Supplementary Material (ESI) for Chemical Communications

A molecular cage of nickel(II) and copper(I): a [{Ni(L)$_2$}$_2$(CuI)$_6$] cluster resembling the active site of nickel-containing enzymes

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Contents

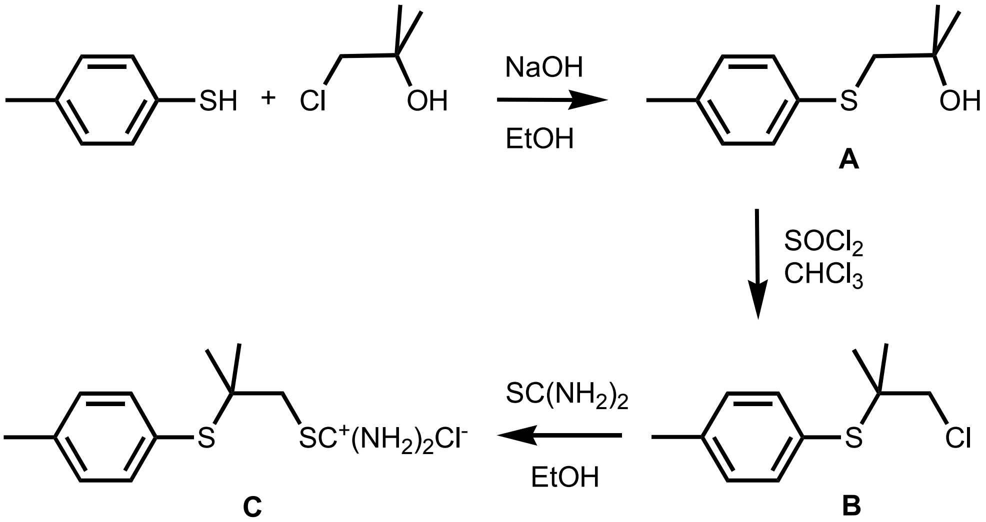
Experimental Methods

Chemicals: All preparations were carried out in reagent grade solvents. All chemicals used in the syntheses were obtained from Acros or Aldrich and were used without further purification unless mentioned otherwise. The complexes were synthesized in an argon atmosphere using standard Schlenk techniques. Solvents were deoxygenated/distilled/purified by bubbling through a stream of argon or by conventional methods and dried over molecular sieves.

Physical Measurements: Elemental analyses were carried out on a Perkin-Elmer series II CHNS/O analyzer 2400. NMR spectra were recorded on a Bruker 300 DPX spectrometer. Temperature was kept constant using a variable temperature unit within the error limit of ±1 K. The software MestReNova was used for the processing of the NMR spectra. Tetramethylsilane (TMS) or the deuterated solvent residual peaks were used for calibration. Mass experiments were performed on a Finnigan MAT 900 equipped with an electrospray interface. Spectra were collected by constant infusion of the sample dissolved in methanol/water or dichloromethane with 1% HOAc.

Electrochemical Measurements: The electrochemistry measurements were performed with an Autolab PGstat10 potentiostat controlled by GPES4 software. A conventional three-electrode system was used, consisting of a static glassy carbon working electrode, a platinum auxiliary electrode and a Ag/AgCl reference electrode. The experiments were carried out in dichloromethane at room temperature in an argon atmosphere with tetrabutylammonium hexafluorophosphate as electrolyte. Under these conditions the ferrocenium–ferrocene couple is located at +430 mV with a peak-to-peak separation of 59 mV. All potentials are reported relative to Ag/AgCl.

