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The theoretical and experimental vibrational studies of thiourea and silver nitrate (2:1) complex

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ABSTRACT

The theoretical and experimental vibrational studies for poly thiourea silver nitrate (2:1) complex using DFT method are performed on the basis of experimental data. During the geometry optimization process one equilibrium structure was found. The Mulliken charges, harmonic vibrational frequencies, Infrared and Raman intensities were calculated on the basis of quantum chemical density functional calculations using firefly (PC GAMESS) Version 7.1G. The clear – cut assignments of observed bands are performed on the basis of potential energy distribution (PED) analysis. Highest Occupied Molecular Orbital (HOMO) and the Lowest Occupied Molecular Orbital (LUMO) are obtained and graphically illustrated with minimum energy. The energy difference between HOMO and LUMO is analyzed. The other molecular properties like molecular electrostatic potential, Mulliken charges and thermodynamic properties of the title compound have also been calculated.

1. Introduction

The centrosymmetric thiourea which is an interesting class of organic compounds coordinate with metal ions forms the non-centrosymmetric stable coordinate complexes [1]. Some of the thiourea metal complexes with NLO properties have been already reported by several researchers [2–8]. Thiourea is found to be crystallizes in the rhombic bipyramidal division of the rhombic system and behaves as a good ligand [9]. The coplanar nature of the C, N and S atoms in the molecule establishes the crystal structure of thiourea [10]. Thiourea can be used as inorganic matrix modifier since it possess a large dipole moment and have the ability to form an extensive network of hydrogen bonds [11, 12]. Vibrational spectra carry significant information about structure, potential energy surfaces and interactions with environment. Silver has been used in the production of coins, craft pieces and since, silver exhibits a high conductivity and their conduction electrons show relatively little resistance to movement under an electric field, it can be used in the field of electronics. Also, their photo chemical properties are extensively used in the field of photography [13]. Poly bis (thiourea) silver (I) nitrate (TuAgN) is one such polymeric semi-organic NLO crystal, characterized for its NLO property where the thiourea is ionically bonded to the silver metal ion. Single crystal X-ray diffraction study reveals that TuAgN crystallizes in non-centrosymmetric space group (C2221) with lattice parameters a = 33.3455(6) Å, b = 45.2957(7) Å, c = 20.3209(5) Å, α = β = γ = 90° and Z = 16 [14].

TuAgN can be extensively studied by spectroscopic and theoretical methods. Molecular spectroscopy is a fundamental tool to establish structure-property relationships. IR, Raman spectroscopic studies along with HOMO-LUMO and hyperpolarizability analysis has been used to elucidate information regarding charge transfer within the molecule. Hence the aim of the present work is to investigate the complete description of the molecular vibrations of the TuAgN. However, the electronic energy, HOMO-LUMO energy and electrostatic potential have also been calculated and discussed in detail.

2. Experimental

TuAgN crystal was synthesized at 60 °C by taking thiourea and silver nitrate 2:1 stoichiometric molar ratio with ultrapure water (resistivity = 18.2 MΩ cm) as the solvent. To the thiourea solution, silver nitrate was added slowly and stirred well for 4 h to get the homogeneous mixture. The synthesized compound has been obtained by the following chemical reaction:

$$2(CH_4N_2S) + AgNO_3 \rightarrow [Ag\,(CH_4N_2S)_2].NO_3.$$

The resultant solution was filtered with Whatman filter paper and allowed for slow evaporation at room temperature. Salt of TuAgN was collected after one week of solvent evaporation. The calculated amount

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of recrystallized salt was dissolved in water and the prepared saturated solution was kept undisturbed in a dust free atmosphere. Recrystallization process was carried out by using millipore water to get the pure crystal suitable for X-ray diffraction.

