made prior to data collection, had an average width at half-height of 0.31°, with a take-off angle of 6.0°. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The H-atom coordinates were found unequivocally from difference Fourier calculations, except those of the water of crystallization. H atoms were included in calculations and not refined. A peak with $\Delta\rho = 1.40\,\text{e}\,\text{Å}^{-3}$ at 1.87 Å from O1 was found in a difference Fourier calculation. Refinement of O atoms at O1 and this site with occupancy factors of 0.8 and 0.2, respectively, resulted in a high displacement parameter for this peak. It was ignored in the final calculations. All calculations were performed using the *TEXSAN* (Molecular Structure Corporation, 1995) program package.

Data collection: Rigaku/AFC diffractometer control software. Cell refinement: Rigaku/AFC diffractometer control software. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

This research was supported by grants from the National Science Foundation of China.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). **C53**, 60–63

Dichloro[*N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)ethylenediamine]samarium(III) Perchlorate

HAI-YING JIN,[a] MASAHARU AKIBA,[a] KEISUKE UMAKOSHI,[a]* YOICHI SASAKI[a] AND KUNINOBU KABUTO[b]

[a]*Division of Chemistry, Graduate School of Science, Hokkaido University, Kita-ku, Sapporo 060, Japan, and* [b]*Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980, Japan. E-mail: umakoshi@teine.chem2.hokudai.ac.jp*

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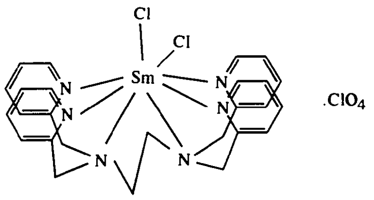
Abstract

The crystal structure of the title compound, $[SmCl_2\{C_2H_4N_2(CH_2C_5H_4N)_4\}]ClO_4$, at room temperature was solved and compared with the previously determined structure of $[Eu^{III}Cl_2(R\text{-tppn})]ClO_4$ [where *R*-tppn is *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)-(*R*)-propylenediamine]. The Sm^{3+} ion is eight-coordinated through the six N atoms of the *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)ethylenediamine ligand and two Cl^- ions. The coordination is best described as dodecahedral with some important distortions.

Comment

The europium(III) complex $[EuCl_2(R\text{-tppn})]ClO_4$ [*R*-tppn is *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)-(*R*)-propylenediamine], (II), which was prepared as a chiral NMR-shift reagent for aqueous solution, has a unique asymmetrically distorted dodecahedral structure (Hazama, Umakoshi, Kabuto, Kabuto & Sasaki, 1996). In order to determine whether the structure is common to other lanthanide(III) ions, we decided to prepare other lanthanide(III) complexes of *R*-tppn and a related ligand, *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen). We report here the X-ray crystal structure of the samarium(III)–tpen complex, $[SmCl_2(tpen)]ClO_4$, (I).



(I)

