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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{Co}-\text{O}) = 0.004\text{ \AA}$
 R factor = 0.043
 wR factor = 0.115
Data-to-parameter ratio = 23.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Barium cobalt chloride selenite, $\text{Ba}_2\text{CoCl}_2(\text{SeO}_3)_2$

Hydrothermally synthesized $\text{Ba}_2\text{CoCl}_2(\text{SeO}_3)_2$ contains [001] chains of corner-linked CoO_4Cl_2 [$d_{\text{av}}(\text{Co}-\text{O}) = 2.073(3)\text{ \AA}$ and $d(\text{Co}-\text{Cl}) = 2.544(2)\text{ \AA}$] octahedra and SeO_3 groups [$d_{\text{av}}(\text{Se}-\text{O}) = 1.702(3)\text{ \AA}$]. These chains stack in the [100] direction, with 10-coordinate Ba^{2+} cations (to seven O and three Cl) binding the chains in the [010] direction. Most of the atoms occupy special positions: Co has site symmetry $2/m$ and Ba, Se, Cl and one O atom have site symmetry m .

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Comment

$\text{Ba}_2\text{CoCl}_2(\text{SeO}_3)_2$ is one of the few well characterized synthetic selenite chlorides. Others include $\text{Co}(\text{HSeO}_3)\text{-Cl}\cdot 3\text{H}_2\text{O}$ (Johnston & Harrison, 2000), built up from one-dimensional chains of vertex-linked $[\text{HSeO}_3]^-$ pyramids and $\text{Co}(\text{OH}_2)_4\text{Cl}_2$ octahedra, and $\text{Cu}_3\text{Er}(\text{SeO}_3)_2\text{O}_2\text{Cl}$ (Berrigan & Gatehouse, 1996), which consists of a three-dimensional network of SeO_3 pyramids, CuO_4Cl_2 octahedra and ErO_8 polyhedra.

In the title compound (Fig. 1), the octahedral cobalt cation (site symmetry $2/m$) is coordinated by four O1 atoms [$d_{\text{av}}(\text{Co}-\text{O}) = 2.073(3)\text{ \AA}$] and two chloride ions. The bond-valence sum (BVS; Brown, 1996) for Co of 1.93 is close to the expected value of 2.00. The $[\text{SeO}_3]^{2-}$ group (Se site symmetry m) adopts its usual pyramidal coordination (Wildner, 1991; Harrison, 1999), with $d_{\text{av}}(\text{Se}-\text{O}) = 1.702(3)\text{ \AA}$ and $\text{BVS}(\text{Se}) = 4.03$ (expected BVS = 4.00). The Ba cation (site symmetry m) is irregularly coordinated by seven O atoms and three chloride ions with $\text{BVS}(\text{Ba}) = 2.11$ (expected value 2.00). The next nearest O atom is some 4.21 \AA distant.

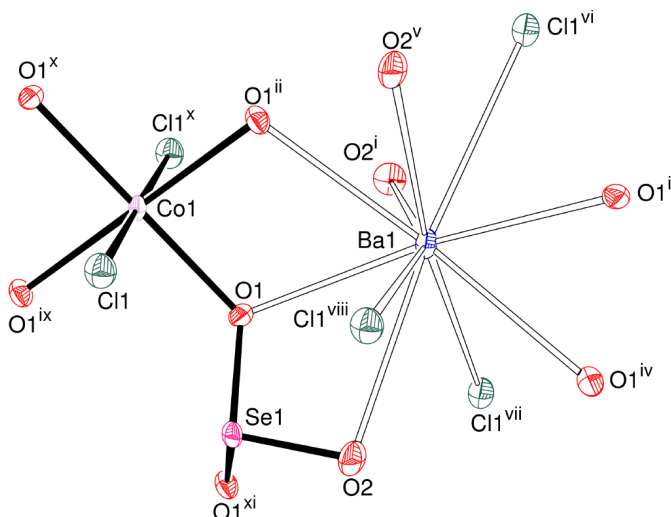


Figure 1
Fragment of $\text{Ba}_2\text{CoCl}_2(\text{SeO}_3)_2$ (50% probability displacement ellipsoids; the symmetry codes are as in Table 1).

