Article

**Supplementary Material**

Synthesis, characterization, catalytic activity, and DFT calculations of Zn(II) hydrazone complexes

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**Table S1**. Structural parameters correlating the geometry of five-coordinate [Zn**L**X2] complexes (**L** = tridentate hydrazone-based ligand; X= pseudohalde, halide or DMSO).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Complex** | *β* (°) | *α* (°) | *τ*1 | *ρ*2 (Å) | References |
| [Zn**L1**(NCS)2]⋅2H2O (**1**) | 149.20(7) | 127.42(10) | 0.36 | 0.6091(3) | This work |
| [Zn**L3**(NCS)2]⋅0.5MeOH3 (**3**) | 147.9(2) | 128.4(3) | 0.32 | 0.6022(11) | [1] |
| [Zn**L4**(N3)2]4 (**4**) | 147.68(10) | 129.4(2) | 0.31 | 0.6165(5) | [2] |
| [Zn**L4**(NCO)2]4 (**5**) | 146.98(8) | 126.41(10) | 0.34 | 0.6462(4) | [2] |
| [Zn**L4**(N3)1.65Cl0.35]4 (**6**) | 148.40(6) | 128.68(8) | 0.33 | 0.5648(2) | [3] |
| [Zn(**L5**)Cl2]⋅0.5H2O5 (**7**) | 147.07(6) | 123.36(5) | 0.40 | 0.6453(3) | [4] |
| [Zn(**L6**)Cl2]6 (**8**) | 146.03(7) | 126.09(5) | 0.33 | 0.6715(2) | [5] |
| [Zn(**HL7**)(NCS)2]7 (**9**) | 151.16(7) | 133.96(8) | 0.29 | 0.5154(3) | [6] |
| [Zn(**HL7**)I2]7 (**10**) | 148.52(8) | 131.46(6) | 0.28 | 0.6628(3) | [6] |
| [Zn(**HL7**)Br2]7 (**11**) | 147.91(8) | 131.83(6) | 0.27 | 0.6528(3) | [6] |
| [Zn(**L8**)Br2]8 (**12**) | 146.06(9) | 129.81(8) | 0.27 | 0.6677(4) | [7] |
| [Zn(**L9**)Cl(DMSO)]9 (**13**) | 149.56(7) | 134.73(6) | 0.25 | 0.5025(3) | [8] |
| [Zn(**L10**)Cl2]10 (**14**) | 144.88(7) | 133.36(6) | 0.19 | 0.6438(3) | [9] |
| [Zn(**L11**)Cl2]11 (**15**) | 143.18(9) | 135.35(8) | 0.13 | 0.6503(4) | [8] |

1 The parameter *τ*5 (*τ*5 = (*β*−*α*)/60, where *β* and *α* are the two largest angles around the central atom) is an index of the degree of trigonality, within the structural continuum between trigonal bipyramidal and square-based pyramidal geometry.

2 *ρ* (Å) is the distance of metal ion from the mean basal plane of square pyramid toward the apical ligand.

3 **L3**= Condensation product of 2-acetylpyridine and trimethylammoniumacetohydrazide chloride (Girard’s T reagent).

4 **L4**= Condensation product of. 2-quinolinecarboxaldehyde and trimethylammoniumacetohydrazide chloride (Girard’s T reagent).

5 **L5** = 2-hydroxyimino-*N'*-[1-(2-pyridyl)ethylidene]propanohydrazide.

6 **L6** = (*E*)-4-(dimethylamino)-*N*′-(pyridin-2-ylmethylene)benzohydrazide.

7 **HL7** = 2-acetyl-pyridylisonicotinoylhydrazone (HAPIH).

8 **L8** = di-2-pyridyl ketone-*N*4-phenyl-3-semicarbazone.

9 **L9** = 2-formylpyridine-*para*-nitro-phenyl hydrazone.

10 **L10**= 2-formylpyridine isonicotinoyl hydrazone.

11 **L11** = 2-formylpyridine-*para*-chloro-phenyl hydrazone.

