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The crystal structure of 3-((1*R*,2*S*)-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium tetrachloridomanganate(II), C₁₀H₁₆Cl₄MnN₂

Abstract

C₁₀H₁₆Cl₄MnN₂, monoclinic, *P*2₁ (no. 4), *a* = 7.28276(7) Å, *b* = 13.22972(12) Å, *c* = 8.01007(7) Å, β = 97.5018(9)°, *V* = 765.155(12) Å³, *Z* = 2, *R*_{gt}(*F*) = 0.0165, *wR*_{ref}(*F*²) = 0.0392, *T* = 123(2) K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.30 × 0.25 × 0.20 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	1.54 mm ^{−1}
Diffractometer, scan mode:	Xcalibur EOS, φ and ω
θ _{max} , completeness:	33.0°, 99.9%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	71011, 5732, 0.028
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 5628
<i>N</i> (<i>param</i>) _{refined} :	177
Programs:	CysAlis ^{PRO} [1], SHELX [2, 3, 5], 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) were dissolved in a few drops of concentrated hydrochloric acid. To this solution 0.126 g (1 mmol) of MnCl₂ were added. This mixture was heated to 80 °C, resulting in an orange coloured solution. Crystals of the title compound were obtained by slow evaporation at room temperature within a few days.

Experimental details

Coordinates of hydrogen atoms attached to nitrogen were refined without any constraints or restraints. The carbon-bound hydrogen atoms were placed using a riding model (AFIX 13/23/43/137) implemented in the SHELXL system [3]. For all hydrogen atoms *U*_{iso} parameters were refined freely.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Mn1	0.32138(3)	0.56787(2)	0.78135(3)	0.01796(4)
Cl1	0.63760(4)	0.57171(3)	0.73648(4)	0.02380(7)
Cl2	0.24580(5)	0.41570(3)	0.91492(4)	0.01983(6)
Cl3	0.15892(6)	0.58125(3)	0.50813(5)	0.02755(8)
Cl4	0.26215(5)	0.69852(3)	0.96716(5)	0.02232(7)
N1	0.93931(19)	0.51775(11)	0.10996(16)	0.0214(2)
H1	1.030(3)	0.5036(17)	0.065(3)	0.028(6)*
C2	0.8661(2)	0.43985(11)	0.18597(18)	0.0205(3)
H2	0.91935(1)	0.37446(8)	0.1824(10)	0.025(5)*
C3	0.7134(2)	0.45432(11)	0.26949(17)	0.0178(2)
C4	0.6383(2)	0.55152(11)	0.26899(19)	0.0211(3)
H4	0.53256(9)	0.56374(4)	0.3241(7)	0.028(5)*
C5	0.7167(2)	0.63026(12)	0.1886(2)	0.0229(3)
H5	0.66544(4)	0.69629(8)	0.1883(17)	0.027(5)*
C6	0.8705(2)	0.61143(13)	0.10902(19)	0.0226(3)
H6	0.92680(5)	0.66456(8)	0.0541(4)	0.031(6)*
N1'	0.68258(17)	0.37281(9)	0.54476(15)	0.0168(2)
H1'	0.654(3)	0.4364(17)	0.576(3)	0.024(5)*
C2'	0.6350(2)	0.36628(11)	0.35596(17)	0.0186(2)
H2'	0.69072(7)	0.30283(5)	0.3169(22)	0.027(5)*
C3'	0.4238(2)	0.35425(14)	0.3303(2)	0.0258(3)
H3'A	0.38483(3)	0.30704(5)	0.23648(4)	0.034(6)*
H3'B	0.36295(6)	0.42032(4)	0.30418(8)	0.029(6)*
C4'	0.3718(2)	0.31201(13)	0.49672(19)	0.0216(3)
H4'A	0.28961(4)	0.35959(6)	0.54699(8)	0.029(6)*
H4'B	0.30747(7)	0.24628(8)	0.47781(2)	0.029(6)*
C5'	0.5542(2)	0.29908(11)	0.61151(19)	0.0199(3)
H5'A	0.53904(8)	0.31489(7)	0.72974(5)	0.029(6)*
H5'B	0.60119(5)	0.22911(8)	0.60578(6)	0.028(6)*
C6'	0.8808(2)	0.35485(13)	0.6083(2)	0.0277(3)
H6'A	0.91965(6)	0.28979(7)	0.56607(9)	0.035(6)*
H6'B	0.89727(4)	0.35382(1)	0.73173(3)	0.041(7)*
H6'C	0.95624(9)	0.40910(10)	0.56916(10)	0.038(7)*

The absolute structure determination succeeded as the derived Flack parameter is found to be near zero with a low standard uncertainty [−0.007(7) from 2650 selected quotients] using Parsons' method [5]. The classical calculation of the Flack parameter showed a similar result [−0.009(10) using all reflections] [3, 5].

Comment

A Cambridge Structural Database [6] survey was performed on nicotine-containing structures. Many of the about fifty structures are metal complexes, which contain neutral nicotine molecules as ligands [7–9]. There is also a small number of structurally-characterized cocrystals containing neutral nicotine as one of the components [10]. Only a very limited number of nicotinium salts have been characterized and further investigated by diffraction methods. Some examples for pyrrolidin-protonated nicotinium cations were found in salts [11] and as cation ligands [12]. However, as a result of the database survey specified above, only five examples of salt structures containing doubly protonated nicotinium cations have been

reported so far [13–17]. This contribution is part of my continuing interest in synthesis, characterization and understanding of hydrogen-bonding schemes of salts of natural products [16–20].

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 tetrachlorido-manganate(II) dianion.

As discussed in one of my preceding contributions [16], the protonation at the nitrogen atom of the pyrrolinyl moiety leads to a second chiral center at N2 (*cf.* the figure), which shows *R* configuration in accord with the literature [16, 17]. Protonation leading to a *R* configuration at the nitrogen atom of the pyrrolinyl moiety seems to be the predominant reaction path.

The four carbon atoms of the pyrrolidinyl moiety are almost planar (RMS deviation = 0.005 Å). This plane encloses an angle of 65.43(7)° with the mean plane of the pyridinyl group. This parameter seems to be variable in different crystal structures and is more or less a consequence of the packing and hydrogen-bonding schemes, respectively. The bond lengths and angles within the *nicH*₂ dication [17] as well as those in the [MnCl₄]^{2−} ion [21] are perfectly in the expected ranges.

Each *nicH*₂ forms two classical, charge supported NH...Cl hydrogen bonds to two adjacent tetrachloridomanganate(II) anions (*cf.* the figure; N1...Cl2^a = 3.1868(14) Å (^a = 1 − *x*, *y*, −1 + *z*); N1'...Cl1 = 3.0857(13) Å) to form a chain structure along the direction [1 0 $\bar{1}$]. The differences in these two bonding parameters are also seen in the lengths of the H...Cl hydrogen bonds, indicating slightly different strengths.

The variation of the Mn–Cl bond lengths are in a narrow range but their differences are in excellent agreement with the hydrogen-bonding scheme of the title structure. The two chlorido ligands Cl1 and Cl2, which are involved in hydrogen bonds, show Mn–Cl distances of 2.3773(4) Å and 2.3780(4) Å, respectively. The Mn–Cl bond length of Cl3 and Cl4 are, as expected, slightly shortened (Mn1–Cl3 = 2.3547(4) Å; Mn1–Cl4 = 2.3571(4) Å).

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