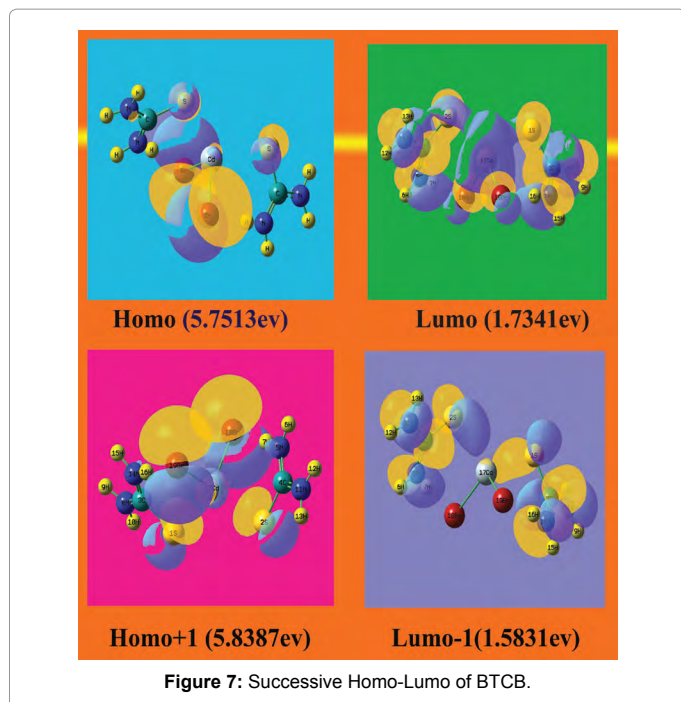


Figure 7: Successive HOMO-LUMO of BTCB.

Parameters	TD-DFT/B3LYP/3-21G
$E_{\text{total}}$ (Hartree)	-11643.95
$E_{\text{HOMO}}$ (eV)	5.7513
$E_{\text{LUMO}}$ (eV)	1.7341
$\Delta E_{\text{HOMO-LUMO gap}}$ (eV)	4.0172
$E_{\text{HOMO-1}}$ (eV)	0.0874
$E_{\text{LUMO+1}}$ (eV)	0.1510
$\Delta E_{\text{HOMO-1-LUMO+1 gap}}$ (eV)	0.0636
Chemical hardness ( $\eta$ )	2.0086
Electronegativity ( $\chi$ )	3.7427
Chemical potential ( $\mu$ )	2.0086
Chemical softness (S)	0.2489
Electrophilicity index ( $\omega$ )	3.4869
Dipole moment	1.9775

Table 8: Calculated energies values, chemical hardness, electro negativity, Chemical potential, Electrophilicity index of Bisthiourea Cadmium Bromide (BTCB).

for the present compound BTCB is calculated as 1.97 Debye. This value is temperate due to the presence of coordinate covalent bond. Hence, the present molecule possesses strong intermolecular interactions.

### Molecular Electrostatic Potential (MEP) analysis

The molecular electrostatic potentials have been used for interpreting and predicting the reactive behaviour of a wide variety of chemical systems in both electrophilic and nucleophilic reactions, the study of biological recognition processes and hydrogen bonding interactions [32,33]. Molecular electrostatic potential (MEP) at a point around a molecule gives an indication of the net electrostatic effect produced at that point by the total charge distribution (electron+nuclei) of the molecule and correlates with dipole moments, electro negatively, partial charges and chemical activity of the molecules. It provides a visual method to understand the relative polarity of the molecule. An electron density iso-surface mapped with electrostatic potential

surface depicts the size, shape, charge density and site of chemical reactivity of the molecules. The different values of the electrostatic potential at the surface are represented by different colours; red represents regions of most negative electrostatic potential, blue represents regions of most positive electrostatic potential and green represents regions of zero potential. Potential increases in the order of red<orange<yellow<green<blue. Molecular electrostatic potential view is mapped up at the level of B3LYP/3-21G (d, p) theory with optimized geometry. The colour code of these maps is in the range between -7.86 a.u. (deepest red) to 7.86 a.u. (deepest blue) in compound. The positive (blue) regions of MEP are related to electrophilic reactivity and the negative (green) regions to nucleophilic reactivity as shown in Figure 8.

