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Crystal structure, electronic properties, and intermolecular interactions of the [Ag(imidazole)₂][ClO₄] complex: A combined DFT, Hirshfeld surface, QTAIM, and RDG study

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RESEARCH ARTICLE



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ABSTRACT

In this study, the [Ag(imidazole)₂][ClO₄] complex was successfully synthesized and its structural and electronic properties were comprehensively investigated using combined experimental and theoretical approaches. The crystal structure was determined by single-crystal X-ray diffraction analysis, while quantum chemical calculations were performed at the DFT/B3LYP/DGDZVP level of theory. A good agreement between the optimized geometry and the experimental structure confirmed the reliability of the theoretical model in describing the structural characteristics of the complex. Hirshfeld surface analysis together with two-dimensional fingerprint plots revealed that the crystal packing is predominantly stabilized by a cooperative network of H...O/O...H, H...H, C...H/H...C, and N...H/H...N intermolecular interactions. Molecular electrostatic potential (MEP) analysis demonstrated that the oxygen atoms of the perchlorate anion constitute the most electron-rich regions, in excellent agreement with the Hirshfeld surface results. Frontier molecular orbital analysis yielded a HOMO-LUMO energy gap of 6.41 eV, indicating high electronic stability and low chemical reactivity of the complex. The HOMO is mainly localized on the perchlorate counterion, whereas the LUMO is distributed over the Ag(I) coordination center and the coordinated imidazole ligands. Furthermore, the Quantum Theory of Atoms in Molecules (QTAIM) and reduced density gradient (RDG) analyses provided detailed insight into the nature of the coordination bonds and weak intermolecular interactions, confirming that van der Waals interactions together with weak hydrogen bonds play a key role in stabilizing the crystal lattice. The combined experimental and theoretical results demonstrate that the structural and electronic stability of the [Ag(imidazole)₂][ClO₄] complex originates from the synergistic contribution of its coordination geometry, favorable electron-density distribution, and cooperative supramolecular interactions.

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1. Introduction

Nitrogen-containing heterocyclic compounds have attracted considerable attention in coordination chemistry, materials science, catalysis, and bioinorganic chemistry due to their versatile electronic properties, strong coordination ability, and wide range of applications [1]. In particular, five-membered aromatic heterocycles are capable of forming stable coordination compounds with transition metal ions due to their electron-rich structures, which significantly influencing the structural, electronic and physicochemical properties of the resulting complexes [2,3]. Consequently, transition metal complexes that incorporate heterocyclic ligands have been extensively investigated due to their structural diversity, flexible coordination behavior, and promising biological, catalytic, and functional applications [4].

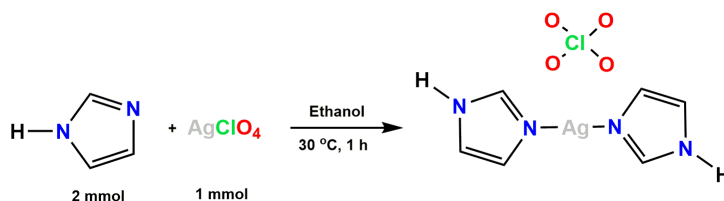
Imidazole is one of the most important nitrogen-containing heterocyclic N-donor ligands owing to its aromatic character, high thermal stability, moderate basicity, and excellent σ -donor ability. The pyridine-like nitrogen atom of the imidazole ring

readily coordinates with transition-metal ions, enabling the formation of coordination compounds with various structural motifs and coordination geometries. These characteristics make imidazole an attractive ligand for the design and synthesis of new coordination compounds with tunable structural and electronic properties [5].

Among transition-metal complexes, silver(I) compounds have attracted considerable attention because of their flexible coordination behavior, variable coordination numbers, and diverse structural architectures. Owing to its d¹⁰ electronic configuration, the Ag(I) ion readily adopts various coordination geometries, including linear, trigonal, and tetrahedral arrangements, which significantly influence crystal packing and intermolecular interactions. In particular, Ag(I)-imidazole complexes have been extensively investigated due to their structural diversity and intriguing electronic and biological properties [6]. However, a comprehensive understanding of their electronic structures and the intermolecular interactions governing crystal packing remains essential to establish

Table 1. Crystal data and structure refinement parameters for [Ag(imidazole)₂]ClO₄ complex.

Parameters	[Ag(imidazole) ₂]ClO ₄
CCDC depository	2563369
Color/shape	Colorless/prism
Chemical formula	[Ag(C ₃ H ₄ N ₂) ₂] ⁺ ·(ClO ₄) ⁻
Formula weight	343.48
Temperature (K)	296(2)
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	P2 ₁ /c (No. 14)
Unit cell parameters	
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.3738(11), 8.5615(8), 10.2360(9)
α, β, γ (°)	90, 90.104(3), 90
Volume (Å ³)	1084.38(17)
<i>Z</i>	4
<i>D</i> _{calc} (g/cm ³)	2.104
μ (mm ⁻¹)	2.110
Absorption correction	Multi-scan
<i>T</i> _{min} , <i>T</i> _{max}	0.4611, 0.7457
<i>F</i> ₀₀₀	672
Crystal size (mm ³)	0.64 × 0.51 × 0.17
Diffractometer	Bruker D8 QUEST
Measurement method	φ and ω scan
Index ranges	-16 ≤ <i>h</i> ≤ 16, -11 ≤ <i>k</i> ≤ 11, -13 ≤ <i>l</i> ≤ 13
θ range for data collection (°)	1.646 ≤ θ ≤ 28.371
Reflections collected	20051
Independent/observed reflections	2663/2286
<i>R</i> _{int}	0.0389
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2663/0/145
Goodness-of-fit on <i>F</i> ²	1.040
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0302, <i>wR</i> ₂ = 0.0696
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0375, <i>wR</i> ₂ = 0.0754
Δρ _{max} , Δρ _{min} (e/Å ³)	0.61, -0.71

**Scheme 1.** Schematic representation of the synthesis of the [Ag(imidazole)₂]ClO₄ complex.

reliable structure–property relationships and for the rational design of new silver(I) coordination compounds [6–8].