X-ray crystal structure determinations: All reflection intensities were measured at 110(2) K using a Nonius KappaCCD diffractometer (rotating anode) with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) under the program *COLLECT*.[1] The program *PEAKREF*[2] was used to refine the cell dimensions. Data reduction was done using the program *EVALCCD*.[3] The structure was solved with the program *DIRDIF08*[4] and was refined on F^2 with *SHELXL-97*.[5] Analytical absorption corrections based on crystal face-indexing were applied to the data using *SADABS*.[5] The temperature of the data collection was controlled using the system *OXFORD CRYOSTREAM 600* (manufactured by *OXFORD CRYOSYSTEMS*). The H-atoms were placed at calculated positions (*AFIX 23* or *AFIX 43* or *AFIX 137*) with isotropic displacement parameters having values 1.2 times Ueq of the attached C atom. Geometry calculations were performed with the *PLATON* program.[6]



Scheme S1. Synthesis of L-thiouronium chloride salt **C**.

Synthesis of 2-methyl-1-[(4-methylphenyl)sulfanyl]propan-2-ol (A). 1-Chloro-2-methyl-2-propanol (6.51 g, 60 mmol) and 4-methylbenzenethiol (7.45 g, 60 mmol) were dissolved in 60 ml ethanol. A solution of NaOH (2.4 g, 60 mmol in 10 ml H_2O) was slowly added to this mixture at room temperature and refluxed for two hours. The formed NaCl was removed by filtration and the solvent was evaporated. The residual oil was partitioned between water and chloroform and extracted into chloroform (2 x 25 ml). All organic layers were combined and dried over $MgSO_4$, evaporated and dried under vacuum to get colorless oil (10.72 g, 91 %). ^{1}H NMR δ_H [300.13 MHz, $CDCl_3$, 298 K] 7.31 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 7.07 (d, ^3J = 8.1 Hz, 2H, phenyl ring), 3.05 (s, 2H, $-S-CH_2-C(CH_3)_2-$), 2.51 (s, 1H, $-OH$), 2.28 (s, 3H, CH_3–phenyl–), 1.26 (s, 6H, $-S-CH_2-C(CH_3)_2-$). ^{13}C NMR δ_C [75.47 MHz, $CDCl_3$, 298 K] 136.08 (Ph–C1), 133.23 (Ph–C4), 129.94 (Ph–C2), 129.59 (Ph–C3), 70.62 ($-C(CH_3)_2-$), 48.97 ($-CH_2-C(CH_3)_2-$), 28.48 ($-C(CH_3)_2-$), 20.81 (CH_3–phenyl–).

Synthesis of 1-[(2-chloro-1,1-dimethylethyl)sulfanyl]-4-methylbenzene (B). A solution of $SOCl_2$ (7.14 g, 60 mmol in 10 ml chloroform) was slowly added to the solution of **A** (10.01 g, 51 mmol in 30 ml chloroform) at room temperature and stirred for an hour. The chloroform and excess thionyl chloride were evaporated under reduced pressure to yield bright yellow oil (10.95 g, 100%). ^{1}H NMR $\delta_\mathbf{H}$ [300.13 MHz, $CDCl_3$, 298 K] 7.37 (d, ^3J = 8.00 Hz, 2H, phenyl ring), 7.14 (d, ^3J = 8 Hz, 2H, phenyl ring), 3.39 (s, 2H, $–S–C(CH_3)_2–CH_2–$), 2.35 (s, 3H, CH_3–phenyl–), 1.68 (s, 6H, $–C(CH_3)_2–$). ^{13}C NMR δ_C [75.47 MHz, $CDCl_3$, 298 K] 136.54 (Ph–C1), 132.96 (Ph–C4), 130.61 (Ph–C2), 130.03 (Ph–C3), 69.78 ($–C(CH_3)_2–$), 50.66 ($–CH_2–C(CH_3)_2–$), 31.23 ($–C(CH_3)_2–$), 20.90 (CH_3–phenyl–).

