

DFT Studies on the Molecular Structure, Electronic and Spectroscopic Properties of Free and Zinc(II) Coordinated N-Alkyl Thiourea Ligands

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The molecular structure, vibrational spectra and non linear optical properties of five thiourea ligands (L) and their zinc chloride complexes; $[\text{ZnL}_2\text{Cl}_2]$ are calculated using DFT/B3LYP method. The results of calculations showed an increase of the C-N double bond characters and decrease of the C-S bond order due to the coordination between Zn^{2+} and thiourea ligands through the S-atom. A low frequency shift for the $\nu(\text{C-S})$ bands and high frequency shift for $\nu(\text{C-N})$ bands are predicted in case of the zinc(II) complexes compared to the free ligands. Also, red shifts for the $\nu(\text{N-H})$ stretches involved in the formation of intramolecular $\text{NH}\cdots\text{Cl}$ H-bonds while the rest of the $\nu(\text{N-H})$ modes undergo blue shifts. High polar character of the C-N and C-S bonds is predicted. Molecular electrostatic potential predicted the higher reactivity of the S-site of the thiourea ligands towards electrophilic attack compared to the N-sites.

Keywords: Thiourea, DFT, Vibrational spectra, Intramolecular H-bond, Non-linear optical.

INTRODUCTION

The study of thiourea and its N-substituted derivatives have great interest¹ in view of the potential use of these compounds as highly selective reagents for the separation of metal cations¹ and in biological applications such as their use as antibacterial, antiviral or antifungal agents^{2,3}. Also the importance of these thioamides is due to the relevance of their binding sites to those in living systems². Their transition metal complexes are also subject of interest due to the special roles played by these compounds in biological processes^{1,4,5}.

The coordination occurs between the metal with sulphur rather than between the metal and nitrogen⁶. It is also found that thiourea ligands can exist in the highly polar structure (Fig. 1). The molecular structure of these compounds is considered to be a resonance hybrid with this highly polar structure. In this work, the molecular structure and vibrational spectra of thiourea (TU), N-methylthiourea (MTU), N,N'-dimethylthiourea (DMTU), tetramethylthiourea (TMTU), diazinane-2-thione (DAT); (Fig. 1) and their zinc chloride complexes $[\text{ZnL}_2\text{Cl}_2]$ are calculated using DFT/B3LYP/6-311+G(d,p) method. The aim of this work is to explain the effect of N-alkyl substitution and metal ion coordination on the molecular structure, reactivity, electronic and spectroscopic properties of these compounds using DFT/B3LYP method.

COMPUTATIONAL METHODS

All calculations for the ligands (L) and their $[\text{ZnL}_2\text{Cl}_2]$ complexes were carried out using Gaussian 03 software⁷ on Pentium IV processor personal computer. The calculations were performed using DFT/B3LYP/6-311+G(d,p) method. The starting input geometry of the $[\text{ZnL}_2\text{Cl}_2]$ complexes are taken from the crystallographic information file (CIF)⁸ where tetrahedral coordination geometry around the zinc atom is considered^{3,9}. GaussView¹⁰ has been used to draw the structures of the optimized geometries and to make assignment for the vibrational modes.

RESULTS AND DISCUSSION

Stabilities, dipole moments (μ) and thermodynamic functions: The energies, dipole moments and thermodynamic functions of the thiourea ligands are shown in Table-1. It was reported that, N-methylthiourea and N,N'-dimethylthiourea exist in the *cis-trans* and *trans-trans* configuration, respectively^{2,11}. The DFT gas phase calculations predicted the *cis*-conformer of N-methylthiourea is more stable than the *trans* one while for N,N'-dimethylthiourea, the *cis-trans* conformer is more stable than the others. The results of energy analysis predicted the *cis*-conformer of N-methylthiourea is more stable than the *trans* one by only 0.2199 kcal/mole. The energy difference between the two conformers is very small which indicates

