Supporting Information

Nickel(II) and nickel(III) Thiosemicarbazone and Hydrazone Complexes: An Unexpected Journey

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1. Experimental section.

2-Acetylthiazole (99%) was obtained from Acros, Girard's P reagent (95%) was obtained from Fluorochem, 2-acetylpyridine (≥99%), and thiosemicarbazide (99%) were obtained from Aldrich (SIGMA CHEMICAL). IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer using the ATR technique in the region 4000−400 cm^{-1} (vs-very strong, s-strong, m-medium, w-weak). ^1H and ^{13}C NMR spectra of ligands were recorded on Varian400/54 PS spectrometer (^1H at 400 MHz; ^{13}C at 125 MHz) at room temperature using TMS as internal standard in DMSO-d_6. Chemical shifts are expressed in ppm (δ) values and coupling constants (J) in Hz. Elemental analyses (C, H, and N) were performed by standard micro-methods using the ELEMENTARVario ELIII C.H.N.S.O analyzer. UV-Vis spectra were recorded at Agilent Cary 3500 UV-Vis spectrometer. Magnetic measurements were performed at 26°C by Evans' method using an MSBMK1 balance (Sherwood Scientific Ltd.) with $Hg[Co(SCN)_4]$ as calibrant; diamagnetic corrections were calculated from Pascal's constants. Molar conductivity of DMSO solutions of the complexes (C = 10^{-3} mol/dm^3) were measured at room temperature (26 °C) on a digital conductivity meter pHenomenal® CO 3100 H. The EPR spectra at room temperature were acquired on a Bruker Elexsys II E540 EPR spectrometer with the following experimental parameters: microwave frequency 9.8 GHz (X band), microwave power 10 mW, modulation amplitude 10 G, modulation

frequency 100 kHz. For measurements, the samples were placed in 1 mm-diameter gas-permeable Teflon tubes (Zeus Industries Inc), and inserted into a quartz EPR cuvette with inner diameter 3 mm (Wilmad-LabGlass, Vineland, NJ, USA).

*1.1. Synthesis of (E)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide (**HL^1**)*

Ligand, **HL^1** was synthesized by the reaction of thiosemicarbazide and 2-acetylthiazole in water according to the previously described method. Yield 1.82 g (91%). Anal. Calcd. (%) for $C_6H_8N_4S_2$: C,35.98; H, 4.03; N, 27.98; S, 32.02. Found (%): C, 35.74; H, 4.26; N, 27.88; S, 31.98. IR (ATR, cm^{-1}): 3434 (vs), 3246 (s), 3188 (vs), 3099 (s), 3071 (s), 2983 (m), 2057 (w), 1778 (w), 1649 (w), 1590 (vs), 1511 (vs), 1481 (vs), 1428 (vs), 1366 (m), 1282 (s), 1166 (w), 1108 (s), 1070 (s), 1041 (m), 848 (m), 759 (m), 713 (w), 638 (w), 525 (w), 503 (w), 445 (w). ^{1}H-NMR (400 MHz, DMSO-d_6), δ (ppm): 2.43 (s, 3H, C5-H), 7.69 (s, 1H, NH_2), 7.80 (d, 1H, C3-H), 7.89 (d, 1H, C2-H), 8.53 (s, 1H, NH_2), 10.67 (s, 1H, NH). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (ppm): 14.12 (C5), 123.06 (C3), 143.75 (C2), 144.70 (C4), 167.52 (C1), 179.44 (C6). Uv-Vis (DMSO): λ_{max} 325 nm (ε, 12670 M^{-1} cm^{-1}).

*1.2. Synthesis of complex [Ni**HL^1**$_2$](BF$_4$)$_2$ (**1**)*

Ligand, **HL^1** (0.040 g, 0.20 mmol) was dissolved in MeOH (10 mL) and solid $Ni(BF_4)_2 \cdot 6H_2O$ (0.068 g, 0.20 mmol) was added. After complete dissolution of $Ni(BF_4)_2 \cdot 6H_2O$ in the reaction mixture, NaN_3 (78 mg, 20 mmol), dissolved in solvent mixture of CH_3CN/H_2O (10/5 mL), was added. Reaction mixture was refluxed for 2 h. After slow evaporation of solvent at room temperature after one-week, green crystals were obtained. Yield: 0.075 g (59 %). Anal. Calcd. (%) for $C_{12}H_{16}B_2F_8N_8NiS_4$: C, 22.77; H, 2.55; N, 17.71; S, 20.26. Found (%): C, 22.75; H, 2.56; N, 17.75; S, 20.25. IR (ATR, cm^{-1}): 3637 (w), 3450 (m), 3395 (m), 3346 (s), 3206 (s), 3129 (m), 3102 (m), 2947 (w), 1633 (s), 1611 (s), 1555 (s), 1489 (m), 1407 (s), 1366 (s), 1311 (m), 1295 (m), 1227 (s), 1169 (s), 1098 (s), 1065 (s), 893 (w), 794 (m), 777 (m), 744 (w), 706 (w), 649 (w), 599 (w), 520 (w), 473 (w). μ_{eff} = 3.5 μ_B. Λ_m = 97.2 µS/cm. Uv-Vis (DMSO): λ_{max} 340 nm (ε, 11776 M^{-1} cm^{-1}), λ_{max} 420 nm (ε, 534 M^{-1} cm^{-1}).

