Data collection

Syntex $P2_1$ upgraded to Nicolet $R3$ diffractometer
ω scans
Absorption correction: ψ scan (*SHELXTL-Plus*; Sheldrick, 1991)
$T_{\min} = 0.431$, $T_{\max} = 0.675$
1335 measured reflections
1178 independent reflections
1045 observed reflections $[F > 3\sigma(F)]$
$R_{\rm int} = 0.031$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 8$
$l = -17 \rightarrow 14$
2 standard reflections monitored every 96 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0376$
$wR = 0.0565$
$S = 0.75$
1045 reflections
93 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0047F^2]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ 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	$U_{\rm eq}$
Cu(1)	1/2	0.1219 (1)	3/4	0.044 (1)
Cu(2)	1/2	0	1/2	0.040 (1)
Cl(1)	0.5013 (1)	0.2272 (1)	0.6280 (1)	0.060 (1)
Cl(2)	0.6562 (1)	0.0008 (2)	0.8322 (1)	0.059 (1)
N(1)	0.6183 (3)	0.1139 (4)	0.5083 (3)	0.049 (2)
C(2)	0.6052 (4)	0.2861 (6)	0.4865 (4)	0.062 (3)
C(3)	0.5107 (5)	0.3236 (6)	0.3883 (4)	0.065 (3)
C(4)	0.4099 (4)	0.2968 (6)	0.3793 (4)	0.064 (3)
N(5)	0.3895 (3)	0.1250 (4)	0.3831 (3)	0.049 (2)
C(6)	0.2912 (4)	0.0965 (7)	0.3736 (4)	0.063 (3)
C(7)	0.7115 (4)	0.0750 (8)	0.6046 (4)	0.066 (3)

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

Cu(1)—Cl(1)	2.234 (2)	Cu(1)—Cl(2)	2.259 (1)
Cu(2)—N(1)	2.016 (5)	Cu(2)—N(5)	2.025 (3)
N(1)—C(2)	1.469 (6)	N(1)—C(7)	1.477 (5)
C(2)—C(3)	1.500 (7)	C(3)—C(4)	1.515 (11)
C(4)—N(5)	1.479 (6)	N(5)—C(6)	1.475 (8)
C(6)—C(7$^{\rm i}$)	1.484 (9)	Cu(2)···Cl(1)	2.855 (2)
Cl(1)—Cu(1)—Cl(2)	99.7 (1)	Cl(1)—Cu(1)—Cl(1$^{\rm ii}$)	133.6 (1)
Cl(2)—Cu(1)—Cl(2$^{\rm ii}$)	126.8 (1)	Cl(2)—Cu(1)—Cl(1$^{\rm ii}$)	100.6 (1)
N(1)—Cu(2)—N(5)	94.3 (2)	N(5)—Cu(2)—N(1$^{\rm i}$)	85.7 (2)
Cu(2)—N(1)—C(2)	116.8 (4)	Cu(2)—N(1)—C(7)	106.0 (4)
C(2)—N(1)—C(7)	113.6 (4)	N(1)—C(2)—C(3)	113.0 (4)
C(2)—C(3)—C(4)	114.0 (6)	C(3)—C(4)—N(5)	112.2 (5)
Cu(2)—N(5)—C(4)	117.0 (2)	Cu(2)—N(5)—C(6)	107.0 (3)
C(4)—N(5)—C(6)	112.9 (5)	N(5)—C(6)—C(7$^{\rm i}$)	107.6 (5)
N(1)—C(7)—C(6$^{\rm i}$)	109.5 (4)		

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

Crystallographic computations were performed using the *SHELXTL-Plus* program package (Sheldrick, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1200). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(μ-diphenylphosphinato-*O*:*O*′)bis(dimethylaluminium)

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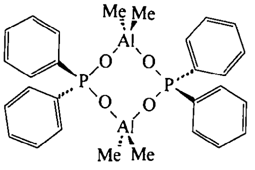
Abstract

The title compound, $[Al_2(C_{12}H_{10}O_2P)_2(CH_3)_4]$, contains discrete centrosymmetric molecules each having a slightly puckered eight-membered $(Al—O—P—O—)_2$ ring. Displacements from the plane of the four O atoms are 0.28 (1) and 0.15 (1) Å for the P and Al atoms, respectively. The Al—O bond distances are 1.781 (3) and 1.794 (3) Å, while the P—O distances are 1.512 (3) and 1.505 (2) Å.