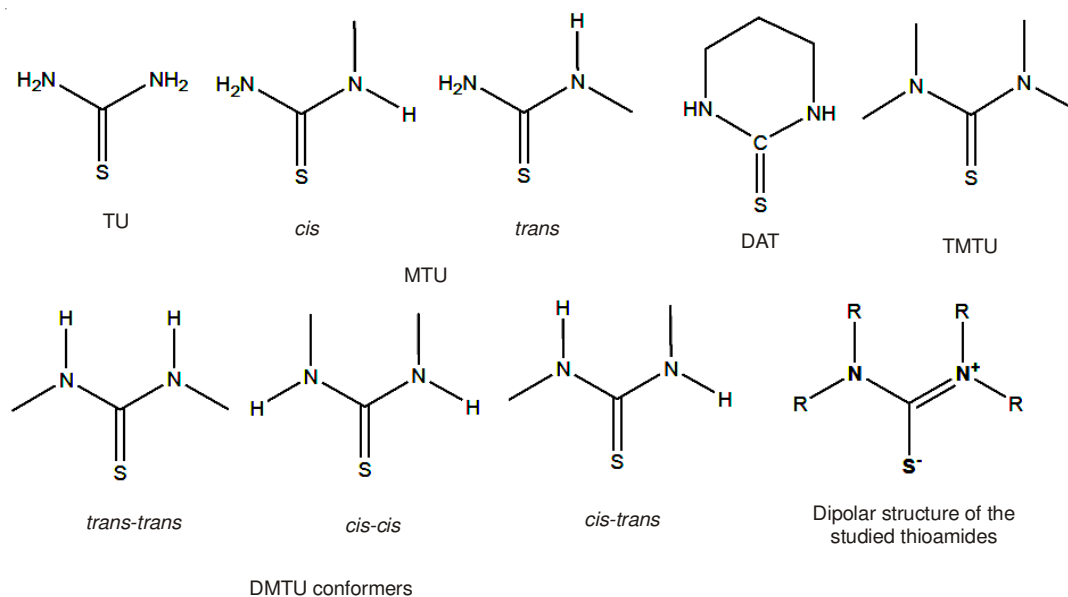
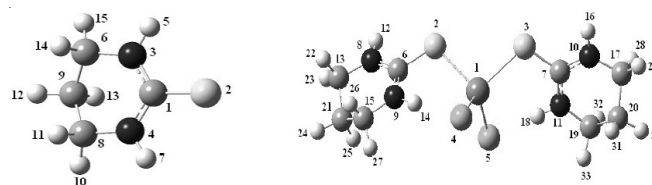


Fig. 1. Structure of the studied thiourea ligands (L)

their coexistence in equilibrium in the gas phase. For N,N'-dimethylthiourea, the calculations showed that the *cis-trans* conformer is more stable than the *trans-trans* one by 0.5242 kcal/mol. In view of the relatively high ΔE value of the *cis-cis* conformer, one can conclude that it should not be observed in the gas phase and the *cis-trans* conformer is the dominant species (Table-1). On other hand, the calculated dipole moment values indicate that the *cis*(MTU) is more polar than the *trans*(MTU) while for N,N'-dimethylthiourea, the *cis-trans* conformer is more polar than the *trans-trans* one.

Molecular geometry: The optimized molecular structure of one of the studied thiourea ligands (L) and its $[\text{ZnL}_2\text{Cl}_2]$ complex as an example are shown in Fig. 2. Selected geometric parameters are summarized in Table-2. For thiourea, the C-S, C1-N3 and C1-N4 bond distances are calculated to be 1.671, 1.365 and 1.365 Å, respectively while for N-methyl-thiourea are predicted to be 1.681, 1.363 and 1.356 Å respectively. One can conclude that the presence of N-alkyl substitution increase the double bond character of the C-N bonds while the single bond character of the C-S bond is increased. For the $[\text{ZnL}_2\text{Cl}_2]$ complexes, the elongation of the C-S bond and the shortening of the C-N bonds increase as the Zn-S interaction increase, in other word, the Zn-S distances decrease. It is noted that the calculated values of the N9-H14 and N11-H18 distances in

case of the complexes **1-4**, are slightly longer than the rest of N-H bonds. This could be attributed to the intramolecular N-H---Cl interactions between the coordinated Cl-atoms with H14 and H18 sites. These results are in good agreement with the available X-ray structure of the studied complexes^{8,9}.

