Electronic Supplementary Information for Dalton Transactions

Hexanuclear [Ni_6L_{12}] metallacrown framework consisting of NiS_4 square-planar and NiS_5 square-pyramidal building blocks†

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Electronic Supplementary Information (ESI)

Experimental Section

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 nickel complexes were synthesized in an argon atmosphere using standard Schlenk techniques. Solvents were deoxygenated by bubbling through a stream of argon or by the freeze–pump–thaw methods and were dried over molecular sieves.

Physical Measurements: Elemental analyses were carried out on a Perkin-Elmer series II CHNS/O analyser 2400. NMR spectra were taken on a Bruker WM 300 MHz spectrometer. Chemical shifts are indicated in ppm relative to tetramethylsilane (TMS). The electrochemistry measurements were performed with an Autolab PGstat10 potentiostat controlled by GPES4 software. A three-electrode system was used, consisting of a platinum working electrode, a platinum auxiliary electrode and an Ag/AgCl reference electrode. The experiments were carried out in dichloromethane at room temperature in an argon atmosphere with tetrabutylammonium hexafluorophosphate (0.10 M) 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. 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 with 1% HOAc.

X-ray crystal structure determinations: Reflections were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) at a temperature of 150 K. The structures were solved with automated Patterson methods using the program DIRDIF[1] and refined with SHELXL-97[2] against F^2 of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[3]

Synthesis of 2-[(4-chlorophenyl)thio]ethanol. (A) 4-Chlorobenzenethiol (8.68 g, 60 mmol) and 2-chloroethanol (4.83 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 at 0 °C. Formed NaCl was removed by filtration after two hours stirring at 60 °C. After evaporating the ethanol under reduced pressure, water was added and the product was extracted with chloroform (2 × 30 ml). The combined chloroform layers were dried with $MgSO_4$ and evaporated to get a colorless oil (yield: 8.46 g, 75%). ^{1}H NMR $\delta_\mathbf{H}$ [300.13 MHz, DMSO-d$_6$, 298 K] 7.33 (s, 4H, phenyl ring), 3.03 (t, 2H, –S–CH_2–CH_2–OH), 3.55 (q, 2H, –S–CH_2–CH_2–OH), 4.96 (t, 1H, –O*H*). ^{13}C NMR δ_C [75.47 MHz, DMSO-d$_6$, 298 K] 130.07 (Ph–C1), 128.82 (Ph–C2), 129.47 (Ph–C3), 135.59 (Ph–C4), 59.70 (–S–CH_2–CH_2–OH), 34.99 (–S–CH_2–CH_2–OH).

Synthesis of 1-chloro-4-[(2-chloroethyl)thio]benzene. (B) To a solution of **A** (8.46 g, 44.8 mmol) in 30 ml chloroform was slowly added a solution of excess $SOCl_2$ (10 g, 84 mmol) in 30 ml chloroform. After an hour stirring the chloroform and excess thionyl chloride were evaporated under reduced pressure to yield 9.28 g of a bright yellow oil (100%). ^{1}H NMR $\delta_\mathbf{H}$ [300.13 MHz, $CDCl_3$, 298 K] 7.31 (2d, 4H, phenyl ring), 3.19 (t, 2H, –S–CH_2–CH_2–Cl), 3.60 (t, 2H, –S–CH_2–CH_2–Cl). ^{13}C NMR δ_C [75.47 MHz, $CDCl_3$, 298 K] 132.73 (Ph–C1), 129.24 (Ph–C2), 131.73 (Ph–C3), 133.08 (Ph–C4), 42.03 (–S–CH_2–CH_2–Cl), 36.28 (–S–CH_2–CH_2–Cl).

