Crystal structure of 1,10-phenanthrolindiium bis(triiodide) monohydrate, $C_{12}H_{12}I_6N_2O$

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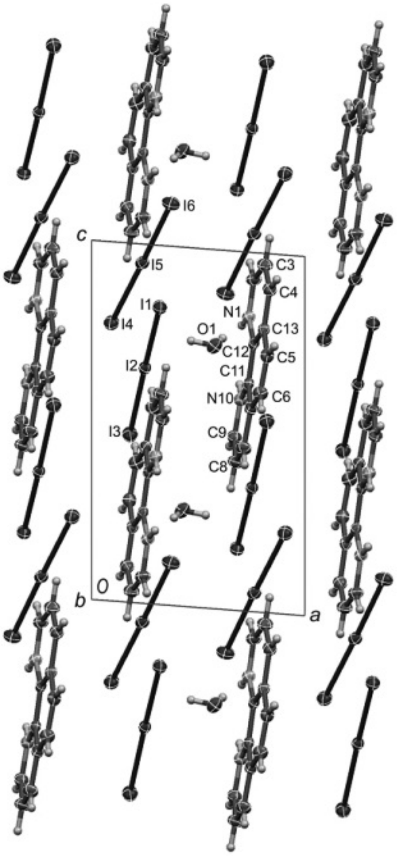
Received July 11, 2014, accepted September 25, 2014, available online October 08, 2014, CCDC no. 1267/4187



Abstract

$C_{12}H_{12}I_6N_2O$, triclinic, $P\bar{1}$ (no. 2), $a = 7.4379(4)$ Å, $b = 11.6193(5)$ Å, $c = 12.4622(6)$ Å, $\alpha = 91.795(4)°$, $\beta = 94.227(4)°$, $\gamma = 95.322(4)°$, $V = 1068.7$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0230$, $wR_{ref}(F^2) = 0.0542$, $T = 295$ K.

Source of material

1,10-Phenanthroline monohydrate (0.5004 g, 2.5 mmol) was slowly, with stirring, added to 73 ml of concentrated (57%) hydroiodic acid. After further stirring and heating up to *ca.* 325 K the mixture was filtered and the clear saturated solution was allowed to stand at room temperature forming single crystals.

Experimental details

All the hydrogen atoms were located in subsequent difference Fourier maps and, for the H atoms bonded to C and N atoms, the riding model with idealized bond lengths and angles was applied. The positions of the H atoms of the water molecule were refined restraining the O–H and H···H distances. The isotropic displacement parameters of H atoms were set to be 1.2 and 1.5 times that of the equivalent isotropic displacement parameters of their parent C, N and O atoms, respectively [16].

Table 1. Data collection and handling.

Crystal:	dark red tabular, size 0.06×0.23×0.29 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	87.21 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	32526, 4649
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4057
$N(param)_{refined}$:	197
Programs:	CrysAlis Pro [15], SHELX [16], MERCURY [17]

Discussion

In our crystal and species engineering research project we are particularly interested in molecular recognition and complementarity issues aiming to exploit and understand the rules governing non-covalent interactions, especially the different types of hydrogen and halogen bonds. Those two common interactions are used to create new systems that develop our understanding of molecular and ionic behavior in the various solid-state environments [1, 2]. Recently, we have developed the concept of the halogenido-ligand exchange synthesis for inorganic-organic halogenidorhodate(III) materials [3, 4]. To better understand structure and properties of those hybrid systems we have determined the structure of some simple salts of nitrogen containing bases like 1,10-phenanthrolindiium bis(triiodide) monohydrate comprising one of the most important organic ligands of many metal complexes and hybrids, the 1,10-phenanthrolindiium cation [5, 6]. The crystal of $C_{12}H_{10}N_2[I_3]_2 \cdot H_2O$ is built up from separated but interacting *via* hydrogen and halogen bonds organic 1,10-phenanthrolindiium $(C_{12}H_{10}N_2)^{2+}$ cations, triiodide I_3^- anions and water molecules. The asymmetric unit contains one formula unit with all the atoms occupying general positions. Cations and I_3^- anions form layers parallel to the *bc* plane of the unit cell. Every second inorganic-organic layer is separated by a water-molecule layer. The $(C_{12}H_{10}N_2)^{2+}$ cations are essentially planar with no atom deviating from the least-squares planes by more than 0.075(4) Å. Their N–C and C–C distances and bond angles are in the expected ranges and are similar to those in previously reported structures [7–9]. Both triiodide anions are not strictly linear with the angles I1–I2–I3 and I4–I5–I6 of 174.891(12) and 178.403(12)°, respectively. Also, the I–I distances show asymmetry of the species: 2.9074(4) (I1–I2), 2.9395(4) (I2–I3) and 2.9290(4) (I4–I5), 2.9199(4) Å (I5–I6). Although the calculated differences of

