Crystal structure of tin octa-μ-chloro-hexachloro-octahedro-molybdate(II), $Sn[(Mo_6Cl_8)Cl_6)]$.

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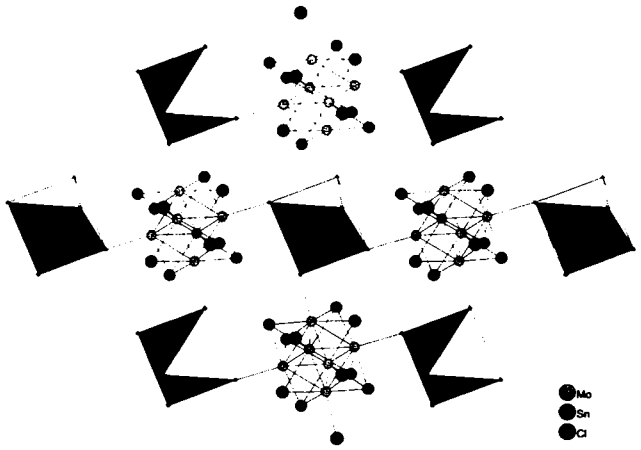

Abstract

$Cl_{14}Mo_6Sn$, cubic, $Pn\bar{3}$ (No. 201), $a = 12.952$ Å, $V = 2172.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.048$, $wR_{ref}(F) = 0.063$, $T = 293$ K.

Source of material

Single crystals of $Sn((Mo_6Cl_8)Cl_6)$ were grown in evacuated quartz tubes from a well ground mixture of $MoCl_2$ [1] and commercial $SnCl_2$ in the molar ratio 2:3 at 1073 K for 19 h. The crystals were yellow, slightly transparent needles.

Experimental details

Due to the sensitivity to moisture all preparative work had to be done in a glove box under Ar-atmosphere.The crystal chosen for the X-ray experiment was mounted on a quartz fibre of 0.1 mm diameter and then encapsulated in a quartz capillary of 0.3 mm diameter.

Discussion

Tin octa-μ-chloro-hexachloro-octahedro-molybdate(II), $Sn[(Mo_6Cl_8)Cl_6]$, has been investigated as part of a project aimed at synthesizing extended molecules with Mo_6Cl_8 as a base. The title compound $Sn[(Mo_6Cl_8)Cl_6]$ is isostructural with $Pb[(Mo_6Cl_8)Cl_6]$ [2], with the Sn atom situated in a chloride octahedron formed by the bridging chlorine atoms. The Mo atoms are, as in all other reported structures of Mo(II)halides, arranged in an octahedron encapsulated in a chlorine cube [3] as shown in the figure. The structure may be described as an double skutterudite. Skutterudite $CoAs_3$ [4] is derived from the aristotype, 'ideal', cubic perovskite, by the concerted rotation of the 'ideal' perovskite octahedron around the three fold axes, ([111] direction). The rotation angle φ in skutterudite is $\varphi \approx 35°$ [5]. Due to the differences in size between the octahedra in the title compond the rotation angle φ will differ. The φ value for the smaller chloride octahedron surrounding tin is 23.8°, and for the bigger chloride octahedron surrounding the Mo_6Cl_8 unit, $\varphi = 36.5°$.

Table 1. Data collection and handling.

Crystal:	yellow needle, size 0.1 × 0.2 × 0.3 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.7 cm^{-1}
Diffractometer, scan mode:	STOE IPDS, φ
$2\theta_{max}$:	56.44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18628, 900
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 253
$N(param)_{refined}$:	33
Programs:	SHELXS 97 [6], Jana 2000 [7]

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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}
Mo	24*h*	0.8649(2)	0.0282(2)	0.963(2)	0.020(8)	0.0266(7)	0.0239(7)	–0.0007(7)	–0.0016(8)	0.0014(7)
Sn	4*c*	1/2	1/2	1/2	0.0292(8)	U_{11}	U_{11}	0.0010(8)	U_{12}	U_{12}
Cl(1)	8*e*	0.1363(4)	*x*	*x*	0.038(2)	U_{11}	U_{11}	–0.008(2)	U_{12}	U_{12}
Cl(2)	24*h*	0.3776(4)	0.6883(4)	0.9337(4)	0.030(3)	0.031(3)	0.030(3)	0.009(2)	–0.003(2)	0.002(2)
Cl(3)	24*h*	0.5891(5)	0.8133(4)	0.0698(5)	0.044(4)	0.020(2)	0.068(5)	–0.004(2)	–0.010(3)	–0.006(3)

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