Fig. 2. B3LYP/6-311+G** optimized molecular geometries and atom numbering scheme of DAT and $[\text{Zn}(\text{DAT})_2\text{Cl}_2]$ complexes

Atom polar tensor (APT) charges: Atom polar tensor charges of the studied compounds are calculated using B3LYP method. Selected APT charge values are given in Table-3. The S- and N-sites are considerably affected by the presence of N-alkyl substituent. The electron releasing N-methyl substituent (+I) increases the negative charge density at the N and S-atoms. The polar character of the C-S and C-N bonds of N-methylthiourea, N,N'-dimethylthiourea and diazinane-2-thione is slightly higher than that for thiourea⁶. Also, the coordination

TABLE-1
CALCULATED TOTAL ENERGIES, DIPOLE MOMENT (μ), THERMODYNAMIC FUNCTIONS AND RELATIVE STABILITIES OF THE THIOUREA LIGANDS USING DFT/B3LYP/6-311G+(d,p) METHOD

Compound		^a E _{corr} (Hartree)	M (Debye)	G (Hartree)	ΔE (kcal/mol)	ΔG (kcal/mol)	K	X
Thiourea	—	-548.2413	5.009	-548.2688				
N-Methylthiourea	<i>cis</i>	-587.5300	5.835	-587.5602	0	0	-	0.6420
	<i>trans</i>	-587.5297	5.037	-587.5597	0.2199	0.3483	1.793	0.3580
N,N'-Dimethylthiourea	<i>cis-cis</i>	-626.8102	5.469	-626.8422	4.9117	5.5798	11584.164	0.0001
	<i>cis-trans</i>	-626.8180	5.740	-626.8511	0	0	-	0.8149
	<i>trans-trans</i>	-626.8171	5.038	-626.8497	0.5242	0.8842	4.405	0.1850
Diazinane-2-thione	—	-664.9301	6.426	-664.9614				

$$^a E_{\text{corr}} = E_{\text{tot}} + \text{ZPVE}$$

TABLE-2
SELECTED BOND DISTANCES AND BOND ANGLES CALCULATED USING
THE B3LYP/6-311+G(d,p) METHOD FOR THE STUDIED COMPOUNDS

Atoms	TU	MTU	DMTU	DAT	TMTU	Atoms	1	2	3	4	5	Exp. ^a
C1-S2	1.671	1.681	1.685	1.686	1.682	Zn1-S2	2.460	2.443	2.445	2.434	2.469	2.341
C1-N3	1.365	1.363	1.363	1.358	1.378	C6-S2	1.714	1.722	1.723	1.726	1.725	1.735
C1-N4	1.365	1.356	1.356	1.358	1.378	Zn1-S3	2.457	2.443	2.445	2.439	2.482	2.341
N3-H5	1.010	1.007	1.007	1.008	-	C7-S3	1.714	1.722	1.723	1.727	1.724	1.735
N3-H6	1.007	1.008	-	-	-	C6-N8	1.353	1.353	1.350	1.350	1.359	1.327
N4-H7	1.010	1.007	1.007	1.008	-	C6-N9	1.331	1.328	1.335	1.330	1.351	1.327
N4-H8	1.007	-	-	-	-	C7-N10	1.352	1.353	1.350	1.350	1.360	1.327
N3-C1-N4	114.650	115.987	115.890	116.430	114.862	C7-N11	1.330	1.328	1.335	1.330	1.350	1.327
S2-C1-N3	122.675	121.983	120.999	121.779	122.572	N8-H12	1.008	1.006	1.008	1.008	-	0.885
S2-C1-N4	122.676	122.017	123.111	121.779	122.566	N8-H13	1.006	1.007	-	-	-	-
						N9-H14	1.028	1.028	1.026	1.027	0.882	-
						N9-H15	1.009	-	-	-	-	-
						N10-H16	1.006	1.006	1.008	1.008	0.882	-
						N10-H17	1.008	1.007	-	-	-	-
						N11-H18	1.028	1.028	1.026	1.027	0.882	-
						N11-H19	1.009	-	-	-	-	-
						H14---Cl4	2.137	2.130	2.148	2.140	2.339	-
						H18---Cl5	2.130	2.130	2.148	2.160	2.339	-

