

Article

Two New Zinc(II) Complexes with Symmetric and Asymmetric 2,6-Diacetylpyridine–Aminoguanidine Schiff Bases: Synthesis, Crystal Structures, and Comparative Study

Marijana S. Regojević ¹, Valentina M. Vukobrat ² , Milica G. Bogdanović ¹ , Marko V. Rodić ¹ ,
Ivana Đ. Borišev ¹ , Berta Barta Holló ¹  and Mirjana M. Radanović ^{1,*} 

- ¹ Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 3, 21000 Novi Sad, Serbia; marijana.kostic@dh.uns.ac.rs (M.S.R.); milica.bogdanovic@dh.uns.ac.rs (M.G.B.); marko.rodic@dh.uns.ac.rs (M.V.R.); ivana.borisev@dh.uns.ac.rs (I.Đ.B.); berta.hollo@dh.uns.ac.rs (B.B.H.)
² “Vinča” Institute of Nuclear Sciences-National Institute of the Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, Vinča, 11351 Belgrade, Serbia; valentina.vukobrat@vin.bg.ac.rs
 * Correspondence: mirjana.lalovic@dh.uns.ac.rs

Abstract

Novel compounds based on symmetric and asymmetric 2,6-diacetylpyridine (DAP) Schiff bases were synthesized. A new salt of the symmetric Schiff base 2,6-diacetylpyridine-bis(aminoguanidine), $L^1 \cdot 3HCl \cdot 2H_2O$, and its zinc(II) complex, $[Zn(L^1)(SCN)_2]$ (**1**), were prepared. By template synthesis, the zinc(II) complex with an asymmetric DAP derivative containing aminoguanidine and thiosemicarbazide moieties (L^2), $[Zn(L^2-H)Cl]$ (**2**), was obtained. All compounds were characterized by elemental analysis, FTIR spectroscopy, molar conductivity, thermogravimetric analysis, antioxidant activity measurements, and, for the complexes, SC-XRD. In **1**, the first complex containing the Schiff base of DAP and aminoguanidine, the chelating ligand coordinates as a pentadentate N_5 donor through the pyridine, two azomethine, and two guanidine imino nitrogen atoms. Two SCN^- are coordinated through sulfur atoms, an uncommon coordination mode with zinc(II). In **2**, the ligand acts as an N_3S tetradentate donor involving one azomethine, one hydrazine, the pyridine nitrogen, and thioamide sulfur atom. The chloride anion completes the coordination sphere. Thermal analysis demonstrated stepwise desolvation of the hydrated ligand, whereas the solvent-free complexes underwent continuous thermal decomposition with characteristic gaseous products. The ligand displayed considerable antioxidant activity, which was markedly diminished upon coordination.

Keywords: guanylhydrazones; thiosemicarbazide; ligand symmetry; single-crystal X-ray diffraction; supramolecular interactions; thermogravimetric analysis; antioxidant activity



Academic Editors: Tamara Topala,
Andreea Elena Bodoki and Luminita
Simona Oprean

Received: 31 July 2026

Revised: 20 August 2026

Accepted: 27 August 2026

Published: 2 September 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Schiff bases are organic compounds containing an azomethine group ($>C=N-$), easily synthesized through the condensation of primary amines with carbonyl compounds. Their structural versatility allows for the tuning of electronic and steric properties by modifying substituents on the amine or carbonyl components, leading to diverse coordination modes with metal ions [1].

They have been extensively studied for their catalytic applications, particularly in asymmetric synthesis, where chiral Schiff base–metal complexes have demonstrated significant efficacy [2]. Additionally, Schiff base complexes exhibit notable photophysical

and magnetic properties, including luminescence and single-molecule magnet behavior, making them of interest in materials science [3,4].

Aminoguanidine Schiff bases and their metal complexes exhibit diverse pharmacological activities, including antiviral, antimalarial, and anticancer effects [5]. They also serve as catalysts and superbases in organic synthesis [6]. Notably, zinc(II) complexes with aminoguanidine Schiff bases demonstrate significant photoluminescence, suggesting potential applications in OLED/PLED technologies [7]. Furthermore, aminoguanidine acts as an antioxidant by inhibiting lipid peroxidation and advanced glycation end-products, offering therapeutic potential in managing oxidative stress-related disorders. These properties position aminoguanidine derivatives as promising candidates in both medicinal chemistry and materials science [8].

DAP is a highly suitable precursor for the synthesis of hydrazone-type Schiff bases. Its versatile coordination behavior enables the formation of unusual geometries, particularly metal complexes with high coordination numbers. It is well established that this ligand readily forms bis-Schiff bases. As a diketone, it also retains the ability to form mono-Schiff bases, leading to metal complexes with coordination geometries distinct from those formed by bis-Schiff bases [9]. So far, asymmetrical Schiff bases have demonstrated certain advantages over their symmetrical counterparts, particularly regarding the structure and coordination geometry of metal ions in biological systems, as well as in reactions involving natural and synthetic components [10]. These findings highlight the significance of synthesizing this type of compound and its corresponding metal complexes.

This study reports the synthesis and structural characterization of a new salt of the Schiff base 2,6-diacetylpyridine-bis(aminoguanidine), $L^1 \cdot 3HCl \cdot 2H_2O$, together with two novel zinc(II) complexes: a complex with the symmetric pentadentate Schiff base derived from DAP and aminoguanidine, $[Zn(L^1)(SCN)_2]$ (**1**), representing the first example of direct coordination of this ligand to a metal center rather than the formation of non-coordinated salts [11], and an asymmetric zinc(II) complex containing a Schiff base derived from DAP, aminoguanidine, and thiosemicarbazide, $[Zn(L^2-H)Cl]$ (**2**), exhibiting a different coordination mode. The newly synthesized compounds were characterized by elemental analysis, infrared spectroscopy, molar conductivity measurements, and thermogravimetric analysis, while their antioxidant activities were also evaluated. The molecular structures of complexes **1** and **2** were unambiguously confirmed by single-crystal X-ray diffraction analysis.

