Poly[di-μ_2-acetato-κ^4O:O'-μ_3-thiourea-κ^3S:S:S-lead(II)]: a redetermination

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The structure of the title polymeric lead(II) thiourea complex, $[Pb(CH_3O)_2\{SC(NH_2)_2\}]_n$, has been redetermined at significantly higher precision using diffractometer data at 100 K. The previous determination used data obtained from multiple-film integrated Weissenberg photographs [Nardelli et al. (1960). Acta Cryst. **13**, 898–904]. The main difference between the two models is in the precision of the bond lengths, angles and cell parameters. In the crystal, the eight-coordinate Pb^{II} atom is chelated by two carboxylate groups and bridged by three S atoms from thiourea ligands. The coordination sphere is completed by an O atom from a third carboxylate group, the second O atom of which binds to a neighbouring Pb^{II} atom, forming a polymeric chain that runs the a axis. Two of these chains are related by centres of symmetry. Intermolecular hydrogen bonds connect neighbouring chains to one another, generating a three-dimensional network.

3D view

Chemical scheme

Structure description

In the polymeric complex, $[Pb(CH_3O)_2\{SC(NH_2)_2\}]_n$, (Fig. 1) an infinite one-dimensional polymeric chain propagates along the a axis (Fig. 2) with the Pb^{II} ions chelated by the O atoms of two carboxylate groups and bridged by three S atoms from thiourea ligands related to a neighbouring Pb atom by a centre of symmetry. The eightfold coordination is completed by an oxygen atom from a third carboxylate group (Fig. 2). The Pb—O bond lengths range from 2.483 (2) to 2.626 (2) Å, while the two unique Pb—S bonds are 3.0701 (9) and 3.1121 (9) Å, respectively. The Pb atom is displaced out of the least-squares planes of the carboxylate groups (A = O1/C1/O2) and (B = O3/C3/O4) by 0.0038 (2) and 0.0078 (3) Å, respectively. The dihedral angles between the mean planes of

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$NB\cdots$O4^i	0.86	1.99	2.836 (4)	169
N2—H2$NA\cdots$O1^{ii}	0.86	2.04	2.883 (4)	168
N1—H1$NA\cdots$O2^{iii}	0.86	2.26	3.021 (4)	148
N1—H1$NB\cdots$O3^{iv}	0.86	2.48	3.311 (4)	163
C4—H4$A\cdots$O4	0.96	2.51	3.225 (5)	131

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $x + 1, y, z$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + 2, -y, -z$.
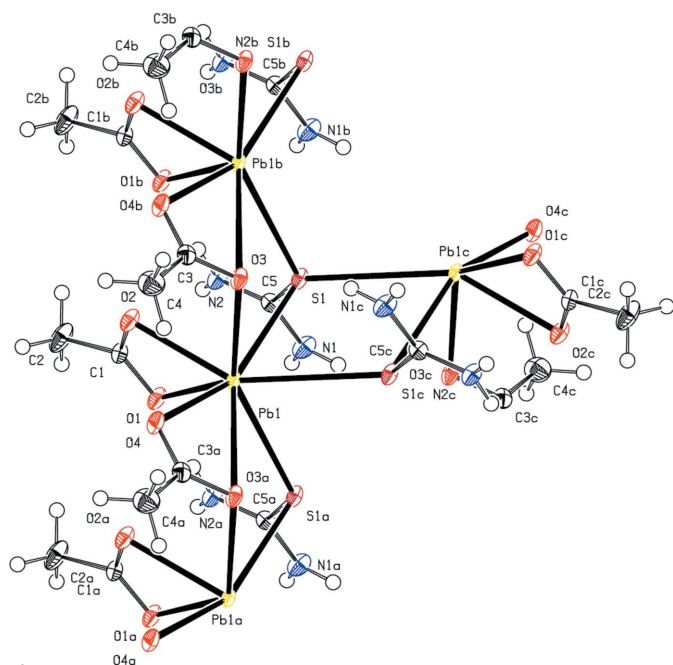
Table 2
Experimental details.

