Metal Complexes of Thiobiurets and Dithiobiurets: Novel Single Source Precursors for Metal Sulfide Thin Film Nanostructures

Karthik Ramasamy, Mohammad A. Malik, Paul O’Brien* and James Raftery

The School of Chemistry and Manchester Materials Center, The University of Manchester, Oxford Road, Manchester, UK M13 9PL.

Supporting Information

* Proofs to

Professor Paul O’Brien

School of Chemistry

The University of Manchester

Oxford Rd, Manchester, M13 9PL

Fax: 44-161 275 4598; Tel: 44-161 275 4653;

E-mail: paul.obrien@manchester.ac.uk
† All preparations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. All reagents were purchased from Sigma-Aldrich chemical company and used as received. Solvents were distilled prior to use. Elemental analysis was performed by the University of Manchester micro-analytical laboratory. In a typical deposition, 0.20 g of the precursor was dissolved in 20 ml tetrahydrofuran in a two-necked 100 ml round-bottom flask with a gas inlet that allowed the carrier gas (argon) to pass into the solution to aid the transport of the aerosol. This flask was connected to the reactor tube by a piece of reinforced tubing. The argon flow rate was controlled by a Platon flow gauge. Seven glass substrates (approx. 1 x 3 cm) were placed inside the reactor tube, which is placed in a CARBOLITE furnace. The precursor solution in a round-bottom flask was kept in a water bath above the piezoelectric modulator of a PIFCO ultrasonic humidifier (Model No. 1077). The aerosol droplets of the precursor thus generated were transferred into the hot wall zone of the reactor by carrier gas. Both the solvent and the precursor were evaporated and the precursor vapour reached the heated substrate surface where thermally induced reactions and film deposition took place. X-ray diffraction studies were performed on a Bruker AXS D8 diffractometer using Cu-Kα radiation. The samples were mounted flat and scanned between 20 to 80 °C in a step size of 0.05 with a count rate of 9 sec. Films were carbon coated using Edward’s E306A coating system before carrying out SEM and EDX analyses. SEM analysis was performed using a Philips XL 30FEG and EDX was carried out using a DX4 instrument. TEM analysis was performed using Philips cm200 instrument

[Fe$_2$(C$_{10}$H$_{20}$N$_3$O$_5$)$_4$(OMe)$_2$] (1) A solution of di-iso-propylcarbamyl chloride (1.0 g, 6 mmol) and sodium thiocyanate (0.49 g, 6 mmol) in acetonitrile (25 mL) was heated to reflux with continuous stirring for 1 h, during which time a fine precipitate of
sodium chloride formed. To the cooled reaction mixture was added diethylamine (1.26 mL, 12 mmol) followed by stirring for 30 min and addition of iron nitrate (0.82 g, 2 mmol). The crude product was precipitated as red powder and recrystallized from tetrahydrofuran to get shiny crystals of dark red which were identified as (1). Yield 0.80 g, (36 %) Mpt : 130 °C, Elemental analysis: Calc. for C_{42}H_{66}N_{12}S_{4}O_{6}Fe: C, 46.9; H, 6.1; N, 15.6; S, 11.9; Fe, 10.4 %. Found: C, 46.5; H, 6.4; N, 15.3; S, 11.4; Fe, 10.2 %.

[Fe(C_{14}H_{28}N_{3}OS)_{3}] (2) We followed the process of making (1) but used di-iso-propylamine (1.49 mL, 12 mmol) followed by stirring for 30 min and addition of iron nitrate (0.82 g, 2 mmol). The crude product was precipitated as red powder and recrystallized from tetrahydrofuran to get shiny crystals of red needles which were identified as (2). Yield 0.95 g (51 %), mpt: 160 °C, Elemental analysis: Calc. for C_{42}H_{84}N_{9}S_{3}O_{3}Fe: C, 55.1; H, 9.1; N, 13.7; S, 10.5; Fe, 6.1 %. Found: C, 54.8; H, 8.9; N, 13.2; S, 9.9; Ni, 5.9 %.