2. Results and Discussion

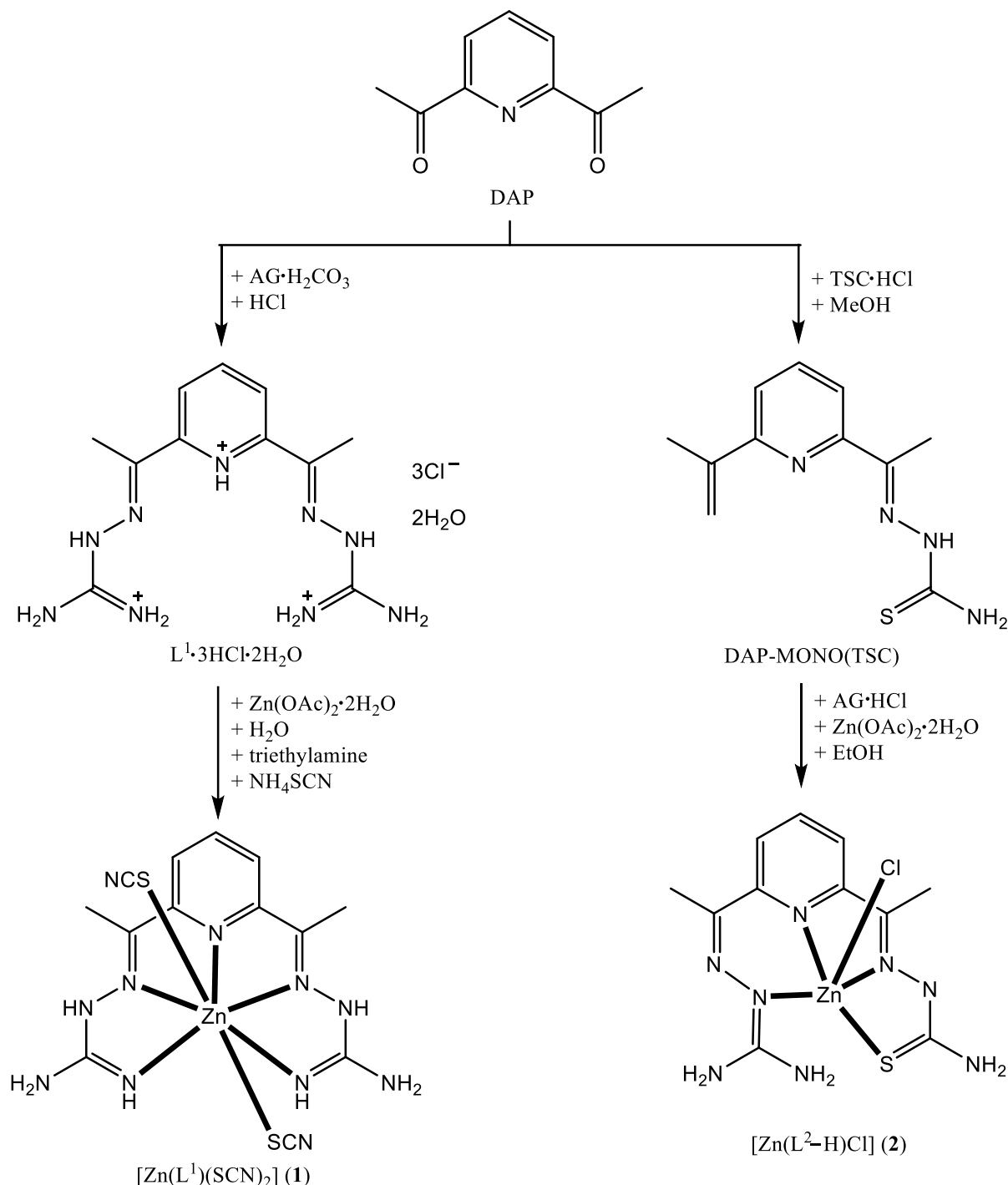
2.1. Compound Syntheses

Synthetic routes for obtaining the ligand $L^1 \cdot 3HCl \cdot 2H_2O$, complex $[Zn(L^1)(SCN)_2]$ (**1**), ligand precursor DAP-MONO(TSC), and complex $[Zn(L^2-H)Cl]$ (**2**) are shown in Scheme 1.

Ligand $L^1 \cdot 3HCl \cdot 2H_2O$ was synthesized by refluxing a reaction mixture of aminoguanidine bicarbonate and DAP in hydrochloric acid solution. Slow evaporation of the resulting solution afforded a pale yellow powder. The results of elemental and thermogravimetric analyses were consistent with the proposed composition of the ligand, the triply protonated Schiff base cation, three chloride anions, and two water molecules.

Direct reactions of this ligand with various metal salts, using different solvent systems, varying the pH, and in the presence of different bases, predominantly resulted in the formation of a white precipitate. Based on IR spectroscopic analysis, this precipitate corresponded to the unreacted ligand. The only successful complexation was achieved in a single reaction carried out in the presence of triethylamine, whereas in all other cases, precipitation remained the dominant process or the isolated products were unsuitable for further characterization. Specifically, the reaction between $Zn(OAc)_2 \cdot 2H_2O$ and $L^1 \cdot 3HCl \cdot 2H_2O$ was performed by briefly refluxing the mixture in water in the presence of triethylamine and

NH_4SCN . Slow evaporation of the resulting yellow solution at room temperature yielded small orange crystals together with a white precipitate of the ligand. The addition of water dissolved the white precipitate, while the orange single crystals of complex $[\text{Zn}(\text{L}^1)(\text{SCN})_2]$ (**1**) were isolated by filtration. The molar conductivity of its DMF solution was consistent with its non-electrolytic nature.



Scheme 1. Synthetic routes for obtaining ligands and complexes.

Yellow single crystals of complex $[\text{Zn}(\text{L}^2\text{-H})\text{Cl}]$ (**2**) containing the asymmetric ligand were obtained by the template reaction of DAP-MONO(TSC), aminoguanidine hydrochloride, and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in a 1:1:1 molar ratio in the presence of EtOH. In this case, the presence of the metal center enabled the condensation reaction between DAP-MONO(TSC)

and aminoguanidine. The obtained crystals were readily soluble in DMF, partially soluble in MeOH and Me₂CO, slightly soluble in MeCN, and insoluble in H₂O and EtOH. The molar conductivity of a DMF solution of **2** was found to be 3 S cm² mol^{−1}, indicating its non-electrolytic nature.

2.2. Crystal and Molecular Structure

To date, only those complex salts in which the Schiff base derived from DAP and aminoguanidine has a role as a counter ion have been obtained in the crystalline state [11]. Complex **1** represents the first structurally characterized coordination compound containing L¹ as a coordinated ligand. The asymmetric unit consists of half of the complex molecule, with Zn1 in a special position on a crystallographic twofold rotation axis passing through the N1 and C3 atoms of the pyridine ring. The remaining part of the complex is generated by the symmetry operation (*i*) 3/2−*x*, *y*, 1−*z*. In this complex, L¹ coordinates to the Zn(II) ion through the pyridine (N1), two azomethine (N2 and N2^{*i*}), and two imino nitrogen atoms (N4 and N4^{*i*}) of the aminoguanidine moieties (Figure 1). The thiocyanate anions act as coligands and are coordinated to the Zn(II) center in a less usual manner, i.e., through the sulfur atoms. The Zn(II) in **1** occupies the central position of a pentagonal bipyramidal coordination environment, formed by the donor atoms of the chelating ligand in the equatorial plane and the sulfur atoms of the thiocyanate ligands in the axial positions (Figure 1). Azomethine N2 (and N2^{*i*}) and N4 (and N4^{*i*}) atoms deviate from the mean plane defined by all five ligating atoms (by ca. 0.12 and 0.17 Å), while the N1 and Zn1 are coplanar.

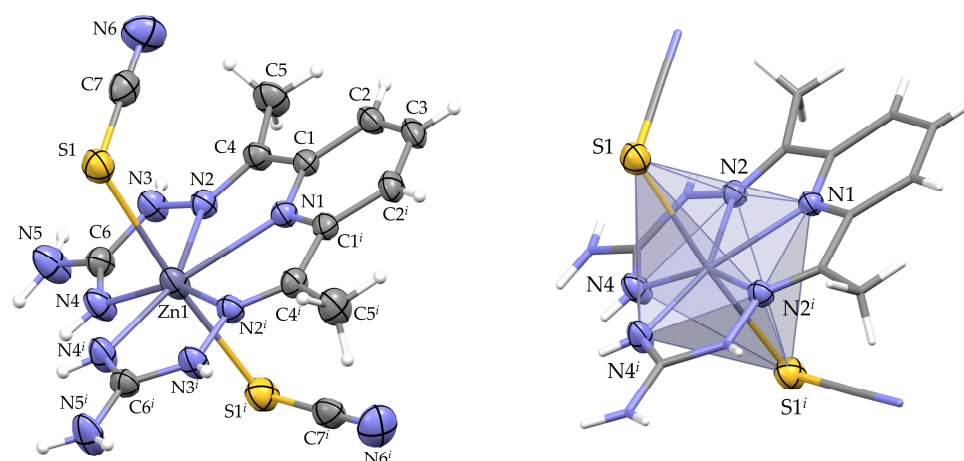


Figure 1. ORTEP representation of the molecular structure of complex **1** showing the atom-labeling scheme (**left**), and the coordination polyhedron of complex **1** (**right**). Thermal ellipsoids are drawn at the 50% probability level; symmetry operation (*i*) 3/2−*x*, *y*, 1−*z*.

A search of the CSD revealed that Zn(II) complexes overwhelmingly exhibit N-coordination of the thiocyanate ligand (nearly 650 reported structures). In contrast, S-coordination, as observed in the present complex **1**, has been reported in only seven structures (refcodes: EBOZUT, JUCIE [12], MAJDUY [13], OCIBAG [14], QUKMAM [15], UPOFAJ [16] and ZIFKOO) [17]. These findings are consistent with Pearson's hard and soft acids and bases (HSAB) theory [18], according to which coordination through the nitrogen atom is generally both thermodynamically and kinetically favored. In the present case, however, this preference is altered by the specific coordination environment created by the chelating ligand. By occupying five coordination sites, the ligand generates a predominantly hard coordination environment around the Zn(II) center, thereby favoring coordination of the softer sulfur donor atoms of the thiocyanate ligands at the remaining two coordination sites. This result is significant as it demonstrates that, due to the pronounced steric effects and rigidity of the ligand structure, coordination of the thiocyanate

ligand occurs through the sulfur atom rather than through the nitrogen atom. Such coordination leaves the nitrogen atoms of the thiocyanate ligands uncoordinated, enabling them to form stronger hydrogen bonds than those with the sulfur atom as acceptor. Thereby, this could further stabilize the crystal structure. In contrast, N-coordination of thiocyanate would limit this possibility, highlighting the important role of steric and structural factors in determining the coordination behavior of thiocyanate ligands.

The molecular structure of complex **2** is shown in Figure 2. The asymmetric Schiff base L^2 coordinates to the Zn(II) through the pyridine nitrogen atom (N1), the hydrazine nitrogen atom (N3) of the aminoguanidine moiety, the azomethine nitrogen atom (N6), and the sulfur atom (S1) of the thiosemicarbazide residue. This coordination mode in **2** results in the formation of one six-membered and two five-membered chelate rings, while the coordination mode observed in **1** affords four five-membered chelate rings. Unlike complex **1**, complex **2** displays a different protonation state of the ligand. The guanidine N4 and N5 nitrogen atoms remain protonated and are not involved in coordination to the Zn(II) center, whereas the N3 donor atom is deprotonated and coordinated to Zn(II), giving rise to a zwitterionic form of the aminoguanidine residue. In addition, deprotonation at the N7 site is consistent with the formulation of the coordinated ligand as L^2-H . The chloride ion acts as a coligand (Figure 2).

