C3	0.3461 (3)	0.5683 (4)	0.1661 (5)	0.058 (2)
C4	0.3078 (3)	0.5561 (4)	0.0582 (5)	0.064 (2)
C5	0.3153 (3)	0.4540 (4)	0.0099 (7)	0.051 (2)
C6	0.3650 (3)	0.3680 (4)	0.0723 (3)	0.041 (2)
C7	0.3722 (3)	0.2544 (4)	0.0269 (3)	0.040 (2)
C8	0.3357 (3)	0.2248 (5)	−0.0813 (4)	0.052 (2)
C9	0.3440 (3)	0.1147 (5)	−0.1117 (4)	0.061 (2)
C10	0.3853 (3)	0.0338 (4)	−0.0364 (4)	0.057 (2)
C11	0.4190 (3)	0.0672 (4)	0.0684 (4)	0.044 (2)
C12	0.4616 (3)	−0.0108 (4)	0.1591 (4)	0.046 (2)
C13	0.4610 (3)	−0.1304 (4)	0.1560 (5)	0.063 (2)
C14	1/2	−0.1893 (6)	1/4	0.076 (4)
N4	0.6548 (3)	0.2077 (4)	0.1865 (3)	0.052 (2)
O1	0.5772 (2)	0.2202 (3)	0.1460 (3)	0.053 (1)
O2	0.6996 (3)	0.2646 (4)	0.1542 (4)	0.091 (2)
O3	0.6839 (2)	0.1334 (3)	0.2573 (3)	0.069 (2)

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

Co1—N1	2.336 (3)	Co1—N3	2.144 (5)
Co1—N2	2.127 (3)	Co1—O1	2.259 (4)
N1—Co1—N2	71.6 (1)	N1—Co1—N1^{i}	84.2 (2)
N1—Co1—N3	137.9 (1)	N2—Co1—N1^{i}	138.9 (1)
N2—Co1—N3	72.8 (1)	O1—Co1—N1^{i}	79.4 (1)
N1—Co1—O1	105.4 (1)	N4—Co1—N2^{i}	145.7 (2)
N2—Co1—O1	75.9 (1)	O1—Co1—N2^{i}	102.2 (1)
N3—Co1—O1	86.8 (1)	O1—Co1—O1^{i}	173.7 (2)

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

Although voids of about 1350 Å were identified by *PLATON* (Spek, 1998), no significant residual electron density was found.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

This work was supported by the China Postdoctoral Science Foundation, the National Science Foundation and Hong Kong Research Grants Council Earmarked Grant CUHK 311/94P.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1249). Services for accessing these data are described at the back of the journal.

References

Barley, M. & Constable, E. C. (1988). *J. Chem. Soc. Dalton Trans.* pp. 2655–2662.
Constable, E. C. (1992). *Tetrahedron*, **48**, 10013–10059.
Constable, E. C., Drew, M. G. B., Forsyth, G. & Ward, M. D. (1988). *J. Chem. Soc. Chem. Commun.* pp. 1450–1452.
Constable, E. C. & Walker, J. V. (1992). *J. Chem. Soc. Chem. Commun.* pp. 884–886.
Fu, Y., Sun, J., Li, Q., Chen, Y., Wang, D., Mak, T. C. W., Tang, W. & Hu, H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2309–2313.
Kopfmann, G. & Huber, R. (1968). *Acta Cryst.* **A24**, 348–351.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Spek, A. L. (1998). *PLATON. Molecular Geometry Program.* Version of 1998. University of Utrecht, The Netherlands.

Acta Cryst. (1999). C**55**, 351–353

Trimethylphosphonium trichlorogermanate(II)

Gabriele Kociok-Köhn, Johannes G. Winter and Alexander C. Filippou*

Institut für Anorganische und Allgemeine Chemie der Humboldt Universität zu Berlin, Hessische Straße 1-2, 10115 Berlin, Germany. E-mail: filippou@chemie.hu-berlin.de

(*Received 23 February 1998; accepted 14 September 1998*)

Abstract

The title compound, $[HPMe_3][GeCl_3]$, features pseudo-tetrahedral $[HP(CH_3)_3]^+$ and trigonal-pyramidal $GeCl_3^-$ units that form a strongly distorted perovskite structure. The Ge^{II} centre shows a distorted octahedral environment with three short Ge—Cl bonds [average Ge—Cl = 2.3071 (9) Å] and three much longer interionic Ge···Cl distances [average Ge···Cl = 4.1372 (12) Å].