From the MEP map of the present compound, the negative regions are mainly localized on cadmium bromide and sulphur atoms. Due to the presence of maximum positive region on the H of  $\text{NH}_2$  groups, there exists the possibility of nucleophilic attack in the region. The above calculated results inferred that the metal atoms coupled strongly in the position of organic lattice region.

### Polarizability and first order hyperpolarizability calculations

Using DFT-B3LYP method and 3-21 G (d, p) basis set, based on the finite-field approach, NLO properties, binding properties, the polarizabilities and first order hyperpolarizabilities of the title molecule are calculated. These parameters are used to find the relationships between the structures of the molecule.

The mean polarizability ( $\alpha$ ), anisotropy of polarizability ( $\Delta\alpha$ ) and the average value of the first hyperpolarizability ( $\langle\beta\rangle$ ) can be calculated using the following equations.

$$\alpha_{\text{tot}} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2]^{\frac{1}{2}}$$

$$\langle\beta\rangle = [(\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{zzz} + \beta_{xxx})^2 + (\beta_{zzz} + \beta_{xxx} + \beta_{yyy})^2]^{\frac{1}{2}}$$

where  $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{yz}, \alpha_{zx}$  and  $\beta_{xxx}, \beta_{yyy}, \beta_{zzz}, \beta_{xyy}, \beta_{yxy}, \beta_{yxx}, \beta_{xyx}, \beta_{yyz}, \beta_{zxx}, \beta_{yzz}, \beta_{zzx}$  are the Polarizability and hyperpolarizability tensors. These are obtained from the output file of Polarizability and hyperpolarizability calculations. The values  $\alpha$  and  $\beta$  of Gaussian output are in atomic units. They have been converted into electronic units.

For ' $\alpha$ ', 1 a.u.=0.1482  $\times 10^{-24}$  esu,

For ' $\beta$ ', 1 a.u.=8.6393  $\times 10^{-33}$  esu

A molecule whose dipole moment, molecular polarizability and first hyperpolarizability values are high will have high active NLO properties.

The first hyperpolarizability and their components  $\beta_x, \beta_y$  and  $\beta_z$  of the present molecule along with related properties such as dipole

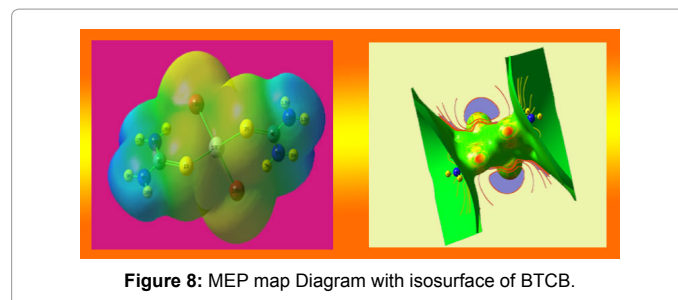


Figure 8: MEP map Diagram with isosurface of BTCB.

moment, average polarizability, anisotropy of polarizability are given in Table 9. In this, the value of dipole moment can be calculated as 4.33 Debye. The dipole moment in the component of  $\mu_z$  is observed as 4.33 D and this value is high. The lowest value of the dipole moment of the molecule compound is  $\mu_y$  component and it is calculated as -0.0089 D. The polarization in different coordinate in the material tuned the optical energy that enters. The calculated value of  $\alpha=153.47 \times 10^{-24}$  esu and  $\Delta\alpha=115.41 \times 10^{-24}$  esu. In the present molecule, the Polarizability is found to be large in amount. This high value of Polarizability shows that the present molecule is rich in NLO property. So the present metallo-organic compound is clearly optically active. The magnitude of the molecular hyperpolarizability  $\beta$ , is one of the important key factors in a NLO system. Because, hyperpolarizability of a system induces optical modulation inside the material and it also stimulating second order harmonic generation in the lattice site. Using (B3LYP/3-21G(d, p)) method, first hyperpolarizability value is calculated as  $\beta=-138.83 \times 10^{-30}$  esu. The high value of hyperpolarizability of the title compound emphasize the generation of the second order harmonic generation with more amplitude. So, the present compound is able to prepare the NLO crystals for enriched electronic applications.

