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Key indicators

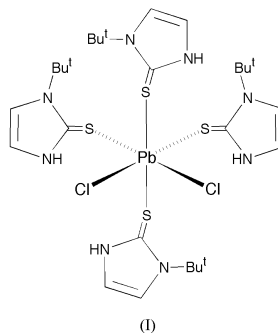
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$
 R factor = 0.047
 wR factor = 0.130
Data-to-parameter ratio = 17.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*cis*-Dichlorotetrakis(2-mercapto-1-*tert*-butylimidazole)lead(II)

The crystal and molecular structure of the title compound, $[\text{PbCl}_2(\text{C}_7\text{H}_{12}\text{N}_2\text{S})_4]$, the first mononuclear lead complex containing a 2-mercapto-1-alkylimidazole ligand to be structurally characterized, has been determined by single-crystal X-ray diffraction. The six-coordinate Pb atom displays a distorted octahedral geometry and is surrounded by four thione groups and two *cis* chloro ligands, with average Pb—S and Pb—Cl bond distances of 2.946 (3) and 3.058 (2) Å, respectively.

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Comment

The coordination chemistry of lead with sulfur-donor ligands is surprisingly underdeveloped despite the purported thiophilicity of this metal. According to a recent survey, only about 16% of all Pb^{II} compounds in the Cambridge Structural Database (CSD; Version 5.24, November 2002; Allen, 2002) contain one or more sulfur-donor groups (Claudio *et al.*, 2003). Heterocyclic thione and thionate ligands are no exception, and very few derivatives of lead have been isolated with such donors, despite the large number of complexes obtained with them for both transition and main group metals (Raper, 1985; Akrivos, 2001). In view of this imbalance and because of our interest in the coordination chemistry of lead with simple thione-type donor ligands, we set out to prepare new complexes with *N*-substituted mercaptoimidazoles. We report here the synthesis, characterization and structure of *cis*-dichlorotetrakis(2-mercapto-1-*tert*-butylimidazole)lead(II), (I), the first mononuclear lead complex containing a 2-mercapto-1-alkylimidazole ligand to be structurally characterized.



The crystal and molecular structure of (I) was determined by single-crystal X-ray diffraction (Fig. 1). The Pb atom in *cis*- $\text{Pb}(\text{Hmim}^{\text{tBu}})_4\text{Cl}_2$ is coordinated by the thione moieties of four mercaptoimidazole groups and by two adjacent chloro ligands in a distorted octahedral environment, with the *trans* and *cis* angles in the approximate ranges 154–170 and 77–112°, respectively. The two Pb—S distances to the thione ligands

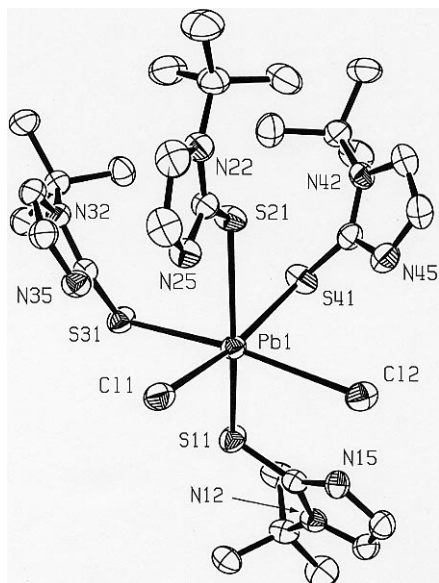


Figure 1
A view of the title compound, showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

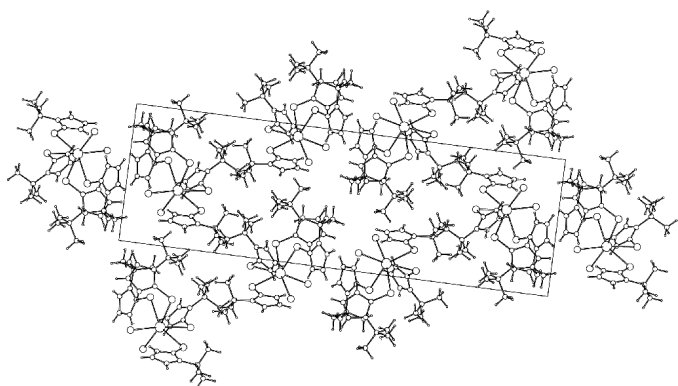


Figure 2
A packing diagram of the title compound, viewed down the *a* axis.

trans to the chlorides (*ca* 2.89 Å) are slightly shorter than those for the mutually *trans* thiones (*ca* 3.00 Å). While these values are only moderately longer than the corresponding bond lengths to the terminal methimazole groups in the dinuclear derivative $\text{Pb}_2(\text{Hmim}^{\text{Me}})_6(\text{NO}_3)_4$ (*ca* 2.84 Å; Bristow *et al.*, 1987), they are comparable to those found in other Pb^{II} complexes with thioureas or heterocyclic thiones (Goldberg & Herbstein, 1972; Herbstein & Kaftory, 1972; Williams *et al.*, 1992). It is also interesting to note that the average C—S bond length in *cis*- $\text{Pb}(\text{Hmim}^{\text{tBu}})_4\text{Cl}_2$ (*ca* 1.71 Å) is very similar to the corresponding averages found for the group 12 metal derivatives $(\text{Hmim}^{\text{tBu}})_4\text{MBr}_2$ (*M* = Zn, Cd, Hg) (*ca* 1.72 Å) or even in free Hmim^{tBu} (1.70 Å; White *et al.*, 2003). The Pb—Cl bond lengths, 3.037 (2) and 3.079 (2) Å, while longer than the mean value found in the CSD for such terminal interactions in six-coordinate Pb^{II} (2.87 Å), are still within the range of observed distances for such bonds (2.617–3.348 Å; Allen, 2002).

