Notes

Synthesis and X-ray Crystal Structure of K$_4$PbTe$_3$·2(en)

C. D. W. Jones,[†,‡] **F. J. DiSalvo,**[†] **and R. C. Haushalter***[‡,§]

Department of Chemistry, Cornell University,
Ithaca, New York 14853, and NEC Research Institute,
4 Independence Way, Princeton, New Jersey 08540

Introduction

The chemistry of polytelluride anions is an active area of research and, for the most part, the binary main-group telluride anions have been well explored.[1] For example, the following discrete tin telluride anions have been structurally characterized by single-crystal X-ray diffraction: [SnTe$_4$$^{4-}$],[2] [Sn$_2Te_7$$^{4-}$],[3] [Sn$_2Te_6$$^{4-}$],[4] [Sn$_2Te_3$$^{2-}$],[5] [HOSnTe$_3$$^{3-}$].[6] The SnTe$_3$$^{2-}$ anion has also been observed by solution NMR, but it has never been isolated in the solid state.[6] There are also more complex one-dimensional chain anions in the tin tellurium system such as [SnTe$_4$$^{2-}$][7] in Cs$_2$SnTe$_4$ and [SnTe$_5$$^{2-}$][8] in K$_2$SnTe$_5$. In the above Zintl anions the tin can be found in both the +4 (preferred) and +2 (Sn$_2$Te$_3$$^{2-}$ only) oxidation states. Moving down group 14, one finds that the lead telluride system is not as structurally rich with only the discrete [Pb$_2$Te$_3$$^{2-}$][9,10] anion being known from single-crystal X-ray diffraction. The Pb$_2$Te$_3$$^{2-}$ anion has a flattened trigonal bipyramidal structure with the lead atoms in the axial positions. This anion has also been observed in NMR with various substitutions: PbSnTe$_3$$^{2-}$, Pb$_2Se_3$$^{2-}$, Pb$_2Se_2Te^{2-}, Pb_2$SeTe$_2$$^{2-}$, and Pb$_2$SSeTe^{2-}.[5] Since lead prefers the +2 oxidation state in these conditions instead of the +4 state, one might expect different anions to be stable in comparison to tin. Indeed, we now report the new lead telluride anion PbTe$_3$$^{4-}$ structurally similar to the Pb$_2$Te$_3$$^{2-}$ anion, but with one of the lead atoms absent.

The synthetic method used here to produce PbTe$_3$$^{4-}$ the direct reduction of an alloy with potassium in ethylenediamine (en), is perhaps not as common as other methods used to prepare polytellurides. High-temperature fusion of the elements, solvent extraction of alloy phases, electrochemical methods, and solventothermal techniques are often used. However, the reduction technique is the oldest technique used to prepare Zintl anions and was in use over 100 years ago, in liquid ammonia solutions, to synthesize the first sodium lead compounds with homopoly-atomic lead Zintl anions.[11] More recently, this method has been used in ammonia with the addition of an encapsulating ligand[10,12] and in room temperature[13] and refluxing[14] ethylenediamine to synthesize crystals with binary main-group telluride anions.

Experimental Section

General. All reactions and manipulations were performed with the careful exclusion of air and water in a high purity helium atmosphere (unless otherwise noted). Starting materials included: potassium metal (Cerac, 99.95%), lead shot (Cerac, 99.999%), tellurium -20 mesh powder (Cerac, 99.5%), and ethylenediamine (Aldrich, 99.5%). The ethylenediamine was dried over CaH$_2$, distilled, reacted with K$_4$Sn$_9$, and distilled again to ensure purity. This procedure has been described previously.[15]

Synthesis. An alloy, of nominal composition PbTe$_2$, was prepared from the direct fusion of stoichiometric amounts of lead and tellurium in a silica tube under a high-purity argon atmosphere. This alloy was powdered, using an agate mortar and pestle, and 0.75 g (1.6 mmole) was added to 9.0 g (approximately 10 mL) of ethylenediamine. While this solution was stirred with a Teflon-coated stir bar, 0.13 g (3.3 mmole) of freshly cut potassium was added. This mixture was stirred for 24 h, after which the brown solution was filtered to remove any remaining solid. Approximately 1.5 mL of this solution was then allowed to sit in a capped vial for several weeks. After this time, several small silver columnar crystals had formed on the vial walls. Selected crystals were analyzed with standardless energy-dispersive X-ray analysis (Hitachi S-2700 SEM with *IMIX*[16] software) to give atomic ratios of 4:1:3.7 for K:Pb:Te (averaged over 10 runs with 100 s of collection time per run). This ratio is in good agreement with the stoichiometry observed from the crystallography considering the analysis was standardless and performed on crystals not specifically prepared for electron microprobe analysis due to their air-sensitive nature. This reaction was reproducible, and crystals with similar color, habit, and composition (by electron microprobe) were also found in the unfiltered reaction mixture. Slow solvent evaporation by only loosely capping the vial aided in producing crystals but also resulted in the precipitation of powders at the bottom of the vial. The same synthetic procedure using an alloy of nominal composition PbTe$_4$ produced a dark purple solution and no similar crystals.