Comment

We have recently become interested in compounds containing Al—O—P linkages as soluble model compounds for aluminophosphate molecular sieves. Only a small amount of work has been carried out in this area and few compounds have been characterized fully. Coates & Mukherjee (1964) studied the reactions of trimethylaluminium with phosphinic acids to give compounds of the type $[Me_2Al(O_2PR_2)]_2$ (R = Me, Ph) and later, reactions of Al_2Me_6 with $HO(O)PX_2$ (X = F, Cl or H) were reported (Schaible, Haubold & Weidlein, 1974; Schaible & Weidlein, 1974). The first crystal structure of this type, namely that of dichloroaluminium diphenylphosphinate, $[Cl_2Al(O_2PPh_2)]_2$, was reported by Sangokoya, Pennington, Robinson & Hrncir (1990).

The crystal structure of the title compound, (1), is found to contain discrete centrosymmetric molecules. The molecule contains a slightly puckered (Al—O—P—O—)$_2$ eight-membered ring, with displacements from the plane of the four O atoms of 0.28 (1) and 0.15 (1) Å for the P and Al atoms, respectively.



(I)

The geometry at the Al and P atoms is approximately tetrahedral (Fig. 1). The two Al—O bond distances are similar, with values of 1.781 (3) and 1.794 (3) Å, as are the two P—O bond distances of 1.512 (3) and 1.505 (2) Å. The P—O—Al angles are not linear and the two differ from each other by 13°. The Al—C distances of 1.931 (4) and 1.945 (4) Å are within the expected range (Power, Bott, Clark, Atwood & Baron, 1990).

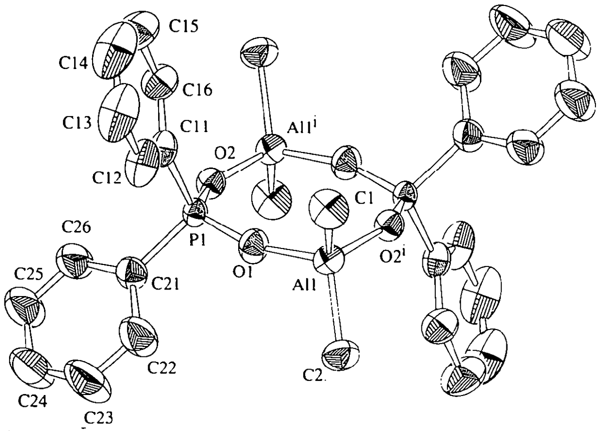


Fig. 1. The molecular structure of $[Me_2Al(O_2PPh_2)]_2$ showing the labelling scheme, with displacement ellipsoids drawn at the 30% probability level and H atoms excluded for clarity. [Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.]

The title compound is isomorphous with $[Cl_2Al(O_2PPh_2)]_2$, in which a similarly small deviation from planarity was observed. Corresponding bond distances and angles for (1) are found to be very similar to those of $[Cl_2Al(O_2PPh_2)]_2$ (Sangokoya *et al.*, 1990).

Molecular weight (cryoscopy) measurements in benzene confirmed that the dimeric species persists in solution (this work; Coates & Mukherjee, 1964). The solid-state MAS ^{31}P NMR spectrum of (1), recorded at a spinning rate of 4.9 kHz, gave a chemical shift of 20.9 p.p.m., which is comparable with the solution value (25.1 p.p.m. in d_8-toluene) if solvent effects are considered. Both chemical shifts were measured relative to 85% H_3PO_4.

Experimental

Working under argon, the title compound was prepared by slowly adding Al_2Me_6 (5.2 mmol) dissolved in toluene to a cold (210 K) suspension of diphenylphosphinic acid (10.4 mmol) in toluene. The solution was allowed to warm slowly to room temperature and after stirring for 8 h, a clear solution had formed. Removal of the volatile materials gave the required product in high yield. Air-sensitive colourless crystals were obtained from toluene and mounted in glass capillaries for X-ray examination.

Crystal data

$[Al_2(C_{12}H_{10}O_2P)_2(CH_3)_4]$
$M_r = 548.48$
Monoclinic
$C2/c$
$a = 11.371 (1)$ Å
$b = 15.433 (1)$ Å
$c = 17.954 (1)$ Å
$\beta = 104.738 (6)°$
$V = 3047.1 (4)$ Å^3
$Z = 4$
$D_x = 1.195$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 39.0$–$45.9°$
$\mu = 2.0$ mm^{-1}
$T = 300$ K
Block
0.65 × 0.50 × 0.40 mm
Colourless

Data collection

Rigaku AFC-7*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.92$, $T_{max} = 1.00$
2568 measured reflections
2151 independent reflections
1902 observed reflections [$F > 4\sigma(F)$]

