O—C(1)—N(1*a*)	129.2 (2)	O—C(1)—C(1*a*)	118.9 (2)
N(1)—C(2)—C(3)	105.2 (2)	N(2)—C(3)—C(2)	107.7 (2)
S—C(4)—N(3)	178.7 (2)		

All crystallographic computations were performed using the *SHELX76* program package (Sheldrick, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1106). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trichloro[(1*H*-benzimidazol-2-ylmethyl)(ethyl)ammonium-*N*^{3}]cobalt(II)

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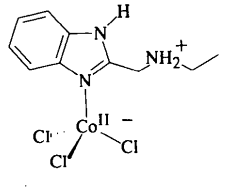
Abstract

The title compound, $[CoCl_3(C_{10}H_{14}N_3)]$, has slightly distorted tetrahedral geometry with monodentate coordination of the protonated ligand. The three Co—Cl distances are 2.2665 (7), 2.2615 (9) and 2.2712 (10) Å. The Co—N distance is 2.029 (2) Å. Antiparallel pairwise packing of molecules allows effective hydrogen bonding of the chloro ligands with both the benzimidazole N [3.439 (2) and 3.699 (2) Å] and ammonium N [3.220 (2) and 3.240 (2) Å] atoms. The respective Cl···H separations are 2.76, 2.90, 2.29 and 2.47 Å.

Comment

As a part of our study of the formation of dinuclear unsymmetrical cobalt(II) complexes, we are investigating the coordination chemistry of cobalt(II) with benzimidazole-containing ligands, which are biologically relevant surrogates for histidine. This type of modeling is of some relevance to bioinorganic chemists, because Co^{II} is used as a spectroscopic or NMR probe for structural changes in reconstituted metalloproteins (Elgren, Ming & Que, 1994; Bertini, Turano & Vila, 1993), as well as being present in the active site of cobalt-dependent methionine aminopeptidase, a non-cobalamin metalloprotein with a dinuclear cobalt species (Roderick & Matthews, 1993). We observed the selective cleavage of the C—N bond linking the 1*H*-benzimidazol-2-ylmethyl and 2-(aminomethyl) moieties by the reaction of Co^{II} perchlorate with a potentially dinucleating unsymmetrical ligand, 6-[bis(1*H*-benzimidazol-2-ylmethyl)aminomethyl]-2-[*N*-(1*H*-benzimidazol-2-ylmethyl)-*N*-(phenylmethyl)aminomethyl]-4-methylphenol (Kamaras, 1994). Site-selective and quantitative C—N bond cleavage in a cobalt(III) polyamine has been observed and a radical reaction mechanism proposed (Calafat & Marzilli, 1993). In order to elucidate whether cleavage of the C—N bond is facilitated by a dinuclear cobalt(II) species or is a typical reaction of cobalt(II) perchlorate with *N*-(1*H*-benzimidazol-2-ylmethyl)alkylamines, we reacted cobalt(II) perchlorate with *N*-(1*H*-benzimidazol-2-ylmethyl)ethylamine. No cleavage was observed and crystals of the title compound, (I), were obtained instead.



(I)

The Co^{II} atom has distorted tetrahedral coordination with three chloride ligands and a 1*H*-benzimidazole ligand. The crystal structure together with the labeling scheme is shown in Fig. 1. The uncoordinated secondary amino group is protonated and compensates the negative charge of the Co^{II}Cl$_3^-$ moiety. The Co atom is displaced from the benzimidazole ligand mean plane (unweighted mean deviation 0.008 Å) by 0.119 (1) Å. The crystal packing (Fig. 2) shows an antiparallel orientation of molecules, allowing effective hydrogen bonding and van der Waals interactions.

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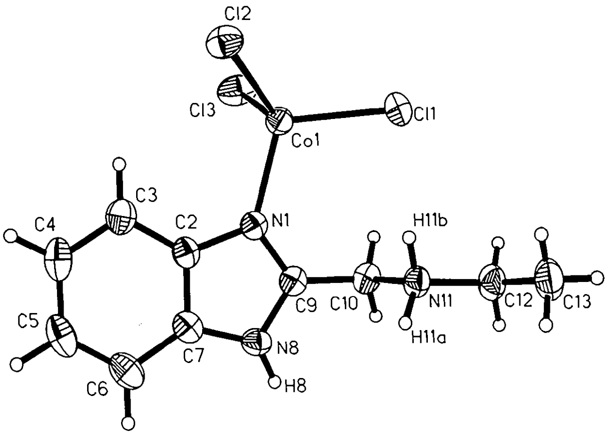

Fig. 1. Molecular structure of the title compound showing 50% probability displacement ellipsoids.

