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Tetraammine(selenito-*O*,*O'*)cobaltate(III) nitrate monohydrate[1]

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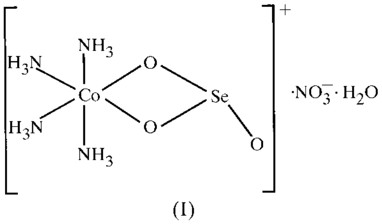
The title compound crystallizes as the monohydrate, $[Co(SeO_3)(NH_3)_4]NO_3\cdot H_2O$. The crystallographic mirror symmetry coincides with the molecular symmetry; the mirror plane passes through the cation, anion and water molecule. The CoN_4O_2 octahedron is distorted, with the selenito group acting as a bidentate ligand through two bridging O atoms to the cobalt. The coordinated Se—O distance is 1.742 (2) Å, whereas the uncoordinated Se—O distance is 1.646 (3) Å. A three-dimensional hydrogen-bonded network exists between $[Co(SeO_3)(NH_3)_4]NO_3$ and the water molecule. The nitrate anion and water molecule form open pores in the structure when hydrogen bonded to two neighboring $[Co(SeO_3)(NH_3)_4]^+$ cations. Selenium participates in two types of relatively close intermolecular interactions with neighboring charged species (Se···N1 and Se···O3), but does not participate in an interaction with a neighboring O2 atom, the nearest contact distance being 4.638 (3) Å.

Comment

As part of studies directed towards the synthesis of selenitoammine cobaltate(III) complexes, the reaction of carbonatotetrammine cobaltate(III) nitrate (Schlessinger, 1960) with selenous acid (H_2SeO_3) gave the title compound, (I) (Salib *et al.*, 1988). The X-ray diffraction analysis of (I) was undertaken in order to deduce the stereochemistry of this complex.



(I)

The molecular structure of (I) (Fig. 1) is similar to that of carbonatotetramminecobaltate(III) bromide (Barclay & Hoskins, 1962). The geometry about the cobalt is distorted, with ammine groups occupying four sites having Co—N bonds in the range 1.946 (3)–1.957 (2) Å and angles approximating that of an octahedron [89.1 (1)–94.8 (2) and 179.7 (2)°]. The SeO_3 moiety acts as a bidentate ligand, forming a four-membered ring through the O atoms with the cobalt. A Co—O distance of 1.942 (2) Å is observed. A nonbonded distance of 2.735 (1) Å separates the Se and Co atoms. Typical Se–first row transition metal single-bond distances are observed in the range 2.40–2.56 Å (Day *et al.*, 1982; Fischer *et al.*, 1981; Herrmann *et al.*, 1983; Rott *et al.*, 1982).

The coordinated Se—O distance is 1.742 (2) Å, whereas the uncoordinated Se—O distance is 1.646 (3) Å; these distances are consistent with single- and double-bonded Se—O character, respectively. Similar distances were reported by Hughes *et al.* (1986) for (selenito-*O*,*O'*)bis(triphenylphosphine)-$O_{bridged}$ = 1.726 (5)–1.746 (5) Å and Se—$O_{terminal}$ = 1.602 (7) Å. In (I), the geometry about Se is pyramidal [O1—Se—O2 104.6 (1)°], with the fourth coordination site occupied by the Se lone pair of electrons.

As with $[Co(NH_3)_4CO_3]Br$ (Barclay & Hoskins, 1962), significant strain is involved in the formation of the four-membered ring in (I). The O1—Co—O1' angle of 78.6 (1)° deviates markedly from the expected angle of 90°. The Co—O1—Se [95.72 (9)°] and O1—Se—O1' [89.9 (1)°] angles are also compressed. Some strain relief may be observed in the angles N2—Co—N2' [94.8 (2)°] and O1—Co—N2 [93.28 (9)°] which are somewhat relaxed.

A slight folding towards N3 [3.1 (2)°] is observed in the equatorial plane of the molecule comprised of O1—O1'—N2—N2' and the selenito fragment, Se—O1—O1'. Barclay & Hoskins (1962) found a similar but more pronounced folding (7°) in the carbonato complex.

An extensive network of N—H···O and O—H···O hydrogen bonding (Fig. 2) is observed for (I) and the water

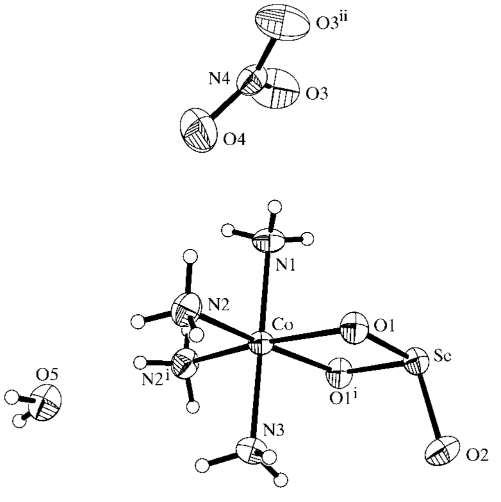


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids and the atomic numbering scheme; symmetry codes as in Table 2.

