Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# (2,2-Dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-$\kappa^2O^4,O^5$)-ethyl(tetrahydrofuran-$\kappa O$)aluminium(III)

**Chien-An Chen, Kuo-Hui Wu and Han-Mou Gau***

Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan
Correspondence e-mail: hmgau@dragon.nchu.edu.tw

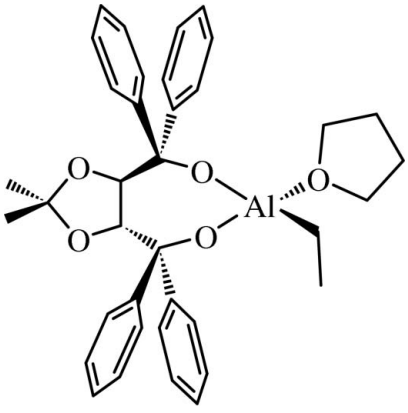
Received 12 September 2007; accepted 1 October 2007

Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.042; $wR$ factor = 0.122; data-to-parameter ratio = 9.3.

The title compound, $[Al(C_2H_5)(C_{31}H_{28}O_4)(C_4H_8O)]$, has a slightly distorted tetrahedral geometry around the $Al^{III}$ metal centre. The bidentate TADDOLate ligand and the $Al^{III}$ metal atom form a seven-membered ring, with an O—Al—O angle of 111.19 (10)°, which is close to the ideal tetrahedral angle. The Al—O—C(alkoxide) angles of 139.17 (17) and 137.95 (17)° are larger than the $sp^3$ bond angle, suggesting substantial $\pi$-donation of the alkoxide O atom to the $Al^{III}$ metal centre.

## Related literature

For related literature, see: Arai *et al.* (1996, 1998); Balsells *et al.* (2002); Gau *et al.* (1996); Gothelf *et al.* (1995); Hafner *et al.* (1992); Hintermann & Togni (2000); Nöth *et al.* (2001); Pu & Yu (2001); Ramón & Yus (2006); Seebach *et al.* (1992); Shao & Gau (1998); Sheen & Gau (2004); Son *et al.* (2003).




## Experimental

### Crystal data

$[Al(C_2H_5)(C_{31}H_{28}O_4)(C_4H_8O)]$
$M_r$ = 592.68
Orthorhombic, $P2_12_12_1$
$a$ = 9.6123 (8) Å
$b$ = 15.7991 (13) Å
$c$ = 21.4207 (18) Å
$V$ = 3253.1 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 293 (2) K
0.80 × 0.23 × 0.19 mm

### Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.748, $T_{max}$ = 1.000
(expected range = 0.733–0.980)
18371 measured reflections
3591 independent reflections
2940 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.050

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.122
$S$ = 1.07
3591 reflections
388 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.14 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Al—O4 | 1.712 (2) | Al—O5 | 1.891 (2) |
| Al—O1 | 1.719 (2) | Al—C32 | 2.040 (3) |
| O4—Al—O1 | 111.19 (10) | O4—Al—C32 | 113.97 (11) |
| O4—Al—O5 | 105.76 (11) | O1—Al—C32 | 118.74 (12) |
| O1—Al—O5 | 101.15 (11) | O5—Al—C32 | 103.97 (11) |

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

This work was supported by a grant from the National Science Council of Taiwan under grant No. NSC 96-2113-M-005-007-MY3.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2463).

## References

Arai, T., Sasai, H., Aoe, K.-i., Okamura, K., Date, T. & Shibasaki, M. (1996). *Angew. Chem. Int. Ed.* **35**, 104–106.
Arai, T., Sasai, H., Yamaguchi, K. & Shibasaki, M. (1998). *J. Am. Chem. Soc.* **120**, 441–442.
Balsells, J., Davies, T. J., Carroll, P. & Walsh, P. J. (2002). *J. Am. Chem. Soc.* **124**, 10336–10348.
Bruker (2000). *SHELXTL*. Bruker AXS Inc., Madison, Winconsin, USA.
Gau, H.-M., Lee, C.-H., Lin, C.-C., Jiang, M.-K., Ho, Y.-C. & Kuo, C.-N. (1996). *J. Am. Chem. Soc.* **118**, 2936–2941.
Gothelf, K. V., Hazell, R. G. & Jørgensen, K. A. (1995). *J. Am. Chem. Soc.* **117**, 4435–4436.
Hafner, A., Duthaler, R. O., Marti, R., Rihs, G., Rothe-Streit, P. & Schwarzenbach, F. (1992). *J. Am. Chem. Soc.* **114**, 2321–2336.
Hintermann, L. & Togni, A. (2000). *Angew. Chem. Int. Ed.* **39**, 4359–4362.
Nöth, H., Schlegel, A. & Suter, M. (2001). *J. Organomet. Chem.* **621**, 231–241.
Pu, L. & Yu, H.-B. (2001). *Chem. Rev.* **101**, 757–824.
Ramón, D. J. & Yus, M. (2006). *Chem. Rev.* **106**, 2126–2208.

 doi:10.1107/S1600536807048052  

Seebach, D., Plattner, D. A., Beck, A. K., Wang, Y. M., Hunziker, D. & Petter, W. (1992). *Helv. Chim. Acta*, **75**, 2171–2209.
Shao, M.-Y. & Gau, H.-M. (1998). *Organometallics*, **17**, 4822–4827.
Sheen, W.-S. & Gau, H.-M. (2004). *Inorg. Chim. Acta*, **358**, 2279–2284.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Son, A. J. R., Thorn, M. G., Fanwick, P. E. & Rothwell, I. P. (2003). *Organometallics*, **22**, 2318–2324.