*1.3. Synthesis of (E)-1-(2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethyl)pyridin-1-ium chloride (**HL²**Cl)*

2-Acetylpyridine 0.363 g (3.00 mmol) and Girard's P reagent 0.563 g (3.00 mmol) were dissolved in ethanol (40 mL) and 1-2 drops of cc. HCl were added. The mixture was refluxed for 2 h. After cooling to the room temperature, a white precipitate was filtered and washed with ethanol. Yield: 0.451 g (52%). Anal. Calcd. (%) for $C_{14}H_{15}ClN_4O$: C, 57.83; H, 5.20; N, 19.27. Found (%): C, 57.80; H, 5.23; N, 19.25. IR (ATR, cm^{-1}): 3425 (s), 3273 (m), 3125 (m), 3054 (s), 2949 (w), 1699 (vs), 1630 (s), 1582 (m), 1485 (vs), 1453 (m), 1433 (s), 1384 (s), 1323 (w), 1263 (s), 1221 (m), 1197 (m), 1150 (w), 1111 (m), 1081 (w), 848 (w), 790 (m), 774 (m), 725 (w), 702 (m), 646 (m), 600 (w), 569 (w). ^{1}H-NMR (400 MHz, DMSO-d_6), δ (ppm): 2.37 (s, 3H, C7-H), 6.14 (s, 2H, C8-H), 7.41 (t, 1H, C4-H), 7.85 (t, 1H, C3-H), 8.13 (d, 1H, C2-H), 8.21 (t, 2H, C10-H), 8.60 (d, 1H, C5-H), 8.67 (t, 1H, C11-H), 9.09 (d, 2H, C9-H), 11.55 (s, 1H, NH). ^{13}C-NMR (125 MHz, DMSO-d_6), δ (ppm): 12.76 (C7), 62.35 (C8), 120.66 (C2), 124.76 (C4), 128.01 (C10), 137.09 (C3), 146.67 (C1[1]), 146.89 (C9), 149.15 (C5), 150.94 (C6), 154.99 (C1), 168.19 (C12). Uv-Vis (DMSO): λ_{max} 289 nm (ε, 12182 M^{-1} cm^{-1}).

*1.4. Synthesis of complex [Ni**L²**(N₃)₃] (**2**)*

Complex was synthesized by the reaction of **HL²**Cl (87 mg, 0.30 mmol) and $Ni(BF_4)_2 \cdot 6H_2O$ (102 mg, 0.30 mmol) in MeOH (20 mL, pH=6). After complete dissolution of $Ni(BF_4)_2 \cdot 6H_2O$ in the reaction mixture, NaN_3 (78 mg, 20 mmol), dissolved in solvent mixture of CH_3CN/H_2O (10/5 mL, pH=5), was added (pH=5). The mixture was refluxed for 2 h (pH=5). After slow evaporation of solvent at room temperature for one day, brown crystals were obtained. Yield: 87 mg (67%). Anal. Calcd. for $C_{17}H_{24}N_{13}ONi$: C 42.90%, H 4.99%, N 37.53%; found: C 43.00%, H 4.95%, N 37.55%. IR (ATR, cm^{-1}): 3267 (w), 3080 (m), 3049 (w), 3023 (m), 2973 (m), 2002 (s), 1633 (w), 1518 (m), 1489 (m), 1461 (m), 1436 (w), 1372 (m), 1339 (w), 1311 (w), 1276 (m), 1219 (w), 1197 (w), 1149 (w), 779 (w), 734 (w), 675 (w). μ_{eff} = 2.1 μ_B. Λ_m = 10.1 µS/cm. Uv-Vis (DMSO): λ_{max} 268 nm (ε, 15692 M^{-1} cm^{-1}), λ_{max} 357 nm (ε, 15576 M^{-1} cm^{-1}).