[Co(C_{14}H_{28}N_{3}OS)_{3}] (3) We followed the process of making (1) but used Co(OAc)_{2} (0.50 g, 2 mmol) and obtained green crystals of (3). Yield 0.51 g, (27 %) Mpt : 198 °C, Elemental analysis: Calc. for C_{42}H_{84}N_{9}S_{3}O_{3}Co: C, 54.9; H, 9.1; N, 13.7; S, 10.4; Co, 6.4 %. Found: C, 54.0; H, 9.0; N, 13.3; S, 9.8; Co, 6.2 %.

[Ni(C_{14}H_{28}N_{3}OS)_{2}] (4) We followed the process of making (1) but used Ni(OAc)_{2} (0.76 g, 3 mmol) and obtained violet crystals of (4). Yield 0.95 g (49 %) Mpt : 177 °C, ^1H NMR (300 MHz; CDCl3; Me4Si): δ 4.70 (m, 4H), 3.5 (m, 4H) 1.0 (d, 24H), 1.2 (d, 24H), Elemental analysis: Calc. For C_{28}H_{56}N_{6}S_{2}O_{2}Ni: C, 53.2; H, 8.8; N, 13.3; S, 10.1; Ni, 9.2 %. Found: C, 53.2; H, 9.0; N, 13.2; S, 9.9; Ni, 9.0 %.

[Cu(C_{14}H_{28}N_{3}OS)_{2}] (5) We followed the process of making (1) but used Cu(NO_3)_{2} .3H_2O (0.73 g, 3 mmol) and obtained green powder of (5). Yield 1.20 g, (62.5 %) Mpt
Elemental analysis: Calc. for C_{28}H_{56}N_{6}O_{2}S_{2}Cu: C, 52.8; H, 8.8; N, 13.2; S, 10.0; Cu, 9.9%. Found: C, 52.3; H, 9.0; N, 13.3; S, 9.6; Cu, 9.7%.

[Zn(C_{14}H_{28}N_{3}OS)_{2}] (6) We followed the process of making (1) but used Zn(OAc)$_2$ (0.67 g, 3 mmol) and obtained white powder of (7). Yield 1.30 g, (67 %) Mpt : 298 °C, $^1$H NMR (300 MHz; CDCl$_3$; Me$_4$Si): δ 4.75 (m, 4H), 3.5 (m, 4H) 1.1 (d, 24H), 1.4 (d, 24H), Elemental analysis: Calc. for C$_{28}$H$_{56}$N$_6$S$_2$O$_2$Zn: C, 52.7; H, 8.7; N, 13.2; S, 10.0; Zn, 10.2%. Found: C, 52.2; H, 8.3; N, 12.7; S, 9.6; Zn, 9.8%.

[Cd(C$_{14}$H$_{28}$N$_3$OS)$_2$] (7) We followed the process of making (1) but used Cd(OAc)$_2$ (0.81 g, 3 mmol) and obtained white powder of (7). Yield 1.49 g, (72 %) Mpt : 109 °C, $^1$H NMR (300 MHz; CDCl$_3$; Me$_4$Si): δ 4.45 (m, 4H), 3.5 (m, 4H) 1.1 (d, 24H), 1.4 (d, 24H), Elemental analysis: Calc. for C$_{28}$H$_{56}$N$_6$S$_2$O$_2$Cd: C, 49.0; H, 8.1; N, 12.2; S, 9.3; Cd, 16.4%. Found: C, 49.2; H, 7.8; N, 7.8; S, 11.8; Zn, 15.8%.

[In(C$_{14}$H$_{28}$N$_3$OS)$_3$] (8) We followed the process of making (1) but used InCl$_3$ (0.45 g, 2 mmol) and obtained white powder of (8). Yield 0.98 g, (49 %) Mpt : 156 °C, $^1$H NMR (300 MHz; CDCl$_3$; Me$_4$Si): δ 5.60 (m, 4H), 4.65 (m, 4H), 3.5 (m, 4H) 1.1 (d, 36H), 1.4 (d, 36H), Elemental analysis: Calc. for C$_{42}$H$_{84}$N$_9$S$_3$O$_3$In: C, 51.8; H, 8.6; N, 12.9; S, 9.8; In, 11.8%. Found: C, 50.7; H, 8.2; N, 12.3; S, 9.5; In, 11.2%.

