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Theoretical molecular structure and vibrational frequencies of $TiX_3(C_2H_6OS)_2$ (X = Cl and Br) complexes

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ÖZET

$TiX_3(C_2H_6OS)_2$ (X = Cl ve Br) komplekslerinin normal frekansları ve bunlara karşılık gelen infrared ve Raman titreşim işaretlemeleri ve bazı önemli yapısal parametreleri (band uzunlukları, band ve dihedral açıları) Lanl2dz baz seti kullanarak B3LYP yoğunluk fonksiyonel metodu yardımıyla kuramsal olarak incelenmektedir. Kuramsal sonuçlar literatürde var olan deneysel veriler ile karşılaştırılmaktadır. Farklı titreşim modları için hesaplanan dalga sayıları baz seti yetersizliğini dengelemek için bu çalışmada önerilen bazı yeni skala faktörleri ile ölçeklenmektedir.

ABSTRACT

The normal mode frequencies and corresponding infrared and Raman vibrational assignments and some important structural parameters (bond lengths, bond and dihedral angles) of $TiX_3(C_2H_6OS)_2$ (X = Cl and Br) complexes have been theoretically examined by means of B3LYP density functional method using Lanl2dz basis set. Theoretical results have been compared against available experimental data in the literature. Calculated wavenumbers for different vibrational modes have been scaled with several new scaling factors proposed in this study to compensate for the approximate basis set deficiencies.

Anahtar Kelimeler

Talyum halojenürü,
Normal mod
frekans,
DFT,
B3LYP,
Lanl2dz

Keywords

Thallium halide,
Normal mode
frequency,
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B3LYP,
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1. Introduction

Thallium complexes have been used for various applications in diverse fields such as photo-electric cells, insoluble anodes, corrosion inhibitors and fungicides [1]. The complexes formed in the thallium (III) halide system are among the most stable metal halide complexes and they have been widely studied [2]. There have been reported studies about structural, equilibrium and dynamic properties of thallium (III) chloride and bromide complexes [3, 4]. Vibrational spectroscopy has been widely used as a standard tool for structural characterization of molecular systems by DFT calculations which shows good agreement with experimental vibrational frequencies of organic and inorganic compounds, if the calculated frequencies are scaled to compensate for the approximate basis set deficiencies and anharmonicity [5-11]. In present study, we have theoretically investigated geometric parameters (bond lengths, bond and dihedral angles) and vibrational wavenumbers of trichlorobis(DMSO)thallium(III) (1) and tribromobis(DMSO)thallium(III) (2) complexes, which are first synthesized by Asadi et al. [12], using B3LYP/Lan12dz model.

2. Calculations

For the calculations, the title complexes were first optimized by B3LYP with Lan12dz basis set in the gas phase. The optimized molecular structures of $TlX_3(DMSO)_2$ (X = Cl and Br) complexes are given in Figure 1. E(RHF) for compound (1) is -279.181417 a.u. whereas E(RHF) is -272.082429 a.u. for Compound (2). After the optimization, in order to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies, harmonic vibrational frequencies and corresponding IR intensities and Raman activities of the title complexes were determined using analytic second derivatives with the B3LYP/Lan12dz method under the keyword freq = Raman and then scaled to generate the corrected frequencies. Scaling factors (α) for selected regions or vibrational modes were calculated using $\alpha_n = \sum (v^{exp} / v^{calc}) / n$ [11]. The optimized geometric structures concerning to minimum on the potential energy surface were provided by solving self-consistent field (SCF) equation iteratively and optimizations were performed without any molecular restrictions. All the calculations were performed using Gaussian 09 program on a personal computer and GaussView program was used for visualization of the structures [13, 14].

Table 1. Some selected bond lengths of $TlX_3(DMSO)_2$ (X = Cl and Br) complexes.

Compound	r(Tl-O) Å		r(Tl-X) Å	
	Exp. ^[11]	B3LYP	Exp. ^[11]	B3LYP
$TlCl_3(DMSO)_2$	2.346	2.310	2.3818	2.5736
	2.394	2.311	2.3975	2.5736
			2.4079	2.5835
			2.5069	2.7034
$TlBr_3(DMSO)_2$	2.383	2.330	2.5069	2.7034
	2.435	2.332	2.5201	2.7382
			2.5288	2.7824

