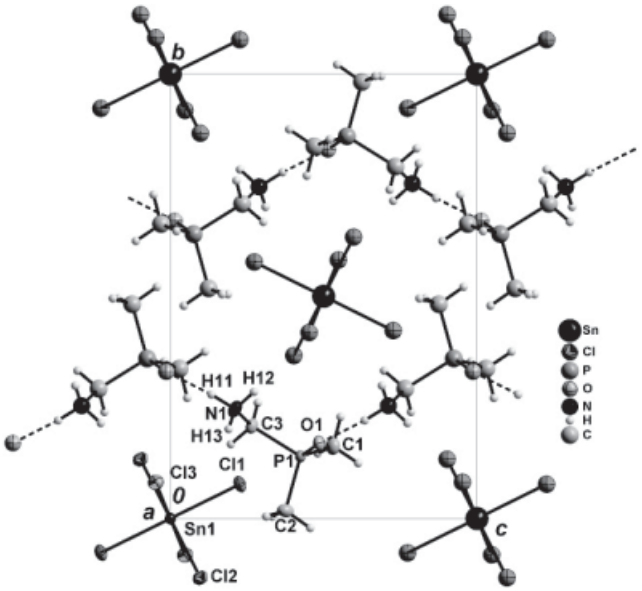
Crystal structure of bis((dimethylphosphoryl)methanaminium)hexachloridostannate(IV), $C_6H_{22}Cl_6N_2O_2P_2Sn$

Charlotte Lambertz, Anne Luppa and Guido J. Reiss*

Institut für Anorganische Chemie und Strukturchemie, Lehrstuhl II: Material- und Strukturforschung, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

Received November 11, 2012, accepted January 24, 2013, available online April 19, 2013, CCDC no. 1267/3959



Abstract

$C_6H_{22}Cl_6N_2O_2P_2Sn$, monoclinic, $P2_1/c$ (no. 14), a = 6.8425(1) Å, b = 14.0497(2) Å, c = 9.9977(2) Å, β = 104.521(2)°, V = 930.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.0145, $wR_{ref}(F^2)$ = 0.0347, T = 105 K.

Table 1. Data collection and handling.

Crystal:	colourless prisms, size 0.196×0.286×0.400 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	24.04 cm^{-1}
Diffractometer, scan mode:	Xcalibur Eos, ω
$2\theta_{max}$:	64.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21161, 3375
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3174
$N(param)_{refined}$:	111
Programs:	CrysAlis PRO [9], SHELX [10], DIAMOND [11]

Source of material

In a typical reaction, 0.38 g (3.55 mmol) (dimethylphosphoryl)-methanamine, *dpma* [1] and 0.62 g (1.77 mmol) $SnCl_4 \cdot 5H_2O$ were dissolved in concentrated hydrochloric acid by heating up the mixture. Upon slow cooling to room temperature, colourless platelets of irregular shape grew from the mother liquor. The **Raman spectrum** was measured using a Bruker MULTIRAM spectrometer (Nd: YAG-Laser at 1064 nm; RT-InGaAs-detector), 4000-70 cm^{-1}: 3238(*w*), 2998(*m*), 2988(*s*), 2954(*m*), 2912(*s*), 1583(*w*), 1484(*w*), 1432(*m*), 1403(*m*), 1313(*w*), 1154(*w*, sh), 1144(*m*), 1104(*w*), 1059(*w*), 1001(*m*), 945(*w*), 917(*w*), 888(*w*), 864(*w*), 778(*w*), 755(*w*), 731(*m*), 668(*s*), 446(*w*), 368(*w*), 310(*vs*, ν_1, Sn–Cl [8]), 273(*m*), 226(*m*), 161(*s*, ν_5, Sn–Cl [8]), 114(*w*), 99(*m*), 78(*w*). **IR** spectroscopic data were collected on a Digilab FT3400 spectrometer using a MIRacle ATR unit (Pike Technologies), 4000-560 cm^{-1}: 3234(*vs*), 3181(*vs*), 3131(*s*, sh), 2997(*s*), 2987(*s*), 2910(*m*), 2700 (*w*, br), 2480 (*w*, br), 1908 (*w*, br), 1596(*m*), 1583(*m*), 1491(*s*), 1420(*m*), 1341(*w*), 1302(*s*), 1149(*vs*), 1104(*vs*), 1058(*w*, sh), 999(*w*), 942(*vs*), 918(*m*), 885(*vs*), 857(*w*, sh), 775(*w*), 756(*w*), 729(*m*), 666(*w*), 537(*w*).

