

3,3'-Dimethyl-1,1'-methylenediimidazolium tetrachlorocobaltate(II)

 A. Zeller,^a E. Herdtweck^{b*} and T. Strassner^a
^aInstitut für Organische Chemie, Lehrstuhl für Physikalische Organische Chemie, Technische Universität Dresden, Bergstraße 66, D-01062 Dresden, Germany, and

^bDepartment Chemie, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching bei München, Germany
Correspondence e-mail: eberhardt.herdtweck@ch.tum.de

Received 5 November 2004

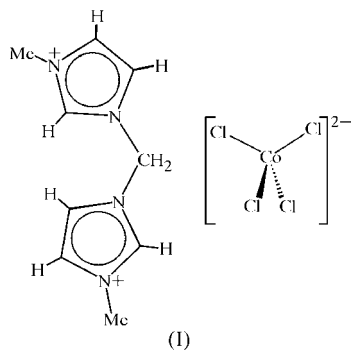
Accepted 22 November 2004

Online 18 December 2004

The title compound, (C₉H₁₄N₄)[CoCl₄], a methylene-bridged bis-imidazolium salt containing a tetrachlorocobaltate anion, is one of the first examples where an alkyl-bridged bis-imidazolium compound could be structurally characterized. Short C—H···Cl contacts between the imidazolium C—H bonds and the Cl atoms of the counter-anion build up a three-dimensional network and indicate that the C—H bonds are strongly polarized.

Comment

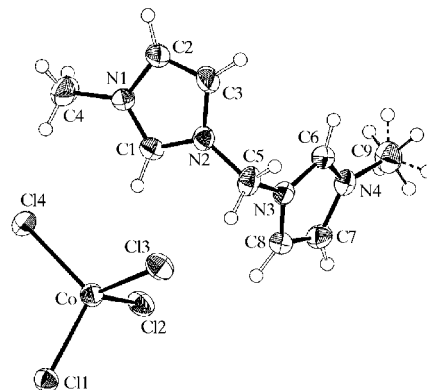
Metal complexes of N-heterocyclic carbenes (NHC) have been shown to be extremely versatile and stable catalysts for a wide range of reactions (Herrmann, 2002). In particular, chelating NHC complexes have been shown to possess enhanced thermal stability, leading to remarkable catalytic properties. For instance, bridged palladium biscarbene complexes have been successfully applied in various catalytic reactions (*e.g.* C—C coupling reactions; Herrmann *et al.*, 1995,



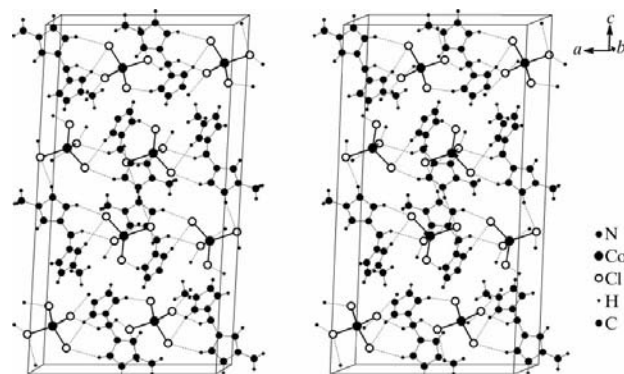
1998), and in particular to C—H activation (Muehlhofer, Strassner & Herrmann, 2002). A convenient synthesis of bridged NHC complexes involves the conversion of basic metal precursors, such as palladium(II) acetate, with a bridged imidazolium salt (Herrmann *et al.*, 1998). We report here the structural characterization of a methylene-bridged imidazolium salt with a tetrachlorocobaltate counter-anion, (I) (Fig. 1).

Previously, only a few reports of solid-state structures of imidazolium salts containing transition metal–halide anions have been published (Dullius *et al.*, 1998; Ortwerth *et al.*, 1998; Hasan *et al.*, 1999, 2001), including the related 1-ethyl-3-methylimidazolium tetrachlorocobaltate (Hitchcock *et al.*, 1993). They all show short contacts between imidazolium H atoms and the halide atoms of the anion, due to ionic interactions.

