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Key indicators

Single-crystal X-ray study
 $T = 120$ K
 Mean $\sigma(\text{C}-\text{C}) = 0.004$ 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>.

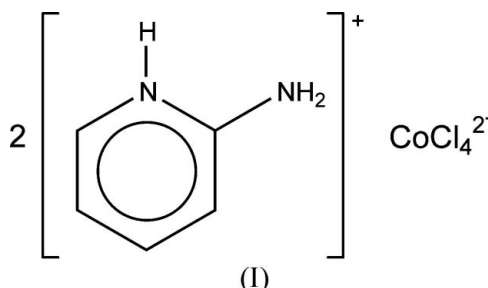
Bis(2-aminopyridinium) tetrachlorocobalt(II)

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In the crystal structure of the title compound, $(\text{C}_5\text{H}_7\text{N}_2)_2\text{[CoCl}_4\text{]}$, 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 $\text{N}-\text{H}\cdots\text{Cl}$ 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).



The asymmetric unit of (I) contains a 2-aminopyridinium cation and half of a $[\text{CoCl}_4]^{2-}$ 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 $\text{C}2-\text{N}1-\text{C}6$ 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 $\text{Cl}-\text{Co}-\text{Cl}$ angles ranging from 109.85 (4) to 115.98 (3)°. The mean $\text{Co}-\text{Cl}$ bond length, 2.27 (7) Å, is close to those observed in similar complexes (Zhang *et al.*, 2005).

There are $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen-bonding interactions between the cations and the anions (Table 2).

Experimental

Solutions of 2-aminopyridine and $\text{CoCl}_2\cdot 2\text{H}_2\text{O}$ 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

(C₅H₇N₂)₂[CoCl₄]
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) Å³

Z = 4
D_x = 1.662 Mg m⁻³
 Mo *K*α 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* > 2σ(*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 > 2σ(*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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.57 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.67 \text{ e } \text{Å}^{-3}$

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, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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

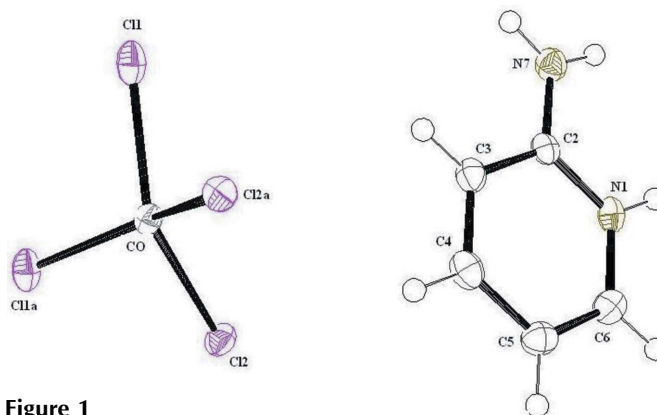
Symmetry codes: (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $x, -y, z - \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

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).

References

- Bis, J. A. & Zaworotko, M. J. (2005). *Cryst. Growth Des.* **5**, 1169–1179.
 Chao, M., Schempp, E. & Rosenstein, R. D. (1975). *Acta Cryst.* **B31**, 2922–2924.
 Jebas, S. R. & Balasubramanian, T. (2006). *Acta Cryst.* **E62**, o2209–o2211.
 Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
 Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
 Smith, G., Bott, R. C. & Wermuth, U. D. (2000). *Acta Cryst.* **C56**, 1505–1506.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Windholz, M. (1976). *The Merck Index*. 9th Edition. Rahway, New Jersey, USA: Merck & Co., Inc.
 Zhang, H., Fang, L. & Yuan, R. (2005). *Acta Cryst.* **E61**, m677–m678.

supporting information

Acta Cryst. (2006). E62, m1818–m1819 [https://doi.org/10.1107/S1600536806026213]

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(I)

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 β = 95.190 (2)°
V = 1562.52 (10) Å³
Z = 4

F(000) = 788
D_x = 1.662 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 2.9–27.5°
 μ = 1.77 mm⁻¹
T = 120 K
 Block, blue
 0.4 × 0.25 × 0.2 mm

Data collection

Bruker–Nonius FR591 rotating anode
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 φ and ω scans
 Absorption correction: multi-scan
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T_{min} = 0.595, *T_{max}* = 0.701
 8864 measured reflections
 1801 independent reflections

1488 reflections with *I* > 2σ(*I*)
R_{int} = 0.032
 θ_{\max} = 27.5°, θ_{\min} = 2.9°
h = -10→10
k = -18→17
l = -17→17
 3 standard reflections every 60 reflections
 intensity decay: none

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.57 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.67 \text{ e } \text{Å}^{-3}$

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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
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, °)

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, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
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) $-x+1/2, -y+1/2, -z+1$; (iii) $x, -y, z-1/2$; (iv) $x+1/2, -y+1/2, z-1/2$.