In recent years, the combination of experimental characterization techniques with density functional theory (DFT) calculations has become a powerful approach to investigate the structural and electronic properties of coordination compounds. Geometry optimization, frontier molecular orbital analysis (HOMO-LUMO), molecular electrostatic potential (MEP) mapping, and global reactivity descriptors provide valuable information regarding molecular stability, electron distribution, and chemical reactivity [9,10]. Furthermore, Hirshfeld surface analysis enables a quantitative evaluation of intermolecular contacts responsible for crystal packing, whereas the Quantum Theory of Atoms in Molecules (QTAIM) and Reduced Density Gradient (RDG) analyses provide detailed insight into the nature of coordination bonds and weak noncovalent interactions at the atomic level [11]. The integration of these experimental and theoretical methods allows a comprehensive interpretation of the relationship between molecular structure, electronic properties, and supramolecular organization.

In the present study, the [Ag(imidazole)₂]ClO₄ complex was successfully synthesized and structurally characterized by single-crystal X-ray diffraction analysis. The experimental findings were complemented by DFT calculations performed at the B3LYP/DGDZVP level. In addition, the structural stability, electronic properties, and intermolecular interactions of the complex were systematically investigated through geometry optimization, frontier molecular orbital (HOMO-LUMO)

analysis, molecular electrostatic potential (MEP) mapping, Hirshfeld surface analysis, QTAIM, and RDG analyses. Unlike previous studies, which have focused primarily on the synthesis, crystal structures, or selected electronic properties of Ag(I)-imidazole complexes, the present work combines complementary experimental and theoretical approaches to provide an integrated understanding of the structural, electronic, and supramolecular characteristics of the complex. Furthermore, the combined application of the Hirshfeld surface, MEP, QTAIM, and RDG analyses enables a detailed correlation between electron density distribution, coordination bonding, and weak intermolecular interactions governing the crystal packing. By integrating experimental observations with theoretical calculations, the present study provides a comprehensive understanding of the relationship between molecular structure, electronic characteristics, and supramolecular organization in the [Ag(imidazole)₂]ClO₄ complex, which contributes to the rational design and fundamental understanding of Ag(I)-imidazole coordination compounds.

2. Experimental

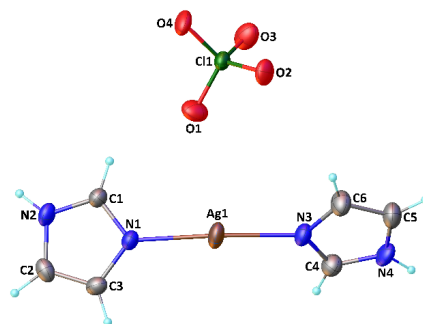
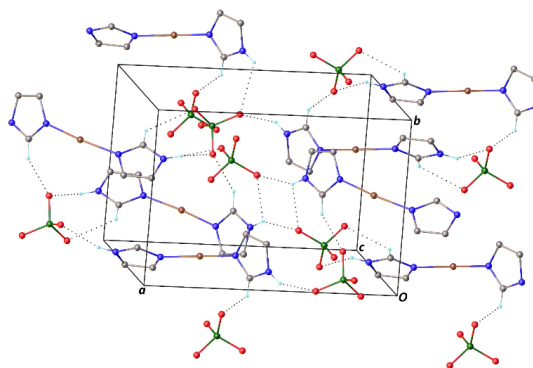
2.1. Computational method

Geometry optimization and calculations of electronic structures were performed using the Gaussian 16W software package [12].

Table 2. Hydrogen bonding geometry for [Ag(imidazole)₂]ClO₄.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
N2–H2N...O4 ⁱ	0.86	2.17	2.941(3)	150
N4–H4N...O2 ⁱⁱ	0.86	2.26	2.998(3)	144
N4–H4N...O1 ⁱⁱⁱ	0.86	2.49	3.151(4)	134
C1–H1...O1	0.93	2.53	3.247(3)	134
C4–H4...O3 ⁱⁱⁱ	0.93	2.59	3.190(4)	123
N2–H2N...O4 ^{iv}	0.86	2.59	3.117(3)	120

Symmetry codes: ⁱ $-x+1, y-1/2, -z+1/2$; ⁱⁱ $-x+2, y-1/2, -z+3/2$; ⁱⁱⁱ $-x+2, -y+1, -z+1$; ^{iv} $x, -y+3/2, z-1/2$.

**Figure 1.** A view of the molecule of [Ag(imidazole)₂]ClO₄, showing the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level, and H atoms are shown as small spheres of arbitrary radii.**Figure 2.** Packing diagram of [Ag(imidazole)₂]ClO₄. Intermolecular N–H...O and C–H...O interactions are shown as dotted lines, and only H atoms involved in hydrogen bonding have been included for simplicity.

The graphical representations of the calculated molecular properties were generated using GaussView 6.1 [13]. Prior to the calculations, the initial geometry of the synthesized complex was obtained from single-crystal X-ray diffraction data, and all computational studies were carried out using this experimentally determined structure as the starting geometry. Full geometry optimization and all subsequent theoretical calculations were performed at the DFT/B3LYP/DGDZVP level of theory [14]. Hirshfeld surface analysis was performed using CrystalExplorer 21.5 based on the experimental single-crystal X-ray diffraction data to investigate intermolecular interactions within the crystal structure [15]. In addition, QTAIM and reduced density gradient (RDG) analyses were carried out using the Multiwfn program, while RDG isosurfaces were visualized using VMD to characterize the nature of chemical bonding and weak non-covalent interactions [16].

