metal-organic compounds

Dimorpholinium tetrachlorido-cobaltate(II)

Xing-Xing Cao, He-Long Cheng, Qing-Liu Feng and Li-Zhuang Chen*

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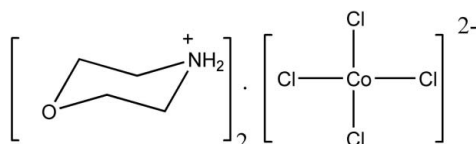Correspondence e-mail: clz1977@sina.com

In the title molecular salt, $(C_4H_{10}NO)_2[CoCl_4]$, the morpholinium cations adopt chair conformations and the tetrachloridocobaltate(II) anion is significantly distorted from regular tetrahedral geometry [Cl—Co—Cl = 102.183 (19)–117.59 (2)°]. The Co—Cl bond lengths for the chloride ions not accepting hydrogen bonds are significantly shorter than those for the chloride ions accepting such bonds. In the crystal, the components are linked by N—H⋯O and N—H⋯Cl and bifurcated N—H⋯(O,Cl) hydrogen bonds to generate (100) sheets.

Related literature

For a phase transition in morpholinium tetrafluoridoborate, see: Szklarz *et al.* (2009); Owczarek *et al.* (2008). For the structure of dimorpholinium pentachloridoantimonate(III), see: Chen (2009).

Experimental

Crystal data

$(C_4H_{10}NO)_2[CoCl_4]$
$M_r = 376.99$
Monoclinic, $P2_1/c$
$a = 6.5952\ (13)$ Å
$b = 13.696\ (3)$ Å
$c = 17.039\ (3)$ Å
$\beta = 92.930\ (2)°$
$V = 1537.1\ (5)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation

$\mu = 1.80$ mm^{-1}
$T = 291$ K
$0.26 \times 0.12 \times 0.08$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{min} = 0.90$, $T_{max} = 1.00$

11708 measured reflections
2997 independent reflections
2761 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.074$
$S = 1.07$
2997 reflections

154 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected bond lengths (Å).

| Co1—Cl1 | 2.3029 (6) | Co1—Cl3 | 2.2455 (6) |
| Co1—Cl2 | 2.2720 (6) | Co1—Cl4 | 2.2811 (6) |

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1C⋯Cl1	0.90	2.39	3.1819 (15)	148
N1—H1D⋯O2^i	0.90	1.97	2.8824 (19)	160
N2—H2C⋯O1^{ii}	0.90	2.47	3.0577 (18)	123
N2—H2C⋯Cl4^{iii}	0.90	2.57	3.3322 (15)	143
N2—H2D⋯Cl1^{iv}	0.90	2.43	3.3003 (15)	164

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; 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*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6916).

References

Chen, L. Z. (2009). *Acta Cryst.* E**65**, m689.
Owczarek, M., Szklarz, P., Jakubas, R. & Lis, T. (2008). *Acta Cryst.* E**64**, o667.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Szklarz, P., Owczarek, M., Bator, G., Lis, T., Gatner, K. & Jakubas, R. (2009). *J. Mol. Struct.* **929**, 48.

supporting information

Dimorpholinium tetrachloridocobaltate(II)

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S1. Experimental

$CoCl_2$ (2.37 g, 10 mmol), morpholine (1.01 g, 10 mmol) and 20% aqueous HCl in a molar ratio of 1:1:1 were mixed and dissolved in sufficient water by heating to 353 K forming a clear solution. The reaction mixture was cooled slowly to room temperature, blue blocks of the title compound were formed, collected and washed with dilute aqueous HCl.

