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Bis(2-aminopyridinium) tetrachlorocobalt(II)

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Key indicators

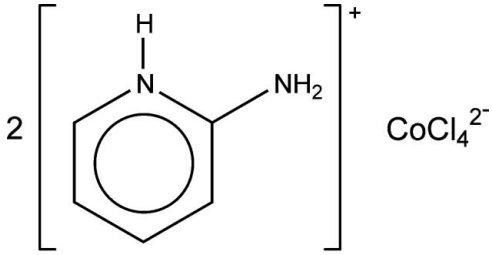
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
R factor = 0.028
wR factor = 0.119
Data-to-parameter ratio = 20.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title compound, $(C_5H_7N_2)_2[CoCl_4]$, the Co^{II} ion is coordinated by four chloride ions. The Co atom lies on a crystallographic twofold rotation axis. The structure is stabilized by an extensive network of N—H···Cl hydrogen bonds.

Comment

2-Aminopyridine is used in the manufacture of pharmaceuticals, especially antihistaminic drugs (Windholz, 1976). As part of our investigation of the reactions of 2-aminopyridine with metals, we report here the crystal structure of the title compound, (I).



(I)

The asymmetric unit of (I) contains a 2-aminopyridinium cation and half of a $[CoCl_4]^{2-}$ anion. The Co atom lies on a crystallographic twofold rotation axis. Protonation of atom N1 of the 2-aminopyridine results in the widening of the C2—N1—C6 angle to 122.7 (2)° . This compares with 117.7 (1)° in neutral 2-aminopyridine (Chao *et al.*, 1975). The bond lengths and angles in (I) are comparable to those in other 2-aminopyridinium complexes (Bis & Zaworotko, 2005; Smith *et al.*, 2000; Jebas & Balasubramanian, 2006). The pyridinium ring deviates somewhat from planarity, with a maximum deviation from the mean plane of 0.026 (2) Å for atom C6.

The anion exhibits tetrahedral geometry, with the Co^{II} ion surrounded by four Cl atoms, with Cl—Co—Cl angles ranging from 109.85 (4) to 115.98 (3)° . The mean Co—Cl bond length, 2.27 (7) Å, is close to those observed in similar complexes (Zhang *et al.*, 2005).

There are N—H···Cl hydrogen-bonding interactions between the cations and the anions (Table 2).

Experimental

Solutions of 2-aminopyridine and $CoCl_2·2H_2O$ in water were mixed in a 1:1 molar ratio and heated at 363 K for 2 h. Blue crystals of (I) were obtained by slow evaporation over a period of one week.

Crystal data

$(C_5H_7N_2)_2[CoCl_4]$
M_r = 390.98
Monoclinic, $C2/c$
a = 8.2152 (3) Å
b = 14.0713 (5) Å
c = 13.5731 (5) Å
β = 95.190 (2)°
V = 1562.52 (10) Å^3
Z = 4
D_x = 1.662 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.77 mm^{-1}
T = 120 (2) K
Block, blue
0.4 × 0.25 × 0.2 mm

Data collection

Bruker–Nonius FR591 rotating-anode diffractometer
φ and ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 2003)
T_{min} = 0.595, T_{max} = 0.701
8864 measured reflections
1801 independent reflections
1488 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 27.5°
3 standard reflections
every 60 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.119
S = 1.26
1801 reflections
87 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.2962P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—Cl2	2.2724 (7)	Co—Cl1	2.2755 (7)
C2—N1—C6	122.7 (2)	Cl2—Co—Cl2^{i}	109.85 (4)
Cl1—Co—Cl1^{i}	109.37 (4)	Cl2—Co—Cl1	115.98 (3)

Symmetry code: (i) $-x, y, -z+\frac{3}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N7—H2A···Cl2^{ii}	0.86	2.42	3.258 (2)	165
N7—H2B···Cl1^{iii}	0.86	2.44	3.286 (2)	169
N1—H1···Cl1^{iv}	0.86	2.58	3.275 (2)	139

Symmetry codes: (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

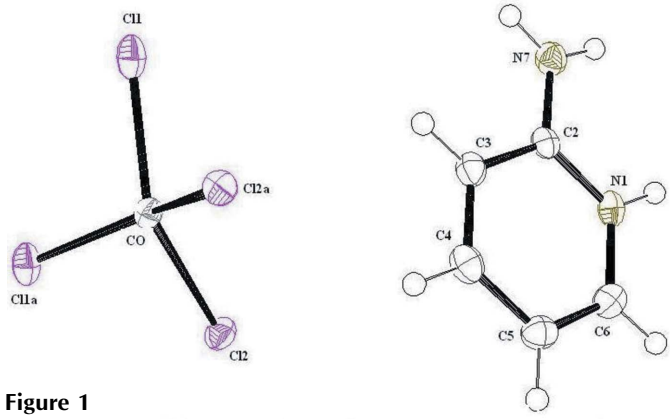


Figure 1
The structure of (I), showing the atom-numbering scheme, with 50% probability displacement ellipsoids. The suffix a indicates the symmetry position $(-x, y, \frac{3}{2}-z)$.