X-ray Crystallography. A crystal of approximate dimensions 0.4 mm × 0.15 mm × 0.1 mm was mounted and sealed in a 0.2 mm (i.d.)

† Cornell University.
‡ NEC Research Institute.
§ Present address: Symyx Technologies, 3100 Central Expressway, Santa Clara, CA 95051.
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Table 1. Crystallographic Data for K$_4$PbTe$_3$·2(en)

empirical formula	K$_4$PbTe$_3$·2(C$_2$H$_8$N$_2$)
fw	866.59 g/mole
unit cell parameters	$a = 9.044(2)$ Å
	$b = 9.325(3)$ Å
	$c = 13.986(5)$ Å
	$\alpha = 71.21(2)°$
	$\beta = 82.77(2)°$
	$\gamma = 65.69(2)°$
unit cell volume	$V = 1017.6(6)$ Å^3
space group	$P\bar{1}$ (No. 2)
formula units per unit cell	$Z = 2$
calculated density	2.83 g/cm^3
temperature	22 °C
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)
absorption coefficient	$\mu = 13.33$ mm^{-1}
$R(F_0)$,^{a} $R_w(F_0)^b$	0.038, 0.043

^{a} $R(F_o) = \sum ||F_o| - |F_c||/\sum |F_o|$. ^{b} $R_w(F_o) = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$; $w = 1/\sigma^2(F_o)$.

Table 2. Atomic Coordinates and Thermal Parameters for the Heavy Atoms

atom	x	y	z	$B_{eq}{}^a$ (Å^2)
Pb(1)	0.788 10(5)	0.321 89(6)	0.765 31(4)	3.70(1)
Te(1)	0.590 14(8)	0.216 20(9)	0.939 36(6)	3.68(2)
Te(2)	0.979 61(9)	0.414 96(9)	0.872 76(6)	3.82(2)
Te(3)	1.034 13(9)	−0.000 37(10)	0.74938(6)	3.93(2)
K(1)	0	0	0	1.79(6)
K(2)	0.734 9(3)	0.402 8(3)	1.084 8(2)	4.91(7)
K(3)	0.333 3(3)	0.115 7(3)	0.8154 (2)	5.02(7)
K(4)	0.762 7(3)	−0.179 6(3)	0.896 0(2)	4.47(7)
K(5)	0	0	0.5	12.7(3)

^{a} $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos \gamma + 2U_{13}aa^*cc^* \cos \beta + 2U_{23}bb^*cc^* \cos \alpha)$.

glass capillary. X-ray intensity data were collected at room temperature on a Rigaku AFC7R automatic four-circle diffractometer with graphite monochromated Mo Kα radiation and a rotating anode generator (50 kV and 250 mA). Cell constants and an orientation matrix were obtained from 19 centered reflections in the range 14.13−19.39°. The data collection consisted of scans of $(1.42 + 0.35 \tan \theta)°$ in the range $5 \leq 2\theta \leq 50°$ which were made using the ω−2θ scan technique at a speed of 16.0°/min (in ω). Of the 3223 reflections collected, 2983 were unique ($R_{int} = 0.023$) and three standard reflections were measured every 150 reflections. The standards decreased by 8.7% over the course of the data collection and a linear correction factor was applied to the data. Corrections were made for Lorentz and polarization effects, and an empirical absorption correction based on ψ-scan data was also applied.