Comment

$[HPMe_3][GeCl_3]$, (1), was originally obtained as a by-product in the course of the attempted crystallization of $GeCl_2(PMe_3)$, (2). Compound (2) was prepared from $GeCl_2$(1,4-dioxane) and $P(CH_3)_3$ in benzene and investigated as an intermediate in the reaction of Cp*M*(CO)$_3$GeCl$_2$H (Cp = C_5H_5; *M* = Mo, W) with $P(CH_3)_3$ to give *trans*-Cp*M*(CO)$_2$[P(CH$_3$)$_3$]GeCl$_2$H (Filippou *et al.*, 1997). Compound (1) was then selectively obtained as a yellow solid from (2) and HCl, and was fully characterized. Compound (1), with its nearly cubic lattice constants, crystallizes in a strongly distorted perovskite structure similar to the low-temperature modification of $[N(CH_3)_4][GeCl_3]$, (3) (Depmeier *et al.*, 1980). The Ge^{II} centre has a distorted octahedral environment with three short Ge—Cl bonds [average Ge—Cl = 2.3071 (9) Å] and three much longer Ge···Cl contacts [average Ge···Cl = 4.1372 (12) Å]. The tendency of Ge^{II} to form trigonal-pyramidal $GeCl_3^-$ units is thus clear. The non-bonded Ge···Cl distances are similar to those in (3) [4.069 (8), 4.122 (8) and 4.322 (4) Å]. However, in (1), the presence of a cation with different substituents leads to a distortion, as is reflected in the different non-bonded Ge···Cl distances; two of these are slightly shorter and one is slightly longer than in (3) (Table 2). Fig. 1 shows compound (1) as the distorted perovskite structure type. Another orthorhombic example of this structure type is given by the powder structure of $[HN(CH_3)_3][GeCl_3]$ (Möller & Felsche, 1982). A rhombohedral variation of the perovskite structure type is demonstrated by the low-temperature form

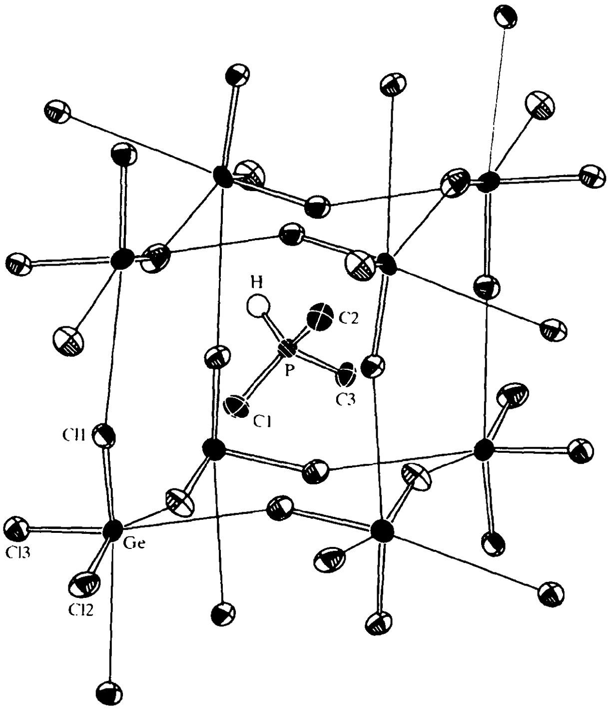

Fig. 1. View (*DIAMOND*; Bergerhoff, 1996) of the structure of $[HP(CH_3)_3][GeCl_3]$ with displacement ellipsoids drawn at the 50% probability level. The asymmetric unit is numbered. Further anions form a cage around the cation, with the longer Ge···Cl contacts represented by thin bonds (see text).

of $CsGeCl_3$ (Christensen & Rasmussen, 1965; Thiele *et al.*, 1987).

In contrast, $RbGeCl_3$ cannot form the perovskite-type structure because of the smaller radius of the cation; it crystallizes in a lattice of lower symmetry (Messer, 1978). A larger cation also leads to structures of lower symmetry (monoclinic and triclinic) and thus to isolated ions in the lattice. This is featured in the structures of a poly(pyrazolyl)germanium(II) derivative (Steiner & Stalke, 1995) and in pilocarpine–trichlorogermanate(II) hemihydrate (Fregerslev & Rasmussen, 1968). A phosphonium cation with a different shape from that of (1) also results in a structure of lower symmetry, as seen in isopropylphosphonium trichlorogermanate(II) (Karnop *et al.*, 1997). $GeCl_3^-$ counter-anions are also found in the structure of a dispirocyclic germylene cation (Karsch *et al.*, 1987) and of a half-sandwich cyclopentadienyl complex cation of Ge^{II} (Kohl *et al.*, 1986, 1989). Bond lengths and angles of the $GeCl_3^-$ unit in (1) are in good agreement with those of the above-mentioned trichlorogermanate compounds.

The title compound displays four contacts that could be regarded as weak hydrogen bonds of types P—H···Cl or C—H···Cl (Table 3). For the pilocarpine derivative (see above), hydrogen bonds were mentioned but not described in detail.