S2. Refinement

All H atoms were placed in calculated positions, with C—H = 0.97 Å and N—H = 0.90 Å, and refined using a riding model, with $U_{iso}(H)=1.2U_{eq}(C, N)$.
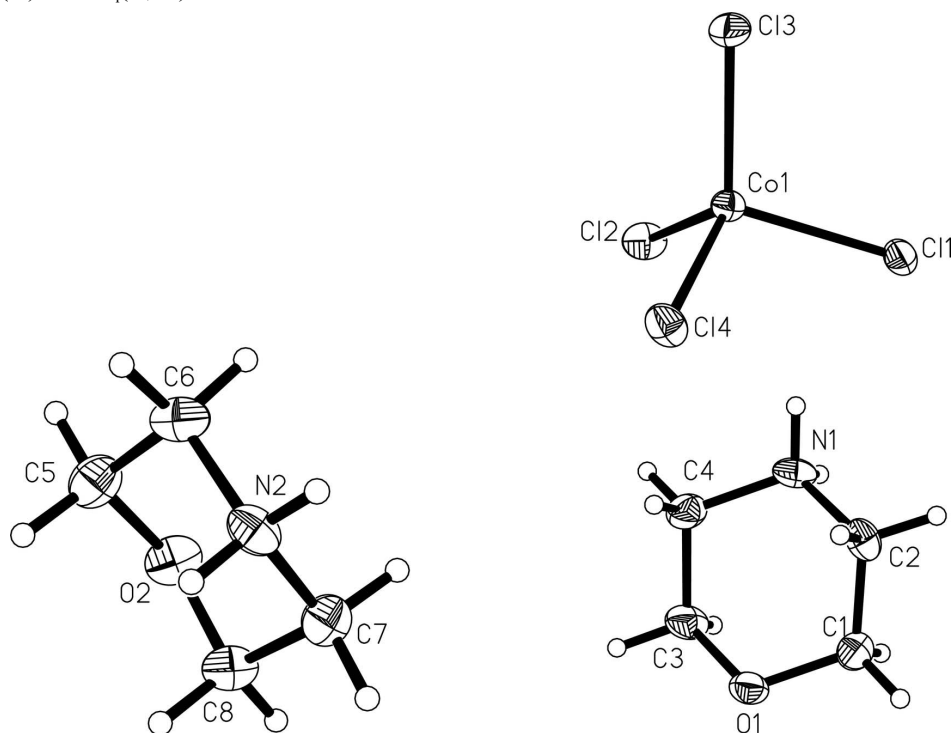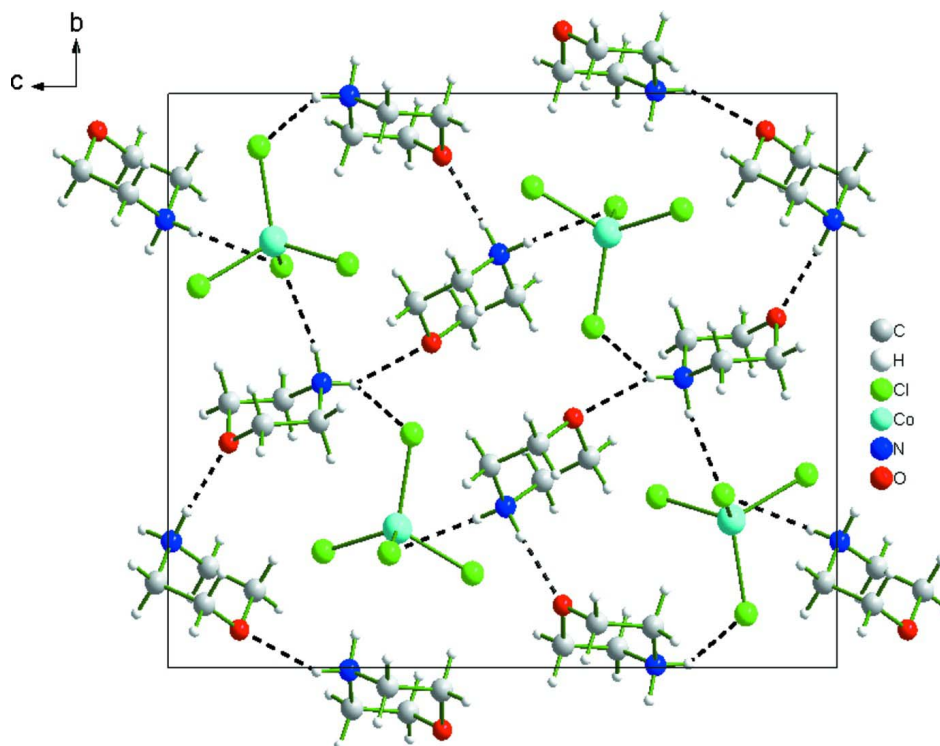

