

Computational Analysis of Dimeric Bismuth(III) Halide Complexes Bearing Thioamide Ligands: Geometry, Reactivity and Electronic Properties

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Abstract

A series of complexes were selected from the literature to investigate the electronic properties of dimeric bismuth(III) halide complexes. Complexes 1–3 contain chloride, bromide, and iodide ligands, respectively, coordinated to the Bi(III) centers through sulfur donor atoms: {[BiCl₂(μ₂-Cl(MtMBZIM)₂)₂].H₂O.CH₃COCH₃} (1), {[BiBr₂(μ₂-Br(MtMBZIM)₂)₂].H₂O} (2) and {[BiI₂(μ₂-I(MtMBZIM)₂)₂].H₂O} (3). The theoretical studies of these complexes were performed using the DFT method with the LANL2DZ basis set, which is suitable for metal ions. The structural differences arising from the substitution of Cl, Br, and I atoms in the complexes were elucidated. In light of the data obtained from the energy values of the frontier molecular orbitals, it was noteworthy that Complex 1 exhibited the highest nucleophilic character, whereas Complex 2 showed the highest electrophilic character. In addition, the ionization potential (IP), electron affinity (EA), chemical potential (μ), chemical hardness (η), electronegativity (χ), and electrophilicity index (ω) values were also calculated.

Keywords

Bismuth(III) halide,
Thioamide,
DFT calculation,
Quantum parameters

Tiyoamid Ligandları İçeren Dimerik Bizmut(III) Halojenür Komplekslerinin Hesaplamalı Analizi: Geometri, Reaktivite ve Elektronik Özellikler

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Özet

Dimerik bizmut(III) halojenür komplekslerinin elektronik özelliklerini incelemek amacıyla literatürden bir dizi kompleks seçilmiştir. 1-3 numaralı kompleksler sırasıyla klorür, bromür ve iyodür ligandları içerir ve bu ligandlar kükürt verici atomlar aracılığıyla Bi(III) merkezlerine koordine edilmiştir: {[BiCl₂(μ₂-Cl(MtMBZIM)₂)₂].H₂O.CH₃COCH₃} (1), {[BiBr₂(μ₂-Br(MtMBZIM)₂)₂].H₂O} (2) ve {[BiI₂(μ₂-I(MtMBZIM)₂)₂].H₂O} (3). Bu komplekslerin teorik çalışmaları, metal iyonları için uygun olan LANL2DZ baz seti kullanılarak Yoğunluk Fonksiyonel Teorisi (DFT) yöntemi ile gerçekleştirilmiştir. Komplekslerde Cl, Br ve I atomlarının yer değiştirmesinden kaynaklanan yapısal farklılıklar aydınlatılmıştır. Sınır moleküler orbitallerinin enerji değerlerinden elde edilen veriler ışığında, Kompleks 1'in en yüksek nükleofilik karakteri sergilediği, buna karşılık Kompleks 2'nin en yüksek elektrofilik karakteri gösterdiği dikkat çekicidir. Ayrıca iyonlaşma potansiyeli (IP), elektron ilgisi (EA), kimyasal potansiyel (μ), kimyasal sertlik (η), elektronegatiflik (χ) ve elektrofiliklik indeksi (ω) değerleri de hesaplanmıştır.

Anahtar kelimeler

Bizmut(III)
halojenür,
Tiyoamid,
DFT Hesaplaması,
Kuantum
Parametreleri

1. INTRODUCTION

Bismuth is a metal located in Group 15 of the periodic table and plays an important role in coordination chemistry [1, 2]. Possessing the electron configuration $[\text{Xe}]4f^{14}5d^{10}6s^26p^3$, bismuth commonly exhibits two oxidation states, +3 and +5 [3]. In particular, the relatively low toxicity of bismuth has increased scientific interest in studies related to this element [4, 5]. Bismuth compounds have been widely used for many years in the treatment of gastrointestinal disorders [6, 7]. Pepto-Bismol®, De-Nol®, and Pylorid® are among the bismuth-containing drugs used for such conditions [8].

According to the Hard and Soft Acids and Bases theory, bismuth(III), which possesses a large ionic radius, shows affinity toward ligands containing nitrogen and oxygen atoms (hard Lewis bases) as well as sulfur-containing ligands (soft Lewis bases) [9]. Among sulfur-containing ligand classes, compounds such as thioamides, thiosemicarbazones, and dithiocarbamates have been widely studied in relation to bismuth(III) complexes [10–13]. In these studies, sulfur is consistently observed to coordinate to the bismuth(III) ion.

