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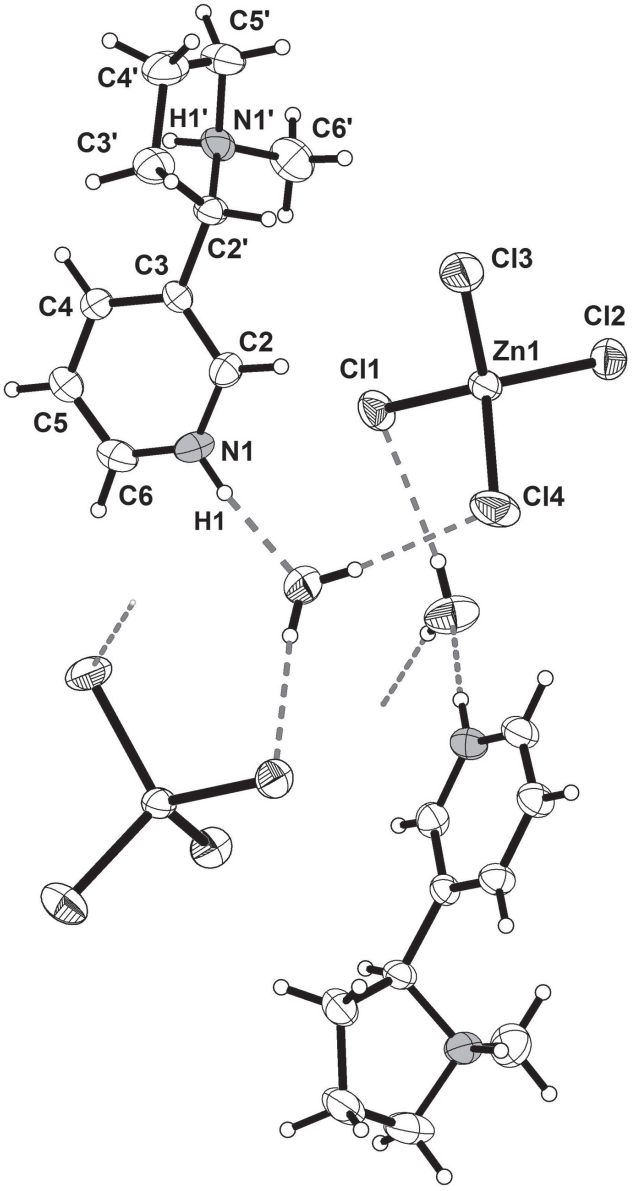
The crystal structure of 3-((1*R*,2*S*)-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium tetrachloridozincate(II) monohydrate, $C_{10}H_{18}Cl_4ZnN_2O$



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Abstract

$C_{10}H_{18}Cl_4ZnN_2O$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 7.0752(1)$ Å, $b = 7.5085(1)$ Å, $c = 29.3383(5)$ Å, $V = 1558.57(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0330$, $wR_{ref}(F^2) = 0.0672$, $T = 290(2)$ K.

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The crystal structure is shown in the figure. 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:	Colourless plate
Size:	0.13 × 0.54 × 0.80 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.25 mm^{-1}
Diffractometer, scan mode:	Xcalibur EOS, ω-scans
θ_{max}, completeness:	28°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	22747, 3750, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3604
$N(param)_{refined}$:	179
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Diamond [4]

Source of materials

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 hydrochloric acid (Merck KGa). To the aforementioned solution 0.136 g (1 mmol; Riedel de Haen) of $ZnCl_2$ were added. This mixture was heated to 85 °C, giving a colourless solution. Colourless plate crystals of the title compound were obtained by slow evaporation at room temperature within a few days.

Raman Spectrum (Bruker MultiRam; resolution: 4 cm^{-1}) [cm^{-1}]: 3092(m), 3066(w), 3031(m), 2964(s, br), 2892(w), 2852(w), 1644(m), 1460(m, br), 1382(w), 1240(m), 1189(m), 1052(s), 1029(s), 902(m), 787(m), 619(m), 562(w), 525(w), 400(br, w), 321(m), 280(s), 220(s), 145(vs) 126 (vs); 100 (vs).