2.2. Synthesis of the [Ag(imidazole)₂]ClO₄ complex

Imidazole (99% purity) and silver perchlorate (AgClO₄, 97% purity) were purchased from Sigma-Aldrich and used without further purification. For the synthesis, 2 mmol of imidazole was dissolved in 10 mL of 98% ethanol and the resulting solution was stirred in an Erlenmeyer flask at 30 °C for 5 min using a magnetic stirrer. In a separate Erlenmeyer flask, 1 mmol of AgClO₄ was dissolved in 5 mL of 98% ethanol and stirred at the same temperature for 5 min. The AgClO₄

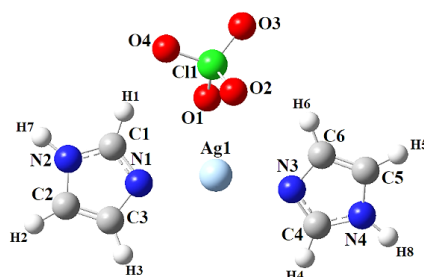
solution was then added dropwise to the imidazole solution under continuous stirring. The reaction mixture was stirred at 30 °C for 60 min. The resulting solution was subsequently stored at +4 °C for approximately 30 days to promote single-crystal growth. At the end of the crystallization period, colorless single crystals suitable for single-crystal X-ray diffraction analysis were obtained, and the synthesized complex was identified as the [Ag(imidazole)₂]ClO₄ complex (Scheme 1).

2.3. X-ray crystallography

X-ray data of [Ag(imidazole)₂]ClO₄ were collected on a Bruker D8 QUEST diffractometer at 296(2) K using graphite-monochromated Mo K α radiation applying the φ and ω scan methods. Data collection was carried out using APEX2 [17] while cell refinement and data reduction were applied using SAINT [17]. The structure was solved by a dual-space algorithm using SHELXT-2018 [18] and refined by means of the full-matrix least-squares calculations on F² using SHELXL-2019 [19]. All H atoms were located in difference maps and then treated as riding atoms, fixing the bond lengths at 0.86 and 0.93 Å for NH and CH atoms, respectively. The displacement parameters of the H atoms were fixed at U_{iso}(H) = 1.2U_{eq}. Crystal data, data collection, and structure refinement details are given in Table 1. OLEX2 [20] was used for the structural plots.

Table 3. Comparison of selected experimental (XRD) and calculated geometrical parameters (bond lengths, Å; bond angles, °) of the [Ag(imidazole)₂][ClO₄] complex.

Bond lengths (Å)	[Ag(imidazole) ₂][ClO ₄]		Bond angles (°)	[Ag(imidazole) ₂][ClO ₄]	
	Calculated	XRD		Calculated	XRD
Ag1—N1	2.278	2.096 (2)	C1—N1—C3	106.5	105.4 (2)
Ag1—N3	2.277	2.103(2)	C1—N1—Ag1	119.8	124.5(18)
N1—C1	1.328	1.319(3)	C3—N1—Ag1	133.7	129.6(17)
N3—C4	1.324	1.317(4)	C4—N3—C6	106.58	105.7 (2)
N1—C3	1.383	1.372(3)	C4—N3—Ag1	133.6	124.2 (2)
N3—C6	1.385	1.361(4)	C6—N3—Ag1	119.7	130.0 (2)
N2—C1	1.358	1.321(3)	C1—N2—C2	108.4	108.3 (2)
N4—C4	1.359	1.323(4)	C4—N4—C5	107.8	108.1 (2)
N2—C2	1.383	1.353(4)	N1—C1—N2	110.9	110.7 (2)
N4—C5	1.385	1.347(4)	N3—C4—N4	110.5	110.9 (3)
C2—C3	1.372	1.338(4)	N1—Ag1—N3	162.9	170.1
C5—C6	1.372	1.353(4)			
Cl1—O1	1.520	1.430(2)			
Cl1—O2	1.522	1.430(19)			
Cl1—O3	1.481	1.427(2)			
Cl1—O4	1.499	1.429(2)			
RMSD	0.077		RMSD	5.11	

**Figure 3.** Optimized molecular structure of the [Ag(imidazole)₂][ClO₄] complex.

3. Results and discussion

3.1. Description of the structure

The molecular structure of [Ag(imidazole)₂][ClO₄] with the adopted atom labeling scheme is shown in Figure 1. The compound crystallizes as a salt in the monoclinic space group *P*2₁/*c* with *Z* = 4. The asymmetric unit of [Ag(imidazole)₂][ClO₄] consists of one Ag(I) cation, two imidazole ligands and one ClO₄[−] anion. The structure of [Ag(imidazole)₂][ClO₄] shows that the silver atom is bound to the nitrogen atoms of two imidazole ligands with a nearly same distance [2.096(2) and 2.103(2) Å] in a slightly bent geometry [N1—Ag1—N3 = 170.08(9)°]. In this arrangement, the two imidazole rings are oriented to each other with an angle of 54.55(17)°. No intramolecular hydrogen bonds are present in the molecular structure of the compound. The crystal structure is stabilized by N—H...O and C—H...O interactions (Figure 2), the geometrical parameters of which are listed in Table 2.

3.2. Optimized geometric structure parameters

The optimized geometrical parameters of the [Ag(imidazole)₂][ClO₄] complex and the corresponding experimental values obtained from single-crystal X-ray diffraction (XRD) analysis are compared in Table 3. The optimized geometry of the [Ag(imidazole)₂][ClO₄] complex is also presented in Figure 3. Overall, a good agreement was observed between the optimized and experimental structures. The root mean square deviation (RMSD) values calculated for bond lengths and bond angles were 0.077 Å and 5.11°, respectively [21], indicating satisfactory consistency between the theoretical and experimental geometries. The small deviations between the calculated and experimental structural parameters can be attributed to the fact that the theoretical calculations were performed in the gas phase, whereas the

experimental structure reflects the influence of crystal packing and intermolecular electrostatic interactions within the crystal lattice [22]. In the complex, the Ag(I) ion is coordinated by the ring nitrogen atoms (N1 and N3) of two imidazole ligands, resulting in an approximately linear coordination geometry. The experimental Ag1—N1 and Ag1—N3 bond lengths were determined to be 2.096(2) and 2.103(2) Å, respectively, whereas both bonds were calculated to be 2.278 Å. The slightly longer Ag—N bond distances obtained from theoretical calculations may be attributed to the absence of crystal packing effects and long-range electrostatic (Coulombic) interactions in the gas-phase model [23]. In the crystal structure, the electrostatic influence of the perchlorate counterion, together with intermolecular interactions, contributes to a more compact coordination environment around the Ag(I) center.