Thioamides, which constitute an important class of sulfur-containing ligands, have attracted considerable attention in coordination chemistry for many years [14]. They can bind to a metal ion through various coordination modes, including monodentate, chelating, and bridging coordination [15–17]. Thioamides containing the functional groups $-\text{N}(\text{H})-\text{C}(=\text{S})-$ and $-\text{N}=\text{C}(-\text{SH})-$ are notable for their biological properties and structural diversity [18–20]. Heterocyclic thioamides are capable of forming complexes with different coordination modes [21]. Through soft acid–soft base interactions, they tend to form stable complexes with the bismuth(III) ion.

When bismuth(III)–thioamide complexes are examined, it is observed that they exhibit significant structural diversity. These complexes are commonly found with square-pyramidal and octahedral molecular geometries [21, 22]. In octahedral complexes, several different isomeric forms may occur. Monomeric octahedral bismuth(III)–thioamides can exist in ionic or neutral forms (facial and meridional), whereas four different isomeric arrangements have been reported for dimeric structures: (i) cis-S, cis-X, (ii) cis-S, trans-X, (iii) trans-S, cis-X, and (iv) bridging-S [12, 22, 24, 25].

In this study, three octahedral bismuth(III) halide–thioamide complexes previously reported in the literature were investigated. These complexes contain chloride, bromide, and iodide ligands and represent different structural environments around the Bi(III) center [24]. Theoretical investigations of this complex were carried out. Density Functional Theory (DFT) using the B3LYP functional with the LANL2DZ basis set was employed for the theoretical calculations, and the GaussView 6.0 interface was used in conjunction with the Gaussian computational package. Based on the obtained results, the quantum chemical parameters of the complexes were

determined, and the effect of the halogen atom was investigated.

2. MATERIAL AND METHOD

The calculations of bismuth(III) halide–thioamide complexes were carried out using Gaussian programs on an Excalibur computer equipped with an Intel Core i7-12700H processor.

The CIF files related to the crystal structures of the complexes were obtained from the study reported in the literature [24]. Density Functional Theory (DFT) calculations were carried out using the B3LYP hybrid exchange-correlation functional [26]. All computational studies were performed with the Gaussian 16W package using the GaussView 6.0 graphical interface. Geometry optimizations of the three bismuth(III) halide complexes were performed employing the LANL2DZ basis set. This basis set incorporates effective core potentials (ECPs), which provide an efficient and reliable description of heavy elements such as bismuth while reducing computational cost. Therefore, the B3LYP/LANL2DZ level of theory was considered appropriate for investigating the structural and electronic properties of the studied Bi(III) complexes. In addition, valuable information regarding the vibrational frequencies of the complexes was obtained.

For various energy calculations of the complexes, formulas derived from the HOMO and LUMO energies were used. All calculated data obtained in Hartree units were converted into electron volts (eV). Using the formulas given below, the ionization potential (IP), electron affinity (EA), chemical potential (μ), chemical hardness (η), electronegativity (χ), and electrophilicity index (ω) values were determined [27, 28].

$$IP = -E_{\text{HOMO}} \quad (1)$$

$$EA = -E_{\text{LUMO}} \quad (2)$$

$$\mu = -\frac{(IP + EA)}{2} \quad (3)$$

$$\eta = \frac{(IP - EA)}{2} \quad (4)$$

$$\chi = \frac{(IP + EA)}{2} \quad (5)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (6)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (7)$$

3. RESULTS

The quantum chemical parameters of the bismuth(III) halide complexes of 5-ethoxy-2-mercaptobenzimidazole and 5-methoxy-2-mercaptobenzimidazole were obtained using the B3LYP functional with the LANL2DZ basis set, and these results were compared with the experimentally obtained X-ray crystallographic data. The optimized complex structures are presented in Figure 1. All three complexes possess a dimeric structure and exhibit an octahedral molecular geometry. The central bismuth ions are connected to each other through $\mu_2\text{-X}$ bridges. Complex 1 adopts a cis-S, cis-X configuration, whereas

complexes 2 and 3 display a trans-S, trans-X arrangement in an octahedral dimeric configuration.

