Fe(II) and Fe(III) dithiocarbamate complexes as single source precursors to nanoscale iron sulfides: A combined synthetic and in-situ XAS approach

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Synthesis of dithiocarbamate salts

\([H_2NMe_2][S_2CNMe_2]\) Me₂NH (15 mmol, 7.50 mL of a 2M solution in THF) was dissolved in further THF (20 mL) CS₂ (0.45 mL, 7.5 mmol) was added slowly dropwise over five mins whereupon a white precipitate began to form. The mixture was stirred for two h, filtered using a Büchner funnel and washed with THF (3 x 10 mL). Yield 1.1200 g, 90 %. ¹H NMR δ/ppm (CDCl₃): 2.78 (s, 6H, CH₃), 3.58 (s, 6H, CH₃), 8.42 (broad s, 2H, [(CH₃)₂N-H₂]). ¹³C{¹H} NMR δ/ppm (CDCl₃): 35.4 (CH₃), 44.8 (CH₃), 210.2 (CS₂). Anal. Calc. for C₅H₁₄N₂S₂: C, 36.11; H, 8.49; N, 16.84. Found: C, 35.56; H, 8.38; N, 16.57. MS(EI): m/z 121 [S₂CN(CH₃)₂ + H⁺].

\([NMe₄][S₂CNET₂]\) To an ice-cooled solution of Me₄NOH (10 mmol, 3.65 g of a 25% wt solution in methanol) and Et₂NH (10 mmol) in methanol (50 mL), CS₂ (10 mmol, 0.60 mL) was added dropwise over five mins. The solution was allowed to come to room temperature and stirred overnight. Methanol was removed in vacuo resulting in a pale yellow crystalline powder. Yield 2.2075 g, 99 %. ¹H NMR δ/ppm (CDCl₃): 1.23 (t, 6H,
= 7.0 Hz, CH$_2$CH$_3$), 4.14 (q, 4H, $J$ = 7.0 Hz, CH$_2$CH$_3$). $^{13}$C{$^1$H} NMR δ/ppm (CDCl$_3$): 12.7 (CH$_2$CH$_3$), 47.5 (CH$_2$CH$_3$), 56.2 (N(CH$_3$)$_4$) 210.6 (CS$_2$). Anal. Calc. for C$_9$H$_{22}$N$_2$S$_2$: C, 48.60; H, 9.97; N, 12.06. Found: C, 48.41; H, 9.54; N, 11.73. MS(EI): m/z 148 [S$_2$CN(CH$_2$CH$_3$)$_2$].

[NMe$_4$][S$_2$CNMeBu] To an ice-cooled solution of Me$_4$NOH (10 mmol, 3.65 g of a 25% wt solution in methanol) and MeBuNH (10 mmol) in methanol (50 mL), CS$_2$ (10 mmol, 0.60 mL) was added dropwise over five mins. The solution was allowed to come to room temperature and stirred overnight. Methanol was removed in vacuo resulting in a pale yellow crystalline powder. Yield 1.1578 g, 98 %. $^1$H NMR δ/ppm (CDCl$_3$): 0.91 (t, 3H, $J$ = 7.4 Hz, S$_2$CN(CH$_3$)(CH$_2$)$_3$CH$_3$), 1.31 (m, 2H, CH$_2$), 1.65 (m, 2H, CH$_2$), 3.51 (s, 3H, S$_2$CN(CH$_3$)(CH$_2$)$_3$CH$_3$), 3.55 (s, 12H, N(CH$_3$)$_4$), 4.14 (m, 2H, CH$_2$). $^{13}$C{$^1$H} NMR δ/ppm (CDCl$_3$): 14.19 (S$_2$CN(CH$_3$)(CH$_2$)$_3$CH$_3$), 20.32 (CH$_2$), 29.44 (CH$_2$), 42.41 (CH$_2$), 59.00 (S$_2$CN(CH$_3$)(CH$_2$)$_3$CH$_3$), 56.17 (N(CH$_3$)$_4$) 211.77 (CS$_2$). Anal. Calc. for C$_{10}$H$_{24}$N$_2$S$_2$: C, 50.80; H, 10.23; N, 11.85. Found: C, 49.47; H, 10.13; N, 11.41. MS(EI): m/z 162 [S$_2$CN(CH$_3$)(CH$_2$)$_3$CH$_3$].

Apparatus used for decomposition studies