inorganic papers

Cobalt hydrogen selenite chloride dihydrate, Co(HSeO$_3$)Cl·2H$_2$O

Magnus G. Johnston 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(Co–O) = 0.002 Å
R factor = 0.022
wR factor = 0.062
Data-to-parameter ratio = 27.5

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

Cobalt hydrogen selenite chloride dihydrate, Co(HSeO$_3$)Cl·2H$_2$O, is built up from a network of *trans* CoO$_4$Cl$_2$ octahedra, *cis* Co(H$_2$O)$_4$Cl$_2$ octahedra and HSeO$_3$ pyramids. These units [d_{av}(Co—O) = 2.075 (2) Å, d_{av}(Co—Cl) = 2.5370 (6) Å and d_{av}(Se—O) = 1.703 (2) Å] share vertices by way of Co—O—Se and Co—Cl—Co bonds to produce a three-dimensional structure. Co of the trans octahedron occupies an inversion centre; Co of the *cis* octahedron and two attached water O atoms lie on a mirror plane. The hydrogen-bonding scheme has been elucidated and involves O—H···O and O—H···Cl interactions. The title compound is isostructural with Cu(HSeO$_3$)Cl·2H$_2$O, although the metal polyhedra are distinctly different in the two phases.

Comment

The title compound represents another example of a hydrogen selenite chloride hydrate, complementing Co(HSeO$_3$)-Cl·3H$_2$O and Cu(HSeO$_3$)Cl·2H$_2$O (Johnston & Harrison, 2000). Co(HSeO$_3$)Cl·2H$_2$O (Figs. 1 and 2) is essentially isostructural with Cu(HSeO$_3$)Cl·2H$_2$O, although the metal coordinations are distinctly different in the two phases.

Co1 (site symmetry $\bar{1}$) has elongated octahedral coordination to four O and two Cl atoms. The *cis* bond angles lie between 88.09 (4) and 91.91 (4)°. The O atoms form bridges to adjacent Se atoms [θ_{av}(Co—O—Se) = 119.8 (8)°] and the Cl atoms link to Co2 cations. The average Co1—O distance of 2.049 (2) Å and the Co1—Cl separation of 2.5989 (6) Å correlate reasonably well with 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). In Cu(HSeO$_3$)Cl·2H$_2$O (Johnston & Harrison, 2000), the distinction between the equatorial Cu—O bonds [$d_{av} =$
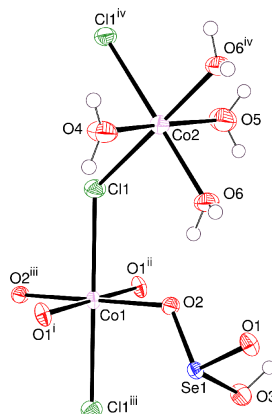
Figure 1
Fragment of Co(HSeO$_3$)Cl·2H$_2$O (50% displacement ellipsoids; arbitrary spheres for the H atoms). Symmetry codes: (i) $\frac{1}{2} + x$, y, $\frac{1}{2} - z$; (ii) $\frac{1}{2} - x$, $-y$, $\frac{1}{2} + z$; (iii) $1 - x$, $-y$, $1 - z$; (iv) x, $\frac{1}{2} - y$, z.
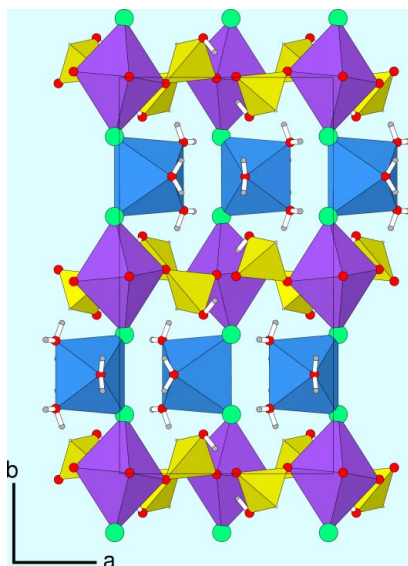
Figure 2
Polyhedral representation of Co(HSeO₃)Cl·2H₂O, viewed approximately normal to (001). Colour key: Co1O₄Cl₂ octahedra purple, Co2(H₂O)₄Cl₂ octahedra blue, HSeO₃E (E = dummy atom representing the lone pair of electrons placed 1.0 Å from Se) pseudo-tetrahedra yellow. The coloured spheres (radii arbitrary) represent O atoms (red), Cl atoms (green), and H atoms (grey).
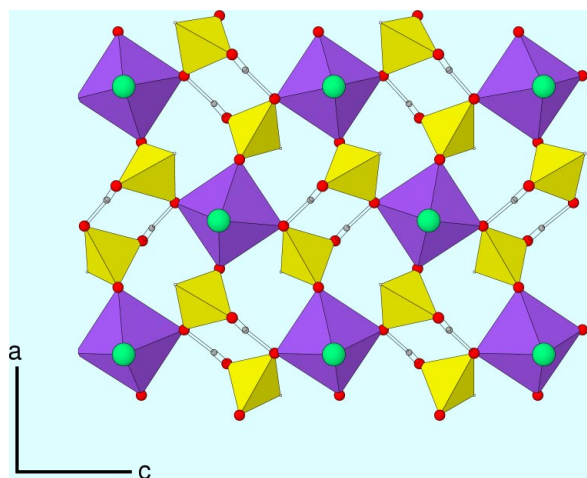