[Fe(C$_6$H$_{12}$N$_3$OS)$_3$] (9) We followed the process of making (1) but used dimethylamine in water (0.92 mL, 12 mmol) and obtained dark red powder of (3). Yield 0.61 g, (51 %) Mpt: 148 °C, Elemental analysis: Calc. for C$_{18}$H$_{36}$N$_9$S$_3$O$_3$Fe: C, 37.3; H, 6.2; N, 21.8; S, 16.6; Fe, 9.6%. Found: C, 37.1; H, 6.4; N, 21.2; S, 16.3; Fe, 9.3%.

[Ni(C$_6$H$_{12}$N$_3$OS)$_2$] (10) We followed the process of making (1) but used dimethylcarbamyl chloride, dimethylamine in water (0.92 mL, 12 mmol) and Ni(OAc)$_2$ obtained violet powder of (10). Yield 1.89 g (46 %). Mpt: 286 °C, $^1$H NMR
[Co(C₆H₁₂N₃S₂)₃] (11) A solution of dimethylthiocarbamyl chloride (1.23 g, 10 mmol) and sodium thiocyanate (0.81 g, 10 mmol) in acetonitrile (40 mL) was heated at reflux with continuous stirring for 1 h, during which time a fine precipitate of sodium chloride formed. To the cooled reaction mixture was added 60 % aqueous dimethylamine (1.49 mL, 20 mmol) followed by stirring for 30 min and addition of cobalt chloride hexahydrate (1.193 g, 5 mmol). The crude product was precipitated as red powder and recrystallised from chloroform and then by tetrahydrofuran to get suitable quality crystals for X-ray crystallography. Yield 1.89 g (30 %). M.pt: 232 °C.

Elemental analysis: Calc. for C₁₈H₃₆N₉S₆Co: C, 34.1; H, 6.1; N, 19.9; S, 30.3; Co, 9.3 %. Found: C, 34.9; H, 6.0; N, 19.7; S, 28.9; Co, 9.1 %.

[Ni(C₆H₁₂N₃S₂)₂] (12) We followed the process of making (11) but used Ni(OAc)₂ (1.24 g, 5 mmol) and obtained brown powder of (12). Yield 1.20 g, (54 %) M.pt: 250 °C, ¹H NMR (300 MHz; CDCl₃; Me₄Si): 3.4 (s, 12 H), 3.15 (s, 12H), Elemental analysis: Calc. for C₁₂H₂₄N₆S₄Ni: C, 32.6; H, 5.8; N, 19.0; S, 29.0; Ni, 13.3 %. Found: C, 32.2; H, 5.4; N, 18.6; S, 27.9; Ni, 12.8 %

[Zn(C₆H₁₂N₃S₂)₂] (13) We followed the process of making (11) but used Zn(OAc)₂ (1.33 g, 5 mmol) and obtained white powder of (13). Yield: 1.44 g (65 %), M.pt: 210 °C, ¹H NMR (300 MHz; CDCl₃; Me₄Si): 3.4 (s, 12 H), 3.15 (s, 12H), Elemental analysis: C, 32.3; H, 5.4; N, 18.8; S, 28.7; Zn, 13.8 % Found C, 32.1; H, 5.7; N, 18.7; S, 28.3; Zn, 14.2 %

[Cd(C₆H₁₂N₃S₂)₂] (14) We followed the process of making (11) but used Cd (OAc)₂ (1.33 g, 5 mmol) and obtained white powder of (14). Yield 1.60 g, (65 %) M.pt: 90 °C, ¹H NMR (300 MHz; CDCl₃; Me₄Si): 3.4 (s, 12 H), 3.15 (s, 12H), Elemental analysis: C, 32.1; H, 5.7; N, 18.7; S, 28.3; Cd, 14.3 %. Found C, 32.0; H, 5.8; N, 18.6; S, 28.4; Cd, 14.4 %.
°C, 1H NMR (300 MHz; CDCl3; Me4Si): 3.4 (s, 12 H), 3.15 (s, 12H), Elemental analysis: Calc. for C12H24N6S4Cd: C, 29.2; H, 4.8; N, 17.0; S, 25.9; Cd, 22.8 %.

