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Bis(1-methylcytosinium) Tetrachlorocobaltate(II), $(C_5H_8N_3O)_2[CoCl_4]$

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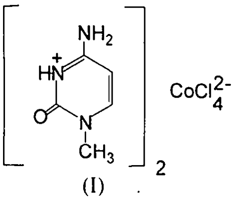
Abstract

The 1-methylcytosinium cations (4-amino-2-oxo-1,2-dihydro-3H^+-pyrimidinium) are protonated at N3. The tetrachlorocobaltate anion has distorted tetrahedral geometry with average Co—Cl bonds of 2.27 (1) Å and Cl—Co—Cl angles in the range 104.7-117.6°.

Comment

The title compound, (I), was originally obtained in low yield when coordination of Co^{II} to 1-MeC was attempted at pH 6. As expected, the yield of the compound increased substantially as the pH was lowered (see *Experimental*).



(I)

There are no unusual structural features in the 1-methylcytosinium cation and the geometry is very similar to that of the corresponding perchlorate salt (Rossi, Caradonna, Marzilli & Kistenmacher, 1979), and close to that of other protonated cytosines (Taylor & Kennard, 1982). The geometry of the $[CoCl_4]^{2-}$ anion deviates from ideal tetrahedral (Lindroos & Lumme, 1991; Søtofte & Nielsen, 1981; Campayo, Navarro, Cano & Foces-Foces, 1987), possibly as a consequence of the involvement of all four Cl atoms in hydrogen bonding; the shortest contact is between Cl1 and H6 of the cytosinium [2.71 (3) Å].

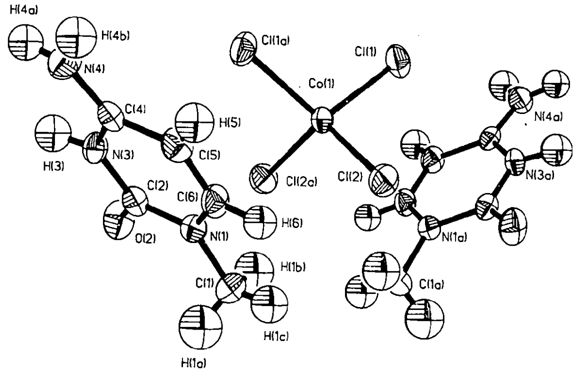


Fig. 1. View of bis(1-methylcytosinium) tetrachlorocobaltate(II) with atomic numbering scheme.

Experimental

The title compound was prepared by mixing 1-methylcytosine ($C_5H_7N_3O$) and $CoCl_2.6H_2O$ in a 2:1 ratio in water. The pH was adjusted to 1.45 with 0.1 *M* HCl. The red solution was evaporated until the free ligand crystallized. After separation of the free ligand by filtration, the solution was allowed to evaporate completely. The blue precipitate obtained was recrystallized from ethanol and light blue prisms were isolated and dried in air (yield 72%).

Crystal data

$(C_5H_8N_3O)_2[CoCl_4]$
$M_r = 453.02$
Monoclinic
$C2/c$
$a = 12.561$ (3) Å
$b = 8.075$ (2) Å
$c = 17.855$ (3) Å
$\beta = 109.38$ (2)°
$V = 1708.1$ (7) Å^3
$Z = 4$
$D_x = 1.762$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 26 reflections
$\theta = 9.6$-34.4°
$\mu = 1.647$ mm^{-1}
$T = 293$ (2) K
Prism
0.3 × 0.16 × 0.14 mm
Light blue

Data collection

Nicolet four-circle diffractometer
Profile-fitted ω scans
Absorption correction: empirical
$T_{min} = 0.934$, $T_{max} = 1.0$
1565 measured reflections
1511 independent reflections
1202 observed reflections $[I > 2\sigma(I)]$