Examination of the imidazole ring bond lengths reveals a close agreement between the theoretical and experimental values. The N1—C1, N2—C1, and N3—C4 bond lengths were experimentally determined as 1.332(3), 1.328(3), and 1.328(3) Å, respectively, while the corresponding calculated values were 1.340, 1.353, and 1.340 Å. Similarly, the C1—C2 and C4—C5 bond lengths were measured as 1.350(3) and 1.350(3) Å in the crystal structure and calculated as 1.365 Å for both bonds. These results demonstrate that the DFT/B3LYP/DGDZVP method successfully reproduces the structural features of the imidazole ligands.

For the perchlorate anion, the experimental Cl1—O bond lengths range from 1.427(2) to 1.430(2) Å, whereas the calculated values fall within the range of 1.481–1.522 Å. The relatively similar calculated Cl—O bond lengths indicate a tendency of the perchlorate group to adopt a more ideal tetrahedral geometry in the optimized structure. The small variations observed in the experimental structure may arise from crystal packing effects, electrostatic interactions, and local environmental influences around the counterion [24].

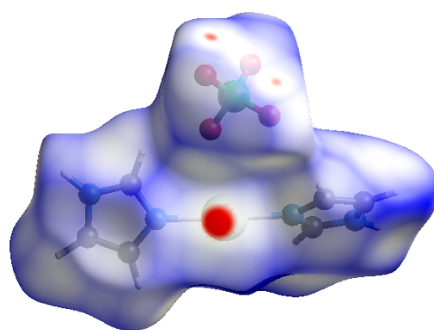


Figure 4. Hirshfeld surface mapped over the d_{norm} for the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex.

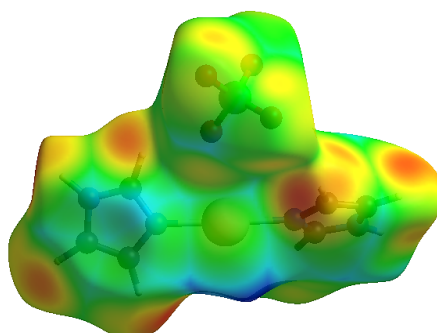


Figure 5. Hirshfeld surface mapped over d_i for the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex.

Bond-angle analysis also shows good agreement between the theoretical and experimental geometries. For example, the N1–C1–N2 angle was measured as $111.2(2)^\circ$ and calculated as 108.4° , while the N3–C4–N4 angle exhibited identical experimental and theoretical values of $111.2(2)^\circ$ and 108.4° , respectively. The most significant geometrical parameter defining the coordination environment, the N1–Ag1–N3 angle, was determined experimentally as 170.1° and calculated as 162.9° . Both values confirm the two-coordinate and nearly linear geometry around the Ag(I) center. The smaller calculated angle can be attributed to the absence of crystal lattice constraints in the gas-phase model, allowing a greater degree of structural relaxation around the coordination sphere.

The good agreement between the optimized and experimental geometries demonstrates that the DFT/B3LYP/DGDZVP level of theory provides a reliable description of the structural characteristics of the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex. The low RMSD values further support the validity of the theoretical model, indicating that it can be confidently used to interpret the electronic structure, bonding characteristics, and molecular properties of the complex.

3.3. Hirshfeld surface analysis

Hirshfeld surface analysis was carried out to investigate the intermolecular interactions that govern the crystal packing of the complex. In this approach, d_i represents the distance from a point on the Hirshfeld surface to the nearest atom within the reference molecule, while d_e corresponds to the distance from the same point to the nearest atom belonging to a neighboring molecule [25]. The normalized contact distance (d_{norm}), derived from these two parameters, enables visualization of intermolecular contacts relative to the corresponding van der Waals radii. On the surface of the d_{norm} , the red regions indicate contacts shorter than the sum of the van der Waals radii, the white regions correspond to the contacts close to van der Waals

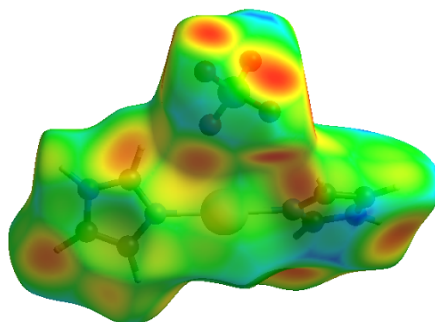
separations, and the blue regions represent longer intermolecular distances [26].

As shown in Figure 4, the d_{norm} surface is dominated by white and light blue regions, while only a few localized red spots are observed. This distribution indicates that the crystal packing is not governed by numerous strong short-range interactions and that a significant proportion of intermolecular contacts occur at or near van der Waals distances [27]. The presence of only a few localized red spots suggests that the short intermolecular contacts are spatially limited and restricted to specific regions of the crystal packing [28]. The relatively small and localized red regions observed around the perchlorate group indicate the presence of short $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ contacts. However, unlike intense red spots generally associated with strong intermolecular interactions, their limited size and intensity suggest that these contacts mainly correspond to weak-to-moderate intermolecular interactions. [29]. In contrast, the localized red area observed near the central region of the molecule indicates the presence of relatively short intermolecular contacts that contribute to the overall packing arrangement.

The d_i surface (Figure 5) exhibits red-orange regions mainly around the peripheral parts of the aromatic ligands, particularly near hydrogen-bearing sites and along the outer boundaries of the molecular surface. These features indicate variations in the internal atomic distances across the Hirshfeld surface. The blue-green regions concentrated around the central part of the molecule and the coordination environment reflect shorter distances between the surface and atoms belonging to the reference molecule [30]. Therefore, the d_i surface reveals the non-uniform spatial distribution of internal atomic distances across the molecular surface, with shorter d_i values concentrated around the central coordination environment and comparatively larger d_i values observed over the outer regions of the ligand framework [26,31].

