The effect of alkyl chain length on the structure of lead(II) xanthates and their decomposition to PbS in melt reactions

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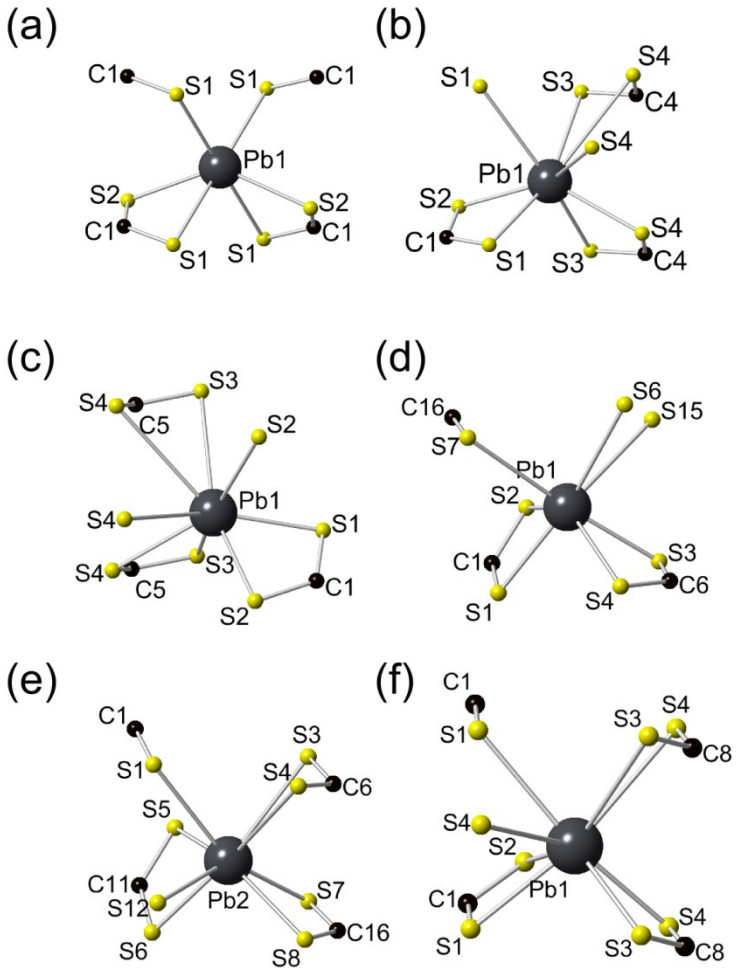
Supporting Information

SI Table 1: Selected distances for lead(II) propylxanthate.

	Length / Å
S(1)-C(1)	1.71(2)
S(2)-C(1)	1.72(2)
S(3)-C(5)	1.73(2)
S(4)-C(5)	1.688(18)
O(1)-C(1)	1.30(3)
O(2)-C(5)	1.32(2)
Pb(1)-S(1)	2.965(5)
Pb(1)-S(2)	2.738(5)
Pb(1)-S(3)	2.788(5)
Pb(1)-S(4)	2.965(5)

SI Table 2: Selected distances for lead(II) hexylxanthate.

	Length / Å
C(1)-O(1)	1.37(2)
C(1)-S(2)	1.654(19)
C(1)-S(1)	1.728(17)
C(8)-O(2)	1.44(2)
C(8)-S(3)	1.63(2)
C(8)-S(4)	1.685(19)
Pb(1)-S(1)	2.811(5)
Pb(1)-S(2)	2.847(4)
Pb(1)-S(3)	3.020(5)
Pb(1)-S(4)	2.799(4)



