1,4-Diazoniabicyclo[2.2.2]octane tetrachlorocobaltate

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Key indicators

Single-crystal X-ray study
$T = 120$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.032
wR factor = 0.078
Data-to-parameter ratio = 22.3

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

The title compound, $(C_6H_{14}N_2)[CoCl_4]$, is isostructural with $(C_6H_{14}N_2)[MCl_4]$ (M = Cu, Zn) and contains doubly protonated dabconium $C_6H_{14}N_2^{2+}$ cations and $[CoCl_4]^{2-}$ tetrahedra. These species interact by way of bifurcated N—H$\cdots$(Cl,Cl) hydrogen bonds to form corrugated chains. The chains interact by way of van der Waals forces and C—H$\cdots$Cl hydrogen bonds.

Comment

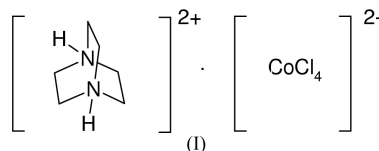The title compound, (I), arose as a side product during our synthetic investigations of organically templated cobalt phosphate networks (Cowley & Chippindale, 1999; Natarajan *et al.*, 2000). It is isostructural with $(C_6H_{14}N_2)[MCl_4]$ (M = Cu, Zn), as described by Brammer *et al.* (2002) and Viossat *et al.* (1984), for the copper and zinc congeners, respectively.


In (I), the $[CoCl_4]^{2-}$ tetrahedron shows slight geometrical deviations from regularity with d_{av}(Co—Cl) = 2.2746 (6) Å and θ_{av}(Cl—Co—Cl) = 109.49 (2)° [spread of angles = 104.56 (2)–114.76 (2)°]. The dabconium (1,4-diazoniabicyclo[2.2.2]octane) cation has typical geometrical parameters $[d_{av}$(N—C) = 1.502 (3) Å, d_{av}(C—C) = 1.530 (3) Å, θ_{av}(C—N—C) = 110.3 (2)° and θ_{av}(N—C—C) = 108.6 (2)°].

The component species in (I) interact by way of bifurcated N—H$\cdots$(Cl,Cl) hydrogen bonds (Table 2), resulting in each chloride ion acting as an acceptor with typical (Brammer *et al.*, 2001) geometrical parameters of d_{av}(N$\cdots$Cl) = 3.298 (2) Å and θ_{av}(N—H$\cdots$Cl) = 132°. The energetics of these interactions and their possible role as synthons in supramolecular chemistry are described in detail by Brammer *et al.* (2002). In (I), these bonds (Fig. 2) result in corrugated polymeric chains which propagate along [001]. The unit-cell packing perpendicular to the chains involves van der Waals forces (Fig. 3) and C—H$\cdots$Cl hydrogen bonds (Brammer *et al.*, 2002; Table 2), assuming these are not merely an artefact of the crystal packing.

Experimental

10 ml of 1 M CoCl$_2$ solution, 10 ml of 1 M H$_3$PO$_4$ solution and 0.5 g dabco (C$_6$H$_{12}$N$_2$) were mixed together in a plastic bottle and heated to 373 K for 24 h, resulting in a blue solution. The solution was cooled
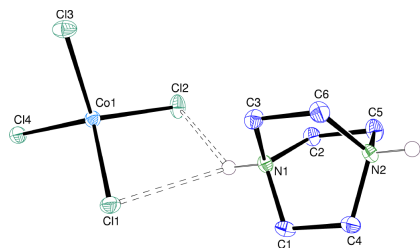
Figure 1
Asymmetric unit of (I) (50% probability displacement ellipsoids, arbitrary spheres for the H atoms, C—H H atoms omitted for clarity and hydrogen bonds indicated by dashed lines).

to room temperature, and plate crystals of (I) grew as water slowly evaporated from the increasingly viscous liquors over several weeks.