Table 4. Energies of HOMO and LUMO orbital and the other quantum chemical properties of the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex.

Molecular orbitals	Energy (eV)	Equation	Energy gap (eV)	I (eV)	A (eV)	η (eV)	χ (eV)	μ_c (eV)	σ (eV ⁻¹)	ω (eV)
H	-6.92	ΔE_{H-L}	6.41	6.92	0.51	3.20	3.71	-3.71	0.31	2.15
L	-0.51									
H-1	-6.97	$\Delta E_{H-1-L+1}$	6.52	6.97	0.45	3.26	3.71	-3.71	0.31	2.12
L+1	-0.45									
H-2	-6.99	$\Delta E_{H-2-L+2}$	6.81	6.99	0.18	3.40	3.58	-3.58	0.29	1.89
L+2	-0.18									

**Figure 6.** Hirshfeld surface mapped over d_e for the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex.

The d_e surface (Figure 6) displays a broader distribution of red-orange regions compared with the d_i surface. These areas are mainly located around the upper part of the perchlorate group, the outer surfaces of the aromatic ligands, and other exposed regions of the molecule. This distribution indicates that intermolecular contacts originating from neighboring molecules are not uniformly distributed across the surface, but are concentrated in specific regions [26,31]. However, the red-orange areas observed on the d_e map should not be interpreted as evidence of strong short contacts. When considered together with the d_{norm} surface, these regions indicate that most external contacts correspond to interactions occurring close to van der Waals separations or to weak-to-moderate intermolecular interactions [30,31].

The two-dimensional fingerprint plots (Figures 7a-d) quantitatively support these observations. $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ contacts make the largest contribution to the Hirshfeld surface, accounting for 43.7% of the total contacts. This substantial percentage highlights the significant involvement of oxygen atoms from the perchlorate anion and hydrogen atoms from the ligands in the crystal packing. However, the absence of extensive red regions around the perchlorate group on the d_{norm} surface suggests that these contacts mainly correspond to weak or moderate $\text{H}\cdots\text{O}$ interactions rather than strong classical hydrogen bonds. $\text{H}\cdots\text{H}$ contacts contribute 21.5% of the total surface area, emphasizing the importance of dispersion forces and van der Waals interactions in stabilizing the crystal structure. $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ contacts account for 8.4% of the surface and can be associated with weak $\text{C}-\text{H}\cdots\pi$ interactions involving the aromatic rings. In addition, $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ contacts contribute 6.8%, indicating that indazole nitrogen atoms also participate as secondary interaction sites within the crystal lattice.

Combining the d_{norm} , d_i , d_e , and fingerprint analyzes reveal that the crystal structure is stabilized not by a single dominant hydrogen-bonding motif, but by a cooperative network of $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ and $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ interactions. While the red-orange regions on the d_i and d_e surfaces indicate preferential localization of intermolecular contacts in specific areas of the molecular surface, the limited red regions on the d_{norm} map demonstrate that most of these interactions are van der Waals-type or weak-to-moderate contacts rather than strong short-range interactions. Consequently, the crystal packing is governed by the cumulative effect of multiple complementary intermolecular interactions that collectively

contribute to the stability of the three-dimensional supramolecular architecture.

3.4. Frontier molecular orbital (HOMO-LUMO) analysis

Frontier molecular orbital theory (FMO) is an important tool to understand the electronic structure, stability, and chemical reactivity of molecular systems [32]. The highest occupied molecular orbital (HOMO) represents the electron-donating ability of a molecule, whereas the lowest unoccupied molecular orbital (LUMO) reflects its electron-accepting capacity [33]. Therefore, the energy levels and spatial distributions of the HOMO and LUMO orbitals provide valuable information about charge-transfer processes and potential reactive sites within a molecule. In addition, the energy difference between the HOMO and LUMO orbitals (E_g) is widely used as an important parameter for evaluating molecular stability and chemical reactivity. In general, molecules with large HOMO-LUMO energy gaps exhibit higher kinetic stability and lower chemical reactivity, whereas systems with smaller energy gaps tend to show higher polarizability, easier charge transfer, and increased reactivity [34].

The HOMO and LUMO energies of the investigated complex were calculated using the optimized geometry, and the corresponding orbital distributions are presented in Figure 8, while the global reactivity parameters are listed in Table 4. The HOMO and LUMO energies were determined to be -6.92 and -0.51 eV, respectively, resulting in a HOMO-LUMO energy gap (ΔE) of 6.41 eV. This relatively large energy gap indicates that the complex possesses high electronic stability and low chemical reactivity. The HOMO is predominantly localized on the oxygen atoms of the perchlorate counterion, whereas the LUMO is mainly distributed over the Ag(I) coordination center and the coordinated imidazole ligands. This distribution suggests a possible redistribution of electron density from the ligand framework toward the coordination environment upon electronic excitation.

Using Koopmans' approximation, several global reactivity descriptors, including ionization potential ($I = -E_{\text{HOMO}}$), electron affinity ($A = -E_{\text{LUMO}}$), electronegativity ($\chi = -\mu_c$), chemical potential ($\mu_c = (E_{\text{HOMO}} + E_{\text{LUMO}})/2$), global hardness ($\eta = (E_{\text{HOMO}} - E_{\text{LUMO}})/2$), global softness ($\sigma = 1/\eta$), and electrophilicity index ($\omega = (\mu_c^2)/2\eta$), were calculated from the frontier molecular orbital energies [35].