**Table S2.** Hydrogen-bond parameters for [Zn**L1**(NCS)2]⋅2H2O (**1**).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| D–H⋅⋅⋅A | D–H (Å) | H⋅⋅⋅A (Å) | D⋅⋅⋅A (Å) | D–H⋅⋅⋅A (°) | Symm.operation on A |
| O1W–H1W⋅⋅⋅O1 | 0.91(4) | 1.89(4) | 2.792(4) | 170(3) |  |
| O1W–H2W⋅⋅⋅O2W | 0.94(4) | 1.96(4) | 2.868(5) | 162(4) |  |
| O2W–H4W⋅⋅⋅S3 | 0.92(4) | 2.81(3) | 3.616(6) | 147(4) |  |
| C8–H8A⋅⋅⋅S2 | 0.96 | 2.896 | 3.737(5) | 146.8 | −1+x, 1+y, z |
| Inter layer C7–H7A⋅⋅⋅O2W | 0.97 | 2.685 | 3.575(5) | 152.7 | 1−x, 2−y, 1−z |
| C10–H10B⋅⋅⋅O1W | 0.96 | 2.686 | 3.579(5) | 155.0 | −1+x, y, z |
| Intra C5–H5B⋅⋅⋅S1 | 0.96 | 2.872 | 3.253(3) | 104.9 |  |
| Intra C9–H9B⋅⋅⋅N3 | 0.96 | 2.381 | 3.022(5) | 123.8 |  |
| Inter layer C9–H9C⋅⋅⋅O1W | 0.96 | 2.528 | 3.476(5) | 169.8 | 1−x, 1−y, 1−z |

**Table S3.** Hydrogen-bond parameters for [Zn(**L2**)2] (**2**).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| D–H⋅⋅⋅A | D–H (Å) | H⋅⋅⋅A (Å) | D⋅⋅⋅A (Å) | D–H⋅⋅⋅A (°) | Symm.operation on A |
| N4–H4B⋅⋅⋅S4 | 0.87 | 2.74 | 3.570(3) | 159.9 | 1−x, −1/2+y, 1/2−z |
| N8–H8B⋅⋅⋅S2 | 0.87 | 2.74 | 3.492(2) | 145.7 | 1−x, 2−y, −z |
| C8–H8⋅⋅⋅N3 | 0.93 | 2.73 | 3.226(3) | 114.3 | 1+x, y, z |
| Intra C5–H5B⋅⋅⋅S1 | 0.96 | 2.68 | 3.168(4) | 112.1 |  |
| Intra C11–H11B⋅⋅⋅S3 | 0.96 | 2.76 | 3.243(3) | 111.7 |  |

**Table S4.** Intermolecular π⋅⋅⋅π interaction parameters for complex **2**.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Cg(I)1 | Cg(J)1 | Cg(I) −Cg(J)2 (Å) | *α*3 (°) | *β*4 (°) | *γ*5 (°) | Slippage6 (Å) | Sym. code on (J) |
| Cg(1) | Cg(1) | 4.0785(15) | 0.02(14) | 24.7 | 24.7 | 1.703 | 2−x, 2−y, 1−z |

1 Labels of aromatic rings: (1) = S1, C1−C3, N1.

2 Cg(I) −Cg(J) = Distance between ring centroids (Ang.).

3 *α* = Dihedral angle between planes (I) and (J) (Deg.).

4 *β* = Angle between Cg(I)−Cg(J) vector and normal to plane (I) (Deg.).

5 *γ* = Angle between Cg(I) −Cg(J) vector and normal to plane (J) (Deg.).

6 Slippage = Distance between Cg(I) and perpendicular projection of Cg(J) on ring I (Ang.).

**Table S5.** DFT calculated and experimental average values of selected bond lengths (Å) and angles (°) for [ZnL1(NCS)2] (**1**), [Zn(L2)2] (**2**) and [ZnL3(NCS)2] (**3**).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Compound** | **1** | | **2** | | **3** | |
| Distances, Å | DFT | exp | DFT | exp | DFT | exp |
| Zn1–N6/Zn1-N6/Zn1-N6 | 1.953 | 1.955 | 2.159 | 2.149 | 1.962 | 1.965 |
| Zn1–N5/Zn1-N5/Zn1-N5 | 1.912 | 1.959 | 2.207 | 2.186 | 1.924 | 1.965 |
| Zn1–N2/Zn1-N2/Zn-N2 | 2.139 | 2.058 | 2.159 | 2.147 | 2.125 | 2.088 |
| Zn1–O1/Zn1-N1/Zn1-O1 | 1.255 | 2.178 | 1.206 | 2.318 | 1.244 | 2.206 |
| Zn1–N1/Zn1-S2/Zn1-N1 | 2.247 | 2.212 | 2.598 | 2.452 | 1.201 | 2.146 |
| O1–C6 /Zn1-S4/N3-C8 | 1.288 | 1.265 | 2.596 | 2.411 | 1.339 | 1.322 |
| Angles, ° |  |  |  |  |  |  |
| N6–Zn1–N1/N1–Zn1–N5/ N1–Zn1–N2 | 104.5 | 101.9 | 88.8 | 84.5 | 74.5 | 74.1 |
| N5–Zn1–N1/N2–Zn1–N5/ N1–Zn1–N5 | 95.2 | 97.9 | 105.2 | 103.1 | 106.2 | 100.5 |
| N5–Zn1–N2/N6–Zn1–N5/ N1–Zn1–N6 | 129.1 | 127.4 | 76.2 | 75.3 | 95.7 | 96.5 |
| N6–Zn1–O1/N2–Zn1–N1/ N1–Zn1–O1 | 91.6 | 96.9 | 76.2 | 73.6 | 145.7 | 147.9 |
| N5–Zn1–O1/N2–Zn1–S4/ N2–Zn1–O1 | 98.0 | 97.8 | 100.3 | 101.2 | 73.0 | 74.0 |

**Table S6.** EHOMO, ELUMO and their energy gaps calculated by using TD-DFT in vacuum at different levels of theory.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | | | [Zn**L1**(NCS)2] (**1**) | | [Zn(**L2**)2] (**2**) | [Zn**L3**(NCS)2] (**3**) |
|  | | EHOMO (eV) | | | –4.970 | –5.054 | –4.903 |
| B3LYP/6-31G | | ELUMO (eV) | | | –2.803 | –2.141 | –2.438 |
|  | | *ΔE*gap(eV) | | | 2.167 | 2.913 | 2.465 |
|  | | | EHOMO (eV) | | –5.163 | –5.245 | –5.124 |
| B3LYP/6-311G(d,p) | | | ELUMO (eV) | | –2.874 | –2.306 | –2.587 |
|  | | | *ΔE*gap(eV) | | 2.289 | 2.939 | 2.537 |
|  | | | EHOMO (eV) | | –4.417 | –4.630 | –4.371 |
| BVP86/6-311G(d,p) | | | ELUMO (eV) | | –3.509 | –2.871 | –3.294 |
|  | | | *ΔE*gap(eV) | | 0.908 | 1.760 | 1.077 |

**Table S7.** Crystal data and structure refinement details for **1** and **2**.

|  |  |  |
| --- | --- | --- |
|  | **1** | **2** |
| formula | C12H20N6O3S3Zn | C12H14N8S4Zn |
| Fw (g mol–1) | 457.89 | 463.92 |
| crystal size (mm) | 0.10 × 0.10 × 0.01 | 0.10 × 0.05 × 0.05 |
| crystal color | colourless | yellow |
| crystal system | triclinic | monoclinic |
| space group | *P* –1 | *P* 21/*c* |
| *a* (Å) | 8.8362(3) | 9.0503(4) |
| *b* (Å) | 8.8934(3) | 13.6692(7) |
| *c* (Å) | 14.5684(7) | 14.9717(8) |
| *α* (º) | 81.964(2) | 90.00 |
| *β* (º) | 86.941(3) | 101.012(5) |
| *γ* (º) | 61.769(2) | 90.00 |
| *V* (Å3) | 998.65(7) | 1818.05(16) |
| *Z* | 2 | 4 |
| calcd density (g cm-3) | 1.523 | 1.695 |
| *F*(000) | 472 | 944 |
| no. of collected reflns | 7430 | 17333 |
| no. of independent reflns | 4532 | 4133 |
| *R*int | 0.0293 | 0.0450 |
| no. of reflns observed | 3161 | 3033 |
| no. parameters | 242 | 230 |
| *R*[*I*> 2σ (*I*)]*1* | 0.0407 | 0.0356 |
| *wR2*(all data)*2* | 0.0898 | 0.0760 |
| *Goof* , *S3* | 1.043 | 1.018 |
| maximum/minimum residual electron density (e Å–3) | +0.33/–0.29 | +0.32/–0.34 |

1 *R* = ∑||*F*o| – |*F*c||/∑|*F*o|.

*2 wR*2 = {∑[*w*(*F*o2 – *F*c2)2]/∑[*w*(*F*o2)2]}1/2.

*3 S* = {∑[*w*(*F*o2 – *F*c2)2]/(*n*/*p*}1/2 where *n* is the number of reflections and *p* is the total number of parameters refined.

|  |  |
| --- | --- |
| (**a**) | (**b**) |

**Figure s1.** (a) A view of the crystal packing of **1** showing complex molecules connected by means of OW-H⋅⋅⋅O, CMe-H⋅⋅⋅S and CMe-H⋅⋅⋅OW hydrogen bonds (dashed blue lines) into layer parallel with the (0 0 1) lattice plain. (b) A side view of the layers parallel with the (0 0 1) lattice plain related by the centers of symmetry showing the function of O1W and O2W in joining the neighboring layers.

|  |  |
| --- | --- |
| PACK1_HydrogenBonding.png  (**a**) | 1_PACK2_Pi_Pi.png  (**b**) |

**Figure s2.** (a) A view of the crystal packing of **2** showing complex molecules connected by means of N–H⋅⋅⋅S hydrogen bonds (dashed blue lines) into layer parallel with the (1 0 0) lattice plain. (b) A side view of the layers showing intermolecular *π*⋅⋅⋅*π* contacts involving 1,3-thiazole rings. Hydrogen atoms not involved in hydrogen bonding are omitted for clarity.

**1H and 13C{1H} NMR spectra of the synthesized propargylamines**

*1-(1-(phenylethynyl)cyclohexyl)pyrrolidine* (**4a**)



**Figure s3**. 1H NMR for 4a.



**Figure s4**. 13C NMR for 4a.

*1-(1-(phenylethynyl)cyclohexyl)piperidine* (**4b**)

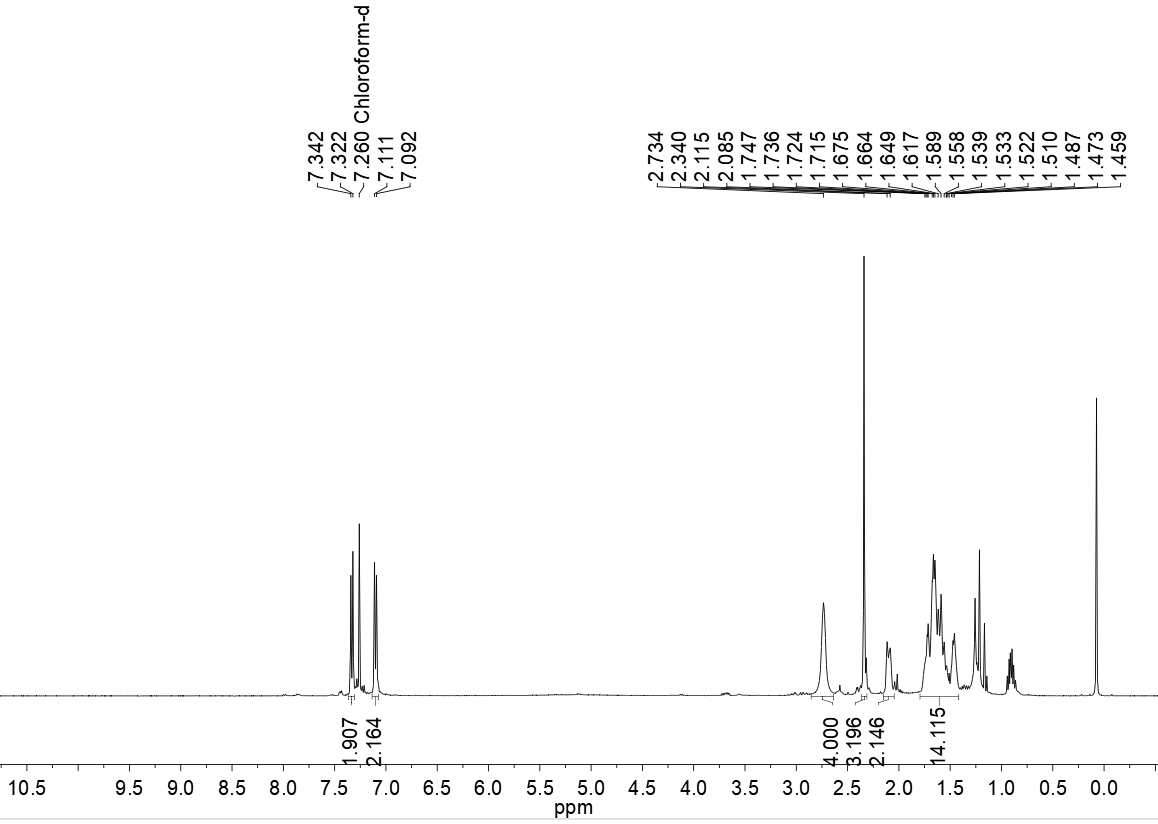


**Figure s5**. 1H NMR for 4b.

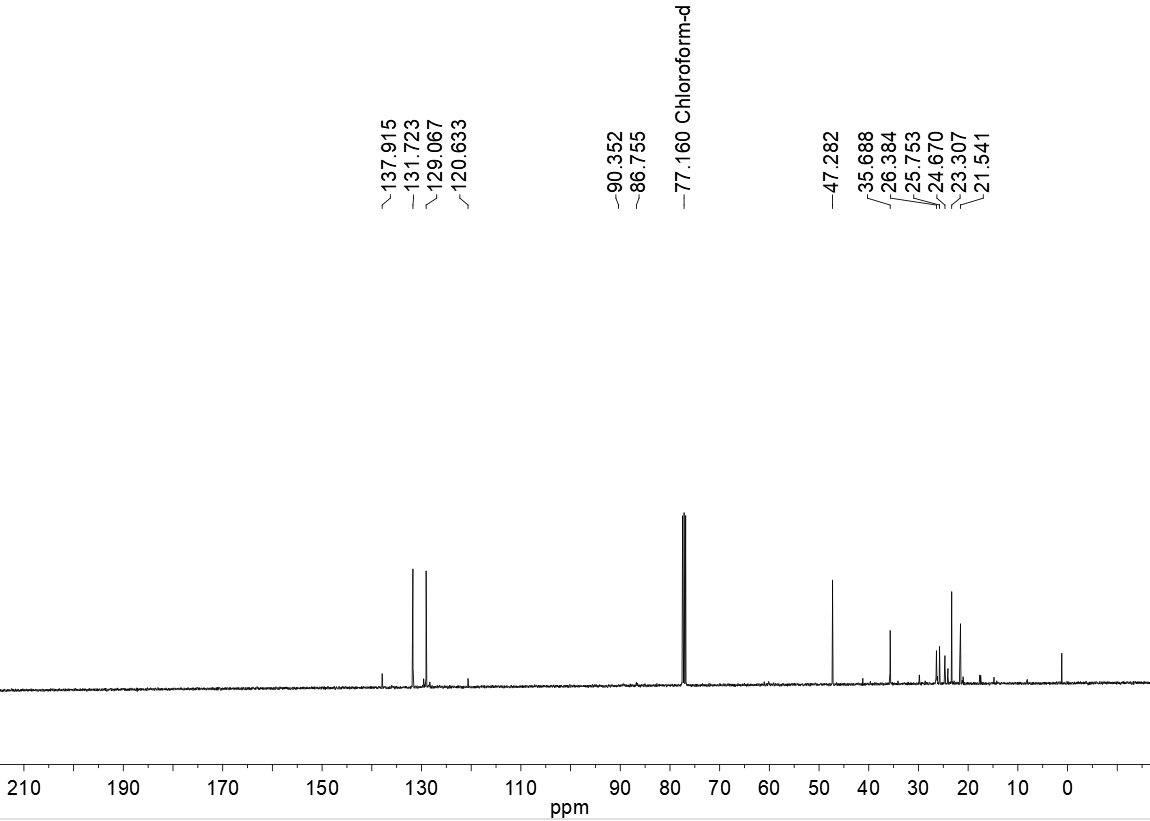


**Figure s6**. 13C NMR for 4b.

*1-(1-(p-tolylethynyl)cyclohexyl)piperidine*(**4c**)



**Figure s7**. 1H NMR for 4c.



**Figure s8**. 13C NMR for 4c.

1*-(3-methyl-1-phenylpent-1-yn-3-yl)pyrrolidine* (**4d**)



**Figure s9**. 1H NMR for 4d.



**Figure s10**. 13C NMR for 4d.

*1-(1-(phenylethynyl)cyclohexyl)piperidine-4-carboxylate* (**4e**)



**Figure s11**. 1H NMR for 4e.



**Figure s12**. 13C NMR for 4e.

*N-octyl-1-(phenylethynyl)cyclohexanamine* (**4f**)



**Figure s13**. 1H NMR for 4f.



**Figure s14**. 13C NMR for 4f.

*1-(3-methyl-1-phenylhex-1-yn-3-yl)pyrrolidine*(**4g**)



**Figure s15**. 1H NMR for 4g.



**Figure s16**. 13C NMR for 4g.

2-methyl-4-(1-(4-phenylpiperazin-1-yl)cyclohexyl)but-3-yn-2-ol (**4h**)



**Figure s17**. 1H NMR for 4h.



**Figure s18**. 13C NMR for 4h.

*1-(1-(oct-1-yn-1-yl)cyclohexyl)piperidine* **(4i)**



**Figure s19**. 1H NMR for 4i.



**Figure s20**. 13C NMR for 4i.

*1-(1-(phenylethynyl)cyclopentyl)piperidine* (**4j**)



**Figure s21**. 1H NMR for 4j.



**Figure s22**. 13C NMR for 4j.

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