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Molecular structure, vibrational spectroscopic and HOMO/LUMO studies of some organotellurium compounds by quantum chemical investigations

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ABSTRACT

Quantum mechanical calculations of geometries, energies and vibrational frequencies of organic mercury and tellurium compounds containing azomethine group, molecules a1-a5 and containing azo group, molecules a6-a10 have been undertaken using density functional theory. The optimized geometrical parameters such as bond lengths, bond angles and dihedral angles showed that only organomercuric compounds have planer structures. The calculation of the total energy and HOMO-LUMO energy gap were showed that organotellurium compounds have higher reactivity than the corresponding organomercuric compounds. As well it showed the HOMO orbitals are localized mainly on tellurium, nitrogen and bromine atoms moieties, while the LUMO of π nature are mostly located on the phenyl ring. The calculated vibrational frequencies of molecules a1 and a7 are in good agreement with experimental frequencies with correlation coefficient r^2 value is 0.9875 and 0.9987, respectively.

1. Introduction

Tellurium chemistry has been the subject of intensive research in the last three decades due to the interest of several research groups in organometallic and supramolecular chemistry of organotellurium compounds [1,2]. There is increasing interest in the synthesis of aromatic organotellurium compounds containing electron donor nitrogen atom at position *ortho* to the tellurium atom [3,4], such as azo group [5] and azomethine group [6,7]. These compounds have high stability due to intra-molecular interaction between tellurium and nitrogen atoms [8,9]. Calculations performed with the use of Density Functional Theory (DFT) have been successfully employed in a number of previous theoretical studies of organotellurium compounds [10-12].

In this study, we report molecular geometry, HOMO-LUMO energy gap and the assignments of IR spectra of some organomercuric and organotellurium compounds containing azo or azomethine groups.

2. Experimental

2.1. Instrumentation and materials

The compounds **a1**-**a10** were prepared according to previously published procedure [13,14]. Infrared spectra were recorded as KBr discs in the range of 4000-400 cm⁻¹ using a Shimadzu FT-IR spectrophotometer at Department of Chemistry, College of Education for Pure Sciences, University of Basrah, Iraq.

2.2. Computational details

All calculations of studied molecules (Figure 1) were performed with Material studio/DMol3 Version 5.5 program [15-17] and using the DFT method [15-17], at the PBE level of theory [18,19] along with standard DNP basis set [17].

## 3. Results and discussion

3.1. Optimized structure

The important structural parameters of the optimized geometries such as bond lengths, bond angles and dihedral angles of the studied molecules **a1-a10** are summarized in Table 1, the optimized structures of these compounds are shown in Figure 2.

In the ArHgCl moiety **a1** and **a6** each mercury atom is linearly coordinated to a chloride and a carbon atom (Angle C-Hg-Cl = 177.307 and 179.451 °), which is fully characterized structurally.

Table 1. Bonds lengths, bond angles and dihedral angles of the studied compounds *.

Compound	Bonds lengths (Å)		Angles bonds (°)		Dihedral angles (°)	
	C1-Hg	Hg-Cl	C1-Hg-Cl	Hg-C1-C2	N=C3-C4-C6	C1-C2-N=C3
a1	2.244	2.449	177.307	105.940	178.939	177.437
	C1-Hg	Hg-Cl	C1-Hg-Cl	Hg-C1-C2	N1=N2-C3-C4	C1-C2-N1=N2
a6	2.190	2.475	179.451	101.706	180.000	180.000