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[1] Systematic name: tetrammine(trioxoselenato-*O*,*O'*)cobalt(III) nitrate monohydrate.

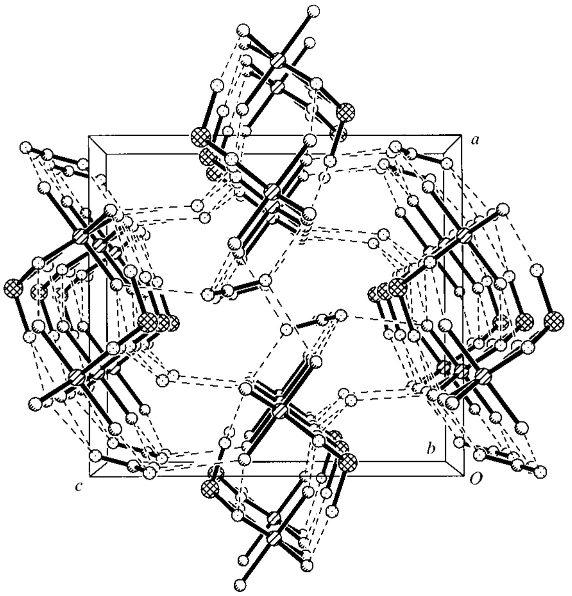

Figure 2
Packing diagram of (I) showing the hydrogen-bond interactions (the view is in the *ac* plane).

molecule. The extensive hydrogen bonding for (I) is expected due to the ability of the SeO_3 moiety to attract the hydrogen from water molecules to form hydrogen selenite or selenous acid. Prior to this work, this behavior was discussed by thermal dehydration of Cu^{II}, Ni^{II} and Co^{II} selenite dihydrates. It was found that the water molecules persist until 523 K and the SeO_3 is transformed into $HSeO_3$ (Emara *et al.*, 1996). Similarly, the related compound $[Co(NH_3)_5SeO_3]Cl$ is very hygroscopic (Salib *et al.*, 1988). In (I), the nitrate anion and water molecule form open pores in the structure when hydrogen bonded to two neighboring $[Co(NH_3)_4SeO_3]^+$ cations. Selenium participates in two types of close intermolecular interactions with neighboring charged species, namely cation–anion [Se···O3 = 3.151 (2) Å; symmetry code: $x + \frac{1}{2}$, y, $-z + \frac{3}{2}$] and cation–cation [Se···N1 = 3.595 (3) Å; symmetry code: $x + \frac{1}{2}$, y, $-z + \frac{3}{2}$] interactions. Additional nearest neighbor contacts with Se are Se···N3($-x + 2$, $-y$, $-z + 1$) = 3.930 (2) Å and Se···O5($-x + \frac{3}{2}$, $-y$, $z + \frac{1}{2}$) = 4.005 (2) Å. Se essentially does not participate in an interaction with a neighboring O2 atom, the nearest contact distance being 4.638 (3) Å.

Experimental

The carbonato complex was prepared initially from an aqueous solution of cobalt(II) nitrate and ammonium carbonate, to which concentrated ammonia solution was added. Oxidation to Co^{III} was effected by H_2O_2 to form the carbonato complex, $[Co(NH_3)_4CO_3]NO_3$ (Schlessinger, 1960). The carbonate group was replaced by an SeO_3 group upon reacting the carbonato complex with an equimolar amount of selenous acid. The resulting red–purple solution was heated to 343 K for several minutes, methanol (200 ml) was added and a red–purple precipitate was obtained. The precipitate was collected by filtration, washed with methanol and filtered (63% yield). Crystals of (I) were obtained by dissolving the crude product in a minimum volume of water to which methanol was added. The crystals were dried over H_2SO_4 in a desiccator. The product was characterized by elemental analysis, UV–vis and IR spectroscopy [m.p. 458 K (decomposition)]. Elemental analysis: $CoH_{12}N_5O_6·H_2O$, calculated: Se 25.0, H 3.8, N 22.2%; found: Se 25.1, H 4.0, N 22.0%. IR [deuterated sample of (I)], $\nu(SeO_3)$: 832 (*s*), 690–790 (*s,b*) cm^{-1}. UV–vis: 18 700 ($^1A_{1g} \rightarrow {}^1T_{1g}$) and 25 800 ($^1A_{1g} \rightarrow {}^1T_{2g}$) cm^{-1}.

