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A hexacoordinated aluminium complex with a new type of seven-membered chelate ring involving a cyclic phosphate ester

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Key indicators

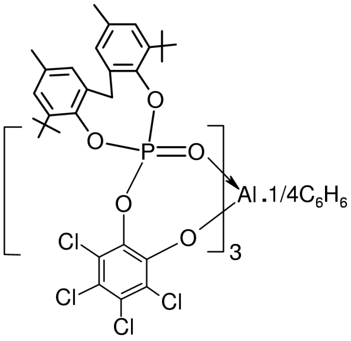
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.046
wR factor = 0.142
Data-to-parameter ratio = 15.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The molecular structure of the title compound, tris[2,3,4,5-tetrachloro-6-(4,8-di-*tert*-butyl-2,10-dimethyl-6-oxo-12*H*-5,7-dioxa-6λ^5-phosphadibenzo[*a*,*d*]cycloocten-6-yloxy)phenoxido]aluminium benzene 0.25-solvate, $[Al(C_{29}H_{30}Cl_4O_5P)_3]\cdot 0.25C_6H_6$, has been determined. The Al atom, with site symmetry 3, is hexacoordinate and is part of a new type of seven-membered chelate ring, with a catecholate O atom forming a covalent bond and a phosphoryl O atom forming a coordinate covalent bond. As expected, the Al—O coordinate bond is longer than the Al—O covalent bond. The phosphocine ring has a tub conformation, with an intramolecular C—H$\cdots$O interaction between one of the ArCH$_2$ H atoms and the phosphoryl O atom.

Comment

Although hexacoordination *via* chelate rings for Al is not uncommon (Arai *et al.*, 1998; Bott *et al.*, 2001; Di Marco *et al.*, 1999; Le *et al.*, 1997; Finnegan *et al.*, 1986), compounds with seven-membered rings are relatively rare, and so far the only example that has been structurally characterized is LiAl(2,2′-bi-1-naphthoxy)$_3$.(THF)$_6$ (THF is tetrahydrofuran; Arai *et al.*, 1998). Here, we report a new type of Al complex, (II), with seven-membered chelate rings. The chelation occurs through a phosphoryl O atom and a catecholate O atom.



(II)

Compound (II) was isolated in the reaction of CH$_2$(6-^{t}Bu-4-Me-C$_6$H$_4$O)$_2$}P(Cl)(1,2-O$_2$C$_6$Cl$_4$), (I) (Kumaraswamy & Kumara Swamy, 2002) with lithium aluminium hydride, in an attempt to substitute the P—Cl bond with a P—H bond. It is most likely formed *via* the hydrolysis product CH$_2$(6-^{t}Bu-4-Me-C$_6$H$_4$O)$_2$}P(O)(OC$_6$Cl$_4$-OH) (Kumaraswamy & Kumara Swamy, 2002).

In the structure of (II) (Fig. 1), the Al atom is bonded to three O atoms of three different tetrachlorocatecholate residues. Three phosphoryl O atoms from three phosphonate residues complete the octahedral geometry at the Al atom.

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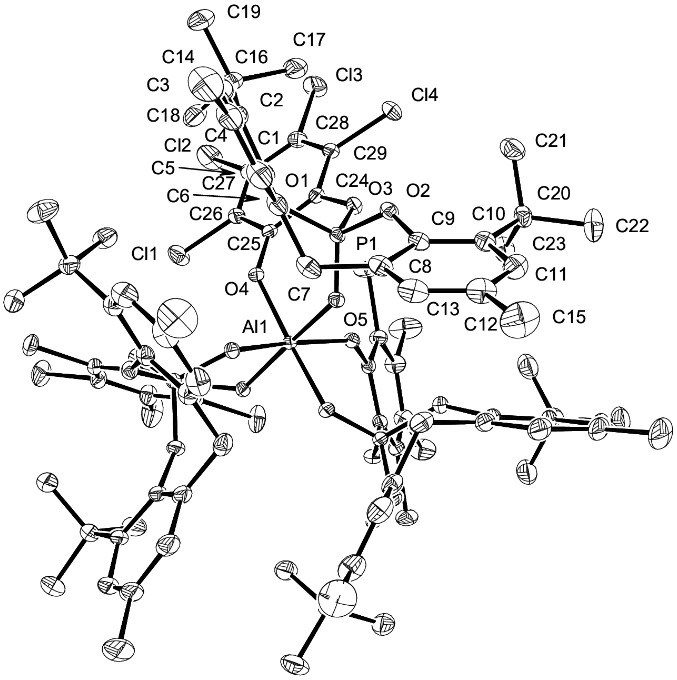

Figure 1
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms have been omitted for clarity.