The structure was solved by direct methods and refined on F by full-matrix least-squares using the *teXsan*[17] crystallographic software package. All the Pb, Te, and K atoms were refined with anisotropic thermal parameters. The ethylenediamine molecules, although easily located, were quite disordered, and thus the C−C and C−N bond lengths were restrained to 1.54 and 1.45 Å, respectively. One of the ethylenediamine molecules was refined with split nitrogen positions with occupancy ratios set to achieve reasonable isotropic thermal parameters. No suitable disorder model could be obtained for the second ethylenediamine, and thus while the C and N positional parameters were refined, their isotropic thermal parameters were fixed (to values similar to those of the C and N atoms of the other ethylenediamine). The positions of the hydrogen atoms were calculated at the end of the refinement (but not included in the refinement). The final least-squares refinement was based on 2089 observed reflections [$I > 3.0\sigma(I)$] and 112 variable parameters and converged with $R(R_w) = 0.038(0.043)$ and GOF = 2.82. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.23 and −2.77 e$^-$/Å^3, respectively. The CIF has been deposited as Supporting

(17) *TeXsan Single-Crystal Analysis Software Package*, version 1.7−1; Molecular Structure Corporation: The Woodlands, TX 77381, 1995.
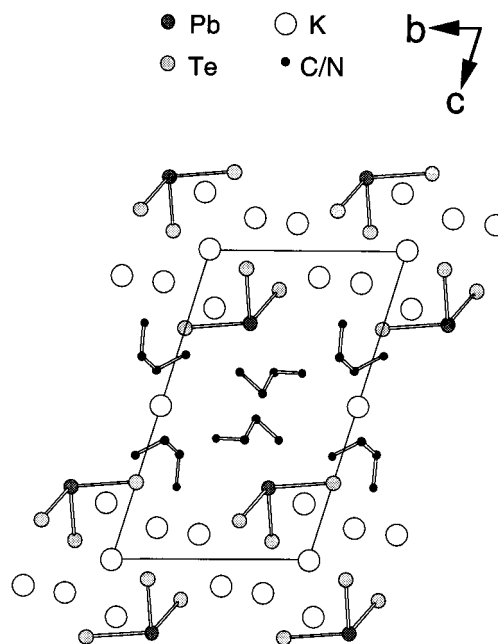
Figure 1. Unit cell of K$_4$PbTe$_3$·2(en) shown down the *a* axis (some atoms, including the some of the split nitrogen atoms on the ethylenediamine molecules, have been removed for clarity).

Information.[18] No higher lattice symmetry or missed additional symmetry was found using the *PLATON*[19] software package.

Results and Discussion

The details from the crystallographic study of K$_4$PbTe$_3$·2(en) are summarized in Table 1 , while Table 2 gives the final atomic coordinates and equivalent isotropic thermal parameters for all the heavy atoms. The unit cell packing down the *a* axis is shown in Figure 1 and illustrates the division between the inorganic and organic components of the compound. The trigonal pyramidal PbTe$_3^{4-}$ anions and four of the five crystallographically distinct K atoms form a "layer" in the *a*−*b* plane (the term "layer" is used loosely here because there is no covalent bonding holding these discrete units together). These layers are bridged by the K(5) atoms and the ethylenediamine molecules.

Of the potassium atoms in the layer, the K(1) atom has a relatively small equivalent isotropic thermal parameter. The maximum electron density on the final difference Fourier map (1.23 e$^-$/Å^3) is also only 0.569 Å from this K(1) position. This might be best explained by looking at the high coordination around K(1). As shown in Figure 2, K(1) lies in the capping position of two trigonal pyramidal PbTe$_3^{4-}$ anions and is thus coordinated to six tellurium atoms. The K(1)−Te distances range from 3.473(1) to 3.638(1) Å and are a little shorter (on average) than the reported values observed in K$_2$Te [3.535 Å],[20] KAuTe [3.623(1) Å],[21] and K$_6$In$_2$Te$_6$·4(en) [range 3.523(3)−3.966(3) Å].[22] The K(1)−Pb distance is 3.7361(8) Å. The K(1) atom is also surrounded by six other potassium atoms [K(2), K(3), K(4)] that have close contact to only four [K(3)] or five [K(2), K(4)] tellurium atoms with distances that range from 3.471(5) to 3.815(5) Å. These potassium atoms sit in a chairlike conformation around K(1) with K(1)−K distances that range

(18) See Supporting Information paragraph at end of text.
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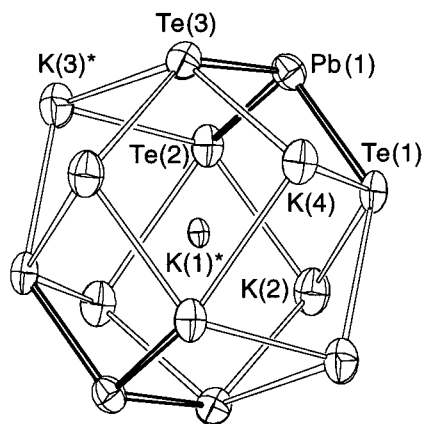(22) Wang, C.; Haushalter, R. C. *Inorg. Chem.* **1997**, *36*, 3806.

Figure 2. Two PbTe$_3^{4-}$ units are shown within the coordination environment of the K(1) atom (the Pb–Te bonds are emphasized). The K(2), K(3), and K(4) atoms are shown connected to the Te atoms [distances range from 3.471(5) to 3.815(5) Å], but the K(1)–Te contacts have been removed for clarity. The thermal ellipsoids are drawn at the 50% probability level.

Table 3. Selected Bond Distances and Angles for the PbTe$_3^{4-}$ Anion

bond distances (Å)		bond angles (deg)	
Pb(1)–Te(1)	2.985(2)	Te(1)–Pb(1)–Te(2)	98.11(4)
Pb(1)–Te(2)	2.957(1)	Te(1)–Pb(1)–Te(3)	101.74(4)
Pb(1)–Te(3)	2.972(2)	Te(2)–Pb(1)–Te(3)	100.36(4)

from 3.852(4) to 4.000(4) Å. The distorted octahedra of closely coordinated tellurium atoms around K(1) and the proximity of the other cations (both Pb and K) may help explain why the K(1) site has a lower equivalent isotropic thermal parameter.

In contrast to K(1), K(5) has a relatively large equivalent isotropic thermal parameter. Since K(5) is bridging the inorganic layers, it has close contact with only two Te(3) atoms [3.539(1) Å]. The rest of its coordination comes from the ethylenediamine molecules with K(5)–N distances of 2.85(2) and 3.2(1) Å, which are reasonable for these types of Zintl compounds.[22,23] The disorder in the nitrogen positions, and the low number of coordinated tellurium atoms, probably leads to the large equivalent isotropic thermal parameter for the K(5) atom. In fact, the anisotropic thermal parameter for K(5) in the direction of the tellurium atoms (along the *c* axis) is roughly equal to those of K(2), K(3), and K(4), but the other two parameters (in the direction of the nitrogen atoms) are 4–5 times larger.[18] A model with a split K(5) atom (two sites off the inversion center) was unsuccessful (the two positions converged back to the inversion center). The possibility that the K(5) site should be refined at reduced occupancy was ruled out both from charge balance arguments and because of the anisotropic nature of the K(5) thermal parameter.

The unique PbTe$_3^{4-}$ anion is also emphasized in Figure 2. This trigonal pyramidal geometry is what would be predicted from a simple VSEPR[24] model, but to the authors' knowledge

this is the first time this unit has been isolated in the solid state for the PbQ$_3^{4-}$ (Q = S, Se, Te) anion series. However, this geometry has been observed for lead(II) before in such anions as [Pb(SePh)$_3^-$].[25] As mentioned, the Pb$_2$Te$_3^{2-}$ anion does contain the "PbTe$_3$" moiety but adopts a trigonal bipyramidal structure.[9,10]

The significant bond lengths and bond angles in the PbTe$_3^{4-}$ anion are given in Table 3. The Pb–Te bond distances compare well with reported values for the two different 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) compounds that contain the Pb$_2$Te$_3^{2-}$ anion: (2,2,2-crypt-K)$_2$Pb$_2$Te$_3$ [2.943(2) Å][9] and (2,2,2-crypt-K)$_2$Pb$_2$Te$_3$·CH$_3$CN [2.954(2)–3.015(1) Å].[10] These Pb–Te distances also agree reasonably well with the sum of the 2-coordinate covalent radius for tellurium (1.42 Å)[26] and the metallic radius of lead (1.50 Å).[27] As expected the Te–Pb–Te bond angles in PbTe$_3^{4-}$ are significantly larger than those for Pb$_2$Te$_3^{2-}$ [92.46(4)° [9] and 92.21(4)–94.33(4)° [10]], due to the removal of the other bonding Pb atom. The larger Te–Pb–Te angles in PbTe$_3^{4-}$ result in Te–Te distances that range from 4.49 to 4.62 Å, much larger than the values in Pb$_2$Te$_3^{2-}$, i.e., 4.25[9] and 4.31–4.34 Å.[10] These values are also much larger than the Te–Te van der Waals distance of 4.12 Å.[28]

In summary, the PbTe$_3^{4-}$ anion is a simple, but new, Zintl telluride. The alloy reduction synthesis in ethylenediamine is a convenient room-temperature technique that might yield other new and interesting Zintl anions from a variety of main-group systems.

Supporting Information Available: The X-ray crystallographic file, in CIF format, is available. Access information is given on any current masthead page.

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