Experimental

A solution of 2-mercapto-1-*tert*-butylimidazole (0.150 g, 0.960 mmol) in methanol (1 ml) was added to a stirred solution of PbCl_2 (0.067 g, 0.240 mmol) in water (5 ml), resulting in the immediate formation of an off-white precipitate and a pale yellow solution. After stirring the suspension for 30 min, the product was isolated by filtration and dried *in vacuo* for 14 h (0.126 g, 58%). NMR data (in CD_2Cl_2): ^1H δ 1.74 [s, 36H, C(CH₃)₃], 6.72 (*d*, $^3J_{\text{H-H}} = 2.3$ Hz, 4H, imidazole H), 6.84 (*d*, $^3J_{\text{H-H}} = 2.3$ Hz, 4H, imidazole H), 11.91 (*br s*, 4 H, NH); ^{13}C δ 28.5 [*q*, $^1J_{\text{C-H}} = 128$ Hz, 12C, C(CH₃)₃], 59.1 [s, 4C, C(CH₃)₃], 114.2 (*d*, $^1J_{\text{C-H}} = 176$ Hz, 4C, imidazole C), 116.3 (*d*, $^1J_{\text{C-H}} = 167$ Hz, 4C, imidazole C), 156.8 (*s*, 4C, C=S). IR data (cm^{-1}): 3137 (*m*), 3096 (*s*), 3015 (*m*), 2974 (*s*), 2917 (*m*), 2884 (*m*), 2782 (*w*), 2729 (*w*), 1576 (*s*), 1474 (*s*), 1455 (*m*), 1414 (*m*), 1399 (*m*), 1369 (*m*), 1312 (*vs*), 1264 (*w*), 1238 (*vs*), 1225 (*s*), 1178 (*w*), 1126 (*m*), 1118 (*m*), 1043 (*w*), 1014 (*w*), 935 (*w*), 913 (*w*), 795 (*m*), 768 (*w*), 723 (*m*), 684 (*s*), 591 (*w*), 546 (*m*), 458 (*w*). Analysis calculated for $\text{C}_{28}\text{H}_{48}\text{Cl}_2\text{N}_8\text{PbS}_4$: C 37.2, H 5.4, N 12.4%; found: C 37.5, H 5.2, N 12.5%.

Crystal data

$[\text{PbCl}_2(\text{C}_7\text{H}_{12}\text{N}_2\text{S})_4]$
M_r = 903.07
Monoclinic, $P2_1/c$
a = 10.268 (1) Å
b = 10.984 (1) Å
c = 34.514 (4) Å
 β = 93.294 (9)°
V = 3886.4 (8) Å³
Z = 4

D_x = 1.543 Mg m⁻³
Cu *K*α radiation
Cell parameters from 25 reflections
 θ = 11.0–20.8°
 μ = 11.97 mm⁻¹
T = 293 (2) K
Irregular, yellow
0.40 × 0.29 × 0.17 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: analytical (Katayama, 1986)
T_{min} = 0.048, *T_{max}* = 0.214
10879 measured reflections
6878 independent reflections
5838 reflections with $I > 2\sigma(I)$

R_{int} = 0.051
 θ_{max} = 66.9°
h = −12 → 12
k = 0 → 13
l = −34 → 41
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.130$
S = 1.03
6878 reflections
404 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0906P)^2 + 2.6577P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.68 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.50 \text{ e \AA}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00190 (9)

Table 1

Selected geometric parameters (Å, °).

Pb1—S31	2.870 (2)	Pb1—Cl1	3.037 (2)
Pb1—S41	2.906 (2)	Pb1—Cl2	3.079 (2)
Pb1—S21	2.930 (2)	Pb1—S11	3.079 (2)
S31—Pb1—S41	92.26 (6)	S21—Pb1—Cl2	101.62 (5)
S31—Pb1—S21	87.51 (5)	Cl1—Pb1—Cl2	93.01 (5)
S41—Pb1—S21	76.93 (5)	S31—Pb1—S11	78.34 (4)
S31—Pb1—Cl1	90.14 (5)	S41—Pb1—S11	81.82 (5)
S41—Pb1—Cl1	166.54 (5)	S21—Pb1—S11	153.93 (5)
S21—Pb1—Cl1	89.95 (5)	Cl1—Pb1—S11	111.64 (5)
S31—Pb1—Cl2	170.34 (5)	Cl2—Pb1—S11	92.01 (4)
S41—Pb1—Cl2	86.79 (6)		

The maximum and minimum electron-density peaks in the final difference Fourier map are 1.14 and 0.90 Å, respectively, from the Pb atom. The H atoms were constrained using a riding model. For the methyl groups, an idealized tetrahedral geometry was used, and the torsion angle about the bond to each methyl group was refined.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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