C126	0.1081 (6)	0.4484 (6)	0.0721 (5)	3.6 (2)
C131	−0.0079 (5)	0.3196 (5)	0.0255 (4)	2.6 (2)
C132	−0.0772 (6)	0.3280 (6)	−0.0058 (5)	3.7 (2)
C133	−0.0883 (7)	0.3167 (7)	−0.0662 (5)	4.6 (3)
C134	−0.0307 (7)	0.2969 (7)	−0.0965 (4)	4.7 (3)
C135	0.0381 (6)	0.2866 (7)	−0.0671 (4)	4.1 (2)
C136	0.0503 (6)	0.2995 (6)	−0.0068 (5)	3.5 (2)
C211	0.1028 (5)	0.1429 (5)	0.0723 (4)	2.8 (2)
C212	0.1596 (6)	0.1902 (6)	0.0962 (5)	3.6 (2)
C213	0.2254 (6)	0.1905 (7)	0.0720 (6)	4.7 (3)
C214	0.2325 (6)	0.1432 (8)	0.0239 (6)	5.4 (3)
C215	0.1790 (6)	0.0950 (8)	0.0012 (5)	5.0 (3)
C216	0.1140 (6)	0.0931 (7)	0.0261 (4)	4.0 (2)
C221	0.0252 (6)	0.0419 (5)	0.1405 (4)	3.1 (2)
C222	0.0898 (7)	0.0212 (7)	0.1748 (5)	4.6 (3)
C223	0.0974 (8)	−0.0555 (8)	0.1983 (6)	6.1 (3)
C224	0.0418 (9)	−0.1086 (7)	0.1867 (6)	7.3 (4)
C225	−0.0222 (9)	−0.0869 (7)	0.1548 (6)	6.4 (4)
C226	−0.0301 (7)	−0.0117 (6)	0.1306 (5)	4.6 (3)
C231	−0.0621 (5)	0.1393 (5)	0.0546 (4)	2.5 (2)
C232	−0.0666 (6)	0.1279 (6)	−0.0065 (4)	3.6 (2)
C233	−0.1328 (8)	0.1284 (8)	−0.0401 (5)	5.4 (3)
C234	−0.1954 (7)	0.1427 (9)	−0.0167 (6)	5.9 (3)
C235	−0.1918 (6)	0.1530 (8)	0.0444 (5)	4.9 (3)
C236	−0.1259 (6)	0.1527 (7)	0.0801 (5)	4.2 (2)
B	0.238	0.210	0.276	16.0

Table 2. *Geometric parameters* (Å, °)

Pd—Cl1	2.386 (3)	Pd—P1	2.290 (2)
Pd—Cl2	2.354 (3)	Pd—P2	2.256 (2)
Cl1—Pd—Cl2	84.89 (9)	Cl2—Pd—P1	172.05 (9)
Cl1—Pd—P1	89.40 (9)	Cl2—Pd—P2	90.8 (1)
Cl1—Pd—P2	175.7 (1)	P1—Pd—P2	94.86 (9)

The tetrafluoroborate anion was refined as a rigid group (ideal tetrahedron with B—F distance of 1.415 Å) with isotropic thermal parameters, those of the F atoms being 20% larger than that of the B atom. Only three of the four F atoms of the BF_4 groups were obvious on the difference Fourier map, and their large temperature factors indicated some possible rotational disorder of this highly symmetric group, which could not be resolved. Hence the fourth F atom was introduced in an estimated position followed by group regularization (B—F = 1.415 Å). The tetrafluoroborate anion was refined further as a rigid group (ideal tetrahedron) with isotropic thermal parameters by means of the *CRYSTALS* program (available with the *MolEN* system), with thermal parameters of the F atoms being 20% larger than those of the B atom.

We thank the Louisiana Educational Quality Support Fund, administered by the Louisiana Board of Regents, for support of this research.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55805 (45 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1035]

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Acta Cryst. (1993). C**49**, 1171–1173

Structure of Pentaaqua(L-serine)holmium(III) Trichloride

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(*Received* 8 *July* 1992; *accepted* 26 *November* 1992)

Abstract

The crystal structure of a holmium(III) complex with L-serine $\{[Ho(C_3H_7NO_3)(H_2O)_5]Cl_3\}$ is reported. As for most cases of lanthanide complexes with amino acids, the coordination number is eight. Each Ho ion is coordinated by two carboxylate O atoms, one hydroxyl O atom of a serine molecule and five other O atoms from water molecules. The Cl anions are not coordinated.

