

Supporting Information

Synthesis of *o*-thiosalicylaldehyde: To a solution of TMEDA (3.25 ml, 21.5 mmol) in anhydrous hexane (30 ml) under Ar was added ⁿBuLi (2.35 M, 9.13 ml, 21.5 mmol) at 0°C followed by benzenethiol (1.03 ml, 10 mmol). The reaction was stirred using a thick magnetic stirrer bar at 0°C for 30 min before being allowed to warm to room temperature and left to stir for 22 h. Dry 1-formylpiperidine (2.66 ml, 24 mmol) was added dropwise such that the temperature did not exceed 70°C and the reaction stirred at room temperature for a further 16 h before being addition HCl (5%, 100 ml). Et₂O (40 ml) was added to the mixture and the organic layer separated. The aqueous layer was further extracted with Et₂O (3 x 20 ml) and the organic extracts combined before drying over MgSO₄. The solution was concentrated *in vacuo* to ca. 5 ml before MeCN (40 ml) was added. Et₂O was then removed *in vacuo* to yield an MeCN solution of crude thiosalicylaldehyde (7.9 mmol, 79%).

Synthesis of [Zn(L)]: A solution of Zn(OAc)₂·2H₂O (0.58 g, 2.65 mmol) in MeOH (5 ml) was added to a solution of thiosalicylaldehyde (5.31 mmol) in MeCN (20 ml). A solution of triethylamine (0.81 g, 8.00 mmol) in MeOH (5 ml) was added to the mixture. A solution of 2,2-dimethyl-1,3-diaminopropane (0.22 g, 2.12 mmol) in MeOH (5 ml) was then added dropwise to the orange solution. The reaction mixture was stirred for 1 h before being filtered to yield the crude product which was recrystallised from CH₂Cl₂ to give yellow crystals of [Zn(L)] (0.97 g, 2.39 mmol, 90%). ¹H-NMR (300.13 MHz, CDCl₃, 298 K): δ_H 8.3 (2H, s, N=CH), 7.3 (2H, d, ArH), 7.2 (2H, d, ArH), 7.2 (2H, t,

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ArH), 7.1 (2H, t, ArH), 3.5 (4H, sb, CH₂), 1.1 (6H, s, CH₃). ¹³C-NMR (300.13 MHz, CDCl₃, 298 K): δ_C 170.58 (N=CH), 137.09 (Ar CH), 137.05 (Ar CH), 131.08 (Ar CH), 129.35 (Ar CH), 122.41 (Ar CH), 122.39 (Ar CH), 68.29 (CH₂), 36.16 (C(CH₃)₂), 24.94 (C(CH₃)₂). IR (KBr, cm⁻¹): 2952 w, 2917 w, 2863 w, 1632 s, 1587 m, 1540 m, 1462 m, 1442 w, 1409 m, 1391 w, 1336 w, 1252 w, 1203 w, 1162 w, 1127 m, 1065 m, 1027 m, 971 w, 868 w, 760 m, 752 m, 721 w, 686 w, 647 w. MS (ES+, m/z): 405 (ZnL^{C3} + H⁺). Elemental analysis: found (calculated for C₁₉H₂₀N₂S₂Zn .0.25 H₂O) C 55.92 (55.88); H 4.94 (5.06); N 6.65 (6.86).

