N(9)—H(93)···O(6^{ii})	0.92	2.08	2.874 (4)	145
N(10)—H(101)···O(10^{v})	0.82	2.17	2.965 (4)	163
N(10)—H(102)···O(3^{viii})	0.90	2.21	3.066 (4)	160
N(10)—H(103)···O(4^{ix})	0.83	2.40	3.190 (4)	160

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

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BR1156). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexaamminecobalt(III) Thiosulfate Chloride Monohydrate

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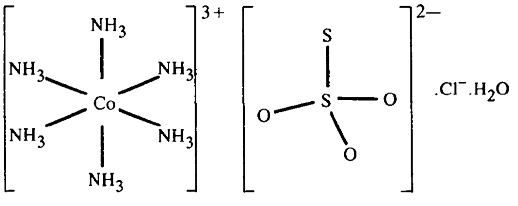
Abstract

The crystal structure of the title compound, $[Co(NH_3)_6](S_2O_3)Cl.H_2O$, consists of discrete ions and water molecules of hydration. The $[Co(NH_3)_6]^{3+}$ cation in the asymmetric unit is distributed between two different symmetry centres. The water molecule and the ions are linked in the crystal by weak hydrogen bonds and interionic contacts.

Comment

The title structure, (I) (Fig. 1), is a member of the family of hexaammine-M^{III} salts, where M = Ru or Co, synthesized and studied by us using different methods (Engelhardt, Reynolds & Sobolev, 1994; Reynolds, Engelhardt & Sobolev, 1994).



(I)

The $[Co(NH_3)_6]^{3+}$ cation is composed of an octahedrally coordinated Co atom bonded to six ammonia ligands with *cis*-N—Co—N angles in the range 88.1 (2)–91.9 (2)°. The Co—N distances vary from 1.955 (2) to 1.965 (3) Å [average value 1.960 (4) Å] and are in good agreement with those in the literature (Restivo, Ferguson & Balahura, 1977; Reynolds, Engelhardt & Sobolev, 1994). The S—S bond length of 1.982 (1) Å and the average S—O distance of 1.467 (2) Å in the $(S_2O_3)^{2-}$ anion also agree with normal values. The hydrogen-bonding network found in (I) comprises O—H···O, N—H···O, N—H···S and N—H···Cl contacts (Table 3) linking water molecules and ions.

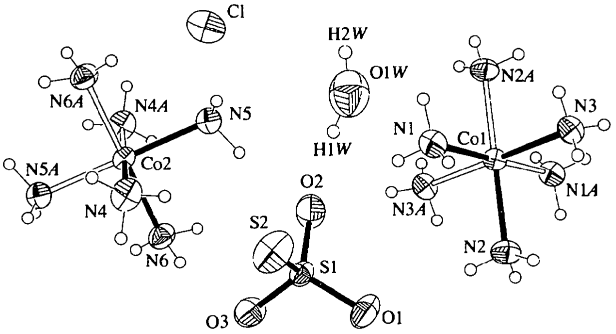


Fig. 1. A general view of the title compound with the atom-numbering scheme and 50% probability ellipsoids. The unshaded bonds correspond to atoms symmetry transformed from those with shaded bonds.

Experimental

Crystals of the title compound were prepared by room-temperature evaporation of a solution of $[Co(NH_3)_6]Cl_3$ to which concentrated $Na_2S_2O_3$ had been added. Crystals (dark-red needles and plates) appeared after about 30 min. One of the needles was cut and prepared for X-ray study.

Crystal data

[$Co(NH_3)_6](S_2O_3)Cl.H_2O$
$M_r = 326.72$
Monoclinic
$P2_1/c$
$a = 7.094\,(1)$ Å
$b = 13.770\,(3)$ Å
$c = 12.648\,(2)$ Å
$\beta = 90.57\,(2)°$
$V = 1235.5\,(4)$ Å^3
$Z = 4$
$D_x = 1.757$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 12 reflections
$\theta = 14.7$–$15.3°$
$\mu = 1.947$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.03 × 0.02 × 0.02 mm
Dark red

Data collection

Siemens $P3/P3$ diffractometer
$2\theta/\theta$ scans
Absorption correction: Gaussian
$T_{min} = 0.963$, $T_{max} = 0.965$
2199 measured reflections
2199 independent reflections

