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Crystal structure of 1,10-phenanthroline bromide dihydrate, $C_{12}H_9N_2Br$

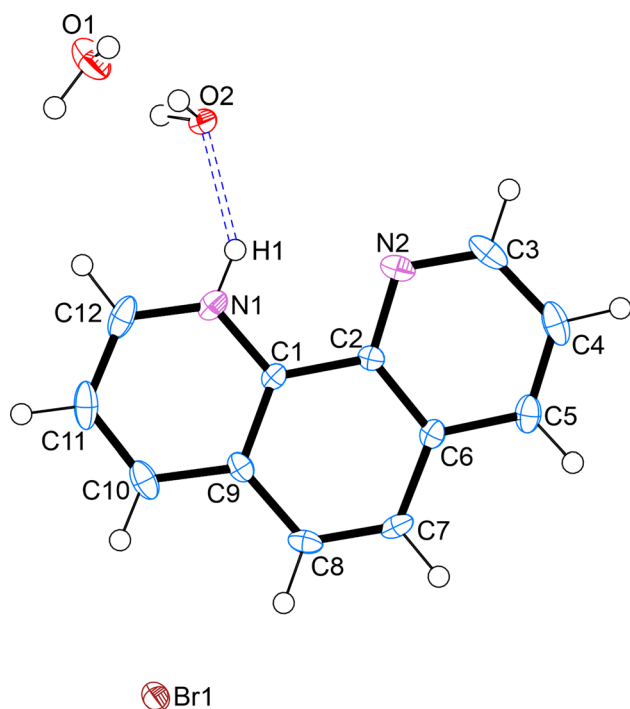


Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.38 × 0.25 × 0.16 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.39 mm ⁻¹
Diffractometer, scan mode:	BRUKER SMART APEX-II, φ and ω
$\theta_{\max}$, completeness:	27.5°, >99 %
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	10,251, 2743, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2596
$N(\text{param})_{\text{refined}}$:	172
Programs:	BRUKER [1, 2], SHELX [3, 4], OLEX2 [5]

1 Source of materials

All reagents are commercially available and were used without further purification. To 1.0 g (5.6 mmol) of 1,10-phenanthroline hydrate was added 20 mL of a methanolic solution of hydrobromic acid (8.2 g, 5.5 mL). Hydrogen peroxide solution (48 %, 5.5 mL) was added dropwise over a period of 20 min under vigorous and continuous stirring at room temperature. After 20 h of stirring, the pink solution was concentrated *in vacuo* at 60–70 °C. The residue was dissolved in water (50 mL) and then extracted with ethyl acetate (3 × 50 mL). The resultant ethyl acetate fractions were combined and concentrated to dryness. This residue was redissolved in dichloromethane and filtered to remove insoluble material. The dichloromethane solution was concentrated *in vacuo* and diethylether added to afford the title compound as a white solid. Crystals of the title compound were initially obtained from a hexane-toluene mixture. Crystals suitable for X-ray diffraction, were obtained by recrystallisation, at ambient temperature, from a mixture of methanol and water by slow evaporation.

2 Experimental details

Data reduction was carried out using the program *SAINT* and empirical absorption corrections were made using *SADABS* [2]. Space group assignment was made using *SHELXS-2013* [3] and the structure refined using full-matrix least-squares minimisation with 2016/6 of *SHELXL* [4] using *OLEX2* as the graphical

