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1-Cyanomethyl-1,4-diazoniabicyclo-[2.2.2]octane tetrachloridocobaltate(II)

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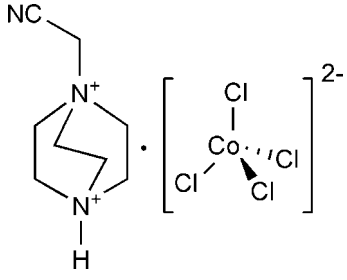
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.046; wR factor = 0.135; data-to-parameter ratio = 21.2.

In the title salt, $(C_8H_{15}N_3)[CoCl_4]$, the four chloride anions coordinate the Co^{II} ion in a distorted tetrahedral geometry. In the crystal, N—H···Cl hydrogen bonds link cations and anions into chains running along the c axis. The crystal packing is further stabilized by weak C—H···Cl and C—H···N interactions.

Related literature

Crystal structures of related Cu and Cd analogs were reported by Wei (2010) and Zhang & Zhu (2012), respectively. For ferroelectric properties of 1,4-diazabicyclo[2.2.2]octane derivatives, see: Zhang *et al.* (2009, 2010).



Experimental

Crystal data

$(C_8H_{15}N_3)[CoCl_4]$
M_r = 353.96
Monoclinic, $P2_1/c$
a = 8.3085 (17) Å
b = 13.604 (3) Å
c = 12.185 (2) Å
β = 93.78 (3)°
V = 1374.3 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.00 mm^{-1}
T = 298 K
0.36 × 0.32 × 0.28 mm

Data collection

Rigaku Mercury70 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.491, T_{max} = 0.571
13757 measured reflections
3152 independent reflections
2724 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.135
S = 0.98
3152 reflections
149 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H10···Cl3^{i}	0.86 (5)	2.52 (5)	3.236 (3)	140 (4)
N2—H10···Cl2^{ii}	0.86 (5)	2.65 (5)	3.225 (3)	125 (4)
C3—H3B···Cl1^{iii}	0.97	2.74	3.647 (4)	156
C7—H7A···Cl2^{iii}	0.97	2.58	3.492 (4)	156
C2—H2A···Cl3^{iv}	0.97	2.73	3.543 (4)	142
C3—H3A···N3^{v}	0.97	2.58	2.983 (4)	105

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, -y+2, -z$; (iii) $-x+1, -y+2, -z$; (iv) $x, -y+\frac{5}{2}, z+\frac{1}{2}$; (v) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *SCXmini Benchtop Crystallography System Software* (Rigaku, 2006); cell refinement: *SCXmini Benchtop Crystallography System Software*; data reduction: *SCXmini Benchtop Crystallography System Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Start-up Projects for Postdoctoral Research Funds (grant No. 1112000064), the Major Postdoctoral Research Funds (grant No. 3212000602) of Southeast University and Jiangsu Planned Projects for Postdoctoral Research Funds (grant No. 1101010B).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5283).

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supplementary materials

Acta Cryst. (2012). E**68**, m665 [doi:10.1107/S1600536812017187]

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Comment

The title compound, (I), has been obtained in the framework of a systematic investigation of dielectric-ferroelectric materials containing 1,4-diazabicyclo[2.2.2]octane (DABCO) (Zhang, Ye *et al.*, 2009; Zhang, Ye *et al.*, 2010). The asymmetric unit of (I) (Fig. 1) contains one cation, $(C_8H_{15}N_3)^{2+}$, and one anion, $(CoCl_4)^{2-}$. All bond lengths and angles are normal and correspond to those observed in isostructural Cu (Wei, 2010) and Cd (Zhang & Zhu, 2012) analogs. The Co centers are coordinated by four Cl atoms with very similar distances in the range of2.2749 (12) to 2.2910 (12) Å. The Cl—Co—Cl bond angles are between 103.21 (4) and 113.85 (5) ° which shows that the coordination polyhedron can be described as a slightly distorted tetrahedron. The ammonium groups of the organic cations are engaged in bifurcated hydrogen bonds to chlorine atoms of two $(CoCl_4)^{2-}$ anions. These weak N—H···Cl interactions cause the formation of a one-dimensional chain along the [0 0 1] (Fig. 2). The crystal packing is further stabilized by the weak intermolecular C—H···Cl and C—H···N interactions (Table 2).