$R_{int} = 0.0234$
$\theta_{max} = 25.06°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 21$
3 standard reflections monitored every 100 reflections intensity variation: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0277$
$wR(F^2) = 0.0577$
$S = 1.099$
1511 reflections
137 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0300P)^2 + 0.6490P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 0.245$ e Å^{-3}
$\Delta\rho_{min} = -0.315$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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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	0.05959 (6)	1/4	0.02601 (15)
Cl2	0.15071 (6)	0.20470 (9)	0.32712 (4)	0.0386 (2)
Cl1	−0.05398 (6)	−0.09866 (9)	0.33682 (4)	0.0395 (2)
N1	0.1342 (2)	0.3240 (3)	0.12121 (12)	0.0288 (5)
N3	0.1072 (2)	0.1459 (3)	0.01372 (13)	0.0283 (5)
C4	0.2122 (2)	0.0804 (3)	0.04387 (14)	0.0272 (6)
C6	0.2395 (2)	0.2592 (4)	0.1537 (2)	0.0324 (6)
C2	0.0621 (2)	0.2646 (3)	0.05027 (15)	0.0290 (6)
C5	0.2805 (2)	0.1406 (4)	0.1189 (2)	0.0332 (6)
O2	−0.0347 (2)	0.3119 (3)	0.01993 (12)	0.0432 (5)
N4	0.2457 (2)	−0.0294 (3)	0.0025 (2)	0.0365 (6)
C1	0.0951 (3)	0.4617 (4)	0.1587 (2)	0.0395 (7)

Table 2. *Selected geometric parameters* (Å, °)

Co1—Cl2	2.2628 (10)	N3—C2	1.383 (4)
Co1—Cl1	2.2791 (8)	C4—N4	1.309 (4)
N1—C6	1.359 (3)	C4—C5	1.416 (4)
N1—C2	1.375 (3)	C6—C5	1.335 (4)
N1—C1	1.464 (4)	C2—O2	1.217 (3)
N3—C4	1.355 (3)		
Cl2—Co1—Cl2^i	117.62 (5)	N4—C4—N3	119.5 (2)
Cl2—Co1—Cl1	104.73 (3)	N4—C4—C5	124.0 (3)
Cl2^i—Co1—Cl1	109.05 (3)	N3—C4—C5	116.4 (2)
Cl1—Co1—Cl1^i	111.80 (5)	C5—C6—N1	123.3 (2)
C6—N1—C2	120.6 (2)	O2—C2—N1	123.8 (3)
C6—N1—C1	121.6 (2)	O2—C2—N3	120.9 (2)
C2—N1—C1	117.8 (2)	N1—C2—N3	115.3 (2)
C4—N3—C2	125.5 (2)	C6—C5—C4	118.7 (2)
C2—N3—C4—N4	−178.7 (3)	C1—N1—C2—N3	173.9 (2)
C2—N3—C4—C5	−0.4 (4)	C4—N3—C2—O2	−177.3 (3)
C2—N1—C6—C5	2.1 (4)	C4—N3—C2—N1	3.3 (4)
C1—N1—C6—C5	−175.8 (3)	N1—C6—C5—C4	1.1 (4)
C6—N1—C2—O2	176.5 (3)	N4—C4—C5—C6	176.4 (3)
C1—N1—C2—O2	−5.5 (4)	N3—C4—C5—C6	−1.9 (4)
C6—N1—C2—N3	−4.1 (4)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Data collection: *P3/PC Diffractometer Program* (Siemens, 1989). Cell refinement: *P3/PC Diffractometer Program.* Data reduction: *SHELXTL-Plus XDISK* (Sheldrick, 1987). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*. Absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C). The space group was checked with *MISSYM* (Le Page, 1987).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71841 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1122]

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[Li{N(Me$_3$SiNPPh$_2$)$_2$}]$_2$.2.5C$_7$H$_8$

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Abstract

The structure of the title compound bis{μ-*P*,*P*'-imido-1:2κ^2*N*''-bis[*P*,*P*-diphenyl-*N*-(trimethylsilyl)phosphine imido](1−)-1κ*N*,1κ*P*:2κ*N*',2κ*P*'}dilithium(*Li*—*Li*), [Li{N[(CH$_3$)$_3$SiNP(C$_6$H$_5$)$_2$]$_2$}]$_2$.2.5C$_7$H$_8$ is reported. There is one molecule of the dimer in the asymmetric unit, two disordered molecules of the toluene solvent close to a centre of symmetry and another disordered solvent molecule situated on a twofold axis.

Comment

Organolithium compounds have received increasing attention in the past few years (see Gregory, Schleyer & Snaith, 1991, for a recent review), especially the amidolithium compounds (R_2NLi), mainly because of their use as proton abstractors in both organic and inorganic syntheses. The title compound, (I) (Pandey & Roesky, 1994; Steiner & Stalke, 1993), is a derivative of the monomer [{Ph$_2$P(Me$_3$SiN)$_2$}Li(thf)$_2$], and is stabilized by a butterfly-like ligand conformation with pseudo-noncrystallographic C_2 symmetry and an Li—Li distance of 2.79 (1) Å.