Supplementary Information

Phosphonium-Templated Iodoplumbates

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Contents

Table S1 Crystal data and structure refinement for $[PMe_4][I]$.

Identification code	1858273
Empirical formula	$C_4H_{12}IP$
Formula weight	218.01
Temperature/K	170.0
Crystal system	tetragonal
Space group	P4/nmm
a/Å	8.1978(10)
b/Å	8.1978(10)
c/Å	6.0037(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	403.47(11)
Z	2
ρ_{calc}g/cm^3	1.794
μ/mm^{-1}	4.061
F(000)	208.0
Crystal size/mm^3	0.2 × 0.1 × 0.015
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.786 to 65.036
Index ranges	$-12 \leq h \leq 10$, $-12 \leq k \leq 12$, $-9 \leq l \leq 9$
Reflections collected	7940
Independent reflections	448 [R_{int} = 0.0702, R_{sigma} = 0.0253]
Data/restraints/parameters	448/0/13
Goodness-of-fit on F^2	1.232
Final R indexes [I>=2σ (I)]	R_1 = 0.0423, wR_2 = 0.0914
Final R indexes [all data]	R_1 = 0.0501, wR_2 = 0.0962
Largest diff. peak/hole / e Å^{-3}	2.90/-1.04

Table S2 Crystal data and structure refinement for $[PMe_4][PbI_3]$.

Identification code	1858275
Empirical formula	$C_4H_{12}I_3PPb$
Formula weight	679.00
Temperature/K	170(2)
Crystal system	hexagonal
Space group	$P6_5$
a/Å	10.0382(8)
b/Å	10.0382(8)
c/Å	23.738(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	2071.5(4)
Z	6
ρ_{calc}g/cm^3	3.266
μ/mm^{-1}	18.987
F(000)	1752.0
Crystal size/mm^3	0.600 × 0.280 × 0.150
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.808 to 61.136
Index ranges	$-14 \leq h \leq 13$, $-14 \leq k \leq 14$, $-33 \leq l \leq 33$
Reflections collected	36416
Independent reflections	4194 [R_{int} = 0.0620, R_{sigma} = 0.0314]
Data/restraints/parameters	4194/1/88
Goodness-of-fit on F^2	1.108
Final R indexes [I>=2σ (I)]	R_1 = 0.0471, wR_2 = 0.1125
Final R indexes [all data]	R_1 = 0.0489, wR_2 = 0.1144
Largest diff. peak/hole / e Å^{-3}	4.45/-4.16
Flack parameter	0.491(10)

A-level alerts in the checkCIF/PLATON report flag residual electron density near the lead atoms. This is due to the strongly absorbing lead iodide atoms and Fourier truncation effects. The nature of the atom as lead is not in doubt.

Table S3 Crystal data and structure refinement for $[P_2C_8H_{22}][Pb_2I_6]$

Identification code	1858274
Empirical formula	$C_8H_{22}I_6P_2Pb_2$
Formula weight	1355.97
Temperature/K	170(2)
Crystal system	monoclinic
Space group	C2/m
a/Å	15.3593(6)
b/Å	11.1506(4)
c/Å	7.9441(3)
α/°	90
β/°	100.8890(10)
γ/°	90
Volume/Å^3	1336.05(9)
Z	2
ρ_{calc}g/cm^3	3.371
μ/mm^{-1}	19.626
F(000)	1164.0
Crystal size/mm^3	0.5 × 0.4 × 0.3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.526 to 66.356
Index ranges	$-22 \le h \le 23$, $-17 \le k \le 15$, $-12 \le l \le 12$
Reflections collected	33343
Independent reflections	2676 [R_{int} = 0.0498, R_{sigma} = 0.0228]
Data/restraints/parameters	2676/18/71
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0661
Final R indexes [all data]	R_1 = 0.0409, wR_2 = 0.0718
Largest diff. peak/hole / e Å^{-3}	3.19/-3.02

Table S4 Crystal data and structure refinement for $[PMePh_3][PbI_3]\cdot MeCN$.

