A Simple Route to Complex Materials: the Synthesis of Alkaline Earth – Transition Metal Sulfides

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1 Materials and Methods

1.1 Materials

All chemicals were purchased from Sigma Aldrich.

1.2 Analytical Equipment

Elemental analysis of the complex was carried out using Flash 2000 Thermo Scientific elemental analyzer in School of Chemistry, The University of Manchester. Thermogravimentric Analysis (TGA) of the complex was carried out by METTLER TOLEDO TGA/DSC 1 STARe system for the complexes under an atmosphere of dry nitrogen. NMR spectra were recorded in CDCl₃ and D₂O solutions on a Bruker Ascend spectrometer operating at 400 MHz, NMR samples for compounds **1** and **2** were prepared under N₂ in glove box. Scanning Electron Microscope images (SEM) and EDX analysis were acquired using Philips XL 30FEG equipped with a DX4 and a FEI Quanta 200 ESEM with EDAX Genesis V4.61. Grazing incidence X-ray diffraction (GIXRD) patterns were obtained Bruker D8 Advance diffractometer (Cu-K α , $\lambda = 1.5418$ Å) - the applied voltage was 40 kV, the current 40 mA and the angle of incidence was 3°. The unit cells were obtained from the GIXRD patterns by use of the PANalytical High Score Plus¹ software with database ICDD P04+2015 to find the peak positions and Miller indices. After that the unit cell refinement was carried out using UnitCell.²

1.3 Synthesis of $[Ca(S_2CO^iP)_2(^iPrOH)_3] - 1$

Adapted from Bezougli *et al.*³ Calcium metal (1.28 g, 16.0 mmol) was suspended in dry ⁱPrOH (100 ml) and the mixture heated to reflux under N₂ for 24 h which resulted in dissolution of the metal and evolution of hydrogen gas, yielding a slightly grey solution. The reaction was cooled to 0 °C and carbon disulfide (2.41 ml, 40 mmol) was added. A clear yellow solution started forming soon after the addition of carbon disulfide. The solution was stirred for 1 h at room temperature and then the solvent was removed *in vacuo*. The product was isolated as powder and stored under N₂ at 0 °C (yield: 5.3 g, 67.6%). M.p. = 48-51 °C.

Calc. for C₁₇H₃₈CaO₅S₄ (%): C 41.6, H 7.8, S 26.0, Ca 8.17; found: C 41.5, H 7.75, S 25.6, Ca 8.53.

FT-IR (cm⁻¹): 3311 (w), 2974 (m), 1459 (m), 1370 (m), 1300 (w), 1185 (s), 1156 (m), 1136 (m), 1081 (s), 1039 (s), 940 (s), 904 (w), 814 (m), 659 (w), 534 (w).

¹H NMR (400 MHz, CDCl₃) δ ppm: 1.27 (d, 6H, (CH₃)₂CHOH), 1.41 (d, 6H, S₂COCH(CH₃)₂), 2.24 (s, 1H, (CH₃)₂CHOH), 4.16 (s, 1H, (CH₃)₂CHOH), 5.61 (s, 6H, S₂COCH(CH₃)₂).

¹³C NMR (400 MHz, CDCl₃) δ ppm: 13.60 (S₂COCH(**C**H₃)₂), 16.61 (**C**H₃)₂CHOH), 57.33 (CH₃)₂**C**HOH), 70.18 (S₂CO**C**H(CH₃)₂), 232.80 (S₂**C**OCH(CH₃)₂).

1.4 Synthesis of $[Ba(S_2CO^iPr)_2] - 2$

Adapted from Bezougli *et al.*³ Barium metal (1.34 g, 9.76 mmol) was suspended in dry ⁱPrOH (100 ml) and the mixture heated to reflux for 16 h under N₂ which resulted in dissolution of the metal and evolution of hydrogen gas, yielding a slightly grey solution. The reaction was cooled to 0 °C and carbon disulfide (1.47 ml, 24.4 mmol) added. The solution was stirred for 1 h at room temperature and then the solvent was removed *in vacuo*. The product was isolated as white powder and stored under N₂ at 0 °C (yield: 3.32 g, 83.6%). M.p. = 168-173 °C.