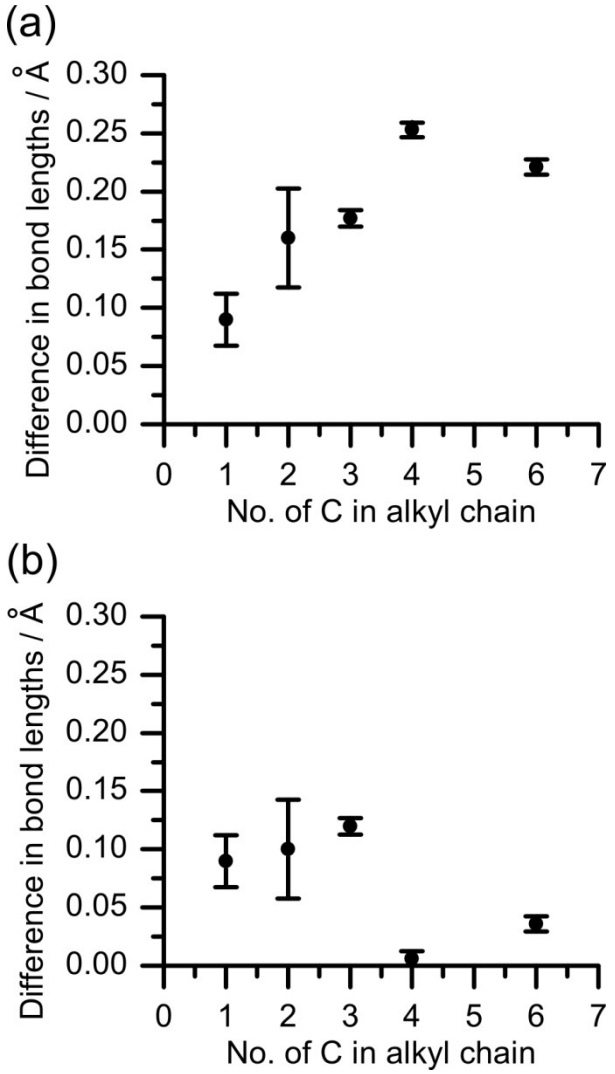
SI Figure 1: The coordination spheres for the lead centres with Pb-S distances of 4 Å displayed for (a) $[Pb(S_2COMe_2)_2]$, (b) $[Pb(S_2COEt_2)_2]$, (c) $[Pb(S_2COPr_2)_2]$, (d, e) $[Pb(S_2COBu_2)_2]$ and (f) $[Pb(S_2COHex_2)_2]$.

SI Table 3: Differences in bond lengths for ligand containing longest Pb-S bond

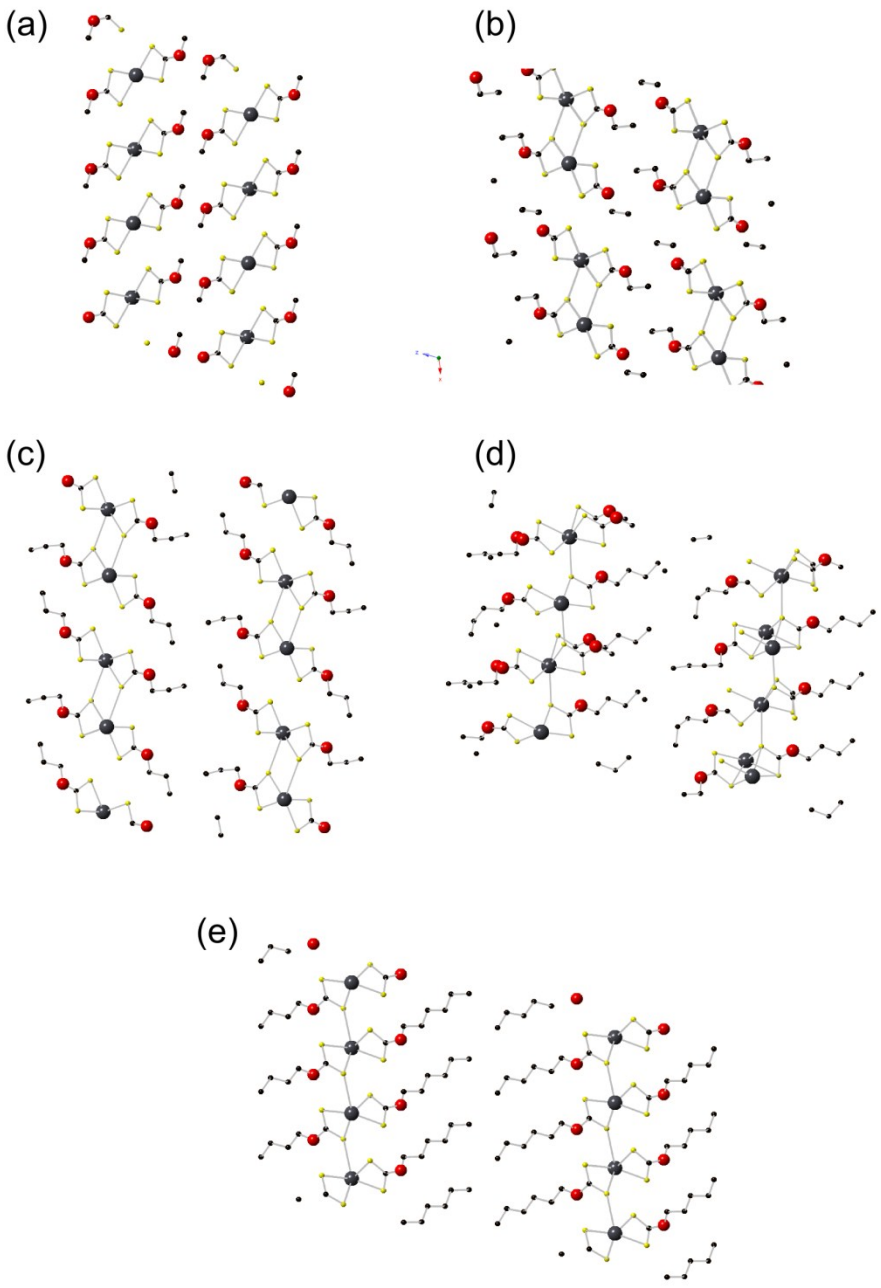
R group	Δ bond lengths	Error in difference
Methyl	0.09	0.022
Ethyl	0.160	0.042
Propyl	0.177	0.007
Butyl	0.253	0.006
Hexyl	0.221	0.006