Identification code	1858276
Empirical formula	$C_{40}H_{39}I_6NP_2Pb_2$
Formula weight	1771.44
Temperature/K	170(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	24.560(2)
b/Å	13.0686(11)
c/Å	16.1499(14)
α/°	90
β/°	110.037(2)
γ/°	90
Volume/Å^3	4869.8(7)
Z	4
ρ_{calc}g/cm^3	2.416
μ/mm^{-1}	10.802
F(000)	3192.0
Crystal size/mm^3	0.530 × 0.500 × 0.470
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.932 to 66.52
Index ranges	$-37 \leq h \leq 37$, $-20 \leq k \leq 20$, $-24 \leq l \leq 24$
Reflections collected	76614
Independent reflections	9334 [R_{int} = 0.0564, R_{sigma} = 0.0331]
Data/restraints/parameters	9334/0/254
Goodness-of-fit on F^2	1.154
Final R indexes [I>=2σ (I)]	R_1 = 0.0371, wR_2 = 0.0783
Final R indexes [all data]	R_1 = 0.0522, wR_2 = 0.0854
Largest diff. peak/hole / e Å^{-3}	2.50/-4.19

A-level alerts in the checkCIF/PLATON report flag residual electron density near the lead atoms. This is due to the strongly absorbing lead iodide atoms and Fourier truncation effects. The nature of the atom as lead is not in doubt.

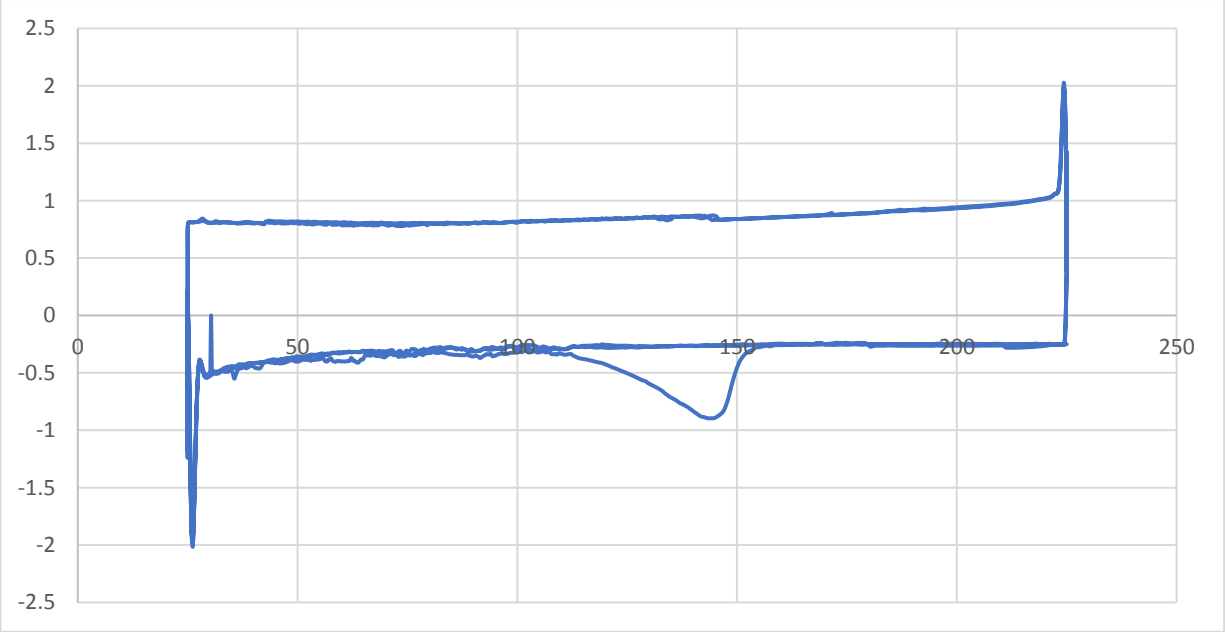
Table S5 Crystal data and structure refinement for $[PHBu_3][PbI_3]$.

