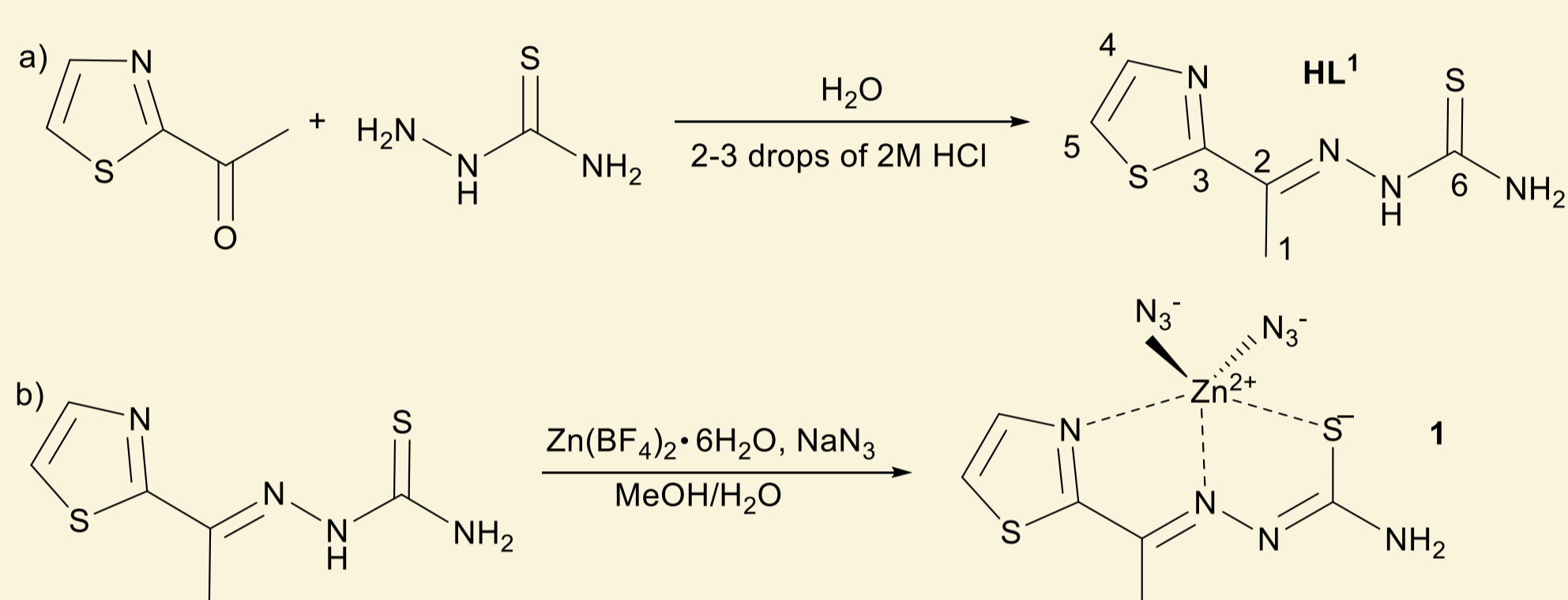# Synthesis of a New Family of Zn(II) Hydrazone Complexes: Characterisation, Catalytic Activity, and DFT Calculations