Comment

The structure of the title compound was investigated in order to continue the study on interaction and coordination of lanthanide ions with amino acids (Głowiak, Dao, Legendziewicz & Huskowska, 1991, and references therein). The structure is that of a linear polymer, in which the Ho ions are connected by serine carboxylate groups. There is pseudosymmetry between the independent structure units of Ho(1) and Ho(2). On moving the cell origin to the point (−0.25, −0.148, 0), the approximate symmetry of the $P2_1/a$ space group could be demonstrated. Eight-coordinated polyhedra of Ho ions take the form of distorted square antiprisms [Δ_{SAP} values

(Drew, 1977) are 0.019 and 0.024 (*FIGURANT*; Starynowicz, 1990) for coordination polyhedra around Ho(1) and Ho(2), respectively]. The Ho—O distances range from 2.27 (1) to 2.41 (2) Å. The valency distances and angles in the serine molecules of the title complex (zwitterion form) are not significantly different from those in the uncoordinated serine structure (Kistenmacher, Rand & Marsh, 1974). Hydrogen bonds of the type O···H···O [2.75 (2)–2.86 (2) Å], O···H···Cl [2.99 (2)–3.75 (2) Å] and N···H···Cl [3.08 (2)–3.33 (2) Å] are present in the structure. A similar linear polymeric structure for the $\mathrm{Ho^{III}}$ complex with threonine has been reported (Głowiak & Dao, 1988).

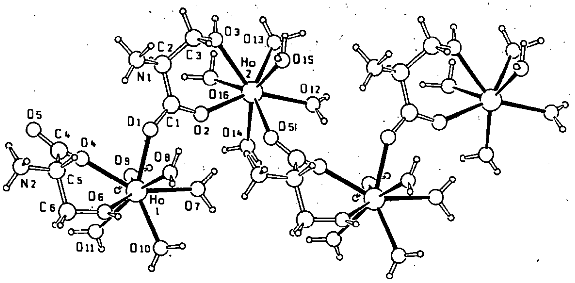

Fig. 1. A *SCHAKAL*88 (Keller, 1988) perspective view of the $[\mathrm{Ho(C_3H_7NO_3)(H_2O)_5]Cl_3}$ structure.

Experimental

Crystal data

$[\mathrm{Ho(C_3H_7NO_3)(H_2O)_5]Cl_3}$
$M_r = 466.5$
Monoclinic
$P2_1$
$a = 8.909\ (2)$ Å
$b = 19.847\ (4)$ Å
$c = 7.602\ (2)$ Å
$\beta = 90.51\ (4)°$
$V = 1344.1$ Å^3
$Z = 4$
$D_x = 2.31$ Mg m^{-3}
$D_m = 2.30$ Mg m^{-3}
Density measured by flotation in $\mathrm{CCl_4/CHBr_3}$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 10\text{–}15°$
$\mu = 6.58$ mm^{-1}
$T = 294$ K
Columns
0.45 × 0.40 × 0.30 mm
Yellow
Crystal source: aqueous solution of $\mathrm{HoCl_3}$ + L-serine (1:1 molar ratio)

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.83$, $T_{\max} = 1.35$
3168 measured reflections
3168 independent reflections

2863 observed reflections [$F > 6\sigma(F)$]
$\theta_{\max} = 32.5°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 20$
$l = -9 \rightarrow 9$
2 standard reflections monitored every 50 reflections
intensity variation: 3%

Refinement

Refinement on F
Final $R = 0.037$
$wR = 0.050$
$S = 4.171$
2863 reflections
288 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Cell refinement: *XTL/XTLE* (Syntex, 1976). Program(s) used to solve structure: *XTL/XTLE* [Patterson syntheses and difference Fourier methods (Syntex, 1976)]. Program(s) used to refine structure: *XTL/XTLE*. Molecular graphics: *SCHAKAL*88 (Keller, 1988).

