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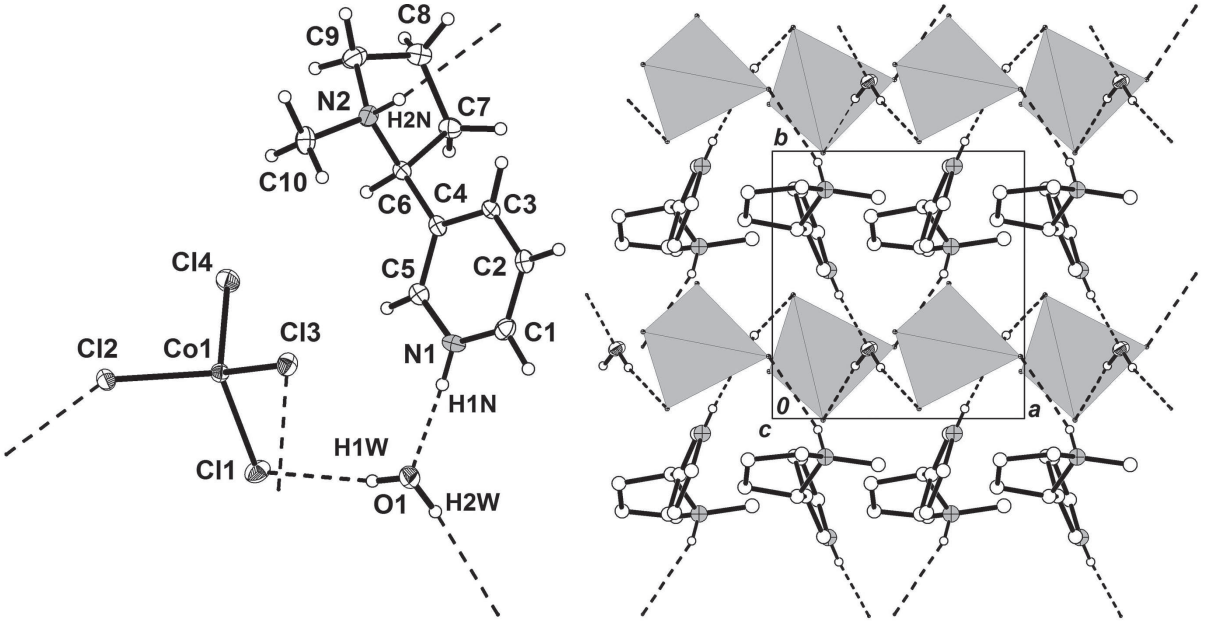
The crystal structure of 3-((1*R*,2*S*)-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium tetrachloridocobaltate(II) monohydrate, $C_{10}H_{18}Cl_4CoN_2O$



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Abstract

$C_{10}H_{18}Cl_4CoN_2O$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 7.0057(3)$ Å, $b = 7.4317(3)$ Å, $c = 29.2510(13)$ Å, $V = 1522.93(11)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0356$, $wR_{ref}(F^2) = 0.0737$, $T = 110$ K.

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Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Blue turquoise plate
Size:	0.59 × 0.25 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	18.2 cm^{-1}
Diffractometer, scan mode:	Xcalibur, φ and ω
$2\theta_{max}$, completeness:	58°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13791, 4052, 0.043
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3865
$N(param)_{refined}$:	217
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], Diamond [4]

Source of material

In a representative experiment 0.16 mL (0.162 g; 1 mmol) *S*-nicotine ((*S*)-3-[1-methylpyrrolidin-2-yl]pyridine) were