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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	0.33235(7)	0.72221(6)	0.62657(2)	0.03149(11)
O1W	0.6448(6)	0.7405(5)	0.50298(12)	0.0562(9)
H1W	0.597(8)	0.811(6)	0.5233(14)	0.082(16)*
H2W	0.689(8)	0.798(6)	0.4798(13)	0.082(16)*
N1	0.8004(6)	0.4450(5)	0.54165(12)	0.0376(8)
H1	0.762(7)	0.540(7)	0.5281(17)	0.043(14)*
N1′	0.7692(6)	0.1462(5)	0.68211(12)	0.0369(9)
H1′	0.786(7)	0.043(6)	0.6693(15)	0.035(13)*
Cl1	0.3209(2)	0.48652(14)	0.57828(4)	0.0428(3)
Cl2	0.03496(15)	0.76693(15)	0.65426(3)	0.0394(2)
Cl3	0.53251(18)	0.6885(2)	0.68610(4)	0.0531(3)
Cl4	0.4349(2)	0.95560(17)	0.58342(4)	0.0575(4)
C2	0.8081(6)	0.4413(5)	0.58728(14)	0.0324(8)
H2	0.772046	0.540726	0.604066	0.039*
C3	0.8691(5)	0.2911(5)	0.60908(12)	0.0267(8)
C4	0.9179(6)	0.1450(6)	0.58296(13)	0.0325(9)
H4	0.960327	0.041586	0.597085	0.039*
C5	0.9041(6)	0.1515(6)	0.53576(14)	0.0364(10)
H5	0.935239	0.052961	0.518069	0.044*
C6	0.8434(6)	0.3062(6)	0.51589(13)	0.0385(10)
H6	0.832494	0.313690	0.484361	0.046*
C2′	0.8895(6)	0.2897(6)	0.66041(12)	0.0309(8)
H2′	0.849295	0.405664	0.672283	0.037*
C3′	1.0873(6)	0.2499(7)	0.67813(14)	0.0422(11)
H3A	1.157224	0.359508	0.682818	0.051*
H3B	1.156057	0.176240	0.656614	0.051*
C4′	1.0607(9)	0.1516(7)	0.72322(16)	0.0526(13)
H4A	1.125026	0.037580	0.722485	0.063*
H4B	1.111298	0.221305	0.748242	0.063*
C5′	0.8526(9)	0.1256(8)	0.72893(15)	0.0535(13)
H5A	0.800882	0.214021	0.749559	0.064*
H5B	0.825863	0.008028	0.741021	0.064*
C6′	0.5640(7)	0.1874(8)	0.68251(18)	0.0524(13)
H6A	0.519860	0.201113	0.651766	0.079*
H6B	0.542879	0.295953	0.699045	0.079*
H6C	0.496665	0.091920	0.696966	0.079*

Experimental details

Coordinates of hydrogen atoms attached to nitrogen were refined without any constraints or restraints. The hydrogen atoms of the water molecule were refined using one O—H distance restraint and one common U_{iso} parameter. The carbon-bound hydrogen atoms were placed using a riding model (AFIX 13/23/43/137) implemented in the SHELXL system using the standard parameters for the 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 [0.007(4) from 1388 selected quotients] using Parsons's method [5]. The classical calculation of the Flack parameter showed a slightly worse result 0.023(18) using all reflections [3, 5].

Comment

A recently conducted Cambridge Structural Database [6] survey on nicotine-containing structures confirms that about fifty structures are deposited that contain a nicotine-fragment. 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-protonated nicotinium salts; (d) and mono-protonated nicotinium as a cationic ligand. As a result of the database survey specified above, only 7 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].