Crystal data	
Chemical formula	[Pb(C$_2$H$_3$O$_2$)$_2$(CH$_4$N$_2$S)]
M_r	401.40
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
a, b, c (Å)	4.4865 (2), 15.7001 (5), 13.6313 (5)
β (°)	91.481 (2)
V (Å^3)	959.85 (6)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	17.78
Crystal size (mm)	0.32 × 0.27 × 0.13
Data collection	
Diffractometer	Bruker APEXII CCD detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.005, 0.099
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	13626, 1893, 1824
R_{int}	0.036
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.015, 0.037, 1.08
No. of reflections	1893
No. of parameters	120
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.88, −1.22

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

Figure 1
The polymeric chain in the structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Atom labels with the suffix a, b and c are related to those with no suffix by the symmetry operations (i), (ii) and (iii) in Table 1.
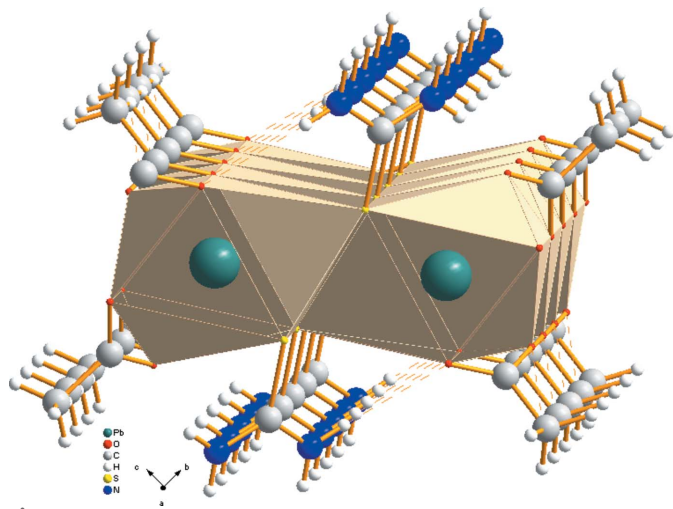

Figure 2
View of a polymeric chain of in the structure of the title compound. For clarity, the [PbO$_5$S$_3$] units are shown as polyhedra, the atoms of the organic ligands are represented as spheres of uniform size selected for each atom type. N—H$\cdots$O and C—H$\cdots$O hydrogen bonds within the chain are shown as dashed lines.
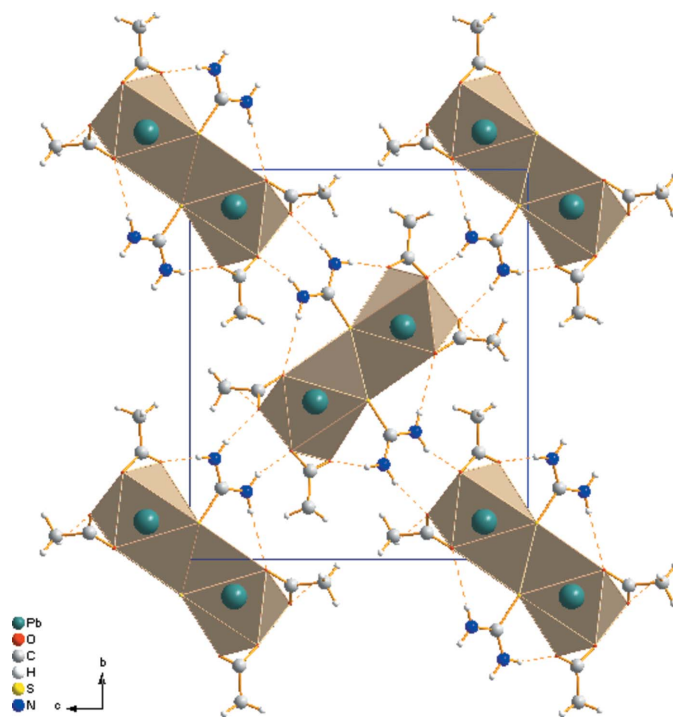

Figure 3
The crystal packing of the title compound viewed along the a axis. N—H$\cdots$O hydrogen bonds are shown as dashed lines (see Table 1 for details).

thiourea ligands (S1/C5/N1/N2) and the carboxylate groups *A* and *B* are 6.93 (18) and 64.37 (19)°, respectively.

In the crystal, H atoms are involved in inter-chain N—H···O and intra-chain N—H···O and C—H···O hydrogen bonds. These link the polymeric chains and stabilize the crystal structure, forming a three-dimensional network (Fig. 3, Table 1).

Synthesis and crystallization

The title compound was obtained from a mixture of (di-aminomethylidene)sulfonium chloride/thiourea (3/2) (Zouihri, 2012) and lead acetate in a molar ratio of 1:1 in ethanol. The mixture was then left for slow evaporation and colourless crystals formed after four days.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. One reflection (011) with $F_o <<< F_c$, likely to have been affected by the beamstop, was omitted from the final refinement.

