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# catena-Poly[[2,2'-bipyridine- $\kappa^2N,N'$ ]lead(II)]-di- $\mu$ -bromido]

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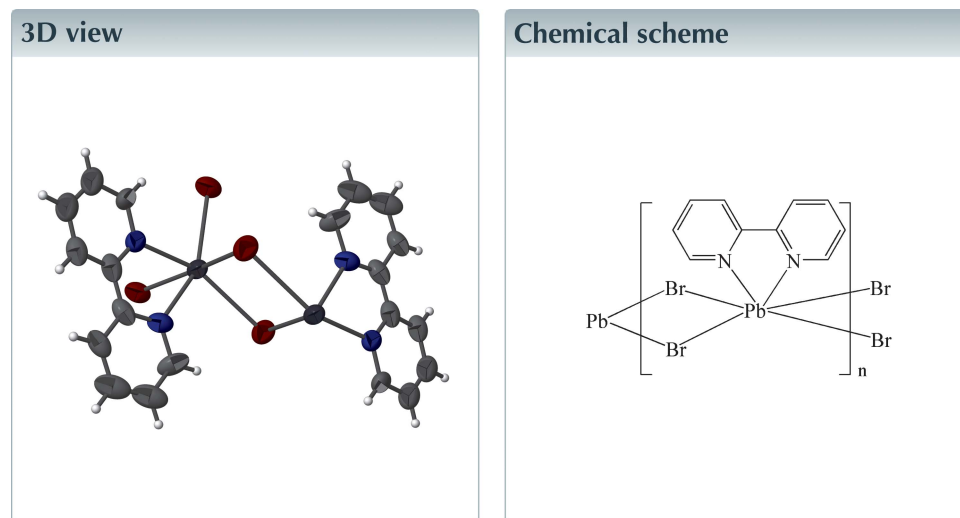
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; one-dimensional coordination polymer; chain structure;  $PbBr_2$  adduct.

CCDC reference: 1479535

Structural data: full structural data are available from iucrdata.iucr.org

The polymeric title compound,  $[PbBr_2(C_{10}H_8N_2)]_n$ , consists of  $\infty^1[PbBr_{4/2}]$  chains running parallel to [001]. Each  $Pb^{II}$  atom is additionally chelated by a 2,2'-bipyridine ligand, completing a distorted octahedral  $Br_4N_2$  coordination set. In the crystal, weak  $C-H \cdots Br$  hydrogen bonds and  $\pi-\pi$  stacking interactions link the  $[PbBr_2(C_{10}H_8N_2)]_n$  chains into a three-dimensional supramolecular structure.



## Structure description

In the context of studies of metal complexes derived from halogen benzoic acids  $X-C_6H_4COOH$ , where  $X$  is F, Cl, Br or I, and ancillary chelating ligands (Zhang *et al.*, 2004; Zhang, 2005, 2006), we originally intended to synthesize a lead(II) complex derived from 6-bromo-2-pyridinecarboxylic acid and 2,2'-bipyridine (bpy). However, we accidentally obtained instead an 1:1 adduct of  $PbBr_2$  with bpy,  $[PbBr_2(C_{10}H_8N_2)]_n$  (Fig. 1), that supposedly formed due to decomposition of the acid under the applied solvothermal conditions.

Both the  $Pb^{II}$  atom and the chelating bpy molecule lie on a twofold rotation axis. In the crystal,  $Pb^{II}$  atoms are bridged by two pairs of Br1 ligands into  $\infty^1[PbBr_{4/2}]$  chains ( $Br-Pb-Br$  and  $Pb-Br-Pb$  angles are 89.87 (6) and 90.13 (6)°, respectively) with a  $Pb \cdots Pb$  distance in the chain of 4.3434 (9) Å (Fig. 1). The closest plane-to-plane distance between two bpy ligands of 3.376 (2) Å indicates the existence of  $\pi-\pi$  interactions, which results in the formation of a layered arrangement of the  $[PbBr_2(C_{10}H_8N_2)]_n$  chains parallel to (100). The layers are associated through weak  $C-H \cdots Br$  hydrogen bonds (Table 1, Fig. 2) into an overall three-dimensional supramolecular set-up.

The chain structure of the title compound resembles that of related cadmium compounds with composition  $[CdX_2(phen)]$  ( $phen = 1,10$ -phenanthroline),  $X = Cl$ , Chen *et al.*, 2003;  $X = Br$ , (Zhang, 2007) or  $[CdCl_2(2,2-bpy)]$  (Zhou *et al.*, 2003).

