Supporting information

Synthesis and crystal structure of a novel binuclear copper complex with the nalidixic acid derivative 1-ethyl-1,4-dihydro-7-methyl-4-oxo-N'-(1H-imidazol-4-ylmethylidene)-1,8-naphthyridine-3-carbohydrazide

Authors

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S1. Synthesis of the ligand and the Cu(II) complex

The first step, which involves the synthesis of the nalidixic acid hydrazide derivative (hzd), was performed according to a similar procedure described by Aboul-Fadl *et al.* 2010.

Nalidixic acid (2.0 mmol, 0.4465 g) was added to 10.0 mL of freshly distilled CH_2Cl_2 followed by the addition of 0.50 mL of triethylamine. The solution was stirred for 15 min and then cooled to 0-5 °C followed by the slow addition of 0.2 mL of methyl chloroformate dissolved in 5.0 mL of dry CH_2Cl_2. The mixture was maintained under stirring for 30 min and then added dropwise to a dispersion of 0.50 mL of hydrazide monohydrate ($N_2H_4{\cdot}H_2O$) in 1.0 mL of dry CH_2Cl_2. The white solid formed was maintained under stirring at room temperature for 5 h in order to assure the complete formation of the hydrazide. After this stage, 5.0 mL of water was added to the suspension and the volume of CH_2Cl_2 was reduced in a rotavapor. The white solid obtained was separated by filtration, washed with several portions of 10 mL of distilled water and dried in a desiccator under P_2O_5.

The precursor hzd formed was used to obtain the ligand h4imi according to the following procedure: 1.5 mmol of 4-imidazolecarboxyaldehyde (4-imi, $C_4H_4N_2O$, 96.09 $gmol^{-1}$) was added to a suspension of 1.5 mmol of hzd ($C_{12}H_{14}N_4O_2$, 246.27 $gmol^{-1}$) in 10.0 mL of methanol. Glacial acetic acid (4 drops) was added as a catalyst. The reaction was kept under stirring for 4 h at room temperature in order to

assure the complete formation of h4imi. The white-pearl solid formed was then separated by filtration, washed several times with cold methanol and dried in a desiccator over P_2O_5 for 2 days. Yield: 43%. Elemental analysis: Calcd. for $C_{16}H_{16}N_6O_2$ (%): C, 59.25; H, 4.97; N, 25.91. Found (%): C, 59.46; H, 5.20; N, 23.02. ESI-QTOF-MS (m/z): 325.1436 [$C_{16}H_{16}N_6O_2+H^+$]. IR ν(N-H) 3235 cm^{-1}, 3170 cm^{-1} and 3126 cm^{-1}, ν_{ar}(C-H) 3065 cm^{-1}, ν_{aly}(C-H) 2968 cm^{-1} and 2928 cm^{-1}, ν(C=O) 1671 cm^{-1} and 1634 cm^{-1}, ν (C=N) 1610.3 cm^{-1},1553 cm^{-1} and 1532 cm^{-1}, ν(C-N) 1501 cm^{-1} and ν(N-N) 1443cm^{-1}.

For [$Cu_{1.5}$(h4imi)Cl]Cl·2(CH_3OH), a 1:1 mixture of $CuCl_2·2H_2O$ (0.50 mmol, 170.48 $gmol^{-1}$) in 10.0 mL of MeOH with h4imi (0.50 mmol, 324.34 $gmol^{-1}$) suspended in 10.0 mL of MeOH was maintained under stirring. The immediate formation of a green solid was observed but the reaction was left for 2 h under stirring in order to assure the complete formation of the complex. The solid was then separated by filtration and washed several times with CH_2Cl_2. Prior to the solid purification, the mother liquor was separated and left for crystallization. After two weeks, green crystals were formed and then evaluated as suitable crystals for X-ray diffraction. Elemental analysis: Calcd. For $Cu_{1.5}C_{18}H_{23}N_6O_4$(%): C, 39.05; H, 4.15; N, 15.18. Found (%): C, 40.07; H, 3.83; N, 17.39.