References

Bruker (2009). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Nardelli, M., Fava, G. & Branchi, G. (1960). *Acta Cryst.* **13**, 898–904.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zouihri, H. (2012). *Acta Cryst.* E**68**, o257.

full crystallographic data

Poly[di-*μ*₂-acetato-*κ*⁴*O*:*O*′-*μ*₃-thiourea-*κ*³*S*:*S*:*S*-lead(II)]: a redetermination

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Poly[di-*μ*₂-acetato-*κ*⁴*O*:*O*′-*μ*₃-thiourea-*κ*³*S*:*S*:*S*-lead(II)]

Crystal data

$[Pb(C_2H_3O_2)_2(CH_4N_2S)]$	$F(000) = 736$
$M_r = 401.40$	$D_x = 2.778$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.4865$ (2) Å	Cell parameters from 214 reflections
$b = 15.7001$ (5) Å	$\theta = 3.1–26.4°$
$c = 13.6313$ (5) Å	$\mu = 17.78$ mm^{-1}
$\beta = 91.481$ (2)°	$T = 100$ K
$V = 959.85$ (6) Å^3	Prism, colourless
$Z = 4$	$0.32 \times 0.27 \times 0.13$ mm

Data collection

Bruker APEXII CCD detector diffractometer	13626 measured reflections
Radiation source: fine-focus sealed tube	1893 independent reflections
Graphite monochromator	1824 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.036$
Absorption correction: multi-scan (SADABS; Bruker, 2009)	$\theta_{max} = 26.0°$, $\theta_{min} = 2.6°$
	$h = -5\rightarrow5$
	$k = -19\rightarrow19$
$T_{min} = 0.005$, $T_{max} = 0.099$	$l = -16\rightarrow16$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.015$	$w = 1/[\sigma^2(F_o^2) + (0.0115P)^2 + 1.9359P]$
$wR(F^2) = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
1893 reflections	$\Delta\rho_{max} = 0.88$ e Å^{-3}
120 parameters	$\Delta\rho_{min} = -1.22$ e Å^{-3}
1 restraint	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pb1	0.74423 (2)	0.09596 (2)	0.12971 (2)	0.01076 (6)
O2	1.0207 (5)	0.22282 (15)	0.19960 (18)	0.0179 (5)
O1	0.6719 (5)	0.24845 (16)	0.08699 (19)	0.0185 (5)
C1	0.8763 (7)	0.2736 (2)	0.1450 (2)	0.0148 (7)
C2	0.9506 (9)	0.3666 (2)	0.1503 (3)	0.0272 (8)
H2A	0.8392	0.3967	0.1002	0.041*
H2B	1.1601	0.3743	0.1406	0.041*
H2C	0.9001	0.3884	0.2135	0.041*
S1	1.22553 (19)	0.09283 (5)	−0.02631 (6)	0.01392 (17)
C3	1.3066 (7)	0.0675 (2)	0.2991 (3)	0.0156 (7)
O3	1.2009 (5)	0.02818 (15)	0.22544 (17)	0.0166 (5)
O4	0.5375 (6)	0.11365 (17)	0.29615 (19)	0.0204 (5)
C5	1.1245 (7)	0.1822 (2)	−0.0929 (2)	0.0127 (6)
N2	1.2377 (6)	0.25730 (18)	−0.0723 (2)	0.0154 (6)
H2NB	1.1832	0.3011	−0.1061	0.019*
H2NA	1.3665	0.2628	−0.0248	0.019*
N1	0.9253 (6)	0.1734 (2)	−0.1662 (2)	0.0194 (6)
H1NA	0.8702	0.2170	−0.2002	0.023*
H1NB	0.8516	0.1240	−0.1795	0.023*
C4	1.1663 (9)	0.0596 (3)	0.3979 (3)	0.0280 (8)
H4A	0.9607	0.0437	0.3892	0.042*
H4B	1.1793	0.1132	0.4316	0.042*
H4C	1.2695	0.0168	0.4359	0.042*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.01374 (8)	0.00827 (8)	0.01006 (8)	−0.00053 (4)	−0.00361 (5)	−0.00080 (4)
O2	0.0227 (12)	0.0117 (12)	0.0188 (13)	−0.0023 (9)	−0.0098 (10)	0.0009 (10)
O1	0.0213 (12)	0.0146 (12)	0.0191 (13)	−0.0020 (9)	−0.0092 (10)	−0.0023 (10)
C1	0.0189 (16)	0.0118 (16)	0.0136 (16)	−0.0018 (13)	−0.0015 (12)	−0.0016 (13)
C2	0.039 (2)	0.0124 (18)	0.029 (2)	−0.0067 (15)	−0.0150 (17)	0.0051 (15)
S1	0.0199 (4)	0.0078 (4)	0.0137 (4)	−0.0009 (3)	−0.0069 (3)	0.0015 (3)
C3	0.0180 (16)	0.0138 (16)	0.0146 (17)	0.0055 (13)	−0.0061 (13)	0.0008 (13)
O3	0.0219 (12)	0.0127 (12)	0.0147 (12)	0.0018 (9)	−0.0084 (9)	−0.0010 (9)
O4	0.0223 (13)	0.0199 (12)	0.0188 (13)	−0.0024 (10)	−0.0045 (10)	−0.0074 (10)
C5	0.0152 (14)	0.0142 (16)	0.0087 (15)	0.0019 (12)	−0.0009 (11)	0.0032 (12)
N2	0.0213 (14)	0.0115 (14)	0.0130 (14)	−0.0018 (11)	−0.0078 (11)	0.0046 (11)
N1	0.0225 (14)	0.0173 (15)	0.0180 (15)	−0.0014 (12)	−0.0086 (11)	0.0063 (12)
C4	0.0267 (19)	0.033 (2)	0.024 (2)	0.0037 (16)	−0.0017 (16)	0.0015 (17)