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

$$B_{\mathrm{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ho(1)	0.05396 (9)	0.0	0.14869 (12)	1.07 (7)
Ho(2)	0.55703 (9)	0.20356 (3)	0.14859 (11)	0.098 (6)
Cl(1)	−0.1766 (8)	0.1116 (5)	−0.3436 (9)	2.6 (4)
Cl(2)	0.3082 (9)	0.1037 (5)	0.6368 (10)	2.6 (4)
Cl(3)	0.4409 (7)	0.4323 (4)	0.1655 (8)	2.6 (4)
Cl(4)	0.0656 (7)	0.2683 (4)	0.8674 (8)	2.5 (4)
Cl(5)	0.5936 (7)	0.3427 (4)	0.6519 (8)	2.6 (4)
Cl(6)	0.9440 (6)	0.3611 (4)	0.3518 (8)	2.2 (3)
O(1)	0.1057 (14)	0.1039 (8)	0.260 (2)	1.7 (10)
O(2)	0.3324 (15)	0.1512 (7)	0.182 (2)	1.3 (10)
O(3)	0.3892 (17)	0.2793 (7)	0.298 (2)	2.7 (11)
O(4)	−0.1764 (14)	0.0558 (10)	0.176 (2)	1.7 (12)
O(5)	−0.3874 (15)	0.0949 (8)	0.2619 (18)	1.4 (9)
O(6)	−0.1073 (15)	−0.0717 (10)	0.313 (3)	4.1 (16)
O(7)	0.3177 (15)	0.0164 (9)	0.099 (2)	1.6 (10)
O(8)	0.156 (2)	−0.0098 (12)	0.432 (2)	4.8 (18)
O(9)	0.068 (2)	0.0704 (11)	−0.088 (2)	3.9 (16)
O(10)	0.1489 (17)	−0.1089 (9)	0.127 (2)	2.2 (11)
O(11)	−0.0923 (17)	−0.0460 (9)	−0.072 (2)	2.5 (11)
O(12)	0.8199 (15)	0.1949 (10)	0.079 (2)	2.0 (11)
O(13)	0.6640 (16)	0.3080 (9)	0.119 (2)	2.6 (12)
O(14)	0.5646 (17)	0.1395 (11)	−0.106 (2)	3.8 (17)
O(15)	0.6498 (18)	0.2197 (8)	0.4342 (17)	2.3 (11)
O(16)	0.4139 (19)	0.2658 (8)	−0.065 (2)	2.5 (13)
N(1)	0.0327 (18)	0.2076 (13)	0.458 (2)	2.0 (11)
N(2)	−0.473 (2)	−0.0116 (12)	0.451 (3)	2.5 (13)
C(1)	0.1984 (17)	0.1554 (11)	0.255 (2)	0.6 (11)
C(2)	0.157 (2)	0.2220 (9)	0.330 (2)	1.6 (12)
C(3)	0.2809 (18)	0.2606 (9)	0.420 (2)	2.1 (11)
C(4)	−0.284 (2)	0.0546 (12)	0.262 (3)	1.6 (14)
C(5)	−0.3152 (19)	−0.0061 (9)	0.389 (2)	1.3 (11)
C(6)	−0.2666 (17)	−0.0747 (8)	0.317 (2)	2.2 (12)

Table 2. *Geometric parameters* (Å, °)

Ho(1)—O(1)	2.28 (2)	Ho(1)—O(4)	2.34 (1)
Ho(1)—O(6)	2.38 (2)	Ho(1)—O(7)	2.41 (1)
Ho(1)—O(8)	2.34 (2)	Ho(1)—O(9)	2.28 (2)
Ho(1)—O(10)	2.33 (2)	Ho(1)—O(11)	2.30 (2)
Ho(2)—O(2)	2.27 (1)	Ho(2)—O(3)	2.41 (1)
Ho(2)—O(5)$^{\mathrm{i}}$	2.37 (2)	Ho(2)—O(12)	2.41 (1)
Ho(2)—O(13)	2.29 (2)	Ho(2)—O(14)	2.32 (2)
Ho(2)—O(15)	2.34 (1)	Ho(2)—O(16)	2.40 (2)
O(1)—C(1)	1.32 (2)	O(2)—C(1)	1.32 (2)
O(4)—C(4)	1.17 (3)	O(5)—C(4)	1.22 (3)
O(6)—C(6)	1.42 (2)	O(3)—C(3)	1.39 (2)
N(1)—C(2)	1.51 (2)	N(2)—C(5)	1.49 (3)
C(1)—C(2)	1.49 (3)	C(2)—C(3)	1.50 (2)
C(4)—C(5)	1.57 (3)	C(5)—C(6)	1.53 (2)
O(1)—C(1)—O(2)	122 (2)	O(1)—C(1)—C(2)	121 (1)
O(2)—C(1)—C(2)	116 (2)	N(1)—C(2)—C(1)	105 (2)

