Crystal structure of lead(II) trioxovanadate(V) chloride, $Pb[VO_3]Cl$

Aytac Sahin and Mehtap Emirdag-Eanes*

Izmir Institute of Technology, Department of Chemistry, Izmir 35430, Turkey

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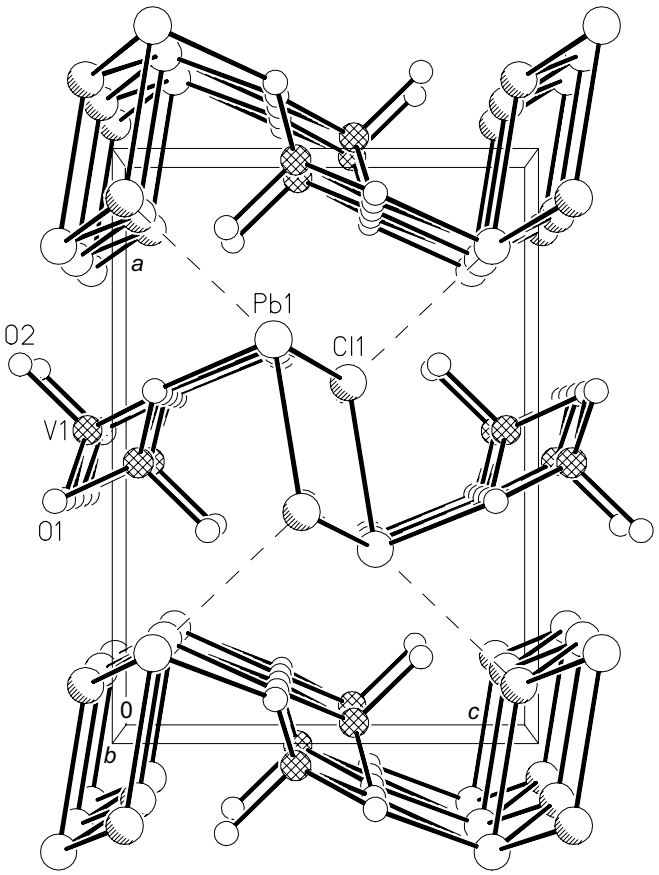

Abstract

ClO_3PbV, orthorhombic, *Pnma* (no. 62), a = 10.022(2) Å, b = 5.288(1) Å, c = 7.171(1) Å, V = 380.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.035, $wR_{ref}(F^2)$ = 0.105, T = 153 K.

Source of material

The following reagents were used as obtained: $NaVO_3$ (Fluka, 98 %) and $PbCl_2$ (Riedel-de Haen, 98 %). $Pb[VO_3]Cl$ was obtained from the reaction of $NaVO_3$ (460.5 mg, 3.3 mmol) and $PbCl_2$ (992 mg, 3.56 mmol). A reaction mixture was loaded into a 23 mL Teflon-lined autoclave. Then 9 mL of 1.7 M $B(OH)_3$ was added. The autoclave was heated at 170 °C for 3 days and then cooled to room temperature. The solid products were recovered by suction filtration and washed with water. The product was a mixture of yellow needle crystals and white powder. Yellow needles of $PbVO_3Cl$ were obtained in approximately 80 % yield and white powder was identified as $PbCl_2$ by using XRD. Examination of these yellow crystals with an EDX-equipped Philips XL 30S FEG SEM gave results consistent with the stated compositions. The EDX, DSC and TG data which are in good agreement are available in the CIF.

Discussion

Vanadium oxide compounds have been studied intensively because of their wide area of applications [1]. However, very few lead chlorovanadates have been synthesized. Only two compounds composed of Pb, V, Cl, and O are known to date, $Pb[VO_4]_2O_9Cl_4$ [2] and $Pb_5[VO_4]_3Cl$ [3]. Hydrothermal techniques are useful for the synthesis of new compounds as single crystals suitable for structural analysis. In this study, $PbVO_3Cl$ was synthesized and its structure was determined.

The crystal structure of the title compound consists of chains of edge-sharing VO_5 square pyramids with *trans* configuration and $[PbCl]^{n+}$ ribbons running along [010]. The VO_5 square pyramids form $[VO_3]^{n-}$ chains running also along [010]. This type of chains is generally observed in AV_3O_7 type compounds [4-6]. $[PbCl]^{n+}$ ribbons wave along [010] and reside between the $[VO_3]^{n-}$ chains. Every $[VO_3]^{n-}$ chain has four $[PbCl]^{n+}$ ribbons as neighbors. There is one unique vanadium atom coordinated by five oxygen atoms in a distorted square pyramid arrangement. The V—O distances are in agreement with the range observed for inorganic compounds [7] and the observed variation in individual distances is compatible with the bond-valence requirements of the individual ions. Vanadium has four long bonds with basal oxygens that range from 1.827(5) Å to 1.928(4) Å. In addition, there is a fifth short bond to the O2 atom of 1.606(6) Å, typical for a V=O group. The VO_5 square pyramid is distorted with an average O1–V–O2 angle of 108.6(3)°. The lead atom is coordinated by both oxygen and chlorine atoms. The atom has two equal bonds to oxygen atoms, with a bond distance of 2.464(4) Å each. The lead atom also has three bonds to chlorine atoms ranging from 2.791(2) Å to 2.979(1) Å and one longer bond to a fourth chlorine atom at 3.277(2) Å. A reason for the small U_{ii} values of the oxygen atoms could not be found.

Table 1. Data collection and handling.

Crystal:	yellow needle, size 0.034 × 0.055 × 0.420 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	472.37 cm^{-1}
Diffractometer, scan mode:	Bruker SMART 1000 CCD, ω
$2\theta_{max}$:	57.76°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4331, 528
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 508
$N(param)_{refined}$:	35
Programs:	SHELXS-97 [8], SHELXL-97 [9]

* Correspondence author (e-mail: mehtapemirdag@iyte.edu.tr)

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(1)	4*c*	0.32991(3)	¼	0.61537(5)	0.0111(4)	0.0103(4)	0.0108(4)	0	–0.00085(9)	0
V(1)	4*c*	0.4726(1)	¼	0.0681(2)	0.0101(8)	0.0040(8)	0.0064(8)	0	0.0000(6)	0
O(1)	8*d*	0.5892(5)	–0.008(1)	0.1133(5)	0.013(2)	0.002(2)	0.009(2)	–0.001(2)	–0.002(1)	–0.002(1)
O(2)	4*c*	0.3599(7)	¼	0.228(1)	0.013(3)	0.006(3)	0.005(3)	0	0.002(3)	0
Cl(1)	4*c*	0.6049(2)	¼	0.5530(3)	0.0113(9)	0.008(1)	0.010(1)	0	–0.0006(7)	0

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