Hydrogen bonding versus packing effects in the crystal structure of 3-((1R,2S)-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium tetraiodidozincate(II), $C_{10}H_{16}I_4ZnN_2$

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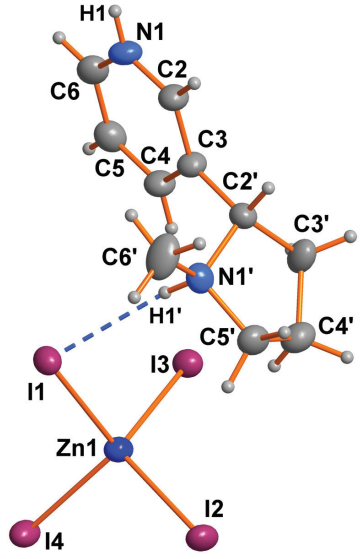

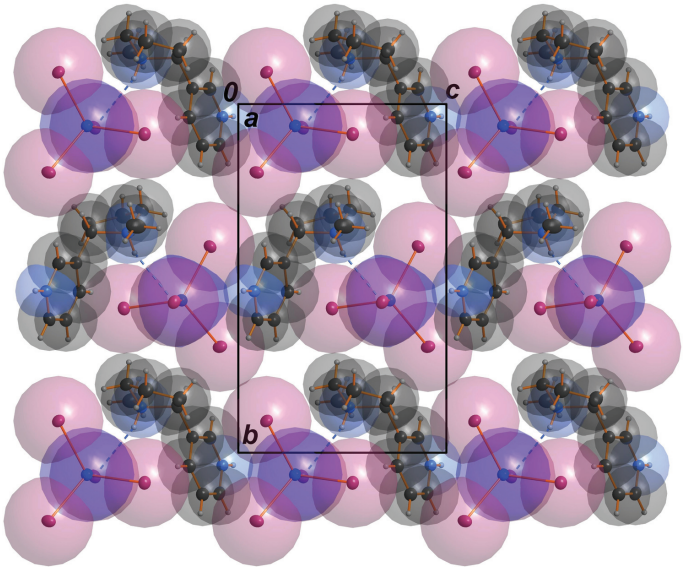

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Abstract

$C_{10}H_{16}I_4ZnN_2$, monoclinic, $P2_1$ (no. 4), $a = 7.3340(1)$ Å, $b = 14.4781(3)$ Å, $c = 8.6768(2)$ Å, $\beta = 94.919(2)°$, $V = 917.93(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0165$, $wR_{ref}(F^2) = 0.0397$, $T = 110$ 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.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.47 × 0.25 × 0.19 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	8.05 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	34.7°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	57483, 7606, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7483
$N(param)_{refined}$:	159
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Diamond [4]