1759 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = -14 \rightarrow 15$
3 standard reflections every 100 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0322$
$wR(F^2) = 0.0816$
$S = 1.078$
2199 reflections
209 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.1391P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.010$
$\Delta\rho_{max} = 0.470$ e Å^{-3}
$\Delta\rho_{min} = -0.596$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0085 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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}
Co1	0	1/2	0	0.0206 (2)
N1	0.0142 (5)	0.3987 (2)	0.1081 (2)	0.0292 (6)
N2	0.2044 (4)	0.5694 (3)	0.0736 (2)	0.0303 (7)
N3	−0.1907 (4)	0.5651 (2)	0.0865 (2)	0.0287 (6)
Co2	1/2	0	0	0.0210 (2)
N4	0.5244 (5)	0.0364 (3)	0.1492 (2)	0.0356 (7)
N5	0.2904 (5)	0.0912 (2)	−0.0169 (3)	0.0323 (7)
N6	0.6785 (5)	0.1023 (3)	−0.0390 (3)	0.0328 (7)
S1	0.50280 (11)	0.31455 (5)	0.13779 (6)	0.0260 (2)
S2	0.4225 (2)	0.25930 (8)	0.27482 (7)	0.0510 (3)
O1	0.5134 (4)	0.4209 (2)	0.1455 (2)	0.0450 (6)
O2	0.3641 (4)	0.2884 (2)	0.0562 (2)	0.0464 (7)
O3	0.6871 (3)	0.2735 (2)	0.1108 (2)	0.0467 (7)
Cl	−0.00444 (12)	0.03708 (7)	0.17484 (6)	0.0409 (3)
O1*W*	−0.0568 (5)	0.2528 (2)	0.3217 (3)	0.0640 (8)

Table 2. *Selected geometric parameters* (Å, °)

Co1—N1	1.955 (3)	Co2—N6	1.961 (3)
Co1—N2	1.964 (3)	S1—O2	1.464 (2)
Co1—N3	1.965 (3)	S1—O3	1.468 (2)
Co2—N4	1.958 (3)	S1—O1	1.470 (2)
Co2—N5	1.957 (3)	S1—S2	1.982 (1)
N1—Co1—N2	89.0 (1)	N4—Co2—N6	90.4 (2)
N1—Co1—N2^{i}	91.0 (1)	N4—Co2—N6^{ii}	89.6 (2)
N1—Co1—N3	88.1 (2)	N5—Co2—N4	90.0 (2)
N1—Co1—N3^{i}	91.9 (2)	N5—Co2—N4^{ii}	90.0 (2)
N2—Co1—N3	91.3 (1)	N5—Co2—N6	90.2 (2)
N2—Co1—N3^{i}	88.7 (1)	N5—Co2—N6^{ii}	89.8 (2)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, -y, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H21···O1	0.82 (5)	2.31 (5)	3.126 (5)	175 (1)
N3—H33···O1^{i}	0.85 (4)	2.14 (5)	2.990 (4)	176 (1)
N4—H41···O1^{ii}	0.88 (5)	2.28 (5)	3.059 (4)	147 (1)
N1—H12···O2	0.78 (4)	2.21 (4)	2.988 (4)	172 (1)
N3—H31···O2^{iii}	0.84 (5)	2.13 (5)	2.965 (4)	173 (1)
N5—H52···O2	0.92 (6)	2.01 (6)	2.914 (4)	166 (1)
N1—H13···O3^{i}	0.91 (5)	1.99 (5)	2.891 (4)	175 (1)
N6—H61···O3	0.86 (5)	2.19 (5)	3.025 (4)	164 (1)
N2—H22···O3^{iv}	0.87 (5)	2.48 (5)	3.278 (4)	153 (1)
N2—H23···O1*W*^{v}	0.82 (5)	2.34 (5)	3.042 (5)	145 (1)
O1*W*—H2*W*···O3^{i}	0.85	2.58	3.225 (5)	133
O1*W*—H1*W*···S2	0.86	2.62	3.459 (4)	166
N4—H43···S2	0.84 (5)	2.75 (5)	3.534 (4)	157 (1)
N6—H62···S2^{vi}	0.91 (6)	2.63 (6)	3.520 (4)	166 (1)
N1—H11···Cl^{v}	0.82 (4)	2.55 (4)	3.343 (4)	166 (1)
N3—H32···Cl^{v}	0.83 (4)	2.59 (4)	3.331 (4)	150 (1)
N4—H42···Cl^{vii}	0.87 (5)	2.56 (5)	3.355 (4)	152 (1)
N5—H51···Cl	0.76 (5)	2.57 (6)	3.303 (4)	163 (1)
N5—H53···Cl^{viii}	0.77 (5)	2.72 (5)	3.338 (4)	138 (1)
N6—H63···Cl^{ix}	0.76 (5)	2.74 (5)	3.473 (4)	163 (1)

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

The title structure was solved by direct methods. H-atom positions were located from a difference Fourier synthesis and refined in the usual way. In the cations, N—H distances are in the range 0.77–0.92 (5) Å. In the water molecule, O—H distances were constrained to be 0.86 Å during refinement.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *PROFIT* (Streltsov & Zavodnik, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Sheldrick, 1984). Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: TA1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Three-Dimensional Iodo-Bridged Mixed-Valence Gold(I,III) Compound, $Cs_2Au^IAu^{III}I_6$

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Abstract

The title compound, dicaesium gold(I) gold(III) hexaiodide, has a distorted perovskite structure. The crystal contains compressed and elongated $[AuI_6]$ octahedra stacked alternately along the [001] and [110] directions by sharing all the corner I atoms. The compound is also characterized by the assembly of the gold complex ions $[Au^II_2]^-$ and $[Au^{III}I_4]^-$. The position of the two halogen atoms in $Cs_2Au^IAu^{III}I_6$ is closer to the midpoint between the two Au atoms than in $Cs_2Au^IAu^{III}Cl_6$. On the other hand, the distortion from the cubic system to the tetragonal system in the iodide is slightly larger than that in the chloride.

