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Synthesis, characterization, DFT calculations and biological activity of derivatives of 3-acetylpyridine and the zinc(II) complex with the condensation product of 3-acetylpyridine and semicarbazide

Supplementary material

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Contents

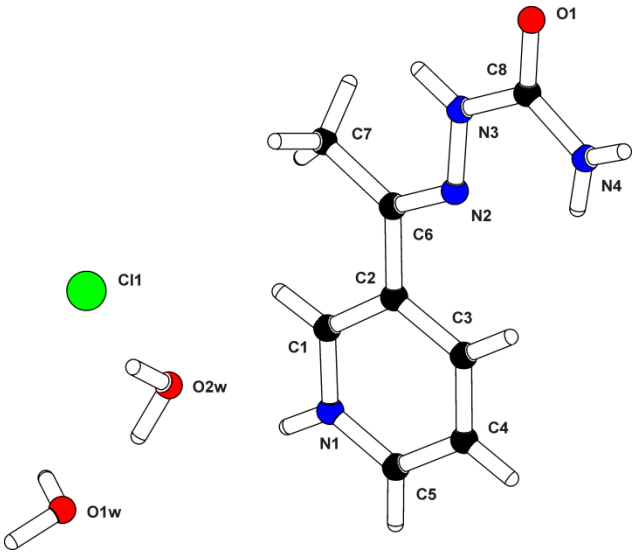

Fig. S1. Representation of the crystallographic structure of compound **HL1**.

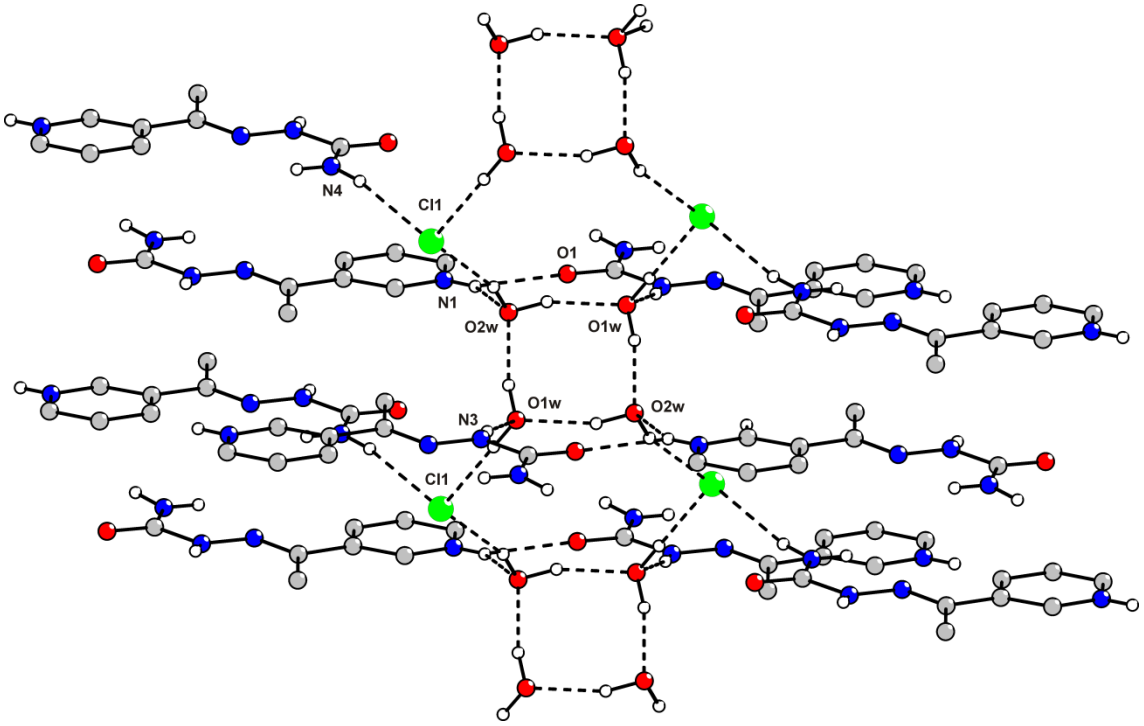

Fig. S2. Hydrogen-bonding network of compound **HL1**.

