Phase control during the synthesis of nickel sulphide nanoparticles from dithiocarbamate precursors

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Supplementary Information



Figure S1 - TGA (black) and DSC (blue) graphs for complexes (a) 1, (b) 2, (c) 3 and (d) 4.



Figure S2 - XRD patterns for materials obtained from (a) 1, (b) 2, (c) 3 and (d) 4, with reference pattern for bulk α -NiS (ICDD card No. 02-1273).



Figure S3 - TEM images of samples prepared from **3** at (a) 150, (b) 180, (c) 260 and (d) 280 °C; (e) average particle size vs. temperature of decomposition; (f) HRTEM image of β-NiS synthesised at 280 °C.



Figure S4 - XRD patterns for samples prepared from 3 at (a) 5, (b) 10, (c) 20 (d) 40 and (e) 50 mM concentration, with reference pattern for bulk α -NiS (ICDD card No. 02-1273).



Figure S5 – TEM images of samples prepared from **3** at (a) 5, (b) 10, (c) 20 (d) 40 and (e) 50 mM concentration.



Figure S6.1 – 13 C NMR spectra of 6, 3 and 2eq. 6 + 3. Mixture explained in S6.4



Figure S6.2 – ¹H NMR spectra of 6, 3 and 2eq. 6 + 3. Mixture explained in S6.43



Figure S6.3 – ¹H NMR spectrum of 2 eq 6 to 3.



Figure S6.4- 13C NMR spectrum of 2 eq 6 to 3. Note S₂C environment 'e' not detected due to low amounts of 3 remaining in solution.



Figure S7 - *in situ* decomposition XAS of 5 plus 3 in oleylamine.



Figure S8 - XAS spectra of 5 and 3 in oleylamine (left), and during heating (right) showing the formation of a square planar complex.

Synthesis of complexes 1-6

 $[Ni(S_2CNMe_2)_2]$ (1) - NaS₂CNMe₂ (2.86 g, 20 mmol) was dissolved in water (50 mL) and added dropwise over 10 min to a solution of NiCl₂·6H₂O (2.38 g, 10 mmol) dissolved in 50 mL of water, whereupon a green precipitate formed. This mixture was vigorously stirred for 2 h, filtered, washed with water (3 x 30 mL) and evaporated to dryness. The resulting green powder was dissolved in 100 mL of dichloromethane (DCM) and stirred with magnesium sulphate for 30 min, after which the mixture was filtered and the filtrate dried *in vacuo*. Yield 2.24 g, 75 %. Anal. Calc. for C₆H₁₂N₂S₄Ni: C, 24.09; H, 4.04; N, 9.37. Found: C, 24.42; H, 4.17; N, 8.81. ¹H NMR δ /ppm (CDCl₃): 3.18 (s, 12H, CH₃). ¹³C{¹H} NMR δ /ppm (CDCl₃): 38.4 (CH₃), 207.7 (CS₂). MS: *m/z* 298 [M⁺], 88 [SCNMe₂]. IR (*v*_{max} cm⁻¹): 1516 (s) [N=C], 970 (s) [C=S].

[Ni(S₂CNEt₂)₂] (**2**) - Prepared following the method above using NaS₂NCEt₂ (4.51 g, 20 mmol). Yield 2.86 g, 81 %. Anal. Calc. for C₁₀H₂₀N₂S₄Ni: C, 33.81; H, 5.67; N, 7.89. Found: C, 33.76; H, 5.66; N, 7.90. ¹H NMR δ/ppm (CDCl₃): 1.22 (t, J = 7.2 Hz, 12H, CH₂CH₃), 3.59 (q, J = 7.2 Hz, 8H, CH₂CH₃). ¹³C{¹H} NMR δ/ppm (CDCl₃): 12.5 (CH₂CH₃), 43.9 (CH₂CH₃), 206.1 (CS₂). MS: m/z 354 [M⁺], 116 [SCNEt₂]. IR (v_{max} cm⁻¹): 1512 (s) [N=C], 991 (s) [C=S].