Experimental

Chloroacetonitrile(0.1 mol, 7.55 g) was added to a CH_3CN (25 ml) solution of 1,4-Diaza-bicyclo[2.2.2]octane (DABCO) (0.1 mol, 11.2 g) with stirring for 1 h at room temperature. 1-(cyanomethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane chloride quickly formed as white solid was filtered, washed with acetonitrile and dried (yield: 80%). $CoCl_2.6H_2O$ (0.01 mol, 2.38 g) and 1 g 36% HCl were dissolved in H_2O (20 ml) and 1-(cyanomethyl)-4-aza-1-azonia-bicyclo[2.2.2]octane chloride (0.01 mol, 1.875 g) in H_2O (20 ml) was added. The resulting solution was stirred until a clear solution was obtained. After slow evaporation of the solvent, blue block crystals of the title compound suitable for X-ray analysis were obtained in about 60% yield.The title compound has no dielectric disuniform from 80 K to 373 K, (m.p. > 373 K).

Refinement

N-bound atom H1 was located on a difference map and isotropically refined. C-bound H atoms were geometrically positioned (C—H 0.97 Å) and refined as riding, with U_{iso}(H) =1.2 U_{eq}(C).

Computing details

Data collection: *SCXmini Benchtop Crystallography System Software* (Rigaku, 2006); cell refinement: *SCXmini Benchtop Crystallography System Software* (Rigaku, 2006); data reduction: *SCXmini Benchtop Crystallography System Software* (Rigaku, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

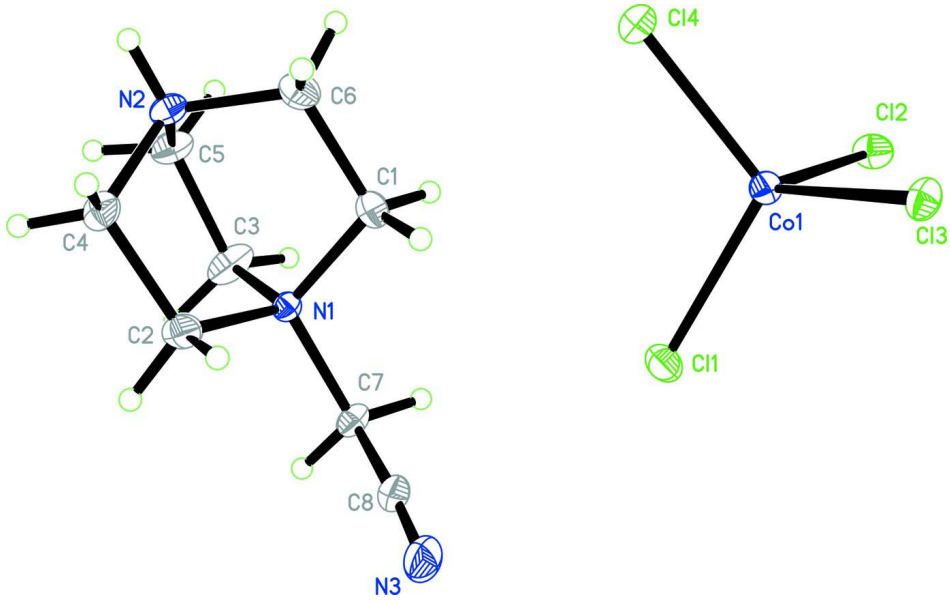

Figure 1

Molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

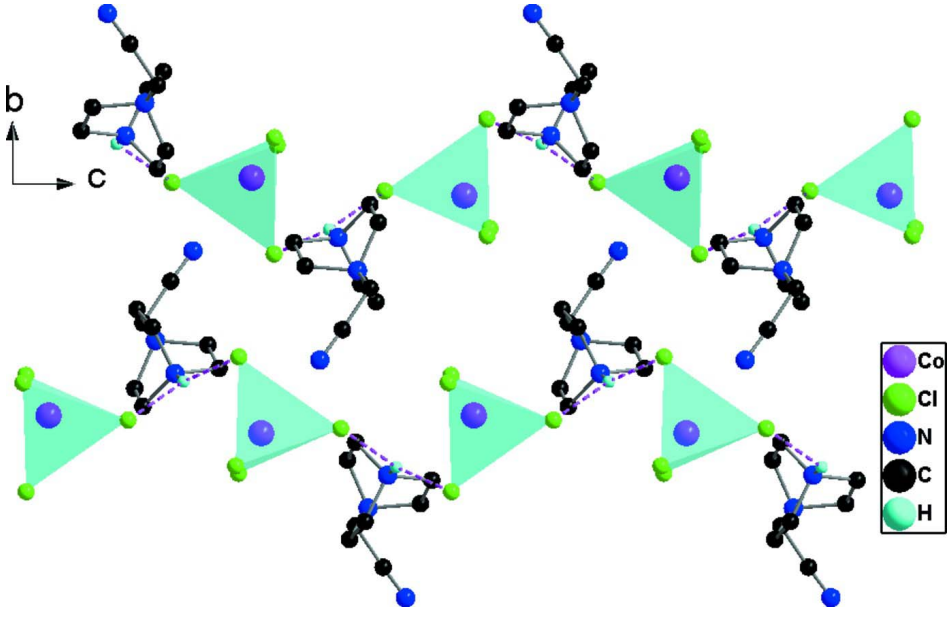

Figure 2

A portion of the crystal packing viewed along the *a* axis. Dotted lines indicate N—H···Cl hydrogen bonds.