Figure 1

The asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

Figure 2

The packing viewed along the *a* axis. Hydrogen bonds are drawn as dashed lines

Dimorpholinium tetrachloridocobaltate(II)

Crystal data

$(C_4H_{10}NO)_2[CoCl_4]$	$F(000) = 772$
$M_r = 376.99$	$D_x = 1.629$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2761 reflections
$a = 6.5952$ (13) Å	$\theta = 2.5$–$26.0°$
$b = 13.696$ (3) Å	$\mu = 1.80$ mm^{-1}
$c = 17.039$ (3) Å	$T = 291$ K
$\beta = 92.930$ (2)°	Block, blue
$V = 1537.1$ (5) Å^3	$0.26 \times 0.12 \times 0.08$ mm
$Z = 4$	

Data collection

Rigaku SCXmini diffractometer	11708 measured reflections
Radiation source: fine-focus sealed tube	2997 independent reflections
Graphite monochromator	2761 reflections with $I > 2\sigma(I)$
Detector resolution: 13.66612 pixels mm^{-1}	$R_{int} = 0.019$
ω scans	$\theta_{max} = 26.0°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan ($CrystalClear$; Rigaku, 2005)	$h = -7 \rightarrow 8$
	$k = -16 \rightarrow 16$
$T_{min} = 0.90$, $T_{max} = 1.00$	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.022$	
$wR(F^2) = 0.074$	
$S = 1.07$	H-atom parameters constrained
2997 reflections	$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.0459P]$
154 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.25$ e Å^{-3}
	$\Delta\rho_{min} = -0.42$ 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}
C1	−0.1713 (3)	0.61037 (13)	0.55358 (11)	0.0444 (4)
H1A	−0.2354	0.6639	0.5801	0.053*
H1B	−0.2756	0.5629	0.5388	0.053*
C2	−0.0788 (3)	0.64794 (13)	0.48120 (10)	0.0404 (4)
H2A	−0.0210	0.5943	0.4526	0.048*
H2B	−0.1819	0.6791	0.4472	0.048*
C3	0.2348 (3)	0.67437 (14)	0.56019 (11)	0.0479 (4)
H3A	0.3349	0.7226	0.5776	0.057*
H3B	0.3043	0.6221	0.5342	0.057*
C4	0.1303 (3)	0.63460 (14)	0.62962 (10)	0.0471 (4)
H4A	0.2296	0.6033	0.6653	0.056*
H4B	0.0696	0.6880	0.6576	0.056*
C5	1.1478 (3)	0.07758 (13)	0.35868 (11)	0.0472 (4)
H5A	1.1997	0.0142	0.3754	0.057*
H5B	1.2597	0.1236	0.3616	0.057*
C6	1.0622 (3)	0.07100 (13)	0.27501 (11)	0.0459 (4)
H6A	1.0223	0.1355	0.2564	0.055*
H6B	1.1652	0.0463	0.2415	0.055*
C7	0.7310 (3)	0.03294 (13)	0.32823 (11)	0.0427 (4)
H7A	0.6226	−0.0150	0.3280	0.051*
H7B	0.6720	0.0957	0.3137	0.051*
C8	0.8328 (3)	0.03920 (13)	0.40899 (10)	0.0428 (4)
H8A	0.7346	0.0588	0.4464	0.051*
H8B	0.8854	−0.0245	0.4245	0.051*
Cl1	0.10686 (6)	0.80041 (3)	0.33040 (2)	0.04020 (12)