[Ni(S₂CN^{*i*}Bu₂)2] (**3**) - ^{*i*}Bu₂NH (3.49 mL, 20 mmol) was added to NaOH (0.80 g, 20 mmol) dissolved in H₂O (50 mL). To this mixture CS₂ (1.20 mL, 20 mmol) was added dropwise over 10 minutes and the mixture stirred overnight. A solution of NiCl₂· 6H₂O (2.38 g, 10 mmol) dissolved in 50 mL of water was added dropwise over 5 minutes, whereupon a green precipitate formed. This mixture was vigorously stirred for 2 h, filtered, washed with water (3 x 30 mL) and evaporated to dryness. The resulting green powder was dissolved in 100 mL of dichloromethane (DCM) and stirred with magnesium sulphate for 30 min, after which the mixture was filtered and the filtrate dried *in vacuo*. Yield 3.97 g, 85 %. Anal. Calc. for C₁₈H₃₆N₂S₄Ni: C, 46.25; H, 7.76; N, 5.99. Found: C, 46.23; H, 7.81; N, 6.03. ¹H NMR δ /ppm (CDCl₃): 0.91 (d, *J* = 6.6 Hz, 24H, CH₃), 2.17 (m, *J* = 6.8 Hz, 4H, CH), 3.40 (d, *J* = 7.7 Hz, 8H, CH₂). ¹³C{¹H} NMR δ /ppm (CDCl₃): 20.1 (CH₃), 27.0 (CH), 56.3 (CH₂), 208.4 (CS₂). MS: *m/z* 467 [M⁺], 171 [S₂CN^{*I*}Bu₂]. IR (*v*_{max} cm⁻¹): 1508 (s) [N=C], 981 (s) [C=S].

[Ni(S₂CNMeBu)₂] (**4**) - Prepared as above using MeBuNH (2.37 mL, 20 mmol). Yield 1.65 g, 43 %. Anal. Calc. for C₆H₁₂N₂S₄Ni: C, 37.60; H, 6.31; N, 7.31. Found: C, 37.51; H, 6.35; N, 7.30. ¹H NMR δ /ppm (CDCl₃): 0.94 (t, *J* = 7.3 Hz, 6H, CH₂(CH₂)₂CH₃), 1.33 (m, 4H, CH₂(CH₂)₂CH₃), 1.61 (m, 4H, CH₂(CH₂)₂CH₃), 3.13 (2, 6H, NCH₃), 3.57 (m, 6H, CH₂(CH₂)₂CH₃). ¹³C{¹H} NMR δ /ppm (CDCl₃): 13.9 ((CH₂)₃CH₃), 19.9 (CH₂), 29.0 (CH₂), 36.5 (CH₃), 51.2 (CH₂), 207.0 (CS₂). MS: *m*/*z* 382 [M⁺], 130 [S₂CNMeBu]. IR (*v*_{max} cm⁻¹): 1512 (s) [N=C], 966 (s) [C=S].

 $(S_2CN^iBu_2)_2$ (**5**) - iBu_2NH (2.62 mL, 15 mmol) was added to NaOH (0.60 g, 15 mmol) in water (50 mL). To this mixture CS₂ (0.90 mL, 15 mmol) was added dropwise over 10 mins and the mixture stirred overnight. An aqueous solution (20 mL) of K₃[Fe(CN)₆] (4.94 g, 15 mmol) was added dropwise over 10 mins and stirred vigorously for two hrs. The solution was filtered using a Büchner funnel, washed with water (1 x 20 mL) and dried *in vacuo*. The resulting beige solid was crushed to a powder using a mortar and pestle, washed with water (3 x 30 mL) and dried *in vacuo*. The resulting beige solid was crushed to a powder using a mortar and pestle, washed with water (3 x 30 mL) and dried *in vacuo* to produce a white powder. Yield 2.7897 g, 91 %. ¹H NMR δ /ppm (CDCl₃): 0.93 (d, *J* = 6.3 Hz, 12H, CH₃), 1.04 (d, *J* = 6.3 Hz, 12H, CH₃), 2.49 (m, 4H, CH), 3.84 (m, 8H, CH₂). ¹³C{¹H}</sup> NMR δ /ppm (CDCl₃): 20.3 (CH₃), 20.5 (CH₃), 26.1 (CH), 28.7 (CH), 61.8 (CH₂), 65.5 (CH₂), 194.3 (CS₂). Anal. Calc. for C₁₈H₃₆N₂S₄: C, 52.89; H, 8.88; N, 6.85. Found: C, 52.73; H, 9.07; N, 6.90. MS: *m/z* 408 [M⁺], 204 [M⁺ - (S₂CN^{*i*}Bu₂)].

(S₂CNMe₂)₂ (6) 97% purity was purchased from Sigma Aldrich.