Found: C, 28.8; H, 4.9; N, 16.7; S, 25.5; Cd, 22.7 %

[In(C6H12N3S2)3] (15) We followed the process of making (11) but used InCl3 (0.72 g, 3.3 mmol) and obtained white powder of (15). Yield 1.4 g, (63%), Mpt: 244 °C. 1H NMR (300 MHz; CDCl3; Me4Si): 3.4 (s, 18 H), 3.15 (s, 18H), 4.38 (s, 2H), Elemental analysis: Calc. for C18H36N9S6In: C, 31.4: H, 5.6: N, 18.3: S, 27.9: In, 16.6 %. Found: C, 31.1: H, 5.1: N, 17.9: S, 27.4: In, 16.2 %.

[Co(C10H20N3S2)3] (16) We followed the process of making (11) but used diethylthiocarbamyl chloride (1.51 g, 10 mmol), diethylamine (1.91 mL, 20 mmol) and Co(OAc)2 (0.83 g, 3.3 mmol) and obtained black crystalline powder of (16). Yield 1.20 g (49 %), Mpt : 190 °C. Elemental analysis: Calc. for C30H60N9S6Co: C, 45.2; H, 7.5; N, 15.8; S, 24.0; Co, 7.3 %. Found: C, 44.9; H, 7.5; N, 15.7; S, 23.7; Co, 7.3 %.

[Ni(C10H20N3S2)2] (17) We followed the process of making (16) but used Ni(OAc)2 (1.24 g, 5 mmol) and obtained brown crystals of (17). Yield 1.5 g, (54%), Mpt : 160 °C. 1H NMR (300 MHz; CDCl3; Me4Si): δ 3.50 (q, 8H), 3.85 (q, 8H) 1.12 (t, 12H), 1.28 (t, 12H), Elemental analysis: Calc. for C20H40N6S4Ni: C, 43.6; H, 7.2; N, 15.2; S, 23.2; Ni, 10.6 %. Found: C, 43.2; H, 7.4; N, 14.7; S, 22.6; Ni, 10.2 %.

[Zn(C10H20N3S2)2] (18) We followed the process of making (16) but used Zn(OAc)2 (1.09 g, 5 mmol) and obtained white powder of (18). Yield 1.5 g, (54%), Mpt : 120 °C. 1H NMR (300 MHz; CDCl3; Me4Si): δ 3.4 (q, 8H), 3.8 (q, 8H) 1.0 (t, 12H), 1.1 (t, 12H), Elemental analysis: Calc. for C20H40N6S4Zn: C, 42.9; H, 7.1; N, 15.0; S, 22.9; Zn, 11.6 %. Found: C, 42.8; H, 7.3; N, 14.9; S, 22.6; Zn, 11.5 %.
We followed the process of making (16) but used Cd(OAc)$_2$ (1.33 g, 5 mmol) and obtained white powder of (19). Yield 1.6 g, (52%), Mpt : 118 °C, $^1$H NMR (300 MHz; CDCl$_3$; Me$_4$Si): $\delta$ 3.45 (q, 8H), 3.9 (q, 8H) 1.1 (t, 12H), 1.3 (t, 12H) Elemental analysis: Calc. for C$_{20}$H$_{40}$N$_6$S$_4$Cd: C, 39.6; H, 6.6; N, 13.8; S, 21.1; Cd, 18.5 %. Found: C, 39.5; H, 6.8; N, 13.8; S, 20.5; Cd, 18.1 %.