Cl2	0.55058 (7)	0.83591 (3)	0.45501 (2)	0.04426 (13)
Cl3	0.59472 (7)	0.79781 (4)	0.23183 (2)	0.04472 (13)
Cl4	0.45151 (7)	0.59332 (3)	0.36450 (3)	0.04461 (13)
Co1	0.44468 (3)	0.757637 (14)	0.342708 (12)	0.02945 (10)
N1	0.0826 (2)	0.71964 (10)	0.50476 (8)	0.0392 (3)
H1C	0.1438	0.7406	0.4618	0.047*
H1D	0.0266	0.7716	0.5277	0.047*
N2	0.8819 (2)	0.00444 (10)	0.27066 (8)	0.0395 (3)
H2C	0.8231	0.0064	0.2218	0.047*
H2D	0.9231	−0.0572	0.2804	0.047*
O1	−0.02319 (19)	0.56588 (8)	0.60621 (7)	0.0402 (3)
O2	0.9955 (2)	0.10839 (9)	0.40987 (7)	0.0454 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0361 (9)	0.0437 (9)	0.0533 (11)	−0.0013 (7)	0.0020 (8)	0.0055 (8)
C2	0.0476 (10)	0.0389 (8)	0.0335 (9)	0.0042 (7)	−0.0083 (7)	−0.0026 (7)
C3	0.0440 (10)	0.0619 (11)	0.0373 (9)	−0.0188 (8)	−0.0023 (8)	0.0045 (8)
C4	0.0601 (11)	0.0511 (10)	0.0292 (9)	−0.0191 (9)	−0.0060 (8)	0.0041 (7)
C5	0.0418 (10)	0.0453 (9)	0.0544 (11)	−0.0079 (8)	0.0031 (8)	−0.0097 (8)
C6	0.0550 (11)	0.0393 (8)	0.0448 (10)	−0.0053 (8)	0.0159 (8)	0.0002 (8)
C7	0.0412 (9)	0.0418 (9)	0.0450 (10)	−0.0019 (7)	0.0015 (8)	−0.0046 (7)
C8	0.0515 (10)	0.0412 (9)	0.0363 (9)	−0.0102 (7)	0.0061 (8)	−0.0041 (7)
Cl1	0.0353 (2)	0.0502 (2)	0.0352 (2)	0.00980 (16)	0.00288 (17)	0.01069 (17)
Cl2	0.0559 (3)	0.0427 (2)	0.0342 (2)	−0.01302 (18)	0.00315 (19)	−0.00842 (17)
Cl3	0.0403 (2)	0.0616 (3)	0.0330 (2)	−0.00275 (18)	0.00952 (18)	0.00554 (18)
Cl4	0.0543 (3)	0.0295 (2)	0.0487 (3)	−0.00623 (16)	−0.0107 (2)	0.00300 (16)
Co1	0.03183 (15)	0.02976 (14)	0.02686 (15)	−0.00168 (7)	0.00255 (10)	0.00081 (7)
N1	0.0550 (9)	0.0368 (7)	0.0266 (7)	−0.0064 (6)	0.0108 (6)	0.0019 (6)
N2	0.0549 (9)	0.0347 (7)	0.0283 (7)	0.0001 (6)	−0.0038 (6)	−0.0015 (5)
O1	0.0462 (7)	0.0356 (6)	0.0384 (6)	−0.0088 (5)	−0.0005 (5)	0.0075 (5)
O2	0.0522 (7)	0.0415 (6)	0.0428 (7)	−0.0124 (6)	0.0053 (6)	−0.0148 (5)

Geometric parameters (Å, º)

C1—O1	1.428 (2)	C6—N2	1.497 (2)
C1—C2	1.495 (2)	C6—H6A	0.9700
C1—H1A	0.9700	C6—H6B	0.9700
C1—H1B	0.9700	C7—N2	1.485 (2)
C2—N1	1.488 (2)	C7—C8	1.503 (2)
C2—H2A	0.9700	C7—H7A	0.9700
C2—H2B	0.9700	C7—H7B	0.9700
C3—N1	1.479 (2)	C8—O2	1.431 (2)
C3—C4	1.502 (2)	C8—H8A	0.9700
C3—H3A	0.9700	C8—H8B	0.9700
C3—H3B	0.9700	Co1—Cl1	2.3029 (6)
C4—O1	1.424 (2)	Co1—Cl2	2.2720 (6)