# supplementary materials

*Acta Cryst.* (2007). E**63**, m2665-m2666 [ **doi:10.1107/S1600536807048052** ]

# (2,2-Dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanolato-$\kappa^2O^4,O^5$)ethyl(tetrahydrofuran-$\kappa O$)aluminium(III)

**C.-A. Chen, K.-H. Wu and H.-M. Gau**

## Comment

The asymmetric C—C bond formation reaction catalyzed by Lewis acidic metals is one of the most important reactions studied in the past decade (Pu & Yu, 2001; Ramón & Yus, 2006). Among the chiral diol ligands developed, α,α,α',α'-tetraaryl-1,3-dioxolane-4,5-dimethanols (TADDOLs) and 1,1'-bi(2-naphthol) (BINOL) are the two ligand types having the most diversified applications. Titanium and aluminium BINOLate complexes have been applied to a variety of asymmetric reactions and crystal structures of complexes of both metals were documented (Balsells *et al.*, 2002; Arai *et al.*, 1996; Nöth *et al.*, 2001). In contrast, applications of TADDOLate ligands mainly focus on titanium catalytic systems and only a few molecular structures of titanium complexes were reported (Seebach *et al.*, 1992; Hafner *et al.*, 1992; Gothelf *et al.*, 1995; Hintermann & Togni, 2000; Sheen & Gau, 2004). Yet, to our knowledge, there is no report of crystal structure of aluminium complex of the TADDOLate ligand. We report here the synthesis and crystal structure of the title compound,(I), an aluminium complex of the TADDOLate ligand.

The molecular structure of (I) has a slightly distorted tetrahedral geometry around the aluminium metal center with short Al—O(TADDOLate) bond lengths of 1.712 (2) and 1.719 (2) Å which are shorter by 0.05 Å than the Al—O(BINOLate) bond distances of 1.762 (1) and 1.754 (1) Å in the tetrahedral Al(BINOLate)py(Et) complex (Son *et al.*, 2003) having a similar seven-membered chelate ring system. The seven-membered chelate TADDOLate O—Al—O angle of 111.19 (10)° is close to the ideal tetrahedral angle comparing to 106.65 (6)° for the Al(BINOLate)py(Et) structure. However, considerable deviations from the tetrahedral geometry are observed for the C—Al—O(TADDOLate) angles of 113.97 (11) and 118.74 (12)°. In comparison with the tetrahedral Ti(TADDOLate)$_2$ (Seebach *et al.*, 1992) and the six-coordinate octahedral TiCl$_2$(TADDOLate)(dppe) (Shao & Gau, 1998) structures, the Al—O(TADDOLate) bond lengths are shorter by 0.07 Å and the TADDOLate O—Al—O bond angle is much larger than the averaged angle of the tetrahedral Ti(TADDOLate)$_2$ complex of 102.5° and the angle of the six-coordinate complex of 98.7 (1)°. The Al—O—C(TADDOLate) angles are observed to be 139.17 (17)° and 137.95 (17)°, indicating considerable π-donation (Gau *et al.*, 1996)) from the alkoxide oxygen donor atom to empty 3 d orbitals of the aluminium(III) metal center. These angles are smaller than the averaged angles of the tetrahedral Ti(IV) complex of 145.3° and the octahedral Ti(IV) complex of 149.5°. However, these angles are larger than the angles of 124.2 (1) and 114.2 (1)° for the Al(BINOLate)py(Et) complex, suggesting a better π-donation ability of the TADDOLate ligand than the BINOLate ligand.

## Experimental

To an ice cold solution of α,α,α',α'-tetraphenyl-2,2-dimethyl- 1,3-dioxolane-4,5-dimethanol (4.67 g, 10.0 mmol) in THF (70 ml) at 273 K, AlEt$_3$ (12.0 ml, 15 wt% in hexane, 10.0 mmol) was added slowly in 30 min. After stirring for 1 h at 273 K, the solution was warmed to room temperature and was allowed to react for another 3.5 h. The volatile material was removed under reduced pressure to give a white residue. The residue was recrystallized from THF (100 ml) at 277 K to afford the first crop of compound (I) (2.07 g, 35.0%). The filtrate was cooled to 248 K to furnish the second crop of the product (2.00 g,

33.8%). The second filtrate was dried and the residue was dissolved in $CH_2Cl_2$. The solution was cooled to 248 K to afford colorless crystals (0.54 g, 9.0%) for molecular structure determination. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.66–7.12 (m, 20H, Ph), 5.02 (d, J = 6.4 Hz, 1H, CH), 4.91 (d, J = 6.4 Hz, 1H, CH), 4.10–3.90 (m, 4H, $OCH_2$), 1.81 (m, 4H, $CH_2$), 0.75 (t, J = 8.0 Hz, 3H, $CH_3$), 0.48 (s, 3H, $OCCH_3$), 0.43 (s, 3H, $OCCH_3$),-0.16 - −0.35 (m, 2H, $AlCH_2$) p.p.m..

### Refinement

All H atoms were treated as riding, with C—H = 0.93–0.98 Å, and with $U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5$U_{eq}$(C). In this investigation, the $U_{eq}$ of C32 was low compared to its neighbors, suggesting a possiblitiy of a heavier atom at this site. However, the $^1$H NMR spectrum of the crystalline material used for the X-ray diffraction study gives exclusive signals of an ethyl group with the C32 bonded to the Al metal center. In the absence of significant anomalous scattering, Friedel pairs were merged prior to the final refinement.