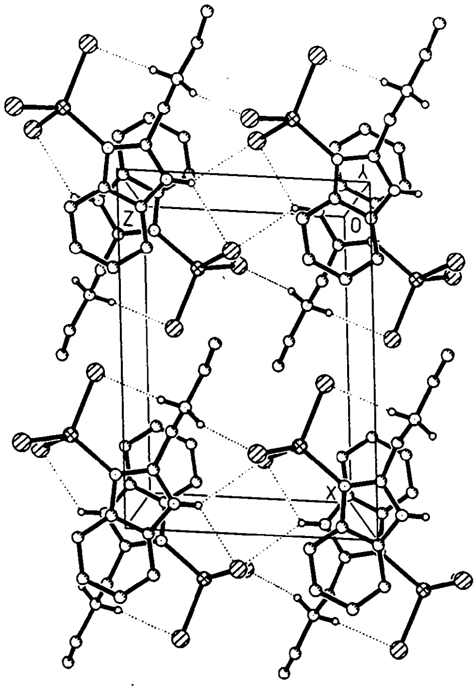

Fig. 2. Packing diagram viewed down the *b* axis. All H atoms attached to C atoms are omitted for clarity. Dotted lines represent hydrogen bonds.

There is an intramolecular hydrogen bond between the chloro ligand Cl1 and one ammonium H atom [Cl1···N11 3.240 (2) Å], and an intermolecular hydrogen bond between the chloro ligand Cl2 and the ammonium H atom of the neighboring molecule [Cl2···N11(x, y, $z+1$) 3.220 (2) Å]. The chloro ligand Cl3 forms two very weak intermolecular hydrogen bonds with the benzimidazole H atoms [Cl3···N8(x, y, $z+1$) 3.699 (2) Å and Cl3···N8($-x$, $-y$, $1-z$) 3.439 (2) Å]. The different degree of hydrogen bonding of the chloro ligands correlates with the increase in the Co—Cl distance in the order Co1—Cl3 [2.2615 (9) Å], Co1—Cl1 [2.2665 (7) Å] to Co1—Cl2 [2.2712 (10) Å]. Comparison with reported structures of tetrahedrally coordinated cobalt(II) complexes having a $\mathrm{Cl_3N}$ donor set shows that the Co—Cl [average 2.266 (2) Å] and Co—N [2.029 (2) Å] distances of the title complex are within the observed ranges of 2.22–2.26 Å for Co—Cl and 2.02–2.05 Å for Co—N distances, respectively (Table 3). The larger N11—Co1—Cl2 and Cl1—Co1—Cl3 angles [115.66 (6) and 115.54 (3)°, respectively] demonstrate the slight distortion from ideal tetrahedral geometry. Bond distances and angles for the benzimidazole and alkylammonium moieties have typical values (Cooley, 1994; Kamaras, 1994; Suzuki, Kanatomi & Murase, 1984).

Experimental

$[\mathrm{Co(ClO_4)_2].6H_2O}$ (150 mg, 0.403 mmol) was added to 2-(ethylaminomethyl)-1*H*-benzimidazole dihydrochloride (100 mg, 0.403 mmol) (Bloom & Day, 1939) dissolved in 10 ml of absolute ethanol, with stirring. Blue crystals (0.071 g, 81% yield) formed upon standing overnight.

Crystal data

$[\mathrm{CoCl_3(C_{10}H_{14}N_3)}]$
$M_r = 341.52$
Monoclinic
$P2_1/c$
$a = 10.9200\,(10)$ Å
$b = 16.409\,(3)$ Å
$c = 7.753\,(6)$ Å
$\beta = 93.89\,(3)°$
$V = 1386.0\,(11)$ Å^3
$Z = 4$
$D_x = 1.637$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 5$–$15°$
$\mu = 1.797$ mm^{-1}
$T = 193\,(2)$ K
Plate
0.4 × 0.3 × 0.1 mm
Dark blue

Data collection

Siemens *P*4/*RA* four-circle diffractometer
ω scans
Absorption correction: none
3137 measured reflections
2413 independent reflections
2246 observed reflections [$I > 2\sigma(I)$]