Experimental

The moisture-sensitive title compound was isolated as colourless columns by evaporation of the solvent over a period of ten days from a solution of $GeCl_2(PMe_3)$ in pentane at room temperature in an atmosphere containing some HCl.

Crystal data

$(C_3H_{10}P)[GeCl_3]$
$M_r = 256.04$
Orthorhombic
Pbca
$a = 12.225\,(2)$ Å
$b = 13.290\,(3)$ Å
$c = 12.387\,(3)$ Å
$V = 2012.5\,(7)$ Å^3
$Z = 8$
$D_x = 1.690$ Mg m^{-3}
D_m not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 5000 reflections
$\theta = 2.80$–$26.24°$
$\mu = 3.806$ mm^{-1}
$T = 180\,(2)$ K
Column
0.84 × 0.30 × 0.27 mm
Colourless

Data collection

Stoe IPDS diffractometer
φ rotation scans
Absorption correction: by integration
$T_{min} = 0.130$, $T_{max} = 0.358$
16 964 measured reflections
1984 independent reflections
1689 reflections with $I > 2\sigma(I)$

$R_{int} = 0.080$
$\theta_{max} = 26.24°$
$h = -15 \rightarrow 15$
$k = -16 \rightarrow 16$
$l = -15 \rightarrow 15$
200 standard reflections
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.085$
$S = 1.044$
1984 reflections
113 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0498P)^2 + 0.4045P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.385$ e Å^{-3}
$\Delta\rho_{min} = -0.594$ e Å^{-3}
Extinction correction: none
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}
Ge	0.24077 (3)	0.25649 (2)	0.97223 (3)	0.04661 (14)
Cl1	0.22883 (6)	0.28650 (6)	1.15454 (6)	0.04872 (19)
Cl2	0.24625 (7)	0.42440 (7)	0.92307 (7)	0.0649 (2)
Cl3	0.05503 (6)	0.23630 (5)	0.94598 (6)	0.04864 (19)
P	0.53625 (5)	0.02725 (5)	0.74875 (6)	0.03528 (17)
C1	0.6031 (3)	−0.0520 (3)	0.8418 (3)	0.0576 (8)
C2	0.4529 (3)	−0.0429 (4)	0.6592 (4)	0.0667 (10)
C3	0.4555 (3)	0.1183 (3)	0.8164 (3)	0.0520 (7)

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

Ge—Cl1	2.2978 (9)	Ge—Cl2^{iii}	4.4583 (13)
Ge—Cl3	2.3095 (9)	P—C1	1.763 (3)
Ge—Cl2	2.3141 (10)	P—C2	1.771 (3)
Ge—Cl3^{i}	3.9742 (11)	P—C3	1.772 (3)
Ge—Cl1^{ii}	3.9791 (12)	P—H	1.28 (3)

Cl1—Ge—Cl3	95.51 (3)	Cl3^{i}—Ge—Cl1^{ii}	106.920 (16)
Cl1—Ge—Cl2	95.34 (3)	Cl1—Ge—Cl2^{iii}	107.96 (3)
Cl3—Ge—Cl2	95.94 (3)	Cl3—Ge—Cl2^{iii}	84.30 (2)
Cl1—Ge—Cl3^{i}	78.86 (2)	Cl2—Ge—Cl2^{iii}	156.59 (4)
Cl3—Ge—Cl3^{i}	171.536 (16)	Cl3^{i}—Ge—Cl2^{iii}	91.391 (16)
Cl2—Ge—Cl3^{i}	90.91 (3)	Cl1^{ii}—Ge—Cl2^{iii}	73.983 (17)
Cl1—Ge—Cl1^{ii}	173.99 (3)	C1—P—C2	111.2 (2)
Cl3—Ge—Cl1^{ii}	78.93 (2)	C1—P—C3	110.91 (19)
Cl2—Ge—Cl1^{ii}	83.07 (3)	C2—P—C3	109.55 (19)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
P—H···Cl3^{i}	1.28 (3)	2.84 (3)	3.6865 (11)	146.3 (5)
C1—H1*C*···Cl3^{ii}	0.92 (5)	2.83 (5)	3.649 (4)	149 (4)
C3—H3*A*···Cl3^{iii}	0.96 (5)	2.81 (5)	3.725 (4)	159 (3)
C3—H3*C*···Cl1^{iv}	0.93 (5)	2.84 (5)	3.647 (4)	146 (4)

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

The structure was solved by the Patterson method. All non-H atoms were refined anisotropically and all H atoms were refined isotropically. The program *XSHAPE* (Stoe, 1997) was used for crystal optimization before a numerical absorption correction implemented in *X-RED* (Stoe & Cie, 1996) was applied. 254 strong reflections with more than six symmetry equivalents for each reflection were used for the optimization. *XSHAPE* is based on the program *HABITUS* (Herrendorf, 1993).