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The ligand (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide (**HL¹**) was obtained from the condensation of 2-acetylthiazole and thiosemicarbazide (Scheme 1a). Upon reacting **HL¹** with $Zn(BF_4)_2 \cdot 6H_2O$ and $NaN_3$ in a solvent mixture of water/methanol, mononuclear Zn(II) complex **1** with the composition $[ZnL^1(N_3)_2]$ was obtained (Scheme 1b). In complex **1**, Zn(II) is pentacoordinated with the thiazole nitrogen, the azomethine nitrogen, and thiolate sulfur atoms from the deprotonated hydrazone ligand, as well as with two azido ligands.
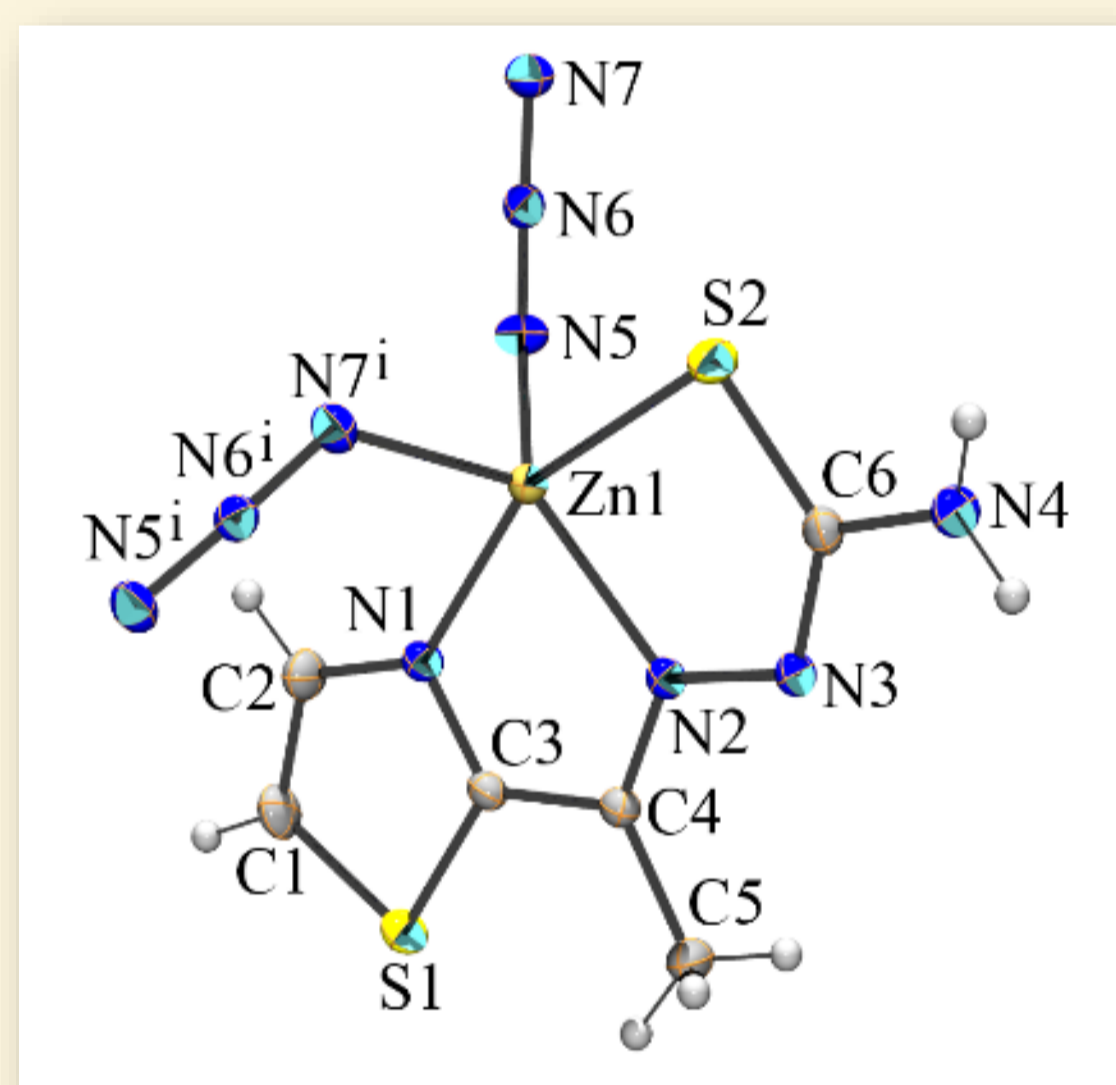
The hydrazone ligand (*E*)-1-(2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethyl)-pyridine-1-ium chloride (**HL²Cl**) was obtained from the condensation reaction of 2-acetylpyridine and Girard's P reagent (Scheme 2a). Reaction of **HL²**Cl with $Zn(BF_4)_2 \cdot 6H_2O$ and $NaN_3$, in a mixture of acetonitrile/water/methanol, gives mononuclear Zn(II) complex **2** with the composition $[ZnL^2(N_3)_2]$ (Scheme 2b). In complex **2**, the ligand is coordinated in its deprotonated, formally neutral, zwitterionic form to Zn(II) ion through the pyridine nitrogen, the imine nitrogen, and the carbonyl oxygen atoms, forming a pentacoordinated complex.