Identification code	1858277
Empirical formula	$C_{12}H_{28}I_3PPb$
Formula weight	791.20
Temperature/K	170(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	16.0770(7)
b/Å	16.3313(9)
c/Å	16.9952(9)
α/°	90
β/°	107.066(2)
γ/°	90
Volume/Å^3	4265.7(4)
Z	8
ρ_{calc}g/cm^3	2.464
μ/mm^{-1}	12.313
F(000)	2848.0
Crystal size/mm^3	0.420 × 0.200 × 0.200
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.728 to 61.136
Index ranges	$-22 \leq h \leq 21$, $-23 \leq k \leq 23$, $-24 \leq l \leq 24$
Reflections collected	208613
Independent reflections	25712 [R_{int} = 0.0807, R_{sigma} = 0.0565]
Data/restraints/parameters	25712/105/608
Goodness-of-fit on F^2	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0552, wR_2 = 0.1097
Final R indexes [all data]	R_1 = 0.1017, wR_2 = 0.1364
Largest diff. peak/hole / e Å^{-3}	3.76/-4.03
Flack parameter	0.260(7)

A-level alerts in the checkCIF/PLATON report are due to disorder of the butyl chains which were modelled as appropriately as possible. The nature of the atoms as carbon is not in doubt. Proximity of the hydrogen atoms is due to the disorder model used.

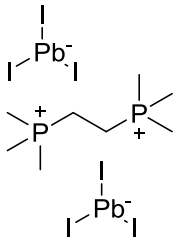
DSC results

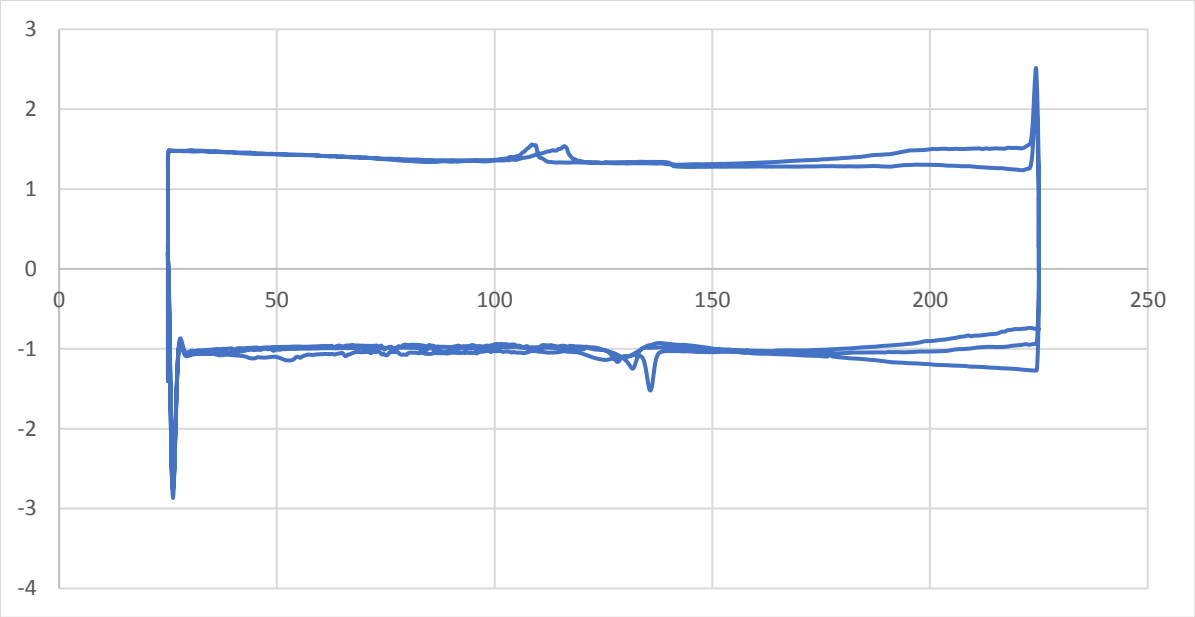
Method: 25 to 225 °C at 10 °Cmin^{-1}, 1 minute isotherm at 225 °C, 225 – 25 °C at 10 °Cmin^{-1}, 1 minute isotherm at 25 °C, 25 to 225 °C at 10 °Cmin^{-1}, 1 minute isotherm at 225 °C, 225 – 25 °C at 10 °Cmin^{-1}.