Crystal data

$(C_6H_{14}N_2)[CoCl_4]$	$D_x = 1.795$ Mg m^{-3}
$M_r = 314.92$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4880
$a = 9.4875$ (2) Å	reflections
$b = 6.7174$ (2) Å	$\theta = 2.9$–$27.5°$
$c = 18.3121$ (5) Å	$\mu = 2.35$ mm^{-1}
$\beta = 92.842$ (1)°	$T = 120$ (2) K
$V = 1165.62$ (5) Å^3	Plate, blue
$Z = 4$	$0.36 \times 0.22 \times 0.08$ mm

Data collection

Nonius KappaCCD diffractometer	2304 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.057$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(Blessing, 1995)	$h = -11 \rightarrow 12$
$T_{min} = 0.485$, $T_{max} = 0.835$	$k = -8 \rightarrow 8$
9112 measured reflections	$l = -23 \rightarrow 22$
2654 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$+ 0.0946P]$
$wR(F^2) = 0.078$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2654 reflections	$\Delta\rho_{max} = 0.57$ e Å^{-3}
119 parameters	$\Delta\rho_{min} = -0.74$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0121 (10)

Table 1
Selected geometric parameters (Å).

Co1—Cl1	2.2672 (6)	Co1—Cl2	2.2751 (6)
Co1—Cl3	2.2694 (6)	Co1—Cl4	2.2867 (6)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$Cl1	0.93	2.77	3.4175 (18)	128
N1—H1$\cdots$Cl2	0.93	2.46	3.1832 (18)	135
N2—H2$\cdots$Cl3^i	0.93	2.75	3.3866 (19)	127
N2—H2$\cdots$Cl4^i	0.93	2.46	3.2064 (18)	138
C1—H3$\cdots$Cl2^{ii}	0.99	2.70	3.488 (2)	137
C1—H4$\cdots$Cl3^{iii}	0.99	2.82	3.589 (2)	135
C2—H6$\cdots$Cl4^{ii}	0.99	2.78	3.588 (2)	140
C3—H7$\cdots$Cl1^{iii}	0.99	2.81	3.376 (2)	117
C4—H9$\cdots$Cl3^i	0.99	2.81	3.409 (2)	119

Symmetry codes: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, 1 - y, -z$; (iii) $2 - x, 1 - y, -z$.
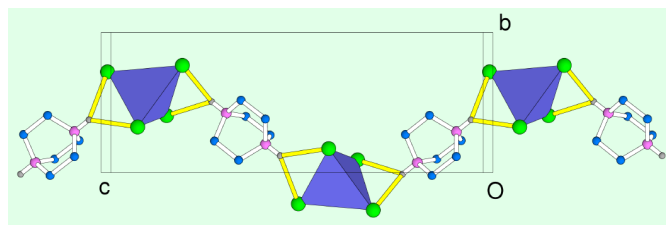
Figure 2
Hydrogen-bonding scheme in (I), leading to corrugated chains of alternating dabconium cations and $[CoCl_4]^{2-}$ tetrahedra. Colour key: CoCl4 tetrahedra blue, Cl atoms green, C atoms blue, N atoms purple, H atoms grey (all radii arbitrary; C—H H atoms omitted for clarity). The H$\cdots$Cl portions of the bifurcated N—H$\cdots$(Cl,Cl) hydrogen bonds are coloured yellow.
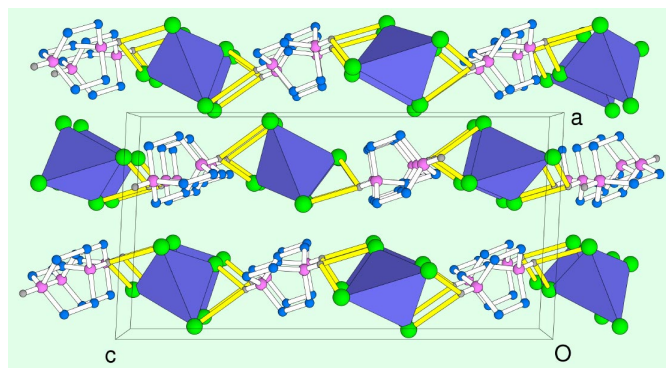
Figure 3
Unit-cell packing in (I), viewed down [010]. Colour key as in Fig. 2.

H atoms were placed in idealized locations and refined by riding on their parent atom, with $U_{iso}(H) = 1.2U_{eq}$(parent atom) in each case.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and ATOMS (Shape Software, 1999); software used to prepare material for publication: *SHELXL*97.

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