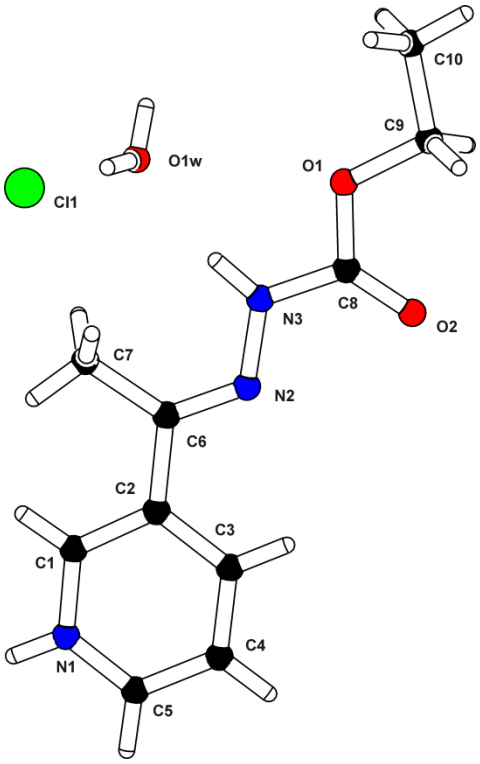

Fig. S3. Representation of the crystallographic structure of compound **HL3**.

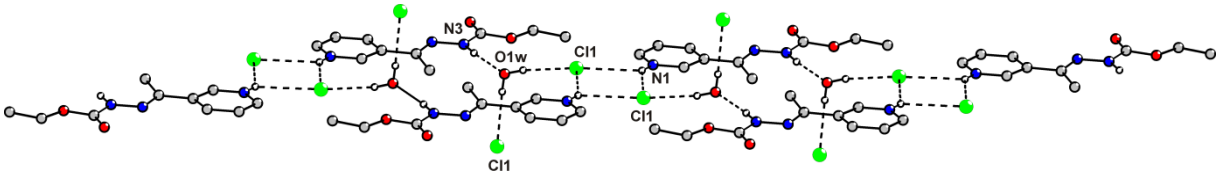

Fig. S4. Hydrogen-bonding network of compound **HL3**.

Table S1

Crystal data and structure refinement details for **HL1**, **HL3** and **1**.

	HL1	**HL3**	**1**
formula	$C_8H_{15}ClN_4O_3$	$C_{10}H_{16}ClN_3O_3$	$C_{16}H_{20}Cl_2N_8O_2Zn$
Fw (g mol^{-1})	250.69	261.71	492.67
crystal size (mm)	0.20× 0.05× 0.05	0.50× 0.10× 0.10	0.20× 0.13× 0.10
crystal color	colourless	colourless	colourless
crystal system	triclinic	monoclinic	orthorhombic
space group	*P*-1	$P2_1/c$	*Pbcn*
a (Å)	6.6772(3)	4.7804(2)	7.43810(10)
b (Å)	8.9768(3)	9.9478(3)	11.6257(2)
c (Å)	11.0700(5)	26.2508(10)	23.9731(5)
α (º)	113.504(2)	90	90
β (º)	94.574(3)	93.338(3)	90
γ (º)	100.428(3)	90	90
V (Å^3)	589.88(4)	1246.22(8)	2073.03(6)
Z	2	4	4
Calc. density (g cm^{-3})	1.411	1.395	1.579
F(000)	264	552	1008
no. of collected reflns	4387	11595	4402
no. of independent reflns	2638	2853	2378
R_{int}	0.0179	0.0294	0.0178
no. of reflns used	2190	2237	1827
no. parameters	170	168	142
$R[I> 2\sigma(I)]^a$	0.0571	0.0381	0.0315
wR_2(all data)^b	0.1594	0.1092	0.0840
Goof , S^c	1.178	1.045	1.053
maximum/minimum residual electron density (e Å^{-3})	+0.57/–0.33	+0.23/–0.20	+0.38/–0.32

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
$^c S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

Table S2

Selected bond lengths (Å) and angles (°) of compounds **HL1**, **HL3** and **1**.

