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Di(aqua)bis[(η5-cyclopentadienyl)tris-(dimethylphosphito-P)cobalt-O,O′,O″]-lanthanum(III) Chloride

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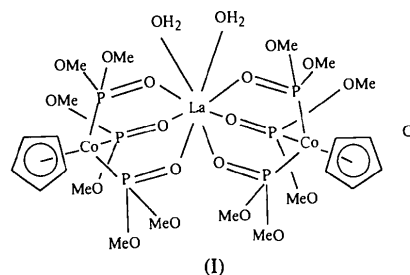
Abstract

The La atom in the title compound, diaqua-$1\kappa^2 O$-bis[2,3(η^5)-cyclopentadienyl]hexakis(μ-dimethyl phosphito)-$1\kappa^3 O{:}2\kappa^3 P{;}1\kappa^3 O{:}3\kappa^3 P$-dicobaltlanthanum chloride, $[Co_2La(C_2H_6O_3P)_6(C_5H_5)_2(H_2O)_2]Cl$, is eight-coordinate The coordination polyhedron around the La atom is nearly a square antiprism, consisting of eight O atoms contributed by two tripodal Co-complex ligands and two water molecules.

Comment

Transition metal complexes containing the O-donor tripodal ligands L_{OR} {L_{OR} = $(C_5H_5)Co[P(O)(OR)_2]_3$, R = CH_3, C_2H_5} have been studied widely (Klaui, 1990). Cyclopentadienyl(aqua)–metal complexes of the type $[CpM(H_2O)_3]^{2+}$ (M = Cr, Co, Rh, Ru) have been characterized (Spreer & Shar, 1981; Kolle & Fuss, 1984; Kolle & Klaui, 1991). We report here the crystal structure of the title compound, (I). To our knowledge this structure is the first characterized of an aqua complex of an early lanthanide metal with such a tripodal ligand.

(I)

The coordination polyhedron around the La atom is nearly a square antiprism, consisting of O1, O2, O3, O4, O5 and O6 contributed by two tripodal groups, and OW and OW2 from two water molecules. One square face (O3, O4, OW2, O5) is nearly planar with no atom displaced by more than 0.044 (5) Å from its mean plane; another (O1, O2, OW1, O6) is almost planar, within 0.115 (5) Å of its mean plane [folded quadrilateral angle about O2⋯O6 168 (1)°]. The La atom is displaced from the plane of O3, O4, OW2 and O5 by 1.327 (2) Å. The angles of the square corners in the square faces are in the range 85.9 (1)–90.0 (2)° and the lengths of the square edges range from 2.843 (6) to 3.147 (6) Å. The twist angle of the square planes is 45 (3)°, which is the mean rotational angle of a square plane from eclipsed square planes (Wilson, 1992).

The average distance (Wilson, 1992) from the La atom to tripodal O atoms is 2.48 (2) Å, which is similar to the distance from the La atom to the phosphine oxide [2.422 (12) or 2.456 (11) Å] in $[La\{S_2P(OEt)_2\}_3(OPPh_3)_2]$ (Pinkerton & Schwarzenbach, 1977). The distances La—OW1 and La—OW2 are 2.651 (5) and 2.619 (5) Å, respectively, which are longer than the La—O(water) distances in $La(OH_2)_6(ClO_4)_3$ (2.48 (3) Å; Glaser & Johansson, 1981), and similar to those in $La(acac)_3(OH_2)_2$ (2.56, 2.58 Å; Phillips, Sands & Wagner, 1968). Hydrogen bonding occurs between the Cl ion and H atoms of the coordinated water molecules [Cl⋯H1W(1 − x, 1/2 + y, 3/2 − z) 2.20, Cl⋯H4W(1 − x, y + 1/2, 3/2 − z) 2.14 Å]. The bond distances between P and O atoms attached to the La atom [average P—O 1.49 (1) Å] are shorter than the bond distances between P and O atoms attached to the methyl group [average P—O 1.59 (3) Å]. These distances are slightly longer than the average P═O distance, 1.46 (5) Å (Corbridge, 1992), in a variety of tetrahedral phosphate compounds, and lie in the range between P—O single and double bonds (Wilson, 1992). These values are similar to those in $[CpCo\{P(O)(OMe)_2\}_2\{P(OMe)_3\}].H_2O$ (Towle, Landon, Brill & Tulip, 1982).
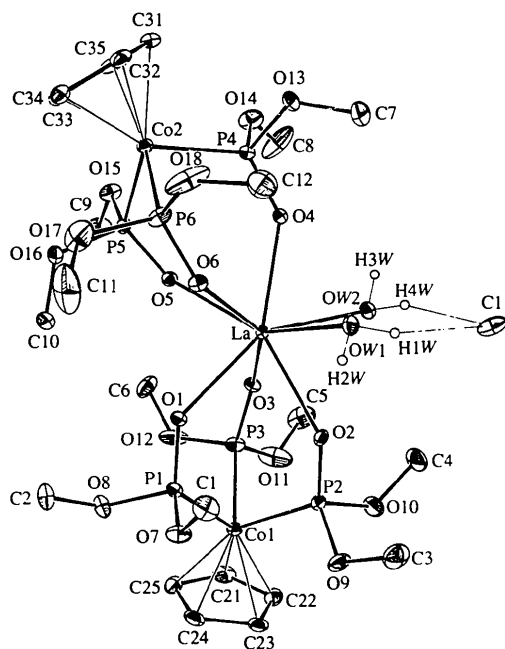
Fig. 1. Molecular structure showing 30% probability displacement ellipsoids. H atoms at C atoms are omitted for clarity.