The crystal structure of (I) (Fig. 1) consists of a monomeric complex cation and a perchlorate anion which is disordered along the Cl(3)—O(4) axis. The Sm—Cl and Sm—N bond lengths are normal and similar to those found in the complexes $[SmCl(OH_2)_2(18\text{-crown-}6)]Cl_2.2H_2O$ (Rogers & Kurihara, 1987), $[Sm(C_{19}H_{14}N_3O_2)_3]$ (Dan, Seth & Chakraborty, 1989) and $Na[Sm(edta)(H_2O)_3].5H_2O$ (Templeton, Templeton, Zalkin & Ruben, 1982). Two bis(2-pyridylmethyl)amino parts of the tpen ligand are in a significantly different steric environment. This is in sharp contrast to the steric structures of the lanthanide(III) complexes of ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate (edta) or its propylenediamine derivative (pdta), where the difference in the steric environments of the two amino–diacetate parts is much less significant (*e.g.* see Hoard, Lee & Lind, 1965; Kabuto, Kabuto, Sasaki, Nishiyama & Umakoshi, 1993; Nakamura, Kurisaki, Wakita & Yamaguchi, 1995). The N(2)—Sm—N(21) coordination angle [89.7 (2)°] is significantly different from the corresponding N(1)—Sm—N(31) angle [121.3 (2)°]. As a result, the N(2) and N(21) atoms are close [3.667 (8) Å], while the N(1) and N(31) atoms are further apart [4.629 (11) Å]. The dodecahedral coordination of (I) consists of four five-fold vertices at Cl(1), Cl(2), N(2) and N(21), due to the short interatomic distance of N(2) and N(21), and four fourfold vertices at N(1), N(11), N(31) and N(41), due to the long interatomic distance between N(1) and N(31) (Fig. 2). A dodecahedron of this sort may be called 'bisdisphenoid' (Wells, 1984). Although dodecahedral coordination has been found for some lanthanide complexes (Wang, Guo, Huang, Zhang & Lu, 1989; Foulon, Durand, Cot, Tijani & Rafiq, 1995), it has not been found for those having multidentate ligands. Such distortions also lead to the marked non-planarity in the N(11), N(21), N(31), N(41) trapezoidal plane; the deviations from this least-squares plane are 0.199 (7) [N(11)], −0.319 (7) [N(21)], 0.324 (7) [N(31)] and −0.204 (7) Å [N(41)]. The Sm^{3+}, Cl(1) and Cl(2) ions deviate by −0.171 (4), 2.474 (4) and −0.448 (9) Å, respectively, from this plane. Similar but less marked non-planarity was observed for the four coordinated carboxyl O atoms of sodium (propylenediaminetetraacetato)europium(III), which is also known as a chiral shift reagent for aqueous solution (Kabuto *et al.*, 1993), and for the four pyridyl N atoms of the tppn complex of dimeric molybdenum(V) (Hazama, Umakoshi, Ichimura, Ikari, Sasaki & Ito, 1995; Saito, Sasaki & Hazama, 1995).

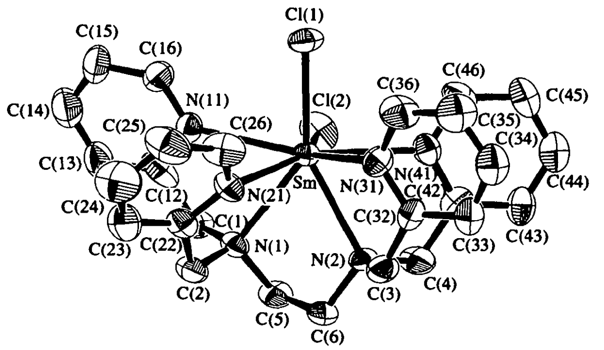


Fig. 1. The molecular structure of the complex cation of (I) with the atomic numbering scheme. Displacement ellipsoids are shown at 50% probability levels.

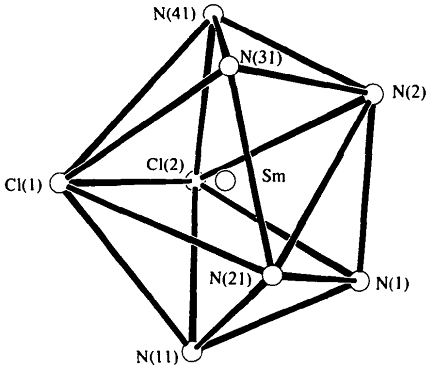


Fig. 2. A perspective view of the distorted dodecahedral geometry around the Sm^{3+} ion. The distances of eighteen edges are as follows (Å): Cl(1)—Cl(2) 3.942 (3), Cl(1)—N(11) 3.469 (7), Cl(1)—N(21) 3.787 (7), Cl(1)—N(31) 3.435 (7), Cl(1)—N(41) 3.773 (7), Cl(2)—N(1) 3.606 (6), Cl(2)—N(2) 4.122 (7), Cl(2)—N(11) 3.374 (6), Cl(2)—N(41) 3.197 (7), N(1)—N(2) 2.94 (1), N(1)—N(11) 2.774 (9), N(1)—N(21) 2.863 (9), N(2)—N(21) 3.667 (8), N(2)—N(31) 2.944 (9), N(2)—N(41) 2.861 (9), N(11)—N(21) 2.974 (9), N(21)—N(31) 3.26 (1) and N(31)—N(41) 2.872 (9).