Source of material

In a representative experiment 0.161 mL (0.162 g; 1 mmol) *S*-nicotine [(*S*)-3-[1-methylpyrrolidin-2-yl]pyridine; Acros Organics] were dissolved in a few drops of concentrated hydroiodic acid (Merck KGa). The hydroiodic acid was purified by a treatment with activated carbon to reduce the iodine concentration. To the aforementioned solution 0.319 g of ZnI_2 (1 mmol; Aldrich) were added. This mixture was heated to 70 °C, giving an orange solution. Almost colourless crystals of the title compound were grown during storage in the refrigerator within a few days. **MP.** 224 °C.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.21305(5)	0.56284(3)	0.72719(4)	0.01823(7)
I1	0.56551(3)	0.56807(2)	0.69202(2)	0.01969(4)
I2	0.13553(3)	0.40892(2)	0.86430(2)	0.02181(5)
I3	0.05004(3)	0.58628(2)	0.45047(2)	0.01973(4)
I4	0.12780(3)	0.69623(2)	0.91159(3)	0.02215(5)
N1	0.7996(4)	0.5366(2)	0.0764(3)	0.0219(6)
H1	0.894578	0.535675	0.024778	0.12(4)*
C2	0.7447(5)	0.4568(3)	0.1376(4)	0.0210(6)
H2	0.809625	0.402554	0.124554	0.025*
C3	0.5912(4)	0.4557(2)	0.2200(4)	0.0185(5)
C4	0.4974(5)	0.5383(2)	0.2363(4)	0.0209(6)
H4	0.393534	0.539216	0.290686	0.025*
C5	0.5580(5)	0.6193(3)	0.1719(4)	0.0229(6)
H5	0.494967	0.674435	0.182105	0.028*
C6	0.7144(5)	0.6169(3)	0.0917(4)	0.0226(6)
H6	0.758727	0.670598	0.049458	0.027*
N1'	0.5881(4)	0.3699(2)	0.4672(3)	0.0199(5)
H1'	0.5647(13)	0.427(3)	0.5016(19)	0.017(11)*
C2'	0.5342(5)	0.3676(2)	0.2940(4)	0.0193(6)
H2'	0.597796	0.315985	0.248946	0.023*
C3'	0.3264(5)	0.3460(3)	0.2823(4)	0.0261(7)
H3A	0.256578	0.399492	0.244492	0.031*
H3B	0.298512	0.294930	0.211794	0.031*
C4'	0.2788(5)	0.3207(3)	0.4453(5)	0.0267(7)
H4A	0.213227	0.370734	0.490262	0.032*
H4B	0.203697	0.265500	0.443118	0.032*
C5'	0.4615(5)	0.3041(3)	0.5369(4)	0.0236(6)
H5A	0.454090	0.317152	0.645805	0.028*
H5B	0.501545	0.240741	0.525636	0.028*
C6'	0.7847(5)	0.3500(3)	0.5088(6)	0.0327(9)
H6A	0.811642	0.288047	0.478272	0.049*
H6B	0.811253	0.356235	0.618591	0.049*
H6C	0.858321	0.392654	0.456536	0.049*

Raman Spectrum. (Bruker MultiRam; resolution: 4 cm^{-1}) [cm^{-1}]: 3101(w), 3046(w), 3020(m), 2950(m, br), 2872(w), 1632(w), 1603(w), 1462(m, br), 1409(w), 1260(w), 1228(m), 1184(m), 1049(m), 1025(m), 967(w), 770(w), 614(w), 420(br, w), 255(w), 165(s, sh), 124(vs), 111 (vs), 81 (s), 72(s). **IR Spectrum**. (Perkin Elmer Frontier MIR; resolution: 4 cm^{-1}) [cm^{-1}]: 3204(s), 3162(vs), 3119(s), 3072(s), 3042(vs), 3016(s), 2965(vs), 2723(m), 1630(m), 1601(s), 1541(s), 1455(s, br), 1405(m), 1372(m), 1311(w), 1248(w), 1184(w), 1087(w), 1011(w), 983(m), 863(m), 788(s), 671(s).

Experimental details

Hydrogen atoms were placed using a riding model (AFIX 13/23/43/137) implemented in the SHELXL program system [3] using the standard parameters for constrained U_{iso}(H) values [3]. The absolute structure determination succeeded as the derived Flack parameter is found to be near zero with a low standard uncertainty [0.009(12) from 3488 selected quotients using Parsons's method [5]]. The classical calculation of the Flack parameter showed a slightly worse result, 0.016(18) using all reflections [3, 5].

Comment

A recently performed Cambridge Structural Database [6] survey on nicotine-containing crystal structures yielded approximately fifty deposited structures. As reported and summarized by one of us [7] structural data are available for (a) metal complexes, which contain neutral nicotine ligands; (b) a small number of co-crystals containing neutral nicotine as one of the components; (c) some examples for pyrrolidinyl-monoprotonated nicotinium salts; and (d) mono-protonated nicotinium as a cationic ligand. As a result of the database survey specified above, only a limited number of examples of salt structures containing doubly protonated nicotinium cations have been reported so far [7–12]. This contribution is part of our continuing interest in synthesis, characterization and understanding of hydrogen-bonding schemes of salts of natural products [7, 11–14]. The choice of a $[ZnI_4]^{2-}$ counter anion is part of our general interest in halogen bonding interactions between iodine containing molecules and ions, regardless of whether they are attractive or repulsive [15–17].