^a[Ref. 8] complexes **1-5**

TU: Thiourea, MTU: N-methylthiourea, DMTU: N,N'-dimethylthiourea, DAT: diazinane-2-thione, TMTU: tetramethylthiourea

TABLE-3
CALCULATED APT CHARGES AT VARIOUS ATOMIC SITES FOR THE STUDIED THIOUREA
LIGANDS; L AND THEIR COORDINATION COMPLEXES; [ZnL₂Cl₂] USING DFT METHOD

Atom	TU	MTU	DMTU	DAT	TMTU	Atom	1	2	3	4	5
C1	1.1854	1.1897	1.1698	1.1769	1.1384	C6	1.2166	1.1758	1.1774	1.1601	1.1743
S2	-0.5967	-0.6508	-0.6314	-0.6875	-0.5998	C7	1.2247	1.1760	1.1774	1.1458	1.1643
N3	-0.7247	-0.7036	-0.7216	-0.7326	-0.7991	S2	-0.6336	-0.6629	-0.6526	-0.6974	-0.7071
N4	-0.7246	-0.7528	-0.7795	-0.7326	-0.7991	S3	-0.6309	-0.6629	-0.6526	-0.6982	-0.6913
H5	0.2273	0.2332	0.1540	0.1952	-	N8	-0.7793	-0.7793	-0.7836	-0.8061	-0.7315
H6	0.2031	0.1964	-	-	-	N9	-0.8027	-0.8085	-0.8486	-0.7960	-0.7924
H7	0.2273	0.1903	0.1890	0.1952	-	N10	-0.7823	-0.7795	-0.7836	-0.7891	-0.7282
H8	0.2030	-	-	-	-	N11	-0.8124	-0.8086	-0.8486	-0.7869	-0.7933
						H12	0.2176	0.2155	0.1638	0.2138	-
						H13	0.2511	0.2557	-	-	-
						H14	0.4057	0.3713	0.3667	0.3894	-
						H15	0.2090	-	-	-	-
						H16	0.2192	0.2156	0.1638	0.2099	-
						H17	0.2532	0.2558	-	-	-
						H18	0.4090	0.3714	0.3667	0.3811	-
						H19	0.2079	-	-	-	-
						Zn	1.3639	1.3569	1.3822	1.3708	1.3514
						Cl	-0.7683	-0.7740	-0.7811	-0.7813	-0.7268
						Cl	-0.7683	-0.7740	-0.7811	-0.7875	-0.7323

TU: Thiourea, MTU: N-methylthiourea, DMTU: N,N'-dimethylthiourea, DAT: diazinane-2-thione, TMTU: tetramethylthiourea

of the Zn²⁺ with the S-atom of the ligand further increases the polar character of these bonds. Moreover, it is found that the formation of N-H---Cl intramolecular H-bonding interactions increases the charge density at the H14 and H18 atoms (almost twice) compared to the other H-atoms. As a result the charge densities at the neighboring N-atoms (N9 and N11) are shifted to more negative charge densities than the corresponding N8 and N10 atoms.