Crystal data

$[Co(SeO_3)(NH_3)_4]NO_3·H_2O$
$M_r = 334.05$
Orthorhombic, *Pnma*
$a = 11.327$ (1) Å
$b = 7.054$ (1) Å
$c = 12.381$ (1) Å
$V = 989.3$ (2) Å^3
$Z = 4$
$D_x = 2.243$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6242 reflections
$\theta = 2.44$–28.29°
$\mu = 5.44$ mm^{-1}
$T = 293$ (2) K
Rod, dark purple
0.30 × 0.08 × 0.05 mm

Data collection

SMART 1K CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.561$, $T_{max} = 0.762$
10 448 measured reflections
1327 independent reflections

1180 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 28.29°$
$h = -15 \rightarrow 15$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.065$
$S = 1.121$
1327 reflections
76 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 1.4436P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max} = 1.15$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Table 1
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Se	0.95043 (3)	1/4	0.68317 (3)	0.02225 (11)
Co	0.80254 (4)	1/4	0.50858 (4)	0.01820 (13)
O1	0.8818 (2)	0.0756 (3)	0.60588 (15)	0.0243 (4)
O2	1.0885 (2)	1/4	0.6418 (3)	0.0322 (7)
N1	0.6632 (3)	1/4	0.6013 (3)	0.0288 (7)
N2	0.7355 (2)	0.0458 (4)	0.4209 (2)	0.0289 (5)
N3	0.9410 (3)	1/4	0.4155 (3)	0.0241 (7)
N4	0.5415 (3)	−1/4	0.6261 (3)	0.0257 (7)
O3	0.5285 (2)	−0.0979 (4)	0.6741 (2)	0.0494 (7)
O4	0.5711 (3)	−1/4	0.5279 (3)	0.0512 (10)
O5	0.7155 (3)	1/4	0.2036 (3)	0.0362 (7)

H atoms were located directly from the difference map and fixed where located in subsequent refinement cycles. H-atom isotropic displacement parameters were defined as $U(H) = 1.5U(N,O)$. A final difference Fourier map showed a relatively large electron-density peak of 1.15 e Å^{-3} at distances of 0.9 and 1.7 Å from H3*B* and N3, respectively. However, this peak is not located in a position suggestive of reasonable bonding geometry.

Table 2
Selected geometric parameters (Å, °).

Se—O2	1.646 (3)	Co—N1	1.952 (3)
Se—O1	1.742 (2)	Co—N2	1.957 (2)
Se—Co	2.735 (1)	N4—O3	1.236 (3)
Co—O1	1.942 (2)	N4—O4	1.260 (5)
Co—N3	1.946 (3)		
O2—Se—O1	104.6 (1)	N1—Co—N2	90.7 (1)
O1—Se—O1^{i}	89.9 (1)	O1—Co—N2^{i}	171.81 (9)
O2—Se—Co	109.6 (1)	N2—Co—N2^{i}	94.8 (2)
O1—Se—Co	44.96 (6)	O1—Co—Se	39.32 (5)
O1^{i}—Co—O1	78.6 (1)	N3—Co—Se	88.5 (1)
O1—Co—N3	89.7 (1)	N1—Co—Se	91.7 (1)
O1—Co—N1	90.5 (1)	N2—Co—Se	132.54 (7)
N3—Co—N1	179.7 (2)	Se—O1—Co	95.72 (9)
O1—Co—N2	93.28 (9)	O3—N4—O3^{ii}	120.5 (4)
N3—Co—N2	89.1 (1)	O3—N4—O4	119.7 (2)

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

Table 3
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3	0.81	2.34	3.027 (3)	144
N1—H1*B*···O4^{i}	0.96	2.18	3.098 (5)	161
N2—H2*A*···O5	0.88	2.26	3.060 (4)	150
N2—H2*B*···O4	0.97	2.13	3.095 (4)	175
N2—H2*C*···O2^{ii}	0.90	2.11	2.989 (3)	166
N3—H3*A*···O1^{ii}	0.91	2.19	3.062 (3)	161
N3—H3*B*···O3^{iii}	0.90	2.50	3.195 (4)	134
O5—H5···O1^{iii}	0.87	1.99	2.821 (3)	159

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

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1235). Services for accessing these data are described at the back of the journal.

References

Barclay, G. A. & Hoskins, B. F. (1962). *J. Chem. Soc.* pp. 586–591.

Day, V. W., Lesch, D. A. & Rauchfuss, T. B. (1982). *J. Am. Chem. Soc.* **104**, 1290–1295.

Emara, A. A. A., Abd El-Hameed, F. S. M. & Khalil, S. M. E. (1996). *Phosphorus Sulfur Silicon*, **112**, 115–120.

Fischer, H., Fischer, E. O., Himmelreich, D., Cai, R., Schubert, U. & Ackermann, K. (1981). *Chem. Ber.* **114**, 3220–3232.

Herrmann, W. A., Weichmann, J., Serrano, R., Blechschmitt, K., Pfisterer, H. & Ziegler, M. (1983). *Angew. Chem. Int. Ed. Engl.* **22**, 314–315.

Hughes, G. R., Minshall, P. C. & Mingos, D. M. P. (1986). *J. Less Common Met.* **116**, 199–209.

Rott, J., Guggolz, E., Rettenmeier, A. & Ziegler, M. (1982). *Z. Naturforsch. Teil B*, **37**, 13–23.

Salib, K. A. R., El-Maraghy, S. B. & Emara, A. A. A. (1988). *Egypt. J. Chem.* **31**, 67–77.

Schlessinger, G. (1960). *Inorg. Synth.* **6**, 173–175.

Sheldrick, G. M. (1994). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.