1-Cyanomethyl-1,4-diazoniabicyclo[2.2.2]octane tetrachloridocobaltate(II)

Crystal data

$(C_8H_{15}N_3)[CoCl_4]$
M_r = 353.96
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc

a = 8.3085 (17) Å
b = 13.604 (3) Å
c = 12.185 (2) Å
β = 93.78 (3)°

V = 1374.3 (5) Å^3
Z = 4
F(000) = 716
D_x = 1.711 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2622 reflections

θ = 3.1–27.5°
μ = 2.00 mm^{-1}
T = 298 K
Block, blue
0.36 × 0.32 × 0.28 mm

Data collection

Rigaku Mercury70 CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.491, T_{max} = 0.571

13757 measured reflections
3152 independent reflections
2724 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −10→10
k = −17→17
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.135
S = 0.98
3152 reflections
149 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.069P)^2 + 4.1266P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Co1	0.22754 (6)	1.23132 (4)	−0.01115 (4)	0.02235 (17)
Cl2	0.22305 (12)	1.24111 (8)	−0.19820 (7)	0.0304 (2)
Cl3	0.19972 (12)	1.39179 (7)	0.04142 (8)	0.0276 (2)
Cl4	0.00899 (12)	1.14672 (8)	0.04230 (8)	0.0321 (2)
Cl1	0.46675 (12)	1.16243 (8)	0.04912 (8)	0.0325 (2)
N2	0.1021 (4)	0.8570 (2)	0.3083 (3)	0.0232 (7)
C8	0.5802 (5)	1.0508 (3)	0.2980 (4)	0.0295 (9)
N1	0.3699 (3)	0.9263 (2)	0.2626 (2)	0.0179 (6)
C7	0.5319 (5)	0.9636 (3)	0.2328 (3)	0.0254 (8)
H7A	0.6120	0.9123	0.2458	0.031*

H7B	0.5270	0.9801	0.1552	0.031*
C2	0.3635 (5)	0.9171 (4)	0.3857 (3)	0.0304 (9)
H2A	0.3699	0.9817	0.4192	0.037*
H2B	0.4545	0.8786	0.4154	0.037*
C6	0.0766 (5)	0.9545 (3)	0.2549 (4)	0.0328 (9)
H6A	0.0331	1.0004	0.3062	0.039*
H6B	0.0000	0.9485	0.1916	0.039*
C5	0.1811 (5)	0.7878 (3)	0.2331 (3)	0.0284 (9)
H5A	0.1173	0.7831	0.1637	0.034*
H5B	0.1883	0.7228	0.2657	0.034*
C4	0.2072 (5)	0.8675 (3)	0.4119 (3)	0.0275 (8)
H4A	0.2297	0.8033	0.4439	0.033*
H4B	0.1526	0.9066	0.4646	0.033*
C1	0.2367 (5)	0.9922 (4)	0.2188 (4)	0.0395 (11)
H1A	0.2344	0.9939	0.1391	0.047*
H1B	0.2553	1.0585	0.2460	0.047*
N3	0.6229 (5)	1.1147 (3)	0.3508 (3)	0.0417 (10)
C3	0.3479 (5)	0.8252 (3)	0.2136 (4)	0.0338 (10)
H3A	0.4283	0.7809	0.2472	0.041*
H3B	0.3620	0.8277	0.1353	0.041*
H10	0.009 (6)	0.840 (4)	0.329 (4)	0.032 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0229 (3)	0.0220 (3)	0.0222 (3)	0.0000 (2)	0.00147 (19)	−0.00076 (19)
Cl2	0.0287 (5)	0.0414 (6)	0.0211 (4)	−0.0016 (4)	0.0011 (3)	−0.0027 (4)
Cl3	0.0320 (5)	0.0209 (5)	0.0305 (5)	−0.0024 (4)	0.0066 (4)	−0.0011 (4)
Cl4	0.0302 (5)	0.0298 (5)	0.0366 (5)	−0.0057 (4)	0.0045 (4)	0.0038 (4)
Cl1	0.0283 (5)	0.0377 (6)	0.0312 (5)	0.0063 (4)	0.0012 (4)	0.0073 (4)
N2	0.0190 (15)	0.0256 (17)	0.0257 (15)	−0.0021 (13)	0.0063 (12)	−0.0035 (13)
C8	0.027 (2)	0.023 (2)	0.038 (2)	−0.0038 (17)	−0.0002 (16)	0.0084 (17)
N1	0.0182 (14)	0.0165 (15)	0.0190 (14)	−0.0004 (12)	0.0023 (11)	−0.0008 (11)
C7	0.0220 (18)	0.026 (2)	0.0294 (19)	−0.0053 (15)	0.0074 (15)	0.0016 (15)
C2	0.0255 (19)	0.047 (3)	0.0185 (17)	−0.0080 (18)	0.0007 (14)	−0.0004 (17)
C6	0.025 (2)	0.031 (2)	0.043 (2)	0.0093 (17)	0.0031 (17)	0.0025 (18)
C5	0.0262 (19)	0.026 (2)	0.034 (2)	−0.0063 (16)	0.0053 (16)	−0.0129 (16)
C4	0.030 (2)	0.035 (2)	0.0182 (16)	−0.0063 (17)	0.0057 (15)	−0.0023 (15)
C1	0.028 (2)	0.031 (2)	0.059 (3)	0.0022 (18)	−0.005 (2)	0.020 (2)
N3	0.052 (2)	0.028 (2)	0.044 (2)	−0.0136 (18)	−0.0076 (18)	0.0070 (17)
C3	0.034 (2)	0.026 (2)	0.044 (2)	−0.0080 (17)	0.0192 (19)	−0.0181 (18)