Synthesis of 2-methyl-2-[(4-methylphenyl)sulfanyl]propythiouronuim chloride (C). A solution of thiourea (3.81 g, 50 mmol in 30 ml ethanol) was added to the solution of **B** (10.74 g, 50 mmol in 30 ml ethanol) and refluxed for six hours. The solvent was evaporated under reduced pressure to get colorless oil. Addition of chloroform to this oil and standing for two hours resulted in a white crystalline solid (13.38 g, 92%). The solid was collected by filtration and washed with chloroform before drying under vacuum. ^{1}H NMR $\delta_\mathbf{H}$ [300.13 MHz, DMSO-d6, 298 K] 9.40 (s, 4H, $–S–C(NH_2)_2{}^+Cl^-$), 7.39 (d, ^3J = 8 Hz, 2H, phenyl ring), 7.23 (d, ^3J = 8 Hz, 2H, phenyl ring) 3.33 (s, 2H, $–S–C(CH_3)_2–CH_2–$), 2.30 (s, 3H, CH_3–phenyl–), 1.26 (s, 6H, $–S–C(CH_3)_2–CH_2–$). ^{13}C NMR δ_C [75.47 MHz, $CDCl_3$, 298 K] 170.17 ($–S–C(NH_2)_2{}^+Cl^-$), 139.44 (Ph–C1), 136.93 (Ph–C3), 129.88 (Ph–C2), 126.52 (Ph–C4), 48.04 ($–S–C(CH_3)_2–CH_2–$), 42.26 ($–S–C(CH_3)_2–CH_2–$), 27.31 ($–S–C(CH_3)_2–CH_2–$), 20.83 (CH_3–phenyl–). MS (ESI): (m/z) calculated for $C_{12}H_{19}N_2S_2$ $[M\text{-}Cl]^+$ requires (monoisotopic mass) 255.10, found 254.91.

Synthesis of [Ni(L)$_2$] (1). A two-necked round bottom flask was charged with Ni(acac)$_2$ (0.771 g, 3 mmol) and the thiouronium salt **C** (1.745 g, 6 mmol). To this 60 ml ethanol was added under argon atmosphere. After 10 minutes stirring at 60 °C, NMe$_4$OH (0.547 g, 6 mmol) was added to the green solution. After the immediate formation of a dark brown colour, the solution was refluxed for two hours then the solvent was evaporated to dryness under reduced pressure. Dichloromethane was added to the residue and filtered through Celite until the filtrate was colorless, in order to remove the tetramethylammonium salt impurities. The filtrate was concentrated to one ml before adding 100 ml hexane and kept at 4 ºC overnight. Analytically pure dark brown flocculent needles were obtained by filtration and dried under vacuum (1.3 g, 91%). ^{1}H NMR δ_H [300.13 MHz, CD_2Cl_2, 303 K]) 7.87 (bs, 4H, phenyl–*ortho–H*), 7.22 (d, 4H, phenyl–*meta–H*), 2.39 (s, 6H, CH_3–Ph), 2.22 (s, 4H, –CH_2–S–), 1.34 (s, 12H, –$C(CH_3)_2$–) ^{13}C NMR δ_C [75.47 MHz, CD_2Cl_2, 303 K] 141.80 (Ph-C4), 135.87 (Ph-C3), 130.08 (Ph-C2), 42.01 (–CH_2–), 26.12 ((–$C(CH_3)_2$–), 21.49 (CH_3–Ph). Elemental Analysis (%), calculated for $C_{22}H_{30}S_4Ni$, C 54.89, H 6.28, S 26.64, found, C 55.17, H 6.66 S 24.55. MS (ESI): (*m/z*) calculated for $C_{22}H_{31}S_4Ni$ $[MH]^+$ requires 481.07, found 480.88.

