Electronic Supplementary Material for CrystEngComm

Electronic Supplementary Information for:

Polymorphism of lead (II) benzenethiolate: a noncentrosymmetric new allotropic form of $Pb(SPh)_2$.

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SYNTHETIC PROCEDURES

Synthesis of β-$Pb(SPh)_2$ powder through metathesis reaction[5]

A solution of benzenethiol (11.0 g, 0.1 mol) in ethanol (100 mL) was added dropwise, under stirring, to a hot (70°C) solution of hydrated lead (II) acetate $Pb(CH_3CO_2)_2$, 3 H_2O (19.0 g, 0.05 mol) in 30 mL of an 80/20 (v/v) ethanol/water mixture, leading to the precipitation of a yellow solid. The mixture was further heated under reflux for 1 hour, then the solid (21.0 g, yield 98%) was filtered, washed with aqueous ethanol ($EtOH/H_2O$: 80/20) and then with pure ethanol, and finally dried under vacuum. mp 201°C. The powder X-ray diagram of the material thus obtained could be indexed using the cell parameters characteristic of β-$Pb(SPh)_2$ (see below crystallographic data).

Recrystallization[4] of β-$Pb(SPh)_2$: its conversion to α-$Pb(SPh)_2$

In a 250 mL Erlenmeyer flask were successively introduced 50 mL of methanol (degassed by nitrogen bubbling), 0.55 g (5 mmol) of benzenethiol, 1.25g (2.95 mmol) of β-$Pb(SPh)_2$ powder and 5 ml of a 0.5 $mol.L^{-1}$ methanolic solution of sodium methoxide (Aldrich). The mixture was briefly stirred by hand and then left without stirring, in the dark and under nitrogen atmosphere, for 3 days. Afterwards, the mixture was filtered and washed with methanol, affording 0.82 g (recrystallization yield: 66%) of crystals which were proved to be α-$Pb(SPh)_2$ by single crystal and powder X-ray analysis (see below crystallographic data).

Crystals of α-$Pb(SPh)_2$ are also obtained when applying the same procedure but replacing sodium methoxide by 2.5 mmol of benzylamine or (S)-1-phenyl ethylamine (recrystallization yields: 58% and 62% respectively). Additionally, in those cases, we were able to recover, for the most part, the fraction of lead (II) benzenethiolate remaining in solution, probably in the form of the complex $[Pb(SPh)_3]^-$: after the filtration of the crystals of α-$Pb(SPh)_2$, the mother-liquor was evaporated, which led to decomposition of the complex; the resulting material was washed with diethyl ether, in which benzenethiol and benzylammmonium or (S)-1-phenyl ethylammonium benzenethiolate are soluble, affording a further crop of lead (II) benzenethiolate collected by filtration; however, this second fraction was shown, by powder X-ray diffraction, to be β-$Pb(SPh)_2$, thus, in the end, unchanged with regard to the starting material. (The formation of the β-phase in these latter conditions can be related to the fact that its precipitation is fast).

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Thermal conversion of crystals of α-$Pb(SPh)_2$ into β-$Pb(SPh)_2$

A sealed tube containing, under a nitrogen atmosphere, crystals (200 mg) of α-$Pb(SPh)_2$, obtained as described above, was placed for one night in an oven heated at 175°C and then taken out of the oven and allowed to cool down to room temperature. The material contained in the tube was then shown, by single crystal and powder X-ray analysis, to be β-$Pb(SPh)_2$ (see below crystallographic data).