Synthesis of 2-[(4-chlorophenyl)thio]ethylimidothiocarbamate hydrochloride (1). To a solution of **B** (9.28 g, 44.8 mmol) in 30 ml ethanol was added a solution of thiourea (3.04 g, 40 mmol) in 60 ml ethanol. After 3 hours of reflux the solvent was evaporated under reduced pressure, which resulted in a solid. This solid was washed with a small amount of ethanol and diethyl ether to obtain a white product in a yield of 9.87 g (78%). ^{1}H NMR $\delta_\mathbf{H}$ [300.13 MHz, DMSO-d$_6$, 298 K] 9.34 (s, 4H, –S– $C(N\mathit{H}_2)_2{}^+Cl^-$), 7.35 (2d, 4H, phenyl ring), 3.42 (t, 2H, –S–CH$_2$–CH_2–), 3.25 (t, 2H, –S–CH_2–CH$_2$–). ^{13}C NMR δ_C [75.47 MHz, DMSO-d$_6$, 298 K] 169.59 (–S–$\mathit{C}(NH_2)_2{}^+Cl^-$), 133.78 (Ph–C1), 130.56 (Ph–C2), 129.18 (Ph–C3), 131.07 (Ph–C4), 30.03 (–S–CH$_2$–CH$_2$–), 31.98 (–S–CH$_2$–CH$_2$–).

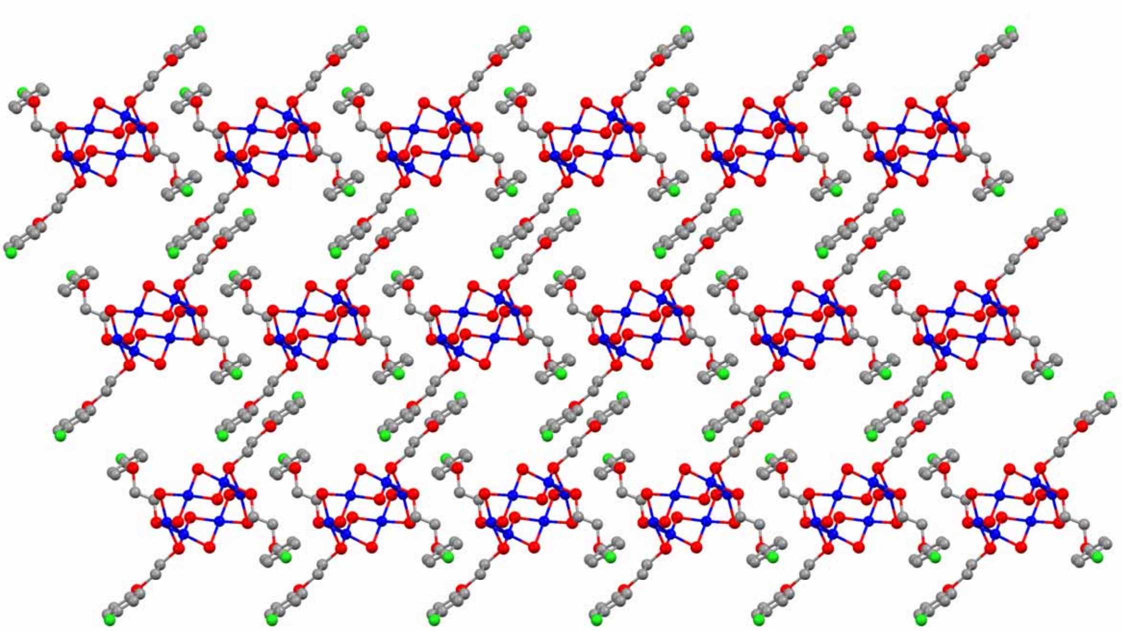

Figure S1. View of π···π stacking of **2** (Cg(5), C(13) - C(18); Cg(6), C(23) - C(28)) along *c* axis. Ni, blue; S, red; Cl, green; I, violet; C, grey. Hydrogens and the groups not involving in packing in this view are omitted for clarity.