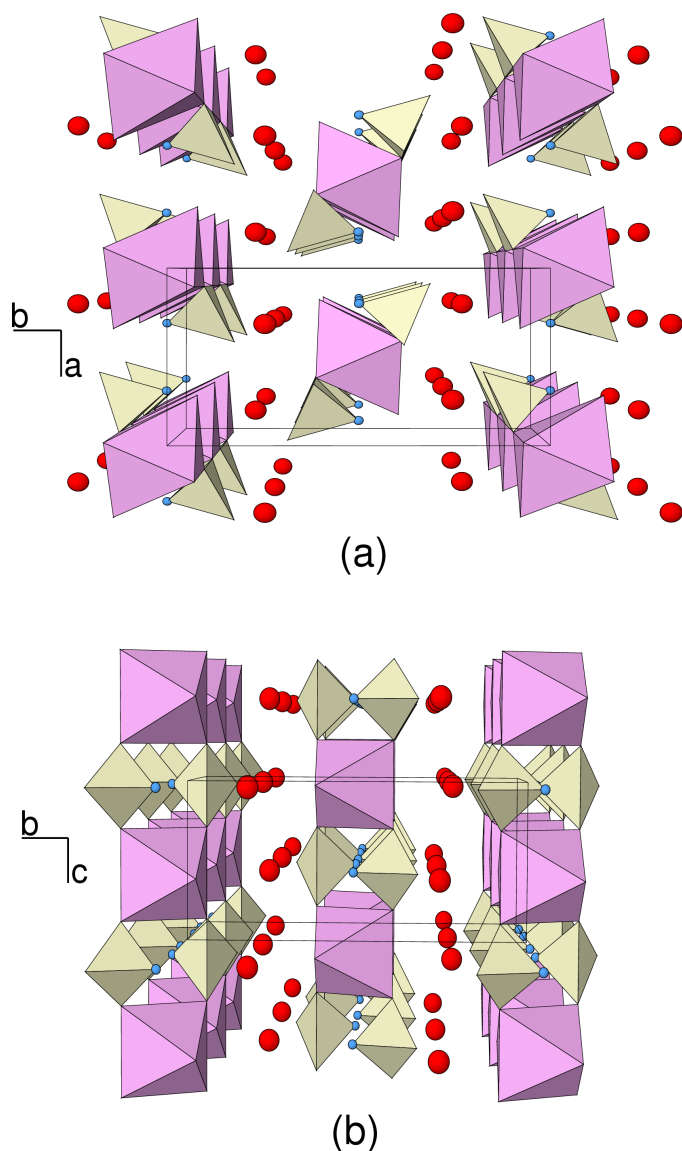


Figure 2
Polyhedral diagrams of $\text{Ba}_2\text{CoCl}_2(\text{SeO}_3)_2$ viewed down (a) [001] and (b) [100]. The SeO_3 pyramids (gold) are represented by SeO_3E tetrahedra, where the dummy atom E, geometrically placed 1.0 Å from Se and indicated by a small blue sphere, represents the Se^{IV} lone pair. CoO_4Cl_2 octahedra are purple and Ba^{2+} cations are represented by red spheres of arbitrary radii.

The geometry of both O atoms is roughly tetrahedral: O1 bonds to one Co, one Se, and two Ba, and O2 (site symmetry m) bonds to one Se and three Ba. Cl1 (site symmetry m) is surrounded by one Co and three Ba atoms in a 'see-saw' geometry, akin to the S-atom coordination in molecular SF_4 . This geometry can be visualized as trigonal bipyramidal with one of the equatorial vertices missing. Here, the Co atom occupies one of the nominal axial positions.

The overall structure (Fig. 2) consists of infinite [001] chains of isolated CoO_4Cl_2 octahedra fused together by pairs of selenite groups. Thus, each Co octahedron corner shares with four SeO_3 groups *via* O1, and each SeO_3 group bridges two Co groups. The Co/Se chains stack on top of each other in the a

direction, with each chain separated by small channels which are probably associated with the Se^{IV} lone pairs. The charge-balancing Ba^{2+} cations bind the chains in the [010] direction, through a variety of corner- and edge-sharing links. Each BaO_7Cl_3 polyhedron is surrounded by six others.