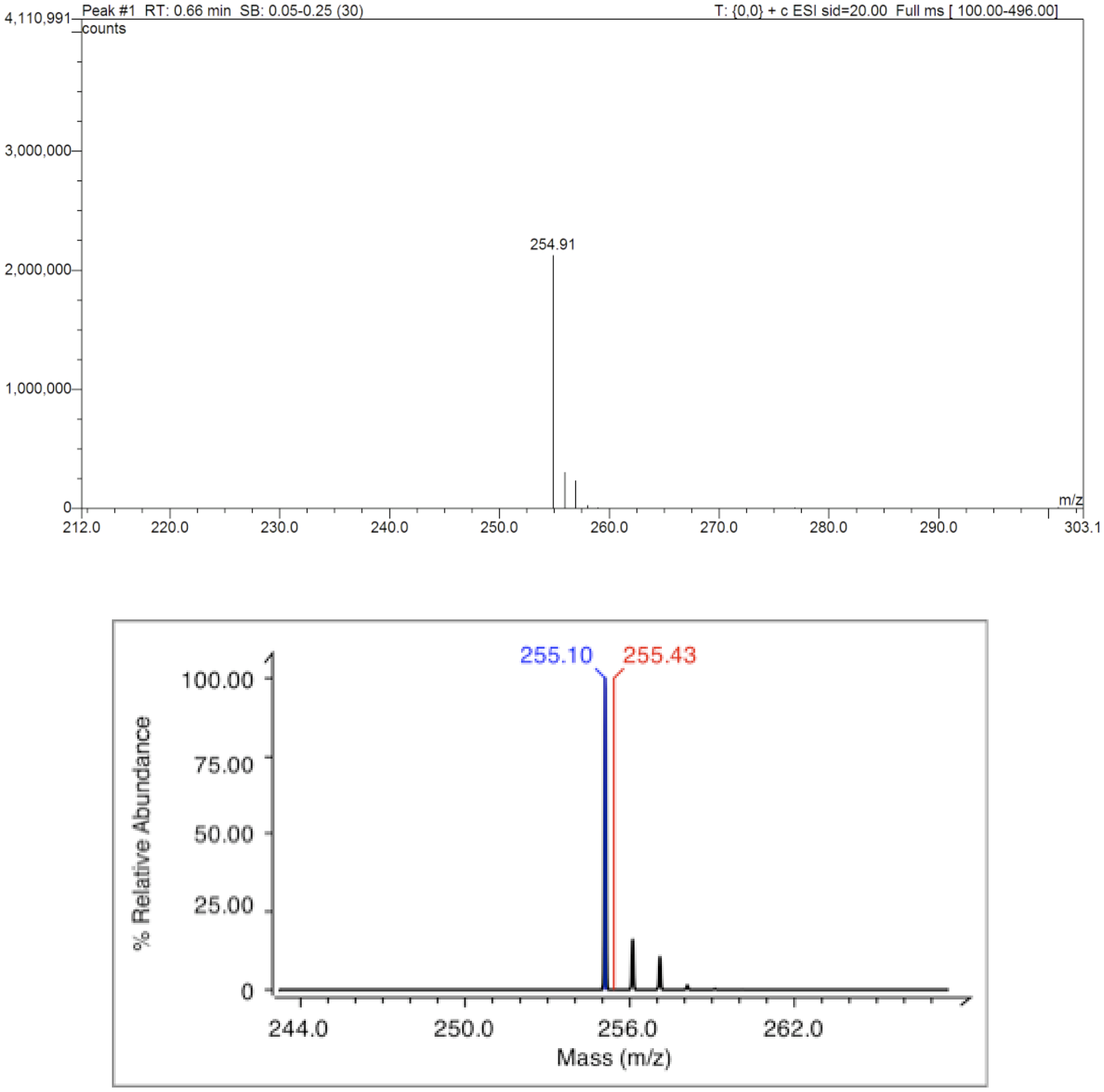


Figure S1. ESI-MS of thiouronium salt of the ligand measured (top) using a methanol/water solution and simulated for $C_{12}H_{19}N_2S_2$ $[M\text{-}Cl]^+$ (bottom).

