Bis(1-carbamoylguanidinium) diaquatetrachlorocobaltate(II)

Colin A. Bremner and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Aberdeen, AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–N) = 0.002 Å
R factor = 0.027
wR factor = 0.068
Data-to-parameter ratio = 29.7

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

The crystal structure of the title compound, $(C_2H_7N_4O)_2[CoCl_4(H_2O)_2]$, contains a molecular network of $(C_2H_7N_4O)^+$ cations and *trans*-$[Co(H_2O)_2Cl_4]^{2-}$ octahedral anions (Co site symmetry $2/m$). An extensive network of N—H$\cdots$Cl, N—H$\cdots$(Cl,Cl), N—H$\cdots$O, O—H$\cdots$O and O—H$\cdots$Cl hydrogen bonds results in a structure with a three-dimensional hydrogen-bond network.

Comment

The title compound, (I), arose as a side product during our synthetic investigations of organically templated cobalt phosphate networks (Cowley & Chippindale, 1999). It is isostructural with $(C_2H_7N_4O)_2[CuCl_4(H_2O)_2]$ (Begley *et al.*, 1988) and $(C_2H_7N_4O)_2[MnCl_4(H_2O)_2]$ (Bremner & Harrison, 2003).


(I)
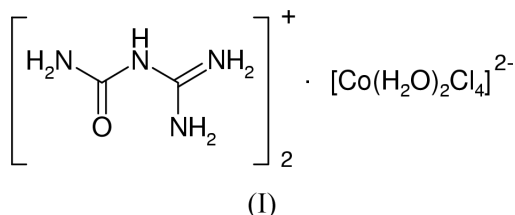
In (I), Co1 (site symmetry $2/m$) has flattened, *trans*, octahedral coordination by two O (water) atoms and four Cl atoms. The *cis* bond angles lie between 84.64 (3) and 95.36 (3)°. The Co—O bond distance of 2.1000 (9) Å and the average Co—Cl separation of 2.4695 (4) Å correlate reasonably well with the ionic radius (IR) sums for the species involved [d_{IR}(Co—O) = 2.09 Å and d_{IR}(Co—Cl) = 2.56 Å], assuming the presence of high-spin Co^{2+} (Shannon, 1976). The $[CuCl_4(H_2O)_2]^{2-}$ grouping in $(C_2H_7N_4O)_2[CuCl_4(H_2O)_2]$ (Begley *et al.*, 1988) is much more distorted, with a Cu—O distance of 1.992 (3) Å and Cu—Cl bond lengths of 2.305 (1) and 2.791 (1) Å, which can be ascribed to a typical Jahn–Teller distortion for the d^9 Cu^{2+} species.