Molecular electrostatic potential (MEP): The molecular electrostatic potential (MEP) is used to study the electrophilic reactivity of the studied thiourea ligands towards attack by positive metal ion such as Zn²⁺ electrophile. The most negative regions are associated with S-atom (-0.0382 to -0.0471 a.u.) rather than the N-atom (+0.0085 to -0.0145 a.u.). From this

point of view, the reactivity of the S-site toward electrophilic attack by a positive metal ion such as Zn²⁺ electrophile is more favored than N-site³ where the former offer more negative electrostatic potential than the latter.

Vibrational spectra: The fundamental vibration modes of the studied compounds are given in Table-4. The calculated harmonic frequencies are scaled down by multiplying their values by a factor of 0.9679¹².

N-H stretching modes: In order to evaluate the effect of the metal ion coordination on the vibrational spectra of the studied thioamides, the shifts in the vibrational frequencies ($\Delta\nu_i^{\text{Scal}}$) and intensities (ΔA_i) due to complex formation have been calculated by using equations proposed by Destexhe *et al.*¹³ and the results are given in Table-5. It can be seen that

TABLE-4
SELECTED STRETCHING VIBRATIONAL FREQUENCIES (ν) (cm^{-1}) AND
VIBRATIONAL INTENSITIES (A) (km mol^{-1}) FOR THE STUDIED COMPOUNDS

No.	TU			MTU			DMTU			DAT			TMTU			Assig.
	Unscal.	Scal.	A	Unscal.	Scal.	A	Unscal.	Scal.	A	Unscal.	Scal.	A	Unscal.	Scal.	A	
1	3694	3575	24.4	3709	3590	50.1	3651	3534	54.9	3642	3525	8.1	-	-	-	ν_{NH}
2	3693	3574	68.9	3648	3531	53.1	-	-	-	-	-	-	-	-	-	ν_{NH}
3	3568	3453	13.6	3580	3465	29.6	3626	3510	20.0	3637	3520	91.3	-	-	-	ν_{NH}
4	3560	3446	46.7	-	-	-	-	-	-	-	-	-	-	-	-	ν_{NH}
5	1419	1373	110.6	1543	1493	377.3	1571	1521	277.4	1574	1523	292.9	1395	1350	199.5	ν_{CN}
6	1405	1360	320.8	1414	1369	18.1	1359	1315	111.9	1343	1300	65.5	1376	1332	184.7	ν_{CN}
7	766	741	11.7	795	769	32.1	736	712	4.6	585	566	8.4	627	607	0.3	ν_{CS}
	1			2			3			4			5			
1	3720	3601	58.5	3723	3603	60.2	-	-	-	-	-	-	-	-	-	ν_{NH}
2	3716	3597	56.9	3723	3603	57.8	-	-	-	-	-	-	-	-	-	ν_{NH}
3	3634	3517	41.4	-	-	-	-	-	-	-	-	-	-	-	-	ν_{NH}
4	3633	3516	123.9	-	-	-	-	-	-	-	-	-	-	-	-	ν_{NH}
5	3591	3476	64.4	3599	3483	38.6	3633	3516	1.7	-	-	-	-	-	-	ν_{NH}
6	3587	3472	63.6	3598	3483	89.9	3633	3516	72.7	3639	3522	59.9	-	-	-	ν_{NH}
7	3252	3148	847.5	3260	3155	1431.1	3294	3188	1428.1	3638	3521	60.1	-	-	-	ν_{NH}
8	3247	3143	830.9	3260	3155	270.4	3293	3187	266.2	3280	3175	898.9	-	-	-	ν_{NH}
9	1511	1462	106.6	1625	1573	242.3	1620	1568	297.4	3272	3167	865.3	1572	1522	247.9	ν_{CN}
10	1509	1461	104.1	1622	1570	269.4	1618	1566	247.8	1631	1579	129.8	1570	1520	255.9	ν_{CN}
11	1404	1359	6.4	1440	1394	35.7	1392	1347	75.4	1627	1575	258.6	1423	1377	105.6	ν_{CN}
12	1399	1354	593.3	1439	1393	40.7	1392	1347	51.1	1349	1306	53.6	1421	1375	116.1	ν_{CN}
13	728	705	6.9	782	757	59.7	727	704	5.2	1349	1306	59.2	616	596	2.4	ν_{CS}
14	727	704	62.0	781	756	6.6	727	704	7.1	576	558	5.5	615	595	10	ν_{CS}