Table S1 Atomic coordinates output for h4imi DFT optimized structure

Atom	X	y	z
C	4.29908492925532	3.10919222023542	-1.49140209129262
N	2.48482754458878	2.58523460573466	-0.21687067470614
H	1.85673920878275	2.50365899091285	-1.02518999215764
O	2.65292519496002	2.44882615280949	2.06052021538461
O	-0.03069280818113	2.07053601195793	-1.20286985575754
N	-1.09930353819085	1.04651566446929	2.60924919115669
N	-3.21851082603991	0.41073790593288	1.91897149026274
N	3.78206390766014	2.91526884267078	-0.33630011425517
C	2.00040181270191	2.33989871371184	1.04134248578708
C	0.13049624475764	1.51734297846901	2.32495507030917
H	0.81749288763598	1.61793870012022	3.15811501338823
C	-1.65392567773408	1.26006459099197	0.29029464832141
C	-2.02054335550967	0.90025195996109	1.59125022848199
C	-2.62258823685082	1.10647655597375	-0.69987467806207

H	-2.35480540679011	1.38479568044798	-1.71261502920917
C	-0.31723465088609	1.77237397381276	-0.04594360088204
C	4.35299165502656	3.23796013045195	-4.01362296049513
N	2.36977348066687	2.84237286049544	-3.03863960804831
C	-4.12448595945281	0.27149175067851	0.96327141797550
C	0.57612765859633	1.87857022183093	1.08699623026490
C	3.70448068859654	3.06184858756041	-2.81078414148027
C	-1.44224021557152	0.65146994938051	3.97485357072492
H	-2.44608776131338	1.01896113981498	4.18749356166393
H	-0.74432869168952	1.17095944789856	4.63292330232160
C	-1.37478806625063	-0.84656542534945	4.18385960621713
H	-2.07850036412660	-1.35523664266965	3.52634276256498
H	-1.63923118875317	-1.08966095049946	5.21582756014556
H	-0.37044822603440	-1.22572264821820	3.98213052346847
C	-3.86137260411546	0.61762713111957	-0.37011423072391
H	-4.63165688605937	0.48393820702617	-1.12045180708595
C	2.20819548965944	2.88980720295532	-4.32987261549675
C	-5.46144471856641	-0.28462029742921	1.34209838739040
H	-5.47139623426898	-0.58210746361133	2.38967081863569
H	-5.70781032891093	-1.15175657474581	0.72435318221666
H	-6.24751767670307	0.45757119084580	1.17819108606811
N	3.38371936424393	3.12519437731751	-4.96613260203776
H	3.51878169580344	3.20696744605624	-5.95867302583803
H	1.27431528266462	2.76128641330775	-4.85607752426869
H	5.38280712754908	3.43477069578023	-4.26287523114046
H	5.35757924884954	3.35833970179129	-1.46330056981211

Table S2 Selected distances of h4imi optimized structure and h4imi coordinated structure

Bond	Distance/ Å	
	crystal	h4imi DFT
O1-C7	1.262(2)	1.2286
C5-N4	1.343(2)	1.3704
N3-N4	1.400(2)	1.3439
N3-C4	1.284(2)	1.2803
C5-C6	1.471(2)	1.4978
C5-O2	1.272(2)	1.2151

Table S3 Selected angles of h4imi optimized structure and h4imi coordinated structure

Angle	crystal	h4imi DFT
O1-C7-C6	125.5(2)	125.14
C7-C6-C5	125.4(2)	125.87
N4-C5-O2	123.3(2)	124.35
C5-N4-N3	107.9(1)	117.83
N4-N3-C4	123.1(2)	120.48
N3-C4-C3	128.5(2)	130.64

Table S4 Selected torsions of h4imi optimized structure and h4imi coordinated structure

Torsions	crystal	h4imi DFT
O1-C7-C6-C5	1.8(3)	-1.31
O2-C5-N4-N3	-2.3(2)	2.84
C5-N4-N3-C4	176.8(2)	177.54
N4-N3-C4-C3	-2.3(3)	1.34
N3-C4-C3-N2	2.9(3)	3.34

Figure S1 Extended structure of the $\{[Cu_{1.5}(h4imi)Cl]Cl\cdot 2(CH_3OH)\}_n$ polymer. The counter ions are intentionally not represented.