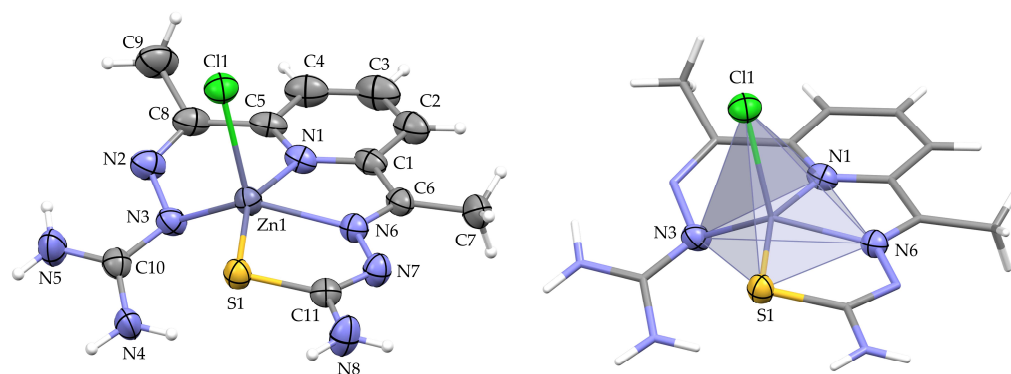


Figure 2. ORTEP representation of the molecular structure of complex **2** (left) and the coordination polyhedron of complex **2** (right). Thermal ellipsoids are drawn at the 50% probability level.

The chelating ligand in complex **2** is not completely planar, which is expected due to steric effects and the spatial arrangement of the ligand around the central metal ion. The donor atoms of the ligand deviate from the planarity significantly more than those in complex **1**. The largest deviations from this least-squares plane are observed for atoms N1 and N2, which are displaced by approximately 0.25 Å.

The coordination geometry of complex **2** was evaluated using the Addison [19] and Holmes [20] methods. The Addison parameter ($\tau_5 = 0.31$) indicates that the coordination environment is better described as a distorted square-pyramid than as a trigonal-bipyramid (Figure 2). The donor atoms of the chelating ligand define the basal plane of the square-pyramidal geometry, while the chloride ion occupies the apical position. The Zn(II) ion is displaced by approximately 0.53 Å from the basal plane toward the apical chloride ligand, further confirming the distorted nature of the coordination environment. However, Holmes analysis places the coordination polyhedron at 51% along the Berry pseudorotation pathway ($D_{3h} \rightarrow C_{2v} \rightarrow C_{4v}$), corresponding to $D_{(SPY-5 \rightarrow TBPY-5)} = 0.49$. This value suggests that the coordination geometry lies approximately midway between the ideal square-pyramidal and trigonal-bipyramidal limits, reflecting the influence of the ligand framework and the associated coordination constraints.

Selected geometrical parameters for **1** and **2** are presented in Table 1. The imine nitrogen atom, N1, is the closest donor atom to the central metal ion, whereas the thiocyanate

sulfur atom exhibits the longest distance from the metal center in **1**. In **2**, the longest M–L bond is Zn1–S1, as expected considering that sulfur acts as a soft base according to Pearson’s HSAB theory [18]. Analysis of the bonds within the aminoguanidine fragment reveals that the azomethine bond length (N2–C4) corresponds to a double bond, unlike the remaining bonds within this fragment, which are shorter than typical single bonds but longer than double bonds. This behavior is consistent with the expected electron delocalization within this part of the ligand [21]. However, in complex **1**, where the amino nitrogen atom is coordinated to the metal center, the electron density remains more localized compared with asymmetric complex **2**, in which such coordination is absent.

Table 1. Selected structural parameters of **1** and **2**.

Bonds	Bond Length, Å		Angles	Angle Values, °	
	1	2		1	2
Zn1–N1	2.317	2.141(2)	N1–Zn1–N4	137.11	/
Zn1–N3	/	2.078(2)	N1–Zn1–N3	/	82.39(8)
Zn1–N2	2.290	/	N1–Zn1–N2	67.00	/
Zn1–N4	2.128	/	N1–Zn1–S1	87.68	154.70(6)
Zn1–N6	/	2.112(2)	N1–Zn1–N6	/	75.15(8)
Zn1–Cl1	/	2.3371(9)	N1–Zn1–Cl1	/	90.59(6)
N1–C5	/	1.338(3)	S1–Zn1–S1 ⁱ	175.37	/
Zn1–S1	2.706	2.4064(7)	C1–N1–C5	/	120.9(2)
N1–C1	1.337	1.342(4)	C1–N1–C1 ⁱ	119.8	/
N2–C8	/	1.293(3)	C4–N2–N3	121.4(2)	/
N6–C6	/	1.296(3)	N2–N3–C6	115.5(2)	/
N6–C7	/	1.384(2)	N3–C6–N5	114.4(2)	/
N2–C4	1.279(3)	/	N3–C6–N4	118.2(2)	/
N3–C10	/	1.344(3)	N4–C6–N5	127.3(3)	/
N7–C11	/	1.318(4)	C8–N2–N3	/	121.1(2)
N4–C10	/	1.322(4)	C6–N6–N7	/	118.3(2)
N2–N3	1.353(3)	1.400(3)	N2–N3–C10	/	108.1(2)
N3–C6	1.366(3)	/	N6–N7–C11	/	112.7(2)
N5–C6	1.342(4)	/	N3–C10–N4	/	122.8(3)
N4–C6	1.285(4)	/	N7–C11–N8	/	115.4(2)
N5–C10	/	1.325(3)	N3–C10–N5	/	118.3(3)
N8–C11	/	1.351(3)	N7–C11–S1	/	128.3(2)
S1–C11	/	1.732(3)	N4–C10–N5	/	119.0(3)
			S1–C11–N8	/	116.3(2)

Symmetry operation: (i) 3/2–x, y, 1–z.

A comparison of the geometrical parameters of the Zn(II) complexes containing symmetric and asymmetric aminoguanidine Schiff bases derived from DAP (Table 1) further reveals more differences reflecting the influence of ligand asymmetry, ligand nature, and coordination mode. The bond between the hydrazine nitrogen atom N3 and the carbon atom C6 to which it is attached is longer in complex **1**, which can be attributed to the absence of its coordination to the metal center. In the asymmetric complex **2**, the hydrazine nitrogen atom N7 is deprotonated and coordinated, resulting in shortening of this bond (N7–C11) due to withdrawal of electron density toward the metal ion. The presence of the thiosemicarbazide moiety on one side of asymmetric complex **2** also influences the structural features of the complex. The softer donor atom from this fragment, sulfur, tends to withdraw electron density from the ligand system. In the symmetric complex **1**, such effects are absent because both ends of the ligand possess the same donor functionality, resulting in a more uniform electron distribution.

Regarding the bond angles (Table 1), particular attention should be given to the C1–N1–C5 angle. In asymmetric complex **2**, the larger value of this angle is most likely a consequence of the uneven electron distribution between different donor groups, leading to a more open angle. In complex **1**, this angle is smaller due to the more uniform electron density distribution in both ligand arms and the resulting more stable geometry. Other variations in bond angles arise from differences in the coordination modes of donor atoms in complexes containing asymmetric and symmetric ligands.

In **1**, the torsion angle N1–C1–C4–N2 ($2.9(3)^\circ$) indicates that the corresponding ligand arm is essentially planar, exhibiting only a slight deviation from coplanarity. On the contrary, in **2**, since the ligand is asymmetric, different torsion angles are expected and reflect the unequal spatial arrangement of the amine precursor residues. The value of $24.1(4)^\circ$ for the corresponding torsion angle N1–C1–C8–N2 indicates a more pronounced deviation of this ligand segment from planarity, resulting from the greater twisting of this arm of the asymmetric ligand. As the azomethine nitrogen atom on this side is not coordinated to Zn(II), this part of the molecule is structurally more flexible, allowing greater torsion and reduced π -conjugation. In contrast, the torsion angle N1–C1–C6–N6 value of $-1.9(4)^\circ$ indicates that the other part of the ligand, where the azomethine nitrogen atom is coordinated, remains essentially planar, preserving efficient π -conjugation and electron delocalization within this segment.