C4—H4A	0.9700	Co1—Cl3	2.2455 (6)
C4—H4B	0.9700	Co1—Cl4	2.2811 (6)
C5—O2	1.427 (2)	N1—H1C	0.9000
C5—C6	1.509 (3)	N1—H1D	0.9000
C5—H5A	0.9700	N2—H2C	0.9000
C5—H5B	0.9700	N2—H2D	0.9000
O1—C1—C2	111.70 (14)	C5—C6—H6B	109.7
O1—C1—H1A	109.3	H6A—C6—H6B	108.2
C2—C1—H1A	109.3	N2—C7—C8	109.66 (14)
O1—C1—H1B	109.3	N2—C7—H7A	109.7
C2—C1—H1B	109.3	C8—C7—H7A	109.7
H1A—C1—H1B	107.9	N2—C7—H7B	109.7
N1—C2—C1	108.73 (14)	C8—C7—H7B	109.7
N1—C2—H2A	109.9	H7A—C7—H7B	108.2
C1—C2—H2A	109.9	O2—C8—C7	110.32 (14)
N1—C2—H2B	109.9	O2—C8—H8A	109.6
C1—C2—H2B	109.9	C7—C8—H8A	109.6
H2A—C2—H2B	108.3	O2—C8—H8B	109.6
N1—C3—C4	109.34 (15)	C7—C8—H8B	109.6
N1—C3—H3A	109.8	H8A—C8—H8B	108.1
C4—C3—H3A	109.8	Cl3—Co1—Cl2	117.59 (2)
N1—C3—H3B	109.8	Cl3—Co1—Cl4	111.892 (19)
C4—C3—H3B	109.8	Cl2—Co1—Cl4	109.01 (2)
H3A—C3—H3B	108.3	Cl3—Co1—Cl1	109.083 (19)
O1—C4—C3	111.56 (14)	Cl2—Co1—Cl1	102.183 (19)
O1—C4—H4A	109.3	Cl4—Co1—Cl1	106.068 (18)
C3—C4—H4A	109.3	C3—N1—C2	110.39 (13)
O1—C4—H4B	109.3	C3—N1—H1C	109.6
C3—C4—H4B	109.3	C2—N1—H1C	109.6
H4A—C4—H4B	108.0	C3—N1—H1D	109.6
O2—C5—C6	110.74 (15)	C2—N1—H1D	109.6
O2—C5—H5A	109.5	H1C—N1—H1D	108.1
C6—C5—H5A	109.5	C7—N2—C6	111.39 (13)
O2—C5—H5B	109.5	C7—N2—H2C	109.3
C6—C5—H5B	109.5	C6—N2—H2C	109.3
H5A—C5—H5B	108.1	C7—N2—H2D	109.3
N2—C6—C5	109.93 (14)	C6—N2—H2D	109.3
N2—C6—H6A	109.7	H2C—N2—H2D	108.0
C5—C6—H6A	109.7	C4—O1—C1	110.33 (13)
N2—C6—H6B	109.7	C5—O2—C8	110.38 (12)
O1—C1—C2—N1	−58.22 (18)	C8—C7—N2—C6	−53.66 (19)
N1—C3—C4—O1	57.4 (2)	C5—C6—N2—C7	52.48 (19)
O2—C5—C6—N2	−55.95 (19)	C3—C4—O1—C1	−58.9 (2)
N2—C7—C8—O2	58.34 (18)	C2—C1—O1—C4	59.74 (19)
C4—C3—N1—C2	−56.12 (19)	C6—C5—O2—C8	61.60 (19)
C1—C2—N1—C3	56.46 (18)	C7—C8—O2—C5	−62.79 (19)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*C*···Cl1	0.90	2.39	3.1819 (15)	148
N1—H1*D*···O2[i]	0.90	1.97	2.8294 (19)	160
N2—H2*C*···O1[ii]	0.90	2.47	3.0577 (18)	123
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Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*+1, −*y*+1/2, *z*−1/2; (iii) −*x*+1, *y*−1/2, −*z*+1/2; (iv) *x*+1, *y*−1, *z*.