IUCrData

ISSN 2414-3146

Redetermination of *catena*-poly[[chloridolead(II)]-μ_2-chlorido-di-μ_2-thiourea-κ^4S:S] at 100 K

Hafid Zouihri,[a]* Khalid Yamni,[a] Youssef Messouss,[b] Najib Tijani[a] and Lahcen Messaoudi[a]

[a]Laboratoire de Chimie des Matériaux et Biotechnologie des Produits Naturels, E.Ma.Me.P.S., Université Moulay Ismail, Faculté des Sciences, Meknès, Morocco, and [b]Centre National de l'Energie, des Sciences et des Techniques Nucléaires, CNESTEN, BP 1382 R.P. Rabat, Morocco. *Correspondence e-mail: hafid.zouihri@gmail.com

Received 12 October 2016
Accepted 31 October 2016

Edited by M. Weil, Vienna University of Technology, Austria

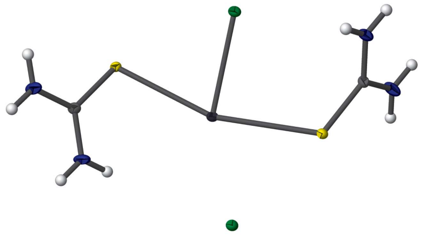
Keywords: crystal structure; redetermination; polymeric lead thiourea salt.

CCDC reference: 1513661

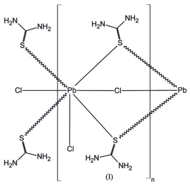
Structural data: full structural data are available from iucrdata.iucr.org

Although the structure rerefinement (CCD data at 100 K) of the polymeric lead(II) thiourea complex, $[PbCl_2{\cdot}2tu]_n$ where (tu = SCN_2H_4), basically confirmed the previous study based on integrated Weissenberg data recorded at room temperature [Nardelli & Fava (1959). *Acta Cryst.* **12**, 727–732]; all atomic positions could be determined with significantly higher precision and accuracy. In addition, all H atoms could be located from difference maps, revealing details of the hydrogen-bonding scheme.

3D view



Chemical scheme



(I)

Structure description

A survey in the Cambridge Structural Database (Groom *et al.*, 2016) shows that the interaction of thiourea (tu) with lead(II) can result in a variety of different compounds and types of coordination. A sixfold coordination of lead by thiourea is found in triclinic $Pb(ClO_4)_2{\cdot}6tu$ (Goldberg & Herbstein, 1972), sevenfold coordination in $PbCl_2{\cdot}2tu$ (Nardelli & Fava, 1959) – which is redetermined in the present work – and eightfold coordination in $PbH(COO)_2{\cdot}4tu{\cdot}H_2O$ (Goldberg & Herbstein, 1973) or $Pb(CHOO)_2{\cdot}2tu$ (Nardelli *et al.*, 1960).

The crystal structure of the title compound comprises an infinite polymeric chain propagating along the *b*-axis direction (Fig. 1) in which the Pb^{II} ions are linked by six bridging atoms, namely four S atoms from two pairs of symmetry-related thiourea ligands and by two symmetry-related Cl^- anions. The distorted sevenfold coordination is completed by another terminal Cl^- anion. The resulting $[PbS_4Cl_3]$ polyhedron can be derived from a distorted trigonal prism formed by four S and two Cl atoms that is capped on one of the lateral faces by another Cl atom. In comparison with the previous determination of the title compound (Nardelli & Fava, 1959) that was based on integrated

Table 1
Comparison of bond lengths (Å) in the current and the previous (Nardelli & Fava, 1959) refinement of poly[μ_2-chlorido-chloridobis(μ_2-thiourea-κ^2S:S)lead(II)].

For the previous refinement: a = 21.20 (4), b = 4.06 (1), c = 12.02 (2) Å; R = 0.114.