### Figures

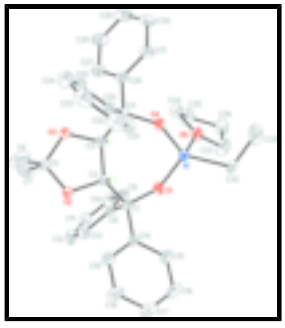


Fig. 1. The molecular structure of (I), with atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms (except tertiary) have been omitted for clarity.

### (2,2-Dimethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanolato- κ$^2$*O*$^4$,*O*$^5$)ethyl(tetrahydrofuran-κ*O*)aluminium(III)

*Crystal data*

| | |
|---|---|
| $[Al(C_2H_5)(C_{31}H_{28}O_4)(C_4H_8O)]$ | $F_{000}$ = 1264 |
| $M_r$ = 592.68 | $D_x$ = 1.210 Mg m$^{-3}$ |
| Orthorhombic, $P2_12_12_1$ | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 6990 reflections |
| $a$ = 9.6123 (8) Å | θ = 2.3–25.6º |
| $b$ = 15.7991 (13) Å | μ = 0.10 mm$^{-1}$ |
| $c$ = 21.4207 (18) Å | $T$ = 293 (2) K |
| $V$ = 3253.1 (5) Å$^3$ | Block, colourless |
| $Z$ = 4 | 0.80 × 0.23 × 0.19 mm |

*Data collection*

| | |
|---|---|
| Bruker SMART 1000 CCD diffractometer | 3591 independent reflections |

| | |
|---|---|
| Radiation source: fine-focus sealed tube | 2940 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.050$ |
| $T = 293(2)$ K | $\theta_{max} = 26.0°$ |
| φ and ω scans | $\theta_{min} = 2.3°$ |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h = -11 \rightarrow 11$ |
| $T_{min} = 0.748$, $T_{max} = 1.000$ | $k = -19 \rightarrow 18$ |
| 18371 measured reflections | $l = -20 \rightarrow 26$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H-atom parameters constrained |
| $wR(F^2) = 0.122$ | $w = 1/[\sigma^2(F_o^2) + (0.0821P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.07$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 3591 reflections | $\Delta\rho_{max} = 0.20$ e Å$^{-3}$ |
| 388 parameters | $\Delta\rho_{min} = -0.14$ e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on $F^2$, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Al | 0.78827 (9) | 0.09324 (5) | 0.85554 (4) | 0.0411 (2) |
| O1 | 0.7584 (3) | 0.09540 (12) | 0.93466 (9) | 0.0542 (5) |
| O2 | 0.7893 (2) | −0.10724 (12) | 1.01477 (9) | 0.0509 (5) |
| O3 | 0.9896 (2) | −0.13100 (13) | 0.96129 (9) | 0.0515 (5) |
| O4 | 0.8597 (2) | −0.00121 (12) | 0.83308 (9) | 0.0471 (5) |
| O5 | 0.9322 (2) | 0.17413 (12) | 0.84797 (11) | 0.0543 (5) |
| C1 | 0.7350 (3) | 0.03898 (17) | 0.98380 (11) | 0.0411 (6) |
| C2 | 0.7832 (3) | −0.05201 (16) | 0.96227 (12) | 0.0401 (6) |
| H2A | 0.7151 | −0.0743 | 0.9324 | 0.048* |
| C3 | 0.9291 (3) | −0.05808 (17) | 0.93323 (12) | 0.0413 (6) |

