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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] Me_2NH (15 mmol, 7.50 mL of a 2M solution in THF) was dissolved in further THF (20 mL) CS_2 (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 %. **^{1}H NMR δ/ppm ($CDCl_3$):** 2.78 (s, 6H, CH_3), 3.58 (s, 6H, CH_3), 8.42 (broad s, 2H, [$(CH_3)_2NH_2$]). **^{13}C{^{1}H} NMR δ/ppm ($CDCl_3$):** 35.4 (CH_3), 44.8 (CH_3), 210.2 (CS_2). **Anal. Calc. for $C_5H_{14}N_2S_2$:** C, 36.11; H, 8.49; N, 16.84. Found: C, 35.56; H, 8.38; N, 16.57. **MS(EI):** *m/z* 121 [$S_2CN(CH_3)_2 + H^+$].

[NMe_4][S_2CNEt_2] To an ice-cooled solution of Me_4NOH (10 mmol, 3.65 g of a 25% wt solution in methanol) and Et_2NH (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 2.2075 g, 99 %. **^{1}H NMR δ/ppm ($CDCl_3$):** 1.23 (t, 6H, *J*

= 7.0 Hz, $\mathrm{CH_2}\mathit{CH}_3$), 4.14 (q, 4H, *J* = 7.0 Hz, $\mathit{CH}_2\mathrm{CH_3}$). **^{13}C{^{1}H} NMR δ/ppm ($CDCl_3$):** 12.7 ($\mathrm{CH_2}\mathit{CH}_3$), 47.5 ($\mathit{CH}_2\mathrm{CH_3}$), 56.2 ($\mathrm{N}(\mathit{CH}_3)_4$) 210.6 ($\mathit{C}\mathrm{S_2}$). **Anal. Calc. for $C_9H_{22}N_2S_2$:** C, 48.60; H, 9.97; N, 12.06. Found: C, 48.41; H, 9.54; N, 11.73. **MS(EI):** *m/z* 148 [$S_2CN(CH_2CH_3)_2$].

[NMe_4][$S_2CNMeBu$] To an ice-cooled solution of Me_4NOH (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, $\mathrm{S_2CN(CH_3)(CH_2)_3}\mathit{CH}_3$), 1.31 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 3.51 (s, 3H, $\mathrm{S_2CN}(\mathit{CH}_3)\mathrm{(CH_2)_3CH_3}$), 3.55 (s, 12H, $\mathrm{N}(\mathit{CH}_3)_4$), 4.14 (m, 2H, CH_2). **^{13}C{^{1}H} NMR δ/ppm ($CDCl_3$):** 14.19 ($\mathrm{S_2CN(CH_3)(CH_2)_3}\mathit{C}\mathrm{H_3}$), 20.32 ($\mathit{C}\mathrm{H_2}$), 29.44 ($\mathit{C}\mathrm{H_2}$), 42.41 ($\mathit{C}\mathrm{H_2}$), 59.00 ($\mathrm{S_2CN}(\mathit{C}\mathrm{H_3})\mathrm{(CH_2)_3CH_3}$), 56.17 ($\mathrm{N}(\mathit{C}\mathrm{H_3})_4$) 211.77 ($\mathit{C}\mathrm{S_2}$). **Anal. Calc. for $C_{10}H_{24}N_2S_2$:** C, 50.80; H, 10.23; N, 11.85. Found: C, 49.47; H, 10.13; N, 11.41. **MS(EI):** *m/z* 162 [$S_2CN(CH_3)(CH_2)_3CH_3$].

Apparatus used for decomposition studies