2. Single crystal X-ray diffraction study.

Crystal data and refinement parameters of compounds **1** and **2** are listed in Table S1. Single crystal X-ray diffraction data were collected at room temperature on an Agilent SuperNova dual-source diffractometer with an Atlas detector equipped with mirror-monochromated Mo–K_α

radiation (λ = 0.71073 Å). Data processing was performed with CrysAlis PRO [1]. The structures were solved by direct methods (SHELXS-2013/1 [2]) and refined by a full-matrix least-squares procedure based on F^2 using SHELXL-2018/3 [3]. All non-hydrogen atoms were refined anisotropically. The nitrogen bonded hydrogen atoms were located in the difference map and refined with the distance restraints (DFIX) with d(N–H = 0.86 Å and with U_{iso}(H) = 1.2U_{eq}(N). All other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

Table S1 Crystal data and structure refinement details for **1** and **2**

	1	**2**
formula	$C_{12}H_{16}B_2F_8N_8NiS_4$	$C_{14}H_{14}N_{13}NiO$
Fw (g mol^{-1})	632.90	439.09
crystal size (mm)	0.20×0.20×0.05	0.40×0.10×0.10
crystal color	red	red
crystal system	monoclinic	triclinic
space group	*P* $2_1/n$	*P* –1
a (Å)	12.5849(6)	7.7318(4)
b (Å)	11.9847(7)	8.6981(6)
c (Å)	16.4909(8)	14.7200(9)
α (º)	90	78.295(6)
β (º)	98.549(5)	83.810(5)
γ (º)	90	69.368(6)
V (Å^3)	2459.6(2)	906.48(10)
Z	4	2
calcd density (g cm^{-3})	1.709	1.609
F(000)	1272	450
no. of collected reflns	11491	7497
no. of independent reflns	5643	4158
R_{int}	0.0355	0.0355
no. of reflns observed	3527	3473

no. parameters	336	263
$R[I> 2\sigma\ (I)]^a$	0.0574	0.0419
wR_2(all data)^b	0.1780	0.1058
Goof, S^c	0.992	1.039
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	+1.04/–0.46	+0.40/–0.50
CCDC	2256752	2256753

$^aR = \sum||F_o| - |F_c||/\sum|F_o|$. $^bwR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
$^cS = \{\sum[(F_o^2 - F_c^2)^2]/(n/p\}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

3. Computational details.

In order to shed some light on the unexpected structure and electronic properties of complex **2** a number of DFT calculations were employed. Starting from the crystal structure coordinates of complex **2** the geometries of the three possible complexes were optimized with Ni(II) as the central metal ion (charge of the complex -1, multiplicity – doublet) and Ni(III) as the central metal ion in low spin (charge 0 and multiplicity doublet) and high spin (charge 0 and multiplicity quartet) state. All the optimizations were done with DFT method, more specifically unrestricted BP86 functional with Grimme D3 empirical dispersion with Becke-Johnson damping using def2TZVP all atoms basis set. The solvent (water) is simulated with PCM implicit solvation method. All the calculations were done in Gaussian09 program package and figures were crated in VMD. Spin population distribution was calculated from optimized wavefunction using Becke atomic space partitioning method [4] and CSD atomic radii [5] with MultiWfn program.

Additional details

Table S2. Selected bond lengths (Å) and angles (°) of complexes **1** and **2**.

1		**2**	
Ni1–S2	2.4141(12)	Ni1–N2	1.855(2)
Ni1–S4	2.4124(13)	Ni1–N1	1.919(2)
Ni1–N1	2.073(3)	Ni1–O1	1.9299(17)
Ni1–N2	2.038(3)	Ni1–N5	1.965(2)
Ni1–N5	2.111(4)	Ni1–N8	1.968(2)

Ni1–N6	2.033(4)	Ni1–N11	1.973(2)
N2–C4	1.291(5)	N2–C6	1.289(3)
N2–N3	1.361(4)	N2–N3	1.380(3)
N3–C6	1.352(6)	N3–C8	1.313(3)
S2–C6	1.680(5)	O1–C8	1.282(3)
N6–C10	1.296(6)	N5–N6	1.194(3)
N6–N7	1.359(5)	N6–N7	1.149(4)
N7–C12	1.337(6)	N8–N9	1.192(3)
S4–C12	1.687(5)	N9–N10	1.146(4)
N4–C6	1.336(6)	N11–N12	1.187(3)
N8–C12	1.324(7)	N12–N13	1.151(4)
B1–F4	1.264(8)		
B1–F2	1.346(8)		
B1–F1	1.350(7)		
B1–F3	1.397(8)		
B2–F8	1.317(8)		
B2–F6	1.326(9)		
B2–F5	1.328(12)		
B2–F7	1.353(12)		
N6–Ni1–N2	172.57(13)	N2–Ni1–N1	82.70(9)
N6–Ni1–N1	96.02(14)	N2–Ni1–O1	82.39(8)
N2–Ni1–N1	78.26(13)	N1–Ni1–O1	164.85(8)
N6–Ni1–N5	77.62(15)	N2–Ni1–N5	91.16(10)
N2–Ni1–N5	97.37(15)	N1–Ni1–N5	88.22(9)
N1–Ni1–N5	88.81(14)	O1–Ni1–N5	89.38(9)
N6–Ni1–S4	82.07(11)	N2–Ni1–N8	179.40(9)
N2–Ni1–S4	102.83(11)	N1–Ni1–N8	97.86(9)
N1–Ni1–S4	93.17(10)	O1–Ni1–N8	97.06(9)
N5–Ni1–S4	159.69(11)	N5–Ni1–N8	89.08(10)