	Bonds lengths (Å)			Angles bonds (°)			Dihedral angles (°)			
Compound	C1-Te	Te-Br1	Te1-Te2	C1-Te-Br1	C1-Te-C1	C1-Te-Te	Te-C1-C2	N=C3-C4-C6	C1-C2-N=C3	C-Te-Te-C
a2	2.165	2.601		94.845			106.311	170.624	166.484	
a3	2.164		2.770			103.000	122.107		134.502	66.470
	2.166					106.063	123.758		-131.369	
a4	2.174	2.724		90.419			108.223		160.184	
	2.192			93.095	107.389		127.836		129.806	
a5	2.171				106.070		128.554		106.614	
	2.160						120.409		94.521	
Compound	C1-Te	Te-Br1	Te1-Te2	C1-Te-Br1	C1-Te-C1	C1-Te-Te	Te-C1-C2	N1=N2-C3-C4	C1-C2-N1=N2	C-Te-Te-C
a7	2.188	2.596		106.100			121.829	-167.505	-164.770	
a8	2.169		2.842			97.263	115.156		-167.761	92.534
	2.153					98.903	118.392		-14.995	
a9	2.172	2.756		93.175	90.360		127.410		141.818	
	2.232			86.790			119.667		65.906	
a10	2.150				93.926		119.968		159.255	
	2.157						121.197		154.019	

* Experimental values: C-Te : 2.158 Å , Te-Br : 2.65 Å , Te-Te: 2.77 Å.
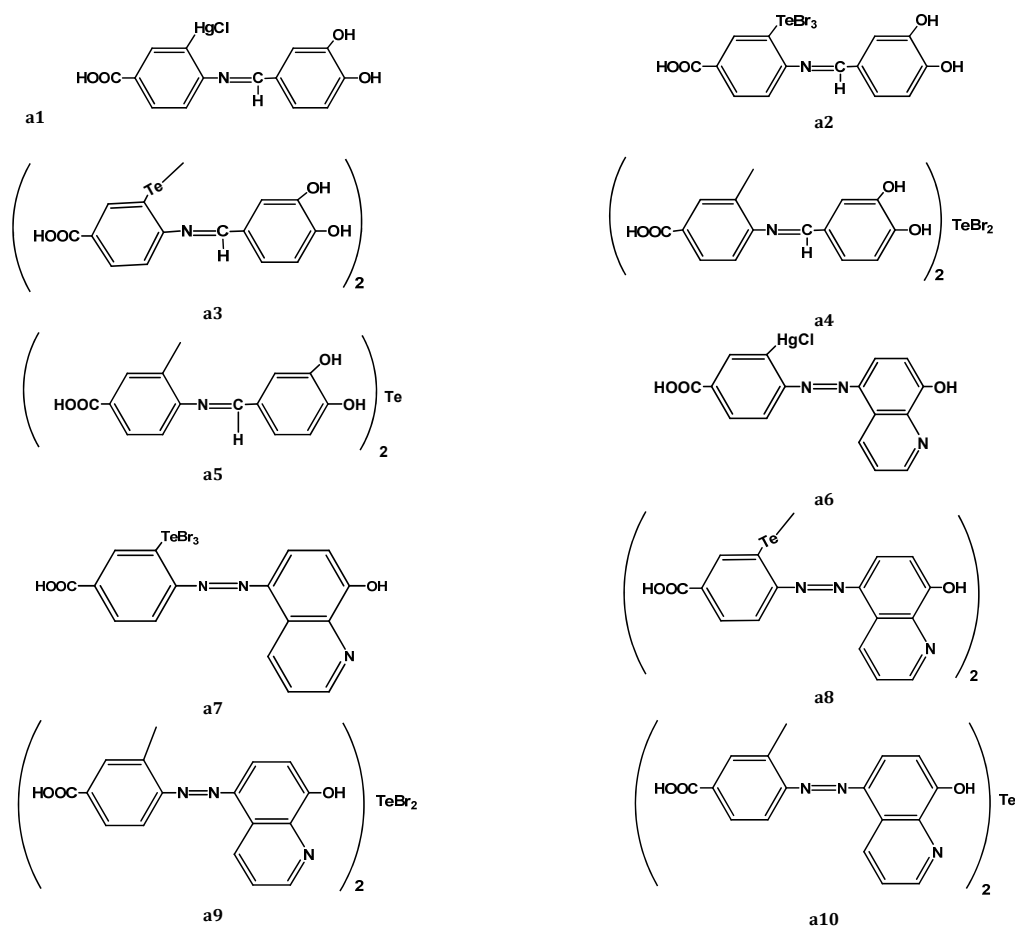
Figure 1. Molecular structure of studied molecules.