| | | | | |
|---|---|---|---|---|
| H3A | 0.9830 | −0.0081 | 0.9455 | 0.050* |
| C4 | 0.9352 (3) | −0.06764 (16) | 0.86033 (13) | 0.0414 (6) |
| C5 | 0.9102 (4) | −0.1571 (2) | 1.01377 (15) | 0.0570 (8) |
| C6 | 0.8713 (8) | −0.2479 (3) | 1.0058 (4) | 0.154 (3) |
| H6A | 0.8170 | −0.2543 | 0.9685 | 0.232* |
| H6B | 0.8178 | −0.2662 | 1.0411 | 0.232* |
| H6C | 0.9541 | −0.2815 | 1.0026 | 0.232* |
| C7 | 0.9958 (6) | −0.1355 (5) | 1.07144 (18) | 0.139 (3) |
| H7A | 1.0136 | −0.0757 | 1.0724 | 0.208* |
| H7B | 1.0825 | −0.1656 | 1.0701 | 0.208* |
| H7C | 0.9453 | −0.1516 | 1.1082 | 0.208* |
| C8 | 0.8179 (3) | 0.07032 (17) | 1.04086 (14) | 0.0443 (6) |
| C9 | 0.9188 (3) | 0.1324 (2) | 1.03385 (16) | 0.0551 (7) |
| H9A | 0.9364 | 0.1541 | 0.9943 | 0.066* |
| C10 | 0.9936 (4) | 0.1627 (2) | 1.0840 (2) | 0.0694 (10) |
| H10A | 1.0616 | 0.2038 | 1.0779 | 0.083* |
| C11 | 0.9680 (4) | 0.1325 (2) | 1.1427 (2) | 0.0743 (11) |
| H11A | 1.0190 | 0.1527 | 1.1765 | 0.089* |
| C12 | 0.8663 (5) | 0.0720 (2) | 1.15179 (17) | 0.0717 (10) |
| H12A | 0.8472 | 0.0521 | 1.1917 | 0.086* |
| C13 | 0.7926 (4) | 0.0409 (2) | 1.10072 (14) | 0.0572 (8) |
| H13A | 0.7250 | −0.0004 | 1.1069 | 0.069* |
| C14 | 0.5786 (3) | 0.03763 (18) | 0.99948 (13) | 0.0444 (6) |
| C15 | 0.4991 (4) | 0.1091 (2) | 0.98485 (17) | 0.0665 (9) |
| H15A | 0.5407 | 0.1551 | 0.9653 | 0.080* |
| C16 | 0.3583 (4) | 0.1116 (3) | 0.9993 (2) | 0.0814 (12) |
| H16A | 0.3067 | 0.1595 | 0.9891 | 0.098* |
| C17 | 0.2938 (4) | 0.0449 (3) | 1.0283 (2) | 0.0812 (12) |
| H17A | 0.1996 | 0.0473 | 1.0381 | 0.097* |
| C18 | 0.3709 (4) | −0.0257 (3) | 1.0425 (2) | 0.0777 (11) |
| H18A | 0.3286 | −0.0716 | 1.0621 | 0.093* |
| C19 | 0.5116 (4) | −0.0291 (2) | 1.02802 (18) | 0.0634 (9) |
| H19A | 0.5619 | −0.0776 | 1.0378 | 0.076* |
| C20 | 0.8713 (3) | −0.15198 (18) | 0.83976 (13) | 0.0453 (6) |
| C21 | 0.7343 (3) | −0.1554 (2) | 0.81897 (14) | 0.0556 (8) |
| H21A | 0.6820 | −0.1060 | 0.8173 | 0.067* |
| C22 | 0.6744 (5) | −0.2314 (3) | 0.80058 (19) | 0.0759 (11) |
| H22A | 0.5826 | −0.2323 | 0.7869 | 0.091* |
| C23 | 0.7490 (5) | −0.3045 (3) | 0.80237 (19) | 0.0827 (13) |
| H23A | 0.7080 | −0.3554 | 0.7905 | 0.099* |
| C24 | 0.8855 (6) | −0.3028 (2) | 0.8218 (2) | 0.0804 (13) |
| H24A | 0.9374 | −0.3525 | 0.8220 | 0.097* |
| C25 | 0.9464 (4) | −0.2273 (2) | 0.84102 (16) | 0.0632 (9) |
| H25A | 1.0381 | −0.2272 | 0.8549 | 0.076* |
| C26 | 1.0860 (3) | −0.06168 (18) | 0.83610 (14) | 0.0471 (7) |
| C27 | 1.2033 (4) | −0.0667 (2) | 0.87345 (17) | 0.0663 (9) |
| H27A | 1.1935 | −0.0754 | 0.9162 | 0.080* |
| C28 | 1.3356 (4) | −0.0589 (3) | 0.8478 (2) | 0.0858 (13) |
| H28A | 1.4136 | −0.0615 | 0.8734 | 0.103* |