SI Table 4: Differences in bond lengths for ligand without longest Pb-S bond

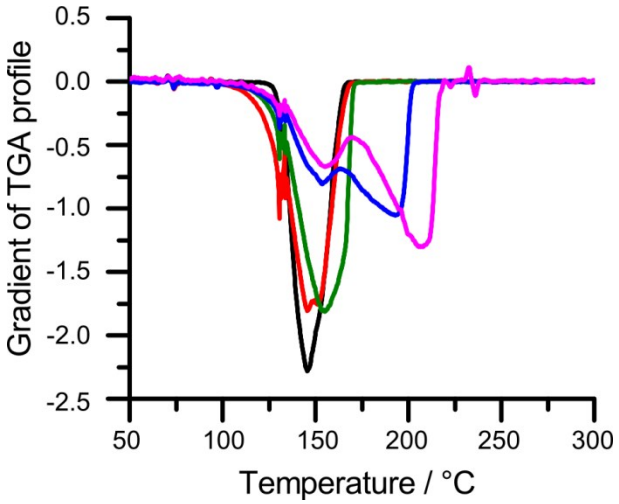
R group	Δ bond lengths	Error in difference
Methyl	0.090	0.022
Ethyl	0.100	0.042
Propyl	0.120	0.007
Butyl	0.006	0.006
Hexyl	0.036	0.006



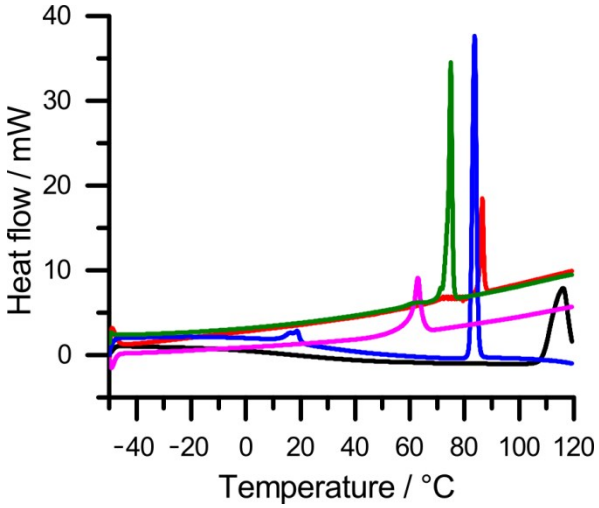
SI Figure 2: The difference in Pb-S bonds with (a) the ligand displaying monodentate character and (b) the ligand displaying bidentate character.



SI Figure 3: Plots of eight complexes viewed down the columns or sheet edges (a) $[Pb(S_2COMe_2)_2]$, (b) $[Pb(S_2COEt_2)_2]$, (c) $[Pb(S_2COPr_2)_2]$, (d) $[Pb(S_2COBu_2)_2]$ and (e) $[Pb(S_2COHex_2)_2]$.



SI Figure 4: The first derivative profiles from the TGA curves for $Pb(S_2COR)_2$ where R is ethyl (black), propyl (red), butyl (green), hexyl (blue) and octyl (pink).



SI Figure 5: The DSC profiles for for $Pb(S_2COR)_2$ where R is ethyl (black), propyl (red), butyl (blue), hexyl (pink) and octyl (green).

SI Table 5: Relative atomic percentages from EDX spectra for lead and sulfur in the nanocrystals formed. The lead M series and sulphur K series were used.

R group of complex	Relative atomic percentage of Pb, %	Relative atomic percentage of S, %
Ethyl	53.27	46.73
Propyl	58.39	41.61
Butyl	53.46	46.54
Hexyl	54.64	45.36
Octyl	49.62	50.38