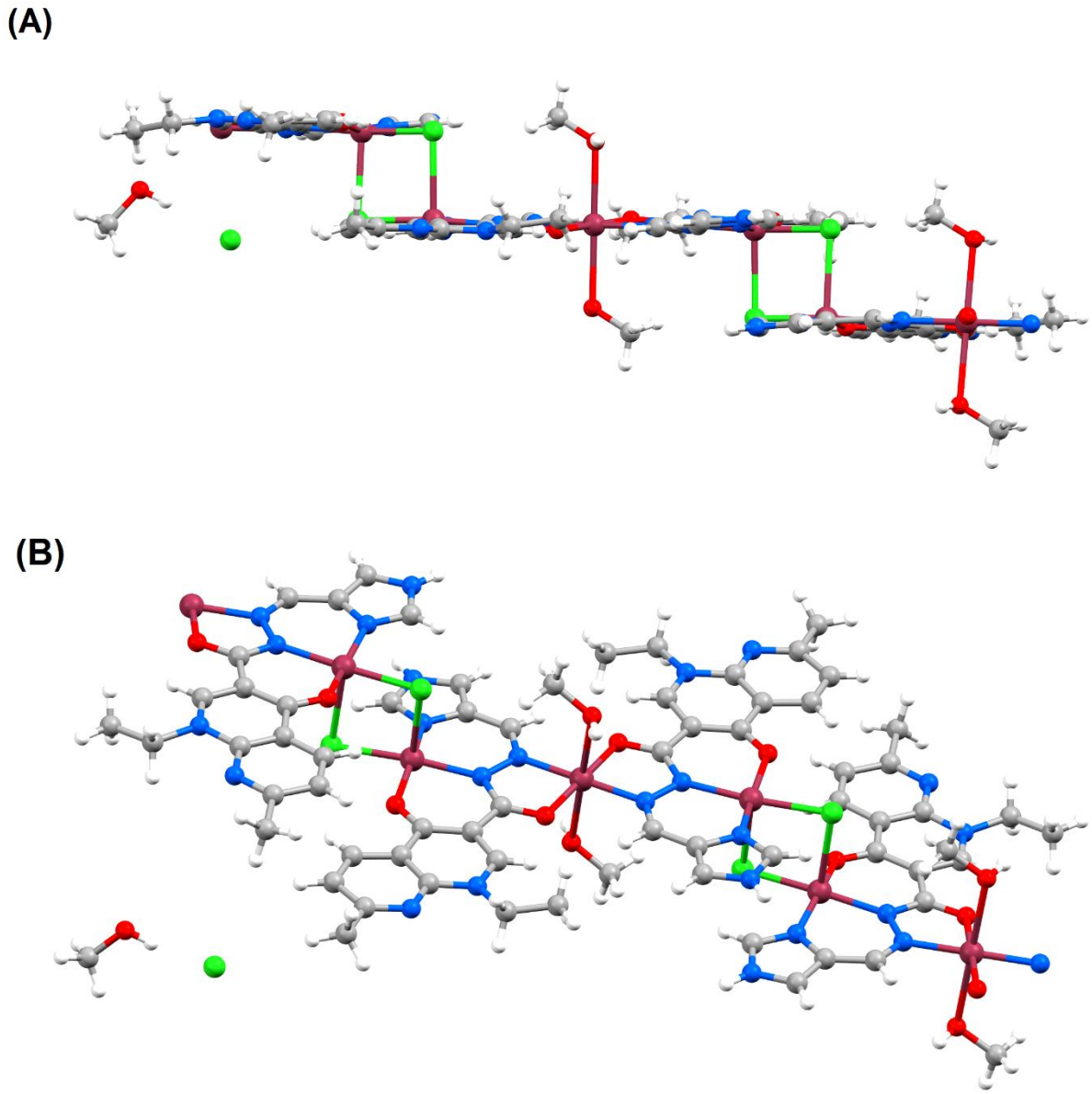

Figure S2 Minimum square planes representation of almost parallel h4imi (22 atoms) molecules. Due to the disorder, the ethyl groups of h4imi were intentionally not picked for the calculation.

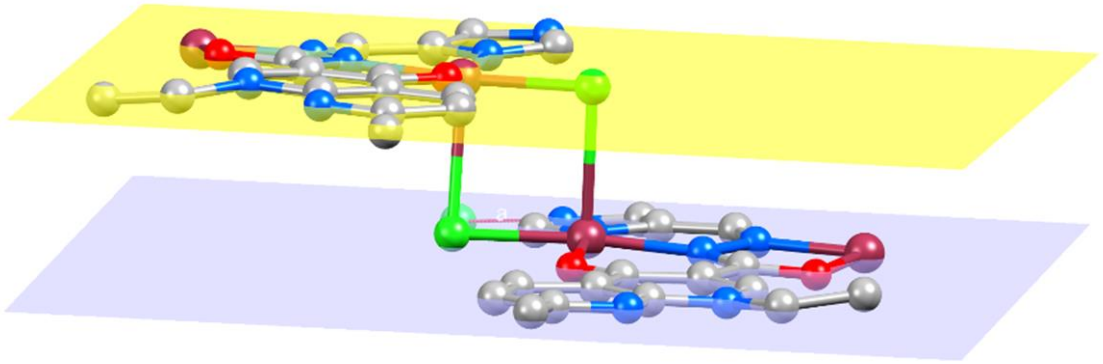

Figure S3 (A) PBE0/def2-TZVP optimized structure of h4imi and (B) comparison between coordinated (X ray data in purple) and non-coordinated h4imi (blue).