In the crystal structure of **1**, crystal packing is governed by hydrogen bonds involving both nitrogen atoms of the aminoguanidine group, as well as the sulfur and nitrogen atoms of the thiocyanate ligands (Figure 3). Nitrogen atoms of the aminoguanidine group act as hydrogen bond donors, forming N3–H31 $\cdots$ N6 i ($2.27(3)$ Å, 149°) and N5–H51 $\cdots$ N6 i ($2.34(3)$ Å, 151°) hydrogen bonds. As the molecule is located in a special position, the same hydrogen-bonded motif is generated by two-fold symmetry, resulting in the formation of chains of molecules propagating along the crystallographic axis c . Additionally, N5–H52 $\cdots$ S1 i ($2.68(3)$ Å, 159°) hydrogen bonds connect neighboring molecules along the crystallographic axis a . The crystal structure is further stabilized by significant π – π stacking interactions between neighboring pyridine rings (Table S2).

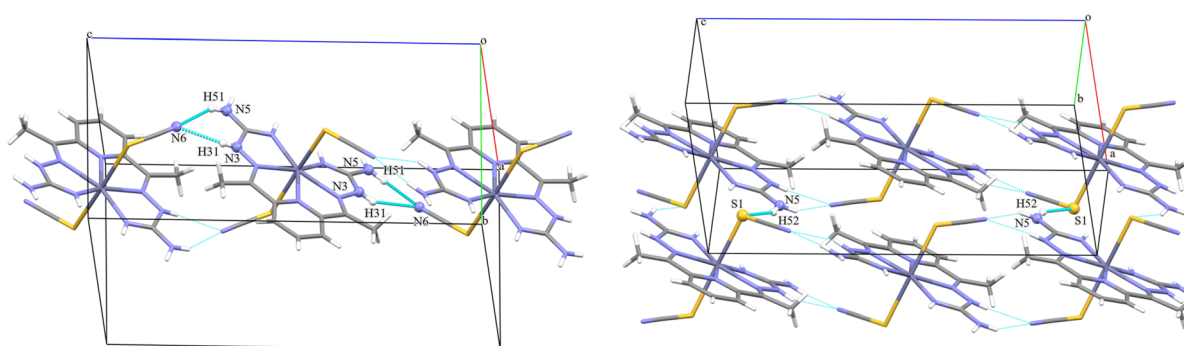


Figure 3. Hydrogen-bonding network in complex **1**.

In the crystal structure of complex **2**, the aminoguanidine moiety participates in the formation of an extensive hydrogen-bonding network that contributes to the structural stability. Two hydrogen bonds, N4 i –H42 i $\cdots$ Cl1 ($2.39(3)$ Å, 162°) and N5 i –H52 i $\cdots$ S1 ($2.71(3)$ Å, 145°), which correspond to the $R^2_2(8)$ graph set motif, connect molecules into chains propagating along crystallographic axis b (Figure 4a). These chains are further connected by N4–H41 $\cdots$ N7 i ($2.28(3)$ Å, 153°) hydrogen bonds into layers parallel to the crystallographic plane ab (Figure 4b). In this motif, each pair of adjacent molecules is linked by two centrosymmetrically related N4–H41 $\cdots$ N7 hydrogen bonds forming a fourteen-membered $R^2_2(14)$ cyclic motif (Figure 4b), incorporating two metal centers from

neighboring molecules. The crystal packing is further stabilized by a moderately strong π - π stacking interaction between two five-membered metallocycles (Zn1-S1-C11-N7-N6) (Table S2) [22].

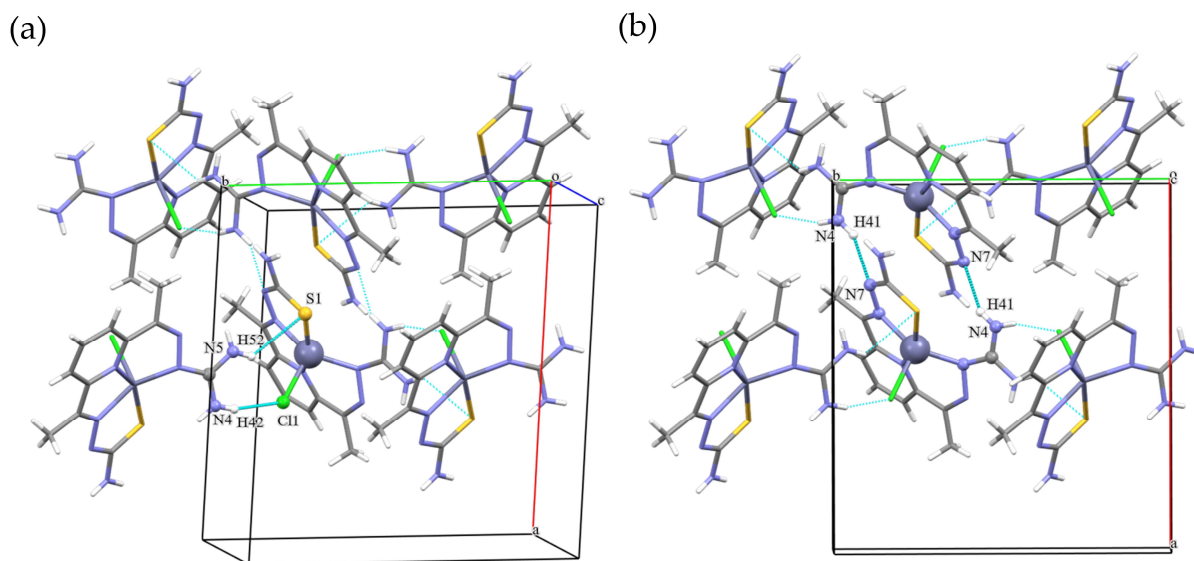


Figure 4. Hydrogen bonding motifs in complex **2** with highlighted graph set motifs, (a) chains propagating along the crystallographic axis *b*, and (b) layer of molecules parallel to the plane *ab*.

The geometrical parameters of the hydrogen bonds present in **2** are summarized in Table S1.

2.3. IR Spectra of $L^1 \cdot 3HCl \cdot 2H_2O$, **1** and **2**

The IR spectrum of ligand $L^1 \cdot 3HCl \cdot 2H_2O$ confirms the successful condensation reaction of the starting diketone (Figures S1 and S2). The absence of the characteristic band corresponding to the C=O group confirms that both carbonyl groups of DAP underwent condensation. The formation of azomethine bonds after condensation was confirmed by the appearance of a band at 1675 cm^{-1} . The broad and intense band at 3295 cm^{-1} indicates the presence of multiple NH groups in the aminoguanidine fragment of $L^1 \cdot 3HCl \cdot 2H_2O$.

The IR spectrum of complex **1** exhibits significant changes compared with the spectrum of the free ligand (Figures S1 and S3). The azomethine $\nu(\text{C}=\text{N})$ band, observed at 1675 cm^{-1} in the ligand spectrum, is shifted to 1644 cm^{-1} in the complex, indicating coordination through the azomethine nitrogen atoms. In addition, the bands in the 1598 – 1566 cm^{-1} region of the ligand spectrum, attributed to pyridine and imino vibrations, exhibit shifts toward lower wavenumbers and changes in intensity upon complex formation, further confirming the involvement of these nitrogen atoms in coordination. The appearance of an intense band at 2068 cm^{-1} in the complex spectrum, absent in the free ligand spectrum, indicates the presence of coordinated thiocyanate ions. Coordination of the pyridine nitrogen atom may also be supported by the weak band in the low-frequency region at approximately 480 cm^{-1} , which can be assigned to $\nu(\text{Zn}-\text{N})$ vibrations.

The IR spectrum of the starting DAP-MONO(TSC) asymmetric L^2 precursor contains bands corresponding to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$, and $\nu(\text{C}=\text{S})$ vibrations, as well as a characteristic band of the pyridine ring (Figure S4). These features confirm the formation of a mono-condensed derivative, as complete conversion of the carbonyl group would result in the disappearance of the $\nu(\text{C}=\text{O})$ band.

In the IR spectrum of DAP-MONO(TSC), the azomethine C=N stretching band appears at 1601 cm^{-1} . In the spectrum of complex **2** (Figure S5), a shift of approximately 26 cm^{-1} toward lower wavenumbers is observed, providing clear evidence for coordination of one azomethine

nitrogen atom. However, an additional band at 1608 cm^{-1} , assigned to the uncoordinated $\text{C}=\text{N}$ group, is also present. Although no pronounced splitting of the bands is observed, this small shift may be attributed to the overlapping contributions of coordinated and free azomethine groups within the same spectral region. Nevertheless, because the vibrations associated with coordination of the azomethine nitrogen atom and the adjacent amino nitrogen atom occur in a similar spectral region and partially overlap, IR analysis alone does not allow reliable discrimination of the coordination site. The final confirmation of the coordination mode was obtained by single-crystal X-ray diffraction analysis.

Bands corresponding to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ vibrations of the pyridine and phenyl rings also appear in the same region or close to it ($1500\text{--}1600\text{ cm}^{-1}$), making confirmation of pyridine nitrogen coordination by IR spectroscopy difficult. However, the shift in the band observed at 637 cm^{-1} in the DAP-MONO(TSC) spectrum toward higher wavenumbers in the spectrum of complex **2** is consistent with coordination of the pyridine nitrogen atom.