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0.0321(6) and 0.0091(6) Å in the I–I distances within I_3^- ions are relatively small, they are statistically significant. A difference of *ca.* 0.4 Å was observed in a compound where both hydrogen bonding and I···I interactions were found [10]. It is worth mentioning that the distortions of both I_3^- ions from point group symmetry $D_{\infty h}$, in the title compound, are caused by the asymmetry of their environments and different strength of interactions in which they are involved. The strengths of those interactions are consistent with the variation of charges on the terminal and central iodine atoms in I_3^- [11, 12]. The C···I and C–H···I contacts are mainly responsible for the deviation from linearity of the $(I–I–I)^-$ ions, whereas mostly the I···I contact of 3.8980(5) Å (all shorter than the sum of the van der Waals radii for relevant atoms [13, 14]) causes the asymmetry of the I–I bond lengths. The water molecules are also involved in hydrogen bonding with 1,10-phenanthrolindiium cations (N···O distances of 2.789(4) and 2.824(4) Å) and triiodide anions (O···I distances of 3.779(3) and 3.544(3) Å) causing further distortions of the trihalide ions.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	0.7044	0.3549	0.7950	0.049
H(2)	2*i*	0.7417	0.3439	0.9708	0.060
H(3)	2*i*	0.8339	0.1770	1.0424	0.066
H(4)	2*i*	0.8682	0.0228	0.9297	0.060
H(5)	2*i*	0.8566	−0.0658	0.7433	0.056
H(6)	2*i*	0.7967	−0.0530	0.5645	0.058
H(7)	2*i*	0.7168	0.0673	0.4070	0.062
H(8)	2*i*	0.6523	0.2398	0.3394	0.067
H(9)	2*i*	0.6460	0.3979	0.4556	0.059
H(10)	2*i*	0.6941	0.3760	0.6297	0.048
H(11)	2*i*	0.466(3)	0.475(4)	0.741(4)	0.082
H(12)	2*i*	0.614(6)	0.544(2)	0.755(4)	0.082

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)	2*i*	0.31875(4)	0.04430(3)	0.82786(2)	0.0510(2)	0.0610(2)	0.0467(2)	0.0043(1)	0.0016(1)	0.0118(1)
I(2)	2*i*	0.24858(3)	0.20088(2)	0.65548(2)	0.0371(1)	0.0384(1)	0.0430(1)	0.0003(1)	0.0056(1)	−0.0019(1)
I(3)	2*i*	0.17931(4)	0.34169(3)	0.46764(2)	0.0594(2)	0.0543(2)	0.0590(2)	0.0035(1)	0.0037(1)	0.0175(1)
I(4)	2*i*	0.09246(4)	0.53347(3)	0.77421(2)	0.0579(2)	0.0582(2)	0.0543(2)	0.0069(1)	0.0073(1)	0.0155(1)
I(5)	2*i*	0.23703(3)	0.39572(2)	0.94757(2)	0.0486(2)	0.0428(2)	0.0417(1)	−0.0013(1)	0.0073(1)	−0.0018(1)
I(6)	2*i*	0.37207(5)	0.25388(3)	1.11948(2)	0.0831(2)	0.0509(2)	0.0468(2)	0.0040(2)	−0.0047(2)	0.0057(1)
N(1)	2*i*	0.7367(4)	0.2910(3)	0.8195(2)	0.044(2)	0.035(2)	0.043(2)	−0.002(1)	0.008(1)	0.002(1)
C(2)	2*i*	0.7608(6)	0.2820(4)	0.9254(3)	0.060(3)	0.051(2)	0.037(2)	−0.005(2)	0.008(2)	−0.003(2)
C(3)	2*i*	0.8133(6)	0.1823(4)	0.9683(3)	0.063(3)	0.060(3)	0.040(2)	−0.003(2)	0.001(2)	0.009(2)
C(4)	2*i*	0.8350(5)	0.0913(4)	0.9010(3)	0.049(2)	0.051(2)	0.049(2)	−0.002(2)	0.003(2)	0.011(2)
C(5)	2*i*	0.8234(5)	0.0034(3)	0.7161(3)	0.047(2)	0.038(2)	0.056(2)	0.006(2)	0.005(2)	0.006(2)
C(6)	2*i*	0.7909(6)	0.0114(3)	0.6099(3)	0.059(2)	0.032(2)	0.054(2)	0.003(2)	0.005(2)	−0.006(2)
C(7)	2*i*	0.7129(6)	0.1309(4)	0.4537(3)	0.059(3)	0.051(3)	0.044(2)	0.002(2)	−0.001(2)	−0.011(2)
C(8)	2*i*	0.6748(6)	0.2330(4)	0.4132(3)	0.062(3)	0.065(3)	0.037(2)	0.001(2)	−0.005(2)	0.002(2)
C(9)	2*i*	0.6698(5)	0.3267(4)	0.4826(3)	0.052(2)	0.052(2)	0.044(2)	0.007(2)	0.000(2)	0.009(2)
N(10)	2*i*	0.6987(4)	0.3161(3)	0.5881(2)	0.045(2)	0.034(2)	0.042(2)	0.005(1)	0.005(1)	0.002(1)
C(11)	2*i*	0.7354(4)	0.2148(3)	0.6337(3)	0.030(2)	0.036(2)	0.039(2)	0.000(1)	0.005(1)	0.003(2)
C(12)	2*i*	0.7608(4)	0.2035(3)	0.7475(3)	0.031(2)	0.035(2)	0.041(2)	−0.002(1)	0.007(2)	−0.001(2)
C(13)	2*i*	0.8081(5)	0.0987(3)	0.7885(3)	0.035(2)	0.037(2)	0.047(2)	−0.003(2)	0.006(2)	0.008(2)
C(14)	2*i*	0.7467(5)	0.1189(3)	0.5651(3)	0.040(2)	0.040(2)	0.044(2)	−0.001(2)	0.003(2)	−0.005(2)
O(1)	2*i*	0.5756(4)	0.4781(3)	0.7325(3)	0.059(2)	0.041(2)	0.065(2)	0.005(1)	0.018(2)	−0.004(1)

Acknowledgments. The authors gratefully acknowledge financial support (publication fee) from the Deutsche Forschungsgemeinschaft (DFG) and the Open Access Publication Fund of the Heinrich-Heine-Universität Düsseldorf. The authors also thank the Fonds der Chemischen Industrie for support.

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