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Hexaaquabis(dimethyl sulfoxide)-yttrium(III) trichloride

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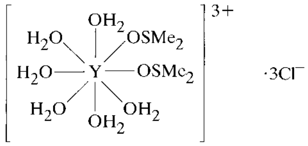
The title compound, $[Y(C_2H_6OS)_2(H_2O)_6]Cl_3$, contains the cation $[Y(H_2O)_6\{(CH_3)_2SO\}_2]^{3+}$ with a distorted square antiprismatic geometry of the eight coordinated O atoms. The six water molecules are coordinated with an average Y—O distance of 2.38 (2) Å, ranging from 2.360 (3) to 2.404 (3) Å. Each water molecule forms two hydrogen bonds to the chloride anions with O—Cl distances ranging from 3.068 (4) to 3.422 (4) Å. The two dimethyl sulfoxide ligands, situated in the *cis* position with the O—Y—O angle equal to 83.22 (11)°, have Y—O distances of 2.269 (3) and 2.278 (3) Å.

Comment

Diffraction from ionic solutions often gives restricted structural information since the two-dimensional radial distribution function obtained can not normally be separated into individual pair distribution functions unless further experiments are carried out. In some cases, where suitable pairs of isotopes are available, the spatial correlation between an ion and its surrounding solvent molecules may be unambiguously determined by isotopic substitution neutron diffraction (Soper *et al.*, 1977). The characterization of crystalline solvated salts is one of the most important sources of information for the structure of liquid solutions since the liquid phase may, in many cases, be regarded as the dynamic analogue of the crystalline phase. The crystalline structure may therefore serve as a model for the local structure of the metal ion in solution. For example, crystalline alum salts, $CsM(SO_4)_2(H_2O)_{12}$, are ideal to model the first hydration sphere of the hexaaqua chromium(III), gallium(III) and indium(III) cations in aqueous solution (Lindqvist-Reis *et al.*, 1998). It has recently been shown, by high resolution EXAFS (extended X-ray absorption fine structure) measurements, that the local environment of the yttrium(III) ion in aqueous solution is very similar to that observed in crystalline $[Y(H_2O)_8]Cl_3\cdot$(15-crown-5), where the water molecules are coordinated to the yttrium(III) ion to form a distorted dodecahedron with Y—O distances ranging from 2.322 (6) to 2.432 (7) Å (Lindqvist-Reis, Lamble *et al.*, 2000). The 15-crown-5 molecules form hydrogen bonds to the hydrated cation and the chloride anions and, in that respect, mimic a second hydration sphere in solution. In dimethyl sulfoxide (DMSO) solutions, the yttrium(III) ion coordinates dmso molecules with an average Y—O distance of 2.36 (1) Å compared with crystalline $[Y\{(CH_3)_2SO\}_8]I_3$ where the dmso molecules are distributed into two groups, one with Y—O distances ranging from 2.311 (4) to 2.320 (4) Å and the other with Y—O distances ranging from 2.352 (4) to 2.368 (4) Å (Lindqvist-Reis, Naslund *et al.*, 2000).



(I)

In the present contribution, we wish to present the structure of the mixed aqua/dmso complex cation $[Y(H_2O)_6\{(CH_3)_2SO\}_2]^{3+}$, (I), where the two different oxygen-donating ligands form a distorted square antiprism (Fig. 1). The six water molecules are coordinated with an average Y—O distance of 2.38 (2) Å, ranging from 2.360 (3) to 2.404 (3) Å. No significant *trans* influence produced by the dmso ligands can be observed. Each water molecule forms two hydrogen bonds to the chloride ions. The average hydrogen-bonded O—Cl distance is 3.18 (9) Å, ranging from 3.068 (4) to 3.422 (4) Å. The two dmso molecules, situated at *cis* positions with the O1—Y—O2 angle equal to 83.22 (11)°, have Y—O distances of 2.269 (3) and 2.278 (3) Å, significantly shorter than those observed in the $[Y\{(CH_3)_2SO\}_8]^{3+}$ cation (Lindqvist-Reis, Naslund *et al.*, 2000). At room temperature, both dmso molecules are disordered over two positions which were both

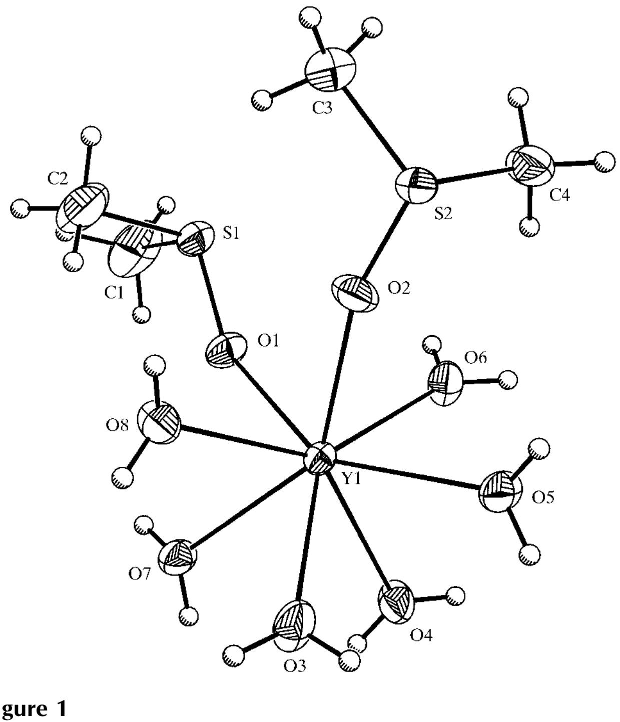


Figure 1
The molecular structure of $[Y(H_2O)_6\{(CH_3)_2SO\}_2]^{3+}$ with displacement ellipsoids drawn at the 30% probability level for all non-H atoms.

resolved and independently refined. The main form (84.30 and 86.48% for S1 and S2, respectively) is transformed into the other by an inversion of the S atom through the plane defined by C1, C2, O1 and Y1 (mean deviation from plane = 0.007 Å). The perpendicular distances of the S1 and S1*A* atoms from this plane are −0.71 and 0.65 Å, respectively (Fig. 2).