Calc. for C₈H₁₄BaO₂S₄ (%): C 23.5, H 3.94, S 31.3, Ba 33.5; found: C 23.8, H 3.89, S 31.4, Ba 33.6.

FT-IR (cm⁻¹): 2972 (w), 2931 (m), 1442 (w), 1381 (m), 1373 (m), 1186 (s), 1158 (s), 1136 (m), 1085 (s), 1035 (s), 926 (s), 904 (w), 813 (m), 654 (w), 585 (w).

¹H NMR (400 MHz, D₂O) δ ppm: 1.24 (d, 6H, OCH(CH₃)₂), 5.44 (s, 1H, OCH(CH₃)₂).

¹³C NMR (400 MHz, D₂O) δ ppm: 20.71 (OCH(*C*H₃)₂), 77.38 (O*C*H(CH₃)₂), 231.98 (S₂*C*O).

1.5 Synthesis of [K(S₂CO(CH₂)₂OCH₃)]

From Al-Shakban *et al.*⁴ Potassium hydroxide (11.22 g, 0.20 mol) was dissolved in 2-methoxyethanol (75 ml) and the reactors were stirred for 6 h at 0 °C, before a solution of carbon disulfide (15.23 g, 12 ml, 0.20 mol) in 2-methoxyethanol (25 ml) was added dropwise to the reaction, resulting in a clear yellow solution. [K(S₂CO(CH₂)₂OCH₃)] was isolated from solution by the addition of THF (100 ml) and shaking the mixture for 15 min. The yellow solid product was dried and recrystallized from 2-methoxyethanol to give [K(S₂CO(CH₂)₂OCH₃)] (19.8 g, 52.1 % yield). M.p. = 216-219 °C.

Calc. for C₄H₇KO₂S₂ (%): C 25.3, H 3.71, S 33.6, K 20.6; found: C 25.5, H 3.79, S 33.5, K 20.8.

FT-IR (cm⁻¹): 2935 (w), 2888 (w), 1442 (m). 1445 (w), 1230 (m), 1134 (m), 1099 (m), 1066 (s), 1018 (m), 844.3 (w), 676.7 (m), 532.5 (m).

¹H NMR (400 MHz, D₂O) δ (ppm) = 3.35 (s, 3H, OCH₃), 3.72 (t, 2H, CH₂CH₂O), 4.50 (t, 2H, CH₂CH₂O).

¹³C NMR (400 MHz, D₂O) δ ppm: 58.15 (O**C**H₃), 70.18 (CH₂**C**H₂O), 72.09 (**C**H₂CH₂O), 232.52 (S₂**C**O).

1.6 Synthesis of [(PPh₃)₂Cu(S₂CO(CH₂)₂OCH₃)] - 3

From Al-Shakban *et al.*⁴ A solution of $[K(S_2CO(CH_2)_2OCH_3)]$ (0.76 g, 4.0 mmol) in chloroform (40 ml) was added to a solution of triphenylphosphine (2.09 g, 8.0 mmol) and CuCl (0.40 g, 4.0 mmol) in the same amount of chloroform. A white precipitate was obtained after continuous stirring for 1 h at room temperature. The solution was filtered to obtain a clear yellow solution. Cooling the yellow solution to -20 °C gave yellow crystals of [bis(triphenylphosphine) copper(I) (2-methoxyethylxanthate) (2.03 g, 67.8% yield). M.p. = 139-143 °C.

Calc. for $C_{40}H_{37}CuO_2P_2S_2$ (%): C 64.98, H 5.05, S 8.66, P 8.39, Cu 8.60; found: C 64.54, H 4.99, S 8.39, P 8.01, Cu 8.25. FT-IR (cm⁻¹): 2876 (w), 1478 (m) 1432 (m), 1235 (w), 1170 (m), 1094 (s), 1065(m), 851 (w), 740 (m), 691 (s), 618 (w). ¹H NMR (400 MHz, CDCl₃) δ ppm: 3.42 (s, 3H, OCH₃), 3.69 (t, 2H,CH₂CH₂O), 4.52 (t, 2H, CH₂CH₂O), 7.05-7.47 (m, 30H, Ph).