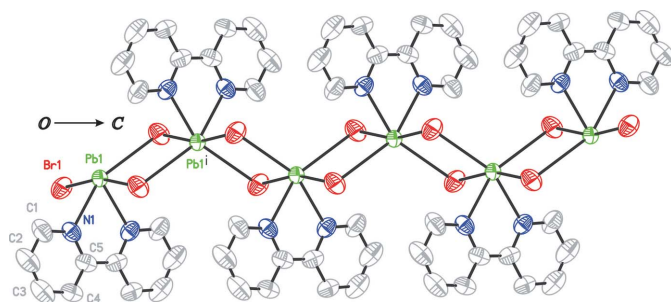
**Table 1**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C2-H2\cdots Br1^i$	0.93	2.98	3.906 (9)	174

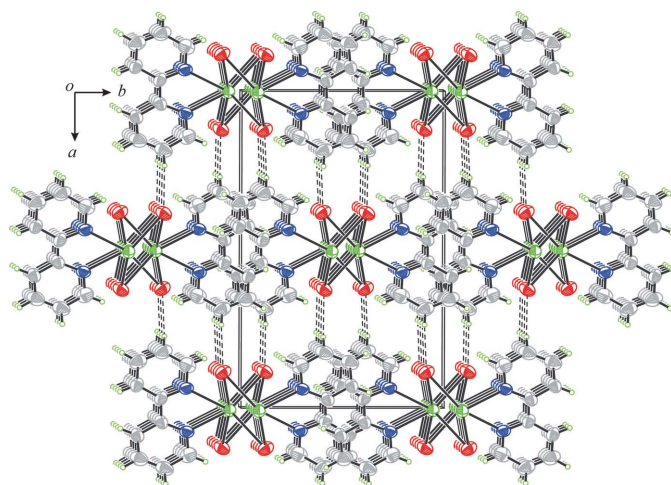
Symmetry code: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$ .

### Synthesis and crystallization

Freshly prepared  $Pb(CH_3COO)_2 \cdot 3H_2O$  (0.1890 g 0.50 mmol), 2,2'-bipyridine (bpy) (0.0399 g 0.25 mmol), 6-bromo-2-pyridinecarboxylic acid (0.0504 g 0.25 mmol), and 15 ml  $CH_3OH/H_2O$  (1:2, v/v) were mixed and stirred for *ca* 2.0 h. Subsequently, the resulting suspension was heated in a 23 ml Teflon-lined stainless steel autoclave at 433 K for 7 days. After the autoclave was cooled to room temperature, yellow crystals with a cuboid form were obtained.



**Figure 1**  
A view of the chain of bromide-bridged  $Pb^{II}$  ions in the title compound extending parallel to [001]. Displacement ellipsoids are drawn at the 40% probability level [symmetry code (i)  $1 - x, y, \frac{1}{2} - z$ ].



**Figure 2**  
A packing diagram of the title compound viewed along [001]. Dashed lines indicate C—H...Br hydrogen bonds.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$[PbBr_2(C_{10}H_8N_2)]$
$M_r$	523.19
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	293
$a, b, c$ (Å)	16.249 (3), 9.878 (2), 8.2425 (16)
$\beta$ (°)	104.79 (3)
$V$ (Å <sup>3</sup> )	1279.2 (4)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	19.41
Crystal size (mm)	0.24 × 0.23 × 0.21
Data collection	
Diffractometer	Rigaku R-Axis RAPID
Absorption correction	Multi-scan ( <i>ABSCOR</i> ; Higashi, 1995)
$T_{min}, T_{max}$	0.013, 0.017
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	4632, 1053, 871
$R_{int}$	0.123
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.583
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.043, 0.124, 1.21
No. of reflections	1053
No. of parameters	58
No. of restraints	21
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	1.64, -1.97

Computer programs: *RAPID-AUTO* (Rigaku, 1998), *CrystalStructure* (Rigaku/MS, 2002), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL97* (Sheldrick, 2008).

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

### Acknowledgements

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## full crystallographic data

*IUCrData* (2016). **1**, x160782 [doi:10.1107/S2414314616007823]

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*Crystal data*

[PbBr<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)]

$M_r = 523.19$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 16.249$  (3) Å

$b = 9.878$  (2) Å

$c = 8.2425$  (16) Å

$\beta = 104.79$  (3)°

$V = 1279.2$  (4) Å<sup>3</sup>

$Z = 4$

$F(000) = 936$

$D_x = 2.717$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 4297 reflections

$\theta = 3.3$ – $24.5$ °

$\mu = 19.41$  mm<sup>-1</sup>

$T = 293$  K

Cuboid, yellow

$0.24 \times 0.23 \times 0.21$  mm

*Data collection*

Rigaku R-AXIS RAPID  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\omega$  scans

Absorption correction: multi-scan

(*ABSCOR*; Higashi, 1995)

$T_{\min} = 0.013$ ,  $T_{\max} = 0.017$

4632 measured reflections

1053 independent reflections

871 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.123$

$\theta_{\max} = 24.5$ °,  $\theta_{\min} = 3.3$ °

$h = -18 \rightarrow 18$

$k = -11 \rightarrow 11$

$l = -9 \rightarrow 8$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.124$

$S = 1.21$

1053 reflections

58 parameters

21 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 35.8179P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.64$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.97$  e Å<sup>-3</sup>

Extinction correction: *SHELXL97* (Sheldrick,  
2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0010 (2)