TU: Thiourea, MTU: N-methylthiourea, DMTU: N,N'-dimethylthiourea, DAT: diazinane-2-thione, TMTU: tetramethylthiourea

TABLE-5
CALCULATED CHANGES IN THE VIBRATIONAL FREQUENCIES ($\Delta\nu^{\text{scal}}$) AND
VIBRATIONAL INTENSITIES (ΔA) FOR THE STUDIED $[\text{ZnL}_2\text{Cl}_2]$ COMPLEXES

$\Delta\nu^{\text{com}}/\Delta\nu^{\text{mon}}$	1		2 ^a		3 ^b		4 ^b		5	
	$\Delta\nu^{\text{cal}}$	ΔA	$\Delta\nu^{\text{scal}}$	ΔA	$\Delta\nu^{\text{scal}}$	ΔA	$\Delta\nu^{\text{scal}}$	ΔA	$\Delta\nu^{\text{scal}}$	ΔA
ν_1/ν_1	25	34.1	14	10.1	-	-	-	-	-	-
ν_2/ν_1	21	32.5	14	7.7	-	-	-	-	-	-
ν_3/ν_2	-57	-27.5	-	-	-	-	-	-	-	-
ν_4/ν_2	-58	55.0	-	-	-	-	-	-	-	-
ν_5/ν_3	22	50.8	18	9.0	7	-18.3	2	-31.4	-	-
ν_6/ν_3	18	50.0	17	60.3	7	52.7	1	-31.2	-	-
ν_7/ν_4	-298	800.8	-376	1378.0	-346	1373.2	-350	890.8	-	-
ν_8/ν_4	-303	784.2	-376	217.3	-347	211.3	-358	857.2	-	-
ν_9/ν_5	89	-4.0	79	-135.0	47	20.0	55	-163.1	171	48.4
ν_{10}/ν_5	87	-6.5	76	-107.9	45	-29.6	51	-34.3	169	56.4
ν_{11}/ν_6	-1	-314.4	25	17.6	32	-36.5	6	-11.9	45	-79.1
ν_{12}/ν_6	-6	272.5	24	22.6	32	-60.8	6	-6.3	44	-68.6
ν_{13}/ν_7	-37	-4.8	-13	27.6	-9	0.6	-9	-2.9	-11	0.3
ν_{14}/ν_7	-38	50.3	-14	-25.5	-9	2.5	-11	14.1	-12	0.3

^aModes ν_7/ν_2 and ν_8/ν_2 ; ^bModes ν_7/ν_1 and ν_8/ν_1

the coordination of the metal ion to the S-atom leads to blue shift in the N-H stretching frequencies (modes ν_1 , ν_2 , ν_5 and ν_6) where the formation of $\text{S} \rightarrow \text{M}$ bonds in all complexes under investigation increases the contribution of the highly polar structure to the thioamide molecules^{3,6}. On other hand, the formation of N-H...Cl intramolecular H-bonding between N9-H14 and N11-H18 with the coordinated chlorine atoms reduces the N-H bond order. As a result these N-H stretching vibrations undergo red shift and increase in their vibrational intensities up to 111 times in case of $[\text{ZnL}_2\text{Cl}_2]$ complexes; **1-4** (modes ν_3 , ν_4 , ν_7 and ν_8) compared to the free ligands (modes ν_2 and ν_4)¹⁴.