N6–Ni1–S2	104.28(10)	N2–Ni1–N11	87.99(10)
N2–Ni1–S2	81.33(9)	N1–Ni1–N11	89.34(9)
N1–Ni1–S2	159.59(10)	O1–Ni1–N11	92.83(9)
N5–Ni1–S2	93.46(10)	N5–Ni1–N11	177.51(10)
S4–Ni1–S2	91.69(5)	N8–Ni1–N11	91.79(10)
		N6–N5–Ni1	115.9(2)
		N9–N8–Ni1	120.8(2)
		N12–N11–Ni1	118.2(2)
		N13–N12–N11	177.2(3)
		N10–N9–N8	177.6(4)
		N7–N6–N5	177.4(4)

Table S3. Ni(II)-N_{Ar}, Ni(II)-N_{imine} and Ni(II)-S_{thione} distances (Å) in octahedral Ni(II)-N_4S_2 complexes with tridentate hydrazone-based NNS-donor ligands.

Complexes	Ni(II)-N_{Ar}	avg.	Ni(II)-N_{imine}	avg.	Ni(II)-S_{thione}	avg.	Refs.
complex **1**	2.073(3) 2.111(4)	2.092	2.033(4) 2.038(3)	2.035	2.414(1) 2.412(1)	2.413	this work
CCDC 974828 (QN ring)	2.159(5) 2.221(4)	2.190	2.017(4) 2.033(5)	2.025	2.449(2) 2.391(2)	2.420	[6]
CCDC 906027 (PY ring)	2.107(2) 2.103(2)	2.105	2.018(2) 2.012(2)	2.015	2.427(1) 2.4142(9)	2.421	[7]
CCDC 906028 (PY ring)	2.102(3) 2.115(3) 2.114(3) 2.120(3)	2.113	2.019(3) 2.022(3) 2.025(2) 2.028(2)	2.023	2.435(1) 2.440(1) 2.419(1) 2.420(1)	2.428	[7]
CCDC 866892 (PY ring)	2.100	2.100	2.005	2.005	2.410	2.410	[8]
CCDC 685929 (PY ring)	2.119(3) 2.105(2)	2.112	2.005(3) 2.008(3)	2.006	2.401(1) 2.431(1)	2.416	[9]
CCDC 626768 (QN ring)	2.139(5) 2.139(6)	2.139	2.006(5) 2.022(4)	2.014	2.372(2) 2.415(2)	2.393	[10]

CCDC 271339 (PZ ring)	2.091	2.091	2.018	2.018	2.418	2.418	[11]
CCDC 244028 (PY RING)	2.144(5) 2.111(5)	2.127	2.011(4) 2.023(4)	2.017	2.449(2) 2.422(2)	2.435	[12]
CCDC 244029 (PY ring)	2.104(4) 2.114(4)	2.109	2.012(3) 1.997(3)	2.004	2.439(1) 2.413(1)	2.426	[12]
CCDC 213952 (PYZL ring)	2.099(2) 2.085(2)	2.092	2.027(2) 2.023(2)	2.025	2.3917(8) 2.3895(9)	2.391	[13]
CCDC 199131 (PY ring)	2.084 2.104	2.094	2.056 2.005	2.031	2.402 2.400	2.401	[14]
CCDC 196028 (PYZL ring)	2.085(2) 2.100(2)	2.092	2.024(2) 2.019(2)	2.021	2.4072(8) 2.4190(9)	2.413	[15]
CCDC 1910631 (PY ring)	2.100(3) 2.102(3)	2.101	2.016(3) 2.003(3)	2.009	2.401(1) 2.447(1)	2.424	[16]
CCDC 1910629 (PY ring)	2.096(3) 2.102(3)	2.099	2.007(3) 2.013(3)	2.010	2.437(9) 2.399(1)	2.418	[17]
CCDC 188748 (PYZL ring)	2.112 2.112	2.112	2.037 2.037	2.037	2.387 2.387	2.387	[18]
CCDC 168861 (PY ring)	2.117(6) 2.098(6)	2.107	2.008(6) 2.005(6)	2.006	2.420(2) 2.416(2)	2.418	[19]
CCDC 157523 (PY ring)	2.087(6) 2.080(5) 2.095(5) 2.087(5)	2.087	2.034(4) 2.036(4) 2.021(5) 2.040(5)	2.033	2.453(2) 2.397(2) 2.395(2) 2.439(2)	2.421	[20]
CCDC 1442107 (PYZL ring)	2.05(2) 2.07(1)	2.06	2.05(1) 2.04(1)	2.045	2.413(6) 2.416(5)	2.414	[21]
CCDC 1062436 (QN ring)	2.172(3) 2.139(3)	2.155	2.049(3) 2.048(2)	2.048	2.377(1) 2.411(1)	2.394	[22]

