Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Two-dimensional network of C–H···Cl–Co hydrogen bonds in the structure of 1,1,4,4-tetraisopropylpiperazinium tetrachlorocobaltate(II)

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Received 26 July 2001
Accepted 30 July 2001
Online 10 August 2001

The reaction of (2-hydroxyethyl)diisopropylammonium chloride with $CoCl_2{\cdot}6H_2O$ has resulted in the unusual formation of a quaternary piperazinium salt with the formula (tippipz)[$CoCl_4$], where tippipz is tetraisopropylpiperazinium ($C_{16}H_{36}N_2^{2+}$). The structure of this compound consists of sheets of organic ammonium dications and inorganic dianions formed by C—H···Cl hydrogen bonds.

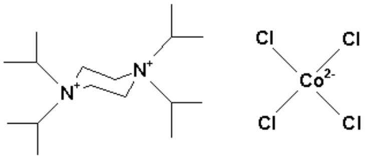
Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.129
Data-to-parameter ratio = 29.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The existence of C—H···Cl hydrogen bonds has been recently reviewed by Aakeröy *et al.* (1999) through a systematic data mining and statistical analysis of the Cambridge Structural Database (Allen & Kennard, 1993). It has been shown that chloride anions are better hydrogen-bond acceptors than neutral chlorine-containing molecules; however, no attention has been given to Cl(—M) groups as potential hydrogen-bond acceptors. The MX_4^{2-} anions in organic–inorganic hybrid solids with the general formula A_2MX_4, in which A (or A_2) is an organic ammonium cation (or ammonium dication), M is a divalent metal ion and X is Cl^- or Br^-, are capable of participating in C—H···Cl, as well as N—H···Cl, hydrogen bonding with organic cations. This behaviour has been reported by several groups (Barbour *et al.*, 1996; Feist *et al.*, 1995; Hitchcock *et al.*, 1993; Mahmoudkhani & Langer, 1999*a*,*b*; Waśkowska, 1994). Indeed, the hydrogen bonding is of importance in assigning and describing some of the microscopic and macroscopic properties in this class of compounds (Mahmoudkhani, 1999). Gillon *et al.* (2000) have recently demonstrated the use of N—H···Cl—M hydrogen-bond synthons in controlling the solid-state structure of some halometallates and in the design of supramolecular aggregates. They have concluded that M—Cl moieties are much better hydrogen-bond acceptors than their organic analogues, C—Cl.



(I)

The title compound, (I), crystallizes in the monoclinic system with space group $P2_1/n$ (No. 14). The asymmetric unit contains an organic dication and an inorganic dianion, as shown in Fig. 1. The coordination geometry of the Co^{II} ion is

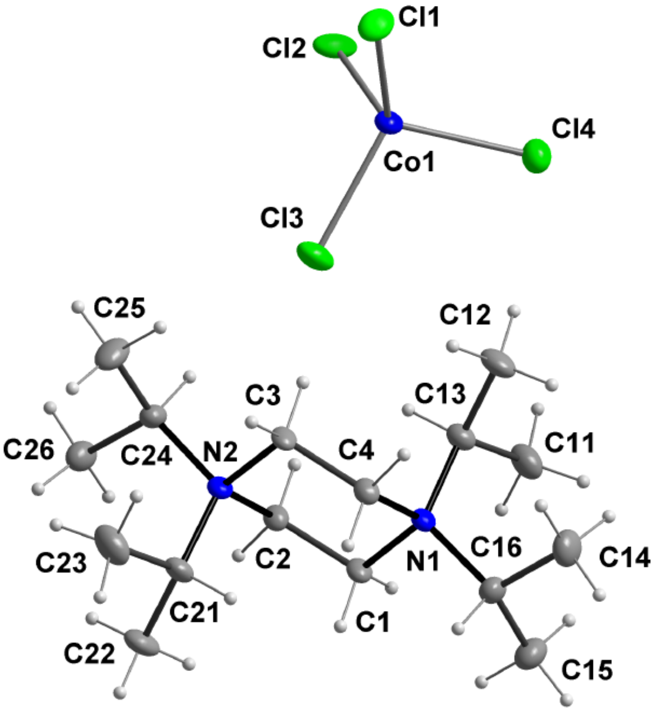


Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

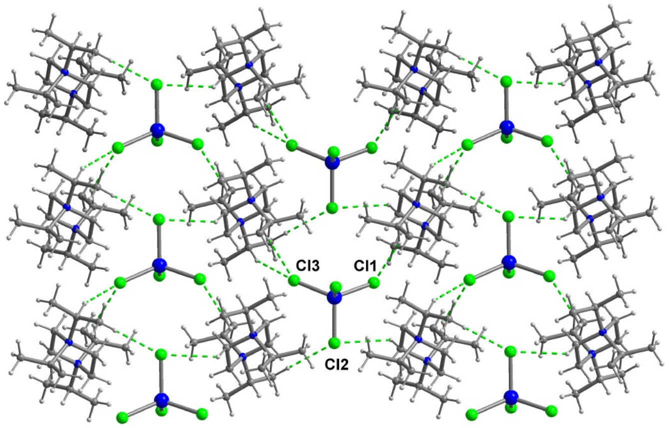


Figure 2
Representation of a hydrogen-bonded sheet in the structure of (I). Notice that only three Cl atoms are involved in the C—H···Cl hydrogen bonding.

