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 – $^1$H NMR spectra of 6, 3 and 2eq. 6 + 3. Mixture explained in S6.43
Figure S6.3 – $^1$H NMR spectrum of 2 eq 6 to 3.
Figure S6.4- 13C NMR spectrum of 2 eq 6 to 3. Note SzC 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(S₂CNMe₂)₂] (I) - Na₂S CNMe₂ (2.86 g, 20 mmol) was 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 C₁₀H₂₀N₂S₂Ni: C, 33.81; H, 5.67; N, 7.89. Found: C, 33.76; H, 5.66; N, 7.90. IR (νmax cm⁻¹): 1512 (s) [N=C], 991 (s) [C=S].

[Ni(S₂CNEt₂)₂] (2) - Prepared following the method above using Na₂S CNEt₂ (4.51 g, 20 mmol). Yield 2.86 g, 81 %. Anal. Calc. for C₁₀H₂₀N₂S₂Ni: C, 33.81; H, 5.67; N, 7.89. Found: C, 33.76; H, 5.66; N, 7.90. IR (νmax cm⁻¹): 1508 (s) [N=C], 991 (s) [C=S].

[Ni(S₂CNBu₂)₂] (3) - 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 C₁₅H₂₆N₂S₂Ni: C, 46.25; H, 7.76; N, 5.99. Found: C, 46.23; H, 7.81; N, 6.03. IR (νmax cm⁻¹): 1516 (s) [N=C], 970 (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 C₁₅H₂₆N₂S₂Ni: C, 37.60; H, 6.31; N, 7.31. Found: C, 37.51; H, 6.35; N, 7.30. IR (νmax cm⁻¹): 12.5 (CH₃ CO), 1.33 (m, 4H, CH₂(CH₂)₂CH₂)), 1.61 (m, 4H, CH₂(CH₂)₂CH₂)), 3.13 (2, 6H, NCH₃)), 3.57 (m, 6H, CH₃(CH₂)₃CH₂), 13C [1H] NMR δ/ppm (CDCl₃): 13.9 ((CH₃)₂CH₂), 19.9 (CH₉), 29.0 (CH₂), 36.5 (CH₃), 51.2 (CH₂), 207.0 (CS₂). MS: m/z 382 [M⁺], 130 [S₂CNMeBu]. IR (νmax cm⁻¹): 1512 (s) [N=C], 966 (s) [C=S].

(S₂CNBu₂)₂ (5) - Bu₂NH (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 K₂[Fe(CN)₄] (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 to produce a white powder. Yield 2.7897 g, 91 %. IR (νmax cm⁻¹): 193 (d, J = 6.6 Hz, 12H, CH₂), 1.04 (d, J = 6.3 Hz, 12H, CH₂), 2.49 (m, 4H, CH), 3.84 (m, 8H, CH₂). 13C [1H] NMR δ/ppm (CDCl₃): 20.3 (CH₃), 20.5 (CH₂), 25.1 (CH), 28.7 (CH), 61.8 (CH₂), 65.5 (CH₃), 194.3 (CS₂). Anal. Calc. for C₁₅H₂₆N₂S₂C: 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⁺ - (S₂CNBu₂)], 172 [M⁺ - (SCN)₂].

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