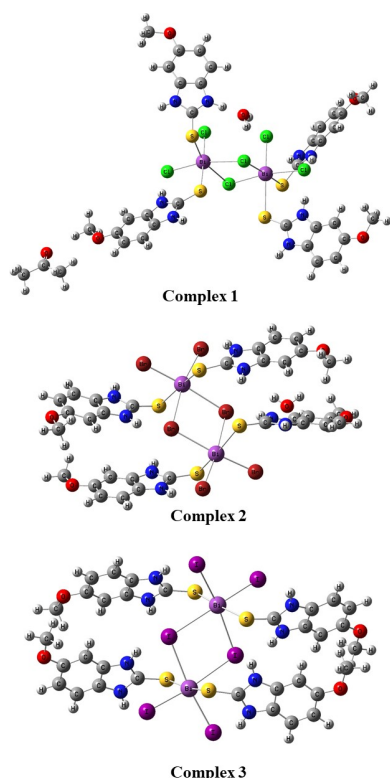


Figure 1. The optimized structures of bismuth(III) halide complexes 1-3

The HOMO–LUMO energy levels and reactivity-related parameters of the bismuth(III) halide complexes are summarized in Table 1. The ionization potential (IP), electron affinity (EA), chemical potential (μ), chemical hardness (η), electronegativity (χ), and electrophilicity index (ω) values were calculated according to Equations (1–7). By comparing the obtained parameters, the effects of structural variations on the electronic properties and reactivity of the dimeric bismuth(III) halide complexes were investigated. The higher HOMO energy level of complex 1 containing a chlorine atom (–5.62 eV) compared to those of the other two complexes (–6.06 eV for 2 and –5.99 eV for 3) indicates that this complex has a greater tendency to donate electrons (Figure 2). In other words, complex 1 exhibits a higher nucleophilic character. The lower LUMO energy of complex 2 (–3.57 eV) compared to the other complexes indicates a higher tendency to accept electrons (–2.03 eV for 1, –2.53 eV for 3). Complex 2 possesses a relatively narrower energy gap compared to the others (by approximately 1.0 eV). This situation is consistent with the behavior of complex 2 as an electron acceptor and with its chemical reactivity. Accordingly, 2 can be considered to have lower kinetic stability. The chemical potential is a concept inversely related to electronegativity. Since complex 2 has a high tendency to accept electrons, it exhibits the highest electronegativity value (4.81 eV). The electrophilicity index also provides supporting results in this regard. It is evident that complex 2 is a strong electrophile [29, 30].

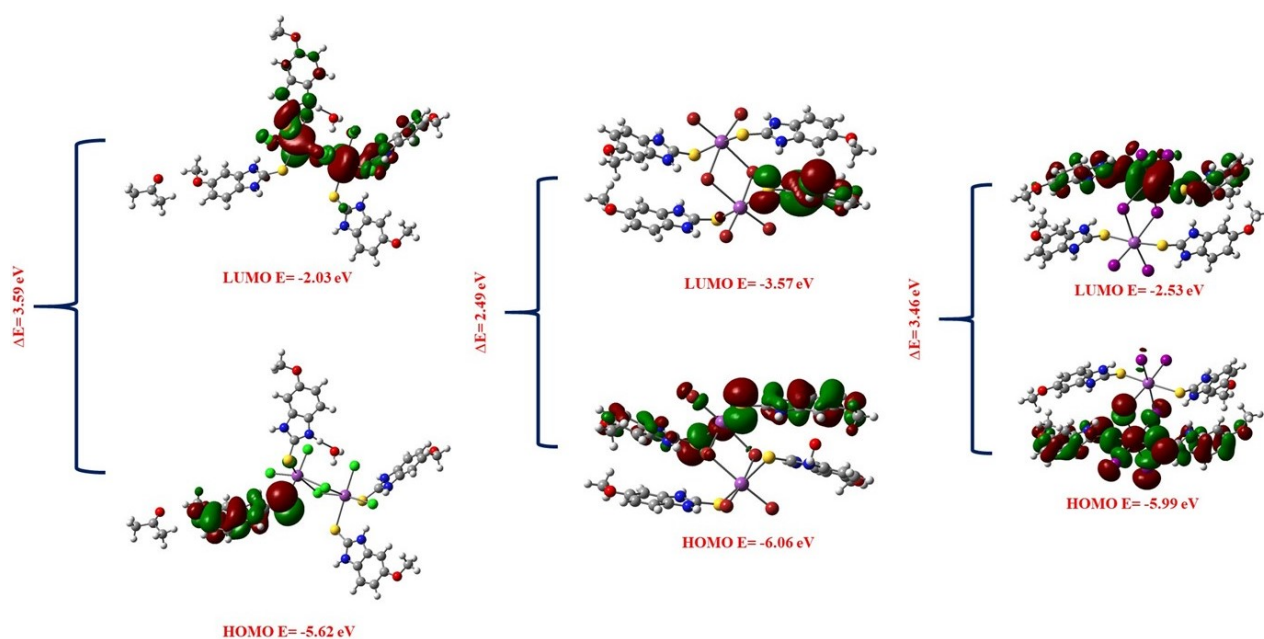


Figure 2. The frontier orbital diagrams of bismuth(III) halide complexes 1-3.