3. Quantum Chemical Calculations

All calculations were performed with the Firefly (PC GAMESS) version 7.1.G, build number 5618 program [15], compiled under Linux operating system. This job was executed on small PC Cluster consisting of three server nodes with 32-bit and 64-bit AMD processors running at 1.8 GHz and 2 GB RAM. The MPICH [16] implementation of MPI standard (Message Passing Interface) for communication between cluster nodes was used. This protocol ensures good performance and complete remote execution environment.

For calculation the structural data from X-ray investigations of crystal were used. The coordinates for particular atoms were established and the *Z*-matrix was built by Molden program [17]. The Z-matrix was directly used in input Firefly files. The optimized structures for all investigated forms of considered complex have been calculated by the HF method. The 3–21 basis set has been employed. The harmonic frequencies and infrared intensities were calculated by the Hartree Fock method with identical basis set. The procedure fol20wed by Fogarasi and Pulay has been employed to the normal coordinate analysis on the investigated molecule [18]. Based on the reference [19], a scaling factor of 0.89 was used for all stretching vibrations. The detailed band vibrations in the IR spectra were explained on the investigated molecule through potential energy distribution (PED) calculations. The Mulliken charges, HOMO and LUMO orbital energies were analyzed directly from Firefly program log files. The graphic interpretation of mentioned properties was made by Modeling and Simulation Kit (MASK) program (version 1.3.0) [20]. In the cases of HOMO, LUMO and electrostatic potentials, graphic illustrations of the isosurface with value equal to 0.01 was used.

The theoretical Raman intensities were calculated according to procedure described by Michalska and Wysokinski [21]. In this calculation the excitation frequency equal to 9398.5 cm^{-1} which corresponds to the wavelength of 1064 nm of frequently used in FT-Raman method.

4. Results and Discussion

4.1. Equilibrium Geometry

One equilibrium theoretical structure is obtained during the optimization process and is shown in Fig. 1. The calculated theoretical vibrational spectrum of this structure contains only positive frequencies which suggest that the optimized geometry of the molecule under study is located at the global energy minimum. The experimental and obtained geometrical parameters are listed in Table 1. From the experimental data, for our investigation we have taken only one unit of TuAgN. It is characteristic that all C-N distances are very similar and it is calculated to be in the region 1.315–1.326 Å. Very similar distances are observed when N—O bond is considered i.e. N_{15}-O_{16} (1.321 Å) and N_{15}-O_{14} (1.320 Å) but much shorter distance is observed for N_{15}-O_{17} (1.216 Å). All N-H distances of amine groups are very similar. In thiourea molecule the considered bond lengths are in the range of 0.997–1.015 Å. Slightly higher distances are observed in the case of nitrogen atom which are involved in intramolecular hydrogen bond i.e. for N_2-H_20, N_7-H_{27} and N_{13}-H_{25} it compasses the value of 1.013 Å, 1.017 Å and 1.015 respectively which are higher than N_2-H_{21} (0.997 Å), N_7-H_{28} (1.000 Å) and N_{13}-H_{26} (0.997 Å). There is no dramatic differences are observed for the calculated bond angle in thiourea silver nitrate complex. All the obtained theoretical geometrical parameters are very well agrees with experimental values [CCDC no. 913226].

