Crystal structure of ammonium triiodide — *N*-formyl-formamide (1:1), $NH_4I_3 \cdot C_2H_3NO_2$

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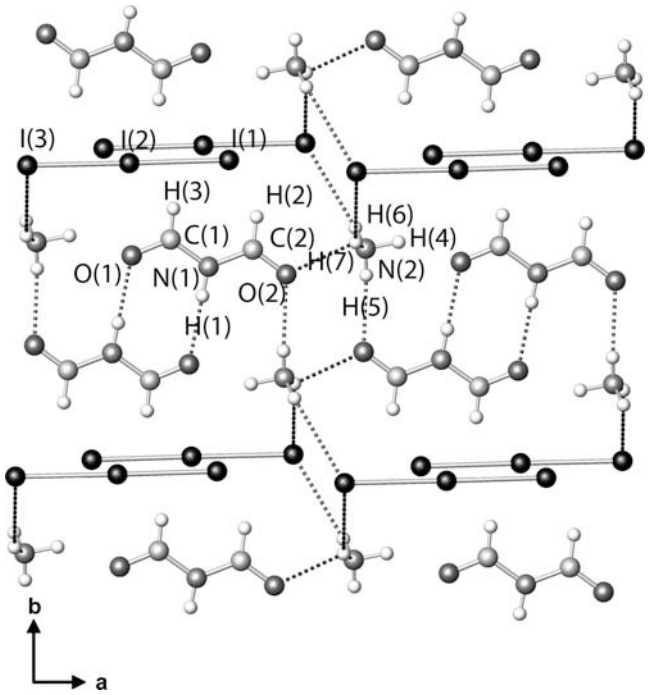

Abstract

$C_2H_7I_3N_2O_2$, monoclinic, $P12_1/c1$ (no. 14), a = 9.7290(6) Å, b = 9.0538(5) Å, c = 12.3633(7) Å, β = 110.403(1)°, V = 1020.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.030, $wR_{ref}(F^2)$ = 0.075, T = 100 K.

Source of material

The title compound was obtained as side product after performing a transport reaction of polymeric NCNCO [1] with iodine at 723 K. Depending on the crystal orientation with respect to the light source, the crystals appear blue and red, respectively.

Experimental details

All hydrogen postions were determined from difference Fourier maps. Hydrogen positions were refined freely with U_{iso}(H) = 1.2 or 1.5 U_{eq} of parent atoms. Otherwise slightly too high, physically questionable, values for U_{iso}(H) were observed.

Discussion

The synthesis and characterization of free *N*-formyl-formamide (or diformamide) and its alkali metal salts have been described already in 1967 [2]. In contrast, only recently, in course of their investigations on resonance stabilized amides, the crystal structure determination, DFT calcualtions and vibrational spectroscopy analysis of diformamide and one of its complex alkali metal salts were published [3]. Ammonium triiodide *N*-formyl-formamide adduct is a new example of a compound containing *N*-formyl-formamide as neutral molecule.

The bond lengths and angles agree very well with those found for the free acid [3]. The almost C_{2v}-symmetric molecule together with the ammonium cations form double chains, hold together by medium stength hydrogen bonds with d(H···A) between 1.90 and 2.30 Å (indicated in the figure as dashed lines). These double chains are arranged parallel to the ab plane, forming layers that alternate with the triiodid counter ions. The distances between the iodine atoms (d(I1—I2) = 2.90 Å, d(I2—I3) = 2.96 Å) and the angle ∠(I1–I2–I3) = 179.4° show a more symmetric molecular structure of the anion compared to that in NH_4I_3 (d(I1—I2) = 2.80 Å, d((I2—I3) = 3.11 Å, ∠(I1–I2–I3) = 178.6°) [4]. Therefore, in this case, the I_3^- ion is better described as $[I–I–I]^-$ with 3c4e-bonds than as a charge-transfer complex $[I–I\cdots I]^-$. We regard the lower number of two hydrogen bonds accepted by the I_3^- unit in the title compound compared to four in NH_4I_3 [4] as the reason for the more symmetric structure. This feature significantly influences the multicenter bonding within the triiodide ion. As in NH_4I_3, only the more ionic end of I_3^- (longer I—I bond) is involved in hydrogen bonding.

Table 1. Data collection and handling.

Crystal:	blue plate, size 0.10 × 0.15 × 0.15 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	91.40 cm^{-1}
Diffractometer, scan mode:	Bruker SMART Apex 1, Bruker AXS, ω
$2\theta_{max}$:	69.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15576, 4284
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3879
$N(param)_{refined}$:	103
Programs:	SHELXS-97, SHELXL-97 [5], ATOMS [6]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.530(4)	0.174(5)	0.010(3)	0.023
H(2)	4*e*	0.787(4)	0.193(5)	0.027(3)	0.024
H(3)	4*e*	0.628(4)	0.453(5)	0.008(3)	0.024
H(4)	4*e*	0.791(5)	0.772(5)	0.534(3)	0.038
H(5)	4*e*	0.891(5)	0.884(5)	0.562(4)	0.038
H(6)	4*e*	0.940(4)	0.738(5)	0.614(4)	0.038
H(7)	4*e*	0.911(4)	0.769(5)	0.478(3)	0.038

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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}
I(1)	4*e*	0.26264(2)	0.48695(2)	0.26391(2)	0.02028(9)	0.0290(1)	0.02278(9)	–0.00135(6)	0.00578(7)	0.00013(6)
I(2)	4*e*	0.56967(2)	0.50598(2)	0.28814(1)	0.02127(9)	0.02031(8)	0.01497(8)	0.00055(5)	0.00552(6)	0.00007(5)
I(3)	4*e*	0.88379(2)	0.52290(2)	0.31463(2)	0.01976(8)	0.02502(9)	0.01980(9)	0.00135(6)	0.00470(6)	–0.00046(6)
O(1)	4*e*	0.4054(2)	0.3287(2)	–0.0072(2)	0.0190(8)	0.0198(9)	0.029(1)	–0.0014(7)	0.0077(7)	0.0000(7)
O(2)	4*e*	0.8862(2)	0.3740(2)	0.0406(2)	0.0180(8)	0.0248(9)	0.0269(9)	–0.0007(7)	0.0088(7)	–0.0015(7)
C(1)	4*e*	0.5239(3)	0.2733(3)	0.0051(2)	0.021(1)	0.017(1)	0.019(1)	–0.0003(8)	0.0059(8)	0.0003(8)
C(2)	4*e*	0.7795(3)	0.2977(3)	0.0294(2)	0.019(1)	0.020(1)	0.022(1)	0.0015(8)	0.0075(9)	–0.0001(9)
N(1)	4*e*	0.6447(2)	0.3569(3)	0.0170(2)	0.0176(9)	0.0167(9)	0.025(1)	0.0008(7)	0.0070(8)	–0.0005(7)
N(2)	4*e*	0.8931(3)	0.7962(3)	0.5464(3)	0.020(1)	0.024(1)	0.033(1)	0.0018(8)	0.0124(9)	–0.0006(9)

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