

## NOTIZEN

### The Crystal Structure of TlBrI<sub>2</sub>(4-methylpyridine-N-oxide)<sub>2</sub>

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Bromo-diiodo-bis(4-methylpyridine-N-oxide)thallium(III), Crystal Structure, Thallium(III) Halide Compounds

The unit cell of TlBrI<sub>2</sub>(4-methylpyridine-N-oxide)<sub>2</sub> is orthorhombic, space group Pnna, with  $a = 1126.9(3)$ ,  $b = 919.8(2)$ ,  $c = 1210.4(3)$  pm, and  $Z = 4$ . The structure consists of discrete TlBrI<sub>2</sub>(4-methylpyridine-N-oxide)<sub>2</sub> molecules which have a distorted trigonal-bipyramidal geometry. The thallium atom is coordinated to two iodine atoms and a bromine atom in equatorial positions, and by two 4-methylpyridine-N-oxide ligands in the axial positions.

### Introduction

Our research on coordination of thallium trihalides with different ligands [1, 2] has lately concentrated on the study of the interhalocompounds of thallium(III) of the type TlXX'<sub>2</sub>·nL ( $X = \text{halide}$ ,  $L = \text{ligand}$ ).

Recently we described the crystal structures of TlBr<sub>2</sub>I(OPPh<sub>3</sub>)<sub>2</sub> [3] and TlBrI<sub>2</sub>(OPPh<sub>3</sub>)<sub>2</sub> [4]. Here, as a continuation of our studies on stabilization of thallium(III) in the complexes indicated above, we report the molecular structure of TlBrI<sub>2</sub>(4-picO)<sub>2</sub> (4-picO = 4-methylpyridine-N-oxide).

### Structure Determination

TlBrI<sub>2</sub>(4-picO)<sub>2</sub> was prepared by oxidation of TlBr with iodine in acetonitrile in the presence of 4-methylpyridine-N-oxide by the method described by Bermejo *et al.* [2]. For the structure determination, the data were collected at room temperature using the automated four-circle diffractometer CAD4 (ENRAF-

NONIUS, Delft) with graphite-monochromated MoK $\alpha$  radiation. The cell constants were determined from the setting angles of 25 reflections (Table I) and

Table I. Crystal data for TlBrI<sub>2</sub>(4-PicO)<sub>2</sub>\*.

Molecular formula	C <sub>12</sub> H <sub>14</sub> BrI <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Tl
Molecular weight	756.34
Crystal class	Orthorhombic
Space group	Pnna (N <sup>o</sup> 52)
Lattice constants	$a = 1126.9(3)$ pm $b = 919.8(2)$ pm $c = 1210.4(3)$ pm
Cell volume	$V = 1254.6 \cdot 10^6$ pm <sup>3</sup>
Formula units	$Z = 4$
Density	$\rho_x = 3.426$ g·cm <sup>-3</sup>

\* Further details of the structure determination have been deposited as Supplementary Publication No. CSD 52808. Copies may be obtained through the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen.

from the systematic absences observed, the space group Pnna was determined. With  $\omega/\theta$  scan mode, 4539 reflections were collected in the range of  $\theta = 3\text{--}32^\circ$ . Corrections for Lorentz and polarization effects and an empirical absorption correction ( $\psi$ -scan) [5] were applied. From 2084 independent reflections ( $R_{\text{int}} = 0.032$ ), 1108 with  $I > 3 \cdot \sigma(I)$  were considered as observed and used for refinement. The structure was solved using the Patterson heavy-atom method, which revealed the positions of the Tl, I and Br atoms. The remaining atoms were located in suc-

Table II. Atomic positional parameters and isotropic thermal parameters [ $\text{pm}^2 \cdot 10^4$ ] for TlBrI<sub>2</sub>(4-PicO)<sub>2</sub>.