Data collection: *IPDS Software* (Stoe, 1998); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program used to prepare the *SHELX* input files: *UTILITY* (Pickardt, 1994); program used to solve and refine structure: *SHELX*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996) and *PLUTON*92 (Spek, 1992); software used to prepare material for publication: *SHELX*97.

This work was supported by the Deutsche Forschungsgemeinschaft.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1290). Services for accessing these data are described at the back of the journal.

References

Bergerhoff, G. (1996). *DIAMOND. Visual Crystal Information System.* University of Bonn, Germany.

Christensen, A. N. & Rasmussen, S. E. (1965). *Acta Chem. Scand.* **19**, 421–428.

Depmeier, W., Möller, A. & Klaska, K.-H. (1980). *Acta Cryst.* B**36**, 803–807.

Filippou, A. C., Winter, J. G., Kociok-Köhn, G. & Hinz, I. (1997). *J. Organomet. Chem.* **544**, 225–231.

Fregerslev, S. & Rasmussen, S. E. (1968). *Acta Chem. Scand.* **22**, 2541–2556.

Herrendorf, W. (1993). PhD thesis, University of Karlsruhe, Germany.

Karnop, M., du Mont, W.-W., Jones, P. G. & Jeske, J. (1997). *Chem. Ber.* **130**, 1611–1618.

Karsch, H. H., Deubelly, B., Riede, J. & Müller, G. (1987). *J. Organomet. Chem.* **336**, C37–40.

Kohl, F. X., Dickbreder, R., Jutzi, P., Müller, G. & Huber, B. (1986). *J. Organomet. Chem.* **309**, C43–46.

Kohl, F. X., Dickbreder, R., Jutzi, P., Müller, G. & Huber, B. (1989). *Chem. Ber.* **122**, 871–878.

Messer, D. (1978). *Z. Naturforsch. Teil B*, **33**, 366–369.

Möller, A. & Felsche, J. (1982). *J. Appl. Cryst.* **15**, 247–248.

Pickardt, J. (1994). *UTILITY*. Technical University Berlin, Germany.

Sheldrick, G. M. (1997). *SHELX97. Program Package for Crystal Structure Solution and Refinement.* University of Göttingen, Germany.

Spek, A. L. (1992). *PLUTON92. Molecular Graphics Program.* University of Utrecht, The Netherlands.

Steiner, A. & Stalke, D. (1995). *Inorg. Chem.* **34**, 4846–4853.

Stoe (1996). *X-RED. Data Reduction Program for Windows.* Version 1.08. Stoe, Darmstadt, Germany.

Stoe (1997). *XSHAPE*. Version 1.02. Stoe, Darmstadt, Germany.

Stoe (1998). *IPDS Software*. Version 2.87. Stoe, Darmstadt, Germany.

Thiele, G., Rotter, H. W. & Schmidt, K. D. (1987). *Z. Anorg. Allg. Chem.* **545**, 148–156.

Acta Cryst. (1999). C**55**, 353-356

A holmium complex of a macrocyclic ligand (DOTA) and its isostructural europium analogue

Franco Benetollo,[a] Gabriella Bombieri,[b] Silvio Aime[c] and Mauro Botta[c]

[a]ICTIMA, CNR, 35127 Padova, Italy, [b]Istituto di Chimica Farmaceutica, Universitá di Milano, Viale Abruzzi 42, 20131 Milano, Italy, and [c]Dipartimento di Chimica IFM, Universitá di Torino, Via P. Giuria 7, 10125 Torino, Italy. E-mail: benetollo@ictr04.ictr.pd.cnr.it

(*Received 28 April 1998; accepted 5 November 1998*)

Abstract

The holmium and europium complexes of the tetra-anion of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (H_4DOTA), namely, sodium aqua(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetato)holmium(III) tetrahydrate, $Na[Ho(C_{16}H_{24}N_4O_8)(H_2O)]\cdot 4H_2O$, and sodium aqua(1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetato)europium(III) tetrahydrate, $Na[Eu(C_{16}H_{24}N_4O_8)(H_2O)]\cdot 4H_2O$, show nine-coordination around the metal ion, with a square antiprismatic coordination geometry involving four N- and four O-donor atoms of the DOTA ligand, and a coordinated water molecule in a capping position.

Comment

Lanthanide(III) complexes with polydentate ligands are of interest because of the possibility of obtaining, with the encapsulation of the metal, stable derivatives which are useful as contrast agents in magnetic resonance imaging (Lauffer, 1987, 1990). The high thermodynamic stability and kinetic inertness of complexes with the