Table 1. The quantum parameters of bismuth(III) halide complexes 1-3.

Compounds	E_{HOMO}	E_{LUMO}	ΔE	IP	EA	μ	η	χ	ω
Complex 1	-5.62	-2.03	3.59	5.62	2.03	-3.83	1.79	3.83	4.07
Complex 2	-6.06	-3.57	2.49	6.06	3.57	-4.81	1.24	4.81	9.31
Complex 3	-5.99	-2.53	3.46	5.99	2.53	-4.26	1.73	4.26	5.24

Mulliken charge analyses were performed to determine the charge distributions in the complexes and to identify nucleophilic and electrophilic regions (Figure 3). In the charge distribution maps, red regions represent negative charges, whereas green regions indicate positive charges [31]. In all three complexes, negative charge localization was primarily observed on the halogen atoms, the oxygen atoms of the ethoxy/methoxy groups, and the nitrogen atoms. Positive charge localization was found predominantly on the bismuth atom, followed by carbon and hydrogen atoms. Atoms with negative charge density correspond to nucleophilic regions, while positively charged atoms indicate electrophilic sites.

While the charge distributions in the bismuth(III) halide complexes were generally consistent, differences were observed in their dipole moments. Complex 1, complex 2, and complex 3 exhibited dipole moment values of 7.0009 D, 3.8298 D, and 2.6146 D, respectively. This variation

can be attributed to differences in charge distribution and molecular symmetry.

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Furthermore, although the formal charge of the bismuth ion is +3, the Mulliken charges of the bismuth center in the complexes were calculated as +1.526, +1.292, and +1.027, respectively. The decrease in charge indicates electron donation from the ligands to the bismuth ion during coordination [32].