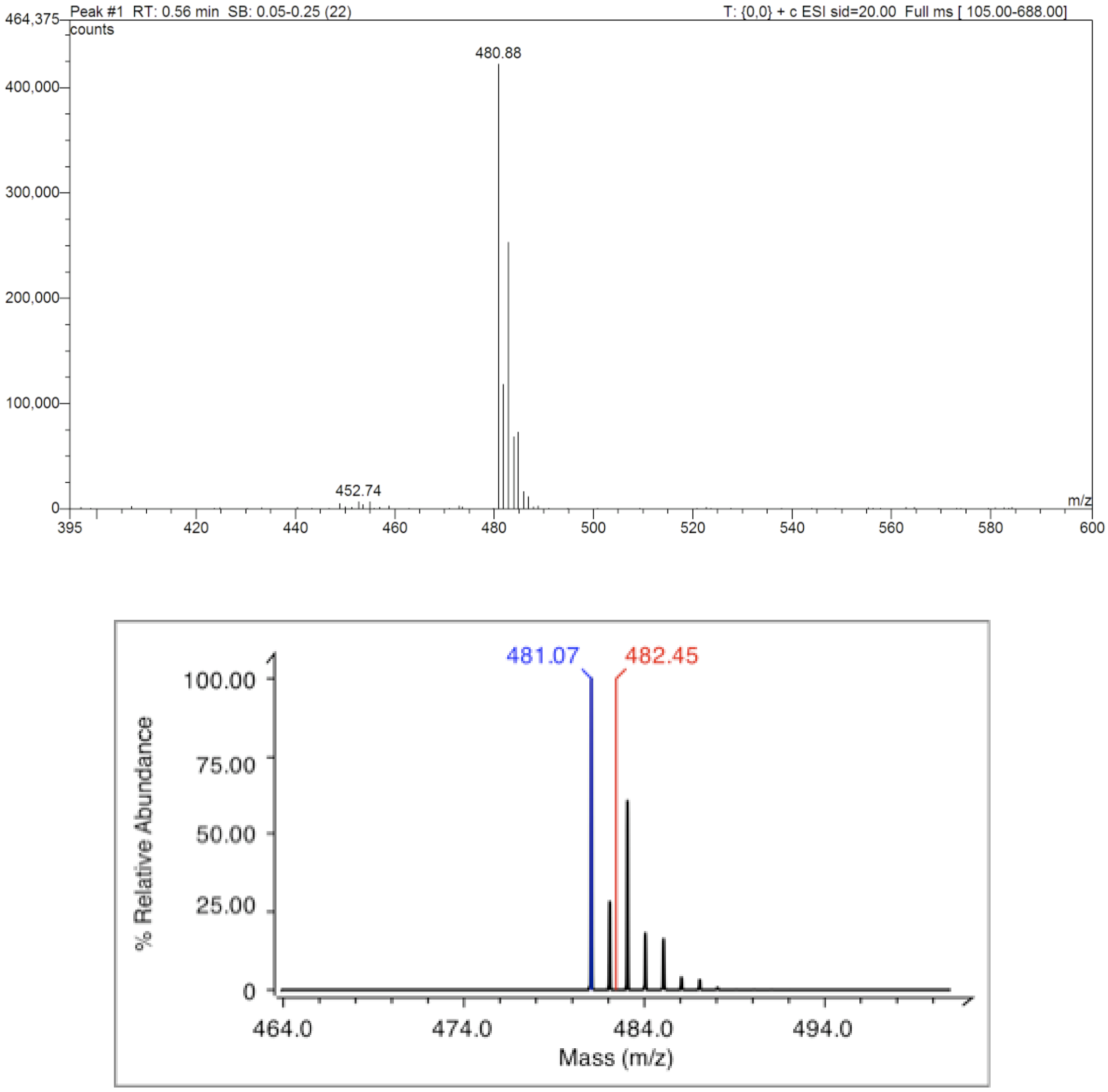


Figure S2. ESI-MS of Ni(L)$_2$ measured (top) using a dichloromethane solution and simulated for $C_{22}H_{31}S_4Ni$ $[MH]^+$ (bottom).