Geometric parameters (Å, º)

Co1—Cl1	2.2749 (12)	C2—C4	1.516 (5)
Co1—Cl4	2.2808 (12)	C2—H2A	0.9700
Co1—Cl2	2.2809 (11)	C2—H2B	0.9700
Co1—Cl3	2.2910 (12)	C6—C1	1.518 (6)
N2—C6	1.487 (5)	C6—H6A	0.9700
N2—C4	1.493 (5)	C6—H6B	0.9700

N2—C5	1.496 (5)	C5—C3	1.510 (6)
N2—H10	0.86 (5)	C5—H5A	0.9700
C8—N3	1.125 (6)	C5—H5B	0.9700
C8—C7	1.469 (6)	C4—H4A	0.9700
N1—C1	1.495 (5)	C4—H4B	0.9700
N1—C7	1.505 (4)	C1—H1A	0.9700
N1—C3	1.506 (5)	C1—H1B	0.9700
N1—C2	1.510 (5)	C3—H3A	0.9700
C7—H7A	0.9700	C3—H3B	0.9700
C7—H7B	0.9700		

Cl1—Co1—Cl4	113.26 (5)	N2—C6—C1	109.0 (3)
Cl1—Co1—Cl2	107.64 (5)	N2—C6—H6A	109.9
Cl4—Co1—Cl2	110.73 (5)	C1—C6—H6A	109.9
Cl1—Co1—Cl3	113.85 (5)	N2—C6—H6B	109.9
Cl4—Co1—Cl3	107.70 (4)	C1—C6—H6B	109.9
Cl2—Co1—Cl3	103.21 (4)	H6A—C6—H6B	108.3
C6—N2—C4	110.1 (3)	N2—C5—C3	109.2 (3)
C6—N2—C5	110.4 (3)	N2—C5—H5A	109.8
C4—N2—C5	108.9 (3)	C3—C5—H5A	109.8
C6—N2—H10	105 (3)	N2—C5—H5B	109.8
C4—N2—H10	106 (3)	C3—C5—H5B	109.8
C5—N2—H10	116 (3)	H5A—C5—H5B	108.3
N3—C8—C7	176.4 (5)	N2—C4—C2	109.0 (3)
C1—N1—C7	111.4 (3)	N2—C4—H4A	109.9
C1—N1—C3	109.8 (3)	C2—C4—H4A	109.9
C7—N1—C3	107.4 (3)	N2—C4—H4B	109.9
C1—N1—C2	109.3 (3)	C2—C4—H4B	109.9
C7—N1—C2	111.0 (3)	H4A—C4—H4B	108.3
C3—N1—C2	107.8 (3)	N1—C1—C6	109.7 (3)
C8—C7—N1	111.0 (3)	N1—C1—H1A	109.7
C8—C7—H7A	109.4	C6—C1—H1A	109.7
N1—C7—H7A	109.4	N1—C1—H1B	109.7
C8—C7—H7B	109.4	C6—C1—H1B	109.7
N1—C7—H7B	109.4	H1A—C1—H1B	108.2
H7A—C7—H7B	108.0	N1—C3—C5	109.5 (3)
N1—C2—C4	109.5 (3)	N1—C3—H3A	109.8
N1—C2—H2A	109.8	C5—C3—H3A	109.8
C4—C2—H2A	109.8	N1—C3—H3B	109.8
N1—C2—H2B	109.8	C5—C3—H3B	109.8
C4—C2—H2B	109.8	H3A—C3—H3B	108.2
H2A—C2—H2B	108.2		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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