Experimental

To a mixture of 2.0 mmol of LaCl₃ and 4.0 mmol of Na[(C₅H₅)Co{PO(OCH₃)₂}₃], 50 ml of dry THF was introduced. The resulting suspension was stirred at room temperature for 24 h and then the precipitate was filtered off. The filtrate was evaporated under reduced pressure to afford yellow powder. The crude product was washed with hexane and then diethyl ether, and dried under high vacuum (yield 72%). Recrystallization of the resultant solid from a solvent pair of THF–ether failed. However, using a solvent pair of wet THF–ether the title compound crystallized. Analysis: calculated for C₂₂H₅₀ClCo₂O₂₀P₆La, C 23.75, H 4.53%; found: C 24.03, H 4.45%.

Crystal data

[Co₂La(C₂H₆O₃P)₆(C₅H₅)₂-
(H₂O)₂]Cl
$M_r = 1112.71$
Monoclinic
$P2_1/c$
$a = 9.065\,(1)$ Å
$b = 21.295\,(3)$ Å
$c = 21.976\,(3)$ Å
$\beta = 98.669\,(1)°$
$V = 4193\,(1)$ Å³
$Z = 4$
$D_x = 1.762$ Mg m⁻³

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.0–13.0°$
$\mu = 2.01$ mm⁻¹
$T = 296\,(2)$ K
Tetragonal
$0.45 \times 0.40 \times 0.30$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans

5375 observed reflections
$[I > 3\sigma(I)]$
$R_{int} = 0.042$

Absorption correction:
ψ scan
$T_{min} = 0.876$, $T_{max} = 1.000$
7695 measured reflections
7301 independent reflections

$\theta_{max} = 25.0°$
$h = -10 \rightarrow 10$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: 0.08%

Refinement

Refinement on F
$R = 0.039$
$wR = 0.048$
$S = 1.068$
5375 reflections
473 parameters
$w = 1/[\sigma^2(F) + 0.003125F^2]$
$(\Delta/\sigma)_{max} = 0.017$

$\Delta\rho_{max} = 0.96$ e Å⁻³
$\Delta\rho_{min} = -0.57$ 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* (Å²)