An alternative obtainment of β-$Pb(SPh)_2$

Actually, β-phase crystals were, at first, obtained, through another way, discovered by serendipity: we were attempting to prepare the compound $[(S)\text{-}C_6H_5\text{-}C(\text{-}CH_3)\text{-}NH_3]^+$, $[Pb(SPh)_3]^-$, using the procedure described by Dean *et al.*[6b] for the synthesis of $[(C_6H_5)_4P]^+$, $[Pb(SPh)_3]^-$ but replacing the reactant tetraphenylphosphonium chloride by (S)-1-phenyl ethylammonium chloride. This attempt failed to afford the desired compound but gave instead β-$Pb(SPh)_2$ in the form of analysable monocrystals, in low yield:

Benzenethiol (3.20 g, 29 mmol) and sodium hydroxide beads (1.04 g, 26 mmol) were successively dissolved in methanol (20 mL), then was added, under stirring, a solution of lead (II) nitrate (2.84 g, 8.6 mmol) in water (10 mL), resulting in the precipitation of a yellow solid. To this mixture was added, at first, a solution of $(S)\text{-}C_6H_5\text{-}C(\text{-}CH_3)\text{-}NH_3]^+$, Cl^- (1.38 g, 8.8 mmol) (previously prepared from the action of HCl on $(S)\text{-}C_6H_5\text{-}C(\text{-}CH_3)\text{-}NH_2$ in diethyl ether, mp 170°C) in methanol (60mL) and then 120 mL of aqueous acetonitrile (CH_3CN/H_2O: 5/1, v/v). The mixture was refluxed, under stirring, for 20 min, then filtered while hot and the insoluble part was discarded. The filtrate was allowed to cool down leading to the precipitation of new crystals which, after one night, were collected by filtration (0.42 g, yield 12%) and shown, by single crystal and powder X-ray analysis, to be β-$Pb(SPh)_2$.

However, the result of this experiment probably depends of factors difficult to control such as the exact speed of cooling of the reaction mixture and is not reproducible: another attempt afforded α-$Pb(SPh)_2$ in 37% yield.

