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Bis(quinolinium) tetrabromidomanganate(II)

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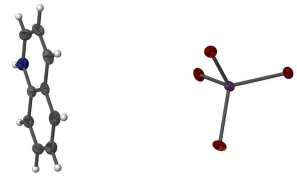
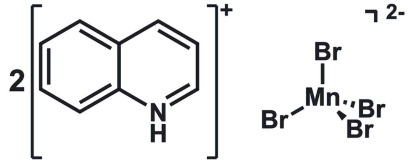
The title compound, $(C_9H_8N)_2[MnBr_4]$, consists of two quinolinium cations and a $[MnBr_4]^{2-}$ anion. The manganese(II) atom, which lies on a twofold rotation axis, is coordinated by four bromide ligands and exhibits a tetrahedral coordination geometry. The $[MnBr_4]^{2-}$ anion and the quinolinium cations are linked by N—H···Br hydrogen bonds. π–π stacking interactions are observed between the quinolinium cations.

3D view



Chemical scheme



Structure description

The molecular structure of the title compound is shown in Fig. 1. The asymmetric unit consists of one quinolinium cation and a half $[MnBr_4]^{2-}$ anion with the Mn^{II} atom lying on a twofold rotation axis. The Mn^{II} atom exhibits a slightly distorted tetrahedral coordination geometry. The crystal structures of similar compounds with the general formula $(QuinH)_2[MX_4]$ (without co-crystallized H_2O; Quin = quinoline; M = Cu, X = Br (Butcher *et al.*, 2010); M = Cu, X = Cl (Lamotte-Brasseur & Vermeire, 1973); M = Cd, X = Cl (Paulus & Göttlicher, 1969) have been reported. Several crystal structures of compounds with the general formula $(QuinH)_2[MX_4]\cdot 2H_2O$ have also been described by Landee *et al.* (2018) (M = Co, Mn, X = Cl; M = Co, Zn, X = Br), Butcher *et al.* (2010) (M = Cu, X = Br), Ye *et al.* (2014) (M = Co, X = Cl), Lynch & McClenaghan (2002) (M = Cu, X = Cl), Slabbert & Rademeyer (2016) (M = Hg, X = Cl; M = Cd, X = Br) and Valdés-Martínez *et al.* (2005) (M = Zn, X = Cl).

In the crystal structure of the title compound, the anion is linked to the cations by N—H···Br hydrogen bonds (Table 1, Fig. 2). Additionally, π–π stacking occurs between two quinolinium cations [$Cg1\cdots Cg1$ = 3.799 (1) Å with ring slippage of 1.7 Å and $Cg1\cdots Cg2$ = 3.6368 (10) Å with ring slippage of 1.3 Å, where $Cg1$ is the centroid of the N1/C1–C4/C9 ring and $Cg2$ is the centroid of the C4–C9 benzene ring].

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Br1^{i}	0.88 (3)	2.69 (3)	3.3815 (14)	137 (2)

Symmetry code: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Synthesis and crystallization

A mixture containing $MnBr_2{\cdot}4H_2O$ (1 mmol) and quinoline (2 mmol) in dry toluene (20 mL) was stirred overnight at 60°C. The solvent was removed under vacuum giving a white solid that was then dissolved in dry EtOH (10 mL) and reacted with 1 eq of HBr (48 wt% in H_2O) overnight. The solvent was removed under vacuum giving a white solid (yield: 73%). Colourless crystals suitable for X-ray diffraction analysis were grown from a solution of EtOH layered with Et_2O.

Refinement

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_9H_8N)_2[MnBr_4]$
M_r	634.91
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	150
a, *b*, *c* (Å)	17.4314 (6), 9.1871 (3), 13.2270 (4)
β (°)	93.7501 (12)
V (Å^3)	2113.69 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	8.19
Crystal size (mm)	0.44 × 0.42 × 0.17
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.12, 0.34
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17446, 2545, 2373
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.041, 1.05
No. of reflections	2545
No. of parameters	118
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.45

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *XP* in *SHELXTL* and *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2006) and *publCIF* (Westrip, 2010).

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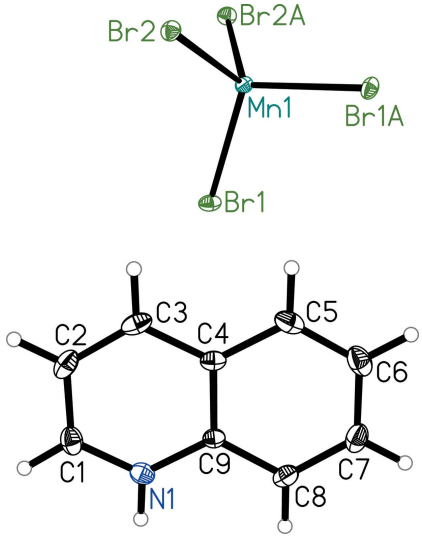

Figure 1
The molecular entities of the title compound with atom labelling and displacement ellipsoids drawn at the 30% probability level.