| | | | | |
|---|---|---|---|---|
| C29 | 1.3516 (5) | −0.0472 (3) | 0.7845 (2) | 0.0850 (13) |
| H29A | 1.4401 | −0.0427 | 0.7673 | 0.102* |
| C30 | 1.2366 (5) | −0.0424 (3) | 0.74697 (19) | 0.0756 (11) |
| H30A | 1.2472 | −0.0344 | 0.7042 | 0.091* |
| C31 | 1.1037 (4) | −0.0495 (2) | 0.77246 (16) | 0.0604 (8) |
| H31A | 1.0262 | −0.0460 | 0.7466 | 0.072* |
| C32 | 0.6370 (3) | 0.13669 (18) | 0.79692 (14) | 0.0493 (7) |
| H32A | 0.5617 | 0.0959 | 0.7951 | 0.059* |
| H32B | 0.5997 | 0.1894 | 0.8131 | 0.059* |
| C33 | 0.6929 (7) | 0.1510 (5) | 0.7327 (2) | 0.136 (2) |
| H33A | 0.6196 | 0.1711 | 0.7061 | 0.203* |
| H33B | 0.7288 | 0.0987 | 0.7164 | 0.203* |
| H33C | 0.7661 | 0.1923 | 0.7343 | 0.203* |
| C34 | 1.0796 (4) | 0.1596 (2) | 0.85889 (19) | 0.0656 (9) |
| H34A | 1.1252 | 0.1406 | 0.8210 | 0.079* |
| H34B | 1.0932 | 0.1174 | 0.8912 | 0.079* |
| C35 | 1.1364 (5) | 0.2442 (3) | 0.8793 (3) | 0.0909 (14) |
| H35A | 1.1299 | 0.2508 | 0.9243 | 0.109* |
| H35B | 1.2327 | 0.2509 | 0.8667 | 0.109* |
| C36 | 1.0441 (5) | 0.3061 (2) | 0.8461 (2) | 0.0835 (12) |
| H36A | 1.0418 | 0.3599 | 0.8678 | 0.100* |
| H36B | 1.0755 | 0.3153 | 0.8036 | 0.100* |
| C37 | 0.9060 (5) | 0.2650 (2) | 0.8471 (3) | 0.0864 (13) |
| H37A | 0.8542 | 0.2820 | 0.8839 | 0.104* |
| H37B | 0.8529 | 0.2805 | 0.8103 | 0.104* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Al | 0.0473 (4) | 0.0348 (4) | 0.0413 (4) | 0.0003 (4) | −0.0033 (3) | 0.0023 (3) |
| O1 | 0.0811 (15) | 0.0354 (9) | 0.0462 (10) | 0.0090 (10) | 0.0087 (10) | 0.0044 (8) |
| O2 | 0.0554 (12) | 0.0430 (10) | 0.0543 (11) | 0.0116 (10) | 0.0114 (10) | 0.0110 (9) |
| O3 | 0.0554 (11) | 0.0510 (11) | 0.0480 (10) | 0.0184 (10) | 0.0080 (10) | 0.0067 (10) |
| O4 | 0.0583 (12) | 0.0414 (10) | 0.0416 (10) | 0.0076 (9) | 0.0008 (9) | 0.0010 (8) |
| O5 | 0.0563 (12) | 0.0367 (10) | 0.0698 (13) | −0.0069 (9) | −0.0054 (11) | 0.0041 (9) |
| C1 | 0.0521 (16) | 0.0353 (13) | 0.0361 (13) | 0.0073 (12) | 0.0022 (11) | −0.0012 (10) |
| C2 | 0.0451 (14) | 0.0328 (12) | 0.0423 (13) | 0.0055 (12) | 0.0049 (12) | 0.0010 (11) |
| C3 | 0.0476 (15) | 0.0336 (12) | 0.0427 (14) | 0.0051 (12) | −0.0006 (12) | −0.0023 (11) |
| C4 | 0.0466 (14) | 0.0356 (13) | 0.0421 (14) | 0.0037 (11) | 0.0032 (12) | −0.0016 (11) |
| C5 | 0.0595 (18) | 0.0489 (17) | 0.0627 (19) | 0.0190 (15) | 0.0135 (15) | 0.0187 (14) |
| C6 | 0.149 (6) | 0.043 (2) | 0.271 (8) | 0.013 (3) | 0.117 (6) | 0.015 (3) |
| C7 | 0.096 (3) | 0.269 (8) | 0.050 (2) | 0.076 (5) | 0.002 (2) | 0.031 (4) |
| C8 | 0.0471 (16) | 0.0377 (14) | 0.0480 (14) | 0.0095 (11) | 0.0006 (12) | −0.0055 (12) |
| C9 | 0.0529 (17) | 0.0457 (16) | 0.0668 (19) | 0.0038 (14) | 0.0051 (15) | −0.0062 (15) |
| C10 | 0.061 (2) | 0.0506 (18) | 0.096 (3) | 0.0026 (17) | −0.014 (2) | −0.0168 (19) |
| C11 | 0.083 (3) | 0.0559 (19) | 0.084 (3) | 0.0126 (19) | −0.032 (2) | −0.020 (2) |
| C12 | 0.100 (3) | 0.060 (2) | 0.0546 (19) | 0.010 (2) | −0.0201 (19) | −0.0032 (16) |
| C13 | 0.071 (2) | 0.0497 (16) | 0.0516 (16) | 0.0009 (16) | −0.0049 (16) | −0.0024 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C14 | 0.0484 (15) | 0.0438 (14) | 0.0409 (14) | 0.0111 (12) | −0.0029 (12) | −0.0063 (12) |
| C15 | 0.071 (2) | 0.060 (2) | 0.069 (2) | 0.0287 (18) | −0.0049 (17) | 0.0004 (17) |
| C16 | 0.066 (2) | 0.077 (3) | 0.101 (3) | 0.036 (2) | −0.012 (2) | −0.005 (2) |
| C17 | 0.048 (2) | 0.091 (3) | 0.104 (3) | 0.019 (2) | −0.001 (2) | −0.021 (2) |
| C18 | 0.053 (2) | 0.067 (2) | 0.113 (3) | 0.0044 (18) | 0.016 (2) | −0.004 (2) |
| C19 | 0.0538 (19) | 0.0514 (18) | 0.085 (2) | 0.0082 (15) | 0.0096 (17) | 0.0002 (17) |
| C20 | 0.0573 (17) | 0.0387 (14) | 0.0399 (14) | −0.0013 (13) | 0.0076 (12) | −0.0029 (11) |
| C21 | 0.0597 (19) | 0.0545 (18) | 0.0526 (16) | −0.0065 (15) | 0.0007 (15) | −0.0047 (14) |
| C22 | 0.077 (3) | 0.076 (3) | 0.075 (2) | −0.026 (2) | 0.001 (2) | −0.012 (2) |
| C23 | 0.109 (4) | 0.062 (2) | 0.077 (2) | −0.034 (2) | 0.016 (2) | −0.0141 (19) |
| C24 | 0.120 (4) | 0.0363 (17) | 0.085 (3) | 0.001 (2) | 0.017 (3) | −0.0081 (17) |
| C25 | 0.079 (2) | 0.0444 (16) | 0.066 (2) | 0.0063 (16) | 0.0037 (18) | −0.0063 (15) |
| C26 | 0.0507 (16) | 0.0388 (14) | 0.0518 (16) | −0.0006 (12) | 0.0094 (13) | −0.0075 (12) |
| C27 | 0.0534 (19) | 0.078 (2) | 0.0673 (19) | 0.0008 (18) | 0.0087 (16) | −0.0037 (18) |
| C28 | 0.0483 (19) | 0.113 (3) | 0.096 (3) | −0.004 (2) | 0.013 (2) | −0.009 (3) |
| C29 | 0.060 (2) | 0.094 (3) | 0.101 (3) | −0.016 (2) | 0.033 (2) | −0.022 (3) |
| C30 | 0.090 (3) | 0.068 (2) | 0.069 (2) | −0.014 (2) | 0.038 (2) | −0.0127 (18) |
| C31 | 0.068 (2) | 0.0567 (18) | 0.0565 (19) | −0.0046 (16) | 0.0150 (16) | −0.0091 (15) |
| C32 | 0.0559 (17) | 0.0358 (14) | 0.0564 (16) | 0.0104 (13) | −0.0090 (13) | 0.0005 (13) |
| C33 | 0.174 (6) | 0.166 (5) | 0.066 (3) | 0.067 (5) | −0.043 (3) | −0.003 (3) |
| C34 | 0.0554 (18) | 0.0527 (18) | 0.089 (2) | −0.0069 (16) | 0.0023 (19) | 0.0076 (18) |
| C35 | 0.085 (3) | 0.071 (3) | 0.117 (4) | −0.023 (2) | −0.024 (3) | 0.010 (2) |
| C36 | 0.103 (3) | 0.051 (2) | 0.097 (3) | −0.019 (2) | −0.018 (3) | 0.010 (2) |
| C37 | 0.082 (3) | 0.0402 (17) | 0.137 (4) | −0.0054 (18) | −0.016 (3) | −0.002 (2) |