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 ($nicH_2$), one tetrachloridozincate(II) dianion and one water molecule. As discussed in our preceding contributions [7, 11, 12], the protonation at the nitrogen atom of the pyrrolinyl moiety creates a second chiral center at N2 (*cf*. the Figure), which shows *R* configuration in accord with the literature. This *R* configuration at the nitrogen atom of the pyrrolinyl moiety seems to be the predominant protonation path. The title structure is isomorphous to the literature known structure of $nicH_2[CoCl_4]\cdot H_2O$ [12]. The four carbon atoms of the pyrrolidinyl moiety are almost planar (RMS deviation = 0.02 Å) with the N1′ atom folded out of this plane by 0.56(1) Å. The best plane defined by the carbon atoms C2′, C3′, C4′, C5′ encloses an angle of 76.9(2) Å with the mean plane of the pyridinyl moiety (see the figure). This parameter represents the flexibility of the nicotin-1,1′-diium cation in the solid state. This variability around the C3—C2′ single bond is obviously more or less a consequence of the packing and hydrogen-bonding schemes, respectively. The bond lengths and angles within the $nicH_2$ dication [7, 11, 12] as well as those in the $[ZnCl_4]^{2-}$ ion [15–17] are in the expected ranges. The Zn–Cl bond lengths of the chlorido ligands of the complex $[ZnCl_4]^{2-}$ anion range from 2.2628(12) Å to 2.2803(12) Å. Comparing the $[ZnCl_4]^{2-}$ anion with related H_3N-R-$ZnCl_3$-complexes [18], which may form an intramolecular NH···Cl hydrogen bond, showed that the Zn—Cl bond lengths are slightly shorter than those in the title salt. The Raman spectrum (see the *Source of Materials* section) supports the finding of a slightly

distorted $[ZnCl_4]^{2-}$ anion. The assignment of the $[ZnCl_4]^{2-}$ anions related Raman signals (80–300 cm^{-1}) is not trivial. A detailed discussion on the assignment of the Raman signals for $[ZnCl_4]^{2-}$ anions has been reported earlier [19]. Raman signals in the 400–3100 cm^{-1} range are as expected [11].

Supramolecular aspects. The nicH_2 dication participates in a classical NH···O hydrogen bond to the water molecule (N···O = 2.724(5) Å; *cf*. the Figure), which is in accord with the isomorphous structure of NicH_2[$CoCl_4$] · H_2O [12]. The NH group of the pyrrolinyl moiety is involved in a very weak NH···Cl hydrogen bond (N2···Cl2′ = 3.509(4) Å; ′ = $x+1$, $y-1$, z). This distance is significantly longer than that [3.309(4) Å] found in the low-temperature structure of the isomorphous structure of nicH_2[$CoCl_4$] · H_2O [12], but in accord with the distance derived from the room-temperature structure [3.539(8) Å] of nicH_2[$CoCl_4$] · H_2O [12]. Temperature has obviously a larger influence on intermolecular interactions than the interchange of Zn(II) by Co(II). The water molecule donates in total two hydrogen bonds to two $[ZnCl_4]^{2-}$ dianions [O1···Cl4 = 3.222(4) Å; O1···Cl1″ = 3.382(4) Å; ″ = $x+1/2$, $-y+3/2$, $-z+1$]. Neglecting the very weak NH···Cl hydrogen bond of the pyrrolidinyl moiety, a hydrogen-bonded chain structure running along the crystallographic *a* direction is obtained. Including the aforementioned very weak NH···Cl hydrogen bond a 2D network parallel to the *ab* plane is constructed by the connection of adjacent chains. This 2D description is also the most reliable description for the low-temperature structure of nicH_2[$CoCl_4$] · H_2O [12].

Outlook. In continuation of this structural study we are still trying to crystallize more nicotin-1,1′-dium tetrahalogenidometallate salts for a detailed comparison and understanding of temperature and element dependent structural changes in groups of isomorphous structures. It may be of interest to test more nicotin-1,1′-dium tetrahalogenidometallate salts in catalysis as for other nicotin-1,1′-dium salts catalytic properties are observed [20, 21].

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