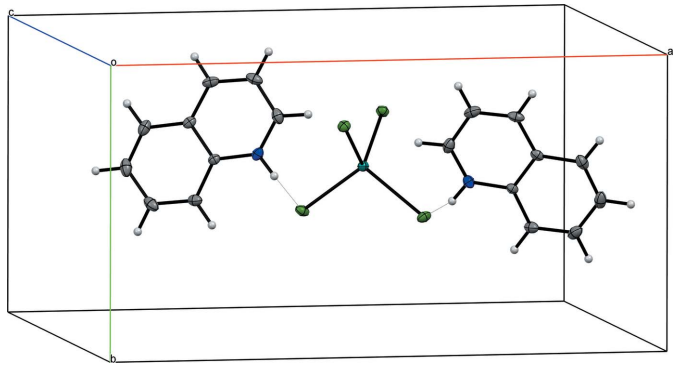

Figure 2
ORTEP representation of the title compound showing the intermolecular hydrogen bonds as dotted lines. Displacement ellipsoids correspond to 30% probability.

full crystallographic data

IUCrData (2019). **4**, x191231 [https://doi.org/10.1107/S2414314619012318]

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Crystal data

$(C_9H_8N)_2[MnBr_4]$
M_r = 634.91
Monoclinic, $C2/c$
a = 17.4314 (6) Å
b = 9.1871 (3) Å
c = 13.2270 (4) Å
β = 93.7501 (12)°
V = 2113.69 (12) Å^3
Z = 4
$F(000)$ = 1212
D_x = 1.995 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9902 reflections
θ = 2.5–30.5°
μ = 8.19 mm^{-1}
T = 150 K
Prism, colourless
0.44 × 0.42 × 0.17 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.12, T_{max} = 0.34
17446 measured reflections
2545 independent reflections
2373 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 28.0°, θ_{min} = 2.3°
h = −22→22
k = −10→12
l = −17→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.041
S = 1.05
2545 reflections
118 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0192P)^2 + 1.7599P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.59434 (2)	0.56020 (2)	0.16817 (2)	0.02499 (5)
Br2	0.55967 (2)	0.23982 (2)	0.38636 (2)	0.02340 (5)
C1	0.90430 (11)	0.7807 (2)	0.56459 (13)	0.0302 (4)
H1B	0.9547	0.7726	0.5418	0.036*
C2	0.87027 (11)	0.66136 (19)	0.60845 (13)	0.0308 (4)
H2	0.8972	0.5717	0.6161	0.037*
C3	0.79790 (11)	0.67462 (18)	0.64031 (12)	0.0282 (4)
H3	0.7741	0.5931	0.6694	0.034*
C4	0.75792 (9)	0.80749 (17)	0.63065 (11)	0.0212 (3)
C5	0.68293 (10)	0.8285 (2)	0.66219 (13)	0.0307 (4)
H5	0.6572	0.7507	0.6930	0.037*
C6	0.64737 (11)	0.9590 (2)	0.64878 (15)	0.0365 (4)
H6	0.5969	0.9718	0.6703	0.044*
C7	0.68442 (11)	1.0755 (2)	0.60344 (15)	0.0337 (4)
H7	0.6585	1.1660	0.5944	0.040*
C8	0.75718 (11)	1.06050 (18)	0.57222 (13)	0.0276 (4)
H8	0.7821	1.1398	0.5420	0.033*
C9	0.79424 (9)	0.92592 (16)	0.58566 (11)	0.0195 (3)
Mn1	0.5000	0.39954 (3)	0.2500	0.01891 (7)
N1	0.86666 (8)	0.90510 (16)	0.55456 (10)	0.0248 (3)
H1A	0.8907 (15)	0.975 (3)	0.524 (2)	0.059 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03363 (10)	0.02137 (8)	0.02065 (8)	−0.00760 (6)	0.00703 (6)	−0.00080 (6)
Br2	0.02595 (9)	0.02263 (8)	0.02159 (8)	0.00227 (6)	0.00134 (6)	0.00346 (6)
C1	0.0259 (9)	0.0378 (9)	0.0268 (8)	0.0056 (7)	0.0025 (7)	−0.0062 (7)
C2	0.0416 (10)	0.0227 (8)	0.0268 (8)	0.0084 (7)	−0.0068 (7)	−0.0050 (7)
C3	0.0438 (11)	0.0196 (8)	0.0205 (7)	−0.0060 (7)	−0.0042 (7)	0.0020 (6)
C4	0.0273 (8)	0.0217 (7)	0.0145 (6)	−0.0064 (6)	0.0004 (6)	−0.0019 (6)
C5	0.0288 (9)	0.0384 (10)	0.0257 (8)	−0.0119 (8)	0.0064 (7)	−0.0053 (7)
C6	0.0241 (9)	0.0514 (12)	0.0343 (10)	−0.0012 (8)	0.0034 (8)	−0.0167 (9)
C7	0.0321 (10)	0.0309 (9)	0.0367 (10)	0.0091 (7)	−0.0083 (8)	−0.0116 (8)
C8	0.0323 (9)	0.0203 (8)	0.0294 (8)	−0.0009 (6)	−0.0048 (7)	0.0005 (6)
C9	0.0222 (8)	0.0193 (7)	0.0168 (7)	−0.0028 (6)	−0.0003 (6)	−0.0011 (5)
Mn1	0.02264 (17)	0.01714 (15)	0.01725 (15)	0.000	0.00363 (12)	0.000
N1	0.0253 (7)	0.0276 (7)	0.0219 (7)	−0.0039 (6)	0.0043 (6)	0.0036 (6)