**Scheme 1.** a) Synthesis of **HL¹** ligand and b) $[ZnL^1(N_3)_2]$ complex (**1**).
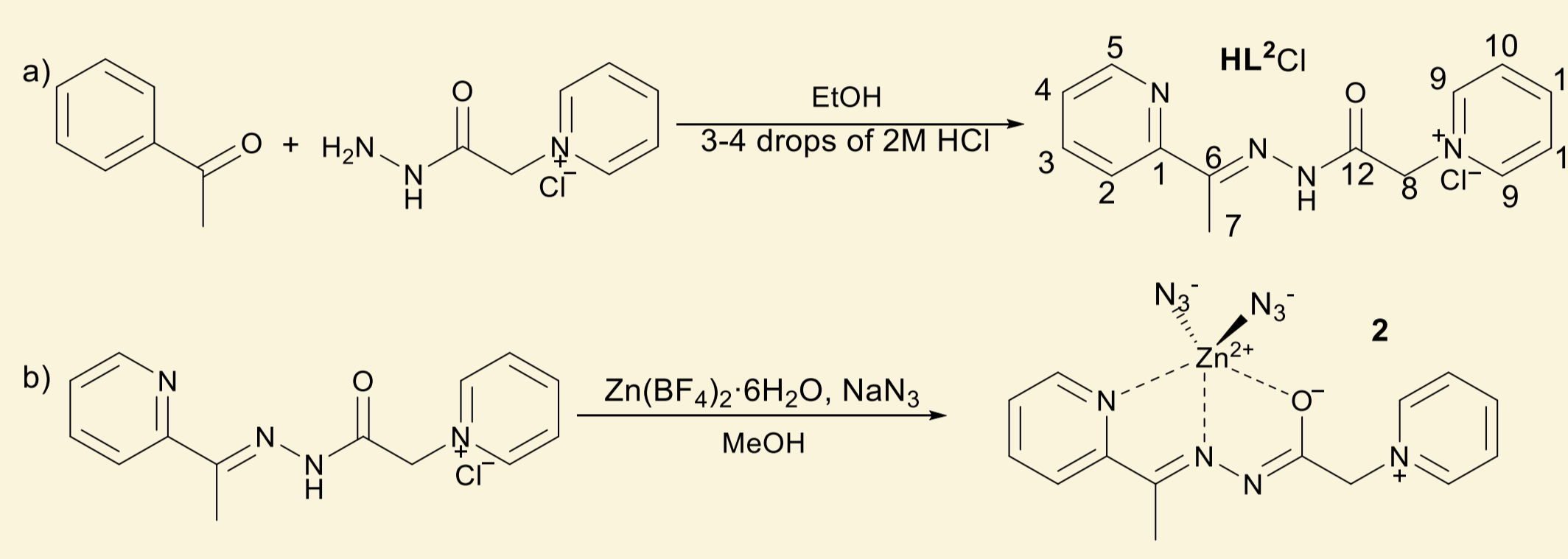