*Geometric parameters (Å, °)*

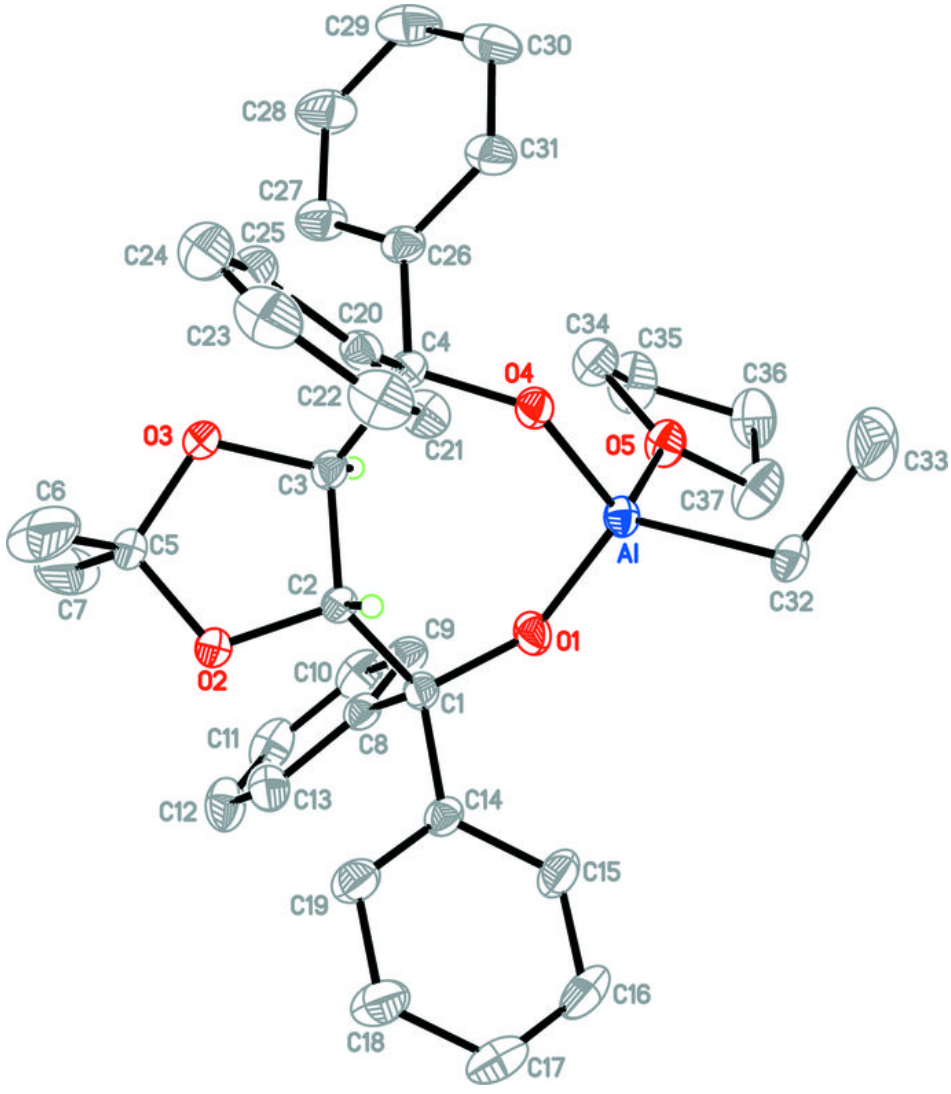
| | | | |
|---|---|---|---|
| Al—O4 | 1.712 (2) | C16—H16A | 0.93 |
| Al—O1 | 1.719 (2) | C17—C18 | 1.374 (6) |
| Al—O5 | 1.891 (2) | C17—H17A | 0.93 |
| Al—C32 | 2.040 (3) | C18—C19 | 1.388 (5) |
| O1—C1 | 1.397 (3) | C18—H18A | 0.93 |
| O2—C5 | 1.404 (4) | C19—H19A | 0.93 |
| O2—C2 | 1.425 (3) | C20—C21 | 1.391 (4) |
| O3—C5 | 1.420 (4) | C20—C25 | 1.393 (5) |
| O3—C3 | 1.423 (3) | C21—C22 | 1.388 (5) |
| O4—C4 | 1.403 (3) | C21—H21A | 0.93 |
| O5—C34 | 1.454 (4) | C22—C23 | 1.361 (6) |
| O5—C37 | 1.458 (4) | C22—H22A | 0.93 |
| C1—C14 | 1.541 (4) | C23—C24 | 1.377 (7) |
| C1—C8 | 1.541 (4) | C23—H23A | 0.93 |
| C1—C2 | 1.579 (3) | C24—C25 | 1.391 (5) |
| C2—C3 | 1.537 (4) | C24—H24A | 0.93 |
| C2—H2A | 0.98 | C25—H25A | 0.93 |
| C3—C4 | 1.570 (4) | C26—C31 | 1.387 (5) |
| C3—H3A | 0.98 | C26—C27 | 1.385 (5) |
| C4—C20 | 1.532 (4) | C27—C28 | 1.392 (5) |
| C4—C26 | 1.543 (4) | C27—H27A | 0.93 |
| C5—C6 | 1.492 (6) | C28—C29 | 1.376 (7) |