Table S4. Hydrogen-bond parameters for complex **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symm. operation on A
N4–H4NA···F6	0.86(3)	2.35(5)	3.117(8)	149(6)	1/2+*x,* 3/2-*y,* -1/2+*z*
N4–H4NB···F1	0.86(7)	2.23(6)	3.074(6)	170(7)	1-*x*,1-*y*,-*z*
N8–H8NA···F8	0.87(5)	2.10(5)	2.914(7)	155(5)	-1/2+*x*, 3/2-*y*,-1/2+*z*
N3–H3N···F2	0.82(4)	2.54(5)	3.187(6)	136(4)	1-*x*,1-*y*,-*z*
N3–H3N···F3	0.82(4)	2.16(5)	2.939(7)	159(4)	1-*x*,1-*y*,-*z*
N8–H8NB···S2	0.84(4)	2.67(4)	3.456(5)	156(5)	1/2-*x,*1/2+*y,*1/2-*z*
N7–H7N···F2	0.85(4)	2.43(5)	2.999(6)	125(4)	1/2-*x,*1/2+*y,*1/2-*z*

Table S5. Octahedral Ni(II)-N_4S_2 complexes with tridentate hydrazone-based NNS-donor ligands.

CCDC NUMBERS	References:
Dicationic complexes:	
CCDC 974828	R. Min, X.-R. Fan, P. Zhou, J. Yan, J.-L. Zhou, S.-C. Zhang, Chin. J. Inorg. Chem. 30 (2014) 1771 [6].
CCDC 906027-906028	C. Graiff, S. Canossa, G. Predieri, J. Struct. Chem. 55 (2014) 493 [7].
CCDC 867991	H.S.Abduelftah, A.Q.Ali, N.E.Eltayeb, S.G.Teoh, H.-K.Fun, Acta Crystallogr. Sect. E: Struct. Rep. Online 68 (2012) m183 [23].
CCDC 867948	H.S. Abduelftah, A.Q. Ali, N.E. Eltayeb, S.G. Teoh, H.-K. Fun, Acta Crystallogr. Sect. E: Struct. Rep. Online 68 (2012) m108 [24].
CCDC 866892	A. Panja, D.M. Eichhorn, Inorg. Chim. Acta 391,(2012) 88 [8].
CCDC 685929	V. Amendola, M. Boiocchi, L. Fabbrizzi, L. Mosca, Chem. Eur. J. 14 (2008) 9683 [9].
CCDC 659219	A.K.Das, S.Seth, S.K. Chattopadhyay, Z Kristallogr Cryst Mater 215 (2000) 481 [25].
CCDC 626768	E. Manoj, M.R.P. Kurup, Polyhedron 27 (2008) 275 [10].
CCDC 611243	A. Jana, S. Konar, S. Ray, S.-M. Peng, G.H. Lee, R.J. Butcher, T.-H. Lu, A.K. Barik, S. Pal, S.K. Kar, Indian J. Chem., Sect A 50 (2011) 1334 [26].
CCDC 271339	M. Li, Q. Sun, Y. Bai, C. Duan, B. Zhang, Q. Meng, Dalton Trans. (2006) 2572 [11].