**Scheme 2.** a) Synthesis of the **HL²**Cl ligand and b) $[ZnL^2(N_3)_2]$ complex (**2**).



**Fig. 1.** Coordination environment of Zn(II) in complex 3. Thermal ellipsoids are drawn at the 30% probability level.

Complex **1** crystallises in the monoclinic crystal system with space group No.14 ($P2_1/c$ cell setting). The unit cell of **1** contains four $[ZnL^1(N_3)]$ asymmetric units. In complex **1**, the Zn(II) site shows a distorted geometry, almost midway between the square pyramid and trigonal bipyramid, established on the basis of a calculated $\tau_5$ parameter of 0.46. The coordination environment of Zn(II) ion in **1** is depicted in Fig. 1.
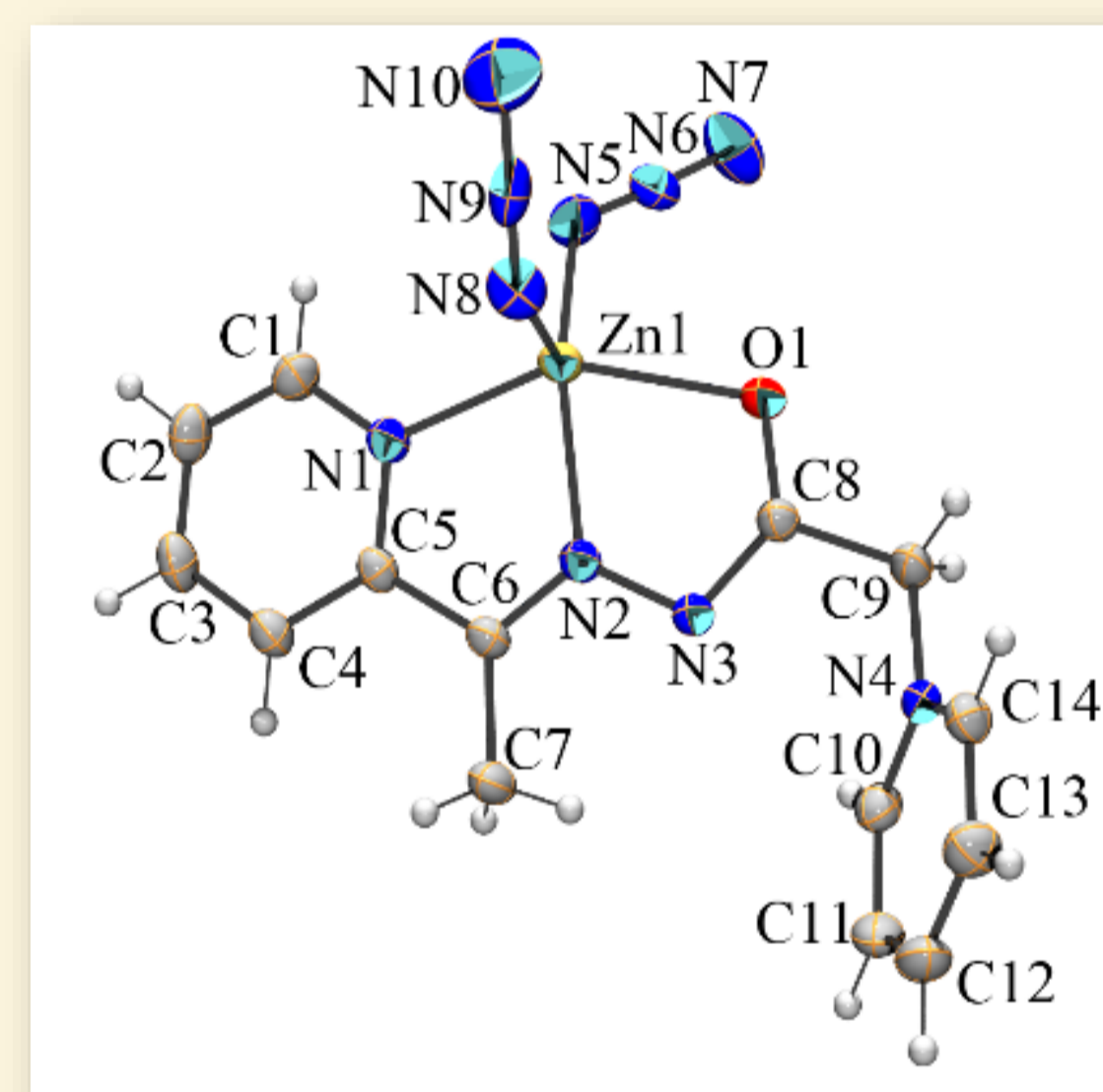


**Fig. 2.** ORTEP[52] representation of the $[ZnL^2(N_3)_2]$ (**2**) complex. Thermal ellipsoids are drawn at the 30% probability level.

The molecular structure of $[ZnL^2(N_3)_2]$ with the atom numbering scheme is shown in Fig. 2. In complex **2**, the Zn(II) ion has fivefold coordination with NNO-set of donor atoms of $L^2$ and two nitrogen atoms (N5 and N8) from the azido ligands. The calculated $\tau_5$ value of 0.08 for $[ZnL^2(N_3)_2]$ indicates that the five-coordination geometry of the Zn(II) ion is slightly distorted square pyramidal.

## Conclusions

Upon reacting (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide (**HL¹**) with $Zn(BF_4)_2 \cdot 6H_2O$ and $NaN_3$, complex **1** with the composition $[ZnL^1(N_3)_2]$ was obtained. The geometry around Zn(II) is distorted, between the square pyramid and trigonal bipyramid. The azide anions bridge Zn(II) ions in a $\mu_{1,3}$ fashion, so as to generate zigzag polymeric chains. The reaction of (*E*)-1-(2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl) ethyl)pyridin-1-ium chloride (**HL²**Cl) with $Zn(BF_4)_2 \cdot 6H_2O$ and $NaN_3$ provides Zn(II) complex **2** with composition $[ZnL^2(N_3)_2]$. The five-coordination geometry of the Zn(II) ion is distorted square pyramidal. In both **1** and **2**, the tridentate ligand is coordinated in its deprotonated form to the Zn(II) ion.

Evaluation of the catalytic properties of the Zn(II) complexes in the KA² reaction shows that the most active compound, when used as a catalyst, is complex **2**. It leads to a 92% isolated yield of the desired propargylamine product. The catalytic activity results are in full agreement with the findings of the DFT calculations. Complex **2** shows the highest value of molecular softness and the lowest value of molecular hardness. The correlation, between experimental and theoretical results, is excellently visualised in the linear relationship between the isolated yield of the desired propargylamine product and the calculated molecular softness, *S*.