### Thermodynamic properties analysis

Thermo dynamic properties provide the necessary information regarding the chemical reactivity. Moreover it is used to discuss the existence and alternation of thermodynamic parameters of the present compound since the molecule is a metal-organic substance. The values of some thermodynamic parameters such as standard heat capacities ( $C_{p,m}^0$ ), standard entropies ( $S_m^0$ ) and standard enthalpy changes ( $\Delta H_m^0$ ) of title molecule by B3LYP/3-21 G (d, p) method are listed in Table 10. On the basis of vibrational analysis, these values were obtained from the theoretical vibrational frequencies. From Table 10, it can be observed that these thermodynamic functions are increased with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation graph between heat capacities, entropies, enthalpy changes and temperatures were shown in Figure 9.

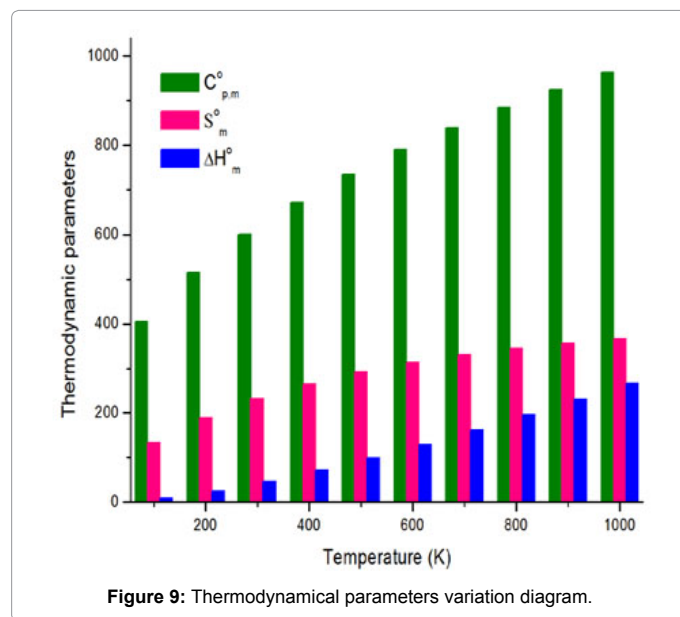
From this observation, it is clear that, the dissociation of atoms related to the temperature is increased up to 1000 K and the molecule has positive entropy-coefficient. In the case of thermodynamical analysis of the molecule, the enthalpy of a system due to the production of metal ion and organic interactions is found to be increased with

Parameter	LSDA 3-21G (d, p) (a.u.)	HF 3-21G (d, p) (a.u.)	Parameter	LSDA 3-21G (d, p) (a.u.)	HF 3-21G (d, p) (a.u.)
$\alpha_{xx}$	-42.9340	-25.6242	$\beta_{xxx}$	0.0349	0.1100
$\alpha_{yy}$	14.7379	22.9900	$\beta_{xxy}$	-0.0424	-0.1562
$\alpha_{zz}$	-136.9602	-139.8447	$\beta_{xyy}$	0.0022	-0.0581
$\alpha_{xz}$	-0.0057	0.0109	$\beta_{yyy}$	0.0047	-0.0409
$\alpha_{yz}$	0.0025	-0.0081	$\beta_{xxz}$	-55.9116	59.7263
$\alpha_{zz}$	-128.8208	-138.6108	$\beta_{yzz}$	24.9887	27.4902
$\alpha_{tot}$	183.312	153.476	$\beta_{yzz}$	-2.6321	10.8741
$\Delta\alpha$	283.314	115.416	$\beta_{zzz}$	-0.0132	0.0178
$\mu_x$	0.0004	0.0021	$\beta_{yzz}$	-0.0041	0.0413
$\mu_y$	-0.0029	-0.0089	$\beta_{zzz}$	-67.2794	-76.2617
$\mu_z$	-1.9775	4.3309	$\beta_{tot}$	-2874.4497	-138.8311
$\mu$	1.9775	4.3309			

**Table 9:** The dipole moments  $\mu$  (D), the polarizability  $\alpha$  (a.u.), the average polarizability  $\alpha_x$  (esu), the anisotropy of the polarizability  $\Delta\alpha$  (esu), and the first hyperpolarizability  $\beta$  (esu) of Bis (thiourea) Cadmium Bromide (BTCB) computed at HF & LSDA with 3-21G (d, p) basis sets.