The 1-carbamoylguanidinium (guanylurea) cation has normal geometrical parameters [d_{av}(N—C) = 1.339 (3) Å], indicating significant delocalization of electrons over the non-hydrogen skeleton (Zaman & Darlow, 1986; Begley *et al.*, 1988) and is essentially planar (for the non-H atoms, the r.m.s. deviation from the least-squares plane = 0.029 Å). A very acute ($\theta = 129$°) intramolecular N4—H9$\cdots$O2 hydrogen bond is present, which is typical for $(C_2H_7N_4O)^+$ (Bremner & Harrison, 2002).
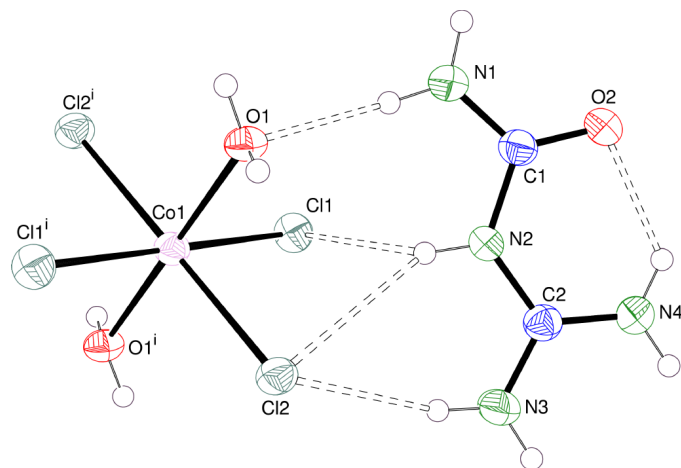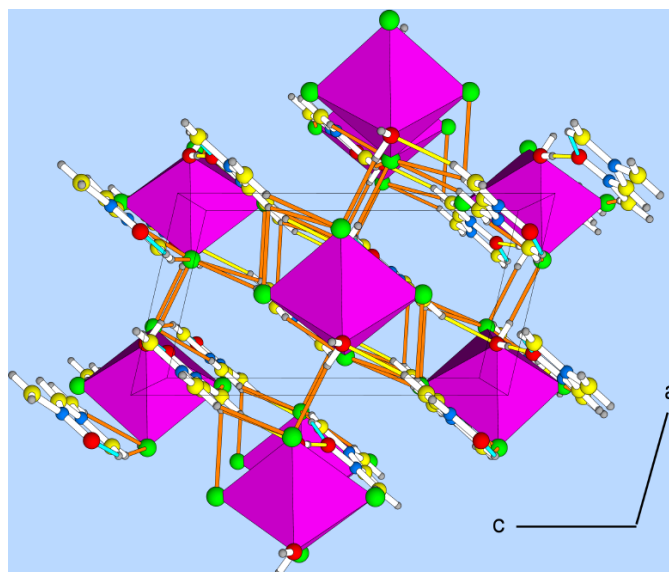
Figure 1
Component species of (I) (50% displacement ellipsoids, arbitrary spheres for the H atoms and hydrogen bonds indicated by dashed lines). [Symmetry code: (i) $-x, 1 - y, -z$.]
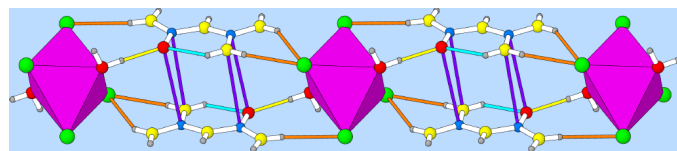
Figure 2
Detail of (I), showing an [010] stack of alternating cation pairs and anions. Colour key: $Co(H_2O)_2Cl_4$ octahedra purple, Cl atoms green, C atoms blue, N atoms yellow, and H atoms grey (all radii arbitrary). The intramolecular H···O, other H···O, H···Cl portions of the hydrogen bonds and the pseudo-π–π-stacking contacts (see text) are coloured light blue, orange, yellow, and purple, respectively.

The component species in (I) interact by way of an extensive hydrogen-bonding network (Table 2). The N—H···Cl hydrogen bonds to chloride ion acceptors involving H5 and H6 are bifurcated [$d_{av}(H \cdots Cl) = 2.72$ Å, $d_{av}(N \cdots Cl) = 3.398 (2)$ Å and $\theta_{av}(N—H \cdots Cl) = 138°$], which is a characteristic 'synthon' bonding motif for these species (Brammer *et al.*, 2001). In this case, the pairs of chloride ions occupy an octahedral edge, with $Cl1 \cdots Cl2$ and $Cl1^v \cdots Cl2^{iv}$ [symmetry codes: (iv) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.] separations of 3.4662 (5) and 3.5190 (5) Å for the interactions involving H5 and H6, respectively. The hydrogen bonds involving H3, H7 and H8 are simple N—H···Cl links [$d_{av}(H \cdots Cl) = 2.52$ Å $d_{av}(N \cdots Cl) = 3.329 (2)$ Å and $\theta_{av}(N—H \cdots Cl) = 159°$]. Overall, Cl1 accepts three and Cl2 accepts five hydrogen bonds.