Experimental details

All hydrogen atoms were identified in difference syntheses. The methyl groups were idealized and refined using rigid groups allowed to rotate about the P–C bond (AFIX 137 option of the SHELXL97 program [10]). The coordinates of all other H-atoms were refined freely. The U_{iso} values of the hydrogen atoms of the NH_3-group were also refined freely. For each methyl and the CH_2-group one common U_{iso} was refined.

Discussion

A limited number of structurally characterized (dimethylphosphoryl)methanamine (*dpma*) containing compounds [1] and only one example of a salt consisting of a *N*-protonated *dpma*H cation, *dpma*HCl, have been reported [2]. Related amino substituted phosphinic anions are already known to be potent tectons (for the term tecton, see [3]) for the construction of hydrogen bonded one- to three-dimensional supramolecular architectures [4]. This structure determination on (*dpma*H)$_2$[$SnCl_6$] is part of our continuing study on hydrogen bonded architectures of methylphosphinic acids and its derivatives [5, 6]. The asymmetric unit of the title compound (*dpma*H)$_2$[$SnCl_6$] consists of one *dpma*H cation in general position and one half of a [$SnCl_6$]$^{2-}$ anion around a centre of inversion. Bond lengths and angles of the *dpma*H cation are in the expected range. The *dpma*H tecton consists of a threefold hydrogen bond donor group at one end (NH_3^+) and a hydrogen bond accepting –P=O group at the other end. In the title structure neighbouring cations are connected head to tail by charge supported N–H···O hydrogen bonds (N–H = 0.894(17) Å; d(NH···O) = 1.775(17) Å; d(N···O) = 2.6479(12) Å; angle: 164.7(16)°) to form one-dimensional zigzag chains along [001] (Fig.1.; first level graph set descriptor: $C^1_1(5)$ [7]). These chains are stacked parallel to each other so that the crests of the waves face each other directly. According to this structural motif, almost hexagonal channels result along [100], which are filled with the [$SnCl_6$]$^{2-}$ anions (Fig. 1). The [$SnCl_6$]$^{2-}$ anion adopts a distorted octahedral geometry (angles of 88.88(1) to 91.12(1)°). Weak charge supported N–H···Cl hydrogen bonds between the chlorine

* Correspondence author (e-mail: reissg@hhu.de)

atoms of the $[SnCl_6]^{2-}$ anion and the NH_3^+ group of the *dpma*H cation are present. Only four out of six chlorido ligands of each $[SnCl_6]^{2-}$ anion are involved in any hydrogen bonding (d(NH···Cl1) = 2.58(2) Å; d(NH···Cl2) 2.73(2) Å) as similarly described for a related $[SnCl_6]^{2-}$ containing salt [8]. The Sn–Cl bonds participating in hydrogen bonding are significantly longer (2.4494(2) and 2.4409(2) Å) than both others (2.4047(3) Å).

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

Atom	Site	x	y	z	U_{iso}
H(11)	4*e*	0.440(2)	0.279(1)	0.134(2)	0.024(4)
H(12)	4*e*	0.411(3)	0.285(2)	0.273(2)	0.043(6)
H(13)	4*e*	0.361(3)	0.201(1)	0.191(2)	0.034(5)
H(3A)	4*e*	0.744(3)	0.262(1)	0.287(2)	0.023(3)
H(3B)	4*e*	0.688(2)	0.169(1)	0.201(2)	0.023(3)
H(2A)	4*e*	0.5302	0.0046	0.3124	0.030(3)
H(2B)	4*e*	0.6743	–0.0213	0.4561	0.030(3)
H(2C)	4*e*	0.7647	0.0045	0.3313	0.030(3)
H(1A)	4*e*	1.0133	0.1467	0.4804	0.024(2)
H(1B)	4*e*	0.9371	0.1245	0.6125	0.024(2)
H(1C)	4*e*	0.9268	0.2287	0.5552	0.024(2)

