

## Pyridinium Tetrabromobis(pyridine)tungstate(III), [(py)<sub>2</sub>H][WBr<sub>4</sub>(py)<sub>2</sub>]

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**Abstract.** [(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>H][WBr<sub>4</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>], C<sub>10</sub>H<sub>11</sub>N<sub>2</sub><sup>+</sup>·C<sub>10</sub>H<sub>10</sub>Br<sub>4</sub>N<sub>2</sub>W<sup>-</sup>, triclinic, *P*1, *a* = 9.504 (1), *b* = 9.683 (1), *c* = 15.196 (1) Å, α = 79.38 (1), β = 78.78 (1), γ = 79.16 (1)°, *Z* = 2, *D*<sub>c</sub> = 2.048 Mg m<sup>-3</sup>, *R* = 0.051 for 3998 reflexions [*I* > 5σ(*I*)]. The structure contains *trans*-[WBr<sub>4</sub>(py)<sub>2</sub>]<sup>-</sup> anions and [(py)<sub>2</sub>H]<sup>+</sup> cations. Average W–Br and W–N bond lengths within the anions are 2.58 (1) and 2.18 (1) Å. The cation pyridine molecules are hydrogen bonded with an N···N separation of 2.73 (2) Å.

**Introduction.** [(py)<sub>2</sub>H][WBr<sub>4</sub>(py)<sub>2</sub>] is the main product in the pyridine reduction of [WBr<sub>4</sub>(py)<sub>2</sub>] at 353 K in vacuum. 2.00 g of [WBr<sub>4</sub>(py)<sub>2</sub>] were allowed to react with 80 ml of pyridine for one hour. The filtrate, diluted with twice the volume of pyridine, was kept at 277 K overnight. One of the extremely oxygen- and moisture-sensitive crystals was sealed under argon together with a drop of the mother-liquor in a glass capillary. The reactivity of the compound prevented rational determination of the experimental crystal density. Also, X-ray structural analysis was the only way of determining the chemical identity of the compound.

Seven crystal faces were identified on an irregularly shaped crystal, and the distances from these spaces to an arbitrary origin inside the crystal estimated. Minimum and maximum values were 0.0875 and 0.225 mm.

The intensity data were collected at 293 (1) K on a computer-controlled CAD-4 (Enraf–Nonius) diffractometer with a graphite-crystal monochromator, Mo *K*α radiation (λ = 0.71069 Å), the ω–2θ scan, 2.5° < 2θ < 55°, a 2θ scan width (°) = 1.0 + 0.2 × tan θ, and an aperture (mm) = 2.5 + 0.9 tan θ; the maximum scan time was 30 s, and background was measured for ¼ the scan time at each of the scan limits.

5789 independent reflexions were collected. All reflexions with *I* < 5σ(*I*) were rejected and the remaining 3998 were used for the solution and refinement of the structure. Structure factors on a relative scale were obtained by applying Lorentz, polarization and absorption corrections to the measured intensities [μ(Mo *K*α) = 10.95 mm<sup>-1</sup>]. The absorption corrections, *A*<sup>\*</sup>, calculated with the measured crystal dimensions (*m*-point Gaussian in-

tegration), were from 5.3 to 23.8. The unit-cell dimensions were determined from the least-squares analysis of 60 randomly chosen reflexions with 2θ values greater than 20°. 2θ values were measured on the diffractometer at 293 (1) K. A centrosymmetric space group was suggested by the |*E*| statistics. Successful solution and refinement of the structure in the centrosymmetric space group supported the choice.

Positions of the heavy atoms were determined from the Patterson map. Pyridine rings were found in the first Fourier calculation based on the |*F*<sub>o</sub>|<sup>2</sup>s with the signs determined by the heavy-atom positions. The structure was refined by full-matrix least-squares techniques with anisotropic temperature factors for W and Br atoms and isotropic for the rest. The structure factors contained the real and imaginary components of anomalous scattering for the heavy atoms. The function minimized in the least-squares procedure was ∑w(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)<sup>2</sup>. An empirical weighting scheme was applied: when |*F*<sub>o</sub>| < 29: *W*<sub>F</sub> = (|*F*<sub>o</sub>|/29)<sup>2.0</sup>; when 29 ≤ |*F*<sub>o</sub>| ≤ 80: *W*<sub>F</sub> = 1.0; when |*F*<sub>o</sub>| > 80: *W*<sub>F</sub> = (80/|*F*<sub>o</sub>|)<sup>5.0</sup>; when sin θ < 0.28: *W*<sub>s</sub> = (sin θ/0.28)<sup>5.0</sup>; when 0.28 ≤ sin θ ≤ 0.43: *W*<sub>s</sub> = 1.0; when sin θ > 0.43: *W*<sub>s</sub> = (0.43/sin θ)<sup>2.0</sup>; *W* = *W*<sub>F</sub>*W*<sub>s</sub>. An isotropic extinction parameter (Zachariasen, 1963; Larson, 1967) was included in the final stage of refinement (*g* = 6.1 × 10<sup>-3</sup>).