The Hg-C distances are 2.24 and 2.19 Å, respectively, are in close agreement with experiment value 2.065 Å [20] for almost linear Ar-Hg-Cl. Similarly, Hg-Cl distance, which are 2.449 and 2.475 Å are close agreement with experiment value 2.326 Å [20].

As could be seen from Table 1, there is fair agreement between the calculated bonds lengths of C-Te, Te-Br and Te-Te bonds with the measured bond lengths [21-26]. Generally, there is no significant difference between the calculated bond lengths. Only a slight increase in N=N length from 1.243 to 1.278 Å on going from molecule **a2** to molecule **a7**. This may be due to intramolecular coordination between tellurium and nitrogen atom [27]. This interaction can be attributed to the overlap of p-orbital on the nitrogen atom with the σ* (Te-C$_{trans}$) molecular orbital (partly responsible for such an interaction) feasible [2].

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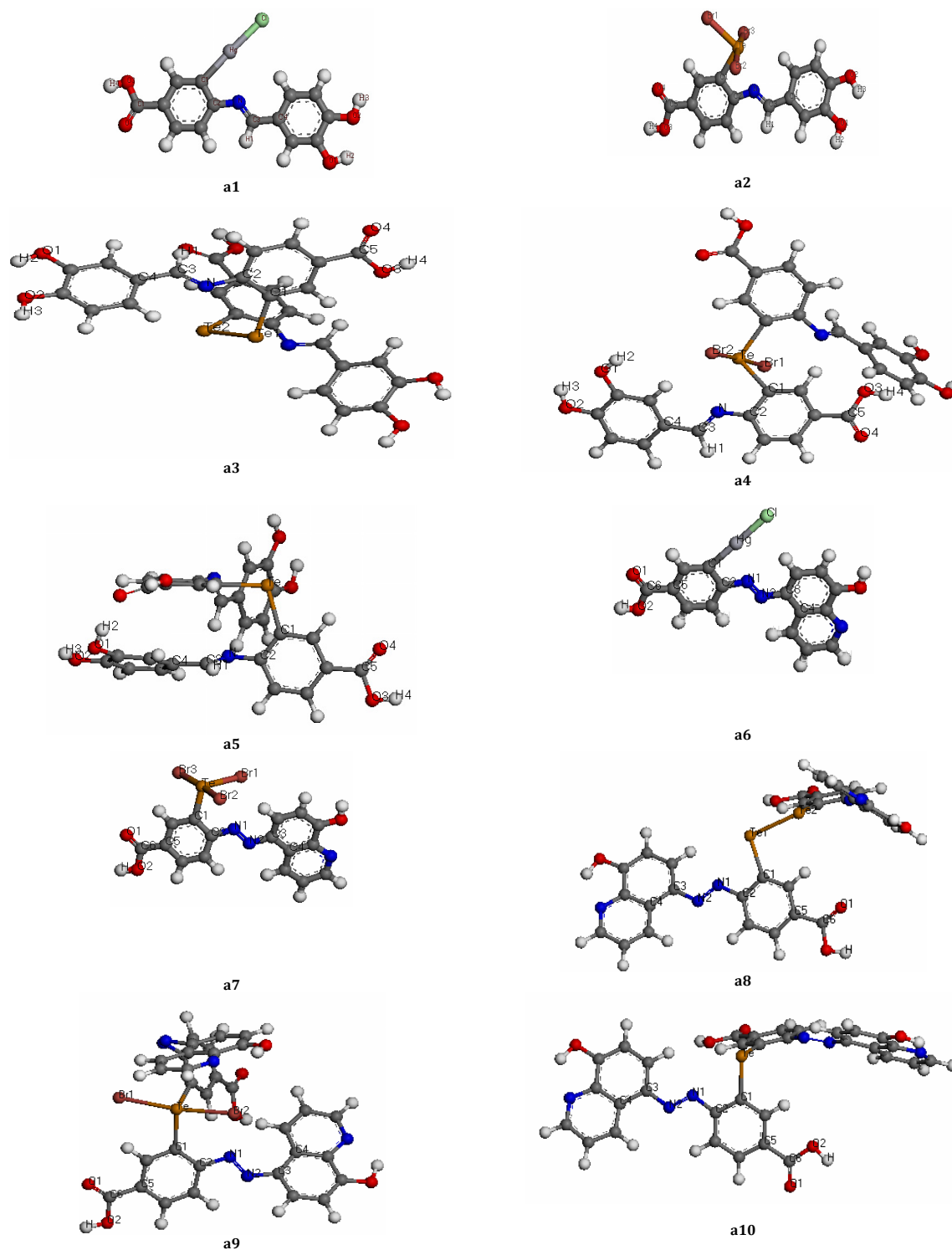