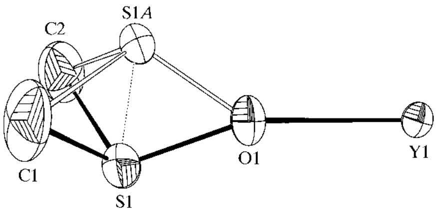


Figure 2
One dmso ligand coordinated to the Y^{3+} cation showing the two disordered positions of the S atom. The displacement ellipsoids are drawn at the 30% probability level. H atoms are not shown for clarity.

Experimental

The title compound was synthesized by dissolving yttrium oxide in dilute hydrochloric acid with stirring and heating. The solution was concentrated by slow evaporation followed by addition of DMSO (DMSO:H_2O = 1:3). After further evaporation in a dessicator, crystals of X-ray quality were obtained. The yttrium and chloride contents were determined by ethylene diamine tetraacetic acid titration and by cation exchange (Dowex 50W–X8, H^+-form), respectively. Identification of the coordinated dmso molecules was achieved by comparing the Raman spectrum (BioRad FTS 6000 spectrometer) of the crystals with that of liquid DMSO.

Crystal data

$[Y(C_2H_6OS)_2(H_2O)_6]Cl_3$
$M_r = 459.61$
Monoclinic, $P2_1/c$
$a = 8.7942\ (11)$ Å
$b = 12.3337\ (15)$ Å
$c = 17.291\ (2)$ Å
$\beta = 101.201\ (2)^\circ$
$V = 1839.7\ (4)$ Å^3
$Z = 4$
$D_x = 1.659$ Mg m^{-3}
$D_m = 1.658$ Mg m^{-3}
D_m measured by flotation in tetrabromoethane/dichloromethane
Mo $K\alpha$ radiation
Cell parameters from 2682 reflections
$\theta = 2.04$–28.53°
$\mu = 3.853$ mm^{-1}
$T = 298\ (2)$ K
Prism, colourless
0.22 × 0.20 × 0.18 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Bruker, 1998)
$T_{\min} = 0.445$, $T_{\max} = 0.500$
10 933 measured reflections
4261 independent reflections
2682 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$
$\theta_{\max} = 28.53^\circ$
$h = -11 \rightarrow 10$
$k = -16 \rightarrow 15$
$l = -22 \rightarrow 19$
Intensity decay: negligible as determined from a repetition of the first 50 frames at the end of the experiment

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.099$
$S = 0.941$
4261 reflections
233 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.49$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Extinction correction: *SHELXL* (Bruker, 1998)
Extinction coefficient: 7 (3) × 10^{-4}

Table 1
Selected geometric parameters (Å, °).

Y1—O2	2.269 (3)	Y1—O8	2.371 (3)
Y1—O1	2.278 (3)	Y1—O7	2.372 (3)
Y1—O5	2.360 (3)	Y1—O6	2.377 (3)
Y1—O4	2.370 (3)	Y1—O3	2.404 (4)
O2—Y1—O1	83.22 (11)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O8—H82···Cl2$^{\rm i}$	0.814 (19)	2.35 (2)	3.138 (4)	162 (4)
O5—H52···Cl3$^{\rm ii}$	0.824 (19)	2.31 (2)	3.120 (4)	167 (4)
O8—H81···Cl3$^{\rm iii}$	0.817 (19)	2.30 (2)	3.118 (4)	174 (5)
O5—H51···Cl2$^{\rm iv}$	0.819 (19)	2.43 (3)	3.189 (4)	155 (5)
O3—H32···Cl2$^{\rm iv}$	0.800 (19)	2.42 (2)	3.207 (4)	170 (5)
O3—H31···Cl3$^{\rm iii}$	0.821 (18)	2.51 (3)	3.253 (4)	152 (4)
O6—H62···Cl2$^{\rm v}$	0.799 (19)	2.67 (3)	3.422 (4)	157 (5)
O7—H72···Cl1	0.83 (2)	2.25 (2)	3.068 (4)	174 (7)
O6—H61···Cl1$^{\rm v}$	0.813 (19)	2.29 (2)	3.099 (4)	176 (5)
O4—H42···Cl1	0.814 (19)	2.33 (2)	3.134 (4)	168 (6)
O7—H71···Cl2	0.814 (19)	2.52 (3)	3.258 (4)	152 (5)
O4—H41···Cl3$^{\rm vi}$	0.811 (19)	2.37 (2)	3.147 (4)	161 (5)

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

Water-H atoms were located on difference Fourier maps but the O—H distances were restrained to 0.82 Å. Methyl-H atoms were generated in ideal positions and were refined as riding on their respective C atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); 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: OS1077). Services for accessing these data are described at the back of the journal.

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