[In(C$_{10}$H$_{20}$N$_3$S$_2$)$_3$] (20) We followed the process of making (16) but used InCl$_3$ (0.73 g, 3.3 mmol) and obtained white powder of (20). Yield 1.2 g, (42%), Mpt: 162 °C, $^1$H NMR (300 MHz; CDCl$_3$; Me$_4$Si): $\delta$ 3.4 (q, 12H), 3.8 (q, 12H) 1.0 (t, 18H), 1.1 (t, 18H) Elemental analysis: Calc. for C$_{20}$H$_{60}$N$_9$S$_6$In: C, 42.1; H, 7.01; N, 14.7; S, 22.4; In, 13.4 %. Found: C, 41.2; H, 7.1; N, 14.2; S, 21.0; In, 13.8 %.

**X-Ray crystallography**

Single-crystal X-ray diffraction data for the compounds were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker APEX diffractometer. The structure was solved by direct methods and refined by full-matrix least squares on F$^2$ All non-H atoms were refined anisotropically. H atoms were included in calculated positions, assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms. All calculations were carried out using the SHELXTL package.$^2$

Crystal data for (1) C$_{42}$H$_{86}$N$_{12}$O$_6$S$_4$Fe$_2$; $M = 1095.17$; black blocks; monoclinic; $P2(1)/c$; $a = 10.466(2)$ Å, $b = 25.355(4)$ Å, $c = 10.328(5)$ Å; $\beta = 95.44(3)^{\circ}$; $V = 2728.5(8)$ Å$^3$; $Z = 2$; $D = 1.333$ Mg/m$^3$; $T = 100(2)$ K; reflections collected = 15681, unique reflections = 5558 [R(int) = 0.0313]; R1 = 0.0510 and wR2 = 0.1160 for [I > 2σ(I)]; R1 = 0.0598 and wR2 = 0.1197 for all data; largest diff. peak and hole = 1.677 and -0.370 e.A$^{-3}$, GOF = 1.144.

Crystal data for (3) C$_{44}$H$_{87}$N$_{10}$O$_3$S$_3$Co, $M = 959.35$, Green needles; monoclinic;
space group $P2_1$ ($n$, $a = 14.055(2)$ Å, $b = 15.727(2)$ Å, $c = 25.394(3)$ Å; $\beta (^\circ) = 96.686(2)$; $V = 5575.5(1)$ Å$^3$; $Z = 4$; $D = 1.143$ Mg/m$^3$; $T = 100(2)$ K, reflections collected = 43979, unique reflections = 11407 [$R(\text{int}) = 0.1028$ ]; $R1 = 0.0701$ and wR2 = 0.2003 for [$I > 2\sigma(I)$]; $R1 = 0.1308$ and wR2 = 0.2235 for all data; Largest diff. peak and hole = 2.250 and -0.601 e.A$^{-3}$, GOF = 0.999.

Crystal data for (4) C$_{28}$H$_{56}$N$_6$O$_2$S$_2$Ni; $M = 631.62$; violet blocks; monoclinic; $P2_1/c$; $a = 21.787$ Å, $b = 13.777$ Å, $c = 11.925$ Å; $\beta = 90.99^\circ$; $V = 3578.9$ Å$^3$; $Z = 4$; $D = 1.172$ Mg/m$^3$; $T = 100(2)$ K; reflections collected = 16324, unique reflections = 6984 [$R(\text{int}) = 0.1107$]; $R1 = 0.0781$ and wR2 = 0.1718 for [$I > 2\sigma(I)$]; $R1 = 0.1877$ and wR2 = 0.2183 for all data; largest diff. peak and hole = 1.379 and -0.994 e.A$^{-3}$, GOF = 0.939. One of the iso-propyl groups in ligand is disordered over two conformations in the ratio of 62:38.

Crystal data for (5) C$_{28}$H$_{56}$N$_6$O$_2$S$_2$Cu; $M = 636.45$; Green blocks; Triclinic; $\alpha = 7.952(2)$ Å, $b = 11.127(3)$ Å, $c = 11.142(3)$ Å; $\alpha = 65.992(6)^\circ$; $\beta = 72.469 (5)^\circ$; $\gamma = 79.123(6)^\circ$; $V = 856.2(4)$ Å$^3$; $Z = 1$; $D = 1.234$ Mg/m$^3$; $T = 100(2)$ K; reflections collected = 5384, unique reflections = 3796 [$R(\text{int}) = 0.0877$]; $R1 = 0.0471$ and wR2 = 0.0682 for [$I > 2\sigma(I)$]; $R1 = 0.1681$ and wR2 = 0.0896 for all data; largest diff. peak and hole = 0.445 and -0.472 e.A$^{-3}$, GOF = 0.491.