CCDC 244028-244029	E. Bermejo, A. Castineiras, I. Garcia-Santos, L.M. Fostiak, J.K. Swearingen, D.X. West, Z. Anorg. Allg. Chem. 631 (2005) 728 [12].
CCDC 213952	N.C. Saha, R.J. Butcher, S. Chaudhuri, N. Saha, Polyhedron 24 (2005) 1015 [13].
CCDC 199131	A. Sreekanth, S. Sivakumar, M.R.P. Kurup, J. Mol. Struct. 655 (2003) 47 [14].
CCDC 196028	D.K. Sau, N. Saha, R.J. Butcher, S. Chaudhuri, Transition Met. Chem. 29 (2004) 75 [15].
CCDC 1910631	W. Clegg, R. W. Harrington, L. K. Leary, Experimental Crystal Structure Determination, 2019 [16].
CCDC 1910629	W. Clegg, R. W. Harrington, L. K. Leary, Experimental Crystal Structure Determination, 2019 [17].
CCDC 188748	N.C. Saha, R.J. Butcher, S. Chaudhuri, N. Saha, Polyhedron 22 (2003) 383 [18].
CCDC 168861	I. Garcia, E. Bermejo, A.K.El Sawaf, A. Castineiras, D.X.West, Polyhedron 21 (2002) 729 [19].
CCDC 157523	N.C. Kasuga, K. Sekino, C. Koumo, N. Shimada, M. Ishikawa, K. Nomiya, J. Inorg. Biochem. 84 (2001) 55 [20].
CCDC 1442107	M. Saha, J. K. Biswas, M. Mondal, D. Ghosh, S. Mandal, D. B. Cordes, A.M.Z. Slawin, T. K. Mandal, N. C. Saha, Inorg. Chim. Acta 483 (2018) 271 [21].
CCDC 1062436	F. Bisceglie, A. Musiari, S. Pinelli, R. Alinovi, I. Menozzi, E. Polverini, P. Tarasconi, M. Tavone, G. Pelosi, J. Inorg. Biochem. 152 (2015) 10 [22].
Monocationic complexes:	
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Table S6. Comparison of Ni(III)–N and Ni(III)–O bond lengths observed in **2** with the corresponding Ni(II)–N and Ni(II)–O bonds found in $[Ni_2\mathbf{L}_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]$ complexes.

	$Ni–N_{Ar}$ (Å)	$Ni–N_{imine}$ (Å)	$Ni–O_{enolate}$ (Å)	$Ni–N_{azido}$ (Å)	Refs.
complex **2**	1.919(2)	1.855(2)	1.930(2)	1.965(2) 1.968(2) 1.973(2)	this work
$[Ni_2\mathbf{L}^3_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]$	2.1850(18) 2.1793(19)	1.9948(17) 1.9962(18)	2.0997(15) 2.1373(16)	2.0851(17) 2.063(2) 2.1400(19) 2.1339(18) 2.064(2) 2.0819(18)	[53]
$[Ni_2\mathbf{L}^4_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot 2H_2O$	2.126(3)	2.017(3)	2.140(2)	2.082(3) 2.101(3) 2.070(3)	[54]
$[Ni_2\mathbf{L}^4_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot 4H_2O$	2.122(2)	1.997(2)	2.083(2)	2.066(2) 2.152(2) 2.109(2)	[54]
$[Ni_2\mathbf{L}^5_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot 6H_2O$	2.077(2)	1.993(2)	2.080(2)	2.085(2) 2.122(2) 2.111(2)	[55]

L^3 = (*E*)-*N*,*N*,*N*-trimethyl-2-oxo-2-(2-(quinolin-2-ylmethylene)hydrazinyl)ethan-1-aminium chloride;

L^4 = (*E*)-*N*,*N*,*N*-trimethyl-2-oxo-2-(2-(1-(thiazol-2-yl)ethylidene)hydrazinyl)ethan-1-aminium chloride;

L^5 = (*E*)-*N*,*N*,*N*-trimethyl-2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethan-1-aminium-chloride.

Table S7. Hydrogen-bond parameters for complex **2**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symm. operation on A
C1–H1···N13	0.93	2.59	3.378(5)	143	1+*x, y, z*
C9–H9B···N5	0.97	2.56	3.424(4)	148	-1+*x*, *y*, *z*
C10–H10···N10	0.93	2.55	3.366(5)	146	*x*, -1+*y*, *z*
C14–H14···N8	0.93	2.36	3.268(4)	166	-1+*x*, *y*, *z*
Intra C7–H7C···N3	0.96	2.54	2.923(3)	104	

Table S8. Intermolecular π···π interaction parameters for complex **2**.

Cg(*I*)[a]	Cg(*J*)[a]	Cg(*I*)···Cg(*J*)[b] (Å)	α[c] (°)	β[d] (°)	γ[e] (°)	Slippage[f] (Å)	Sym. code on (*J*)
Cg(1)	Cg(1)	3.4922(15)	0.03(12)	24.7	24.7	1.461	2-*x,* 1-*y,* 1-*z*
Cg(2)	Cg(2)	4.016(2)	0.0(2)	28.4	28.4	1.912	1-*x,*1-*y,*-*z*

[a] Labels of aromatic rings: (1) = N(1),C(1),C(2),C(3),C(4),C(5); (2) = N(4),C(10),C(11),C(12),C(13),C(14).

[b]Cg(*I*)···Cg(*J*) = Distance between ring centroids (Ang.).

[c]α = Dihedral angle between planes (*I*) and (*J*) (Deg).

[d]β = Angle between Cg(*I*)–Cg(*J*) vector and normal to plane (*I*) (Deg).

[e]γ = Angle between Cg(*I*)–Cg(*J*) vector and normal to plane (*J*) (Deg).