The overall structural features of the complex cation in (I) are very similar to those of (II), which has an optically active arrangement of the coordination atoms induced by a fixed *gauche* configuration of the diamine part due to the methyl group at the asymmetric C atom. Each complex cation in the crystal of (I) has a similar optically active arrangement of the coordinating atoms. There are equal amounts of enantiomeric pairs in the crystal of (I).

Experimental

A methanol solution (10 ml) of tpen (581.6 mg, 1.37 mmol) was mixed with a methanol solution (10 ml) of $SmCl_3.6H_2O$ (500 mg, 1.37 mmol). The mixture was refluxed for 90 min. To the resulting mixture was added sodium perchlorate (400 mg, 3.27 mmol) in methanol (5 ml) to give a white precipitate. Yield: 380 mg (37.2%). Analysis: found C 41.96, H 3.99, N 11.05, Cl 14.11%; calculated for $C_{26}H_{28}Cl_3N_6O_4Sm$ C 41.90, H 3.79, N 11.28, Cl 14.27%. Vapor diffusion of diethyl ether into a concentrated acetonitrile solution of the complex gave colourless crystals suitable for the X-ray structure determination.

Crystal data

$[SmCl_2(C_{26}H_{28}N_6)]ClO_4$
$M_r = 745.27$
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Monoclinic
$P2_1/a$
$a = 15.804\ (2)$ Å
$b = 15.112\ (2)$ Å
$c = 12.684\ (2)$ Å
$\beta = 104.89\ (1)°$
$V = 2927.5\ (7)$ Å^3
$Z = 4$
$D_x = 1.691$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 12.54–14.80°$
$\mu = 2.33$ mm^{-1}
$T = 296$ K
Plate
0.35 × 0.20 × 0.08 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.42$, $T_{\max} = 0.83$
9196 measured reflections
8838 independent reflections
4915 observed reflections
$[I > 3\sigma(I)]$

$R_{\rm int} = 0.022$
$\theta_{\max} = 30°$
$h = -22 \rightarrow 21$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 17$
3 standard reflections
monitored every 150 reflections
intensity decay: 0.22%