The final *R* values were: *R* = ∑(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)/∑|*F*<sub>o</sub>| = 0.051, and *R*<sub>w</sub> = [∑w(|*F*<sub>o</sub>| – |*F*<sub>c</sub>|)<sup>2</sup>/∑w*F*<sub>o</sub><sup>2</sup>]<sup>1/2</sup> = 0.052. The average shift-to-error ratio for all parameters was 0.07 in the final cycle. A difference Fourier map gave no peaks greater than 1 e Å<sup>-3</sup>.

All calculations were performed on the CDC Cyber computer of RRC Ljubljana with the XRAY system of

Table 1. Positional parameters (×10<sup>5</sup>) and thermal parameters for W and Br atoms with standard deviations

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
W(1)	0	0	0	2.11 (2)
W(2)	½	0	½	2.06 (2)
Br(11)	230 (11)	–19831 (11)	13923 (7)	3.17 (4)
Br(12)	27599 (11)	–1330 (12)	–1181 (7)	3.41 (4)
Br(21)	51462 (11)	26657 (10)	45079 (8)	3.34 (4)
Br(22)	74437 (11)	–6500 (11)	39695 (8)	3.35 (4)

crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), adapted by Professor L. Golič.

Atomic scattering factors for neutral atoms tabulated by Cromer & Mann (1968) and the values for  $f'$  and  $f''$  for the anomalous-dispersion correction compiled by Cromer (1965) were applied.

The positional parameters for W and Br atoms are listed in Table 1 and for the remaining (non-hydrogen) atoms in Table 2.\*

A projection of the structure in the  $yz$  plane and the atom-numbering scheme are presented in Fig. 1. Interatomic distances and angles are in Table 3.

**Discussion.** Coordination compounds of  $W^{III}$  are rare. Isolated octahedral structures were found with the following stoichiometries:  $WX_3L_3$  ( $X = Cl, Br; L =$  pyridine) (Brenčič, Čeh & Križelj, 1977) and  $[(L)_2H][WBr_4(L)_2]$  ( $L =$  pyridine, 4-methylpyridine) (Brenčič, Čeh & Šegedin, 1979).

The structure of  $[(py)_2H][WBr_4(py)_2]$  has the cationic part formed from two pyridines held together by a hydrogen bond ( $N \cdots H \cdots N$ ), together with octahedral

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34595 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional parameters ( $\times 10^4$ ) and thermal parameters ( $\times 10$ ) for C and N atoms, with standard deviations

The isotropic temperature factor is in the form  $\exp[-B(\sin \theta/\lambda)^2]$ .

	x	y	z	B ( $\text{Å}^2$ )
N(1)	-393 (9)	1621 (9)	884 (6)	28 (2)
C(11)	304 (12)	2778 (12)	669 (8)	34 (2)
C(12)	28 (16)	3858 (15)	1179 (10)	45 (3)
C(13)	-969 (16)	3785 (16)	1964 (10)	47 (3)
C(14)	-1682 (15)	2586 (14)	2211 (9)	43 (3)
C(15)	-1343 (12)	1539 (12)	1665 (8)	34 (2)
N(2)	3858 (9)	56 (9)	3869 (6)	27 (2)
C(21)	2581 (12)	-456 (12)	4015 (8)	35 (2)
C(22)	1821 (16)	-417 (16)	3323 (10)	46 (3)
C(23)	2339 (19)	118 (19)	2472 (13)	53 (3)
C(24)	3659 (17)	683 (17)	2306 (11)	50 (3)
C(25)	4336 (14)	637 (13)	3006 (9)	39 (2)
N(3)	3534 (13)	6238 (13)	2618 (8)	44 (2)
C(31)	3821 (17)	6895 (16)	1767 (11)	48 (3)
C(32)	5040 (17)	7473 (17)	1471 (11)	50 (3)
C(33)	5984 (18)	7400 (18)	2055 (11)	51 (3)
C(34)	5666 (21)	6811 (21)	2935 (14)	59 (4)
C(35)	4419 (18)	6207 (18)	3219 (11)	51 (3)
N(4)	1138 (14)	5014 (14)	3420 (9)	47 (3)
C(41)	1223 (17)	3599 (16)	3670 (10)	48 (3)
C(42)	65 (17)	2962 (16)	4195 (10)	48 (3)
C(43)	-1209 (16)	3843 (15)	4454 (10)	45 (3)
C(44)	-1294 (14)	5293 (14)	4192 (9)	41 (3)
C(45)	-107 (14)	5812 (14)	3687 (9)	39 (2)