[f]Slippage = Distance between Cg(*I*) and perpendicular projection of Cg(*J*) on ring (*I*) (Ang).

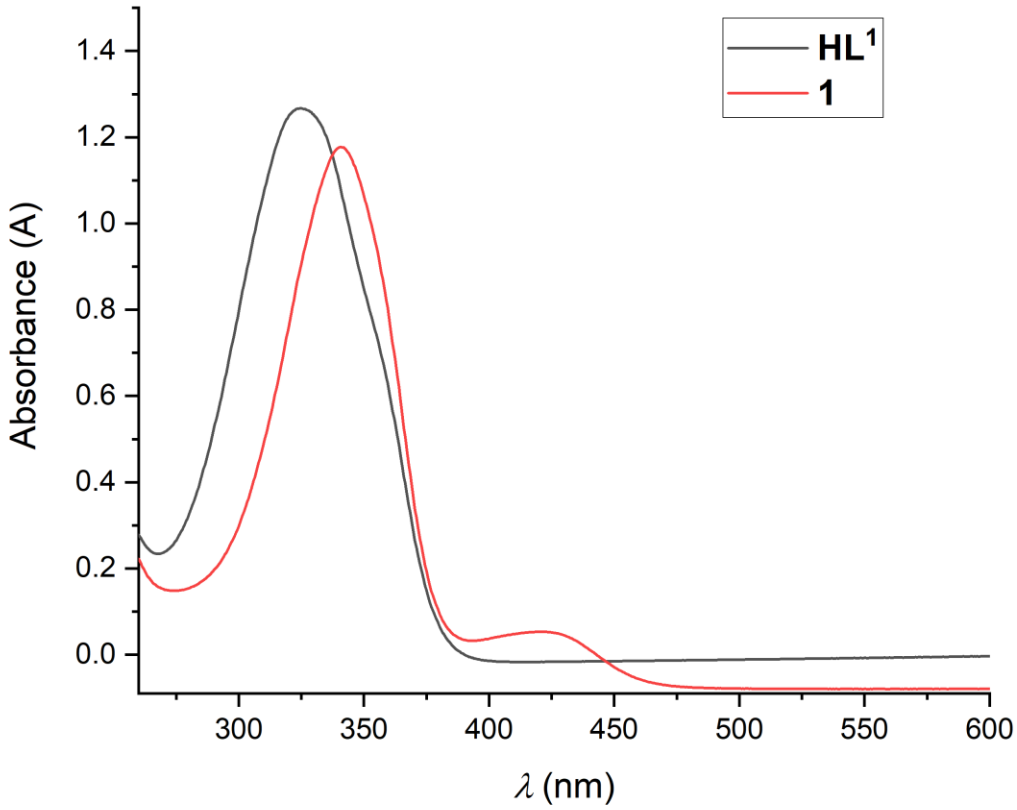


Figure S1. Absorption spectra of ligand **HL**[1] and complex **1**.