Description. The asymmetric unit of the title structure contains one 3-((1*R*,2*S*)-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium (nicotin-1,1′-dium) dication ($nicH_2$) and one tetraiodidozincate(II) dianion. As discussed several times [7, 11, 12], the protonation at the nitrogen atom of the pyrrolinyl moiety creates a second chiral center at N1′ (*cf*. left part of the Figure), which shows *R* configuration in all reliable crystal structures deposited in the Cambridge Structural database so far. The four carbon atoms of the pyrrolidinyl moiety (C2′, C3′, C4′, C5′) are almost planar (RMS deviation = 0.07 Å) and the N1′ atom is folded out of this plane by 0.53(1) Å. The aforementioned plane defined by the carbon atoms C2′, C3′, C4′ & C5′ encloses an angle of 67.5(2)° with the mean plane of the pyridinyl moiety (see the Figure). The rotation around the C3—C2′ single bond causes a certain flexibility of the $nicH_2$ dication and the final orientation is more or less a consequence of the packing and the hydrogen-bonding scheme, respectively. The bond lengths and angles within the $nicH_2$ dication [7, 11, 12] as well as those in the $[ZnI_4]^{2-}$ ion [18–20] are in the expected ranges. The Zn—I bond lengths of the complex $[ZnI_4]^{2-}$ anion are: Zn1—I1 2.6298(4) Å, Zn1—I2 2.6117(4) Å, Zn1—I3 2.6109(4) Å and Zn1—I4 2.6176(4) Å. Small alterations of the Zn—I bond lengths are well known for hydrogen bonded $[ZnI_4]^{2-}$ anion. [18], whereas in the case of a salt that doesn't contain classical hydrogen bonds the Zn—I distances are almost equilibrated [19]. In the title structure the longest Zn—I bond length [Zn1—I1 2.6298(4) Å] correlates with the shortest hydrogen bond (see below).

The Raman spectrum (see the Source of materials section) supports the finding of a slightly distorted $[ZnI_4]^{2-}$ anion. The assignment of the $[ZnI_4]^{2-}$ anion-related Raman signals (80–300 cm^{-1}) is in accord with the literature [20–22]. The symmetrical stretch mode (ν_1) perfectly fits with a report of Lutz and Pfitzner [22]. The same is true for a shoulder at 165 cm^{-1}, which can be assigned as ν_3 [20]. The ν_1 and ν_4 modes are expected to appear between 40 and 60 cm^{-1}. They can't be assigned beyond doubt, as the spectral range of our spectrometer starts at 50 cm^{-1} and the two signals detected in this range are seriously shifted with respect to the expectation.

Supramolecular aspects. The $nicH_2$ participates in one classical NH···I hydrogen bond between the methylpyrrolidin-1-ium-2-yl moiety and one iodido ligand of the complex $[ZnI_4]^{2-}$ anion [N1′···I1 = 3.481(3) Å; H···I1 = 2.63 Å; *cf.* left part of the Figure]. The NH^+ function of the pyridin-1-ium-3-yl moiety is located between the iodido ligands I2 and I4 of a neighboring $[ZnI_4]^{2-}$ anion [N1···I2′ = 3.695(3) Å; N1···I4′ = 3.711(3); *cf.* right part of the Figure; ′ = 1 + x, y, −1 + z]. In this structure the NH^+ function of the pyridin-1-ium-3-yl moiety forms a very weak hydrogen bond which is perhaps better described as a combined hydrogen bond/Coulomb-type/van-der-Waals type interaction [23]. Our classification is supported by the fact that two aromatic CH functions of the pyridin-1-ium-3-yl have C···I distances, which are almost in the same range [C6···I4′ = 3.711(4) Å; C2···I4′ 3.918(4) Å] as the aforementioned N1···I2′ and N1···I4′ distances.

Outlook. It may be of interest to test more nicotin-1,1′-dium tetrahalogenidometallate salts in catalysis as for other nicotin-1,1′-dium salts some catalytic properties are observed [24, 25].

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