Comment

Mixed-valence systems with perovskite-type structures have attracted much attention in view of high-temperature superconductors such as $La_{2-x}Ba_xCuO_4$ (Bednorz & Müller, 1986) and $Ba_{1-x}K_xBiO_3$ (Cava *et al.*, 1988). In these systems, interesting physical properties such as superconductivity depend remarkably on the valence states present and the crystal structure. From these viewpoints, we have systematically investigated the relationship between the physical properties and the crystal structures of $Cs_2Au^IAu^{III}X_6$ (X = Cl, Br, I), which are well known as three-dimensional halogen-bridged mixed-valence gold compounds (Kojima, Kitagawa, Ban, Amita & Nakahara, 1990, 1991; Kitagawa, Kojima, Matsushita, Ban & Tsujikawa, 1991; Kitagawa, Kojima & Nakajima, 1991; Kitagawa, Kojima & Sakai, 1991; Kitagawa, Sato, Kojima, Kikegawa & Shimomura, 1991*a*,*b*; Kitagawa, Kojima, Takahashi & Mori, 1993). The crystal structure of $Cs_2Au_2X_6$ determined by powder X-ray diffraction (Brauer & Sleater, 1970) and the crystal structure analysis of $Cs_2Au_2Cl_6$ using a single crystal (Tindemans-v. Eijndhoven & Verschoor, 1974) have been reported. The characteristic properties of the crystal structure and mixed valence of $Cs_2Au_2X_6$ are analogous to those of $BaBiO_3$, which is the parent compound of the superconductors $Ba_{1-x}(K \text{ or } Rb)_xBiO_3$ and $BaPb_{1-x}Bi_xO_3$. Therefore, these gold compounds are interesting materials for research on Cu-free high-T_c superconductors.

An X-ray single-crystal analysis of $Cs_2Au_2I_6$ has not been reported, even though the atomic coordinates and interatomic distances in $Cs_2Au_2I_6$ are indispensable for band calculations and analysis of the physical properties. One probable reason is the difficulty in obtaining a suitable single crystal of $Cs_2Au_2I_6$. Very recently, we have succeeded in carrying out an X-ray single-crystal analysis of $Cs_2Au_2I_6$.

Fig. 1 shows the crystal structure of $Cs_2Au_2I_6$. The Au(1) atom is surrounded by four I(1) atoms in a perfectly square-planar arrangement. The Au(1)—I(1) distance [2.646 (2) Å] is in good agreement with that for the $[AuI_4]^-$ anion in other mixed-valence compounds: $K_2[AuI_2][AuI_4]$ [2.648 (3) and 2.639 (3) Å] (Strähle, Gelinek, Kolmel & Nemcek, 1979), $Rb_2[AuI_2][AuI_4]$ [2.643 (2) Å] (N. Matsushita, unpublished results) and $Rb_2Ag[AuI_2]_2[AuI_4]$ [2.637 (4) and 2.633 (5) Å] (Werner & Strähle, 1979). Crystal structures of mononuclear complexes of Au^{III} surrounded by four I atoms in a square-planar arrangement have not been reported to the best of our knowledge. On the other hand, the Au(2) atom is linearly coordinated by two I(2) atoms, as shown in Fig. 1. The Au(2)—I(2) distance [2.586 (3) Å] is close to that for the $[AuI_2]^-$ anion in the mixed-valence compounds $K_2[AuI_2][AuI_4]$ [2.564 (3) Å] (Strähle *et al.*, 1979), $Rb_2[AuI_2][AuI_4]$ [2.570 (3) Å] (N. Matsushita, unpublished results) and $Rb_2Ag[AuI_2]_2[AuI_4]$ [2.570 (9) and 2.549 (9) Å] (Werner & Strähle, 1979), and it is longer than that found in $[n\text{-}Bu_4N][AuI_2]$ [2.529 (1) Å] (Braunstein, Müller & Bogge, 1986) where $[n\text{-}Bu_4N]^+$ is the tetra(n-butyl)ammonium ion. Therefore, Au(1) is formally trivalent and Au(2) is formally monovalent. The crystal is built up from square-planar $[AuI_4]^-$ anions, linear $[AuI_2]^-$ anions and Cs^+ cations, and the compound may be described as $Cs_2[Au^II_2][Au^{III}I_4]$.

The Au^I—I distances in $[AuI_2]^-$ in the mixed-valence compounds are longer than that in the compound containing discrete $[AuI_2]^-$ ions. The I atom in

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