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CRISTALLOGRAPHIC DATA

1 - Crystallographic data for α-Pb(S-C_6H_5)$_2$

a- checkcif report for α-Pb(S-C_6H_5)$_2$

```
Bond precision:  C-C = 0.0090 A          Wavelength=0.71073
Cell:        a=27.0798(13) b=5.7437(3) c=7.452(3)
             alpha=90      beta=90     gamma=90
Temperature: 293 K
                Calculated                Reported
Volume          1159.1(5)                 1159.0(4)
Space group     Pmcn                      P m c n
Hall group      -P 2n 2a                  ?
Moiety formula  C12 H10 Pb S2             ?
Sum formula     C12 H10 Pb S2             C12 H10 Pb S2
Mr              425.54                    425.51
Dx,g cm-3       2.439                     2.439
Z               4                         4
Mu (mm-1)       14.876                    14.880
F000            784.0                     784.0
F000'           772.45
h,k,lmax        36,7,10                   36,7,10
Nref            1565                      1558
Tmin,Tmax       0.135,0.304               0.113,0.300
Tmin'           0.044
Correction method= AbsCorr=MULTI-SCAN
Data completeness=
Ratio = 0.996              Theta(max)= 29.000
R(reflections)= 0.0357(    wR2(reflections)= 0.0627(
987)                       1558)
S = 1.033        Npar= 79
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT761_ALERT_1_A CIF Contains no X-H Bonds ....
PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles ..   ?

Alert level B

PLAT230_ALERT_2_B Hirshfeld Test Diff for   S1A   -   S1B   14.35 su
PLAT232_ALERT_2_B Hirshfeld Test Diff (M-X) Pb   -   S1A   13.70 su

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Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without
a literature citation. This should be contained in the
_exptl_absorpt_process_details field.
Absorption correction given as multi-scan
PLAT048_ALERT_1_C MoietyFormula Not Given .....   ?
PLAT125_ALERT_4_C No _symmetry_space_group_name_Hall Given ....   ?

PLAT128_ALERT_4_C Non-standard setting of Space-group Pnma Pmcn
PLAT152_ALERT_1_C Supplied and Calc Volume s.u. Inconsistent ?
PLAT194_ALERT_1_C Missing _cell_measurement_reflns_used datum ....
PLAT195_ALERT_1_C Missing _cell_measurement_theta_max datum . ?
PLAT196_ALERT_1_C Missing _cell_measurement_theta_min datum .. ?
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Pb - S1B 5.03 su
PLAT242_ALERT_2_C Check Low Ueq as Compared to Neighbors for S1A
PLAT301_ALERT_3_C Main Residue Disorder ..... 12.00 Perc.
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang . 9
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C1 - C2 1.38 Ang.
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C1 - C6 1.37 Ang.
PLAT366_ALERT_2_C Short? C(sp?)-C(sp?) Bond C2 - C3 1.37 Ang.
PLAT720_ALERT_4_C Number of Unusual/Non-Standard Label(s) 5
PLAT764_ALERT_4_C Overcomplete CIF Bond List Detected (Rep/Expd) 1.20 Ratio

b- Table 1. Crystal data and structure refinement for α-Pb(S-C_6H_5)$_2$

Empirical formula	C12 H10 Pb S2
Formula weight	425.51
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	orthorhombic, P m c n
Unit cell dimensions	a = 27.0798(13) A alpha = 90 deg.
	b = 5.7437(3) A beta = 90 deg.
	c = 7.452(3) A gamma = 90 deg.
Volume	1159.0(4) A^3
Z, Calculated density	4, 2.439 Mg/m^3
Absorption coefficient	14.878 mm^-1
F(000)	784
Crystal size	0.20 x 0.12 x 0.08 mm
Theta range for data collection	4.21 to 29.00 deg.
Limiting indices	-36<=h<=30, -7<=k<=7, -10<=l<=10
Reflections collected / unique	11520 / 1558 [R(int) = 0.0632]
Completeness to theta = 29.00	99.6 %
Absorption correction	Multi-sacn
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1558 / 0 / 79
Goodness-of-fit on F^2	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.0527
R indices (all data)	R1 = 0.0901, wR2 = 0.0627
Largest diff. peak and hole	1.066 and -1.816 e.A^-3

2 – Crystallographic data for β-Pb(S-C_6H_5)$_2$

a- checkcif report for β-Pb(S-C_6H_5)$_2$

Bond precision: C-C = 0.0126 A Wavelength=0.71073
Cell: a=27.1492(11) b=6.0119(2) c=7.2935(3)
alpha=90 beta=90 gamma=90

	Calculated	Reported
Volume	1190.43(8)	1190.43(8)
