Crystal structure of 4,4′-bipyridinium dibromide, $(C_{10}H_{10}N_2)Br_2$

B.-S. Zhang and Y.-Q. Zheng*

Ningbo University, Institute for Solid State Chemistry, Municipal Key Laboratory of Inorganic Materials Chemistry, Ningbo, Zhejiang, 315211 P. R. China

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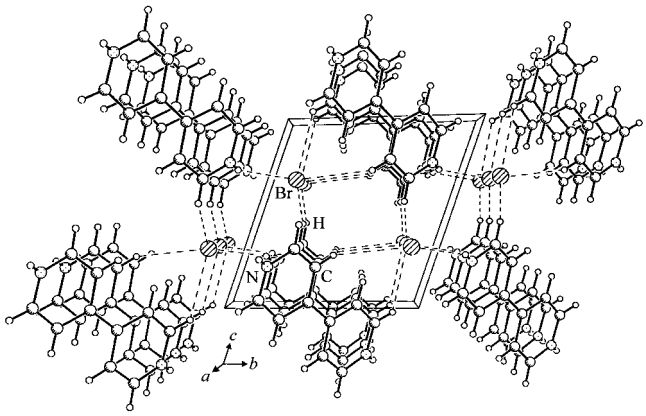

Abstract

$C_{10}H_{10}Br_2N_2$, triclinic, $P\bar{1}$ (No. 2), $a = 4.8975(6)$ Å, $b = 7.654(1)$ Å, $c = 7.9711(9)$ Å, $\alpha = 70.468(9)°$, $\beta = 87.029(9)°$, $\gamma = 77.15(1)°$, $V = 274.5$ Å^3, $Z = 1$, $R_{gt}(F) = 0.034$, $wR_{ref}(F^2) = 0.091$, $T = 293$ K.

Source of material

A 23 ml teflon-lined stainless steel autoclave was charged with a suspension of 0.341 g (1.724 mmol) $MnCl_2 \cdot 4H_2O$, 0.264 g (1.671 mmol) 4,4′-bipyridine, 8 ml H_2O and 0.445 g (0.215 mmol) W_6Br_{12} and heated at 453 K for 4 days. After the autoclave was cooled to room temperature, the solid was filtered off. The resulting orange filtrate was allowed to stand at room temperature and slow evaporation for 2 months afforded yellow pillar-like crystals. The synthesis was originally directed to synthesize the 4,4′-bipyridine bridged $[W_6Br^i_8]$ cluster compounds with divalent transition metals. $[H_2(4,4'\text{-bpy})]Br_2$ was sirendipitously obtained. A series following experiments directed to $[H_2(4,4'\text{-bpy})]Br_2$ by hydrothermal reaction of 4,4′-bipyridine and HBr was unsuccessful. The further experiments show that the hydrothermal hydrolysis of 0.445 g (0.215 mmol) W_6Br_{12} in 8 ml at 453 K for 4 days gave a very strong acidic solution, which is considered to be a precondition for formation of the protonated 4,4′-bipyridinium cations. At the same time, the used W_6Br_{12} is the Br^- anion source. Without addition of $MnCl_2 \cdot 4H_2O$, a hydrothermal reaction of W_6Br_{12} and 4,4′-bipyridine in H_2O could not afford $[H_2(4,4'\text{-bpy})]Br_2$, suggesting that $MnCl_2 \cdot 4H_2O$ is the enhancing agent for formation of $[H_2(4,4'\text{-bpy})]Br_2$. The reason for the formation of a bromide rather than any chloride is at moment unclear.

Discussion

The title compound consists of 4,4′-bipyridinium cations $[H_2(4,4'\text{-bpy})]^{2+}$ and Br^- anions. The 4,4′-bipyrinum cations are centered at the crystallographic 1*e* positions and display perfect coplanarity. Along the [100] direction, the 4,4′-bipyridinium cations are stacked via π-π stacking inteactions with a mean interplanar distance of 3.32 Å to generate 1D columnar chains, which are further interlinked by Br^- anions. The Br atoms are each tetrahedrally hydrogen bonded to three columnar chains with d(N–H···Br) = 3.20 Å and d(C–H···Br) = 3.51 Å – 3.65 Å.

Table 1. Data collection and handling.

Crystal:	yellow pillar-like, size 0.20 × 0.22 × 0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	73.45 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1676, 1242
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1116
$N(param)_{refined}$:	70
Programs:	SHELXS-97 [1], SHELXL-97 [2]

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

Atom	Site	x	y	z	U_{iso}
HN	2*i*	1.177(9)	0.134(6)	0.279(6)	0.03(1)
H(1)	2*i*	0.9185	0.2599	0.4445	0.053
H(2)	2*i*	0.5317	0.4748	0.2873	0.053
H(3)	2*i*	0.7959	0.3288	–0.1422	0.053
H(4)	2*i*	1.1775	0.1194	0.0278	0.053

* Correspondence author (e-mail: zhengcm@nbu.edu.cn)

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}
Br	2*i*	1.61714(7)	–0.15985(5)	0.32705(4)	0.0442(3)	0.0523(3)	0.0455(2)	0.0006(2)	–0.0059(1)	–0.0177(2)
N	2*i*	1.0740(7)	0.1806(5)	0.2438(5)	0.032(2)	0.044(2)	0.052(2)	–0.004(1)	–0.010(1)	–0.001(1)
C(1)	2*i*	0.8918(8)	0.2774(5)	0.3248(5)	0.049(2)	0.057(2)	0.036(2)	–0.006(2)	–0.011(2)	–0.007(2)
C(2)	2*i*	0.6609(7)	0.4052(5)	0.2310(4)	0.045(2)	0.048(2)	0.034(2)	–0.002(1)	–0.004(1)	–0.014(1)
C(3)	2*i*	0.8176(7)	0.3190(5)	–0.0240(5)	0.040(2)	0.045(2)	0.040(2)	–0.000(1)	–0.001(1)	–0.016(1)
C(4)	2*i*	1.0451(7)	0.1939(5)	0.0777(5)	0.037(2)	0.046(2)	0.055(2)	–0.001(1)	0.001(2)	–0.014(2)
C(5)	2*i*	0.6211(6)	0.4301(4)	0.0526(4)	0.030(1)	0.033(1)	0.034(1)	–0.006(1)	–0.001(1)	–0.009(1)

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