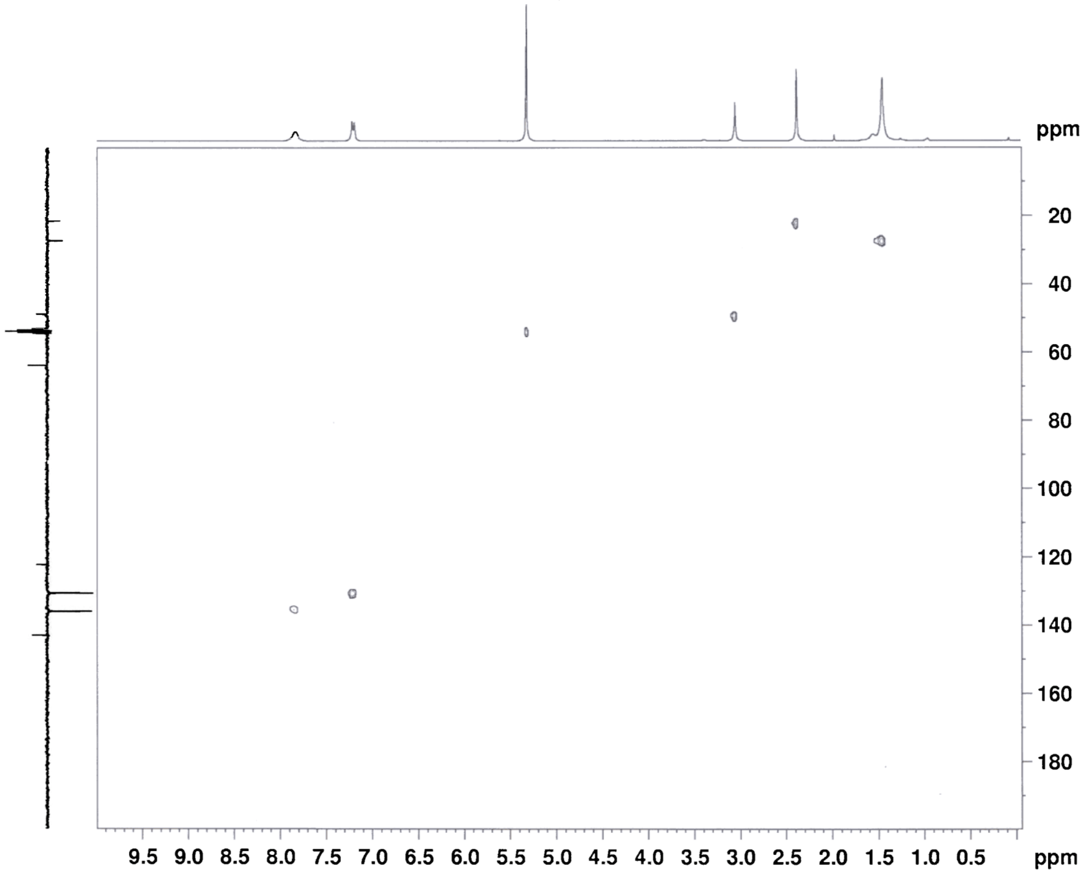


Figure S3: ^{13}C–^{1}H HSQC spectrum of $[\{Ni(L)_2\}_2(CuI)_6]$ **2** in CD_2Cl_2 at 293 K.