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.68536(8)	0.27516(8)	0.62651(2)	0.01216(12)
Cl1	0.58248(16)	0.03651(14)	0.58422(4)	0.0195(2)
Cl2	0.98516(13)	0.23205(14)	0.65618(3)	0.01433(19)
Cl3	0.70087(15)	0.50581(13)	0.57563(3)	0.0162(2)
Cl4	0.48691(15)	0.32424(16)	0.68651(4)	0.0206(2)
O1	0.3828(4)	0.2610(5)	0.50334(11)	0.0190(7)
H1W	0.430(7)	0.189(8)	0.5221(18)	0.023*
H2W	0.328(7)	0.198(7)	0.4822(17)	0.023*
N1	0.2217(5)	0.5556(5)	0.54291(12)	0.0143(7)
H1N	0.263(7)	0.463(7)	0.5305(17)	0.017*
N2	0.2092(5)	0.8564(5)	0.68463(12)	0.0138(7)
H2N	0.181(7)	0.958(7)	0.6719(16)	0.017*
C1	0.1791(6)	0.6961(6)	0.51645(14)	0.0159(8)
H1	0.190(7)	0.678(7)	0.4841(16)	0.019*
C2	0.1123(6)	0.8516(6)	0.53605(15)	0.0149(8)
H2	0.087(7)	0.953(7)	0.5193(17)	0.018*
C3	0.0872(6)	0.8581(6)	0.58315(14)	0.0133(8)
H3	0.049(7)	0.966(7)	0.5966(16)	0.016*
C4	0.1324(5)	0.7093(6)	0.60983(13)	0.0110(7)
C5	0.2032(6)	0.5577(6)	0.58861(14)	0.0132(8)
H5	0.229(7)	0.454(7)	0.6034(16)	0.016*
C6	0.0987(6)	0.7081(6)	0.66094(14)	0.0131(8)
H6	0.146(7)	0.600(7)	0.6722(17)	0.016*
C7	−0.1084(6)	0.7432(6)	0.67575(14)	0.0153(8)
H7A	−0.168(8)	0.623(7)	0.6796(16)	0.018*
H7B	−0.183(7)	0.812(7)	0.6508(16)	0.018*
C8	−0.0960(7)	0.8456(6)	0.72151(15)	0.0175(9)
H8A	−0.150(7)	0.962(7)	0.7211(18)	0.021*
H8B	−0.151(7)	0.790(7)	0.7474(16)	0.021*
C9	0.1170(7)	0.8665(7)	0.73092(16)	0.0200(9)
H9A	0.169(7)	0.776(8)	0.7482(17)	0.024*
H9B	0.152(7)	0.985(7)	0.7450(17)	0.024*
C10	0.4199(6)	0.8271(7)	0.68619(17)	0.0191(9)
H10A	0.442(7)	0.715(8)	0.7022(17)	0.023*
H10B	0.479(8)	0.935(7)	0.7053(17)	0.023*
H10C	0.461(7)	0.826(7)	0.6537(18)	0.023*

dissolved in a few drops of concentrated hydrochloric acid. To this solution 0.240 g (1 mmol) of $CoCl_2{\cdot}6H_2O$ were added. This mixture was heated to 80 °C, resulting in a blue-turquoise coloured solution. Crystals of the title compound were obtained by slow evaporation within 2 days.

Experimental details

Coordinates of hydrogen atoms were refined without any constraints or restraints. Their U_{iso} values were set to $1.2U_{eq}$ of the parent atoms. The absolute structure was established by refinement of the Flack parameter (−0.009(11) from 1458 selected quotients) using Parsons' method [5]. The classical refinement of the Flack parameter gave a similar result (−0.012(23)) [3].

Comment

Only a limited number of nicotinium salts have been characterized structurally although nicotine and its derivatives are of general interest. Further surveys of crystal structures containing such mono and diprotonated nicotinium cations were recently carried out [6]. To the best of our knowledge, only four examples of salts containing doubly protonated nicotinium cations have been reported so far [6–9]. This contribution is part of our continuing interest in synthesis, characterisation and understanding of hydrogen bonding schemes of tetrahalogenido- and hexahalogenidometallates [10] on the one hand and pyridinium salts on the other hand [11].

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 (*nic*H_2), one tetrachloridocobaltate(II) dianion and one water molecule. The bond lengths and angles within these moieties are in the expected ranges. As discussed recently [5], the protonation at the nitrogen atom of the pyrrolidinylium moiety leads to a second chiral center at N2 (*cf*. left part of the figure), which shows *R* configuration. The four carbon atoms of the pyrrolidinylium moiety are almost planar (RMS deviation = 0.0797 Å). This plane encloses an angle of 81.3(1)° with the plane of the pyridinylium group. The *nic*H_2 participates in a classical NH···O hydrogen bond to the water molecule (N···O = 2.722(5) Å; *cf*. left part of the figure). The NH group of the pyrrolinyl moiety is involved in a NH···Cl hydrogen bond (N2···Cl2′ = 3.309(4) Å; ′ = $x-1$, $y+1$, z). The water molecule donates in total two hydrogen bonds to two other $CoCl_4^{2-}$ dianions (O1···Cl1 = 3.215(3) Å; O1···Cl3″ = 3.300(3) Å; ″ = $x-{}^1/_2, -y+{}^1/_2, -z+1$; *cf*. the figure). The variance of the Co-Cl bond lengths excellently reflects the hydrogen bonding scheme: the three chloride ligands (Cl1—Cl3) involved in hydrogen bonds show Co—Cl distances ranging from 2.2727(11) Å to 2.2950(11) Å, whereas the Co—Cl4 bond length with 2.2684(12) Å is slightly shorter. In the title structure, each *nic*H_2/H_2O unit is surrounded by three $CoCl_4^{2-}$ anions. In total, the hydrogen bonding interactions construct a network parallel to the *ab* plane (cf. right part of the figure). Within these layers $CoCl_4^{2-}$ anions and water molecules are arranged in hydrogen bonded chains along the *a* direction with the *nic*H_2 dications connecting adjacent ones.

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