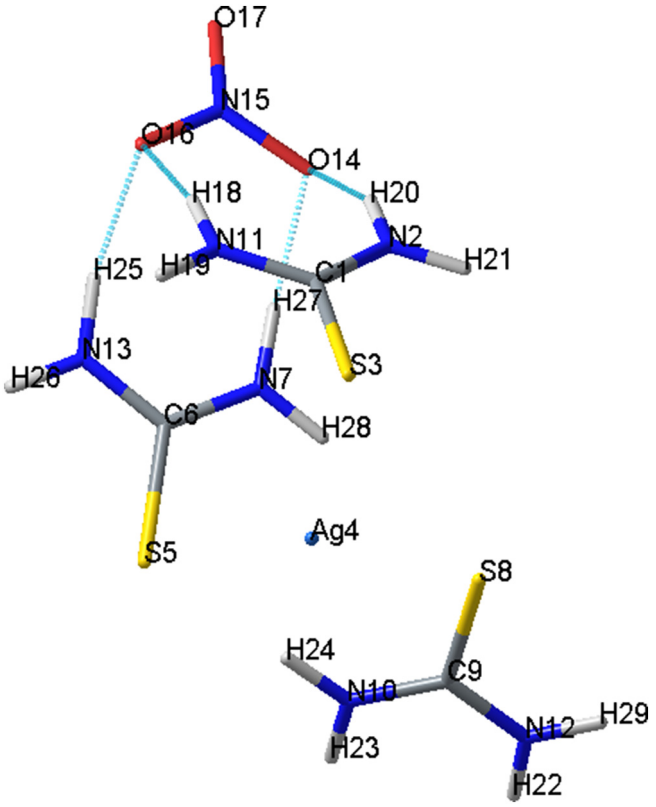

Fig. 1. Optimized structure of TuAgN.

4.2. Mulliken Population Analysis

The Mulliken population analysis of TuAgN is done by MASK program. All nitrogen atoms of TuAgN have negative charge (i.e.) nitrogen atoms of both thiourea and silver nitrate have negative charge. But N_{15}

Table 1
Experimental and calculated geometrical parameters

Bond	Bond length [Å]		Angle	Bond angle [°]	
	Expt [14]	Theory		Expt. [14]	Theory
Ag_4—S_5	2.509	2.842	Ag_4—S_5—C_6	97	87
Ag_4—S_8	2.697	2.849	Ag_4—S_8—C_9	110	113
C_1—N_2	1.311	1.318	C_1—N_2—H_20	124	121
C_1—N_{11}	1.296	1.317	C_1—N_2—H_{21}	120	119
C_1—S_3	1.750	1.797	C1—N_{11}—H_{18}	127	123
C_6—N_7	1.319	1.317	C_1—N_{11}—H_{19}	121	119
C_6—N_{13}	1.303	1.315	C_1—S_3—AG_4	101	89
C_9—N_{10}	1.300	1.317	C_6—N_7—H_{27}	123	122
C_9—N_{12}	1.312	1.326	C_6—N_7—H_{28}	125	120
N_2—H_20	0.850	1.013	C_6—N_7—O_{14}	124	123
N_2—H_{21}	0.840	0.997	C_6—N_{13}—H_{25}	130	121
N_7—H_{27}	0.850	1.017	C_6—N_{13}—H_{26}	115	119
N_7—H_{28}	0.840	1.000	C_9—N_{10}—H_{23}	120	122
N_7—O_{14}	2.268	2.822	C_9—N_{10}—H_{24}	122	121
N_{10}—H_{23}	0.840	1.000	C_9—N_{12}—H_{22}	125	123
N_{10}—H_{24}	0.850	1.007	C_9—N_{12}—H_{29}	122	119
N_{11}—H_{18}	0.850	1.015	N_2—C_1—S_3	123	121
N_{11}—H_{19}	0.850	0.997	N_7—O_{14}—N_{15}	113	112
N_{12}—H_{22}	0.850	0.999	O_{14}—N_{15}—O_{16}	134	117
N_{12}—H_{29}	0.850	0.998	O_{14}—N_{15}—O_{17}	134	121
N_{13}—H_{25}	0.850	1.015	S_3—Ag_4—S_5	120	129
N_{13}—H_{26}	0.840	0.997	S_3—Ag_4—S_8	114	115
N_{15}—O_{16}	1.225	1.321	S_3—C_1—N_{11}	120	120
N_{15}—O_{17}	1.247	1.216	S_5—C_6—N_7	121	121
O_{14}—N_{15}	1.268	1.320	S_5—C_6—N_{13}	119	119
S_3—AG_4	2.580	2.753	S_8—C_9—N_{10}	122	122
S_5—C_6	1.722	1.800	S_8—C_9—N_{12}	118	118
S_8—C_9	1.743	1.777			