Coordination of the sulfur donor atom in **2** is supported by the decrease in intensity and shift toward lower wavenumbers of the band located at 817 cm^{-1} in the DAP-MONO(TSC) spectrum (by approximately 9 cm^{-1}).

2.4. Thermal Properties

The thermal properties of the compounds were analyzed by coupled thermogravimetric-mass spectrometric (TG-MS) measurements in an inert atmosphere. The ligand is obtained as a hydrochloride salt with two lattice water molecules per ligand molecule. In contrast, the two zinc(II) complexes are obtained without a lattice solvent. These differences most significantly affect the thermal properties. Namely, the thermal decomposition pattern of the ligand is complex, with numerous more or less overlapping mass-loss steps, whereas the complexes decompose in only one significant mass-loss step. The ligand's mass decreases from the start of the heating process (Figure 5). Up to about $115\text{ }^{\circ}\text{C}$, 13.2% of mass is lost through at least three overlapping processes, as indicated by the derivative thermogravimetric (DTG) peaks at 47, 62, and $100\text{ }^{\circ}\text{C}$. This mass loss exceeds the water content in the ligand (8.56%), suggesting that HCl evaporates together with water in this temperature range. Mass spectrometric analysis of the evolved gaseous products in this range revealed signals at m/z 17 and 18, which correspond to water evolution (Figure 6). At the very beginning of the process, the m/z 36 fragment, characteristic of HCl evolution, was also observed. In the next step, with two corresponding DTG peaks at 152 and $186\text{ }^{\circ}\text{C}$, the mass loss is 10.5%, somewhat more than that corresponding to one molecule of HCl (8.66%). Besides HCl, water was also detected by MS. The third desolvation step, with a DTG maximum at $252\text{ }^{\circ}\text{C}$, results in a mass loss of 10.1% up to $287\text{ }^{\circ}\text{C}$, and the same fragments were detected as in the previous step. The overall mass loss of 33.8% up to about $290\text{ }^{\circ}\text{C}$, attributed to the release of water and HCl, is close to their calculated total content of 34.56%. The additional TG-MS data suggest that partial loss of HCl may occur upon storage, accompanied by the uptake of additional water. Nevertheless, the general trend is that water is released first, as expected, whereas at higher temperatures, above $130\text{ }^{\circ}\text{C}$, the evaporation of HCl takes place. Above $300\text{ }^{\circ}\text{C}$, the ligand decomposes. Two DTG peaks associated with this decomposition are observed at 344 and $382\text{ }^{\circ}\text{C}$, with a corresponding mass loss of 23.7%. Above $400\text{ }^{\circ}\text{C}$, the decomposition process of the ligand slows down and continues at a steady rate, leading to the formation of a carbonaceous residue. In this range, no stable intermediates are observed, and the decomposition process is not complete up to $600\text{ }^{\circ}\text{C}$. All dehydration, dehydrochlorination, and decomposition processes are accompanied by endothermic heat effects.

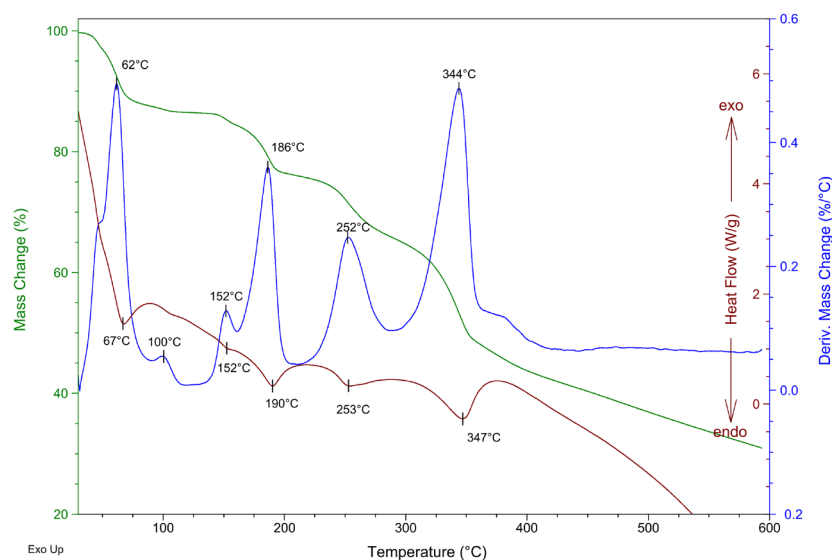


Figure 5. TG (green), DTG (blue), and DSC (brown) curves of $L^1 \cdot 3HCl \cdot 2H_2O$ in argon.

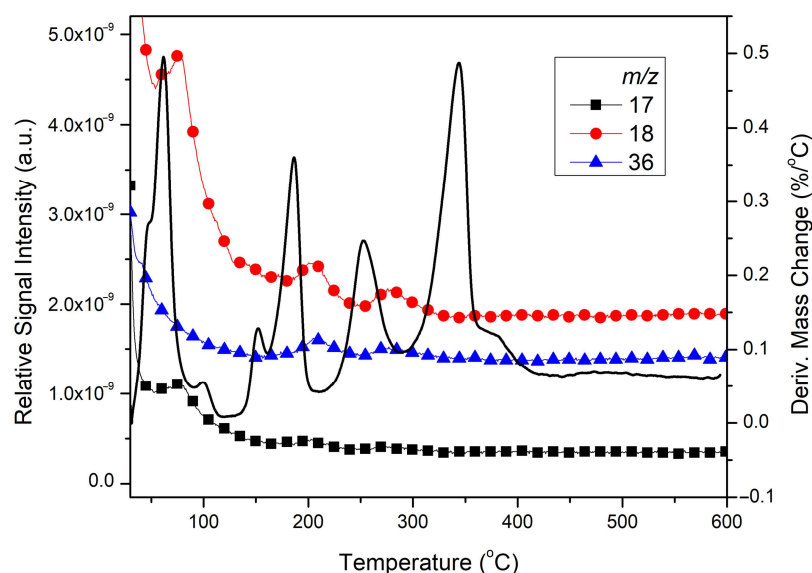


Figure 6. Characteristic fragments of $L^1 \cdot 3HCl \cdot 2H_2O$.

Complex **1** starts to decompose at room temperature at a steady rate, with continual mass loss of about 4.1% up to 237 °C onset. Above this temperature, the course of the TG curve changes, and the mass loss becomes more pronounced, although no well-defined mass-loss step is observed (Figure 7). The mass loss up to 600 °C is 39.6%. Above 600 °C, the mass decrease slows somewhat, but the thermal decomposition is not finished up to 700 °C. On the DTG curve, two overlapping maxima at 262 and 279 °C are detected. The decomposition process is followed by an endothermic peak at 254 °C. The thermal behavior of complex **2** and its TG, DTG, and DSC curves are very similar to that of complex **1** despite the different ligands. The decomposition of **2** also starts at room temperature, with a steady and continuous mass loss of about 1% up to 205 °C. Above this temperature, a small mass-loss step of 1% is detected with a DTG maximum at 236 °C. Above 250 °C, the decomposition of complex **2** becomes more intense and continues up to about 370 °C, with a mass loss of 21.9%. The corresponding DTG peaks are detected at 297 and 330 °C. At higher temperatures, the decomposition slows down and does not complete up to 700 °C. The overall decomposition process is followed by endothermic heat effects, with the only clearly detectable DSC peak appearing at 301 °C.

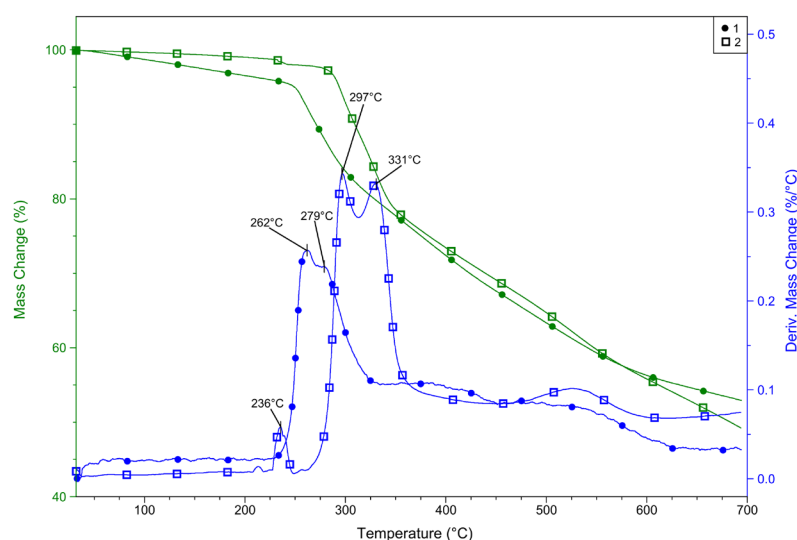


Figure 7. TG (green) and DTG (blue) curves of complexes **1** and **2** in argon.