Experimental

The crystals were prepared by hydrothermal reaction of BaCO_3 (0.592 g, 3 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.427 g, 6 mmol), SeO_2 (0.334 g, 3 mmol) and 15 ml H_2O . Reactants were placed in a 23-ml capacity, teflon-lined steel bomb and 1 M HNO_3 was added until the pH of the solution was about 1. The bomb was heated for 3 d at 453 K. Upon cooling the bomb to room temperature over 3 h, the resulting solids were recovered by vacuum filtration and washing with water. A few very pale purple needles of $\text{Ba}_2\text{CoCl}_2(\text{SeO}_3)_2$ were isolated from a mixture of unidentified pink and white powders.

Crystal data

$\text{Ba}_2\text{Co}(\text{SeO}_3)_2\text{Cl}_2$	Mo $K\alpha$ radiation
$M_r = 658.44$	Cell parameters from 2656 reflections
Orthorhombic, $Pnmm$	$\theta = 3.2\text{--}32.5^\circ$
$a = 6.7635$ (4) Å	$\mu = 18.70 \text{ mm}^{-1}$
$b = 12.6454$ (7) Å	$T = 293$ (2) K
$c = 5.3866$ (3) Å	Needle, pale purple
$V = 460.70$ (5) Å ³	$0.48 \times 0.02 \times 0.02 \text{ mm}$
$Z = 2$	
$D_x = 4.746 \text{ Mg m}^{-3}$	

Data collection

Bruker SMART1000 CCD diffractometer	902 independent reflections
ω scans	837 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$R_{\text{int}} = 0.053$
$T_{\text{min}} = 0.030$, $T_{\text{max}} = 0.602$	$\theta_{\text{max}} = 32.5^\circ$
3658 measured reflections	$h = -10 \rightarrow 10$
	$k = -17 \rightarrow 19$
	$l = -8 \rightarrow 4$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$\Delta\rho_{\text{max}} = 6.37 \text{ e \AA}^{-3}$
$wR(F^2) = 0.115$	$\Delta\rho_{\text{min}} = -2.51 \text{ e \AA}^{-3}$
$S = 1.13$	Extinction correction: SHELXL (Sheldrick, 1997)
902 reflections	Extinction coefficient: 6.6 (13) $\times 10^{-3}$
39 parameters	
$w = 1/[\sigma^2(F_o^2) + (0.0817P)^2 + 0.2871P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected geometric parameters (Å, °).

Ba1—O2 ⁱ	2.700 (6)	Co1—O1 ⁱⁱ	2.075 (3)
Ba1—O1	2.813 (3)	Co1—O1 ^{ix}	2.075 (3)
Ba1—O1 ⁱⁱ	2.813 (3)	Co1—O1	2.075 (3)
Ba1—O1 ⁱⁱⁱ	2.875 (4)	Co1—O1 ^x	2.075 (3)
Ba1—O1 ^{iv}	2.875 (4)	Co1—Cl1 ^x	2.5465 (19)
Ba1—O2	3.043 (3)	Co1—Cl1	2.5465 (19)
Ba1—O2 ^v	3.043 (3)	Se1—O2	1.685 (6)
Ba1—Cl1 ^{vi}	3.2480 (12)	Se1—O1 ^{xi}	1.713 (3)
Ba1—Cl1 ^{vii}	3.2480 (12)	Se1—O1	1.713 (3)
Ba1—Cl1 ^{viii}	3.305 (2)		
Se1—O1—Co1	122.54 (18)	Co1—Cl1—Ba1 ^{viii}	171.41 (8)
Co1—Cl1—Ba1 ^{xii}	92.06 (4)	Ba1 ^{xii} —Cl1—Ba1 ^{viii}	83.17 (4)
Co1—Cl1—Ba1 ^{xiii}	92.06 (4)	Ba1 ^{xiii} —Cl1—Ba1 ^{viii}	83.17 (4)
Ba1 ^{xii} —Cl1—Ba1 ^{xiii}	112.04 (6)		

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, y, 1 - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (v) $x, y, 1 + z$; (vi) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (viii) $1 - x, -y, 1 - z$; (ix) $-x, -y, z$; (x) $-x, -y, 1 - z$; (xi) $x, y, -z$; (xii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (xiii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The highest difference peak is 0.76 Å from Ba1 and the deepest difference hole is 0.76 Å from Ba1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL97*.

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