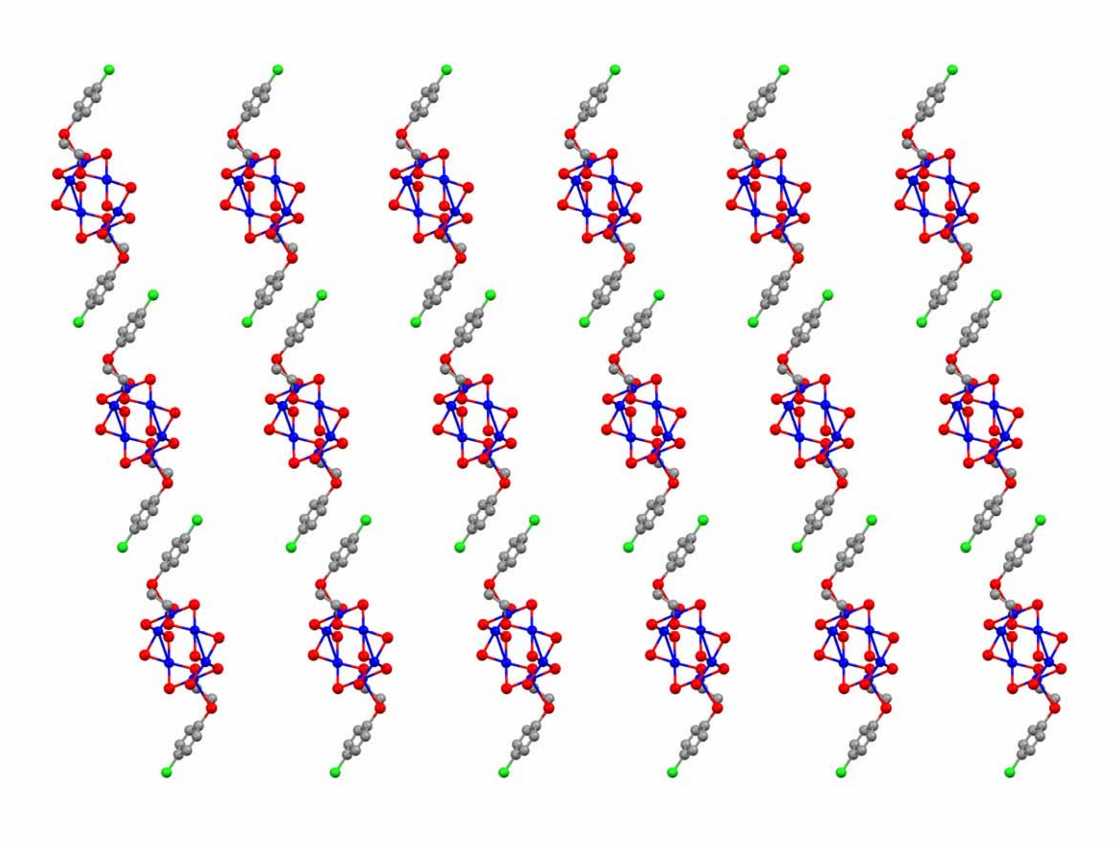

Figure S2. View of π···π stacking of **2** (Cg(9), C(53) - C(58)) along *a* axis. Ni, blue; S, red; Cl, green; I, violet; C, grey. Hydrogens and the groups not involving in packing in this view are omitted for clarity.