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Abstract

$C_{12}H_9N_2Br$, triclinic, $P\bar{1}$ (no. 2), $a = 7.4005(13)$ Å, $b = 9.4122(16)$ Å, $c = 9.7916(17)$ Å, $\alpha = 98.235(9)^\circ$, $\beta = 101.744(8)^\circ$, $\gamma = 111.005(7)^\circ$, $V = 605.69(18)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0209$, $wR_{\text{ref}}(F^2) = 0.0514$, $T = 100(2)$ K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.27857 (3)	0.11119 (2)	0.39455 (2)	0.01755 (6)
C1	0.2385 (2)	0.53193 (18)	0.09434 (17)	0.0127 (3)
C2	0.2639 (2)	0.50116 (19)	−0.04636 (17)	0.0127 (3)
C3	0.3853 (3)	0.5947 (2)	−0.2254 (2)	0.0239 (4)
H3	0.452233	0.680111	−0.263100	0.029*
C4	0.3189 (3)	0.4420 (2)	−0.3101 (2)	0.0245 (4)
H4	0.342367	0.426193	−0.401814	0.029*
C5	0.2205 (3)	0.3168 (2)	−0.25956 (18)	0.0201 (4)
H5	0.173606	0.213046	−0.315849	0.024*
C6	0.1895 (2)	0.34372 (19)	−0.12275 (17)	0.0146 (3)
C7	0.0864 (3)	0.2206 (2)	−0.06086 (19)	0.0177 (3)
H7	0.034209	0.114959	−0.113832	0.021*
C8	0.0620 (3)	0.2519 (2)	0.07111 (19)	0.0184 (4)
H8	−0.007522	0.168157	0.109724	0.022*
C9	0.1397 (2)	0.4098 (2)	0.15393 (17)	0.0150 (3)
C10	0.1217 (3)	0.4493 (2)	0.29392 (19)	0.0221 (4)
H10	0.054542	0.368921	0.336870	0.027*
C11	0.2008 (3)	0.6029 (3)	0.36799 (19)	0.0269 (4)
H11	0.190301	0.629276	0.462577	0.032*
C12	0.2961 (3)	0.7194 (2)	0.3037 (2)	0.0245 (4)
H12	0.350287	0.826140	0.354079	0.029*
N1	0.3119 (2)	0.68247 (17)	0.17224 (15)	0.0176 (3)
H1	0.369124	0.755292	0.132193	0.021*
N2	0.3598 (2)	0.62597 (17)	−0.09655 (16)	0.0181 (3)
O1	0.8326 (2)	1.11613 (18)	0.37689 (15)	0.0307 (3)
H1A	0.945807	1.112674	0.376812	0.046*
H1B	0.793038	1.063350	0.436555	0.046*
O2 ^a	0.4789 (4)	0.9793 (3)	0.1546 (3)	0.0180 (6)
H2A ^a	0.597107	1.018192	0.211287	0.027*
H2B ^a	0.414019	1.021318	0.196234	0.027*
O3 ^a	0.5536 (7)	0.9525 (4)	0.1155 (4)	0.0410 (9)
H3A ^a	0.625915	1.028255	0.187770	0.061*
H3B ^a	0.516342	0.995625	0.051017	0.061*

interface [5]. Hydrogen atom positions were calculated geometrically and refined using the riding model.

3 Comment

For several decades, phenanthroline derivatives have been used primarily as colourimetric indicators for transition metals ions. This application and the structural rigidity of phenanthrolines have generated interest in the preparation and structural studies of phenanthrolines with pendant photo- and electroactive molecules [6]. The 1,10-phenanthroline and its derivatives have been largely unexplored as chromophores to stabilize transition metal complexes in contrast to the related 2,2'-bipyridine and 2,2',6,6''-terpyridine structures [7]. Coordination chemistry

of 1,10-phenanthroline has encouraged the synthesis of new structures which could serve as electron acceptors when chelated to appropriate metal ions. Studies on the use of different phenanthrolines have shown their importance as ion-selective electrochemical sensors, as fluorometric sensors, and as agents for selective ion transport, especially for the detection and transport of Li^+ [8].

The asymmetric unit of the title crystal structure contains one 1,10-phenanthroline-1-ium cation, one bromide anion and two free water molecules. One of the two water molecules is disordered over two positions with equal site occupancies. The title compound is solvatomorphic as the 1,10-phenanthroline bromide monohydrate structure reported by Buttery and co-workers [9]. All geometric parameters are within the expected ranges [10] and a least-squares fit calculation comparing the phenanthroline ions in these two crystal structures (title structure and monohydrate [9]) shows the r.m.s. deviation of bond lengths to be 0.0174 Å [11].

The 1,10-phenanthroline bromide dihydrate reported here however, crystallizes in the $P\bar{1}$ space group with an different packing arrangement. The crystal structure is composed of extended sheets of phenanthroline cations with the bromide anions arrayed on both sides of the sheets out of the plane of the polyaromatic cation. The molecules stack along the a-axis with an interplanar separation of 3.329 Å and are supported by π - π interactions. In the crystal, there is evidence of hydrogen bonding interactions between the water molecules and the bromide ion as well as the pyridinium hydrogen. Charge-assisted hydrogen bonds are observed between H(1B)⋯Br(1) at 2.495 Å and H(2B)⋯Br(1) at 2.534 Å. In addition, there are strong hydrogen bonds between N-H(1)⋯O(2) at 1.929 Å as well as the two water molecule with H(2A)⋯O(1) at 1.946 Å.

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