N(1)—C(2)—C(3)	110 (1)	C(1)—C(2)—C(3)	116 (1)
O(3)—C(3)—C(2)	110 (1)	O(4)—C(4)—O(5)	127 (2)
O(4)—C(4)—C(5)	121 (2)	C(5)—C(4)—O(5)	112 (2)
N(2)—C(5)—C(4)	115 (2)	N(2)—C(5)—C(6)	109 (2)
O(6)—C(6)—C(5)	105 (1)	C(4)—C(5)—C(6)	114 (1)

Symmetry code: (i) $1 + x, y, z$.

This work has received the support of project CPBP 01.12.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55815 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1017]

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Acta Cryst. (1993). C**49**, 1173–1175

Structures of the Cadmium Halide Complexes [{$CdCl_2$(dmso)(MeOH)}$_n$] and [{$CdBr_2$(dmso)(MeOH)}$_n$] with Coordinated Dimethyl Sulfoxide and Methanol

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(*Received* 14 *September* 1992; *accepted* 17 *November* 1992)

Abstract

Cadmium chloride and bromide form halogen-bridged polymeric chain complexes *catena*-poly[{(dimethyl sulfoxide)(methanol)cadmium}di-μ-chloro] [{$CdCl_2$(dmso)(MeOH)}$_n$] (dmso = dimethyl sulfoxide) and *catena*-poly[{(dimethyl sulfoxide)(methanol)cadmium}di-μ-bromo] [{$CdBr_2$(dmso)(MeOH)}$_n$] with Cd in octahedral coordination. With the chloride, the dmso and MeOH ligands are in *trans* positions. The hydroxylic proton of the coordinated methanol enters into hydrogen bonding with the O atom of a dmso ligand coordinated to an adjacent Cd centre in the same chain. The bromide differs in having the dmso and MeOH ligands in *cis* positions, with each chain now linked to its four neighbours through hydrogen bonding.

Comment

The two compounds have polymeric chain structures with six-coordinate cadmium centres bridged by halogen pairs. The chain simplicity distinguishes them from most of the other single-chain structures which cadmium chloride and bromide are found to produce (Nieuwenhuyzen, 1992). Each Cd carries a methanol and a dimethyl sulfoxide (dmso) ligand but whereas the two ligands are *trans* in the chloride (1), they are *cis* in the bromide (2). In (1), there is intrachain hydrogen bonding between the methanol and dmso ligands carried by adjacent Cd centres (Fig. 1) with the whole structure conforming to the 2_1 screw-axis relationship. Deviation from strict linearity is very slight with Cd···Cd···Cd angles of 179.3 (1)°. By contrast, the *cis* positioning in (2) means that there is chain zigzag, and the Cd···Cd···Cd angle is 130.2 (1)°. Both the zigzag and the linear chains can be related to the bonding within an original, but now degraded, CdX_2 layer lattice.

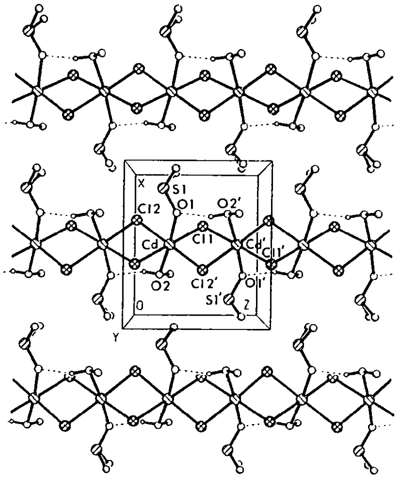

Fig. 1. Chain relationships for [{$CdCl_2$(dmso)(MeOH)}$_n$] (1) showing the intrachain hydrogen bonding. The coordinates of Cd are ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} + z$) and Cd′ ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 + z$); the x and y coordinates are therefore close to ($\frac{1}{2}$, $\frac{1}{2}$). In the extended structure, Cd atoms of the four neighbouring chains lie close to the cell edges parallel to the z axis.

0108-2701/93/061173-03$06.00