Geometric parameters (Å, º)

Br1—Mn1	2.5073 (2)	C5—H5	0.9500
Br2—Mn1	2.4986 (2)	C6—C7	1.404 (3)
C1—N1	1.320 (2)	C6—H6	0.9500
C1—C2	1.391 (3)	C7—C8	1.366 (3)

C1—H1B	0.9500	C7—H7	0.9500
C2—C3	1.361 (3)	C8—C9	1.401 (2)
C2—H2	0.9500	C8—H8	0.9500
C3—C4	1.407 (2)	C9—N1	1.366 (2)
C3—H3	0.9500	Mn1—Br2^{i}	2.4986 (2)
C4—C9	1.410 (2)	Mn1—Br1^{i}	2.5073 (2)
C4—C5	1.411 (2)	N1—H1A	0.88 (3)
C5—C6	1.356 (3)		
N1—C1—C2	120.10 (17)	C8—C7—C6	120.94 (17)
N1—C1—H1B	119.9	C8—C7—H7	119.5
C2—C1—H1B	119.9	C6—C7—H7	119.5
C3—C2—C1	119.18 (16)	C7—C8—C9	118.70 (16)
C3—C2—H2	120.4	C7—C8—H8	120.6
C1—C2—H2	120.4	C9—C8—H8	120.6
C2—C3—C4	120.86 (16)	N1—C9—C8	120.85 (15)
C2—C3—H3	119.6	N1—C9—C4	117.91 (14)
C4—C3—H3	119.6	C8—C9—C4	121.23 (15)
C3—C4—C9	118.32 (15)	Br2—Mn1—Br2^{i}	108.068 (14)
C3—C4—C5	123.69 (16)	Br2—Mn1—Br1	113.799 (6)
C9—C4—C5	117.98 (15)	Br2^{i}—Mn1—Br1	106.734 (5)
C6—C5—C4	120.45 (17)	Br2—Mn1—Br1^{i}	106.733 (5)
C6—C5—H5	119.8	Br2^{i}—Mn1—Br1^{i}	113.798 (6)
C4—C5—H5	119.8	Br1—Mn1—Br1^{i}	107.877 (14)
C5—C6—C7	120.70 (17)	C1—N1—C9	123.62 (15)
C5—C6—H6	119.7	C1—N1—H1A	115.4 (18)
C7—C6—H6	119.7	C9—N1—H1A	121.0 (17)
N1—C1—C2—C3	0.2 (3)	C7—C8—C9—N1	179.22 (16)
C1—C2—C3—C4	−0.9 (2)	C7—C8—C9—C4	−0.2 (2)
C2—C3—C4—C9	1.0 (2)	C3—C4—C9—N1	−0.5 (2)
C2—C3—C4—C5	−179.94 (16)	C5—C4—C9—N1	−179.59 (14)
C3—C4—C5—C6	−178.77 (17)	C3—C4—C9—C8	178.94 (15)
C9—C4—C5—C6	0.3 (2)	C5—C4—C9—C8	−0.2 (2)
C4—C5—C6—C7	−0.1 (3)	C2—C1—N1—C9	0.3 (3)
C5—C6—C7—C8	−0.3 (3)	C8—C9—N1—C1	−179.57 (16)
C6—C7—C8—C9	0.4 (3)	C4—C9—N1—C1	−0.2 (2)

Symmetry code: (i) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Br1^{ii}	0.88 (3)	2.69 (3)	3.3815 (14)	137 (2)

Symmetry code: (ii) −*x*+3/2, *y*+1/2, −*z*+1/2.