De-solvation of toluene peak at ca. 100 °C.

1,2-bis(trimethylphosphonio)ethane triiodoplumbate (II), **$[P_2C_8H_{22}][Pb_2I_6]$**

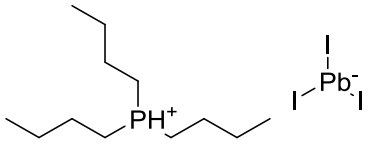


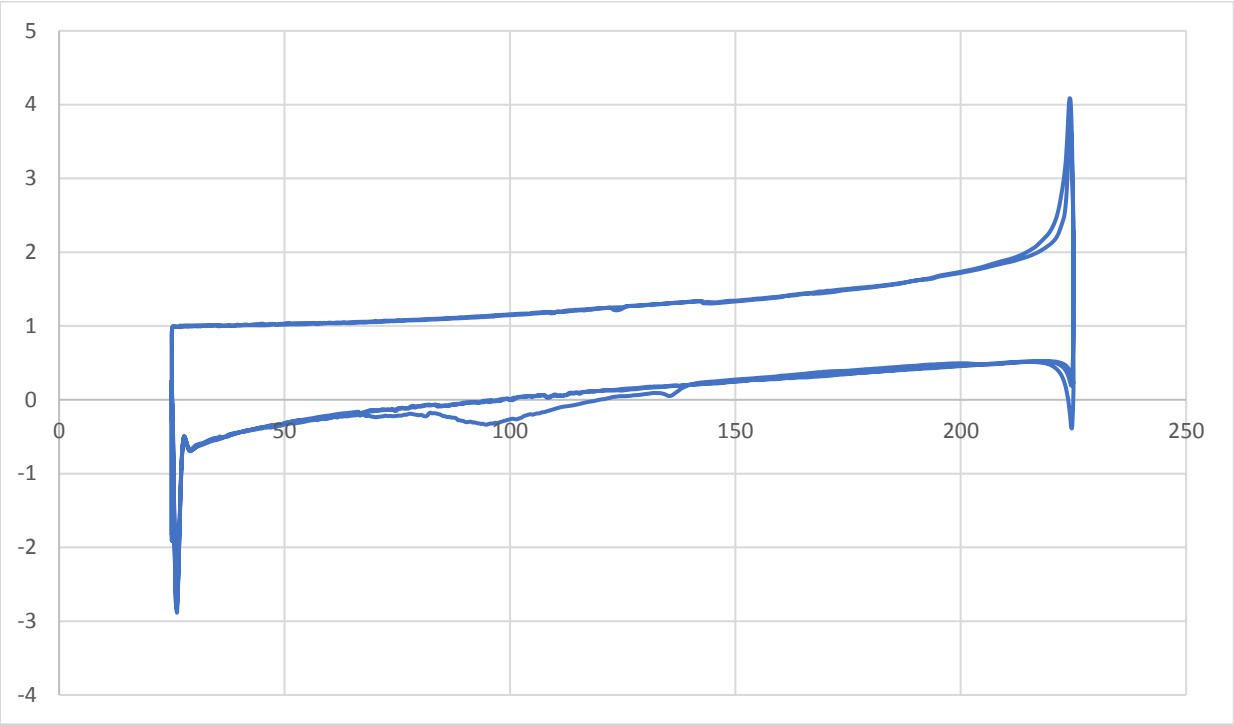


No observed events.