Geometric parameters (Å, º)

Pb1—O1	2.483 (2)	S1—Pb1^{ii}	3.1121 (9)
Pb1—O4	2.489 (3)	C3—O3	1.261 (4)

Pb1—O2	2.520 (2)	C3—O4^{ii}	1.265 (4)
Pb1—O3	2.626 (2)	C3—C4	1.507 (5)
Pb1—C1	2.858 (3)	O4—C3^{i}	1.265 (4)
Pb1—S1	3.0701 (9)	C5—N2	1.311 (4)
Pb1—S1^{i}	3.1121 (9)	C5—N1	1.330 (4)
O2—C1	1.259 (4)	N2—H2NB	0.8600
O1—C1	1.259 (4)	N2—H2NA	0.8600
C1—C2	1.499 (5)	N1—H1NA	0.8600
C2—H2A	0.9600	N1—H1NB	0.8600
C2—H2B	0.9600	C4—H4A	0.9600
C2—H2C	0.9600	C4—H4B	0.9600
S1—C5	1.726 (3)	C4—H4C	0.9600
O1—Pb1—O4	93.25 (8)	C1—C2—H2C	109.5
O1—Pb1—O2	52.18 (8)	H2A—C2—H2C	109.5
O4—Pb1—O2	76.03 (8)	H2B—C2—H2C	109.5
O1—Pb1—O3	127.07 (8)	C5—S1—Pb1	99.88 (10)
O4—Pb1—O3	84.07 (8)	C5—S1—Pb1^{ii}	121.89 (12)
O2—Pb1—O3	76.25 (7)	Pb1—S1—Pb1^{ii}	93.05 (2)
O1—Pb1—S1	86.73 (6)	O3—C3—O4^{ii}	123.1 (3)
O4—Pb1—S1	156.73 (6)	O3—C3—C4	120.9 (3)
O2—Pb1—S1	85.78 (6)	O4^{ii}—C3—C4	115.9 (3)
O3—Pb1—S1	77.53 (5)	C3—O3—Pb1	118.0 (2)
C1—Pb1—S1	85.29 (7)	C3^{i}—O4—Pb1	106.9 (2)
O1—Pb1—S1^{i}	76.36 (6)	N2—C5—N1	120.3 (3)
O4—Pb1—S1^{i}	109.57 (6)	N2—C5—S1	121.5 (3)
O2—Pb1—S1^{i}	128.52 (6)	N1—C5—S1	118.2 (3)
O3—Pb1—S1^{i}	153.29 (5)	C5—N2—H2NB	120.0
S1—Pb1—S1^{i}	93.05 (2)	C5—N2—H2NA	120.0
C1—O2—Pb1	92.08 (19)	H2NB—N2—H2NA	120.0
C1—O1—Pb1	93.8 (2)	C5—N1—H1NA	120.0
O2—C1—O1	121.9 (3)	C5—N1—H1NB	120.0
O2—C1—C2	118.6 (3)	H1NA—N1—H1NB	120.0
O1—C1—C2	119.6 (3)	C3—C4—H4A	109.5
O2—C1—Pb1	61.80 (17)	C3—C4—H4B	109.5
O1—C1—Pb1	60.11 (17)	H4A—C4—H4B	109.5
C2—C1—Pb1	178.3 (3)	C3—C4—H4C	109.5
C1—C2—H2A	109.5	H4A—C4—H4C	109.5
C1—C2—H2B	109.5	H4B—C4—H4C	109.5
H2A—C2—H2B	109.5		

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2*NB*⋯O4^{iii}	0.86	1.99	2.836 (4)	169
N2—H2*NA*⋯O1^{ii}	0.86	2.04	2.883 (4)	168

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N1—H1*NB*···O3ᵛ	0.86	2.48	3.311 (4)	163
C4—H4*A*···O4	0.96	2.51	3.225 (5)	131

Symmetry codes: (ii) $x+1, y, z$; (iii) $x+1/2, -y+1/2, z-1/2$; (iv) $x-1/2, -y+1/2, z-1/2$; (v) $-x+2, -y, -z$.