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted R-factor wR and goodness of fit S are based on  $F^2$ , conventional R-factors R are based on F, with F set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on  $F^2$  are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Pb1	0.5000	0.43060 (8)	0.2500	0.0502 (5)
Br1	0.62002 (14)	0.3951 (2)	0.0295 (3)	0.0700 (6)
C1	0.3595 (8)	0.2242 (10)	-0.0180 (13)	0.073 (6)
H1	0.3389	0.3078	-0.0624	0.087*
C2	0.3177 (7)	0.1061 (13)	-0.0845 (14)	0.086 (5)
H2	0.2692	0.1106	-0.1733	0.103*
C3	0.3485 (8)	-0.0188 (10)	-0.0181 (17)	0.086 (5)
H3	0.3206	-0.0979	-0.0626	0.103*
C4	0.4210 (8)	-0.0256 (7)	0.1147 (16)	0.061 (4)
H4	0.4416	-0.1092	0.1590	0.073*
C5	0.4628 (6)	0.0925 (9)	0.1811 (12)	0.059 (4)
N1	0.4320 (7)	0.2174 (8)	0.1147 (12)	0.055 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Pb1	0.0539 (7)	0.0463 (6)	0.0447 (6)	0.000	0.0023 (4)	0.000
Br1	0.0603 (14)	0.0770 (12)	0.0718 (12)	0.0152 (10)	0.0151 (9)	0.0157 (9)
C1	0.074 (15)	0.092 (13)	0.043 (9)	0.022 (11)	-0.002 (10)	-0.022 (9)
C2	0.060 (11)	0.098 (10)	0.101 (12)	-0.010 (9)	0.022 (10)	-0.046 (10)
C3	0.060 (11)	0.098 (10)	0.101 (12)	-0.010 (9)	0.023 (10)	-0.046 (10)
C4	0.063 (9)	0.050 (6)	0.083 (9)	-0.009 (6)	0.041 (8)	-0.010 (6)
C5	0.060 (9)	0.049 (6)	0.081 (9)	-0.008 (6)	0.042 (8)	-0.010 (6)
N1	0.045 (9)	0.062 (8)	0.059 (8)	-0.003 (7)	0.011 (7)	-0.016 (7)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

Pb1—N1	2.504 (7)	C1—H1	0.9300
Pb1—N1 <sup>i</sup>	2.504 (15)	C2—C3	1.3900
Pb1—Br1	3.006 (2)	C2—H2	0.9300
Pb1—Br1 <sup>i</sup>	3.006 (2)	C3—C4	1.3900
Pb1—Br1 <sup>ii</sup>	3.128 (2)	C3—H3	0.9300
Pb1—Br1 <sup>iii</sup>	3.128 (2)	C4—C5	1.3900
Br1—Pb1 <sup>iii</sup>	3.128 (2)	C4—H4	0.9300
C1—C2	1.3900	C5—N1	1.3900
C1—N1	1.3900	C5—C5 <sup>i</sup>	1.433 (17)

N1—Pb1—N1 <sup>i</sup>	65.5 (6)	C2—C1—H1	120.0
N1—Pb1—Br1	85.0 (3)	N1—C1—H1	120.0
N1 <sup>i</sup> —Pb1—Br1	83.7 (6)	C1—C2—C3	120.0
N1—Pb1—Br1 <sup>i</sup>	83.7 (3)	C1—C2—H2	120.0
N1 <sup>i</sup> —Pb1—Br1 <sup>i</sup>	85.0 (6)	C3—C2—H2	120.0
Br1—Pb1—Br1 <sup>i</sup>	166.60 (8)	C2—C3—C4	120.0
N1—Pb1—Br1 <sup>ii</sup>	155.8 (2)	C2—C3—H3	120.0
N1 <sup>i</sup> —Pb1—Br1 <sup>ii</sup>	90.8 (4)	C4—C3—H3	120.0
Br1—Pb1—Br1 <sup>ii</sup>	97.52 (7)	C5—C4—C3	120.0
Br1 <sup>i</sup> —Pb1—Br1 <sup>ii</sup>	89.87 (6)	C5—C4—H4	120.0
N1—Pb1—Br1 <sup>iii</sup>	90.8 (2)	C3—C4—H4	120.0
N1 <sup>i</sup> —Pb1—Br1 <sup>iii</sup>	155.8 (4)	C4—C5—N1	120.0
Br1—Pb1—Br1 <sup>iii</sup>	89.87 (6)	C4—C5—C5 <sup>i</sup>	122.73 (11)
Br1 <sup>i</sup> —Pb1—Br1 <sup>iii</sup>	97.52 (7)	N1—C5—C5 <sup>i</sup>	117.27 (9)
Br1 <sup>ii</sup> —Pb1—Br1 <sup>iii</sup>	113.19 (9)	C5—N1—C1	120.0
Pb1—Br1—Pb1 <sup>iii</sup>	90.13 (6)	C5—N1—Pb1	119.9 (5)
C2—C1—N1	120.0	C1—N1—Pb1	120.0 (5)

Symmetry codes: (i)  $-x+1, y, -z+1/2$ ; (ii)  $x, -y+1, z+1/2$ ; (iii)  $-x+1, -y+1, -z$ .

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 $\cdots$ Br1 <sup>iv</sup>	0.93	2.98	3.906 (9)	174

Symmetry code: (iv)  $x-1/2, -y+1/2, z-1/2$ .