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Refinement of crystal structure of tris[pyrrolidine-2-one] hydrogen tribromide, $(C_4H_7NO)_3HBr_3$

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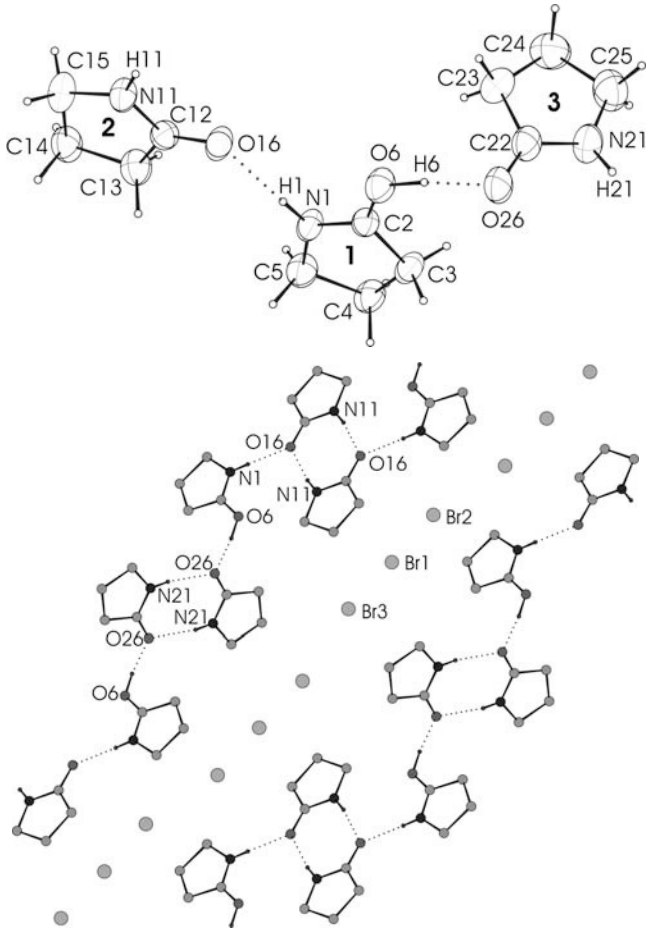

Abstract

$C_{12}H_{22}Br_3N_3O_3$, monoclinic, $P12_1/a1$ (no. 14), a = 11.932(2) Å, b = 10.091(2) Å, c = 15.514(3) Å, β = 105.19(2)°, V = 1802.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.038, $wR_{ref}(F^2)$ = 0.114, T = 293 K.

Source of material

The title compound was prepared as followed: to a 200 ml flask cooled in an ice bath and equipped with a dropping funnel and a condenser, successively 20 ml of MeOH and 25 g (one drop per second) of a solution of HBr (30 % in acetic acid) were added while maintaining the internal temperature under 10 °C. Element of bromine (16 g, 0.1 mole), was then added by the dropping funnel (2 drops per second). The solution was stirred for 10 minutes and became orange. Commercial pyrrolidin-2-one (25.3 g, 0.3 mole) was then added by the dropping funnel (2 drops per second). After 15 minutes the title complex started to precipitate. This one was collected after one hour, washed with diethyl oxide and dried under vacuum to give 25.8 g violet crystals (yield 51 %). The final product was recrystallised from acetic acid for crystallographic studies.

Experimental details

The hydrogen atoms of CH_2 groups were inserted at calculated positions with $U_{iso}(H) = 1.2\ U_{eq}$(carrier atoms). H1, H6, H11 and H21 atoms involved in hydrogen bonding were first located from a difference Fourier map and then refined with the same isotropic thermal parameter.

Discussion

In a previous work [1] we prepared and structurally characterized methylpyrrolidone hydrotribromide, a new brominating reagent. In order to promote this reagent, it was necessary to compare it with commercial pyrrolidone hydrotribromide. Pyrrolidin-2-one gave a crystalline complex with bromine; the red brick solid was identified as a mixture of $(C_4H_7NO)_2 \cdot Br_2$ (A) and $C_4H_7NO \cdot HBr$ (B) [2]. More recently, the same entities were prepared [3]. A change in the structure of the lactam was noted which conferred a different requirement for stability upon these complexes. The empirical formula for lactam-hydrogen bromide and bromine was assumed $(C_4H_7NO)_3 \cdot HBr \cdot Br_2$ (C). The stability might be due to the formation of Br_3^- species, as it was observed since a long time in many other complexes of halogen and hydrohalides with organic compounds [4-7]. The Br_3^- species would interact with lactam derivatives to form stable unified complexes. A crystal structure of compound C recrystallised from chloroform was described in [8].

