Crystal structure of lead chloride thiocyanate, PbCl(SCN)

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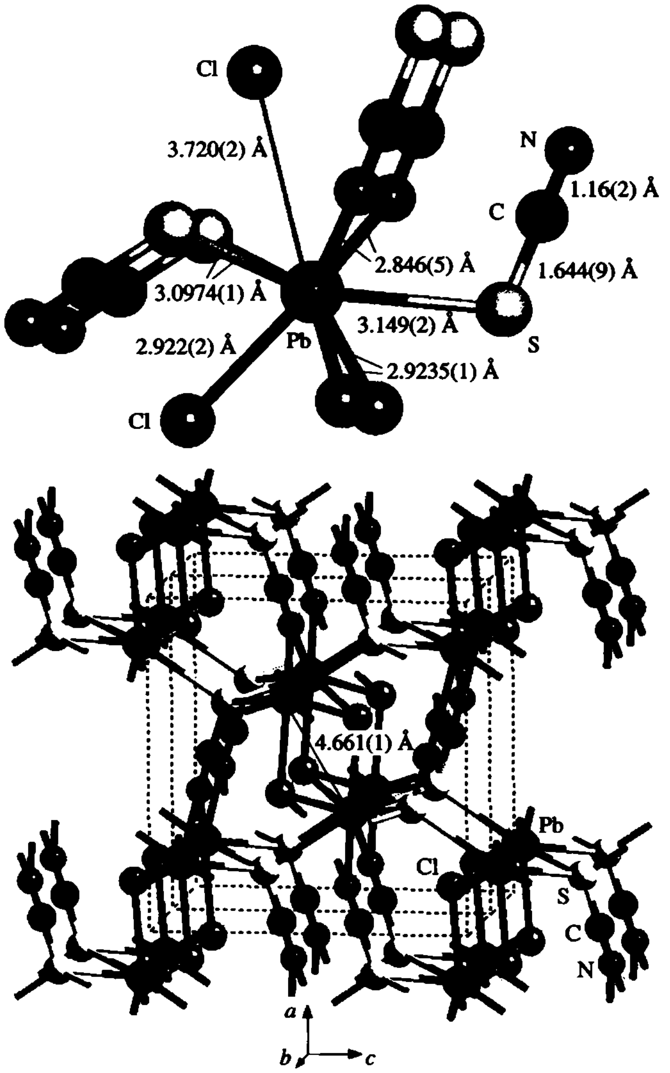

Abstract

CClNPbS, orthorhombic, *Pnma* (no. 62), $a = 10.166(1)$ Å, $b = 4.255(1)$ Å, $c = 9.589(1)$ Å, $V = 414.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.067$, $T = 293$ K.

Source of material

PbCl(SCN) was prepared from $PbCl_2$ and KSCN: 0.5 mmol of $PbCl_2$ were dissolved in 100 mL of water with the stoichiometric amount of KSCN. The mixture was refluxed during one hour and the resulting clear solution was slowly evaporated at room temperature, yielding millimeter sized, transparent needles of PbCl(SCN).

Discussion

The lead atom is coordinated to three sulfur atoms and two nitrogen atoms from five thiocyanate groups (figure, top). The metal environment is completed by three chlorine atoms. This coordination scheme can be described as a bicapped trigonal prism, the capping atoms being a sulfur atom at 3.149 Å and a chlorine atom at 2.922 Å. The position of the potential third cap is occupied by a chlorine atom, but the Pb—Cl distance, 3.72 Å, is too long to be considered. This environment is very similar to the one observed in BaCl(SCN) where the cation is located at the centre of a tricapped trigonal prism [1]. Among lead compounds, the present environment is not unusual: a mono- or a bicapped trigonal prismatic arrangement is observed in several chlorides or bromides as $NH_4Pb_2Cl_5$, $NH_4Pb_2Br_5$ or $[Co(NH_3)_6](Pb_4Cl_{11})$ [2-4]. This shows that the lone pair effect is very weak in the chemistry of Pb(II) compounds, even with electronegative ligands. The N atom is bridging two Pb atoms along the *b* axis and the S atom is μ_3 coordinated towards Pb. SCN^- is a highly versatile ambidentate ligand with fifteen modes of coordination: two terminal modes and thirteen multidentate bridging modes, ranging from bi- to hexadentate [5]. The present pentadentate mode (Va in ref [5]) is rather rare, but has already been observed in BaCl(SCN) and $Na_4Mg(SCN)_6$ [1]. The chlorine atoms are μ_3-coordinated under forming tetrahedra. Lead polyhedra are edge-connected through two chlorine bridges, leading to a Pb—Pb distance equal to 4.661 Å (figure, bottom). They are also face-connected, along the *b* axis, through three bridges (μ_2-N, μ_2-S and μ_2-Cl) with a Pb—Pb distance equal to the *b* parameter. These connections result in the formation of double chains, extending along the *b* axis and centred on the centres of symmetry. Finally, the 3D crystal structure of PbCl(SCN) is designed by linking these chains through the bridging thiocyanate groups.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.06 × 0.16 × 0.5 mm
Wavelength:	Ag K_α radiation (0.56085 Å)
μ:	226.89 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, ω/φ
$2\theta_{max}$:	42.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2518, 544
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 468
$N(param)_{refined}$:	31
Programs:	SIR92 [6], SHELXS-97 [7], SHELXL-97 [8], WinGX [9]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb	4*c*	0.18928(3)	¾	0.08053(3)	0.0226(3)	0.0210(3)	0.0261(2)	0	–0.0016(1)	0
Cl	4*c*	–0.0972(2)	¾	0.1044(2)	0.017(1)	0.016(1)	0.0221(9)	0	–0.0014(7)	0
S	4*c*	0.1370(2)	¼	0.3087(2)	0.015(1)	0.020(1)	0.0176(8)	0	0.0004(8)	0
C	4*c*	–0.0173(9)	¼	0.3600(8)	0.021(4)	0.013(4)	0.017(3)	0	0.001(3)	0
N	4*c*	–0.1260(8)	¼	0.3961(8)	0.018(4)	0.032(5)	0.025(3)	0	–0.003(3)	0

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