Due to the low-intensity mass loss of both complexes up to temperatures above 200 °C, the evolved gaseous products were expected to be below the detection limit in this range. With increasing decomposition intensity, gaseous fragments originating from the ligands became detectable. For complex **1**, signals were observed at $m/z = 16$ (NH_2), 17 (NH_3 , OH), 18 (H_2O), 28 (N_2 , CNH_2), and 30 (N_2H_2 , CH_4N), while for complex **2**, signals were detected at $m/z = 16$, 17, 18, 27, 28, 30, and 36. For complex **2**, the signal at $m/z = 36$ indicated the evolution of HCl , consistent with its composition. The signal at $m/z = 27$ could suggest the evolution of HCN . Also, the latter, as well as the remaining signals, could be attributed to gaseous decomposition products of the organic ligands.

2.5. Antioxidative Properties

The free ligand L^1 was found to possess considerable antioxidant capacity (1.66 mg TE/g), a result that fits well with the range of nitrogen-containing functional groups distributed throughout its structure (Figure 8). Two of these in particular, the imine moiety and the aminoguanidine fragment, provide sites through which electron or hydrogen atom transfer to $\text{DPPH}^\bullet$ can occur, and it is this donor character that most plausibly accounts for the ligand's pronounced scavenging behavior.

A markedly different picture emerged once the ligand was coordinated to Zn(II) . Instead of the expected improvement, complex **1** ($[\text{Zn}(\text{L}^1)(\text{SCN})_2]$) displayed a substantial loss of activity (0.41 mg TE/g). The nitrogen atoms that had previously supported radical scavenging in the free ligand are specifically those recruited for metal binding: once the imine nitrogen and the guanidine/aminoguanidine N-H groups are involved in coordination, their lone pairs and dissociable protons are no longer accessible for interaction with the $\text{DPPH}^\bullet$ radical. No compensation can be expected from the Zn(II) center itself, since its d^{10} electronic configuration prevents any redox contribution, and the presence of two thiocyanate co-ligands occupies further coordination positions, reducing still more the number of sites that remain open for radical interaction.

The loss of activity was less pronounced in complex **2** ($[\text{Zn}(\text{L}^2\text{-H})\text{Cl}]$), formed from the asymmetric DAP-aminoguanidine ligand containing a thiosemicarbazide group; its activity was slightly higher than that of complex **1** (0.48 mg TE/g). This difference can likely be attributed to the sulfur atom present in the thiosemicarbazide fragment. Owing to its greater polarizability, sulfur can contribute to the stabilization of radical intermediates, and its presence alongside nitrogen donors introduces an asymmetric electronic environment

quite unlike the uniformly nitrogen-coordinated sphere found in complex **1**, a distinction that could plausibly account for the modest increase in reactivity (Figure 8).

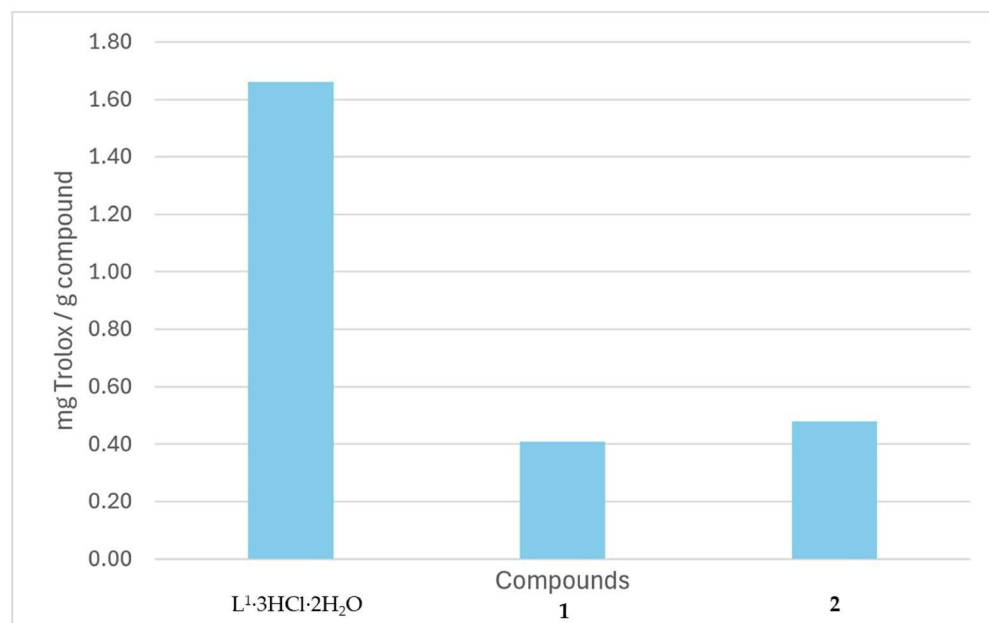


Figure 8. Antioxidant activity for L^1 , **1** and **2**.

3. Materials and Methods

Aminoguanidine hydrogen carbonate, aminoguanidine hydrochloride, 2,6-diacetylpyridine, thiosemicarbazide hydrochloride, and hydrochloric acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ammonium thiocyanate was obtained from Fluka (Buchs, Switzerland), triethylamine from Merck (Darmstadt, Germany), and diethyl ether from Lach-Ner (Neratovice, Czech Republic). All reagents were of analytical grade and used without further purification, except for the precursor for the synthesis of the asymmetric DAP derivative, DAP-MONO(TSC), prepared according to the previously reported procedure [23], described below.

3.1. Synthesis of $L^1 \cdot 3HCl \cdot 2H_2O$

Aminoguanidine hydrogen carbonate (0.136 g, 1 mmol) was dissolved in 10 cm³ of HCl (0.2 mol dm^{−3}), and DAP (0.080 g, 0.5 mmol) was added to the resulting solution. The reaction mixture was refluxed for 1 h and then transferred to an evaporating dish. After standing for five days at room temperature, the pale yellow precipitate was collected by filtration and dried in air. Yield: 0.038 g (48.72%). Anal. Calc. C₁₁H₂₄N₉O₂Cl₃ (420.72): C, 31.40; H, 5.75; N, 30.14. Found: C, 31.58; H, 5.93; N, 30.08.

3.2. Synthesis of 2,6-Diacetylpyridine-Mono(thiosemicarbazone), DAP-MONO(TSC) [23]

DAP (0.815 g, 5 mmol) was dissolved in 25 cm³ of methanol at room temperature. This solution was added dropwise over 3 h, with continuous stirring at room temperature, to a solution of thiosemicarbazide hydrochloride (0.650 g, 5 mmol) in 25 cm³ of methanol. The resulting yellow precipitate was collected by filtration and washed with diethyl ether. Yield: 0.72 g (60.76%).

3.3. Synthesis of $[Zn(L^1)(SCN)_2]$ (**1**)

A mixture of Zn(OAc)₂·2H₂O (0.022 g, 0.1 mmol) and $L^1 \cdot 3HCl \cdot 2H_2O$ (0.042 g, 0.1 mmol) was suspended in 4 cm³ of water, and triethylamine (5 drops) was added. The reaction mixture was refluxed for 15 min, after which NH₄SCN (0.050 g, 0.66 mmol)

was added. After three days, small orange crystals were isolated from the yellow solution by filtration and washed with methanol. Yield: 0.027 g (58.70%). Molar conductivity (Λ_M , DMF): 21 S cm² mol^{−1}. Anal. Calc. C₁₃H₁₇N₁₁S₂Zn (456.86): C, 34.18; H, 3.75; N, 33.73; S, 14.04. Found: C, 34.76; H, 3.92; N, 33.83; S, 14.19.

3.4. Synthesis of [Zn(L²-H)Cl] (2)

A mixture of Zn(OAc)₂·2H₂O (0.022 g, 0.1 mmol), DAP-MONO(TSC) (0.023 g, 0.1 mmol), and aminoguanidine hydrochloride (0.011 g, 0.1 mmol) was suspended in 15 cm³ of ethanol and heated for several minutes until complete dissolution. After five days, yellow single crystals were isolated from the yellow solution by filtration and washed with ethanol. Yield: 0.029 g (74.17%). Molar conductivity (Λ_M , DMF): 3 S cm² mol^{−1}. Anal. Calc. C₁₁H₁₆N₈SClZn (393.20): C, 35.44; H, 3.52; N, 26.30; S, 17.20. Found: C, 35.72; H, 3.44; N, 26.51; S, 17.33.