T(K)	$C_{p,m}^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$S_m^0$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_m^0$ (kcal mol <sup>-1</sup> )	Observed Peak Endothermic signal
100.00	404.94	133.84	9.12	-
200.00	515.37	189.18	25.37	199.08
298.15	599.21	231.74	46.12	247.66
300.00	600.64	232.44	46.55	-
400.00	672.28	265.82	71.53	-
500.00	734.53	292.01	99.47	-
600.00	789.68	312.88	129.76	-
700.00	839.23	329.92	161.92	-
800.00	884.25	344.20	195.65	-
900.00	925.51	356.40	230.70	-
1000.00	963.62	366.95	266.87	-

**Table 10:** Thermodynamic parameters at different temperatures at the B3LYP/3-21G (d, p) level for Bis (thiourea) Cadmium Bromide (BTCB).



**Figure 9:** Thermodynamical parameters variation diagram.

consecutive saturation between the successive temperatures (e.g., 300 K-400 K). At low temperature, it is found that, the specific heat capacity of the present compound falls down rapidly and obeys the Debye  $T^3$  law.

### TGA/DTA analysis

The Thermo gravimetric analysis and differential thermal analysis for BTCB have been performed at a heating rate of 10°C/min in nitrogen and are reported in Figure 10. In the analytical graph, there are two endothermic peaks which are observed at 199.08°C and 247.66°C. The peaks are observed due to the liberation of bromide and cadmium atoms from the crystal which are due to the weak coordination covalent interaction with thiourea. The formation of the metal complex with thiourea in the inner coordination sphere indicates greater thermal stability of the crystal [34]. The TGA analysis curves show that the occurring of weight loss which is about 81.01% in the temperature range 178-602°C and this is due to the detachment of metal bromide.

## Natural Bond Orbital (NBO) analysis

Using DFT/B3LYP level, the Natural Bond Orbital (NBO) calculations are performed in order to understand various second order interactions between the filled orbital of base system and vacant orbital of ligand system and vice versa, which is a measure of the inter-molecular delocalization or hyper-conjugation. The NBO investigation facilitates the most accurate possible natural Lewis structure with the orientation of electron density. The useful aspect of the NBO method is that it gives information about interactions of both filled and virtual orbital interactions. In this case, the second-order Fock-matrix is carried out to evaluate the donor-acceptor interactions in the NBO basis. For each donor (i) and acceptor (j), the stabilization energy [E(2)] associated with the delocalization  $i \rightarrow j$  is determined as

$$E(2) = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\epsilon_i - \epsilon_j}$$

where  $q_i$  is the donor orbital occupancy;  $\epsilon_i$  and  $\epsilon_j$  are the diagonal elements (orbital energies) and  $F(i, j)$  is the off-diagonal NBO Fock-matrix element. In NBO analysis, large value of E(2) shows the intensive interaction between electron-donors and electron-acceptors and greater the extent of conjugation of the whole system, the possible intensive interactions are given in Table 11. The second-order perturbation theory analysis of Fock-matrix in NBO basis shows strong intra-molecular hyper-conjugative interactions of  $\sigma$  and  $\pi$  electrons. The intra molecular hyper-conjugative interactions are formed by the orbital overlap between the thiourea segments and metal-bromide. Though the metal bromide is connected symmetrically with thiourea by coordinate covalent bond, the strong intra-molecular hyper-conjugative interaction is taking place between the lone pair of S1 and  $\sigma$  of Cd17-Br18 that weakens the respective bonds leading to the stabilization of 6.07 kJ mol<sup>-1</sup>. The another intra molecular hyper-conjugative interaction is formed by the orbitals of S2-C4 and Cd17-Br (18 and 19) overlap between thiourea and cadmium atom and bond orbital by spending 6.05 kJ mol<sup>-1</sup> which results in ICT causing stabilization of metal organic system. Simultaneously, the interaction is taking place between S2-C4 and N11-H (12 and 13) by spending 3.30 kJ mol<sup>-1</sup>. This view shows the mutual coupling of thiourea and Cd in left moiety. The same amount of energy has been spent to form the interaction between C-S and Cd in right moiety of the total system. Thus, a strong intra molecular hyper-conjugative interaction has occurred between metal atom and thiourea. From these interactions, it is notable that, in the case of Cd-Br, the electron density move towards Br from Cd by making it positive. In the case of C-S and N-H,