¹³C NMR (400 MHz, CDCl₃) δ ppm: 59.15 (O**C**H₃), 70.24 (CH₂**C**H₂O), 71.90 (**C**H₂CH₂O), 128.40 (Ph), 129.46 (Ph), 133.66 (Ph), 133.94 (Ph), 226.84 (S₂**C**O).

1.7 Preparation of Thin Films

For the deposition of the $CaCu_2S_2$ thin films, The precursor was prepared by sequentially dissolving $[(PPh_3)_2Cu(S_2CO(CH_2)_2OMe)]$ (0.118, 0.00016mol) and $[Ca(S_2CO'Pr)_2(^{i}PrOH)_3]$ (0.0392 g, 0.00008mol) in 4 mL dry THF under an N₂ atmosphere in glove box. A clear yellow solution was obtained, precursors were directly coated on glass substrates, which were cleaned by ultra-sonication for 15 min in water and then 15 min in acetone. The prepared precursors were spin-coated at the spinning speed of 1000 rpm for CaCu_2S_2 followed by immediate annealing for 1h at 300 °C. CaS, BaS, CuS, CaCu_2S_2, β - BaCu_2S_2, and β - BaCu_4S₃ were deposited by the same method. The experimental conditions are summarised in Table S1.

Compound	Complex(1) (g, mol)	Complex (2) (g, mol)	Complex (3) (g, mol)	THF (ml)	R.P.M	Temperature (°C)	Pictures of films
CaS	(0.245, 0.0005)	.		4	3000	300	
BaS		(0.2, 0.0005)		4	1200	550	
CuS			(0.147, 0.0002)	4	1000	300	
CaCu ₂ S ₂	(0.0392, 0.00008)		(0.118, 0.00016)	4	1000	300	
β- BaCu ₂ S ₂		(0.0366, 0.00009)	(0.132, 0.00018)	4	1000	550	
β- BaCu ₄ S ₃		(0.0126, 0.0000311)	(0.0916, 0.000124)	4	1000	580	

Table S1. The experimental conditions for the preparation of CaS, BaS, CuS, CaCu₂S₂, β - BaCu₂S₂, and β - BaCu₄S₃ films. The films were heated at different temperatures for 1h.

2 Thermogravimetric analysis of compounds 1-3



Figure S1. Thermogravimetric analysis of $[Ca(S_2CO^{i}Pr)_2(^{i}PrOH)_3]$ (**1**, black), $[Ba(S_2CO^{i}Pr)_2]$ (**2**, red) and $[(PPh_3)_2Cu(S_2CO(CH_2)_2OMe)]$ (**3**, blue).

3 GIXRD Data

Table S2. Lattice	parameters of th	e thin films as	determined by	GIXRD.
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Compound	structure	Lattice constant (Å)			
Compound	structure	Experimental	Literature		
CaS	cubic	<i>a</i> = 5.699 (2)	<i>a</i> = 5.694		
CaCu ₂ S ₂	Hexagonal	a = 3.949 (3) c = 6.520 (3)	<i>a</i> = 3.940 <i>c</i> = 6.523		
BaS	cubic	<i>a</i> = 6.392(6)	<i>a</i> = 6.388		
BaCu₂S₂ at 550 °C	Orthorhombic	a = 9.215 (1) b = 4.059 (1) c = 10.387 (1)	a = 9.273 b = 4.053 c = 10.380		
(mix between α and $\beta)$	Tetragonal	a = 3.907(7) b =3.907(7) c = 12.648(7)	a = 3.907 b = 3.907 c = 12.640		
β- BaCu₂S₂	Tetragonal	a = 3.907 (3) b = 3.907 (3) c = 12.648(3)	<i>a</i> = 3.907 <i>b</i> = 3.907 <i>c</i> = 12.640		
β- BaCu₄S₃	Orthorhombic	a = 4.053(1) b = 13.848(3) c = 10.377(2)	a = 4.058 b = 13.863 c = 10.373		
Cu _{1.73} S	Orthorhombic	a = 11.810(1) b = 27.020(7) c = 13.435(1)	a = 11.820 b = 27.050 c = 13.430		



Figure S2. GIXRD of $BaCu_2S_2$ showing the mixed α (orthorhombic) and β (tetragonal) phases present in films prepared at 550 °C.