$[WBr_4(py)_2]^-$  anions. Ligands in the octahedron are in *trans* positions. The unit cell contains two independent  $[WBr_4(py)_2]^-$  groups located at the center of inversion. The eclipsed configuration of the pyridine rings is a consequence of the symmetry. Four Br atoms form a nearly perfect square around the W.

W—Br and W—N bond lengths are 2.574–2.582 and 2.184 and 2.191 Å, and are comparable to those found in  $[(pic)_2H][WBr_4(pic)_2]$  ( $pic =$  4-methylpyridine). Angles between pyridines and the equatorial planes of the  $[WBr_4(py)_2]^-$  groups are 87 and 89°. Pyridine rings are parallel to the Br(11)—Br(12) and Br(21)—Br(22<sup>ii</sup>) directions.

A bridging H atom is inferred to lie between N atoms in the cation as the  $N \cdots N$  distance is 2.73 (2) Å. This is longer than that found in  $[(py)_2H]_2P_2S_8$ , 2.66 Å

Table 3. Dimensions of the  $[WBr_4(py)_2]^-$  ions, with standard deviations in parentheses

W(1)—Br(11)	2.582 (1) Å	Br(11)···Br(12)	3.627 (1) Å
W(1)—Br(12)	2.574 (1)	Br(12)···Br(11 <sup>i</sup> )	3.665 (1)
W(1)—N(1)	2.184 (9)	N(1)···Br(11)	3.397 (8)
W(2)—Br(21)	2.574 (1)	N(1)···Br(12)	3.383 (8)
W(2)—Br(22)	2.577 (1)	N(1)···Br(11 <sup>i</sup> )	3.367 (9)
W(2)—N(2)	2.191 (9)	N(1)···Br(12 <sup>i</sup> )	3.369 (10)
Br(11)—W(1)—Br(12)	89.4 (1)°	Br(21)···Br(22)	3.658 (1)
N(1)—W(1)—Br(11)	90.5 (2)	Br(22)···Br(21 <sup>ii</sup> )	3.626 (1)
N(1)—W(1)—Br(12)	90.2 (2)	N(2)···Br(21)	3.370 (10)
N(1)—W(1)—Br(11 <sup>i</sup> )	89.5 (2)	N(2)···Br(22)	3.375 (9)
N(1)—W(1)—Br(12 <sup>i</sup> )	89.8 (2)	N(2)···Br(21 <sup>ii</sup> )	3.391 (8)
Br(21)—W(2)—Br(22)	90.5 (1)	N(2)···Br(22 <sup>ii</sup> )	3.390 (8)
N(2)—W(2)—Br(21)	89.6 (2)		
N(2)—W(2)—Br(22)	89.7 (2)	Symmetry code	
N(2)—W(2)—Br(21 <sup>ii</sup> )	90.4 (2)	(i) $-x, -y, -z$	
N(2)—W(2)—Br(22 <sup>ii</sup> )	90.3 (2)	(ii) $1-x, y, 1-z$	

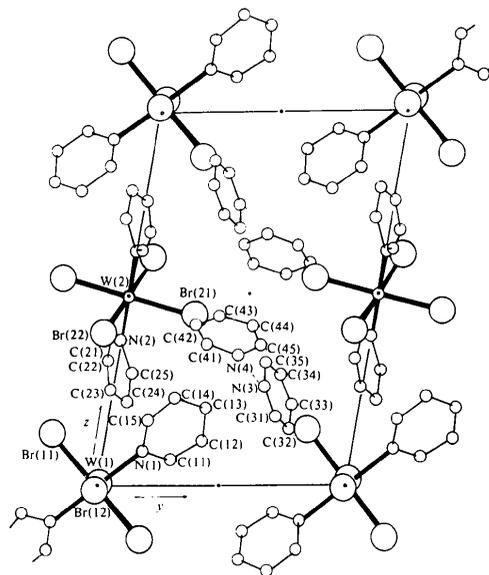


Fig. 1. Projection of the structure in the  $yz$  plane and the atom-numbering scheme.