Atom	$x$	$y$	$z$	$B_{\text{eq}}$
Tl	0.23597(9)	0.250	0.250	2.40(2)
I	0.1050(2)	0.3492(2)	0.0781(1)	3.49(3)
Br	0.4735(2)	0.250	0.250	2.21(4)
O	0.250	0.500	0.344(2)	2.7(4)
N	0.250	0.500	0.453(2)	2.2(4)
C(1)	0.343(2)	0.440(3)	0.510(2)	3.2(4)
C(2)	0.347(2)	0.443(3)	0.624(2)	3.4(5)
C(3)	0.250	0.500	0.683(3)	3.7(7)
C(4)	0.250	0.500	0.809(3)	6(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, defined as:

$$B_{\text{eq}} = (4/3)[a^2 B_{11} + \dots + ab B_{12} \cos \gamma + \dots]$$

Estimated standard deviations for the least significant figure are in parentheses. Parameters with no standard deviations were fixed by symmetry.

\* Reprint requests to Dr. W. Hiller.

ceeding difference Fourier syntheses [6]. Hydrogen atoms were not included. In the last refinement all atoms (non-H) were assigned anisotropic temperature parameters. Final refinement converged at  $R = 0.053$ ,  $R_w = 0.063$  for 83 variables. Positional and thermal parameters are given in Table II\*.

### Discussion

The structure of bromo-diiodo-bis(4-methylpyridine-N-oxide)thallium(III) consists of discrete monomeric molecules in which the Tl atom is penta-coordinated. The molecule has a trigonal-bipyramidal structure with the halide atoms occupying equatorial positions, and the 4-picoline N-oxide ligands in the axial positions (Fig. 1). The bond an-

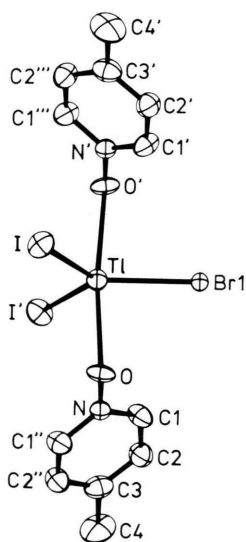


Fig. 1. The structure of  $\text{TlBrI}_2(4\text{-PicO})_2$ .

Table III. Bond lengths (pm) and angles (deg) for  $\text{TlBrI}_2(4\text{-PicO})_2$ .

Bond lengths		Bond angles	
Tl—O	257.0(3)	I—Tl—I'	113.97(3)
Tl—Br	267.6(1)	I—Tl—Br	123.02(2)
Tl—I	271.0(1)	I'—Tl—Br	123.02(2)
O—N	133(1)	I—Tl—O	94.1(1)
N—C(1)	137(1)	I—Tl—O'	89.7(1)
C(1)—C(2)	138(1)	Br—Tl—O	86.47(1)
C(2)—C(3)	140(1)	Br—Tl—O'	86.47(1)
C(3)—C(4)	152(2)	O—Tl—O'	172.95(2)
		Tl—O—N	116.3(1)
		O—N—C(1)	120.1(5)
		O—N—C(1'')	120.1(5)
		C(1)—N—C(1'')	119.8(9)
		N—C(1)—C(2)	121.1(9)
		C(2)—C(3)—C(2'')	119(1)
		C(2)—C(3)—C(4)	120.3(6)
		C(2'')—C(3)—C(4)	120.3(6)

gles in the equatorial plane are  $113.97(3)^\circ$  and  $123.02(2)^\circ$ , the bond angles to the axial positions are between  $86.47(1)^\circ$  and  $94.1(1)^\circ$  which indicates a distorted geometry (Table III). The thallium-iodine distance is similar to those reported for triiodo-bis(3-methylpyridine-N-oxide)thallium [1], and the thallium bromide distance is greater than found in  $\text{TlBrI}_2(\text{OPPh}_3)_2$  (258.0(1) pm) [4], but similar as in  $\text{TlBr}_3(\text{C}_5\text{H}_5\text{N})_3$  [7]. The Tl—O bond lengths (257 pm) are longer than the expected value of 221 pm derived from Paulings covalent radii [8].

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