Crystal data for (17) C$_{20}$H$_{40}$N$_6$S$_4$Ni; $M = 551.53$; Brown needles; Triclinic; $\alpha = 9.4941(2)$ Å, $b = 11.4556(2)$ Å, $c = 13.758(2)$ Å; $\alpha = 89.628^\circ$; $\beta = 89.726(3)^\circ$; $\gamma = 67.548(3)^\circ$ $V = 1382.9(4)$ Å$^3$; $Z = 2$; $D = 1.325$ Mg/m$^3$; $T = 100(2)$ K; reflections collected = 8092, unique reflections = 5529 [$R(\text{int}) = 0.0221$]; $R1 = 0.0477$ and wR2 = 0.0991 for [$I > 2\sigma(I)$]; $R1 = 0.0651$ and wR2 = 0.1037 for all data; largest diff. peak and hole = 0.553 and -0.326 e.A$^{-3}$, GOF = 1.112.

Crystal data for (18) C$_{20}$H$_{40}$N$_6$S$_4$Zn; $M = 558.19$; colourless blocks; monoclinic;
p2(1)/n; $a = 9.092(8)$ Å, $b = 11.505(1)$ Å, $c = 26.955(2)$ Å; $\beta = 98.79(2)^\circ$; $V = 2786.4(4)$ Å$^3$; $Z = 4$; $D = 1.331$ Mg/m$^3$; $T = 100(2)$ K; reflections collected = 23865, unique reflections = 6650; $R_1 = 0.0360$ and $wR_2 = 0.0492$ for $|I > 2\sigma(I)|$; $R_1 = 0.0686$ and $wR_2 = 0.0541$ for all data; largest diff. peak and hole = 0.860 and -0.443 e.A$^{-3}$, GOF = 0.743. CCDC reference numbers: 715969(1), 715962(3), 715960(4), 715965(5), 715963(17), 692257(18) respectively.
Fig. S1. XRD pattern of cobalt sulfide thin films deposited from a) [Co(C_{14}H_{28}N_{3}OS)_{2}], b) [Co(C_{10}H_{20}N_{3}S_{2})_{2}] and c) [Co(C_{10}H_{20}N_{3}S_{2})_{3}] respectively.
Fig. S2. XRD pattern of copper sulfide, nickel sulfide and iron sulfide thin films deposited from a) [Cu(C14H28N3OS)2], b) [Ni(C14H28N3OS)2] and c) [Fe(C14H28N3OS)3] respectively.
Fig. S3. XRD pattern of zinc sulfide, cadmium sulfide and nickel sulfide thin films deposited from a) \([\text{Cd(C}_6\text{H}_{12}\text{N}_3\text{S}_2)_2]\) b) \([\text{Zn(C}_6\text{H}_{12}\text{N}_3\text{S}_2)_2]\) and c) \([\text{Ni(C}_6\text{H}_{12}\text{N}_3\text{OS})_2]\) respectively.
**Fig. S4.** SEM and AFM images of ZnS (a and c), CdS (b and d) thin films deposited from [Zn(C\textsubscript{6}H\textsubscript{12}N\textsubscript{3}S\textsubscript{2})\textsubscript{2}] and [Cd(C\textsubscript{6}H\textsubscript{12}N\textsubscript{3}S\textsubscript{2})\textsubscript{2}]
**Fig. S5** HRTEM images of a and b) cobalt sulfide thin films deposited from [Co(C_{10}H_{20}N_{3}S_{2})_{2}] and [Co(C_{10}H_{20}N_{3}S_{2})_{3}], c) iron sulphide thin film deposited from [Fe(C_{14}H_{28}N_{3}OS)_{3}].
References:
