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Crystal structure of 1,2-vinylenbis(triphenylphosphonium) tetrabromoplumbate(II), $[Ph_3P–CH=CH–PPh_3][PbBr_4]$

R. Blachnik*, H. Reuter, T. Wiest and H. Eickmeier

Universität Osnabrück, Institut für Chemie, Barbarastr. 7, D-49076 Osnabrück, Germany

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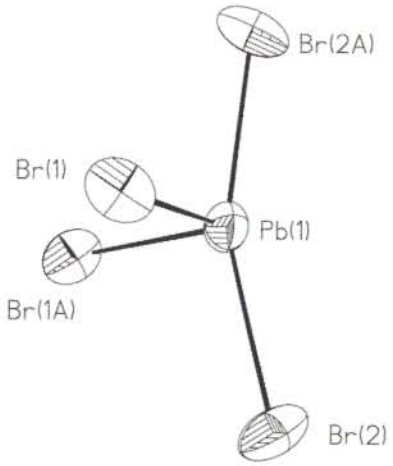

Abstract

$C_{38}H_{32}Br_4P_2Pb$, monoclinic, $C12/c1$ (No. 15), a = 10.913(2) Å, b = 17.618(4) Å, c = 19.848(4) Å, β = 99.97(3)°, V = 3758.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.043, $wR_{ref}(F^2)$ = 0.096, T = 293 K.

Source of material

$PbBr_2$ and $[Ph_3P\text{-}CH=CH\text{-}PPh_3][Br_2]$ were both dissolved in aqueous HBr, the solutions were mixed and water was slowly evaporated. After several hours a fine crystalline yellow powder precipitated. For the preparation of single crystals 1.5 g of this product and 5 ml H_2O were filled into a glass ampoule which was sealed and heated to 453 K. The ampoule was cooled with a rate of 10 K/min to ambient temperature.

Discussion

Lead atom is coordinated by four bromide ligands, in form of a trigonal ψ-bipyramide with one equatorial position occupied by the s^2-pair. The axial Pb—Br bond lengths are 2.99 Å, the equatorial lengths 2.70 Å, Br(ax)–Pb–Br(eq) angles are in the range 95.53° to 99.42°, the bond angle between the two axial Br-atoms is 159.0°. The data agree with those observed in comparable bromoplumbates(II) [1]. The distorted ψ-bipyramide was so far not observed in the structure of lead bromides with organic cations. Cations and anions form waved layers, which are stacked along the a-axis in the order A,A,A. Bond distances and bond angles in the cation agree well with the data of Stang and Zhdankin [2]. The compound was investigated with a differential scanning calorimeter. Between 153 K and 423 K no phase transition was detected.

Table 1. Data collection and handling.

Crystal:	bright yellow block, size 0.31 × 0.34 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	88.52 cm^{-1}
Diffractometer, scan mode:	Siemens P4, 2θ/ω
$2\theta_{max}$:	46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3252, 2535
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1851
$N(param)_{refined}$:	206
Program:	SHELXLTL [3]

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

Atom	Site	x	y	z	U_{iso}
H(1)	8*f*	–0.1073	0.7597	0.2771	0.063
H(11)	8*f*	–0.1543	0.7573	0.4029	0.070
H(12)	8*f*	–0.2429	0.8271	0.4816	0.072
H(13)	8*f*	–0.1210	0.9146	0.5511	0.073
H(14)	8*f*	0.0765	0.9361	0.5387	0.070
H(15)	8*f*	0.1662	0.8712	0.4581	0.057
H(31)	8*f*	0.3294	0.6939	0.3817	0.054
H(32)	8*f*	0.5194	0.7412	0.3661	0.070
H(33)	8*f*	0.5346	0.8648	0.3299	0.078
H(34)	8*f*	0.3626	0.9409	0.3052	0.081
H(35)	8*f*	0.1688	0.8941	0.3195	0.061
H(21)	8*f*	0.0743	0.6775	0.4862	0.066
H(22)	8*f*	0.1033	0.5503	0.5217	0.075
H(23)	8*f*	0.1394	0.4588	0.4449	0.090
H(24)	8*f*	0.1492	0.4895	0.3344	0.074
H(25)	8*f*	0.1210	0.6140	0.2979	0.060

* Correspondence author (e-mail: rblachnik@rz.uni-osnabrueck.de)

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}
Pb(1)	4*e*	0	0.08888(3)	1/4	0.0596(4)	0.0425(3)	0.0671(4)	0	–0.0033(3)	0
Br(1)	8*f*	–0.0720(1)	–0.02069(8)	0.33039(6)	0.0736(8)	0.0871(8)	0.0455(6)	0.0149(6)	0.0167(5)	0.0096(5)
Br(2)	8*f*	0.2552(1)	0.11984(9)	0.32813(7)	0.0567(7)	0.115(1)	0.0685(8)	–0.0328(7)	0.0173(6)	–0.0283(7)
P(1)	8*f*	0.0799(2)	0.7533(1)	0.3607(1)	0.040(1)	0.043(1)	0.026(1)	–0.001(1)	0.0029(9)	0.0005(9)
C(1)	8*f*	–0.0217(8)	0.7575(5)	0.2786(4)	0.033(5)	0.056(5)	0.037(5)	–0.003(4)	0.006(4)	–0.005(4)
C(10)	8*f*	0.0132(8)	0.8073(5)	0.4216(4)	0.052(5)	0.035(4)	0.022(4)	0.010(4)	0.001(4)	–0.001(3)
C(11)	8*f*	–0.108(1)	0.7940(6)	0.4296(6)	0.057(7)	0.055(6)	0.067(7)	0.000(5)	0.021(6)	0.003(5)
C(12)	8*f*	–0.160(1)	0.8349(6)	0.4772(6)	0.054(6)	0.049(6)	0.085(8)	0.006(5)	0.034(6)	–0.003(6)
C(13)	8*f*	–0.087(1)	0.8878(6)	0.5182(6)	0.087(8)	0.050(6)	0.053(6)	0.023(6)	0.034(6)	0.004(5)
C(14)	8*f*	0.030(1)	0.9003(6)	0.5109(5)	0.086(8)	0.053(6)	0.036(5)	0.020(6)	0.006(5)	–0.012(5)
C(15)	8*f*	0.084(1)	0.8615(5)	0.4629(4)	0.054(6)	0.054(6)	0.031(5)	–0.003(5)	–0.002(4)	0.002(4)
C(30)	8*f*	0.2308(8)	0.7881(5)	0.3512(4)	0.046(5)	0.042(5)	0.025(4)	–0.001(4)	0.005(4)	–0.003(4)
C(31)	8*f*	0.3356(8)	0.7432(5)	0.3659(5)	0.044(5)	0.046(5)	0.049(5)	–0.001(4)	0.014(4)	0.004(4)
C(32)	8*f*	0.4487(9)	0.7715(6)	0.3572(6)	0.037(5)	0.061(6)	0.074(7)	–0.008(5)	0.004(5)	–0.006(6)
C(33)	8*f*	0.457(1)	0.8457(7)	0.3350(6)	0.063(7)	0.080(8)	0.057(7)	–0.020(6)	0.024(5)	–0.001(6)
C(34)	8*f*	0.355(1)	0.8915(6)	0.3204(6)	0.082(8)	0.050(6)	0.075(8)	–0.012(6)	0.026(6)	0.024(5)
C(35)	8*f*	0.239(1)	0.8636(6)	0.3287(5)	0.050(6)	0.051(6)	0.054(6)	–0.004(5)	0.015(5)	0.006(5)
C(20)	8*f*	0.0929(8)	0.6562(5)	0.3879(5)	0.040(5)	0.042(5)	0.046(6)	–0.011(4)	0.004(4)	–0.003(4)
C(21)	8*f*	0.089(1)	0.6398(6)	0.4558(5)	0.060(6)	0.053(6)	0.050(6)	–0.012(5)	0.006(5)	–0.008(5)
C(22)	8*f*	0.106(1)	0.5637(6)	0.4767(6)	0.055(6)	0.057(7)	0.071(7)	–0.015(5)	–0.005(5)	0.036(6)
C(23)	8*f*	0.128(1)	0.5090(6)	0.4306(8)	0.051(7)	0.038(6)	0.14(1)	0.006(5)	0.018(7)	0.010(7)
C(24)	8*f*	0.134(1)	0.5271(6)	0.3647(7)	0.053(6)	0.048(6)	0.089(9)	–0.011(5)	0.022(6)	–0.007(6)
C(25)	8*f*	0.1166(9)	0.6013(5)	0.3429(5)	0.048(5)	0.045(6)	0.060(6)	0.006(4)	0.016(4)	–0.003(5)

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References

1. Sienkiewicz, A. V.; Kokozay, V. V.: Crystal structure of lead(II) complexes with 2,2′-iminodiethanol. Z. Naturforsch. **49b** (1994) 615-620.
2. Stang, P. J.; Zhdankin, V. V.: Preparation and chemistry of bis[phenyl]-[[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene. J. Am. Chem. Soc. **113** (1991) 4571-4576.
3. Sheldrick, G. M.: Program Package SHELXTL, Release 5.1. Bruker Analytical X-Ray Instruments Inc, Madison (WI 53719), USA 1997.