Bond	Current refinement	Previous refinement
Pb—Cl1	2.7451 (8)	2.75 (4)
Pb—Cl2	3.1708 (7)	3.17 (3)
Pb—Cl1^{i}	3.1635 (7)	3.28 (3)
Pb—S1	3.0057 (7)	3.02 (3)
Pb—S1^{ii}	3.0494 (7)	3.04 (3)
Pb—S2^{i}	2.9923 (7)	3.10 (3)
Pb—S2	2.9494 (7)	2.92 (3)
S1—C1	1.732 (3)	1.68 (9)
S2—C2	1.739 (3)	1.78 (17)
C1—N1	1.322 (4)	1.40 (12)
C1—N2	1.328 (4)	1.35 (14)
C2—N3	1.320 (4)	1.32 (20)
C2—N4	1.323 (4)	1.34 (17)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N4—H1A⋯Cl1^{i}	0.86	2.53	3.299 (3)	150
N4—H1B⋯Cl2^{ii}	0.86	2.50	3.336 (3)	163
N3—H2A⋯Cl1^{i}	0.86	2.78	3.494 (4)	142
N3—H2A⋯S1^{iii}	0.86	2.85	3.421 (3)	126
N3—H2B⋯Cl1^{iv}	0.86	2.44	3.285 (3)	168
N1—H3A⋯Cl2^{v}	0.86	2.72	3.480 (4)	149
N1—H3A⋯S2^{v}	0.86	2.75	3.414 (3)	135
N1—H3B⋯Cl2^{vi}	0.86	2.37	3.232 (4)	175
N2—H4A⋯Cl2^{v}	0.86	2.49	3.304 (3)	159
N2—H4B⋯Cl1^{vii}	0.86	2.44	3.275 (3)	164

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x, -y, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-\frac{3}{2}, z-\frac{1}{2}$; (iv) $x, y-1, z$; (v) $-x, -y, z+\frac{1}{2}$; (vi) $x, y+1, z$; (vii) $-x+\frac{1}{2}, y+\frac{1}{2}, z+\frac{1}{2}$.

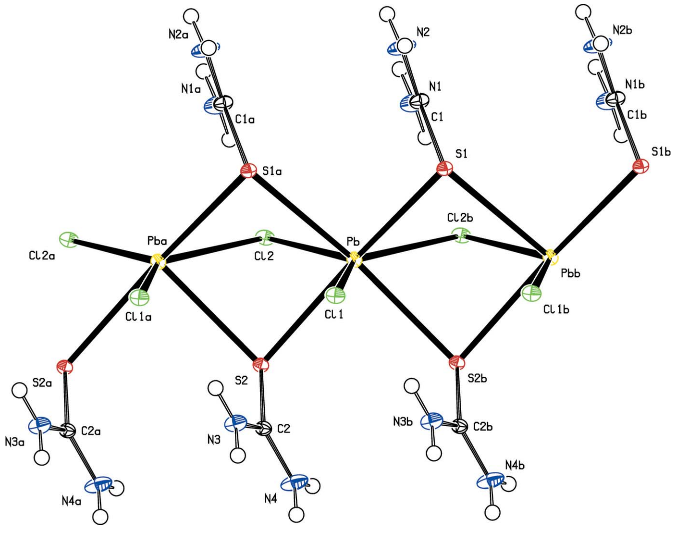


Figure 1
The polymeric chain in the crystal structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. [Symmetry codes: (a) $x, y+1, z$; (b) $x, y-1, z$.]

Table 3
Experimental details.

Crystal data	
Chemical formula	[$PbCl_2(CH_4N_2S)_2$]
M_r	430.33
Crystal system, space group	Orthorhombic, $Pna2_1$
Temperature (K)	100
a, b, c (Å)	21.1951 (6), 4.0280 (1), 11.9433 (3)
V (Å^3)	1019.65 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	17.43
Crystal size (mm)	0.46 × 0.17 × 0.14
Data collection	
Diffractometer	Bruker APEXII CCD detector
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.040, 0.087
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	23237, 6206, 5867
R_{int}	0.032
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.904
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.018, 0.041, 1.04
No. of reflections	6206
No. of parameters	101
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.18, −2.38
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.315 (4)