Figure 3
Polyhedral representation of a sheet of Co1 and Se centred groups in Co(HSeO₃)Cl·2H₂O, viewed down [010] ($-0.20 < y < 0.20$), showing the squashed eight-ring voids bridged by pairs of hydrogen bonds (H···O portion coloured red). Otherwise, the colour key is as in Fig. 2.

1.976 (2) Å] and apical Cu—Cl [d = 2.8066 (5) Å] bonds is more extreme, and can be ascribed to a typical Jahn–Teller distortion for the d^9 Cu²⁺ ion.

The pyramidal geometry of the [HSeO₃]⁻ moiety and the lengthened protonated Se—O3H bond in the title compound are typical for the hydrogen selenite group (Verma, 1999). The unobserved Se^{IV} lone pair of electrons is presumed to occupy the fourth vertex of a tetrahedron and, as such, is directed into empty space at an angle of about 35° with respect to a projection of the Se—E (E = lone pair) vector on to (010). The Co1 and Se polyhedra form [Co(HSeO₃)₂Cl₂]²⁻ layers which
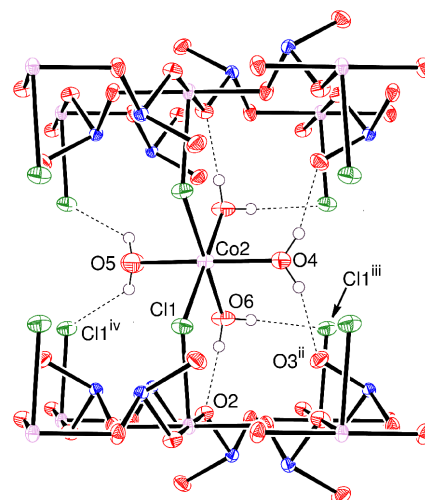
Figure 4
Section of Co(HSeO₃)Cl·2H₂O (50% displacement ellipsoids; arbitrary spheres for the H atoms), showing the hydrogen bonds (dashed lines) associated with the water molecules bonded to Co2. Atom H1 has been omitted for clarity and the symmetry codes are as in Table 2.

propagate in the (010) plane. These layers encapsulate polyhedral eight-rings (Fig. 3), each of which is stabilized by a pair of intra-sheet Se—O3—H1···O1 hydrogen bonds.