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

	x	y	z	U_{eq}
La	0.2096 (1)	0.1398 (1)	0.3852 (1)	0.032 (1)
Co1	0.0000 (1)	0.0598 (1)	0.2040 (1)	0.042 (1)
P1	−0.0778 (2)	0.1434 (1)	0.2450 (1)	0.044 (1)
P2	0.0095 (2)	0.0106 (1)	0.2905 (1)	0.047 (1)
P3	0.2320 (2)	0.0866 (1)	0.2272 (1)	0.054 (1)
O1	0.0135 (5)	0.1741 (2)	0.2998 (2)	0.047 (3)
O2	0.0620 (5)	0.0451 (2)	0.3499 (2)	0.049 (3)
O3	0.2975 (4)	0.1046 (2)	0.2913 (2)	0.045 (3)
O7	−0.2429 (6)	0.1330 (3)	0.2596 (3)	0.070 (4)
O8	−0.1070 (6)	0.1939 (3)	0.1892 (2)	0.067 (4)
O9	−0.1543 (7)	−0.0178 (3)	0.2927 (3)	0.082 (4)
O10	0.1050 (8)	−0.0515 (3)	0.2879 (3)	0.096 (6)
O11	0.3284 (8)	0.0310 (5)	0.2049 (4)	0.138 (9)
O12	0.2637 (8)	0.1410 (4)	0.1825 (2)	0.118 (8)
C1	−0.2797 (10)	0.1330 (5)	0.3206 (4)	0.088 (8)
C2	−0.1831 (11)	0.2493 (4)	0.1958 (5)	0.089 (7)
C3	−0.1854 (13)	−0.0476 (6)	0.3471 (5)	0.117 (10)
C4	0.2173 (12)	−0.0717 (4)	0.3346 (5)	0.103 (9)
C5	0.4709 (13)	0.0155 (6)	0.2267 (7)	0.134 (15)
C6	0.3517 (15)	0.1891 (4)	0.1964 (4)	0.113 (14)
C21	0.0406 (11)	0.0291 (5)	0.1192 (4)	0.079 (8)
C22	−0.0174 (11)	−0.0187 (4)	0.1482 (3)	0.070 (7)
C23	−0.1566 (9)	−0.0020 (4)	0.1590 (3)	0.066 (6)
C24	−0.1859 (10)	0.0571 (4)	0.1365 (4)	0.077 (6)
C25	−0.0581 (13)	0.0783 (4)	0.1111 (3)	0.086 (10)
OW1	0.0926 (6)	0.0901 (2)	0.4777 (2)	0.054 (3)
OW2	0.3906 (5)	0.0474 (2)	0.4236 (2)	0.053 (3)
Co2	0.3638 (1)	0.3251 (1)	0.4707 (1)	0.040 (1)
P4	0.4624 (2)	0.2350 (1)	0.4986 (1)	0.045 (1)
P5	0.3637 (2)	0.3021 (1)	0.3747 (1)	0.041 (1)
P6	0.1404 (2)	0.2883 (1)	0.4666 (1)	0.062 (1)
O4	0.4009 (5)	0.1766 (2)	0.4683 (2)	0.049 (3)
O5	0.3350 (5)	0.2366 (2)	0.3516 (2)	0.042 (2)
O6	0.0949 (4)	0.2287 (2)	0.4338 (2)	0.046 (3)
O13	0.4659 (8)	0.2265 (3)	0.5710 (2)	0.084 (6)
O14	0.6354 (6)	0.2384 (3)	0.4949 (3)	0.088 (6)
O15	0.5220 (6)	0.3253 (3)	0.3593 (2)	0.070 (4)
O16	0.2568 (7)	0.3485 (2)	0.3318 (2)	0.074 (5)
O17	0.0328 (8)	0.3447 (4)	0.4344 (5)	0.146 (13)
O18	0.0889 (11)	0.2886 (4)	0.5295 (4)	0.162 (9)
C7	0.4662 (14)	0.1650 (5)	0.5966 (4)	0.102 (10)
C8	0.7138 (12)	0.1984 (5)	0.4735 (8)	0.16 (2)
C9	0.5648 (11)	0.3162 (5)	0.2998 (4)	0.098 (8)
C10	0.1390 (11)	0.3274 (4)	0.2872 (4)	0.084 (7)
C11	−0.1087 (13)	0.3371 (8)	0.4187 (8)	0.21 (3)
C12	0.0786 (15)	0.2338 (6)	0.5661 (5)	0.124 (12)
C31	0.4955 (11)	0.3673 (4)	0.5446 (4)	0.073 (7)

C32	0.3503 (12)	0.3844 (4)	0.5434 (4)	0.071 (7)
C33	0.3035 (10)	0.4170 (4)	0.4887 (4)	0.070 (6)
C34	0.4230 (11)	0.4172 (4)	0.4558 (4)	0.074 (8)
C35	0.5405 (11)	0.3858 (4)	0.4902 (5)	0.082 (8)
Cl	0.7480 (2)	0.4619 (1)	0.9854 (1)	0.091 (2)