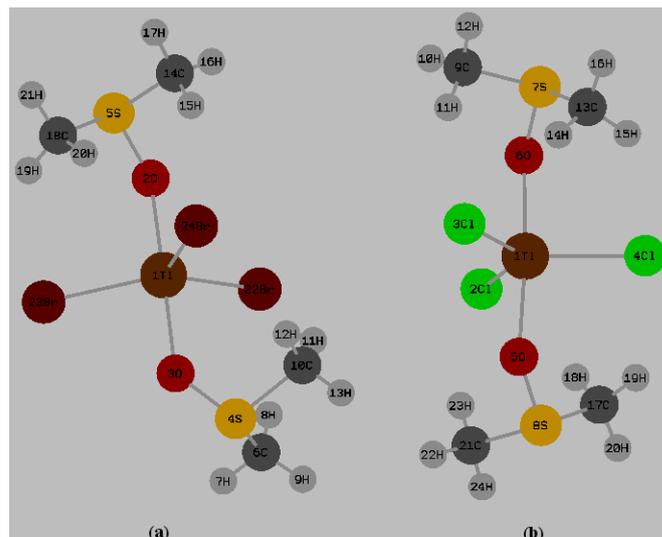


Figure 1. Optimized molecular structures of $TlBr_3(DMSO)_2$ (a) and $TlCl_3(DMSO)_2$ (b) complexes.

3. Results and discussion

Some of the calculated bond lengths of (1) and (2) are given in Table 1. The selected parameters are very important for these structures and, especially, Tl-X bond is only difference between two structures. Both experimental and calculated $r(Tl-O)$ and $r(Tl-X)$ distances of (2) are longer than those of (1). Mulliken charge distributions for (1) / (2) were calculated as Tl = 1.069099 / 0.972760, Cl(2) / Br(22) = -0.463963 / -0.432426, Cl(3) / Br(23) = -0.463973 / -0.389814, Cl(4) / Br(24) = -0.480368 / -0.489520, O(5) / O(2) = -0.704982 / -0.706100 and O(6) / O(3) = -0.705090 / -0.707730. Experimental bond distances and calculated mulliken charge distributions are in good agreement. For instance, considering Tl = 1.069099 / 0.972760, it is seen that thallium of (1) more electropositive than that of (2) which leads to a stronger electrostatic attraction and so a shorter bond length between the neighboring oxygen atoms and thallium atom for (1). Depending on the ionic radii of halides Tl-Cl and Tl-Br bond lengths are different. The shortest O-H, S-H and Cl-H distances were calculated as 2.911 Å, 2.429 Å and 2.639 Å for (1) and 2.922 Å, 2.428 Å and 2.638 for (2). These distances suggest possible internal hydrogen bondings [15]. $\angle(O-Tl-O)$, $\angle(Cl-Tl-Cl)$, $\angle(Br-Tl-Br)$ bond angles, in agreement with [16], were calculated as 175.93° (1) / 177.92° (2), (115.93°, 115.92°, 128.15°) and (114.04°, 117.73°, 128.23°), respectively. $\angle(Cl, Cl, Tl, Cl)$ and $\angle(Br, Br, Tl, Br)$ dihedral angles were found as 179.98° and 179.43° which propose a trigonal plane around the metal [12].

Both (1) and (2) compounds consist of 24 atoms, so they have 66 vibrational modes according to $3N-6$, and belong to the point group C_1 with only identity (E) symmetry element or operation. It is difficult to determine the vibrational assignments of these complexes due to their low symmetry. According to the calculations, 28 normal vibrational modes of both conformations are below 400 cm^{-1} and others are above 400 cm^{-1} . All the theoretical vibrational modes obtained in this study are given in Tables 2-3. Regarding

our calculations and previously reported data [12], we have provided a reliable correspondence.

In general for both (1) and (2) calculated vibrational wavenumbers are approximately similar. For instance, CH₃ antisymmetric and symmetric vibrations have been calculated as 3002 cm⁻¹, 2915 cm⁻¹ for (1) and 2999 cm⁻¹, 2913 cm⁻¹ for (2). It can be withdrawn from the results that

when compared to stretching modes, vibrational wavenumbers of bending modes are more sensitive to the alterations of halide atoms attached to thallium. Atomic radius of bromide is larger than chloride, so it hinders the bending ability of O-Tl-O group resulting a lower force constant (F(Br)_{O-Tl-O} = 0.0319, F(Cl)_{O-Tl-O} = 0.0528).

Table 2. Experimental and calculated vibrational wavenumbers (cm⁻¹) of TlCl₃(DMSO)₂ complex.