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

Weissenberg data (room-temperature measurement), the current redetermination reveals not only a higher precision but also a significantly higher accuracy, in particular for the C═S, C—C and C—N bond lengths (Table 1). In contrast to the previous study, the H atoms could be determined in the

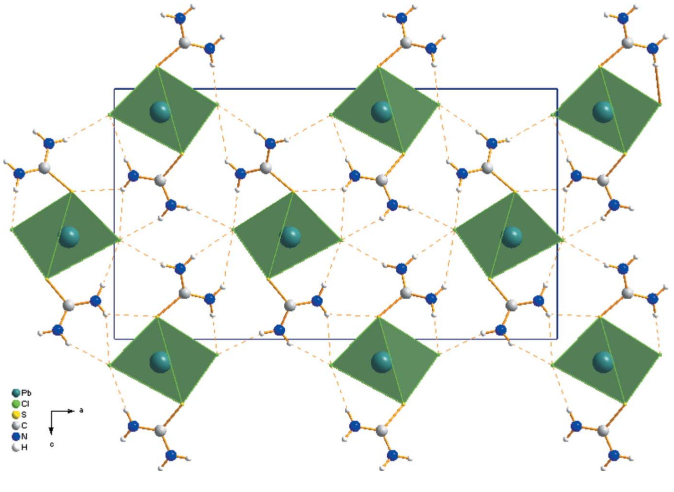


Figure 2
The crystal packing of the title compound viewed along the b axis. The coordination sphere around the Pb^{II} atom is given in the polyhedral representation; N—H⋯Cl and N–H⋯S hydrogen bonds are shown as dashed lines (see Table 2 for details).

current study. All of them are involved in hydrogen-bonding interactions. Intra-chain N—H⋯Cl hydrogen bonds as well as interchain N—H⋯Cl and N—H⋯S hydrogen bonds (Table 2) are observed in the crystal, leading to a three-dimensional network structure (Fig. 2).

Synthesis and crystallization

To obtain the title compound, (diaminomethylidene)-sulfonium chloride–thiourea (3/2) (Zouihri, 2012) (1 mmol) in ethanol (10 ml) was added dropwise to an aqueous solution (5 ml) of lead chlorate (2 mmol). The resulting solution was allowed to stand at room temperature. After two weeks, colourless crystals with good quality were obtained from the filtrate and dried in air.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The same atom labelling as in the previous study (Nardelli & Fava, 1959) was used for better comparison (Table 1). All hydrogen atoms could be localized in difference Fourier syntheses. The structure was refined as an inversion twin (Table 3), using 5385 Friedel pairs. Reflections (200) and (201) were omitted from the refinement due to obstruction from the beam stop.

References

Bruker (2009). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Goldberg, I. & Herbstein, F. H. (1972). *Acta Cryst.* B**28**, 410–415.

Goldberg, I. & Herbstein, F. H. (1973). *Acta Cryst.* B**29**, 246–250.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Nardelli, M. & Fava, G. (1959). *Acta Cryst.* **12**, 727–732.

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.

IUCrData (2016). **1**, x161745 Zouihri *et al.* • $[PbCl_2(CH_4N_2S)_2]$ **3 of 3**

full crystallographic data

IUCrData (2016). **1**, x161745 [https://doi.org/10.1107/S2414314616017454]

Redetermination of *catena*-poly[[chloridolead(II)]-μ_2-chlorido-di-μ_2-thiourea-κ^4*S*:*S*] at 100 K

Hafid Zouihri, Khalid Yamni, Youssef Messouss, Najib Tijani and Lahcen Messaoudi

catena-Poly[[chloridolead(II)]-μ_2-chlorido-di-μ_2-thiourea-κ^2*S*:*S*]

Crystal data

$[PbCl_2(CH_4N_2S)_2]$
$M_r = 430.33$
Orthorhombic, $Pna2_1$
$a = 21.1951\ (6)$ Å
$b = 4.0280\ (1)$ Å
$c = 11.9433\ (3)$ Å
$V = 1019.65\ (5)$ Å^3
$Z = 4$
$F(000) = 784$
$D_x = 2.803$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 318 reflections
$\theta = 1.5$–$28.3°$
$\mu = 17.43$ mm^{-1}
$T = 100$ K
Prism, colourless
0.46 × 0.17 × 0.14 mm