Figure S3. GIXRD of Cu₂S showing the chalcocite copper sulfide phase presents in film prepared at 300 °C.

Table S3. Mass absorption coefficient (MAC), length absorption coefficient (LAC) data obtained for CaS, CuS, β -BaCu₂S₂ and β -BaCu₄S₃ at an incident angle of 3° (which is what was used for the GIXRD experiment). The data was calculated using the PANalytical High Score Plus¹ software with database ICDD P04+2015. The film thickness was determined through SEM (ESI Figure S4).

Compound	MAC (cm ² g ⁻¹)	LAC (cm ⁻¹)	Path length (µm)	Penetration depth (µm)	Thickness of the film (μm)
CaS	131.1	169.1	272	~ 7.12	0.96
BaS	298.1	633.4	72.7	~ 1.90	0.73
CuS	59.95	164.9	279	~ 7.31	0.81
$CaCu_2S_2$	82.13	179.86	256	~ 6.7	0.74
β- BaCu ₂ S ₂	182.7	516.5	89.2	~ 2.33	2.5
β- BaCu ₄ S ₃	142.6	384.5	112	~ 3.13	2.6



Figure S4. Film thickness measurements obtained for (a) CaS, (b) BaS, (c) CuS, (d) $CaCu_2S_2$, (e) β -BaCu₂S₂ and (f) β -BaCu₄S₃.

4 SEM and EDX data



Figure S5. EDX elemental mapping for $CaCu_2S_2$ showing a homogenous distribution of the elements.



Figure S6. EDX elemental mapping for β -BaCu₂S₂ showing a homogenous distribution of the elements.



Figure S7. EDX elemental mapping for β -BaCu₄S₃ showing a homogenous distribution of the elements.



Figure S8. EDX elemental mapping for $Cu_{1.73}$ S showing a homogenous distribution of the elements.

Compound	Ca (at.%)	Ba (at.%)	Cu (at.%)	S (at.%)
CaS	49.9			50.1
BaS		50.1		49.9
CuS			63.4	36.6
$CaCu_2S_2$	19.6		42.8	37.6
β - BaCu ₂ S ₂		22.2	39.9	37.9
β- BaCu ₄ S ₃		12.1	49.5	38.4

Table S4. Compositional analysis of films determined by EDX.

In order to probe C inclusion in the final films, we deposited CaS, BaS, CuS, BaCu₂S₂ and BaCu₄S₃ films on silicon substrates (to avoid any carbon signal from glass), and coated the films with Au/Pd source using (Quorum-Q150TES). The Au/Pd films thickness is \approx 18 nm. Note that we were unable to obtain C content for CaCu₂S₂ films, as the films did not bind well to the surface of the Si substrate. However, it is reasonable to assume that it would behave in a manner analogous to the other systems.

Table S5. EDX values of CaS, BaS, CuS, $BaCu_2S_2$ and $BaCu_4S_3$ films on silicon substrates. Note that the Au/Pd signal is from coating the sample.

Compound	Ca (at.%)	Ba (at.%)	Cu (at.%)	S (at.%)	Au (at.%)	Pd (at.%)	C (at.%)
CaS	46.0			49.6	2.21	2.07	0.12
BaS		51.4		41.3	4.56	2.62	0.11
CuS			62.5	35.2	1.44	0.76	0.1
β -BaCu ₂ S ₂		23.6	37.0	35.8	2.20	1.11	0.28
β-BaCu ₄ S ₃		15.1	47.5	34.0	2.04	1.06	0.27



Figure S9. EDX measurements obtained for (a) CaS, (b) BaS, (c) CuS, (d) β - BaCu₂S₂ and (e) β -BaCu₄S₃ on silicon substrates.

5 Raman Data



Figure S10. Raman spectra of $Cu_{1.7}S$ and $CaCu_2S_2$ were measured using a Renishaw 1000 Micro-Raman System equipped with a 514 nm laser.

6 References

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