		HL1	
N1–C1	1.344(3)	C1–N1–C5	123.3(2)
N1–C5	1.328(4)	C2–C6–N2	113.8(2)
N2–N3	1.363(3)	C6–N2–N3	119.1(2)
C8–O1	1.233(3)	N2–N3–C8	119.0(2)
N4–C8	1.337(4)	N3–C8–O1	119.1(2)
		HL3	
N1–C1	1.335(2)	C1–N1–C5	123.44(15)
N1–C5	1.327(2)	C2–C6–N2	114.94(13)
N2–N3	1.3670(19)	C6–N2–N3	117.70(13)
C8–O1	1.3395(19)	N2–N3–C8	117.93(13)
C8–O2	1.200(2)	N3–C8–O1	108.01(13)
C9–O1	1.450(2)	C8–O1–C9	116.48(13)
		1	
Zn1–N1	2.0552(16)	N1–Zn1–Cl1	105.09(5)
Zn1–Cl1	2.2298(6)	N1–Zn1–N1^{i}	112.55(9)
N1–C1	1.353(2)	N1–Zn1– Cl1^{i}	109.14(5)
N1–C5	1.334(3)	Cl1–Zn1–Cl1^{i}	116.02(4)
C6–N2	1.280(3)	C1–N1–C5	117.96(18)
N2–N3	1.367(2)	C2–C6–N2	112.99(17)
C8–N3	1.374(3)	C6–N2–N3	121.19(17)
C8–O1	1.237(2)	N2–N3–C8	116.83(17)
N4–C8	1.325(3)	N3–C8–O1	119.95(19)

Symmetry transformations used to generate equivalent atoms: (i) –x, y, –z+0.5.

Table S3

Hydrogen bonding geometry of compounds **HL1**, **HL3** and **1**.

D – H ⋯ A	*d*(D – H)/ Å	*d*(H ⋯ A)/ Å	*d*(D ⋯ A)/ Å	<(DHA)/ º	Symmetry transformation for acceptors
HL1					
N1–H1N···O1	0.85(4)	2.33(3)	2.930(3)	127(3)	x, y, z–1
N1–H1N···O2w	0.85(4)	2.08(4)	2.814(4)	144(3)	
O1w–H1w···Cl1	0.93(3)	2.20(3)	3.131(3)	178(5)	–x, –y+2, –z+1
N3–H2N···O1w	0.87(3)	2.11(3)	2.966(3)	170(3)	x, y, z+1
O1w–H2w···O2w	0.94(4)	1.87(3)	2.800(4)	169(3)	–x+1, –y+2, –z+1
N4–H3N···Cl1	0.86(2)	2.80(2)	3.523(2)	143(3)	x, y–1, z
O2w–H3w···Cl1	0.93(3)	2.21(3)	3.109(3)	161(3)	
N4–H4N···Cl1	0.86(4)	2.48(4)	3.333(3)	169(3)	–x, –y+1, –z+2
O2w–H4w···O1w	0.94(3)	1.92(3)	2.815(3)	159(4)	
HL3					
N1–H1N···Cl1	0.858(17)	2.801(19)	3.3868(15)	127.0(14)	x–1, y–1, z
N1–H1N···Cl1	0.858(17)	2.441(16)	3.1651(14)	142.6(16)	–x, –y+1, –z
O1w–H1w···Cl1	0.90(2)	2.30(2)	3.1823(16)	167(2)	x+1, y, z
O1w–H2w···Cl1	0.90(2)	2.24(2)	3.1393(16)	178.8(18)	
N3–H2N···O1w	0.872(16)	2.050(17)	2.909(2)	168.1(15)	
1					
N4–H2N···O1	0.85(2)	2.04(2)	2.883(3)	175(2)	x+0.5, –y–0.5, –z
N3–H1N···O1	0.870(17)	2.266(18)	3.133(2)	175(2)	x–0.5, –y–0.5, –z

Table S4

Computed NMR data (at COSMO-SSB-D/ET-pVQZ, in ppm) of **1** and assignment to atoms.

Atoms	Conf. A (in blue in Fig.2)	Atoms	Conf. B (in red in Fig. 2)[a]
	^{1}H		
H(C1)	8.91, 8.89	H(C5)	8.86, 8.86
H(C5)	8.65, 8.64	H(C3)	8.76, 8.76
H(C3)	8.54, 8.54	H(N3)	8.17, 8.17
H(N3)	8.23, 8.21	H(C1)	7.94, 7.94
H(C4)	7.54, 7.54	H(C4)	7.66, 7.66
H(N4)	6.42, 6.37, 4.84, 4.77	H(N4)	6.46, 6.46, 4.89, 4.89
H(C7)	average 2.11	H(C7)	average 1.75
	(2.44, 2.41, 1.95, 1.95, 1.95, 1.93)		(2.09, 2.09, 1.75, 1.75, 1.40, 1.40)
	^{13}C		
C8	148.29, 147.62	C8	147.19, 147.19
C5	144.82, 144.77	C5	147.10, 147.10
C1	143.48, 143.46	C1	141.14, 141.14
C6	140.10, 140.06	C6	138.31, 138.31
C3	137.02, 136.73	C3	137.75, 137.75
C2	132.44, 132.42	C2	132.12, 132.12
C4	125.52, 125.35	C4	126.52, 126.52
C7	10.86, 10.86	C7	9.03, 9.03

a) identical because of C_2 symmetry present in conformer

Table S5

Cartesian coordinates of optimized structures of **1**, **HL1** and $ZnCl_2$(**HL1**)$_1$

1

Zn	-0.021872	-2.435718	0.416255
Cl	-0.985717	-3.717146	-1.193439
N	6.560823	1.585014	0.564518
O	8.629906	2.528799	0.654573
N	-1.461127	-1.079485	1.028726
Cl	0.937232	-3.266491	2.301896
C	4.387905	0.687770	1.993261
N	5.536665	1.068810	-0.153347
N	-5.593095	1.087559	0.136849
N	7.785733	1.888840	-1.392596
N	1.427242	-1.288016	-0.515883
O	-8.733792	2.236656	-0.940627
C	4.492843	0.636526	0.493786
C	-3.457552	0.186655	0.535151
C	2.426502	-0.751098	0.212819
C	-4.483108	0.151358	-1.855481
N	-6.637404	1.393168	-0.667472
C	1.354049	-1.025689	-1.836816
N	-7.750673	2.347248	1.142347
C	-1.364739	-0.473092	2.229545
C	-3.343983	0.812465	1.793177
C	-2.478976	-0.760146	0.204080
C	7.720472	2.043648	-0.048152
C	3.320025	0.346598	-1.721360
C	-2.295210	0.478795	2.642699
C	3.409376	0.081073	-0.339771
C	-4.560692	0.498518	-0.393995
C	2.290806	-0.211517	-2.471143
C	-7.781472	2.004825	-0.169407
H	2.202787	-0.015476	-3.539111
H	5.140069	0.029060	2.457997
H	3.398393	0.398998	2.359144
H	4.582481	1.714024	2.346152
H	8.522249	2.388677	-1.879423
H	6.941586	1.640028	-1.901943
H	2.435654	-1.033478	1.265637
H	-5.227419	-0.620040	-2.113925
H	-3.493351	-0.207401	-2.152726
H	-4.706494	1.044067	-2.462528
H	6.545421	1.645403	1.584572
H	0.528030	-1.490325	-2.376027
H	-7.022188	1.952282	1.732316
H	-8.636686	2.598186	1.568818

H	-0.525657	-0.775155	2.856860
H	-4.080606	1.561310	2.085239
H	-2.505491	-1.312421	-0.735357
H	4.059852	0.996636	-2.188982
H	-2.187688	0.953709	3.617197
H	-6.660906	1.151473	-1.660302

HL1-protonated

C	3.322852	0.330947	0.240385
N	-2.776361	1.578297	-0.210733
C	0.206420	-2.382513	-0.170368
N	0.966034	-0.048043	0.082899
N	2.228800	-0.517536	0.084164
C	-2.519186	-1.091751	0.221365
N	3.043430	1.653528	0.312600
C	-0.009206	-0.902963	-0.035670
C	-1.364157	-0.322448	-0.017710
O	4.468287	-0.158353	0.266813
C	-3.900039	0.862732	0.020357
C	-1.544429	1.047138	-0.240449
C	-3.782835	-0.498897	0.241869
H	-2.867948	2.579552	-0.383438
H	0.917327	-2.582787	-0.988656
H	-0.717074	-2.924212	-0.394176
H	0.639466	-2.795978	0.755535
H	-0.722341	1.725733	-0.446839
H	-4.676895	-1.088756	0.432419
H	-2.433961	-2.161299	0.407405
H	3.793453	2.267076	0.613526
H	2.081894	1.947847	0.462527
H	-4.837303	1.410528	0.015388
H	2.447393	-1.514271	0.021032

HL1-deprotonated

C	3.338996	0.287789	-0.077393
N	-3.798367	-0.530629	-0.185869
C	0.171817	-2.332397	0.162174
N	0.963867	-0.015523	-0.039878
N	2.219761	-0.528045	-0.013083
C	-1.572276	1.150333	0.125781
N	3.103798	1.624483	-0.103754
C	-0.036480	-0.846784	0.039719
C	-1.385405	-0.242599	0.006923
O	4.475283	-0.229244	-0.069142
C	-3.941510	0.802302	-0.067822
C	-2.546203	-1.025045	-0.149599
C	-2.858247	1.675591	0.085538
H	0.678210	-2.724300	-0.735760
H	-0.758173	-2.889098	0.302010

H	0.821243	-2.547339	1.027118
H	-2.471215	-2.107480	-0.261825
H	-3.028334	2.749102	0.178354
H	-0.706778	1.801065	0.253680
H	2.159571	1.947218	-0.301429
H	3.882826	2.217602	-0.370749
H	-4.963651	1.187664	-0.095607
H	2.406105	-1.530499	0.052250

$ZnCl_2(HL1)_1$

C	2.808560	-1.251555	0.290750
N	-3.220889	0.747389	0.919575
C	-0.686232	-3.227081	-0.545310
N	0.459355	-1.168131	0.124648
N	1.608905	-1.907150	0.151255
C	-2.925892	-1.219927	-1.068723
N	3.906896	-2.011958	0.316648
C	-0.655489	-1.774946	-0.179212
C	-1.895819	-0.987408	-0.141194
O	2.852927	0.011768	0.385744
C	-4.178564	0.531247	-0.003959
C	-2.113057	-0.006899	0.844934
C	-4.079297	-0.443381	-1.001694
Zn	0.980703	0.884644	0.389007
H	0.010708	-3.433556	-1.373549
H	-1.691464	-3.547953	-0.832414
H	-0.371961	-3.835538	0.319913
H	-1.368148	0.146897	1.630777
H	-4.892819	-0.586213	-1.713103
H	-2.815218	-1.982931	-1.840265
H	4.807916	-1.560801	0.430953
H	3.863228	-3.024026	0.264344
H	-5.069879	1.158751	0.065820
H	1.573280	-2.919872	0.047289
Cl	0.579834	2.110100	-1.446601
Cl	0.680591	1.778280	2.438838