3.5. Analytical Techniques

Elemental analyses (C, H, N, and S) of the air-dried complexes were performed using a Thermo Scientific FlashSmart CHNS analyzer (Thermo Fisher Scientific, Waltham, MA, USA). IR spectra were recorded in the 4000–400 cm^{−1} region using a Thermo Nicolet iS20 FTIR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a Smart iTRTM ATR sampling accessory. Molar conductivities of freshly prepared complex solutions ($c = 1 \times 10^{-3}$ mol dm^{−3}) were determined using a Jenway 4510 conductivity meter (Cole-Parmer, Stone, Staffordshire, UK). The thermal decomposition of L¹·3HCl·2H₂O and complexes **1** and **2** was investigated using a simultaneous thermogravimetric-differential scanning calorimetric analyzer (SDT Q600, TA Instruments, New Castle, DE, USA). Samples of 1–3 mg were heated from room temperature to 700 °C at 10 °C min^{−1} under argon or air flowing at 50 mL min^{−1}. The sample pan was an alumina crucible, and an empty alumina crucible was used as the reference pan. Online coupled thermogravimetric–mass spectrometric analysis (TG-MS) was carried out on a simultaneous thermal analyzer (SDT Q600, TA Instruments, New Castle, DE, USA) coupled with a mass spectrometer (Hidden Analytical HPR20/QIC, Hidden Analytical Ltd., Warrington, UK) under the above-listed experimental conditions. Selected ions between $m/z = 1$ –135 were monitored in multiple ion detection mode (MID).

3.6. Crystal Structure Determination

All measurements were performed at room temperature. Instrument control and data reduction were accomplished using CrysAlis PRO 1.171.41.93a [24]. Crystal structures were solved with the iterative dual-space algorithm implemented in SHELXT [25] and refined using SHELXL [26]. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions and refined according to the riding model. The final crystal structures were subjected to internal validation using PLATON (version 120923) [27], while external validation was performed against the Cambridge Structural Database (CSD) [28] employing the MOGUL [29] knowledge base available within Mercury CSD [30]. Pertinent crystallographic data are given in Table S3. The crystallographic data presented in this study have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 2575418 and 2575419. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures> (accessed on 30 July 2026).

3.7. Determination of DPPH• Radical Neutralization Capability

The antioxidant activity of the synthesized compounds was evaluated by determining their DPPH• radical scavenging capacity using a slightly modified procedure described by

Soler-Rivas et al. [31]. This method is based on the spectrophotometric monitoring of the reduction of the stable nitrogen-centered radical DPPH• (2,2-diphenyl-1-picrylhydrazyl), which changes from its violet-colored radical form to the yellow-colored reduced form (DPPH-H). The DPPH• solution in methanol exhibits a characteristic absorption maximum at 515 nm. In the presence of electron- or hydrogen-donating compounds, the DPPH radicals are neutralized, resulting in a decrease in absorbance accompanied by the loss of the purple color.

The synthesized compounds were dissolved in a 5% (*v/v*) DMF/methanol solution, and a series of concentrations (10–40 mg mL^{−1}) was prepared. The assay was performed in 96-well microplates by mixing 50 µL of sample solution with 160 µL of DPPH solution and 90 µL of methanol to obtain a final volume of 300 µL. The DPPH solution was initially prepared as a 0.4 mmol L^{−1} solution in 96% ethanol and subsequently diluted fourfold with methanol to achieve an absorbance of 0.9 at 515 nm. Blank samples (solvent replacing the tested sample) and matrix blanks (sample and solvent without DPPH solution) were analyzed in parallel.

Trolox standard solutions (1–100 mg mL^{−1}) were prepared simultaneously for construction of the calibration curve. The same volumes of DPPH solution and methanol were added to the Trolox standards as to the tested samples. Absorbance was recorded at 515 nm after 60 min of incubation. Antioxidant activity was expressed as milligrams of Trolox equivalents per gram of dry sample weight (mg TE g^{−1} dsw).

4. Conclusions

Novel salt of symmetric Schiff base 2,6-diacetylpyridine-bis(aminoguanidine)—L¹·3HCl·2H₂O, its first complex [Zn(L¹)(SCN)₂] (1) and novel complex with asymmetric ligand 2,6-diacetylpyridine-mono(thiosemicarbazone)-mono(aminoguanidine) L²—[Zn(L²—H)Cl] (2) were successfully synthesized and comprehensively characterized. Structural investigations demonstrated that the coordination behavior of the ligands is strongly influenced by their symmetry and donor set, resulting in distinct coordination geometries.

The ligand L¹ acts as a pentadentate N₅ donor, while two thiocyanate ligands complete the coordination sphere through sulfur atoms. The observed S-coordination of thiocyanate is uncommon for Zn(II) complexes and can be attributed to the specific coordination environment imposed by the chelating ligand. The asymmetric ligand L² adopts an N₃S coordination mode in 2. The asymmetric donor set influences both the molecular geometry and the electronic structure of the complex, leading to differences in bond lengths, bond angles, and torsion angles compared with the symmetric analog.

Thermal analysis showed that the novel ligand salt, crystallizing as a hydrate hydrochloride, undergoes an initial desolvation/dehydrochlorination process, whereas the solvent-free Zn(II) complexes decompose continuously without well-defined intermediate stages, confirming the proposed decomposition mechanisms. Antioxidant studies revealed that the activity is governed primarily by the ligand L¹·3HCl·2H₂O structure rather than the redox-inactive Zn(II) center, with the asymmetric complex exhibiting slightly higher radical-scavenging activity than the symmetric analog. Overall, these findings demonstrate that ligand design, particularly its symmetry and donor atom arrangement, governs coordination behavior, thermal properties, and functional performance, providing valuable guidelines for the rational design of new Schiff base coordination compounds.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/inorganics14090232/s1>, Table S1: Hydrogen bonding geometry parameters for complexes 1 and 2; Table S2. Selected geometric parameters of π – π stacking interactions in 1 and 2; Table S3. Crystallographic and refinement details; Figure S1. FTIR spectrum of DAP;

Figure S2. FTIR spectrum of $L^1 \cdot 3HCl \cdot 2H_2O$; Figure S3. FTIR spectrum of **1**; Figure S4. FTIR spectrum of DAP-MONO(TSC); Figure S5. FTIR spectrum of **2**.

Author Contributions: Conceptualization, M.S.R. and M.M.R.; methodology, M.S.R., B.B.H. and M.M.R.; investigation, M.S.R., M.G.B., I.Đ.B., V.M.V. and B.B.H.; resources, M.M.R.; writing—original draft preparation, M.S.R., and M.M.R.; writing—review and editing, M.V.R., M.M.R. and B.B.H.; visualization, M.S.R., M.G.B., B.B.H. and I.Đ.B.; supervision, M.V.R., M.M.R. and B.B.H.; funding acquisition, B.B.H. and M.M.R. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the financial support of the Provincial Secretariat for Higher Education and Scientific Research (Grant No. 003864137 2025 09418 003 000 000 001 04 004) and Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grants No. 451-03-33/2026-03/200125 & 451-03-34/2026-03/200125).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

DAP	Diacetylpyridine
DAP-MONO(TSC)	Diacetylpyridine-monothiosemicarbazone
AG·H ₂ CO ₃	Aminoguanidine bicarbonate
AG·HCl	Aminoguanidine hydrochloride
DTG	Derivative thermogravimetry
OLED/PLED	Organic light-emitting diode/polymer light-emitting diode
TG-MS	Thermogravimetric–mass spectrometry
SC-XRD	Single-crystal X-ray diffraction

References

1. Kumar, M.; Pailvi, Tuli, H.; Khare, R. Synthesis, Characterization and Biological Studies of Novel Schiff Base viz. Bis-1,1'-(pyridine-2,6-diyl-dieth-1-yl-1-ylidene) biguanidine and Their Transition Metal Complexes. *Asian J. Chem.* **2019**, *31*, 799–804. [\[CrossRef\]](#)
2. Zhang, W.; Loebach, J.L.; Wilson, S.R.; Jacobsen, E.N. Enantioselective Epoxidation of Unfunctionalized Olefins Catalyzed by Salen Manganese Complexes. *J. Am. Chem. Soc.* **1990**, *112*, 2801–2803. [\[CrossRef\]](#)
3. Borisov, S.M.; Pommer, R.; Svec, J.; Peters, S.; Novakova, V.; Klimant, I. New Red-Emitting Schiff Base Chelates: Promising Dyes for Sensing and Imaging of Temperature and Oxygen via Phosphorescence Decay Time. *J. Mater. Chem. C Mater.* **2018**, *6*, 8999–9009. [\[CrossRef\]](#)
4. Miyasaka, H.; Clérac, R.; Wernsdorfer, W.; Lecren, L.; Bonhomme, C.; Sugiura, K.; Yamashita, M. A Dimeric Manganese(III) Tetradentate Schiff Base Complex as a Single-Molecule Magnet. *Angew. Chem. Int. Ed.* **2004**, *43*, 2801–2805. [\[CrossRef\]](#)
5. Chourasiya, S.S.; Kathuria, D.; Nikam, S.S.; Ramakrishnan, A.; Khullar, S.; Mandal, S.K.; Chakraborti, A.K.; Bharatam, P.V. Azine-Hydrazone Tautomerism of Guanylhyazones: Evidence for the Preference Toward the Azine Tautomer. *J. Org. Chem.* **2016**, *81*, 7574–7583. [\[CrossRef\]](#)
6. Buvaylo, E.A.; Kokozay, V.N.; Vassilyeva, O.Y.; Skelton, B.W.; Nesterova, O.V.; Pombeiro, A.J.L. Copper(II) Complex of the 2-Pyridinecarbaldehyde Aminoguanidine Schiff Base: Crystal Structure and Catalytic Behaviour in Mild Oxidation of Alkanes. *Inorg. Chem. Commun.* **2017**, *78*, 85–90. [\[CrossRef\]](#)