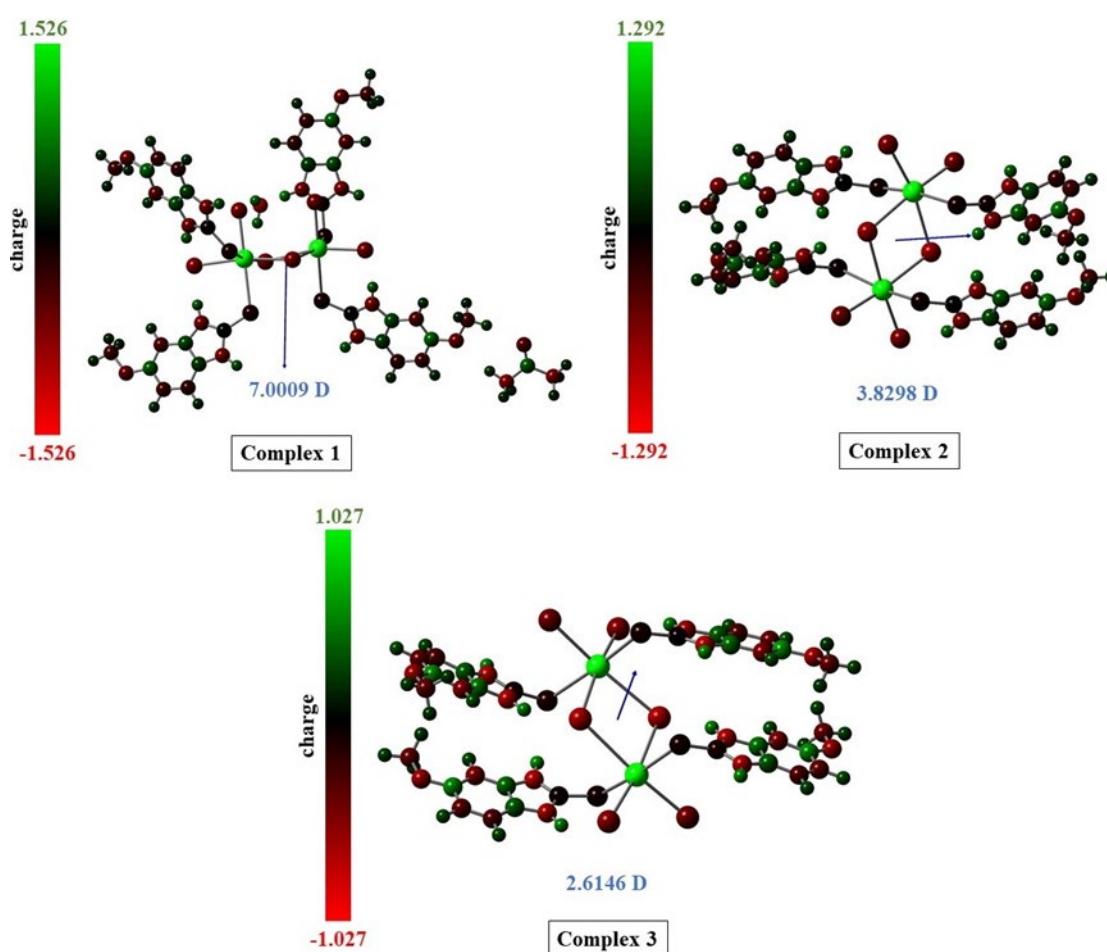


Figure 3. Atomic charge distributions of the complexes 1-3 from Mulliken charge analysis.

The selected bond lengths and bond angles obtained from the optimized geometries are summarized in Table 2 together with the corresponding experimental crystallographic values. Overall, the calculated geometrical parameters show good agreement with the experimental data, confirming the reliability of the B3LYP/LANL2DZ level of theory for describing Bi(III) halide complexes. As expected, the Bi-X bond distances increase in the order $\text{Cl} < \text{Br} < \text{I}$, reflecting the progressive

increase in the atomic radius of the halogen atoms. The calculated Bi-Cl, Bi-Br, and Bi-I bond lengths are consistent with the corresponding experimental values and reproduce the observed structural trends. Furthermore, the S1-Bi1-S2 bond angle of complex 1 was calculated as 79.20° , indicating a cis arrangement of the sulfur donor atoms, whereas the corresponding angles of complexes 2 and 3 (167.90° and 171.81° , respectively) confirm a trans disposition. In addition, several bond

angles around the bismuth center deviate from the ideal octahedral values of 90° and 180° , revealing a distorted octahedral coordination environment. This distortion can be attributed to the presence of bridging halide ligands and the stereochemical influence of the Bi(III) center. The close correspondence between the calculated and experimental geometrical parameters demonstrates that the optimized structures adequately represent the molecular geometries observed in the solid state.

Table 2. The selected bond lengths and angles of bismuth(III) halide complexes **1-3** (exp. data in bracket).