(Minshall & Sheldrick, 1978), but shorter than those in [(pic)<sub>2</sub>H][WBr<sub>4</sub>(pic)<sub>2</sub>], 2.77 Å, and [(pyH)<sub>2</sub>]-[(Cl<sub>3</sub>Fe)<sub>2</sub>O(py)], 2.75 Å (Drew, McKee & Nelson, 1978).

The angle between the N(3)–C(33) and N(4)–C(43) directions is 15.5°. Pyridine rings are twisted by 76°. The corresponding values in [(pic)<sub>2</sub>H]<sup>+</sup> are 7 and 24°. This difference could be the reason for the closer contact of the two N atoms in the [(pic)<sub>2</sub>H]<sup>+</sup> case.

All four pyridine rings are planar within 0.02 Å. Distances and angles are normal. The shortest interionic interaction is between C(43)(*x*, *y*, *z*) and C(45)(–*x*, 1–*y*, 1–*z*), 3.40 (2) Å.

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### 3-Cyanopyridinium Tetrachloroferrate(III)–3-Cyanopyridine

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**Abstract.** [C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>][FeCl<sub>4</sub>].C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>, *M<sub>r</sub>* = 406.8, *C*2/*c*, *a* = 33.520 (5), *b* = 7.586 (1), *c* = 14.610 (4) Å, β = 107.9 (2)°, *V* = 3535.2 Å<sup>3</sup>, *D<sub>m</sub>* = 1.55 (2); *D<sub>x</sub>* = 1.53 Mg m<sup>–3</sup>, *Z* = 8. Final *R<sub>w</sub>* = 0.049 for 1556 counter reflexions. The unit cell contains tetrahedral tetrachloroferrate anions, 3-cyanopyridinium cations and 3-cyanopyridine molecules. N–H···N hydrogen bonding occurs between the cation and the solvent molecule.

**Introduction.** The crystal structure study of the title compound was undertaken after the compound appeared as a by-product during a series of reactions between iron(III) chloride and cyanopyridine. Anhydrous iron(III) chloride was added to a large excess of 3-cyanopyridine in dichloromethane. An intense brown-red colour developed. The reaction seemed to be quite complex. If the mixture was immediately filtered to remove excess iron(III) chloride, a yellow complex crystallized from the filtrate. The crystals were washed with ether and dried.

The crystal system was determined from precession photographs (Mo *K*α, λ = 0.71069 Å). Systematic extinctions *h*0*l*, *l* = 2*n* + 1, *hkl*, *h* + *k* = 2*n* + 1

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indicated space group *C*2/*c*. *D<sub>m</sub>* was measured by flotation in a tetrachloromethane–dichloromethane mixture.

A crystal 0.6 × 0.3 × 0.1 mm was set up about [001] on an automatic four-circle diffractometer and cell dimensions and orientation matrix were obtained by least squares from the setting angles of nine reflexions. The intensities of 3099 independent reflexions with sin θ/λ < 0.59 Å<sup>–1</sup> were measured by a θ/2θ scan at room temperature. Mo *K*α radiation and a take-off angle of 3° were used with a graphite monochromator set in front of the counter. An asymmetric scan starting 0.5° before the *K*α<sub>1</sub> peak and finishing 0.7° after the *K*α<sub>2</sub> peak was used because of tailing of the diffraction peaks. The scan speed was 1.5° min<sup>–1</sup>. The measurements were corrected for Lorentz and polarization effects. No absorption correction was applied (μ = 1.47 mm<sup>–1</sup>). Each structure factor was assigned a standard deviation σ = (F × ΔI)/I where *I* was the integrated intensity and ΔI the error. Of the 3099 reflexions, only 1556 with *F* > 3σ were used in subsequent calculations.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974), including *f'*