7. Radanović, M.M.; Vojinović-Ješić, L.S.; Jelić, M.G.; Sakellis, E.; Barta Holló, B.; Leovac, V.M.; Rodić, M.V. Synthesis, Structures, and Photoluminescence of Two Novel Zinc(II) Compounds Containing 2-Acetylpyridine-Aminoguanidine. *Inorganics* **2022**, *10*, 147. [\[CrossRef\]](#)
8. Chakraborty, M.; Mohanty, M.; Dinda, R.; Sengupta, S.; Kumar Chattopadhyay, S. Cu(II) Complexes of a Bio-Compatible Aminoguanidine Schiff Base: Histidine Sensing and DNA-Binding Studies. *Polyhedron* **2022**, *211*, 115554. [\[CrossRef\]](#)
9. Naskar, S.; Mishra, D.; Kumar Chattopadhyay, S.; Corbella, M.; Blake, A.J. Versatility of 2,6-Diacetylpyridine (Dap) Hydrazones in Stabilizing Uncommon Coordination Geometries of Mn(II): Synthesis, Spectroscopic, Magnetic and Structural Characterization. *Dalton Trans.* **2005**, *34*, 2428–2435. [\[CrossRef\]](#)
10. Ejidike, I.P.; Ajibade, P.A. Transition Metal Complexes of Symmetrical and Asymmetrical Schiff Bases as Antibacterial, Antifungal, Antioxidant, and Anticancer Agents: Progress and Prospects. *Rev. Inorg. Chem.* **2015**, *35*, 191–224. [\[CrossRef\]](#)
11. Valdés-Martínez, J.; Alstrum-Acevedo, J.H.; Toscano, R.A.; Hernández-Ortega, S.; Espinosa-Pérez, G.; West, D.X.; Helfrich, B. Tetrachlorocuprate(II) Salts of Heterocyclic Aminoguanidonium (Guanylhyaazonium) Ions. *Polyhedron* **2002**, *21*, 409–416. [\[CrossRef\]](#)
12. Zhang, H.; Jiang, X.; Zhang, Y.; Duanmu, K.; Wu, C.; Lin, Z.; Xu, J.; Yang, J.; Huang, Z.; Humphrey, M.G.; et al. Toward Strong UV–Vis–NIR Second-Harmonic Generation by Dimensionality Engineering of Zinc Thiocyanates. *J. Am. Chem. Soc.* **2024**, *146*, 28329–28338. [\[CrossRef\]](#)
13. Pramanik, A.; Das, G. Aryl Azo Imidazole Assisted Self-Assembly of D10 Metal Complexes: Influence of Halogen Substitution and Counter Ions. *Polyhedron* **2010**, *29*, 2999–3007. [\[CrossRef\]](#)
14. Chen, Q.; Bi, Y.; Chen, J. Pseudohalide-Directed Assembly of Two Zinc(II) Coordination Polymers with a 3,4-Bis(3-Pyridyl)-5-(4-Pyridyl)-1,2,4-Triazole Tecton. *Z. Anorg. Allg. Chem.* **2016**, *642*, 1445–1449. [\[CrossRef\]](#)
15. Saha (Halder), S.; Sen, C.; Roy, S.; Mallick, D.; López-Torres, E.; Sinha, C. Structure and Photochromism of Zn(II) Thiocyanato Complexes of 1-Alkyl-2-((o-Thioalkyl)Phenylazo)imidazole. *Polyhedron* **2015**, *97*, 240–247. [\[CrossRef\]](#)
16. Moon, D.; Choi, J.-H. Synthesis, Crystal Structure, Infrared Spectroscopy and Hirshfeld Surface Analysis of *Cis*-(Thiocyanato-KN)(1,4,8,11-Tetraazacyclotetradecane-KN⁴)Chromium(III)(μ -1,3-Thiocyanato-KN,*S*)Trichloridozincate. *J. Coord. Chem.* **2021**, *74*, 969–982. [\[CrossRef\]](#)
17. Mori, H.; Tanaka, S.; Mori, T.; Maruyama, Y. Crystal Structures and Electrical Resistivities of Three-Component Organic Conductors: (BEDT-TTF)2MM'(SCN)4 [M = K, Rb, Cs; M' = Co, Zn, Cd]. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1136–1144. [\[CrossRef\]](#)
18. Pearson, R.G. Hard and Soft Acids and Bases. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539. [\[CrossRef\]](#)
19. Addison, A.W.; Rao, T.N.; Reedijk, J.; van Rijn, J.; Verschoor, G.C. Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds Containing Nitrogen–Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-Bis(N-Methylbenzimidazol-2'-yl)-2,6-Dithiaheptane]Copper(II) Perchlorate. *J. Chem. Soc. Dalton Trans.* **1984**, *13*, 1349–1356. [\[CrossRef\]](#)
20. Holmes, R.R. Five-Coordinated Structures. In *Progress in Inorganic Chemistry*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1984; pp. 119–235.
21. Lalovic, M.; Leovac, V.; Vojinovic-Jesic, L.; Rodic, M.; Jovanovic, L.; Cesljevic, V. Dioxidovanadium(V) Complexes with Pyridoxalaminoguanidine: Synthesis, Spectral and Structural Characterization. *J. Serbian Chem. Soc.* **2013**, *78*, 1161–1170. [\[CrossRef\]](#)
22. Malenov, D.P.; Janjić, G.V.; Medaković, V.B.; Hall, M.B.; Zarić, S.D. Noncovalent Bonding: Stacking Interactions of Chelate Rings of Transition Metal Complexes. *Coord. Chem. Rev.* **2017**, *345*, 318–341. [\[CrossRef\]](#)
23. Martinez-Martinez, M.P.; Garcia-Vargas, M.; Muñoz-Leyva, J.A. Thiosemicarbazones Derived from 2,6-Diacetylpyridine as Tri- and Pentadentate Ligands of Heavy Metal Ions. *Spectrochim. Acta A* **1986**, *42*, 701–704. [\[CrossRef\]](#)
24. Rigaku Oxford. *Diffraction CrysAlisPro Software System*; Rigaku Corporation: Wroclaw, Poland, 2019.
25. Sheldrick, G.M. SHELXT—Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. A Found. Adv.* **2015**, *71*, 3–8. [\[CrossRef\]](#)
26. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. C Struct. Chem.* **2015**, *71*, 3–8. [\[CrossRef\]](#)
27. Spek, A.L. Structure Validation in Chemical Crystallography. *Acta Crystallogr. D Biol. Crystallogr.* **2009**, *65*, 148–155. [\[CrossRef\]](#)
28. Groom, C.R.; Bruno, I.J.; Lightfoot, M.P.; Ward, S.C. The Cambridge Structural Database. *Acta Crystallogr. B Struct. Sci. Cryst. Eng. Mater.* **2016**, *72*, 171–179. [\[CrossRef\]](#)
29. Bruno, I.J.; Cole, J.C.; Kessler, M.; Luo, J.; Motherwell, W.D.S.; Purkis, L.H.; Smith, B.R.; Taylor, R.; Cooper, R.I.; Harris, S.E.; et al. Retrieval of Crystallographically-Derived Molecular Geometry Information. *J. Chem. Inf. Comput. Sci.* **2004**, *44*, 2133–2144. [\[CrossRef\]](#)

30. Macrae, C.F.; Sovago, I.; Cottrell, S.J.; Galek, P.T.A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G.P.; Stevens, J.S.; Towler, M.; et al. *Mercury 4.0: From Visualization to Analysis, Design and Prediction*. *J. Appl. Crystallogr.* **2020**, *53*, 226–235. [[CrossRef](#)]
31. Soler-Rivas, C.; Espín, J.C.; Wichers, H.J. An Easy and Fast Test to Compare Total Free Radical Scavenger Capacity of Foodstuffs. *Phytochem. Anal.* **2000**, *11*, 330–338. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.