Figure 2. Optimization geometries structures of the studied molecules.

For tellurium(II) compounds **a5** and **a10** both lone pairs of electrons around tellurium should be stereo chemically active according to VSEPR (Valence Shell Electron Pair Repulsion) theory [28], the geometry of the tellurium atom in compound a5 is relative to the tetrahedral geometry, where C-Te-C angle is 106.07°. While geometry of the tellurium atom in compound a10 is a distorted pseudo-tetrahedral [27], C-Te-C angles are

93.9°. This is due to high secondary intramolecular coordination between tellurium and nitrogen atom in this compound [29]. On the other hand, the C-Te-C angle for the tellurium(IV) compounds **a4** and **a9** (covering the range 90.08-107.38 °) are significantly lower than the putative value of 120 ° for trigonal bipyramidal geometry due to the stereo chemical activity of the lone pair on tellurium atom [30].

Table 2. Values of Total energy and LUMO-HOMO energy gap of studied compounds in Hartree unit.

Compound	Total energy	HOMO	LUMO	$\Delta E_{(LUMO-HOMO)}$
		Energy	Energy	
a1	-19767.3034778	-0.20750	-0.11965	0.08785
a2	-15229.8885967	-0.17632	-0.13959	0.03673
a3	-15016.6729209	-0.17360	-0.10248	0.07112
a4	-13550.5167344	-0.20574	-0.12309	0.08265
a5	-8402.8083298	-0.17584	-0.10006	0.07578
a6	-19877.6762863	-0.21148	-0.14248	0.06900
a7	-15334.2428367	-0.21059	-0.16402	0.04657
a8	-15237.4436071	-0.18269	-0.13639	0.04630
a9	-2044.5778558	-0.16680	-0.13649	0.03031
a10	-2017.828634	-0.17381	-0.13448	0.03933

In the case of aryl tellurium (IV) tribromide **a2** and **a7**, the presence of an electron-rich Br atom of the neighboring molecule (close to Te(IV) atom having a lone pair as per VSERP theory) in the lattice is of particular interest [30]. The overall coordination geometry around the tellurium atom is trigonal bipyramidal. Due to the presence Br group, that will weaken the Lewis acidity of the tellurium atom will further prevent intramolecular interaction, leading to the formation of molecular species with conformation consistent with the VSEPR theory [31], therefore the distance of C1-Te in compound **a7** is longer (2.188 Å) and angle Te-C1-C2 is largest (121.82 °) compared with other compounds. While in the compound **a2** the case is reverse (C1-Te is 2.165 Å and Te-C1-C2 is 94.84 °), this may be due to steric or electronic effects for bromine atoms.

In the ditelluride system **a3** and **a8**, the Te-Te bond is likely to influence the repulsion between loin pairs. The steric interaction between aromatic rings is due to small C-Te-Te-Te dihedral angles (66.47 and 92.53 °). This is a consequence of rotation around the C-Te bonds which take place because of the proximity of the phenyl rings of each other.