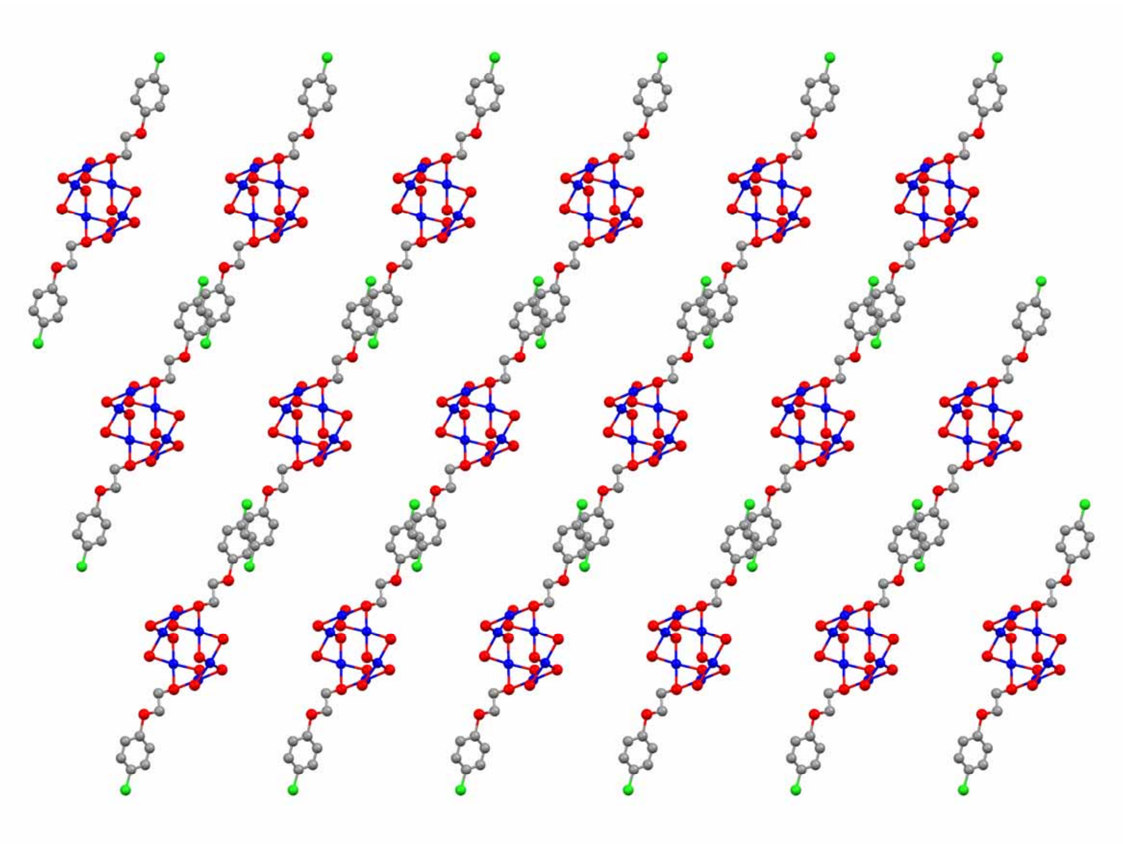

Figure S3. View of π···π stacking of **2** (Cg(10), C(63) - C(68)) along *a* axis. Ni, blue; S, red; Cl, green; I, violet; C, grey. Hydrogens and the groups not involving in packing in this view are omitted for clarity.

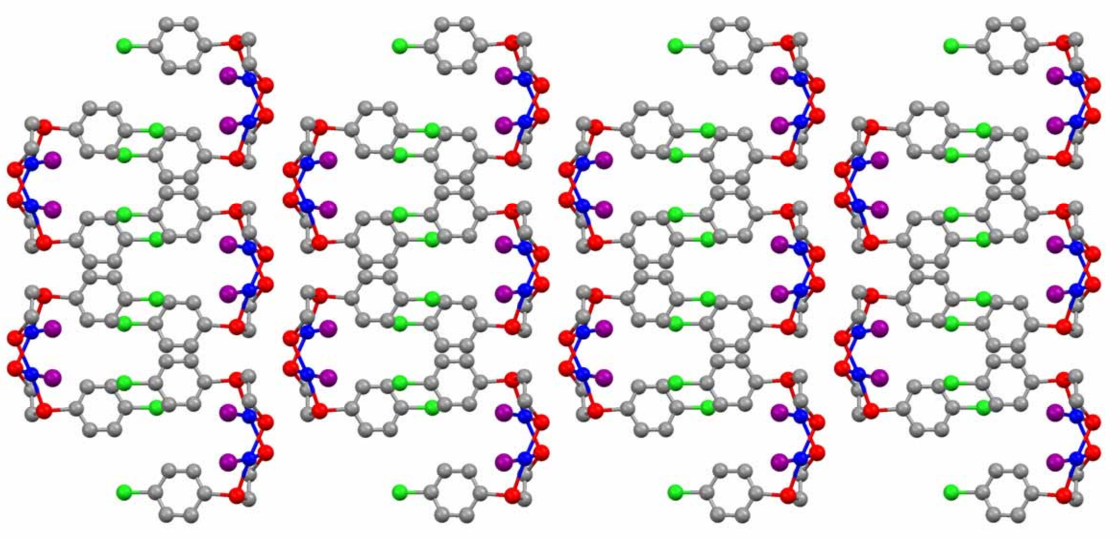

Figure S4. View of packing of **3** along *a* axis. Ni, blue; S, red; Cl, green; I, violet; C, grey. Hydrogens are omitted for clarity.

References:

1. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smiths and C. Smykalla, in *The DIRDIF99 program system, Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, **1999**.
2. G. M. Sheldrick, in *SHELXL-97. Program for crystal structure refinement*, University of Göttingen, Germany, **1997**.
3. A. L. Spek, J. Appl. Cryst., **2003**, 36, 7.