Refinement

Refinement on F
$R = 0.049$
$wR = 0.043$
$S = 2.248$
4915 reflections
359 parameters
H atoms not located
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.828$
$\Delta\rho_{\max} = 1.34$ e Å^{-3}
$\Delta\rho_{\min} = -1.14$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sm	0.23345 (3)	0.21658 (2)	0.04975 (4)	0.03175 (9)
Cl(1)	0.1087 (1)	0.3340 (1)	0.0467 (2)	0.0483 (7)
Cl(2)	0.3578 (2)	0.3354 (2)	0.0451 (2)	0.0611 (8)
Cl(3)	0.6160 (2)	0.0024 (2)	0.3725 (2)	0.0599 (8)
O(1)†	0.6069 (7)	0.0988 (7)	0.3530 (10)	0.073 (4)
O(2)†	0.5562 (8)	−0.0398 (8)	0.289 (1)	0.084 (4)
O(3)†	0.5940 (8)	−0.0080 (9)	0.477 (1)	0.097 (5)
O(4)	0.7057 (4)	−0.0206 (5)	0.3839 (5)	0.081 (3)
O(5)‡	0.603 (2)	0.049 (2)	0.450 (2)	0.13 (1)
O(6)‡	0.588 (1)	0.034 (2)	0.256 (2)	0.116 (8)
O(7)‡	0.570 (1)	−0.080 (2)	0.358 (2)	0.110 (8)
N(1)	0.3049 (4)	0.1197 (4)	−0.0754 (5)	0.037 (2)
N(2)	0.3257 (4)	0.0852 (4)	0.1584 (5)	0.040 (2)
N(11)	0.1951 (4)	0.2592 (4)	−0.1624 (5)	0.041 (2)
N(21)	0.1266 (4)	0.1044 (4)	−0.0653 (6)	0.042 (2)
N(31)	0.1575 (4)	0.1422 (4)	0.1952 (6)	0.045 (2)
N(41)	0.3097 (4)	0.2534 (4)	0.2548 (6)	0.044 (2)
C(1)	0.3337 (5)	0.1808 (5)	−0.1531 (7)	0.046 (3)
C(2)	0.2473 (5)	0.0470 (5)	−0.1380 (7)	0.046 (3)
C(3)	0.2670 (6)	0.0270 (5)	0.2061 (7)	0.050 (3)
C(4)	0.3996 (5)	0.1222 (6)	0.2441 (8)	0.063 (3)
C(5)	0.3871 (5)	0.0801 (5)	−0.0047 (7)	0.046 (3)
C(6)	0.3670 (5)	0.0261 (5)	0.0881 (7)	0.047 (3)
C(12)	0.2551 (6)	0.2293 (5)	−0.2183 (8)	0.054 (3)
C(13)	0.2419 (7)	0.2471 (6)	−0.3281 (8)	0.064 (3)
C(14)	0.1678 (8)	0.2969 (6)	−0.3840 (8)	0.075 (4)
C(15)	0.1072 (7)	0.3274 (6)	−0.3276 (8)	0.064 (3)
C(16)	0.1224 (6)	0.3055 (5)	−0.2160 (7)	0.052 (3)
C(22)	0.1502 (5)	0.0651 (5)	−0.1478 (7)	0.043 (3)
C(23)	0.0879 (6)	0.0366 (6)	−0.2414 (8)	0.064 (3)
C(24)	−0.0013 (7)	0.0492 (7)	−0.245 (1)	0.090 (4)
C(25)	−0.0251 (7)	0.0883 (7)	−0.158 (1)	0.081 (4)
C(26)	0.0403 (5)	0.1134 (5)	−0.0671 (9)	0.059 (3)
C(32)	0.2088 (5)	0.0789 (5)	0.2579 (7)	0.041 (2)
C(33)	0.2044 (6)	0.0627 (6)	0.3651 (8)	0.052 (3)
C(34)	0.1459 (7)	0.1093 (7)	0.4066 (8)	0.066 (4)
C(35)	0.0911 (7)	0.1694 (7)	0.3410 (9)	0.071 (4)
C(36)	0.0980 (6)	0.1857 (6)	0.2350 (9)	0.065 (4)
C(42)	0.3725 (5)	0.1958 (5)	0.3102 (7)	0.047 (3)
C(43)	0.4129 (5)	0.2061 (6)	0.4193 (7)	0.053 (3)
C(44)	0.3897 (6)	0.2789 (7)	0.4733 (7)	0.060 (3)
C(45)	0.3252 (7)	0.3376 (6)	0.4193 (8)	0.064 (3)
C(46)	0.2854 (6)	0.3228 (5)	0.3078 (8)	0.053 (3)

† Site occupancy = 0.63 (1). ‡ Site occupancy = 0.37 (1).

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

Sm—Cl(1)	2.645 (2)	Sm—N(11)	2.680 (6)
Sm—Cl(2)	2.673 (2)	Sm—N(21)	2.566 (6)
Sm—N(1)	2.619 (6)	Sm—N(31)	2.692 (7)
Sm—N(2)	2.634 (6)	Sm—N(41)	2.630 (7)
Cl(1)—Sm—Cl(2)	95.64 (6)	N(1)—Sm—N(11)	63.1 (2)
Cl(1)—Sm—N(1)	143.3 (1)	N(1)—Sm—N(21)	67.0 (2)
Cl(1)—Sm—N(2)	145.5 (2)	N(1)—Sm—N(31)	121.3 (2)
Cl(1)—Sm—N(11)	81.3 (1)	N(1)—Sm—N(41)	123.9 (2)
Cl(1)—Sm—N(21)	93.2 (2)	N(2)—Sm—N(11)	131.2 (2)
Cl(1)—Sm—N(31)	80.1 (2)	N(2)—Sm—N(21)	89.7 (2)
Cl(1)—Sm—N(41)	91.3 (2)	N(2)—Sm—N(31)	67.1 (2)
Cl(2)—Sm—N(1)	85.9 (1)	N(2)—Sm—N(41)	65.8 (2)
Cl(2)—Sm—N(2)	101.9 (2)	N(11)—Sm—N(21)	69.0 (2)
Cl(2)—Sm—N(11)	78.1 (1)	N(11)—Sm—N(31)	139.7 (2)
Cl(2)—Sm—N(21)	144.2 (2)	N(11)—Sm—N(41)	150.4 (2)
Cl(2)—Sm—N(31)	139.0 (2)	N(21)—Sm—N(31)	76.7 (2)
Cl(2)—Sm—N(41)	74.1 (1)	N(21)—Sm—N(41)	140.3 (2)
N(1)—Sm—N(2)	68.2 (2)	N(31)—Sm—N(41)	65.3 (2)