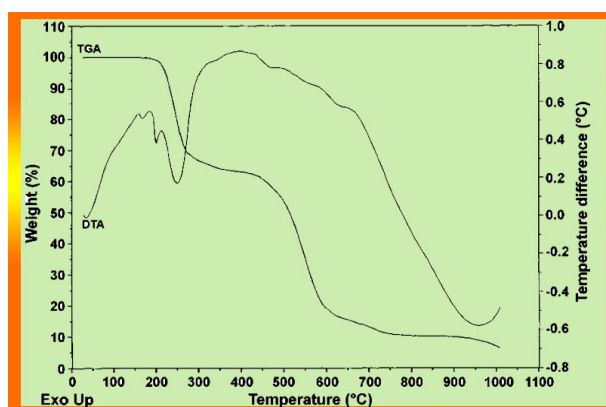


Figure 10: TGA/DTA curve for BTCB.

Donor (i)	Type of bond	Occupancy	Acceptor (j)	Type of bond	E(2) kcal/mol	E(j) - E(i) a.u.	F(i, j) a.u.
S1	$\sigma$	1.999	Cd17	$\sigma^*$	20.58	88.22	0.159
S1	$\sigma$	1.999	Cd17-Br18	$\sigma^*$	6.07	7.70	0.04
S1	$\sigma$	1.999	Cd17-Br19	$\sigma^*$	5.44	5.88	0.020
S1	$\sigma$	1.999	C3-N14	$\sigma^*$	23.63	0.21	0.067
S1-C3	$\sigma$	1.977	N8	$\sigma^*$	1.15	2.14	0.045
S1-C3	$\sigma$	1.977	N14	$\sigma^*$	1.16	2.16	0.045
S1-C3	$\sigma$	1.977	N8-H9	$\sigma^*$	3.29	1.01	0.052
S1-C3	$\sigma$	1.977	N14-H15	$\sigma^*$	3.24	1.02	0.051
S1-C3	$\sigma$	1.977	Cd17-Br18	$\sigma^*$	0.09	0.73	0.007
S1-C3	$\sigma$	1.977	Cd17	$\sigma^*$	1.84	0.71	0.034
S2	$\sigma$	1.999	C4-N5	$\sigma^*$	23.63	0.21	0.066
S2	$\sigma$	1.999	Cd17	$\sigma^*$	20.57	0.32	0.073
S2	$\sigma$	1.999	Cd17-Br18	$\sigma^*$	5.46	0.34	0.040
S2	$\sigma$	1.999	Cd17-Br19	$\sigma^*$	6.05	0.34	0.042
S2-C4	$\sigma$	1.977	Cd17	$\sigma^*$	0.73	0.71	0.022
S2-C4	$\sigma$	1.977	N5-H6	$\sigma^*$	3.24	1.02	0.051
S2-C4	$\sigma$	1.977	N11-H12	$\sigma^*$	3.30	1.01	0.052
C3-N14	$\pi$	0.498	C3	$\pi^*$	0.55	1.06	0.043
C3-N8	$\sigma$	1.994	N8-H9	$\sigma^*$	0.60	1.26	0.025
C3-N14	$\pi$	1.996	C3-N14	$\pi^*$	4.79	0.34	0.041
C4	$\sigma$	1.999	Cd17	$\sigma^*$	0.05	10.20	0.022
C4-N5	$\pi$	1.996	Cd17	$\pi^*$	0.37	0.44	0.012
C4-N5	$\pi$	1.996	C4-N5	$\pi^*$	7.76	0.48	0.103
C4-N11	$\sigma$	1.994	Cd17	$\sigma^*$	0.15	0.96	0.011
N5-H6	$\sigma$	1.985	S2-C4	$\sigma^*$	4.45	0.86	0.055
N5-H7	$\sigma$	1.986	C4-N11	$\sigma^*$	4.11	1.09	0.060
N5-H7	$\sigma$	1.986	Cd17	$\sigma^*$	0.54	0.73	0.019
N5-H7	$\sigma$	1.986	Cd17-Br18	$\sigma^*$	0.22	0.75	0.012
N5-H7	$\sigma$	1.986	Cd17-Br19	$\sigma^*$	0.07	0.75	0.007
N8	$\sigma$	1.998	C3-N14	$\sigma^*$	75.42	0.23	0.123
N8-H9	$\sigma$	1.988	C3	$\sigma^*$	2.89	1.41	0.057
N8-H10	$\sigma$	1.990	C3	$\sigma^*$	2.60	1.58	0.057
N11	$\sigma$	1.998	C4-N5	$\sigma^*$	75.89	0.23	0.123
N11-H 13	$\sigma$	1.990	C 4 - N 5	$\sigma^*$	3.72	1.12	0.058
N11-H13	$\sigma$	1.990	Cd17	$\sigma^*$	0.05	0.75	0.006
N14	$\sigma$	1.998	C3	$\sigma^*$	5.87	14.81	0.264
N14-H15	$\sigma$	1.985	C3	$\sigma^*$	2.49	1.40	0.053
N14-H16	$\sigma$	1.986	C3	$\sigma^*$	1.48	1.38	0.040
N14-H16	$\sigma$	1.986	Cd17-Br18	$\sigma^*$	0.07	0.75	0.007
N14-H16	$\sigma$	1.986	Cd17-Br19	$\sigma^*$	0.22	0.75	0.012
Cd17-Br18	$\sigma$	1.970	H16	$\sigma^*$	0.06	1.34	0.008
Cd17-Br18	$\sigma$	1.970	S1-C3	$\sigma^*$	0.05	0.60	0.005
Cd17-Br19	$\sigma$	1.970	N14	$\sigma^*$	0.05	1.93	0.009
Cd17-Br19	$\sigma$	1.970	H16	$\sigma^*$	0.34	1.34	0.019
Cd17-Br19	$\sigma$	1.970	N14-H16	$\sigma^*$	4.39	0.79	0.053
Br18	$\sigma$	2.000	N5-H7	$\sigma^*$	20.03	0.58	0.097
Br19	$\sigma$	2.000	N14-H16	$\sigma^*$	20.00	0.58	0.097
Cd17	$\sigma$	1.999	Cd17-Br18	$\sigma^*$	19.82	0.02	0.042
Cd17	$\sigma$	1.999	Cd17-Br19	$\sigma^*$	19.93	0.02	0.042