The title crystal structure is built up from [bis(pyrrolidine-2-one)-pyrrolidine-2-onium]$^+$ cation and $[Br_3]^-$ anion (figure, top). The pyrrolidine-2-onium entity (1) is linked by strong hydrogen bonds to the two pyrrolidine-2-one molecules (2, 3) formed with the N1 nitrogen and O6 oxygen atoms (N1–H1···O16 and O6–H6···O26: 2.725(4) Å, 175(4)° and 2.502(4)Å, 172(7)°, respectively). Moreover each pyrrolidine-2-one molecule [N11/C12-C15/O16 or N21/C22-C25/O26], forms a centrosymmetric dimer within which the molecules are held together by two N–H···O hydrogen bonds: N11–H11···O16^{i} (2.964(4) Å, 171(4)°) and N21–H21···O26^{ii} (2.998(5) Å, 171(4)°) (symmetry codes (i): $-x,-y,-z$;

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(ii): 1–*x*,–*y*,1–*z*). These values agree well with mean values of 2.92(7) Å and 166(9)° found for N–H···O bonds in crystals of monoamides [9]. The configuration of this cation may be compared with that determined in the pyrrolidine-2-one [10]. Nevertheless, the N1—C2 bond (1.265(4) Å) is significantly shorter than that reported in pyrrolidine-2-one (1.335(2) Å). Since the three $[Br_3]^-$ are not located at inversion center, they are neither centrosymmetric nor linear. The angle Br2–Br1–Br3, 178.15(2)° and the bond lengths *d*(Br1—Br2) = 2.528(1) Å and *d*(Br1—Br3) = 2.556(1) Å are in good agreement with the values reported in the hexakis(*N*,*N*-dimethylformamide-*O*)aluminium(III) tris(tribromide) with a similar symmetry [11]. The crystal packing is characterized by the presence of layers parallel to (101) plane, consisting of $[Br_3]^-$ anions (figure, bottom). The cations are placed in sandwich between these layers. The crystalline cohesion is ensured by many van der Waals contacts, the shortest being 3.361(1) Å.

Table 1. Data collection and handling.

Crystal:	violet parallelepiped, size 0.15 × 0.22 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	67.25 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	60.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10628, 5237
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2079
$N(param)_{refined}$:	204
Programs:	SIR92 [12], SHELXL-97 [13], CAMERON [14], WinGX [15]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.271(3)	0.161(4)	0.088(2)	0.055(8)
H(3A)	4*e*	0.5353	0.1175	0.2631	0.058
H(3B)	4*e*	0.4716	0.2289	0.3038	0.058
H(4A)	4*e*	0.5830	0.2701	0.1769	0.058
H(4B)	4*e*	0.5058	0.3767	0.2087	0.058
H(5A)	4*e*	0.3741	0.3544	0.0776	0.059
H(5B)	4*e*	0.4444	0.2356	0.0509	0.059
H(6)	4*e*	0.327(6)	0.034(6)	0.291(1)	0.15(3)
H(11)	4*e*	–0.063(3)	0.049(3)	–0.087(3)	0.055(8)
H(13A)	4*e*	0.1928	0.2312	–0.1172	0.060
H(13B)	4*e*	0.1204	0.3373	–0.0798	0.060
H(14A)	4*e*	0.0627	0.2299	–0.2488	0.065
H(14B)	4*e*	0.0009	0.3504	–0.2157	0.065
H(15A)	4*e*	–0.1425	0.2204	–0.1989	0.065
H(15B)	4*e*	–0.0892	0.1048	–0.2444	0.065
H(21)	4*e*	0.452(3)	0.081(4)	0.552(2)	0.055(8)
H(23A)	4*e*	0.1676	0.1108	0.3908	0.075
H(23B)	4*e*	0.2344	0.2281	0.3592	0.075
H(24A)	4*e*	0.1507	0.2308	0.5036	0.090
H(24B)	4*e*	0.2212	0.3463	0.4738	0.090
H(25A)	4*e*	0.3744	0.2956	0.5844	0.085
H(25B)	4*e*	0.3045	0.1782	0.6132	0.085