The title structure was solved by the heavy-atom method (*DIRDIF*; Beurskens *et al.*, 1992). The non-H atoms were refined anisotropically, except for the O(1), O(2), O(3), O(5), O(6) and O(7) atoms of the perchlorate ion. The perchlorate ion is rotationally disordered along the Cl(3)—O(4) axis. The occupancies of the disordered O atoms were refined with the constraints that the occupancies of the O(1), O(2) and O(3) atoms and those of the O(5), O(6) and O(7) have the same value, and that the sum of the occupancies of the two groups is unity. In the final cycle of the refinement, the occupancies of the O(1), O(2), O(3) and O(5), O(6), O(7) groups were 0.63 (1) and 0.37 (1), respectively. No attempt was made to locate the H atoms in the structure analysis. The final cycle of full-matrix least-squares refinement gave an R value of 0.049 ($wR = 0.043$). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1992) and *BOND* (Yoshioka & Hirotsu, 1980).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS*. Program(s) used to solve structure: *PATTY* in *DIRDIF92*. Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: TA1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis[bis(triphenylphosphoranylidene)ammonium] Pentachlorofluoroosmate(IV) Hydrate, $[(C_6H_5)_3P{=}N{=}P(C_6H_5)_3]_2$-$[OsFCl_5].H_2O$

CLEMENS BRUHN AND WILHELM PREETZ*

Institut für Anorganische Chemie, Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany. E-mail: sunac026@talos.ac.uni-kiel.de

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Abstract

The structure of the title compound, $(C_{36}H_{30}NP_2)_2$-$[OsCl_5F].H_2O$, has been determined by single-crystal X-ray diffraction at 208 K. The octahedral $[OsCl_5F]^{2-}$ complex anions are completely ordered in an A_2B-type lattice. The monoclinic unit cell contains four formula units, each with a solvent water molecule linked to the F atom by a hydrogen bond [O···F 2.737 (8) Å]. The Os—F bond [1.960 (4) Å] is weakened by *trans* influence and, correspondingly, the Os—Cl1 bond [2.307 (2) Å] *trans* to Os—F is strengthened compared with the average Os—Cl bond length along the Cl—Os—Cl axes of 2.339 Å.

Comment

We are currently studying the spectroscopic properties of inorganic octahedral complexes. The present work was performed in order to confirm the results obtained from vibrational and NMR spectroscopy for the heteroleptic series $[MCl_{6-n}F_n]^{2-}$ (M = Os, Ir, Pt; n = 1–5; Preetz & Ruf, 1986; Alyoubi, Greenslade, Foster & Preetz, 1990; Bruhn, Drews, Meynhardt & Preetz, 1995). Until recently, structure analyses of mixed-halogeno complexes have failed because of total or partial disorder in the packing of the complexes in the anion sublattice. Using the twofold organic cation *N,N'*-methylenedipyridinium (Brüdgam & Hartl, 1986), which forms *AB*-type salts, ordered structures of all compounds of the series $[OsCl_{6-n}F_n]^{2-}$ (n = 2–5) became accessible, with each Os—F and Os—Cl bond clearly distinguishable (Bruhn & Preetz, 1994*a*,*b*, 1995*a*,*b*, 1996). Unfortunately, the *N,N'*-methylenedipyridinium salt of $[OsCl_5F]^{2-}$ crystallizes in space group $P\bar{1}$, with the central ion located on the inversion center causing disorder in the F—Os—Cl axis. This problem is overcome by crystallizing the mixed-ligand complex with bis(triphenylphosphoranylidene)ammonium as cation to give a completely ordered A_2B-type lattice. In the course of our work on mixed F/Cl complexes of Os^{IV}, we isolated the title complex, (I), by ion-exchange chromatography.