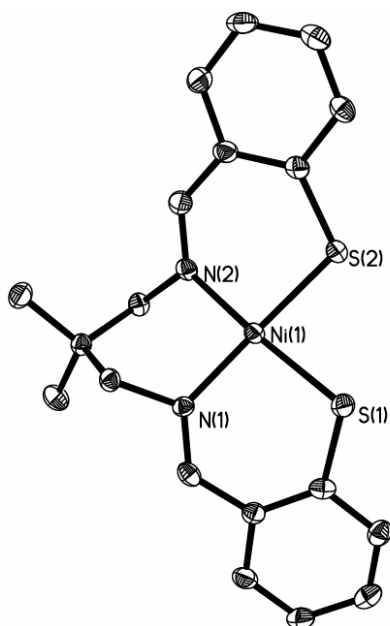
Synthesis of [Ni(L)]: Ni(NO₃)₂.6H₂O (0.58 g, 2.0 mmol) in MeOH (3 ml) was added to a solution of [Zn(L)] (0.81 g, 2.0 mmol) in CH₂ (15 ml) and the solution stirred for 2 h. Excess MeOH was added to the brown solution and the precipitate collected by filtration in air. The crude product was washed with cold MeOH and recrystallised from CH₂Cl₂ to give brown crystals of [Ni(L)] (0.71 g, 1.8 mmol, 92 %). ¹H-NMR (300.13 MHz, CDCl₃, 298 K): δ_H 7.70 (2H, s, N=CH), 7.26 (4H, m, ArH), 7.19 (2H, dd, ArH), 7.00 (2H, dd, ArH), 3.62 (4H, s, CH₂), 1.04 (6H, s, CH₃). ¹³C-NMR (300.13 MHz, CDCl₃, 298 K): δ_C 165.20 (N=CH), 145.40 (Ar CH), 133.60 (Ar CH), 130.80 (Ar CH), 130.69 (Ar CH), 130.41 (Ar CH), 122.17 (Ar CH), 69.65 (CH₂), 34.78 (C(CH₃)₂), 24.36 (C(CH₃)₂). IR (KBr, cm⁻¹): 2959 s, 2924 s, 1615 vs, 1586 vs, 1540 s, 1446 s, 1427 m, 1389 m, 1221 s, 1128 m, 1079 s, 1061 m, 1035 m, 948 m, 747 vs, 720 m. MS (ES+, m/z): 399 (M + H⁺), 797 (2 x M + H⁺). Elemental analysis: found (calculated for C₁₉H₂₀N₂S₂Ni) C 57.19 (57.17); H 5.08 (5.05); N 6.94 (7.02).

Syntheses of 1 and 2: To a stirred suspension of [Ni(L)] (0.27 g, 0.67 mmol) in toluene (20 ml) was added Fe₂(CO)₉ (0.24 g, 0.67 mmol). After 72 h the mixture was filtered and solvent removed *in vacuo* from the filtrate. Column chromatography (silica gel, CH₂Cl₂ : toluene, 1 : 1) yielded orange / brown [NiL]{Fe(CO)₃}₂, **2** (0.16 g, 0.23 mmol, 34%), and red / brown [NiL]Fe(CO)₃, **1** (0.11 g, 0.21 mmol, 31%), as the first and second bands, respectively.

1: IR (KBr, cm⁻¹): 2958 w, 2930 w, 2045 vs, 1973 vs, 1614 m, 1589 m, 1538 w, 1462 m, 1385 w, 1368 w, 1250 w, 1219 w, 1081 w, 1026 w, 752 m, 623 m, 614 m. MS (FAB, m/z): 538 (M⁺), 510 ([M-CO]⁺), 482 ([M-2CO]⁺), 398 ([M-Fe(CO)₃]⁺). Elemental analysis: found (calculated for C₂₂H₂₀N₂S₂O₃NiFe) C 48.98 (49.02); H 3.67 (3.74); N 5.07 (5.20).

2: IR (KBr, cm⁻¹): 2962 w, 2936 w, 2050 vs, 2000 vs, 1977 vs, 1636 m, 1591 m, 1575 m, 1524 w, 1484 m, 1457 m, 1384 m, 1261 m, 1129 w, 1080 w, 1026 w. MS (FAB, m/z): 678 (M⁺), 622 ([M-2CO]⁺), 538 ([M-Fe(CO)₃]⁺), 482 ([M-Fe(CO)₅]⁺), 398 ([M-Fe₂(CO)₆]⁺). Elemental analysis: found (calculated for C₂₅H₂₀N₂S₂O₆NiFe₂) C 44.19 (44.23); H 2.84 (2.97); N 4.04 (4.13).

X-ray Crystal Structure of [Ni(L)]:



Crystallographic data for [Ni(L)]: $C_{19}H_{20}N_2S_2Ni$, $M = 399.20$, triclinic, $a = 8.5701(2)$, $b = 9.057(2)$, $c = 11.767(3)$ Å, $\alpha = 76.164(3)$, $\beta = 87.506(3)$, $\gamma = 89.673(3)^\circ$, $U = 866.0(6)$ Å³, $T = 150(2)$ K, space group P-1, $Z = 2$, μ (Mo-K α) = 1.333 mm⁻¹, 7692 data collected, 3955 independent reflections ($R_{int} = 0.033$). Final $R1$ [$I > 2\sigma(I)$] = 0.0401, $wR2$ [all data] = 0.0649.

Electronic Spectra of **1**, **2** and [Ni(L)] recorded in CH₂Cl₂ solution.