Trace	Melt	Recrys.
1	125.5	116
2	135.833	108.667
3	131.667	

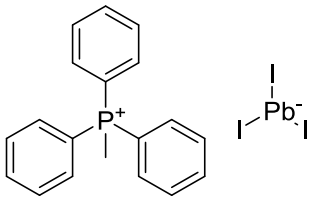
Tributylphosphonium triiodoplumbate (II), **[PHBu$_3$][PbI$_3$]**

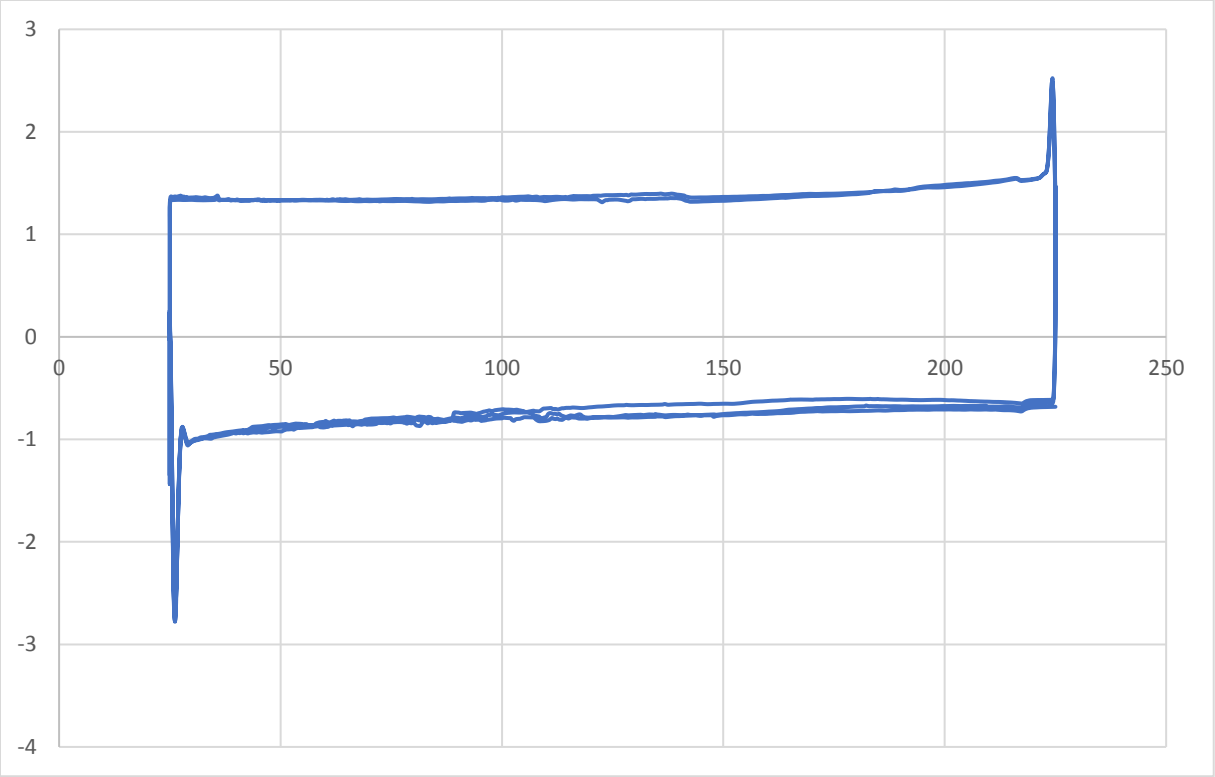




First trace: de-solvation at 94.33; no other noticeable differences.

Methyltriphenylphosphonium triiodoplumbate (II) , **[PMePh$_3$][PbI$_3$]·MeCN**





No observed events.

Tetramethylphosphoium triiodoplumbate (II), **[PMe_4][PbI_3]**