Table 3. 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}
Sn(1)	2*a*	0	0	0	0.00803(4)	0.00915(4)	0.00749(4)	–0.00006(3)	0.00230(3)	–0.00038(3)
Cl(1)	4*e*	0.10131(4)	0.07717(2)	0.22657(3)	0.0140(1)	0.0168(1)	0.0095(1)	–0.00216(9)	0.00342(9)	–0.00324(8)
Cl(2)	4*e*	–0.14686(4)	–0.13328(2)	0.09752(3)	0.0142(1)	0.0129(1)	0.0141(1)	–0.00175(8)	0.00575(9)	0.00171(8)
Cl(3)	4*e*	–0.31885(4)	0.08168(2)	–0.04766(3)	0.0100(1)	0.0144(1)	0.0148(1)	0.00219(8)	0.00276(9)	0.00021(8)
P(1)	4*e*	0.66796(4)	0.13998(2)	0.42420(3)	0.0123(1)	0.0098(1)	0.0075(1)	0.00035(9)	0.00323(9)	0.00023(8)
O(1)	4*e*	0.4995(1)	0.16965(6)	0.48639(8)	0.0156(4)	0.0140(4)	0.0106(3)	0.0006(3)	0.0060(3)	–0.0011(3)
N(1)	4*e*	0.4431(2)	0.24628(8)	0.2108(1)	0.0145(4)	0.0177(4)	0.0124(4)	–0.0005(4)	0.0029(3)	0.0046(3)
C(3)	4*e*	0.6506(2)	0.20804(8)	0.2659(1)	0.0139(5)	0.0145(5)	0.0099(4)	0.0017(4)	0.0046(4)	0.0020(4)
C(2)	4*e*	0.6582(2)	0.01789(8)	0.3754(1)	0.0176(5)	0.0111(4)	0.0175(5)	0.0003(4)	0.0071(4)	–0.0009(4)
C(1)	4*e*	0.9148(2)	0.16259(9)	0.5303(1)	0.0151(5)	0.0188(5)	0.0126(5)	0.0003(4)	0.0018(4)	0.0006(4)

Acknowledgments. We would like to thank E. Hammes for technical support. Funding by the 'Lehrförderfond' of the Heinrich-Heine-Universität Düsseldorf is gratefully acknowledged.

References

1. Varbanov, S.; Agopian, G.; Borisov, G.: Polyurethane foams based on dimethylaminomethylphosphine oxide adducts with ethylene and propylene oxides. Eur. Polym. J. **23** (1987) 639-642.
2. Reiss, G. J.; Joergens, S.: (Dimethylphosphoryl)methanaminium chloride. Acta Crystallogr. **E68** (2012) o2899-o2900 and literature cited therein.
3. Metrangolo, P.; Resnati, G.: Tectons: Definition and Scope. In: *Encyclopedia of Supramolecular Chemistry* (Eds. J. L. Atwood, J. W. Steed, K. J. Wallace), p. 1484-1492. Abingdon, Taylor & Francis 2007.
4. Chen, S.-P.; Zhang, Y.-Q.; Hu, L.; He, H.-Z.; Yuan, L.-J.: Hydrogen-bonded assembly of aminophosphonic anions: different 1D, 2D and 3D supramolecular architectures. CrystEngComm **12** (2010) 3327-3336.
5. Reiss, G. J.; Engel, J. S.: Ethane-1,2-diylbis(methylphosphinic acid). Acta Crystallogr. E64 (2008). o400.
6. Meyer, M. K.; Graf, J.; Reiss, G. J.: Dimeric, or not dimeric, that is the question. Two neighboring I_3^- ions enclosed in cavities of a complex host structure. Z. Naturforsch. **B65** (2010) 1462-1466.
7. Grell, J.; Bernstein, J.; Tinhofer, G.: Investigation of Hydrogen Bond Patterns A Review of Mathematical Tools For the Graph Set Approach. Crystallogr. Rev. **8** (2002) 1-56.
8. Reiss, G. J.; Helmbrecht, C.: Bis(diisopropylammonium) hexachloridostannate(IV). Acta Crystallogr. **E68** (2012) m1402-m1403.
9. Agilent Technologies: *CrysAlis PRO* Software system, version 1.171.35.15, Agilent Technologies UK Ltd, Oxford, UK 2011.
10. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
11. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 3.2i. Crystal Impact, Bonn, Germany 2012.