Table 11: Second order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intra-molecular bonds of the Bis (thiourea) Cadmium Bromide (BTCB).

the electron clouds are pulled by C and N by leaving S neutral. The increased electron density at the Br and N atoms leads to the elongation of respective bond length and a lowering of the corresponding stretching modes. The electron density (ED) is transferred from the n(Br) to the anti-bonding of  $\sigma^*$  and  $\pi^*$  orbital of the BTCB explaining

both the elongation and the red shift. This view is strongly validated by Mulliken charge analysis.

## Conclusions

FT-IR, FT-Raman, UV, NMR and quantum chemical calculation studies have been performed on Bis Thiourea Cadmium Bromide (BTCB) to identify its structural and spectroscopic properties. A complete vibrational analysis of BTCB was performed with HF and DFT method using 3-21G (d, p) basis set. From the UV-Visible spectra, it is monitored that, the entire electronic transitions shifted bathochromically due to the substitutional effect. From the Mulliken charge analysis, the entire charge levels of the molecule are altered on par with due to the substitution. The electrical, optical and bio molecular properties are profoundly investigated using frontier molecular orbital. From NMR analysis, it is concluded that the chemical property of the metal is directly coupled with organic molecules and this shows that the present metal complex molecule have an additional chemical property. The MEP map is performed and from this, the change of the chemical properties of the compound is also discussed. The TGA/DTA curves recorded for the crystal confirmed its thermal stability. The correlations between the statistical thermodynamics and temperature are also obtained. It is seen that the heat capacities, entropies and enthalpies increase with the increasing temperature owing to the intensities of the molecular vibrations increase with increasing temperature. Furthermore, the average Polarizability, the first order hyperpolarizability and total dipole moment of title molecule have been calculated and the results are discussed. These results indicate that the title compound is a good candidate of nonlinear optical materials. In NBO analysis, both filled and virtual orbital interactions are discussed.

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