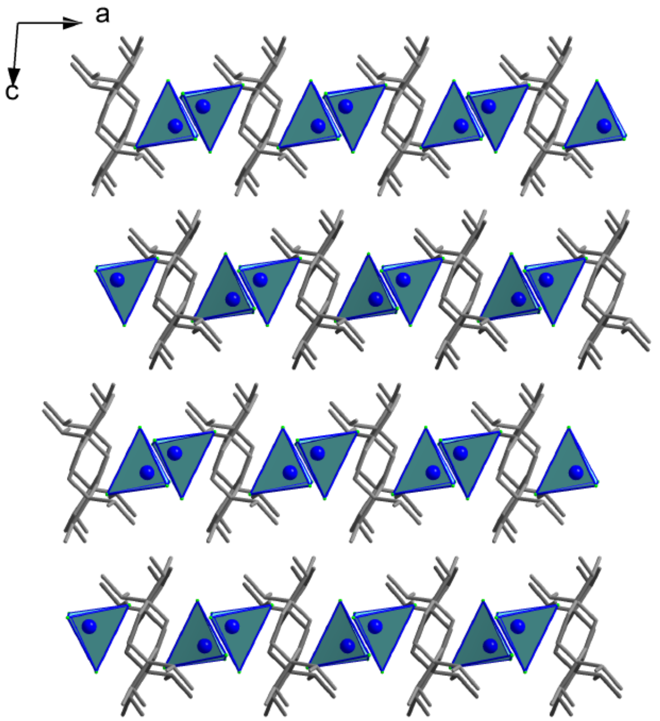


Figure 3
A view along the *b* axis showing parallel sheets, each comprising alternating orientations of $CoCl_4$ tetrahedra.

distorted tetrahedral, with a mean Co—Cl bond distance of 2.282 (9) Å. Only three Cl atoms are involved in hydrogen bonds of the C—H···Cl type with C atoms of neighbouring organic dications, while the Cl4 atom does not act as a hydrogen-bond acceptor. However, atoms Cl3 and Cl2 are acceptors of two hydrogen bonds each from atoms C13 and C24, and atoms C25 and C1, respectively (see Table 2 for the geometry). The C—H···Cl hydrogen bonds link organic dications and inorganic dianions together to form sheets parallel to the *ab* plane (see Fig. 2). In each sheet, $CoCl_4$ tetrahedra adopt alternating up and down orientations parallel to the *b* axis while having the same arrangement parallel to the *a* axis. There is no significant interaction between the sheets thus the solid material exhibits a layered structure. In comparison with the crystal structure of bis[(2-chloroethyl)diisopropylammonium] tetrachlorocobaltate (Mahmoudkhani & Langer, 1999*b*), the title compound shows no disorder even at room temperature. This may be attributed to the relative strengths arising from the C—H···Cl hydrogen bonds.

Experimental

The synthesis and structure of (2-hydroxyethyl)diisopropylammonium chloride, (II), is described elsewhere (Mahmoudkhani & Langer, 1999*c*); ^1H NMR (400 MHz, D_2O): δ 1.33 (*d*, 6.4, CH_3), 1.34 (*d*, 6.4, CH_3), 3.27 (*t*, 5.6, CH_2—N), 3.76 (*m*, 6.4, CH), 3.86 (*t*, 5.6, CH_2—O). In a small round-bottomed flask with a capacity of 25 ml, 110 mmol of (II) was added to a solution of 50 mmol of $CoCl_2 \cdot 6H_2O$ in ethanol (15 ml). The mixture was refluxed for about 1 h. Solvents were removed by azeotropic distillation with toluene. After gently removing toluene under vacuum, a blue highly viscous oily material was obtained which was kept in a desiccator over silica gel; ^1H NMR (400 MHz, $CDCl_3$): δ_H 1.40 (*d*, 6.4), 1.52 (*d*, 6.4), 3.05 (*s*, br), 3.60 (*s*, br), 4.20 (*s*, br). Blue plate crystals of the title compound suitable for diffraction analysis were obtained after 8 months growth from the oily product (yield 20–30%).

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Crystal data

$(C_{16}H_{36}N_2)[CoCl_4]$
$M_r = 457.20$
Monoclinic, $P2_1/n$
$a = 7.1245\ (3)$ Å
$b = 17.1830\ (7)$ Å
$c = 17.3367\ (7)$ Å
$\beta = 94.640\ (1)^\circ$
$V = 2115.41\ (15)$ Å^3
$Z = 4$

$D_x = 1.436$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5489 reflections
$\theta = 1$–32°
$\mu = 1.32$ mm^{-1}
$T = 183\ (2)$ K
Plate, blue
0.60 × 0.50 × 0.04 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min} = 0.505$, $T_{\max} = 0.949$
24 763 measured reflections

7391 independent reflections
4998 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 32.8^\circ$
$h = -10 \rightarrow 10$
$k = -26 \rightarrow 24$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.129$
$S = 0.99$
7391 reflections
252 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2{\rm P}]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.92$ e Å^{-3}
$\Delta\rho_{\min} = -1.08$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—Cl1	2.2904 (6)	Co1—Cl3	2.2819 (6)
Co1—Cl2	2.2688 (6)	Co1—Cl4	2.2883 (6)
Cl2—Co1—Cl1	104.74 (2)	Cl3—Co1—Cl1	118.33 (3)
Cl2—Co1—Cl3	108.33 (2)	Cl3—Co1—Cl4	106.25 (2)
Cl2—Co1—Cl4	109.37 (3)	Cl4—Co1—Cl1	109.63 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1B···Cl2	0.99	2.80	3.319 (2)	113
C13—H13···Cl3$^{\rm i}$	1.00	2.78	3.665 (2)	148
C21—H21···Cl1$^{\rm ii}$	1.00	2.60	3.482 (2)	147
C24—H24···Cl3$^{\rm i}$	1.00	2.68	3.628 (2)	157
C25—H25B···Cl2$^{\rm iii}$	0.98	2.74	3.713 (2)	174

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1+x, y, z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

The H atoms were constrained to idealized geometries using the appropriate riding model.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2001); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000).

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