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(1)	4*e*	0.26920(3)	0.48775(4)	0.24021(3)	0.0454(2)	0.0511(2)	0.0470(2)	–0.0008(2)	0.0062(2)	–0.0022(2)
Br(2)	4*e*	0.12472(4)	0.49653(4)	0.08850(3)	0.0587(3)	0.0660(3)	0.0449(2)	–0.0024(2)	–0.0029(2)	–0.0010(2)
Br(3)	4*e*	0.41998(4)	0.48284(5)	0.39145(3)	0.0615(3)	0.0889(4)	0.0500(3)	0.0031(3)	–0.0074(2)	–0.0054(2)
N(1)	4*e*	0.3316(3)	0.1772(3)	0.1199(2)	0.037(2)	0.049(2)	0.035(2)	–0.007(2)	–0.001(1)	0.002(2)
C(2)	4*e*	0.3626(3)	0.1323(3)	0.1987(2)	0.036(2)	0.040(2)	0.036(2)	–0.001(2)	0.007(2)	–0.004(2)
C(3)	4*e*	0.4771(3)	0.1869(4)	0.2488(2)	0.035(2)	0.057(2)	0.044(2)	0.000(2)	–0.003(2)	–0.003(2)
C(4)	4*e*	0.5068(3)	0.2875(4)	0.1855(2)	0.041(2)	0.051(2)	0.048(2)	–0.012(2)	0.004(2)	–0.002(2)
C(5)	4*e*	0.4120(3)	0.2707(4)	0.0974(3)	0.048(2)	0.051(2)	0.046(2)	–0.009(2)	0.008(2)	0.004(2)
O(6)	4*e*	0.3027(2)	0.0476(3)	0.2290(2)	0.046(2)	0.057(2)	0.043(2)	–0.011(1)	0.005(1)	0.009(1)
N(11)	4*e*	–0.0301(3)	0.1058(3)	–0.1102(2)	0.048(2)	0.046(2)	0.036(2)	–0.007(2)	0.004(2)	0.005(1)
C(12)	4*e*	0.0719(3)	0.1472(4)	–0.0621(2)	0.040(2)	0.042(2)	0.038(2)	0.002(2)	0.008(2)	–0.005(2)
C(13)	4*e*	0.1162(4)	0.2533(4)	–0.1109(2)	0.055(3)	0.047(2)	0.045(2)	–0.006(2)	0.011(2)	–0.000(2)
C(14)	4*e*	0.0280(4)	0.2602(4)	–0.2024(3)	0.061(3)	0.056(2)	0.044(2)	0.005(2)	0.013(2)	0.010(2)
C(15)	4*e*	–0.0728(4)	0.1695(4)	–0.1965(3)	0.064(3)	0.051(2)	0.038(2)	–0.001(2)	–0.003(2)	0.002(2)
O(16)	4*e*	0.1212(2)	0.1035(2)	0.0129(2)	0.042(2)	0.062(2)	0.037(1)	–0.006(1)	–0.001(1)	0.007(1)
N(21)	4*e*	0.3913(4)	0.1227(4)	0.5236(2)	0.063(3)	0.074(3)	0.042(2)	0.003(2)	0.003(2)	0.008(2)
C(22)	4*e*	0.3439(4)	0.0960(4)	0.4395(3)	0.053(3)	0.053(2)	0.041(2)	–0.002(2)	0.008(2)	0.014(2)
C(23)	4*e*	0.2327(4)	0.1713(5)	0.4092(3)	0.048(3)	0.076(3)	0.058(3)	0.004(2)	0.002(2)	0.003(2)
C(24)	4*e*	0.2218(4)	0.2525(5)	0.4875(3)	0.069(3)	0.086(4)	0.075(4)	0.014(3)	0.025(3)	0.005(3)
C(25)	4*e*	0.3277(4)	0.2176(5)	0.5635(3)	0.077(4)	0.077(3)	0.056(3)	–0.008(3)	0.014(3)	–0.010(3)
O(26)	4*e*	0.3853(3)	0.0184(3)	0.3936(2)	0.060(2)	0.071(2)	0.038(2)	0.018(2)	0.007(1)	0.011(1)

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