Assignment ^a	Exp.IR ^a	Exp.Raman ^a	Cal. Freq.	Cor. Freq.	IR Intensity	Raman Activite	Scaling Factors
CH ₃ a-str	3000 m	3003 s	3209	3002	1.98	38.48	0.9354
CH ₃ s-str	2914 m	2915 vs	3073	2915	0.89	98.44	0.9485
CH ₃ a-bend	1433 s	-	1506	1429	91.90	0.11	0.9486
CH ₃ a-bend	1411 s	1407 m	1492	1415	5.00	15.69	-
CH ₃ a-bend	1401 s	-	1475	1399	25.47	1.38	-
CH ₃ s-bend	1312 s	-	1408	1312	16.90	0.48	0.9318
S-O str	1021 vs	-	756	1021	99.75	5.42	1.3505
SC ₂ a-str	706 m	714 m	633	710	10.41	23.49	1.1217
SC ₂ s-str	672 w	677 m	586	675	0.05	4.93	1.1511
SC ₂ -bend	-	411 w	334	411	1.11	2.60	1.2305
SC ₂ -sciss	-	332 w,sh	255	332	0.78	1.05	1.3020
Tl-O str	-	308 m,sh	234	308	1.43	8.92	1.3162
Tl-Cl str	-	289 vs	243	289	0.85	48.44	1.1893
O-Tl-O bend	-	118 m	109	118	1.05	2.56	1.0826
O-Tl-Cl bend	-	87 w,sh	90	87	6.48	3.49	0.9667

^a Taken from Ref. [12]. Exp: experimental, Cal: calculated, Freq: frequency, Cor: corrected, bend: bending, str: stretching, sciss: scissoring, s: symmetric, a: asymmetric, vs: very strong, s: strong, m: medium, w: weak, sh: shoulder.

Table 3. Experimental and calculated vibrational wavenumbers (cm⁻¹) of TlBr₃(DMSO)₂ complex.

Assignment ^a	Exp. IR ^a	Exp. Raman ^a	Cal. Freq.	Cor. Freq.	IR Intensity	Raman Activite	Scaling Factors
CH ₃ a-str	2997 w	3002 s	3209	2999	2.06	78.40	0.9347
CH ₃ s-str	2913 m	2913 vs	3075	2913	16.28	88.76	0.9473
CH ₃ a-bend	1432 m	-	1501	1426	9.98	0.54	0.9500
CH ₃ a-bend	-	1412 w	1488	1414	0.30	2.63	-
CH ₃ a-bend	1401 m	-	1474	1400	5.75	0.15	-
CH ₃ a-bend	1383 s	-	1461	1388	10.42	0.11	-
CH ₃ s-bend	1314 m	-	1404	1314	8.97	0.10	0.9359
S-O str	1021 vs	-	758	1021	82.44	0.36	1.3470
SC ₂ a-str	707 w	714 m	632	710	0.63	6.69	1.1242
SC ₂ s-str	669 w	676 m	586	672	0.51	3.07	1.1476
SC ₂ -bend	-	409 vw	319	409	0.95	1.55	1.2821
SC ₂ -sciss	-	334 w	251	334	0.85	2.69	1.3307
Tl-O str	-	308 w	222	308	0.47	1.44	1.3874
Tl-Br str	-	202 m,sh	169	213	0.14	4.72	1.2574
Tl-Br str	-	190 vs	144	181	1.38	23.67	-
O-Tl-O bend	-	112 s,b	102	112	0.63	20.69	1.0980

^a Taken from Ref. [12]. Exp: experimental, Cal: calculated, Freq: frequency, Cor: corrected, bend: bending, str: stretching, sciss: scissoring, s: symmetric, a: asymmetric, vs: very strong, s: strong, m: medium, w: weak, sh: shoulder.

The biggest difference between the experimental and calculated infrared wavenumbers is 4 cm⁻¹ for (1) and 6 cm⁻¹ for (2) while the biggest difference for Raman values is 8 cm⁻¹ for (1) and 11 cm⁻¹ for (2). It can be seen from Tables 2-3 that average scaling factor for B3LYP/Lan12dz model is found as 1.1135 for (1) and 1.1452 for (2). Check et al.'s correction factor was 1.1670 of B3LYP method for Lan12dz basis set on a set of 36 metal halide molecules [11].

Determined scaling factors in this study are similar with previously reported value.

4. Conclusions

The theoretical applications of B3LYP method with Lan12dz effective core basis set for TlX₃(C₂H₆OS)₂ (X = Cl and Br) complexes have been completed with good results. Comparing the computed vibrational frequencies with the experimental data available in the literature, a set of scaling

factors is derived. The results obtained in this study also indicate that B3LYP/LanL2dz method is reliable and it makes easier the understanding of vibrational spectrum and structural parameters of the title complexes.

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