The Al—O bond to the catecholate O atom is shorter than that to the phosphoryl O atom; this is expected, because the latter are pure coordinate bonds. All these Al—O distances fall within the range 1.862–1.967 Å observed in other chelate complexes of Al (Arai *et al.*, 1998; Bott *et al.*, 2001; Di Marco *et al.*, 1999; Finnegan *et al.*, 1986; Le *et al.*, 1997). The P—O distances also fall in the normal range (Kumaraswamy & Kumara Swamy, 2002).

The seven-membered ring comprising atoms Al1, O4, C25, O1, C24, P1 and O5 has a 'rowing boat' type of conformation, with atoms P1, O4 and C25 on the same side of the plane comprising the rest of the atoms. To our knowledge, this complex represents a new type of chelate system, with the ligand readily generated *via* the hydrolysis of pentacoordinate chloro-phosphorus compounds (Kumara Swamy *et al.*, 1998; Kumaraswamy & Kumara Swamy, 2002).

The eight-membered phosphocine ring has a tub conformation. As noted before (Kumara Swamy *et al.*, 2001), this feature may be a result of an intramolecular C—H···O interaction between the phosphoryl atom O5 and one of the ArCH$_2$ H atoms. The relevant C7···O5 distance is 3.141 (3) Å and the C7—H7*B*···O5 angle is 138°.

Experimental

The synthesis of (II) was carried out as follows. To a stirred solution of (I) (1.27 g, 1.965 mmol) in dry THF (20 ml), lithium aluminium hydride (0.074 g, 1.96 mmol) was added slowly in small portions over about 10 min at 273 K, and the reaction mixture was stirred continuously for 24 h. The solvent was removed *in vacuo* and dry toluene (10 ml; containing traces of benzene) was added. Filtration followed by concentration of the filtrate to 4 ml afforded crystals of (II) [m.p. 543 K (charring)]. Spectroscopic analysis: ^{1}H NMR (CDCl$_3$, 200 MHz, δ, p.p.m.): 1.00 (*s*, 18H, ^{t}Bu-H), 2.28, 2.33 (2*s*, 6H, Ar-CH$_3$), 2.60 (*d*, $^2J_{HH}$ = 15.7 Hz, 1H, CH$_A$H$_X$), 4.35 (*d*, $^2J_{HH}$ = 15.7 Hz, 1H, CH$_A$H$_X$), 6.30–7.20 (*m*, 4H, Ar-H); ^{31}P NMR (CDCl$_3$, δ, p.p.m.): −14.0 (*ca* 93%), −14.4 (*ca* 7%). Analysis, calculated for $C_{88.5}H_{91.5}AlCl_{12}O_{15}P_3$: C 54.78, H 4.72%; found: C 53.95, H 4.56%.

Crystal data

$[Al(C_{29}H_{30}Cl_4O_5P)_3]\cdot 0.25C_6H_6$
M_r = 1940.41
Trigonal, $R\overline{3}$
a = 22.4062 (7) Å
c = 33.854 (2) Å
V = 14718.8 (12) Å^3
Z = 6
D_x = 1.313 Mg m^{-3}

Mo *K*α radiation
Cell parameters from 8257 reflections
θ = 2.7–20.4°
μ = 0.46 mm^{-1}
T = 298 (2) K
Block, colourless
0.55 × 0.50 × 0.50 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.633, T_{max} = 0.831
28 911 measured reflections

5770 independent reflections
4591 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 25.0°
$h = -26 \rightarrow 26$
$k = -26 \rightarrow 26$
$l = -26 \rightarrow 40$

Refinement

Refinement on F^2
$R(F)$ = 0.046
$wR(F^2)$ = 0.142
S = 1.07
5770 reflections
365 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.09P)^2 + 7.037P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Al1—O4	1.8461 (15)	P1—O2	1.5494 (16)
Al1—O5	1.9448 (15)	P1—O3	1.5588 (16)
P1—O5	1.4736 (16)	P1—O1	1.5594 (17)
O4^i—Al1—O4	97.09 (7)	O2—P1—O3	100.98 (9)
O4—Al1—O5^i	90.58 (6)	O5—P1—O1	116.99 (9)
O4^i—Al1—O5	169.98 (8)	O2—P1—O1	106.01 (9)
O4—Al1—O5	88.31 (6)	O3—P1—O1	105.83 (9)
O5^i—Al1—O5	83.18 (7)	C9—O2—P1	127.37 (15)
O5—P1—O2	112.42 (9)	C25—O4—Al1	138.90 (14)
O5—P1—O3	113.13 (9)	P1—O5—Al1	124.90 (9)

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

Table 2
C—H···O interaction geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7*B*···O5	0.97	2.35	3.141 (3)	138

H atoms were placed geometrically and refined using a riding model, with CH$_2$ distances constrained to 0.97 Å with U_{iso}(H) = 1.2U_{eq}(C), and CH$_3$ distances constrained to 0.96 Å with U_{iso}(H) = 1.5U_{eq}(C). The residual electron density after refining the main molecule was modelled as benzene (since it did not fit to toluene); the solvent used did show traces of benzene.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine

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structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX*-6a (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.

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