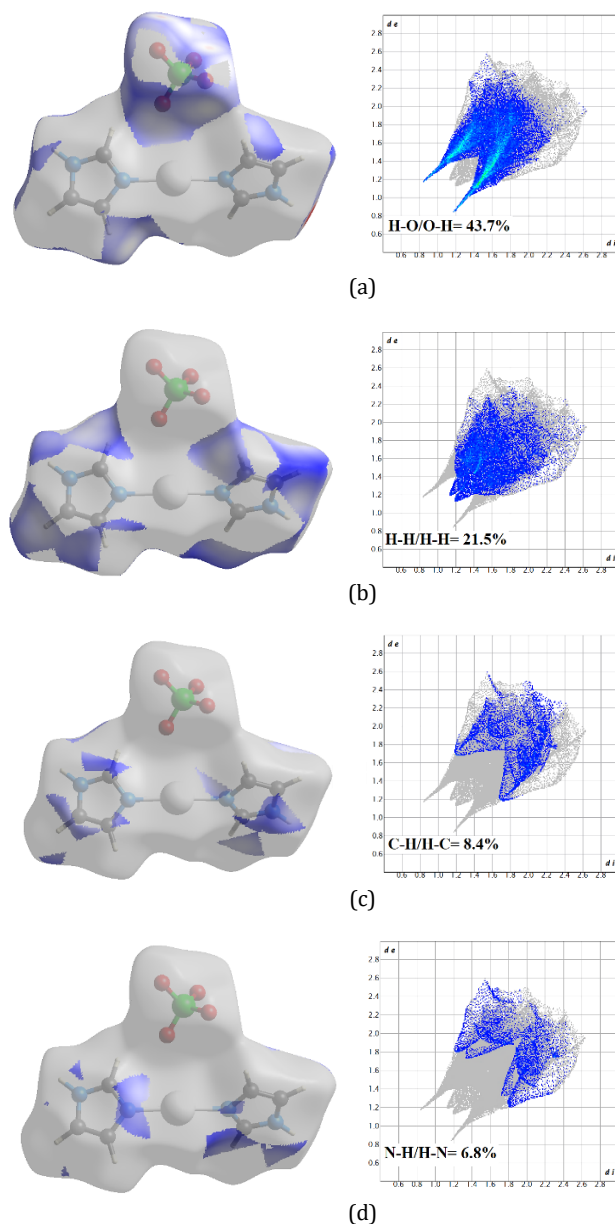


Figure 7. Decomposed two-dimensional fingerprint plots and the corresponding Hirshfeld surfaces for the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex showing (a) $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, (b) $\text{H}\cdots\text{H}$, (c) $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$, and (d) $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ contacts.

The ionization potential and electron affinity values were found to be 6.92 and 0.51 eV, respectively. The high global hardness value ($\eta = 3.20$ eV) and the low softness value ($\sigma = 0.31$ eV⁻¹) indicate that the complex has a rigid and electronically stable structure. The calculated electronegativity ($\chi = 3.71$ eV) and the chemical potential ($\mu = -3.71$ eV) support the tendency of the system to retain its electron density, whereas the electrophilicity index ($\omega = 2.15$ eV) indicates that the complex exhibits a moderate electrophilic character. Furthermore, the energy gaps calculated for the $\text{H}-1/\text{L}+1$ and $\text{H}-2/\text{L}+2$ orbital pairs were 6.52 and 6.81 eV, respectively, confirming that the electronic structure is generally characterized by wide energy separations.

For comparison, HOMO-LUMO energy gaps of 5.66 and 5.08 eV have been reported for ethyl 1*H*-imidazole-1-carboxylate and its perchlorate complex [8], respectively, while a value of 5.70 eV was calculated for *N*-methoxy-*N*-methyl-1*H*-imidazole-1-carboxamide [36]. The HOMO-LUMO energy gap obtained for the present complex (6.41 eV) is higher than those reported for

these imidazole derivatives and is consistent with the values reported for similar $\text{Ag}(\text{I})$ -imidazole complexes, such as $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$. Furthermore, the relatively large energy gaps observed for all of these systems indicate that imidazole-derived complexes generally have low chemical reactivity and a high resistance to charge transfer processes [8,36].

The results obtained demonstrate that the investigated complex possesses high electronic stability and low chemical reactivity. The calculated HOMO-LUMO parameters and global reactivity descriptors confirm the stable electronic nature of the complex and provide a theoretical explanation for its chemical behavior in agreement with the experimental findings.

3.5. Molecular electrostatic potential (MEP) analysis

Molecular electrostatic potential (MEP) analysis is a widely used theoretical approach to visualize the charge distribution on a molecular surface and identify potential reactive sites [37].

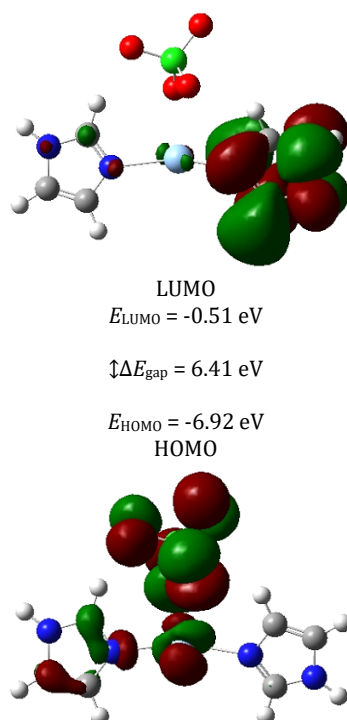


Figure 8. HOMO and LUMO orbital distributions of the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex.

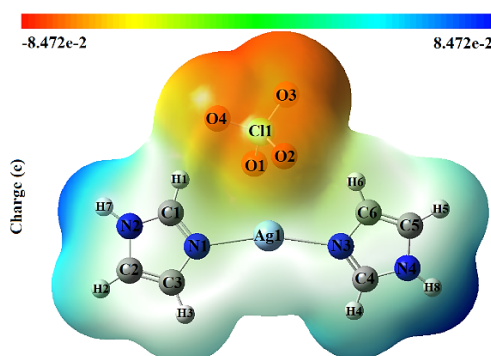


Figure 9. Molecular electrostatic potential (MEP) surface of the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex showing the distribution of the electrostatic potential over the molecular surface.