| | | | |
|---|---|---|---|
| C5—C7 | 1.523 (6) | C28—H28A | 0.93 |
| C6—H6A | 0.96 | C29—C30 | 1.369 (6) |
| C6—H6B | 0.96 | C29—H29A | 0.93 |
| C6—H6C | 0.96 | C30—C31 | 1.393 (5) |
| C7—H7A | 0.96 | C30—H30A | 0.93 |
| C7—H7B | 0.96 | C31—H31A | 0.93 |
| C7—H7C | 0.96 | C32—C33 | 1.494 (6) |
| C8—C9 | 1.388 (4) | C32—H32A | 0.97 |
| C8—C13 | 1.385 (4) | C32—H32B | 0.97 |
| C9—C10 | 1.379 (5) | C33—H33A | 0.96 |
| C9—H9A | 0.93 | C33—H33B | 0.96 |
| C10—C11 | 1.368 (6) | C33—H33C | 0.96 |
| C10—H10A | 0.93 | C34—C35 | 1.508 (5) |
| C11—C12 | 1.382 (6) | C34—H34A | 0.97 |
| C11—H11A | 0.93 | C34—H34B | 0.97 |
| C12—C13 | 1.393 (5) | C35—C36 | 1.500 (6) |
| C12—H12A | 0.93 | C35—H35A | 0.97 |
| C13—H13A | 0.93 | C35—H35B | 0.97 |
| C14—C19 | 1.378 (5) | C36—C37 | 1.478 (6) |
| C14—C15 | 1.398 (4) | C36—H36A | 0.97 |
| C15—C16 | 1.389 (6) | C36—H36B | 0.97 |
| C15—H15A | 0.93 | C37—H37A | 0.97 |
| C16—C17 | 1.372 (6) | C37—H37B | 0.97 |
| O4—Al—O1 | 111.19 (10) | C18—C17—C16 | 118.7 (4) |
| O4—Al—O5 | 105.76 (11) | C18—C17—H17A | 120.6 |
| O1—Al—O5 | 101.15 (11) | C16—C17—H17A | 120.6 |
| O4—Al—C32 | 113.97 (11) | C17—C18—C19 | 120.5 (4) |
| O1—Al—C32 | 118.74 (12) | C17—C18—H18A | 119.8 |
| O5—Al—C32 | 103.97 (11) | C19—C18—H18A | 119.8 |
| C1—O1—Al | 139.17 (17) | C14—C19—C18 | 121.7 (3) |
| C5—O2—C2 | 111.5 (2) | C14—C19—H19A | 119.2 |
| C5—O3—C3 | 110.5 (2) | C18—C19—H19A | 119.2 |
| C4—O4—Al | 137.95 (17) | C21—C20—C25 | 117.6 (3) |
| C34—O5—C37 | 109.0 (3) | C21—C20—C4 | 120.4 (3) |
| C34—O5—Al | 126.35 (19) | C25—C20—C4 | 122.0 (3) |
| C37—O5—Al | 122.7 (2) | C20—C21—C22 | 121.2 (3) |
| O1—C1—C14 | 109.3 (2) | C20—C21—H21A | 119.4 |
| O1—C1—C8 | 108.0 (2) | C22—C21—H21A | 119.4 |
| C14—C1—C8 | 109.6 (2) | C23—C22—C21 | 120.5 (4) |
| O1—C1—C2 | 108.3 (2) | C23—C22—H22A | 119.7 |
| C14—C1—C2 | 109.7 (2) | C21—C22—H22A | 119.7 |
| C8—C1—C2 | 111.9 (2) | C22—C23—C24 | 119.6 (4) |
| O2—C2—C3 | 104.1 (2) | C22—C23—H23A | 120.2 |
| O2—C2—C1 | 109.8 (2) | C24—C23—H23A | 120.2 |
| C3—C2—C1 | 116.3 (2) | C23—C24—C25 | 120.5 (4) |
| O2—C2—H2A | 108.8 | C23—C24—H24A | 119.7 |
| C3—C2—H2A | 108.8 | C25—C24—H24A | 119.7 |
| C1—C2—H2A | 108.8 | C24—C25—C20 | 120.6 (4) |
| O3—C3—C2 | 104.6 (2) | C24—C25—H25A | 119.7 |