For steric reasons, the N—CH—N units in the two imidazole moieties point in opposite directions. The N1—C1 and N2—C1 (and N3—C6 and N4—C6) bonds are almost identical, which indicates delocalization within these bonds. The dihedral angle between the imidazole rings is 72.96 (9)°. The Co atom of the counter-anion is surrounded by four Cl[−] ions in a tetrahedral fashion [Co—Cl = 2.2679 (7)–2.2911 (7) Å]. As previously observed for analogous compounds, several short contacts are formed between C—H bonds and Cl atoms of the anion. In the case of (I), they are established by imidazolium ring H atoms, as well as by both H atoms of the methylene bridge and one H atom of the methyl group (Table 2). This shows a possible polarization of all C—H bonds adjacent to an N atom in an imidazolium salt, and not only of the central C—H bond in the N—CH—N unit, which is deprotonated during the formation of metal–NHC complexes.


Figure 1

A perspective view of (I), showing the atom-numbering scheme and the disorder in the C9 methyl group (dashed lines). Displacement ellipsoids are drawn at the 50% probability level.


Figure 2

A stereoview of the unit cell of (I), showing the hydrogen-bonding network.

As can be seen from Fig. 2 and Table 2, the most acidic H atoms take part in C—H...Cl contacts, which build up a bilayer structure parallel to the *ab* plane. Contacts such as C2—H21...Cl3^{iv} [symmetry code: (iv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$], which are longer but still within the sum of the relevant van der Waals radii (2.95 Å; Bondi, 1964), connect these layers into a three-dimensional network.

Experimental

The title compound was prepared by reaction of 1,1'-dimethyl-3,3'-methylenediimidazolium dibromide (Muehlhofer, Strassner, Herdtweck & Herrmann, 2002) with cobalt(II) chloride hexahydrate in refluxing tetrahydrofuran/ethanol (2:1) for 10 h. The resulting light-blue precipitate was isolated by filtration and washed with tetrahydrofuran (yield 73%). Elemental analysis revealed a 1:1 mixture of the tetrachloro- and corresponding tetrabromocobaltate compounds. Analysis calculated for C₉H₁₄Br₂Cl₂CoN₄: C 23.10, H 3.02, N 11.97%; found: C 23.15, H 3.01, N 11.98%. Crystals of (I) were obtained selectively by slow diffusion of tetrahydrofuran into a solution of the product in dimethyl sulfoxide.

Crystal data

(C ₉ H ₁₄ N ₄)[CoCl ₄]	$D_x = 1.623 \text{ Mg m}^{-3}$
$M_r = 378.97$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3026 reflections
$a = 15.2885 (1) \text{ \AA}$	$\theta = 1.5\text{--}25.2^\circ$
$b = 7.1995 (1) \text{ \AA}$	$\mu = 1.78 \text{ mm}^{-1}$
$c = 28.2539 (3) \text{ \AA}$	$T = 173 (1) \text{ K}$
$\beta = 94.0770 (4)^\circ$	Plate, light blue
$V = 3102.02 (6) \text{ \AA}^3$	$0.38 \times 0.20 \times 0.05 \text{ mm}$
$Z = 8$	