In the MEP maps, red and orange regions represent negative electrostatic potential and high electron density, whereas blue regions correspond to positive electrostatic potential and electron-deficient areas. Green regions indicate nearly neutral electrostatic potential values. Therefore, MEP maps provide valuable information to assess molecular reactivity and intermolecular interaction tendencies [38].

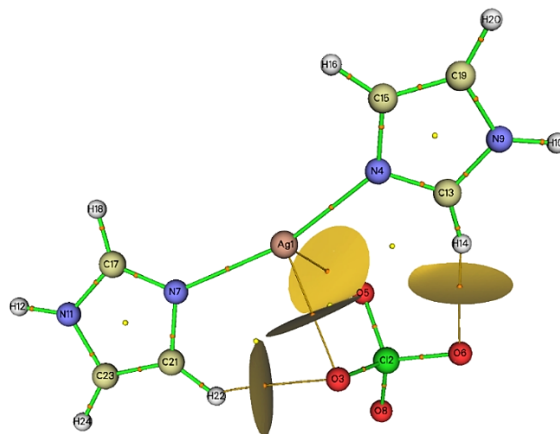
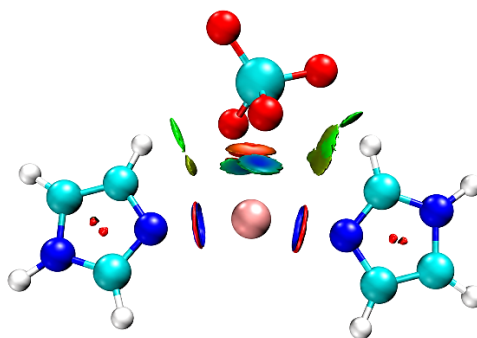
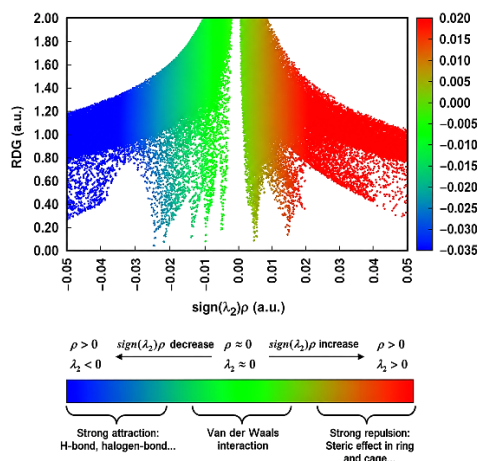
The calculated MEP surface of the investigated complex is presented in Figure 9, with electrostatic potential values ranging from -8.472×10^{-2} to $+8.472 \times 10^{-2}$ a.u. Examination of the surface reveals that the most negative electrostatic potential regions are concentrated around the O1–O4 oxygen atoms of the perchlorate anion. This observation indicates that these oxygen atoms possess a high electron density and constitute the primary nucleophilic centers of the complex. On the contrary, the positive electrostatic potential regions are located mainly around the hydrogen atoms of the imidazole ligands and, to a lesser extent, in the vicinity of the Ag(I) coordination center. These electron-deficient regions are more susceptible to interactions with nucleophilic species. The extensive green-colored areas distributed over the molecular

surface suggest a relatively balanced charge distribution throughout the structure. The negative potential regions surrounding the perchlorate oxygen atoms and the positive regions associated with the ligand hydrogen atoms reveal the presence of complementary electrostatic sites within the molecule. These findings are consistent with Hirshfeld surface analysis, where $\text{H} \cdots \text{O}/\text{O} \cdots \text{H}$ contacts were found to make the largest contribution (43.7%) to crystal packing, highlighting the significant role of electrostatic interactions between oxygen and hydrogen atoms in stabilizing the crystal structure. Overall, the MEP results indicate that the perchlorate oxygen atoms act as the principal nucleophilic centers, whereas the hydrogen atoms of the imidazole ligands represent the main electrophilic regions of the complex. When considered together with the HOMO–LUMO analysis, the results demonstrate a distinct differentiation of electron density between the ligand framework and the coordination environment, which significantly influences the intermolecular interaction behavior of the complex.

Table 5. Topological parameters obtained by QTAIM analysis for [Ag(imidazole)₂]ClO₄.

Interactions	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$G(r)$	$V(r)$	$ V(r) /G(r)$	$E_{\text{int}}(\text{kcal/mol})$
Ag-N ₄	0.06240	0.23729	-0.01211	0.07150	-0.08369	1.17048	-26.25
Ag-N ₇	0.06220	0.23889	-0.01203	0.07175	-0.08379	1.17280	-26.28
Ag...O ₃	0.02268	0.09627	0.00041	0.02365	-0.02324	0.98266	-7.29
Ag...O ₅	0.02545	0.10781	0.00018	0.02714	-0.02733	0.98700	-8.57
C ₁₃ -H ₁₄ ...O ₆	0.01428	0.05444	0.00201	0.01161	-0.00961	0.82773	-3.01
C ₂₁ -H ₂₂ ...O ₃	0.01005	0.03961	0.00172	0.00817	-0.00644	0.78824	-2.02

D: Distance (Å); $\rho(r)$ (a.u.): Density of electrons; $\nabla^2\rho(r)$ (a.u.): Laplacian of electron density; $V(r)$ (a.u.): Potential energy density; (E_{int}) (kcal/mol): Interaction energy.

**Figure 10.** Graphical representation of the AIM analysis of the [Ag(imidazole)₂]ClO₄ complex.**Figure 11.** RDG and isosurface density plots of the [Ag(imidazole)₂]ClO₄ complex.