H atoms were placed in calculated positions, with C—H = 0.93 Å and N—H = 0.86 Å, and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C,*N*).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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(I)

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$c = 13.5731$ (5) Å
$\beta = 95.190$ (2)°
$V = 1562.52$ (10) Å^3
$Z = 4$
$F(000) = 788$
$D_x = 1.662$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 2.9$–27.5°
$\mu = 1.77$ mm^{-1}
$T = 120$ K
Block, blue
0.4 × 0.25 × 0.2 mm

Data collection

Bruker–Nonius FR591 rotating anode diffractometer
φ and ω scans
Absorption correction: multi-scan SADABS (Sheldrick, 2003)
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8864 measured reflections
1801 independent reflections
1488 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.9°$
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 17$
$l = -17 \rightarrow 17$
3 standard reflections every 60 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.119$
$S = 1.26$
1801 reflections
87 parameters
0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 0.2962P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C2	0.0862 (3)	0.30455 (18)	0.44634 (18)	0.0176 (6)

H2	−0.0701	0.3131	0.6568	0.028*
C3	−0.0066 (3)	0.27692 (19)	0.5235 (2)	0.0208 (6)
H3	−0.0671	0.221	0.5182	0.025*
C4	−0.0082 (3)	0.33173 (19)	0.6060 (2)	0.0236 (6)
C5	0.0835 (3)	0.41657 (19)	0.6152 (2)	0.0240 (6)
C6	0.1703 (3)	0.44272 (18)	0.5399 (2)	0.0226 (6)
H6	0.2305	0.4987	0.5444	0.027*
N1	0.1702 (3)	0.38769 (15)	0.45715 (17)	0.0200 (5)
H1	0.2256	0.4063	0.4099	0.024*
N7	0.0986 (3)	0.25322 (16)	0.36481 (16)	0.0227 (5)
H2A	0.1588	0.2729	0.3204	0.027*
H2B	0.0463	0.2004	0.3567	0.027*
H1A	0.0841	0.4537	0.672	0.029*
Co	0	0.04217 (3)	0.75	0.01744 (19)
Cl1	−0.10210 (9)	−0.05131 (4)	0.86658 (5)	0.0261 (2)
Cl2	0.21666 (8)	0.13498 (5)	0.80332 (5)	0.0234 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0140 (11)	0.0201 (13)	0.0182 (13)	0.0030 (10)	−0.0014 (10)	0.0034 (10)
C3	0.0179 (13)	0.0225 (14)	0.0217 (13)	−0.0022 (11)	0.0005 (11)	0.0038 (11)
C4	0.0199 (14)	0.0295 (14)	0.0219 (14)	0.0007 (11)	0.0051 (11)	0.0037 (12)
C5	0.0240 (14)	0.0233 (14)	0.0245 (15)	0.0017 (11)	0.0018 (11)	−0.0027 (12)
C6	0.0194 (14)	0.0202 (13)	0.0280 (15)	0.0007 (10)	0.0008 (11)	0.0000 (11)
N1	0.0183 (11)	0.0204 (11)	0.0219 (12)	0.0006 (9)	0.0048 (9)	0.0062 (9)
N7	0.0229 (12)	0.0240 (11)	0.0215 (12)	−0.0012 (9)	0.0043 (9)	0.0016 (10)
Co	0.0164 (3)	0.0163 (3)	0.0202 (3)	0	0.0048 (2)	0
Cl1	0.0254 (4)	0.0240 (4)	0.0306 (4)	0.0031 (3)	0.0120 (3)	0.0083 (3)
Cl2	0.0218 (4)	0.0214 (4)	0.0270 (4)	−0.0053 (2)	0.0022 (3)	0.0001 (3)

Geometric parameters (Å, º)

C3—C4	1.361 (4)	N1—C2	1.360 (3)
C3—C2	1.405 (4)	N1—H1	0.86
C3—H3	0.93	N7—C2	1.333 (3)
C4—H2	0.93	N7—H2A	0.86
C5—C4	1.411 (4)	N7—H2B	0.86
C5—H1A	0.93	Co—Cl2	2.2724 (7)
C6—C5	1.350 (4)	Co—Cl2^{i}	2.2724 (7)
C6—N1	1.364 (4)	Co—Cl1	2.2755 (7)
C6—H6	0.93	Co—Cl1^{i}	2.2755 (7)
C2—N7—H2A	120	C6—N1—H1	118.7
C2—N7—H2B	120	C6—C5—C4	118.5 (3)
H2A—N7—H2B	120	C6—C5—H1A	120.7
C2—N1—C6	122.7 (2)	N1—C6—H6	119.7
C2—N1—H1	118.7	N1—C2—C3	117.5 (2)

C2—C3—H3	119.9	N7—C2—N1	118.7 (2)
C3—C4—C5	120.5 (3)	N7—C2—C3	123.8 (2)
C3—C4—H2	119.8	Cl1—Co—Cl1^{i}	109.37 (4)
C4—C3—C2	120.2 (2)	Cl2—Co—Cl2^{i}	109.85 (4)
C4—C3—H3	119.9	Cl2—Co—Cl1	115.98 (3)
C4—C5—H1A	120.7	Cl2^{i}—Co—Cl1	103.08 (2)
C5—C4—H2	119.8	Cl2—Co—Cl1^{i}	103.08 (2)
C5—C6—N1	120.6 (3)	Cl2^{i}—Co—Cl1^{i}	115.98 (3)
C5—C6—H6	119.7		

Symmetry code: (i) $-x$, y, $-z+3/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H2*A*···Cl2^{ii}	0.86	2.42	3.258 (2)	165
N7—H2*B*···Cl1^{iii}	0.86	2.44	3.286 (2)	169
N1—H1···Cl1^{iv}	0.86	2.58	3.275 (2)	139

Symmetry codes: (ii) $-x+1/2$, $-y+1/2$, $-z+1$; (iii) x, $-y$, $z-1/2$; (iv) $x+1/2$, $-y+1/2$, $z-1/2$.