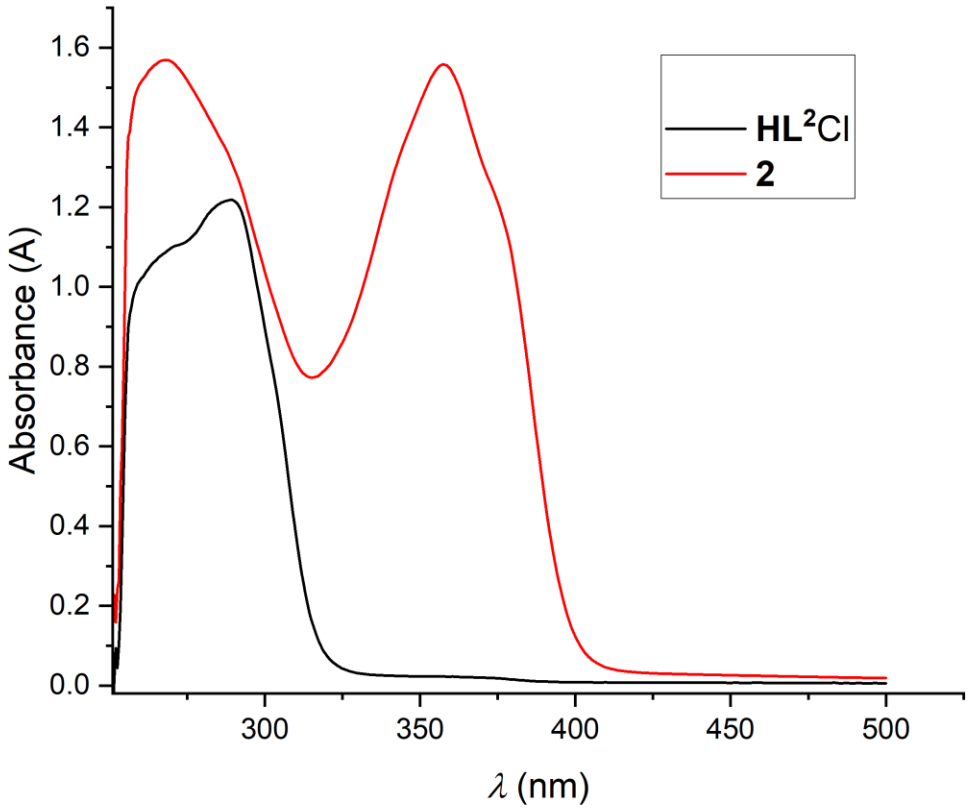
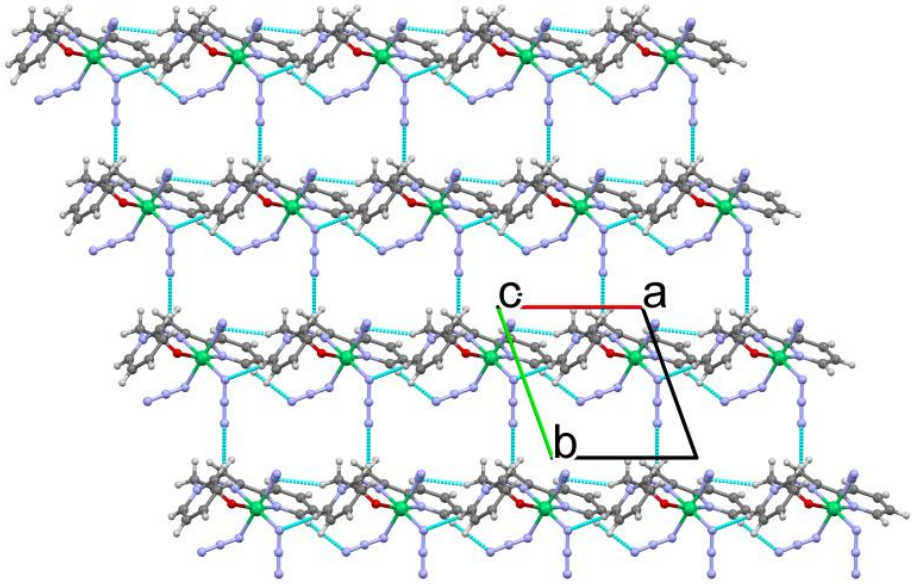
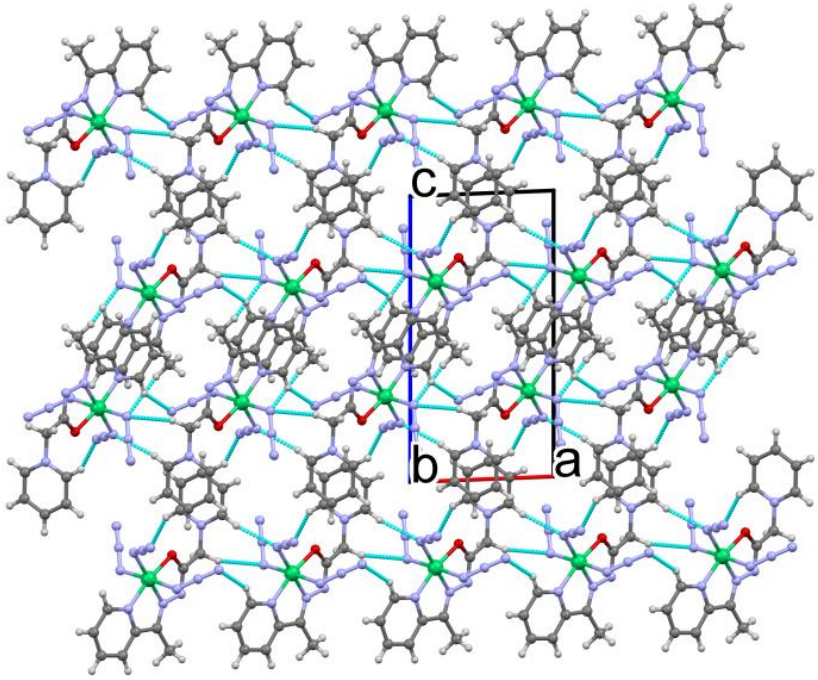


Figure S2. Absorption spectra of ligand **HL^2**Cl and complex **2**.



(a)



(b)

Figure S3. Crystal packing of complex **2**. (a) Hydrogen-bonded layer parallel with the (001) lattice plane generated by intermolecular C–H···N hydrogen bonds viewed along [001] direction. (b) Side view of the (001) layers showing π···π contacts between aromatic rings.

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