3.6. AIM (atoms in molecules) and non-covalent interactions reduced density gradient (NCI-RDG) analysis

The AIM theory is a quantum chemistry that models the interactions inside molecular systems using topological analysis of electron density. [39,40]. The atoms in molecules (AIM) and noncovalent interactions (NCI) were estimated to study the intramolecular and intermolecular interactions between the Ag(I) cation and the imidazole molecule. The quantum theory of atoms in molecules (QTAIM) has been used as a relativistic topological property to calculate interaction energies and bond critical points (BCPs). Figure 10 depicts bond critical points, or the equilibrium locations of donor and acceptor atoms. The AIM results showed that the Ag(I) complex is characterized by BCPs, which are collected in detail in Table 5. The title complex is stabilized by two weak intramolecular hydrogen bonds, H...O, as indicated by the figure and table. The analysis results indicate that the C-H...O hydrogen bond is indicative of weak H-bonds, as indicated by the values of $\nabla^2\rho(r)$

> 0 and $H(r) > 0$. $H(r)$ indicates weaker hydrogen connections of a purely electrostatic nature. These critical intermolecular Ag-N interactions contribute to the stability of the complex with $\nabla^2\rho(r) > 0$ and $H(r) < 0$ ratios. These findings characterize the weakly ionic closed-shell interactions. Also, since the Ag...O interactions in the silver complex have the condition $0.5 < |V(r)|/G(r) < 1$, the covalent character of the bonds is dominant. The stability of the [Ag(imidazole)₂]ClO₄ complex was analyzed in more detail using electron density and reduced density gradient (RDG) studies of its non-covalent interactions (NCI). Figure 11 shows the 3D RDG isofacial densities of the compound as well as the 2D scattering plot. The steric effects are shown by the red regions at the centers of the imidazole rings in the complex, and represent the cyclic effect of the ring. The bluish-green patches in the 3D isosurface represent the presence of weak hydrogen bonds. The NCI analysis confirms the presence of hydrogen bond and van der Waals interactions in the synthesized compound.

4. Conclusions

In this study, the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex was successfully synthesized and its molecular structure was comprehensively elucidated by single-crystal XRD analysis. The crystal structure revealed that the Ag(I) center adopts an approximately linear two-coordinate geometry through coordination with the ring nitrogen atoms of two imidazole ligands, while the perchlorate anion is present as a noncoordinating counterion within the crystal lattice. Geometry optimization performed at the DFT/B3LYP/DGDZVP level showed excellent agreement with the experimental crystal structure, as evidenced by the low RMSD values obtained for both bond lengths and bond angles. The minor discrepancies between the calculated and experimental geometries can be attributed to the absence of crystal-packing effects and long-range electrostatic (Coulombic) interactions in the gas-phase calculations.

Hirshfeld surface analysis, together with two-dimensional fingerprint plots, demonstrated that the crystal packing is not governed by a single dominant hydrogen bond, but rather by a cooperative network of $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$, $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$, and $\text{N}\cdots\text{H}/\text{H}\cdots\text{N}$ contacts. The predominance of $\text{H}\cdots\text{O}/\text{O}\cdots\text{H}$ interactions highlights the significant role of the oxygen atoms of the perchlorate anion in stabilizing the crystal lattice. The distributions observed on the d_{norm} , d_i , and d_e surfaces further confirmed that these contacts are concentrated in specific regions of the molecular surface and are predominantly weak-to-moderate van der Waals-type interactions rather than strong classical hydrogen bonds. These findings are fully supported by the molecular electrostatic potential (MEP) analysis, where the oxygen atoms of the perchlorate anion constitute the most electron-rich regions, whereas the hydrogen atoms of the imidazole ligands represent the most electron-deficient sites. The excellent agreement between the Hirshfeld and MEP analyses demonstrates that the calculated electrostatic potential distribution is directly reflected in the experimentally observed crystal packing.

Frontier molecular orbital analysis revealed a relatively large HOMO-LUMO energy gap of 6.41 eV, indicating high electronic stability and low chemical reactivity of the complex. The HOMO is predominantly localized on the oxygen atoms of the perchlorate counterion, whereas the LUMO is mainly distributed over the Ag(I) coordination center and the coordinated imidazole ligands, suggesting that electronic excitation is accompanied by electron-density redistribution from the counterion toward the coordination sphere. In agreement with this observation, the calculated high global hardness, low global softness, and moderate electrophilicity further confirm the electronically stable nature of the complex. Moreover, the larger HOMO-LUMO energy gap compared with those reported for structurally related imidazole derivatives and their coordination compounds indicates that the synthesized complex has enhanced resistance toward electron-transfer processes.

The QTAIM and RDG analyses provided further insight into the origin of the structural stability of the complex. Topological analysis revealed that the Ag–N coordination bonds exhibit closed-shell interaction characteristics, whereas the Ag $\cdots$ O contacts possess a noticeable partial covalent contribution. In contrast, the C–H $\cdots$ O interactions were found to be predominantly electrostatic in nature. The RDG analysis confirmed that the crystal lattice is primarily stabilized by weak hydrogen bonds together with van der Waals interactions. These findings complement the Hirshfeld surface and MEP analyses, demonstrating that the supramolecular organization of the complex is governed by the synergistic contribution of coordination, electrostatic, and dispersion interactions.

The excellent agreement among the single-crystal X-ray diffraction data, DFT geometry optimization, Hirshfeld surface

analysis, MEP mapping, frontier molecular orbital calculations, and QTAIM/RDG analyses provides a consistent description of the structural and electronic properties of the $[\text{Ag}(\text{imidazole})_2]\text{ClO}_4$ complex. The results demonstrate that the remarkable stability of the complex arises not only from the coordination geometry around the Ag(I) center but also from the favorable electron-density distribution, the large HOMO-LUMO energy separation, and the synergistic interplay of electrostatic, van der Waals, and coordination interactions throughout the crystal lattice. Overall, these findings provide valuable insight into the relationship between molecular structure, electronic characteristics, and supramolecular organization in Ag(I)-imidazole coordination compounds. The integrated experimental and theoretical approach presented herein provides a comprehensive understanding of the structure–property relationships in Ag(I)-imidazole complexes and establishes a reliable foundation for the rational design of new silver(I) coordination compounds with tailored structural and functional properties. Furthermore, the methodology and comprehensive interpretation presented in this study may serve as a useful reference for future experimental and theoretical investigations of structurally related Ag(I) coordination compounds.

Supporting information

CCDC-2563369 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered to.
Sample availability: Samples of the compounds are available from the author.

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