The hydrogen-bonding scheme in (I) results in stacks of alternating $[Co(H_2O)_2Cl_4]^{2-}$ octahedra and pairs of 1-carbamoylguanidinium species propagating along [010] (Fig. 2), which are held together by the O1—H1···O2^i, N1—H3···Cl1^{iii}, N3—H6···Cl2^{iv}, and N4—H8···Cl2^{iv} bonds (see Table 2 for the acceptor-atom symmetry codes). There may be pseudo π–π-stacking interactions involving the parallel 1-carbamoylguanidinium pairs, with resulting short contact distances of $C1 \cdots N4^{vi} = 3.346 (2)$ Å and $C2 \cdots O2^{vi} = 3.364 (2)$ Å [symmetry code: (vi) $1 - x, 1 - y, 1 - z$].

Figure 3
Unit-cell packing in (I), viewed down [010]. Colour key as in Fig. 2 (pseudo-π–π-stacking contacts have been omitted for clarity).

The stacks are fused into $(10\bar{1})$ pseudo-sheets by way of the N1—H4···O1, N2—H5···(Cl1, Cl2), N3—H6···Cl1^v, and N3—H7···Cl2 bonds, which in turn are crosslinked by the O1—H2···Cl2^{ii} bonds (symmetry codes as in Table 2), resulting in a three-dimensional structure.

Experimental

Crystal data

$(C_2H_7N_4O)_2[CoCl_4(H_2O)_2]$	$D_x = 1.818$ Mg m^{-3}
$M_r = 443.00$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 3083
$a = 6.3488 (3)$ Å	reflections
$b = 11.3392 (5)$ Å	$\theta = 2.6$–$32.4°$
$c = 11.5436 (5)$ Å	$\mu = 1.75$ mm^{-1}
$\beta = 103.118 (1)°$	$T = 293 (2)$ K
$V = 809.34 (6)$ Å^3	Block, purple
$Z = 2$	$0.26 \times 0.19 \times 0.13$ mm

Data collection

Bruker SMART1000 CCD diffractometer	2914 independent reflections
	2160 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan	$\theta_{max} = 32.5°$
(*SADABS*; Bruker, 1999)	$h = -8 \rightarrow 9$
$T_{min} = 0.650$, $T_{max} = 0.810$	$k = -17 \rightarrow 17$
7802 measured reflections	$l = -16 \rightarrow 17$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{max} < 0.001$
2914 reflections	$\Delta\rho_{max} = 0.37$ e Å^{-3}
98 parameters	$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Co1—O1	2.1000 (9)	N2—C2	1.3577 (17)
Co1—Cl1	2.4332 (4)	N2—C1	1.3926 (16)
Co1—Cl2	2.5057 (3)	N3—C2	1.3170 (17)
O2—C1	1.2297 (18)	N4—C2	1.3066 (19)
N1—C1	1.3212 (19)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O2[i]	0.84	1.82	2.6587 (13)	179
O1—H2$\cdots$Cl2[ii]	0.87	2.37	3.1465 (10)	149
N1—H3$\cdots$Cl1[iii]	0.86	2.59	3.4349 (12)	170
N1—H4$\cdots$O1	0.86	2.12	2.9586 (17)	166
N2—H5$\cdots$Cl1	0.86	2.66	3.2905 (14)	132
N2—H5$\cdots$Cl2	0.86	2.77	3.5040 (13)	144
N3—H6$\cdots$Cl2[iv]	0.86	2.56	3.3245 (14)	148
N3—H6$\cdots$Cl1[v]	0.86	2.87	3.4749 (12)	129
N3—H7$\cdots$Cl2	0.86	2.48	3.2743 (15)	155
N4—H8$\cdots$Cl2[iv]	0.86	2.50	3.2778 (13)	151
N4—H9$\cdots$O2	0.86	2.03	2.6571 (16)	129

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

The H atoms attached to atom O1 were located in difference maps and refined by riding in their as-found positions. The other H atoms were placed in idealized locations [d(N—H) = 0.86 Å] and refined by riding on their parent atom, with U_{iso}(H) = $1.2U_{eq}$(parent atom) in all cases.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; 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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