$R_{\mathrm{int}} = 0.0208$
$\theta_{\mathrm{max}} = 25°$
$h = -12 \rightarrow 12$
$k = -19 \rightarrow 1$
$l = -1 \rightarrow 9$
3 standard reflections monitored every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.0300$
$wR(F^2) = 0.0861$
$S = 1.046$
2410 reflections
157 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.8951P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\mathrm{max}} = 0.002$
$\Delta\rho_{\mathrm{max}} = 0.305$ e Å^{-3}
$\Delta\rho_{\mathrm{min}} = -0.537$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Co1	0.22861 (3)	0.10592 (2)	0.21894 (4)	0.02805 (13)
Cl1	0.42480 (6)	0.10832 (4)	0.33476 (9)	0.0403 (2)
Cl2	0.20637 (6)	0.21211 (4)	0.03152 (8)	0.0374 (2)
Cl3	0.17483 (7)	−0.00638 (4)	0.06254 (9)	0.0474 (2)
N1	0.1129 (2)	0.10510 (10)	0.4130 (3)	0.0272 (4)
C2	−0.0101 (2)	0.12886 (14)	0.3950 (3)	0.0283 (5)
C3	−0.0789 (2)	0.16007 (15)	0.2514 (3)	0.0371 (6)
C4	−0.2011 (2)	0.1759 (2)	0.2721 (4)	0.0420 (6)
C5	−0.2537 (2)	0.1624 (2)	0.4305 (4)	0.0439 (6)
C6	−0.1863 (2)	0.1324 (2)	0.5729 (4)	0.0415 (6)
C7	−0.0629 (2)	0.11553 (13)	0.5515 (3)	0.0312 (5)
N8	0.0298 (2)	0.08442 (12)	0.6624 (3)	0.0319 (4)
C9	0.1322 (2)	0.07925 (13)	0.5748 (3)	0.0276 (5)
C10	0.2514 (2)	0.04938 (13)	0.6555 (3)	0.0307 (5)
N11	0.3299 (2)	0.11941 (12)	0.7211 (3)	0.0303 (4)
C12	0.4485 (2)	0.0911 (2)	0.8103 (4)	0.0394 (6)
C13	0.5295 (2)	0.1630 (2)	0.8605 (4)	0.0485 (7)

Table 2. *Selected geometric parameters and hydrogen-bonding geometry* (Å, °)

Co1—N1	2.029 (2)	Co1—Cl2	2.2712 (10)
Co1—Cl3	2.2615 (9)	C10—N11	1.502 (3)
Co1—Cl1	2.2665 (7)	N11—C12	1.499 (3)
N1—Co1—Cl3	103.88 (6)	Cl3—Co1—Cl2	105.64 (5)
N1—Co1—Cl1	109.03 (7)	Cl1—Co1—Cl2	107.30 (3)
Cl3—Co1—Cl1	115.51 (3)	C9—C10—N11	110.7 (2)
N1—Co1—Cl2	115.74 (6)	C12—N11—C10	112.0 (2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11B···Cl1	0.88	2.47	3.240 (2)	147
N11—H11A···Cl2^{i}	0.98	2.29	3.220 (2)	157
N8—H8···Cl3^{i}	0.94	2.90	3.699 (2)	144
N8—H8···Cl3^{ii}	0.94	2.76	3.439 (2)	130

Symmetry codes: (i) $x, y, 1 + z$; (ii) $-x, -y, 1 - z$.

Table 3. *Comparison of the* Co—Cl *and* Co—N *bond distances for mononuclear* Co^{II} *tetrahedral complexes having a* 3Cl + 1N *coordination donor set*

*M*1 is bis(acetonitrile)(15-crown-5)–Co^{II}, MeCN is acetonitrile, *M*2 is 2,6-dimorpholino-4-phenyl-1,3,5-oxadiazinium, *L*1 is tetrahydrothiamine, *M*3 is tris(pyridine)[salicylaldehyde-(*S*)-methylisothiosemicarbazonato]–Co^{II} and *L*2 is (1*H*-benzimidazol-2-ylmethyl)ethylammonium.

	Co—Cl	Co—N	Reference
[$CoCl_3$(thiamine)]	2.267 (1) 2.283 (1) 2.260 (1)	2.046 (3)	(*a*)
[*L*1H]$^+$.[$CoCl_3$*L*1]$^-$	2.287 (1) 2.273 (2) 2.260 (1)	2.050 (5)	(*b*)
[*M*3]$^+$.[$CoCl_3$(pyridine)]$^-$	2.261 (4) 2.248 (3) 2.246 (3)	2.052 (5)	(*c*)
[*M*2]$^+$.[$CoCl_3$MeCN]$^-$	2.249 (2) 2.249 (2) 2.229 (2)	2.047 (2)	(*d*)
[*M*1]$^+$.2[$CoCl_3$MeCN]$^-$	2.239 (3) 2.230 (3) 2.225 (3)	2.02 (1)	(*e*)
[$CoCl_3$*L*2]	2.2665 (7) 2.2712 (10) 2.2615 (9)	2.029 (2)	(*f*)

References: (*a*) Aoki, Hu, Yamazaki & Adeyemo (1990); (*b*) Bau *et al.* (1988); (*c*) Divjakovic, Leovac, Ribar, Argay & Kalman (1982); (*d*) Hartung, Beyer, Gutierrez-Puebla, Fernandez & Olk (1992); (*e*) Kireeva, Bulychev, Strelsova, Belsky & Dunin (1992); (*f*) this study.

All H atoms were clearly visible from difference Fourier maps. Methyl H atoms were located using a ΔF synthesis with toroidal averaging and were included in subsequent calculations as a group of idealized tetrahedral geometry riding on the methyl C atom with isotropic temperature factors equal to $1.5U_{eq}$. Nitrogen H atoms, located from a ΔF map, were refined isotropically. All other H atoms were placed in geometrically calculated positions and were constrained to ride on their respective C atoms with isotropic temperature factors equal to $1.2U_{eq}$.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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