Data collection

Bruker APEXII CCD detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)
$T_{min} = 0.040$, $T_{max} = 0.087$
23237 measured reflections
6206 independent reflections
5867 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 40.0°$, $\theta_{min} = 2.6°$
$h = -38 \rightarrow 36$
$k = -7 \rightarrow 5$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.041$
$S = 1.04$
6206 reflections
101 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0121P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.18$ e Å^{-3}
$\Delta\rho_{min} = -2.38$ e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.315 (4)

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.

Refinement. Refined as a 2-component inversion twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Pb	0.10368 (2)	0.29058 (2)	0.09284 (2)	0.00922 (2)
Cl1	0.23177 (4)	0.24529 (17)	0.06240 (7)	0.01151 (10)
Cl2	−0.01146 (3)	−0.21081 (15)	0.10426 (7)	0.01147 (13)
S2	0.09634 (4)	−0.20155 (16)	−0.08955 (7)	0.00909 (11)
S1	0.15296 (4)	0.78245 (15)	0.26068 (7)	0.00912 (11)
C1	0.10345 (13)	0.6395 (9)	0.3655 (3)	0.0122 (4)
C2	0.15858 (15)	−0.1690 (6)	−0.1838 (2)	0.0102 (4)
N3	0.21531 (14)	−0.2855 (6)	−0.1607 (3)	0.0145 (4)
H2A	0.2453	−0.2656	−0.2088	0.017*
H2B	0.2223	−0.3812	−0.0975	0.017*
N1	0.04268 (13)	0.5872 (8)	0.3479 (3)	0.0187 (5)
H3A	0.0195	0.5066	0.4004	0.022*
H3B	0.0263	0.6338	0.2839	0.022*
N2	0.12793 (14)	0.5659 (8)	0.4648 (2)	0.0185 (5)
H4A	0.1043	0.4854	0.5166	0.022*
H4B	0.1674	0.5988	0.4772	0.022*
N4	0.14795 (14)	−0.0218 (8)	−0.2809 (2)	0.0196 (5)
H1A	0.1780	−0.0023	−0.3289	0.024*
H1B	0.1110	0.0543	−0.2961	0.024*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.00719 (4)	0.01007 (3)	0.01040 (4)	0.00009 (2)	0.00000 (5)	−0.00047 (9)
Cl1	0.0079 (3)	0.0156 (2)	0.0110 (2)	0.00059 (18)	0.0001 (2)	−0.00040 (17)
Cl2	0.0080 (2)	0.0163 (2)	0.0101 (4)	−0.00025 (15)	0.0003 (2)	−0.0017 (2)
S2	0.0074 (3)	0.0108 (2)	0.0090 (3)	−0.00018 (17)	0.0008 (2)	−0.00054 (19)
S1	0.0080 (3)	0.0107 (2)	0.0086 (3)	−0.00211 (18)	0.0000 (2)	0.0005 (2)
C1	0.0103 (12)	0.0157 (10)	0.0107 (11)	−0.0031 (8)	0.0007 (8)	0.0012 (9)
C2	0.0097 (11)	0.0118 (9)	0.0091 (10)	0.0014 (7)	0.0004 (9)	−0.0004 (7)
N3	0.0087 (11)	0.0224 (11)	0.0125 (11)	0.0045 (8)	0.0014 (9)	0.0029 (8)
N1	0.0075 (10)	0.0341 (14)	0.0146 (11)	−0.0044 (9)	−0.0003 (9)	0.0046 (11)
N2	0.0114 (12)	0.0343 (15)	0.0099 (10)	−0.0059 (10)	−0.0019 (9)	0.0063 (9)
N4	0.0127 (12)	0.0342 (14)	0.0119 (11)	0.0076 (10)	0.0033 (9)	0.0081 (10)