Due to a substantial secondary intramolecular coordination between Te and N, it is of interest to note that the twist dihedral angles of both the N-phenyl and C-phenyl ring out of the plane C-C=N-C in the Schiff base moiety, molecules **a1** to **a5** or C-N=N-C in the azo moiety, molecules **a6** to **a7** is less than 15 °. From the dihedral angles measurement, observed two molecules **a1** and **a6** have a planar structure (dihedral angle ≈180 °), the angle N=C2-C4-C6 is 178.93 ° and C1-C2-N=C3 is 177.43 ° for compound **a1**, while angle N1=N2-C3-C4 is 180 ° and C1-C2-N1=N2 is 180.00 ° for compound **a6**. The rest compounds have non planar structures (dihedral angles are 49-170 °), Table 1.

3.2. Energies calculation

Molecular orbital and their properties are very useful for physicists and chemists. In particular, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and their energy gap reflect the chemical activity of the molecule [32,33]. Higher value of HOMO of a molecule has a tendency to donate electrons to appropriate accepter molecule with low energy, empty molecular orbitals [34].

The total energy and HOMO-LUMO energy gaps the studied molecules **a1**-**a10** are summarized in Table 2. The values of LUMO-HOMO energy gap and total energy of the organomercuric compounds **a1** and **a6**, which are $\Delta E_{LUMO-HOMO}$ energy gap 0.0878 and 0.0690 Hartree; Total energy -19767.3 and -19877.6 Hartree, are relatively higher compared with the corresponding organtellurium compounds. This indicates a high stability and high chemical hardness of these compounds. Molecules **a2** and **a9** showed the lowest gap values (0.0367 and 0.0303 Hartree), reflecting their chemical reactivity compared with other studied molecules. This may be due to presence bromine atoms.

3.3. HOMO LUMO analysis

The HOMO orbitals are localized mainly on tellurium, nitrogen and bromine atoms moieties. Whereas the LUMO of π nature are mostly located on the phenyl ring. The HOMO-LUMO transition implies an electron density transfer to the phenyl ring from tellurium atom. The visualization of HOMO-LUMO gap and HOMO and LUMO orbitals for compound **a2** and **a8** are shown in Figure 3 and 4.
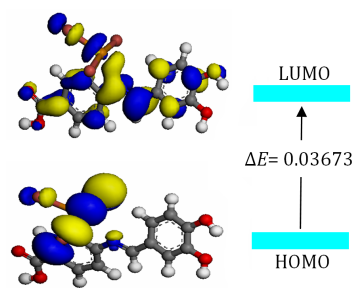
Figure 3. HOMO and LUMO orbitals of compound **a2**.
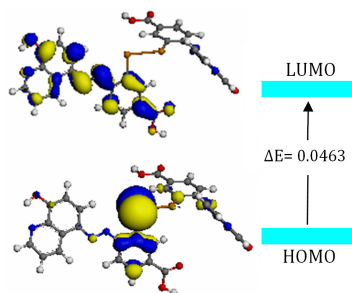
Figure 4. HOMO and LUMO orbitals of compound **a8**.

3.4. Vibrational frequencies

Assignments for the complex systems can be proposed on the basis of frequency agreement between the computed harmonics and the observed fundamentals.

The calculated frequencies for the optimized geometry and the experimental wave numbers together with the proposed assignments for compounds **a1** and **a7** are given in Table 3 and 4, respectively. The vibrational spectral data obtained from the solid-phase FT-IR spectra based on the results of the normal coordinates calculations. The observed and the calculated spectra reflect a reasonable agreement for the vibrational frequencies. Based on the comparison of the calculated and experimental results, assignments of fundamental frequencies incorporate the observed band frequencies in the infrared spectra of the studied species confirmed by establishing a one-to-one correlation between observed and theoretically calculated frequencies.

Table 3. Calculated vibrational frequencies (cm⁻¹) and the observed frequencies of compound **a1**.