$R_{int} = 0.048$
$\theta_{max} = 60°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 17$
$l = -20 \rightarrow 19$
3 standard reflections monitored every 150 reflections
intensity decay: 13.2%

Refinement

Refinement on F
$R = 0.062$
$wR = 0.089$
$S = 2.25$
1893 reflections
170 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.001F^2]$
$(\Delta/\sigma)_{max} = 0.08$

$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX76* (Sheldrick, 1976) for C, H, O and P atoms, and *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1) for Al

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}
P1	0.17587 (8)	0.34179 (6)	0.40911 (5)	0.0485 (6)
Al1	0.42955 (9)	0.33478 (6)	0.54316 (6)	0.0633 (6)
O1	0.2853 (2)	0.3511 (2)	0.4771 (2)	0.0754 (16)
O2	0.0922 (2)	0.2685 (2)	0.4164 (1)	0.0627 (13)
C1	0.5546 (5)	0.3257 (4)	0.4883 (3)	0.096 (3)
C2	0.4474 (5)	0.4243 (3)	0.6215 (3)	0.095 (3)
C11	0.2249 (3)	0.3257 (3)	0.3234 (2)	0.066 (2)
C12	0.2986 (4)	0.3866 (4)	0.3017 (3)	0.100 (3)
C13	0.3381 (6)	0.3734 (7)	0.2362 (5)	0.138 (5)
C14	0.3039 (6)	0.3037 (8)	0.1925 (4)	0.153 (6)
C15	0.2306 (6)	0.2385 (5)	0.2119 (3)	0.126 (4)
C16	0.1891 (4)	0.2517 (3)	0.2777 (3)	0.088 (3)
C21	0.0951 (4)	0.4410 (2)	0.3998 (2)	0.072 (2)
C22	0.1412 (6)	0.5123 (4)	0.4453 (4)	0.137 (4)
C23	0.0830 (7)	0.5900 (4)	0.4342 (6)	0.179 (6)
C24	−0.0270 (7)	0.5976 (4)	0.3841 (5)	0.149 (5)
C25	−0.0773 (6)	0.5278 (5)	0.3408 (4)	0.143 (4)
C26	−0.0171 (5)	0.4503 (3)	0.3498 (4)	0.111 (3)

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

Al1—O1	1.781 (3)	P1—O1	1.512 (3)
Al1—O2^{i}	1.794 (3)	P1—O2	1.505 (2)
Al1—C1	1.931 (4)	P1—C11	1.782 (4)
Al1—C2	1.945 (4)	P1—C21	1.771 (4)
O1—Al1—O2^{i}	101.3 (2)	C21—P1—O1	107.1 (2)
C1—Al1—O1	110.1 (2)	C21—P1—O2	109.5 (2)
C2—Al1—O1	106.8 (2)	C21—P1—C11	107.9 (2)
C1—Al1—O2^{i}	109.7 (2)	Al1—O1—P1	162.4 (2)
C2—Al1—O2^{i}	109.8 (2)	Al1^{i}—O2—P1	149.1 (2)
C1—Al1—C2	117.8 (2)	C12—C11—P1	119.6 (4)
O1—P1—O2	114.2 (1)	C16—C11—P1	120.7 (3)
C11—P1—O1	109.7 (2)	C22—C21—P1	121.3 (4)
C11—P1—O2	108.3 (2)	C26—C21—P1	121.8 (3)

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

The large U_{ij} terms observed for some phenyl C atoms may indicate disorder. H atoms were placed in calculated positions with a common refined displacement parameter. Nine reflections were omitted as likely to be suffering from extinction.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

The authors would like to thank the EPSRC for support (DJB) and for funds to purchase the X-ray diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1033). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Ethanol)(2,3,7,8,12,13,17,18-octaethylporphinato)manganese(III) Perchlorate

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Abstract

The crystal structure of $[Mn(C_{36}H_{44}N_4)(C_2H_6O)]ClO_4$ has been determined. The average Mn—N$_p$ bond distance is 1.997 (5) Å and the axial Mn—O bond length is 2.145 (2) Å. The manganese(III) ion has a displacement of 0.17 Å from the mean plane of the 24-atom porphinato core.

Comment

The title compound, [Mn(OEP)(EtOH)]ClO$_4$ (EtOH is ethanol and OEP is the dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin), (I), was obtained in our attempted preparation of [Mn(OEP)]$_2$O from CHCl$_3$ and hexanes. The source of the ethanol ligand is believed to be the stabilizer in CHCl$_3$.

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