Data collection

Nonius KappaCCD area-detector diffractometer	2784 independent reflections
φ and ω rotation scans	2509 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan, (DENZO; Nonius, 2001)	$R_{\text{int}} = 0.044$
$T_{\text{min}} = 0.562, T_{\text{max}} = 0.916$	$\theta_{\text{max}} = 25.2^\circ$
32 195 measured reflections	$h = -18 \rightarrow 18$
	$k = -8 \rightarrow 8$
	$l = -33 \rightarrow 33$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 4.883P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.067$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
2784 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
166 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Co—Cl1	2.2805 (7)	N2—C5	1.461 (3)
Co—Cl2	2.2911 (7)	N3—C5	1.457 (3)
Co—Cl3	2.2679 (7)	N3—C6	1.333 (3)
Co—Cl4	2.2746 (7)	N3—C8	1.380 (3)
N1—C1	1.313 (3)	N4—C6	1.324 (3)
N1—C2	1.365 (3)	N4—C7	1.376 (3)
N1—C4	1.467 (4)	N4—C9	1.468 (3)
N2—C1	1.327 (3)	C2—C3	1.336 (4)
N2—C3	1.374 (3)	C7—C8	1.340 (3)
Cl1—Co—Cl2	110.45 (2)	Cl2—Co—Cl3	105.49 (2)
Cl1—Co—Cl3	113.94 (2)	Cl2—Co—Cl4	108.69 (2)
Cl1—Co—Cl4	109.15 (2)	Cl3—Co—Cl4	108.95 (2)

Table 2

Hydrogen-bond geometry (Å, °).

	D—H	H...A	D...A	D—H...A
C1—H11...Cl2	0.95	2.72	3.606 (2)	155
C2—H21...Cl3 ⁱ	0.95	2.91	3.557 (3)	127
C3—H31...Cl4 ⁱⁱ	0.95	2.65	3.524 (3)	153
C4—H42...Cl3 ⁱⁱⁱ	0.98	2.73	3.479 (3)	134
C5—H51...Cl1 ⁱⁱ	0.99	2.73	3.484 (2)	133
C5—H52...Cl3	0.99	2.71	3.573 (3)	145
C7—H71...Cl1 ^{iv}	0.95	2.69	3.582 (2)	157
C8—H81...Cl2	0.95	2.76	3.556 (3)	141

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

The C9 methyl group is disordered over two sets of positions, with occupancies of 0.61 (3) and 0.39 (3). Methyl H atoms were located from difference Fourier syntheses and refined as part of rigid rotating groups, with C—H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C—H distances of 0.99 and 0.95 Å, respectively, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *KappaCCD Server Software* (Nonius, 2001); cell refinement: *DENZO* (Nonius, 2001); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

We are indebted to Professor W. A. Herrmann for his generous and continuous support of our work. We are grateful for financial support from Süd-Chemie International.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1598). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Dullius, J. E. L., Suarez, P. A. Z., Einloft, S., de Souza, R. F., Dupont, J., Fischer, J. & De Cian, A. (1998). *Organometallics*, **17**, 815–819.
- Hasan, M., Kozhevnikov, I. V., Siddiqui, M. R. H., Femoni, C., Steiner, A. & Winterton, N. (2001). *Inorg. Chem.* **40**, 795–800.
- Hasan, M., Kozhevnikov, I. V., Siddiqui, M. R. H., Steiner, A. & Winterton, N. (1999). *Inorg. Chem.* **38**, 5637–5641.
- Herrmann, W. A. (2002). *Angew. Chem. Int. Ed.* **41**, 1290–1309.
- Herrmann, W. A., Elison, M., Fischer, J., Koecher, C. & Artus, G. R. J. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2371–2374.
- Herrmann, W. A., Reisinger, C.-P. & Spiegler, M. (1998). *J. Organomet. Chem.* **557**, 93–96.
- Hitchcock, P. B., Seddon, K. R. & Welton, T. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2639–2943.
- Muehlhofer, M., Strassner, T., Herdtweck, E. & Herrmann, W. A. (2002). *J. Organomet. Chem.* **660**, 121–126.
- Muehlhofer, M., Strassner, T. & Herrmann, W. A. (2002). *Angew. Chem. Int. Ed.* **41**, 1745–1747.
- Nonius (2001). *KappaCCD Server Software* and *DENZO*. Nonius BV, Delft, The Netherlands.
- Ortwerth, M. F., Wyzlic, M. J. & Baughman, R. G. (1998). *Acta Cryst.* **C54**, 1594–1596.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.