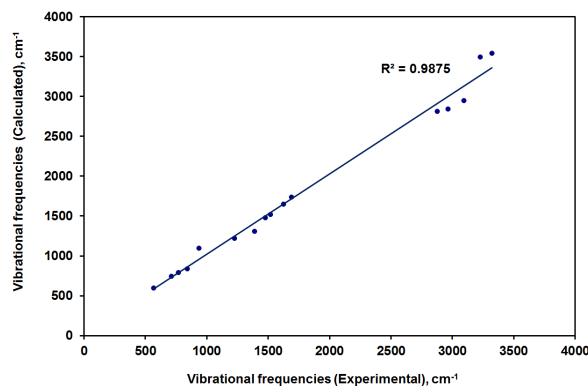| Calculated	Experimental	Assignment
3544	3321	υ(O-H)
3499	3225	υ(O-H)
2949	3095	υ(C-H) aromatic
2844	2963	υ(C-H) aliphatic
2818	2876	υ(C-H) aliphatic
1739	1690	υ(C=O)
1652	1624	υ(C=N)
1522	1518	υ(C=C)
1479	1477	δ(C-H) aliphatic
1311	1389	δ(C-N)
1222	1225	δ(C-O)
1097	935	δ(C-H) aromatic
840	841	δ(C-H) aromatic
789	770	δ (O-H)
Correlation coefficient = 0.9875		

Table 4. Calculated vibrational frequencies (cm⁻¹) and the observed frequencies of compound **a7**.

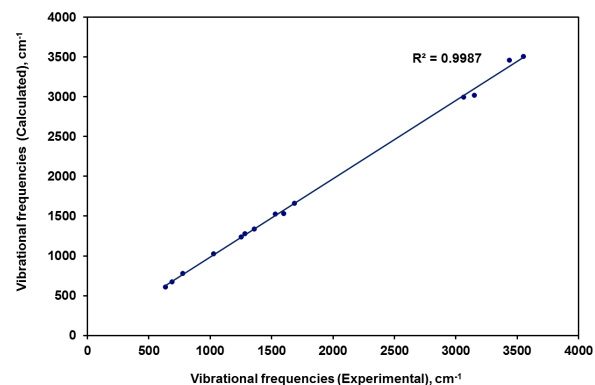| Calculated	Experimental	Assignment
3511	3550	υ(O-H)
3465	3435	υ(O-H)
3018	3150	υ(C-H) aromatic
2995	3066	υ(C-H) aromatic
1660	1685	υ(C=O)
1528	1601	υ(N=N)
1522	1531	υ(C=C)
1342	1359	δ(C=C)
1279	1282	δ(C-N)
1241	1251	δ(C-O)
1028	1030	δ(C-C)
778	775	δ(C-H) aromatic
668	688	δ (O-H)
613	636	δ (O-H)
Correlation coefficient = 0.9987		

The calculated frequencies are slightly higher than the observed values for the majority of the normal modes. Many different factors may be responsible for the discrepancies between the experimental and computed spectra of the compound. Factors such as environment, anharmonicity, intermolecular interaction and limited basis set [34]. The vibrational analyses are summarized in Table 3 and 4. A linearity between the experimental and the calculated wave numbers can be estimated by plotting the calculated *vs.* experimental wavenumbers, Figure 5 and 6. The values of the correlation coefficients (r^2) were 0.9875 and 0.9987; provide good linearity between the calculated and the experimental wave numbers.

and distorted pseudo-tetrahedral, while the Te(IV) compounds have trigonal bipyramidal geometry. The calculations indicate the organotellurium compounds have higher reactivity than organomercuric compounds.

Figure 6. Graphical correlation between experimental and calculated vibration data of compound **a7**.

Figure 5. Graphical correlation between experimental and calculated vibration data of compound **a1**.

4. Conclusions

The molecules containing Hg atom have planer structures. The vibrational frequencies analysis by PBE level agrees satisfactorily with experimental results. The optimized structure of the Te(II) compounds have tetrahedral geometry

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