Electronic Supplementary Information for Dalton Transactions

The Complex Story of a Simple Brønsted Acid: Unusual Speciation of HBr in an Ionic Liquid Medium

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Supplementary Experimental Details:

Materials: Details for the purification of starting materials and methods used in preparation of the liquid formed from a 2:1 mole ratio of HBr and 1-methylimidazole, as used in this work (including and ^{1}H-NMR characterisation), are available in the literature.[1] Crystals of $[(Hmim)_3Br]^{2+}\cdot Br^-\cdot[H_2Br_3]^-$ co-exist in equilibrium with the pure liquid of their own accord, at temperatures < 20 °C.

X-Ray Diffraction: A suitable crystal was selected from the mother liquid and mounted to a glass fibre using the oil-drop method.[2] Diffraction data were collected on a Nonius KappaCCD diffractometer (graphite-monochromated MoK α radiation). The structure was solved by direct methods. The programs COLLECT,[3] SHELXS-97 and SHELXL-97,[4] were used for data reduction, structure solution and structure refinement, respectively: $C_{12}H_{23}Br_5N_6$, M_r = 650.91 g mol^{-1}, crystal size 0.20 x 0.20 x 0.20 mm^3, hexagonal, *P-62c*, a = 13.2000(10) Å, b = 13.2000(10) Å, c = 7.1170(10) Å, V = 1073.93(19) Å^3, Z = 2, ρ_{calc} = 2013 kg m^{-3}, μ = 9.362 mm^{-1}, Mo Kα radiation, λ = 0.71073 Å, T = 173(2) K, 2θ*max* = 25.05°, reflections collected/unique = 13151/685, R_{int} = 0.0851, $R1$ = 0.0364, $wR2$ = 0.0789, (I > 2σ(I)), largest diff. peak and hole 0.659 and -0.791 e Å^{-3}. Refinement of F^2 was performed against all reflections.

Complete X-ray crystallographic data can be obtained from the Cambridge Crystallographic Data Centre, quoting the number CCDC-812944. All non-hydrogen atoms were refined anisotropically. H atoms of the 3-methyl-1H-imidazolium cation were geometrically fixed and allowed to ride on the attached atoms and the hydrogen H(7) was found in the difference map and refined with riding temperature factor.

Supplementary Tables

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $[(Hmim)_3Br]^{2+}\cdot Br^-\cdot[H_2Br_3]^-$. U(eq) is defined as 1/3 the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3252(9)	3896(8)	7500	28(2)
C(2)	4167(10)	3797(13)	7500	43(3)
N(3)	3907(11)	2735(13)	7500	44(3)
C(4)	2762(19)	2111(14)	7500	95(6)
C(5)	2334(12)	2849(14)	7500	65(5)
C(6)	3190(11)	4990(10)	7500	45(3)
Br(1)	6667	3333	7500	36(1)
Br(2)	6496(1)	6496(1)	0	37(1)
Br(3)	10000	0	5000	31(1)

Table 2. Bond lengths [Å] and angles [°] for $[(Hmim)_3Br]^{2+}\cdot Br^{-}\cdot[H_2Br_3]^{-}$.

N(1)-C(2)	1.278(16)
N(1)-C(5)	1.305(18)
N(1)-C(6)	1.486(13)
C(2)-N(3)	1.266(19)
C(2)-H(2)	0.9500
N(3)-C(4)	1.31(2)
N(3)-H(3)	0.8800
C(4)-C(5)	1.35(2)
C(4)-H(4)	0.9500
C(5)-H(5)	0.9500
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
Br(2)-H(7)	1.87(7)
C(2)-N(1)-C(5)	108.4(11)
C(2)-N(1)-C(6)	127.8(11)
C(5)-N(1)-C(6)	123.8(10)
N(3)-C(2)-N(1)	111.5(12)
N(3)-C(2)-H(2)	124.3
N(1)-C(2)-H(2)	124.3
C(2)-N(3)-C(4)	106.6(11)
C(2)-N(3)-H(3)	126.7
C(4)-N(3)-H(3)	126.7
N(3)-C(4)-C(5)	108.3(14)
N(3)-C(4)-H(4)	125.9
C(5)-C(4)-H(4)	125.9
N(1)-C(5)-C(4)	105.3(13)
N(1)-C(5)-H(5)	127.4
C(4)-C(5)-H(5)	127.4
N(1)-C(6)-H(6A)	109.5
N(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
N(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5

Symmetry transformations used to generate equivalent atoms.

Table 3. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[(Hmim)_3Br]^{2+}\cdot Br^-\cdot[H_2Br_3]^-$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	24(5)	20(5)	43(6)	0	0	14(5)
C(2)	28(6)	40(8)	73(9)	0	0	27(7)
N(3)	37(7)	50(7)	60(7)	0	0	33(6)
C(4)	75(12)	35(7)	185(17)	0	0	35(9)
C(5)	32(7)	34(7)	131(13)	0	0	19(6)
C(6)	41(6)	24(6)	80(9)	0	0	23(6)
Br(1)	19(1)	19(1)	72(1)	0	0	9(1)
Br(2)	31(1)	31(1)	47(1)	0(1)	0(1)	14(1)
Br(3)	32(1)	32(1)	28(1)	0	0	16(1)

Table 4. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for $[(Hmim)_3Br]^{2+}\cdot Br^-\cdot[H_2Br_3]^-$.

	x	y	z	U(eq)
H(2)	4944	4440	7500	51
H(3)	4399	2468	7500	53
H(4)	2311	1281	7500	114
H(5)	1536	2649	7500	78
H(6A)	3283	5288	8787	68
H(6B)	2431	4827	7004	68
H(6C)	3817	5577	6709	68
H(7)	6460(190)	6000(200)	2500	55

References:

1. G. Driver and K. E. Johnson, *Green Chem.*, 2003, **5**, 163-169.
2. T. Kottke and D. Stalke, *J. Appl. Crystallogr.*, 1993, **26**, 615-619.
3. *Nonius COLLECT,Nonius BV, Delft, The Netherlands*, 2002.
4. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.