C1 (bond lengths)	C2 (bond lengths)	C3 (bond lengths)
Bi1-S1: 2.828 (2.692)	Bi1-S1: 2.887 (2.857)	Bi1-S1: 3.017 (2.894)
Bi1-S2: 3.112 (2.794)	Bi1-S2: 3.034 (2.784)	Bi1-S2: 2.901 (2.769)
Bi1-Cl1: 2.589 (2.710)	Bi1-Br1: 2.824 (2.748)	Bi1-I1: 2.991 (2.948)
Bi1-Cl2: 2.649 (2.625)	Bi1-Br2: 2.771 (2.712)	Bi1-I2: 3.066 (2.982)
Bi1-Cl3: 2.989 (2.782)	Bi1-Br3: 3.226 (3.050)	Bi1-I3: 3.368 (3.228)
Bi1-Cl3*: 3.062 (2.919)	Bi1-Br3*: 3.177 (3.029)	Bi1-I3*: 3.466 (3.242)
S1-Cl1: 1.779 (1.719)	S1-Cl1: 1.761 (1.694)	S1-Cl7: 1.757 (1.718)
S2-C9: 1.747 (1.708)	S2-C9: 1.761 (1.740)	S2-C15: 1.762 (1.718)
C1-N1: 1.378 (1.341)	C1-N1: 1.365 (1.340)	C7-N1: 1.373 (1.347)
C1-N2: 1.353 (1.337)	C1-N2: 1.374 (1.340)	C7-N2: 1.332 (1.372)
C9-N3: 1.380 (1.337)	C9-N3: 1.371 (1.329)	C15-N3: 1.365 (1.334)
C9-N4: 1.404 (1.341)	C9-N4: 1.404 (1.332)	C15-N4: 1.374 (1.350)
C1 (bond angles $^\circ$)	C2 (bond angles $^\circ$)	C3 (bond angles $^\circ$)
S1-Bi1-S2: 79.20 (80.90)	S1-Bi1-S2: 167.90 (176.90)	S1-Bi1-S2: 171.81 (175.29)
S1-Bi1-Cl1: 89.79 (90.17)	S1-Bi1-Br1: 94.10 (87.14)	S1-Bi1-I1: 93.91 (87.85)
S1-Bi1-Cl2: 96.77 (92.65)	S1-Bi1-Br2: 86.94 (84.00)	S1-Bi1-I2: 89.05 (84.44)
S1-Bi1-Cl3: 159.49 (175.44)	S1-Bi1-Br3: 91.20 (105.26)	S1-Bi1-I3: 89.52 (100.70)
S1-Bi1-Cl3*: 85.45 (92.52)	S1-Bi1-Br3*: 85.20 (90.61)	S1-Bi1-I3*: 84.95 (90.80)
S2-Bi1-Cl1: 168.92 (170.37)	S2-Bi1-Br1: 97.80 (94.59)	S2-Bi1-I1: 94.08 (96.16)
S2-Bi1-Cl2: 89.79 (93.62)	S2-Bi1-Br2: 89.50 (93.25)	S2-Bi1-I2: 91.87 (97.80)
S2-Bi1-Cl3: 101.10 (97.03)	S2-Bi1-Br3: 91.20 (77.48)	S2-Bi1-I3: 88.60 (77.08)
S2-Bi1-Cl3*: 75.30 (79.62)	S2-Bi1-Br3*: 83.60 (87.95)	S2-Bi1-I3*: 86.90 (85.18)
Cl1-Bi1-Cl2: 92.70 (90.35)	Br1-Bi1-Br2: 97.70 (97.66)	I1-Bi1-I2: 96.20 (92.97)
Cl1-Bi1-Cl3: 88.81 (91.62)	Br1-Bi1-Br3: 88.20 (83.31)	I1-Bi1-I3: 90.90 (87.24)
Cl1-Bi1-Cl3*: 102.90 (97.32)	Br1-Bi1-Br3*: 167.40 (173.32)	I1-Bi1-I3*: 172.80 (178.60)
Cl2-Bi1-Cl3: 103.70 (91.53)	Br2-Bi1-Br3: 173.90 (170.74)	I2-Bi1-I3: 172.80 (174.86)
Cl2-Bi1-Cl3*: 164.30 (170.73)	Br2-Bi1-Br3*: 94.90 (88.35)	I2-Bi1-I3*: 90.90 (87.26)
Cl3-Bi1-Cl3*: 74.91 (83.09)	Br3-Bi1-Br3*: 79.20 (91.23)	I3-Bi1-I3: 81.90 (92.65)

4. DISCUSSION AND CONCLUSION

In this study, a theoretical calculation investigation was carried out on bismuth(III) halide complexes of thioamide-derived ligands containing methoxy and ethoxy groups. The effect of the variation of halogen atoms on the electronic properties of the selected dimeric complexes was elucidated. Accordingly, among

complexes 1, 2, and 3 containing chlorine, bromine, and iodine atoms, respectively, bromide was found to have a greater influence on the electrophilic character compared to the others. In this context, the high electronegativity exhibited by Complex 2 indicates that bromine-containing complexes may be noteworthy for future studies. In addition, it is noteworthy that Complex 1, which contains chlorine-an electronegative atom-exhibited the highest

nucleophilic character. According to the charge distribution analysis, electron transfer in the bismuth(III) halide complexes can be considered to occur from the ligands toward the metal center. Furthermore, the magnitude of the dipole moments of the three selected bismuth(III) halide complexes indicates their potential to provide insights into possible application areas in future studies. The calculated Bi–X bond distances followed the expected trend of $\text{Cl} < \text{Br} < \text{I}$, reflecting the increasing atomic size of the halogen atoms. In addition, the S–Bi–S bond angles confirmed the *cis* arrangement in complex 1 and the *trans* arrangement in complexes 2 and 3, while deviations from ideal octahedral geometry indicated the influence of bridging halide ligands and the stereochemically active lone pair of the Bi(III) center. Furthermore, the optimized geometrical parameters showed good agreement with the available experimental crystallographic data.

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