The four O and two Cl atoms around Co2 (site symmetry m) form a distorted *cis* Co(H₂O)₄Cl₂ octahedron [d_{av}(Co—O) = 2.100 (3) Å]. The *cis* and *trans* bond angles lie in the ranges 87.04 (8)–92.68 (7) and 173.00 (12)–179.19 (6)°, respectively. The [Co2(H₂O)₄Cl₂] octahedra are isolated from each other, and bridge the (010) [Co(HSeO₃)₂Cl₂]²⁻ sheets *via* Co1—Cl1—Co2—Cl1—Co1 bonds to produce a three-dimensional structure. The hydrogen bonds (Table 2 and Fig. 4) associated with the Co2-polyhedron water molecules include O—H···O and O—H···Cl links. In Cu(HSeO₃)Cl·2H₂O, a Jahn–Teller distortion led to long bonds to two of the *trans* water-molecule O atoms [2.229 (3) and 2.634 (5) Å], two short symmetry-equivalent Cu–OH₂ links [2.0244 (16) Å] and a short Cu—Cl bond [d = 2.3127 (5) Å].

Experimental

A mixture of 7 ml 0.5 M 'H₂SeO₃' solution (dissolved SeO₂), 8 ml 1 M LiCl solution and 0.714 g (3 mmol) CoCl₂·6H₂O were sealed in a 23 ml capacity Teflon-lined hydrothermal bomb, and heated to 473 K for 6 d. After cooling over a few hours and opening the bomb, there was no solid product. The resultant red liquor was placed in a Petri dish and, after 10 d, purple chunky crystals of the title compound were recovered by vacuum filtration. These were not rinsed, as the crystals redissolve very easily. Co(HSeO₃)Cl·2H₂O crystals appear to be stable when stored in a dry atmosphere.

Crystal data

Co(HSeO₃)Cl·2H₂O	Mo $K\alpha$ radiation
$M_r = 258.38$	Cell parameters from 5736
Orthorhombic, *Pnma*	reflections
$a = 9.3384$ (4) Å	$\theta = 3.5$–32.5°
$b = 17.3447$ (7) Å	$\mu = 9.42$ mm⁻¹
$c = 7.3198$ (3) Å	$T = 293$ (2) K
$V = 1185.60$ (9) Å³	Chunk, purple
$Z = 8$	$0.35 \times 0.16 \times 0.08$ mm
$D_x = 2.895$ Mg m⁻³	

Data collection

Bruker SMART1000 CCD diffractometer	2199 independent reflections
ω scans	1923 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)	$R_{int} = 0.025$
	$\theta_{max} = 32.5°$
$T_{min} = 0.137$, $T_{max} = 0.519$	$h = -13 \rightarrow 14$
11031 measured reflections	$k = -22 \rightarrow 26$
	$l = -9 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.062$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.92$ e Å^{-3}
2199 reflections	$\Delta\rho_{min} = -0.94$ e Å^{-3}
80 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.0007 (2)

Table 1
Selected geometric parameters (Å, °).

Co1—O1^i	2.0403 (14)	Co2—O5	2.155 (3)
Co1—O2	2.0578 (14)	Co2—Cl1	2.4751 (6)
Co1—Cl1	2.5989 (6)	Se1—O2	1.6779 (15)
Co2—O6	2.0809 (17)	Se1—O1	1.6851 (14)
Co2—O4	2.083 (2)	Se1—O3	1.7530 (15)
Cl1^{ii}—Co2—Cl1	90.13 (3)	Se1—O1—Co1^{iii}	116.90 (8)
Co2—Cl1—Co1	129.26 (2)	Se1—O2—Co1	122.75 (8)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H1···O1^i	0.90	1.74	2.641 (2)	173
O4—H2···O3^{ii}	0.85	2.00	2.8123 (18)	159
O5—H3···Cl1^{iii}	0.82	2.73	3.387 (2)	138
O6—H4···O2	0.82	1.93	2.750 (2)	175
O6—H5···Cl1^{iv}	0.88	2.50	3.3741 (18)	177

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

The H atoms were located from difference maps and refined by riding in their as-found positions.

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: *SHELXS*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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