C=S and C-N stretching modes: In IR spectrum of thiourea ligands, the characteristic bands of the $\nu(\text{C}=\text{S})$ and $\nu(\text{C}-\text{N})$ is expected in the frequency regions; 700-600 cm^{-1} and at about 1500 cm^{-1} , respectively. As shown in Table-5, a low frequency shift in the $\nu(\text{C}=\text{S})$ bands and a high frequency shift in the $\nu(\text{C}-\text{N})$ bands are predicted for the complexes compared to free ligands. These spectral shifts are due to the $\text{S} \rightarrow \text{Zn}^{2+}$ coordination where the increase of the interaction between Zn^{2+} and S-atom.

Frontier molecular orbitals: The frontier molecular orbitals (FMO) can offer a reasonable qualitative prediction of

TABLE-6
CALCULATED FRONTIER MOLECULAR ORBITALS ENERGIES (eV) FOR THE STUDIED COMPOUNDS

Compound	E _{HOMO}	E _{LUMO}	ΔE	Compound	E _{HOMO}	E _{LUMO}	ΔE
TU	-5.9174	-0.6599	5.2576	1	-6.7455	-0.9701	5.7754
MTU	-5.7264	-0.5328	5.1936	2	-6.5438	-0.7263	5.8176
DMTU	-5.5830	-0.5146	5.0684	3	-6.3030	-0.6822	5.6208
TMTU	-5.4859	-0.5850	4.9008	4	-6.4521	-0.6193	5.8328
DAT	-5.6121	-0.4792	5.1329	5	-6.1866	-1.0868	5.0997

TU: Thiourea, MTU: N-methylthiourea, DMTU: N,N'-dimethylthiourea, DAT: diazinane-2-thione, TMTU: tetramethylthiourea

the excitation properties and the ability of electron transport^{15,16}. The energies of the HOMO and LUMO orbital of studied thiourea ligands; L and their [ZnL₂Cl₂] complexes were investigated using DFT/B3LYP method and the results are given in Table-6. The results of the FMO energy analysis showed that the energy difference between the HOMO and LUMO decreased due to the presence of alkyl substituent at the N-atom of the studied ligands. In case of the [ZnL₂Cl₂] complex, the coordination of the Zn²⁺-ion with the thiourea ligands through the S-atom increases the energy of the HOMO more than the LUMO so, the transition energies are increased and blue shift is predicted.

Non-linear optical properties (NLO): The NLO properties have an important role in communication technology and optical memory devices¹⁷. The NLO properties are related to the energy gap (ΔE) between HOMO and LUMO. The smaller ΔE value, the more shift of the absorption band towards the visible region^{18,19} and the higher NLO properties. It is found that, the presence of alkyl substituents at the N-sites of thiourea molecule decrease the value of ΔE so; increase the NLO properties. These results show that the N-alkyl thiourea ligands are better NLO material than thiourea. In contrast, the calculations predicted larger energy gaps (ΔE) and so higher excitation energies in case of the [ZnL₂Cl₂] complexes compared to the free ligands. As a result, the NLO properties are predicted to decrease for the former compared to the latter.

Conclusion

The molecular geometries and vibrational spectra of five thiourea ligands (L) and their [ZnL₂Cl₂] complexes are calculated using B3LYP method. There C-N bonds are shortened and the C-S bonds are elongated due to the coordination of the Zn²⁺ to the thiourea ligands through the S-atom. As a result a blue shift in the ν(C-N) modes and red shift in the ν(C-S) stretches. The degree of infrared spectral shifts is inversely proportional to the Zn-S distances. Careful analysis of the NH stretching modes predicted red shift for the ν(N-H) involved in the intramolecular N-H...Cl interactions while the stretching frequencies of the other ν(N-H) modes undergo blue shift. Molecular electrostatic potential study showed that the zinc ion as electrophile tends to attack on the S-atom of thiourea ligands rather than the N-sites. The atom polar tensor charge analyses confirmed the high polarity of the C-N and C-S bonds.

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