Table 2. Selected geometric parameters (Å, °)

La—O1	2.491 (4)	La—O2	2.478 (4)
La—O3	2.440 (4)	La—OW1	2.651 (5)
La—OW2	2.619 (5)	La—O4	2.449 (4)
La—O5	2.519 (4)	La—O6	2.478 (4)
Co1—P1	2.161 (2)	Co1—P2	2.161 (2)
Co1—P3	2.164 (2)	P1—O1	1.503 (4)
P1—O7	1.592 (6)	P1—O8	1.622 (5)
P2—O2	1.512 (4)	P2—O9	1.610 (6)
P2—O10	1.586 (7)	P3—O3	1.493 (4)
P3—O11	1.592 (9)	P3—O12	1.575 (8)
Co2—P4	2.166 (2)	Co2—P5	2.165 (2)
Co2—P6	2.160 (2)	P4—O4	1.479 (4)
P4—O13	1.598 (5)	P4—O14	1.584 (6)
P5—O5	1.494 (4)	P5—O15	1.601 (6)
P5—O16	1.589 (6)	P6—O6	1.487 (5)
P6—O17	1.639 (8)	P6—O18	1.523 (10)
O2···OW1	2.946 (6)	O1···O2	2.968 (6)
O6···O1	3.144 (6)	O6···OW1	3.108 (6)
O3···OW2	3.147 (6)	O3···O5	3.105 (7)
O5···O4	2.843 (6)	O4···OW2	2.918 (6)
OW1—La—O1	111.8 (1)	OW1—La—O2	69.8 (1)
OW1—La—O3	138.2 (1)	OW2—La—O1	143.5 (1)
OW2—La—O2	76.8 (1)	OW2—La—O3	76.9 (1)
OW2—La—OW1	75.9 (2)	O4—La—O1	144.3 (1)
O4—La—O2	141.4 (1)	O4—La—O3	116.3 (1)
O4—La—OW1	82.9 (1)	O4—La—OW2	70.2 (1)
O5—La—O1	80.9 (1)	O5—La—O2	145.1 (1)
O5—La—O3	77.5 (1)	O5—La—OW1	143.4 (1)
O5—La—OW2	114.9 (1)	O5—La—O4	69.9 (1)
O6—La—O1	78.6 (1)	O6—La—O2	121.0 (1)
O6—La—O3	144.2 (1)	O6—La—OW1	74.5 (1)
O6—La—OW2	136.0 (1)	O6—La—O4	74.4 (1)
O6—La—O5	74.8 (1)	O2—La—O1	73.3 (2)
O2—La—O3	73.4 (2)	O1—La—O3	75.1 (2)
O2···O1···O6	89.8 (2)	O1···O2···OW1	92.3 (2)
O5···O3···OW2	87.6 (2)	O2···OW1···O6	91.0 (2)
O3···OW2···O4	86.3 (2)	O5···O4···OW2	97.4 (2)
O3···O5···O4	88.4 (2)	O1···O6···OW1	85.9 (2)

The structure was solved by Patterson method and difference Fourier techniques and refined using full-matrix least squares on F. Final refinement was performed with anisotropic displacement parameters for all non-H atoms and fixed isotropic displacement parameters ($U_{iso} = 0.08$ Å^2) and calculated positions for all H atoms, except those at H$_2$O which were refined with isotropic displacement parameters and fixed positional parameters obtained from the difference Fourier function.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: MolEN (Fair, 1990). Structure solution: SHELX76 (Sheldrick, 1976). Structure refinement: SHELX76. Molecular graphics: ORTEPII (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: KH1012). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Trimethyl[(trimethylstannyl)methyl]ammonium Iodide

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Abstract

The crystal and molecular structure of the title compound, [Sn(C$_4$H$_{11}$N)(CH$_3$)$_3$]I, has been determined [alternative coordination nomenclature: (trimethyl)(trimethylammoniomethyl)tin(IV) iodide]. Both the Sn and N atoms are in tetrahedral environments.

Comment

The Sn—C$_{sp^3}$ bond lengths in the title compound, (I), range from 2.126 (6) to 2.182 (5) Å and valency angles about Sn range from 102.7 (2) to 113.7 (2)°. The Sn—CH$_2$ bond length is longer than all three Sn—Me bond