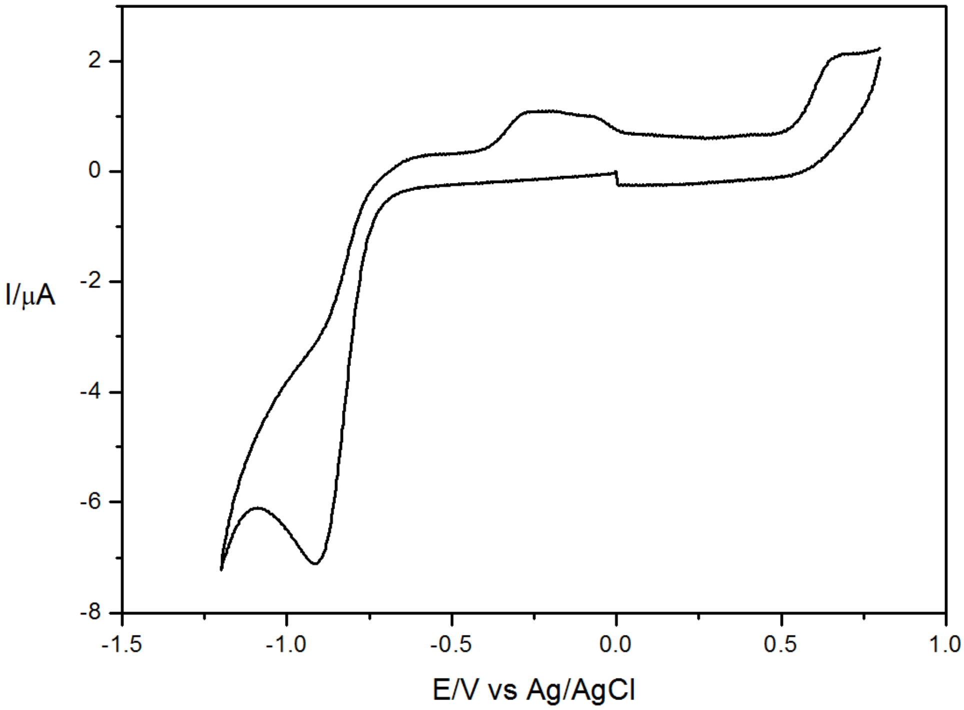


Figure S4: Cyclic voltammogram of 0.5 mM solution of **2** in CH_2Cl_2 containing 0.05 M $(NBu_4)PF_6$. Scan rate 100 mV s^{-1}. Static glassy carbon disc working, Pt wire counter electrodes used with Ag/AgCl reference electrode.

Table S1. Selected interatomic distances (Å) and angles (°) of $[\{Ni(L)_2\}_2(CuI)_6]$ **2**.

Cu1···Cu1A	2.6032(10)	Cu2···Cu2A	4.0309(10)
Cu1···Cu3	5.3644(2)	Cu1···Cu2	3.9844(9)
Ni1···Ni1A	6.6421(9)	Ni1···Cu1	3.5495(9)
Ni1···Cu2	3.8655(9)	Ni1···Cu3	3.5982(10)
Ni1–S6	2.1641(14)	Ni1–S9	2.2028(16)
Ni1–S16	2.1757(15)	Ni1–S19	2.1932(14)
Cu1–S6	2.2925(14)	Cu2–S6	2.4417(15)
Cu1–I1	2.5955(8)	Cu1–I2	2.5271(8)
Cu2–I2A	2.6337(7)	Cu2–I3A	2.6296(7)
S6–Ni1–S9	92.17(6)	S9–Ni1–S19	90.04(6)
S16–Ni1–S19	92.08(6)	S6–Ni1–S16	85.82(6)
S6–Ni1–S19	176.89(6)	S9–Ni1–S16	176.47(6)
S6–Cu1–I1	109.11(4)	I1–Cu1–I2	124.21(3)
S6–Cu1–I2	126.61(4)	S6–Cu2–I2A	110.40(4)
I2A–Cu2–S16A	99.90(4)	I3A–Cu2–S16A	107.65(4)
S6–Cu2–I3A	98.61(4)	S6–Cu2–S16A	122.29(5)
I2A–Cu2–I3A	119.38(3)		

Crystallographic data of complex 2. $C_{44}H_{60}Cu_6I_6Ni_2S_8$, Fw = 2105.46, dark brown needles, 0.04 × 0.07 × 0.24 mm^3, triclinic, P–1 (no. 2), a = 11.6566(5), b = 14.1559(4), c = 19.9857(7) Å, α = 86.088(1), β = 84.143(1), γ = 70.505(2) °, V = 3090.5(2) $Å^3$, Z = 2, D_x = 2.263 g cm^{-3}, μ = 5.915 mm^{-1}. 67305 Reflections were measured up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.62 $Å^{-1}$. An absorption correction based on multiple measured reflections was applied (0.48–0.87 correction range). 12170 Reflections were unique (R_{int} = 0.063), of which 8494 were observed [$I > 2\sigma(I)$]. 607 Parameters were refined. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0361/0.0553. $R1/wR2$ [all refl.]: 0.0742/0.0634. S = 1.022. Residual electron density between −0.90 and 0.98 $eÅ^{-3}$.

References:

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