Geometric parameters (Å, º)

Pb—Cl1	2.7451 (8)	C1—N2	1.328 (4)
Pb—S2	2.9494 (7)	C2—N3	1.320 (4)
Pb—S2$^{\rm i}$	2.9923 (7)	C2—N4	1.323 (4)
Pb—S1	3.0057 (7)	N3—H2A	0.8600
Pb—S1$^{\rm ii}$	3.0494 (7)	N3—H2B	0.8600
Pb—Cl2	3.1708 (7)	N1—H3A	0.8600
S2—C2	1.739 (3)	N1—H3B	0.8600
S2—Pb$^{\rm ii}$	2.9924 (7)	N2—H4A	0.8600

S1—C1	1.732 (3)	N2—H4B	0.8600
S1—Pb^{i}	3.0493 (7)	N4—H1A	0.8600
C1—N1	1.322 (4)	N4—H1B	0.8600
Cl1—Pb—S2	84.82 (2)	Pb—S1—Pb^{i}	83.40 (2)
Cl1—Pb—S2^{i}	90.03 (2)	N1—C1—N2	119.1 (3)
S2—Pb—S2^{i}	85.36 (2)	N1—C1—S1	121.9 (3)
Cl1—Pb—S1	77.79 (2)	N2—C1—S1	118.9 (2)
S2—Pb—S1	162.54 (2)	N3—C2—N4	119.9 (3)
S2^{i}—Pb—S1	93.035 (19)	N3—C2—S2	122.0 (2)
Cl1—Pb—S1^{ii}	72.76 (2)	N4—C2—S2	118.2 (2)
S2—Pb—S1^{ii}	93.01 (2)	C2—N3—H2A	120.0
S2^{i}—Pb—S1^{ii}	162.79 (2)	C2—N3—H2B	120.0
S1—Pb—S1^{ii}	83.40 (2)	H2A—N3—H2B	120.0
Cl1—Pb—Cl2	136.433 (18)	C1—N1—H3A	120.0
S2—Pb—Cl2	64.09 (2)	C1—N1—H3B	120.0
S2^{i}—Pb—Cl2	115.26 (2)	H3A—N1—H3B	120.0
S1—Pb—Cl2	131.19 (2)	C1—N2—H4A	120.0
S1^{ii}—Pb—Cl2	78.92 (2)	C1—N2—H4B	120.0
C2—S2—Pb	112.77 (10)	H4A—N2—H4B	120.0
C2—S2—Pb^{ii}	118.89 (10)	C2—N4—H1A	120.0
Pb—S2—Pb^{ii}	85.36 (2)	C2—N4—H1B	120.0
C1—S1—Pb	92.99 (11)	H1A—N4—H1B	120.0
C1—S1—Pb^{i}	119.38 (11)		

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *y*−1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H1*A*···Cl1^{iii}	0.86	2.53	3.299 (3)	150
N4—H1*B*···Cl2^{iv}	0.86	2.50	3.336 (3)	163
N3—H2*A*···Cl1^{iii}	0.86	2.78	3.494 (4)	142
N3—H2*A*···S1^{v}	0.86	2.85	3.421 (3)	126
N3—H2*B*···Cl1^{ii}	0.86	2.44	3.285 (3)	168
N1—H3*A*···Cl2^{vi}	0.86	2.72	3.480 (4)	149
N1—H3*A*···S2^{vi}	0.86	2.75	3.414 (3)	135
N1—H3*B*···Cl2^{i}	0.86	2.37	3.232 (4)	175
N2—H4*A*···Cl2^{vi}	0.86	2.49	3.304 (3)	159
N2—H4*B*···Cl1^{vii}	0.86	2.44	3.275 (3)	164

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *y*−1, *z*; (iii) −*x*+1/2, *y*−1/2, *z*−1/2; (iv) −*x*, −*y*, *z*−1/2; (v) −*x*+1/2, *y*−3/2, *z*−1/2; (vi) −*x*, −*y*, *z*+1/2; (vii) −*x*+1/2, *y*+1/2, *z*+1/2.