Space group	P21ca	P 21 c a
Hall group	P -2ac 2a	?
Moiety formula	C12 H10 Pb S2	?
Sum formula	C12 H10 Pb S2	C12 H10 Pb S2
Mr	425.54	425.54
Dx,g cm-3	2.374	2.374
Z	4	4
Mu (mm-1)	14.485	14.485
F000	784.0	784.0
F000'	772.45	
h,k,lmax	35,7,9	35,7,9
Nref	1404(2746)	2205
Tmin,Tmax	0.135,0.235	0.103,0.282
Tmin'	0.060	

Correction method= AbsCorr=MULTI-SCAN
Data completeness= 1.57(0.80) Theta(max)= 27.520
R(reflections)= 0.0270(1822) wR2(reflections)= 0.0454(2205)
S = 1.032 Npar= 136

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT761_ALERT_1_A CIF Contains no X-H Bonds ..... ?
PLAT762_ALERT_1_A CIF Contains no X-Y-H or H-Y-H Angles .... ?

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field.
Absorption correction given as multi-scan
PLAT048_ALERT_1_C MoietyFormula Not Given ..... ?
PLAT062_ALERT_4_C Rescale T(min) & T(max) by 0.83
PLAT125_ALERT_4_C No _symmetry_space_group_name_Hall Given .. ?
PLAT128_ALERT_4_C Non-standard setting of Space group Pca21 . P21ca
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for S1
PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang . 13

b - Table 1. Crystal data and structure refinement for β-Pb(S-C_6H_5)$_2$

Empirical formula	C12 H10 Pb S2
Formula weight	425.54
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	orthorhombic, P 21 c a
Unit cell dimensions	a = 27.1492(11) A alpha = 90.000(4) deg.
	b = 6.0119(2) A beta = 90.000(4) deg.
	c = 7.2935(3) A gamma = 90.000(3) deg.
Volume	1190.43(8) A^3
Z, Calculated density	4, 2.374 Mg/m^3
Absorption coefficient	14.485 mm^-1
F(000)	784
Crystal size	0.2 x 0.12 x 0.08 mm
Theta range for data collection	3.39 to 27.52 deg.
Limiting indices	-24<=h<=35, -7<=k<=7, -9<=l<=9
Reflections collected / unique	10365 / 2205 [R(int) = 0.0458]
Completeness to theta = 27.52	99.8 %
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2205 / 1 / 136
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0270, wR2 = 0.0427
R indices (all data)	R1 = 0.0422, wR2 = 0.0454
Absolute structure parameter	0.123(8)
Largest diff. peak and hole	0.720 and -0.849 e.A^-3

3 – X-ray powder diffraction

Powder X-ray diffraction measurements were carried out on a D8 Bruker diffractometer using Cu-K$\alpha_{1,2}$ radiation, equipped with a linear Vantec super speed detector. Powder X-Ray patterns of samples of α-Pb(SPh)$_2$ and β-Pb(SPh)$_2$ showed that all reflections are indexed in the unit cells obtained from X-ray diffraction of the single crystal studies (X-ray patterns given in the main text).

DSC ANALYSIS

Differential scanning calorimetry (DSC) measurements were performed on a DSC-2010 TA Instruments system.
DSC analysis were carried out by loading sample (approximately 5 mg) in a nearly hermetic aluminum capsule which was then located in the system unit (nitrogen atmosphere) and heated from room temperature up to 450°C with a 5°C/min ramp rate.

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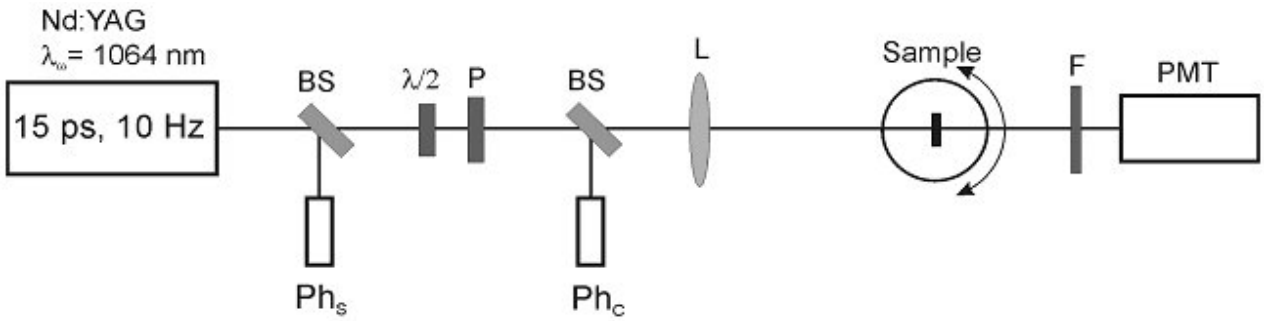
SHG EXPERIMENTS

The properties of the SHG were studied for a fundamental wavelength at 1064 nm from a Q-switch Nd:YAG laser (Model Continuum Leopard D-10) with a pulse duration of 15 ps and a mean power density of 1.0 mJ per pulse at the repetition frequency of 10 Hz. The energy of the fundamental beam was changed with a half-wave plate and a Glan polarizer. The beam was focused on the sample passing through a convergent lens with a focal length of 250 mm.

The crystals of the studied samples and POM were crushed and sieved in order to assure almost the same crystallites size (range of 125-250 μm). The studied powder was placed between two microscope slides. All experiments were done at the same conditions and the amount of used material of studied samples was the same (40 mg).

The SH signal was detected by a photomultiplier (Hamamatsu R1828-01), then integrated by a box-car and processed by a LabVIEW program.



Experimental setup of SHG: BS: beam splitter, λ/2: half wave plate, P: Glan polarizer, L: convergent lens (250 mm), F: selective spectral filter (532 nm), Phs: synchronization photodiode, Phc: control photodiode, PMT: photomultiplier.