| | | | |
|---|---|---|---|
| O3—C3—C4 | 109.1 (2) | C20—C25—H25A | 119.7 |
| C2—C3—C4 | 116.3 (2) | C31—C26—C27 | 118.4 (3) |
| O3—C3—H3A | 108.9 | C31—C26—C4 | 117.0 (3) |
| C2—C3—H3A | 108.9 | C27—C26—C4 | 124.6 (3) |
| C4—C3—H3A | 108.9 | C26—C27—C28 | 120.7 (3) |
| O4—C4—C20 | 108.9 (2) | C26—C27—H27A | 119.7 |
| O4—C4—C26 | 107.5 (2) | C28—C27—H27A | 119.7 |
| C20—C4—C26 | 109.5 (2) | C29—C28—C27 | 120.2 (4) |
| O4—C4—C3 | 108.8 (2) | C29—C28—H28A | 119.9 |
| C20—C4—C3 | 110.8 (2) | C27—C28—H28A | 119.9 |
| C26—C4—C3 | 111.3 (2) | C30—C29—C28 | 119.7 (4) |
| O2—C5—O3 | 107.1 (2) | C30—C29—H29A | 120.1 |
| O2—C5—C6 | 109.5 (4) | C28—C29—H29A | 120.1 |
| O3—C5—C6 | 108.8 (4) | C29—C30—C31 | 120.4 (3) |
| O2—C5—C7 | 108.0 (3) | C29—C30—H30A | 119.8 |
| O3—C5—C7 | 106.7 (3) | C31—C30—H30A | 119.8 |
| C6—C5—C7 | 116.3 (6) | C26—C31—C30 | 120.6 (4) |
| C5—C6—H6A | 109.5 | C26—C31—H31A | 119.7 |
| C5—C6—H6B | 109.5 | C30—C31—H31A | 119.7 |
| H6A—C6—H6B | 109.5 | C33—C32—Al | 111.2 (3) |
| C5—C6—H6C | 109.5 | C33—C32—H32A | 109.4 |
| H6A—C6—H6C | 109.5 | Al—C32—H32A | 109.4 |
| H6B—C6—H6C | 109.5 | C33—C32—H32B | 109.4 |
| C5—C7—H7A | 109.5 | Al—C32—H32B | 109.4 |
| C5—C7—H7B | 109.5 | H32A—C32—H32B | 108.0 |
| H7A—C7—H7B | 109.5 | C32—C33—H33A | 109.5 |
| C5—C7—H7C | 109.5 | C32—C33—H33B | 109.5 |
| H7A—C7—H7C | 109.5 | H33A—C33—H33B | 109.5 |
| H7B—C7—H7C | 109.5 | C32—C33—H33C | 109.5 |
| C9—C8—C13 | 117.4 (3) | H33A—C33—H33C | 109.5 |
| C9—C8—C1 | 120.2 (3) | H33B—C33—H33C | 109.5 |
| C13—C8—C1 | 122.4 (3) | O5—C34—C35 | 105.1 (3) |
| C10—C9—C8 | 121.7 (3) | O5—C34—H34A | 110.7 |
| C10—C9—H9A | 119.1 | C35—C34—H34A | 110.7 |
| C8—C9—H9A | 119.1 | O5—C34—H34B | 110.7 |
| C11—C10—C9 | 120.1 (4) | C35—C34—H34B | 110.7 |
| C11—C10—H10A | 119.9 | H34A—C34—H34B | 108.8 |
| C9—C10—H10A | 119.9 | C36—C35—C34 | 103.0 (3) |
| C10—C11—C12 | 119.9 (3) | C36—C35—H35A | 111.2 |
| C10—C11—H11A | 120.1 | C34—C35—H35A | 111.2 |
| C12—C11—H11A | 120.1 | C36—C35—H35B | 111.2 |
| C11—C12—C13 | 119.6 (4) | C34—C35—H35B | 111.2 |
| C11—C12—H12A | 120.2 | H35A—C35—H35B | 109.1 |
| C13—C12—H12A | 120.2 | C37—C36—C35 | 103.8 (3) |
| C8—C13—C12 | 121.3 (3) | C37—C36—H36A | 111.0 |
| C8—C13—H13A | 119.4 | C35—C36—H36A | 111.0 |
| C12—C13—H13A | 119.4 | C37—C36—H36B | 111.0 |
| C19—C14—C15 | 117.5 (3) | C35—C36—H36B | 111.0 |
| C19—C14—C1 | 124.3 (3) | H36A—C36—H36B | 109.0 |

| | | | |
|---|---|---|---|
| C15—C14—C1 | 118.2 (3) | O5—C37—C36 | 106.1 (3) |
| C16—C15—C14 | 120.4 (4) | O5—C37—H37A | 110.5 |
| C16—C15—H15A | 119.8 | C36—C37—H37A | 110.5 |
| C14—C15—H15A | 119.8 | O5—C37—H37B | 110.5 |
| C17—C16—C15 | 121.2 (4) | C36—C37—H37B | 110.5 |
| C17—C16—H16A | 119.4 | H37A—C37—H37B | 108.7 |
| C15—C16—H16A | 119.4 | | |

**Fig. 1**


C29
C30
C28
C31
C27
C25
C24
C26
C23
C20
C4
C34
C35
C36
C22
O4
O3
C21
O5
C33
C6
C3
C37
C5
Al
C2
C32
C7
C9
O2
O1
C10
C1
C11
C8
C12
C13
C14
C15
C19
C16
C18
C17