

α -Tris(2,4-pentanedionato- κ^2 O,O')-aluminium(III) at 240, 210, 180, 150 and 110 K: a new δ phase at 110 K

Lars S. von Chrzanowski,* Martin Lutz and Anthony L. Spek

Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands
Correspondence e-mail: l.vonchrzanowski@chem.uu.nl

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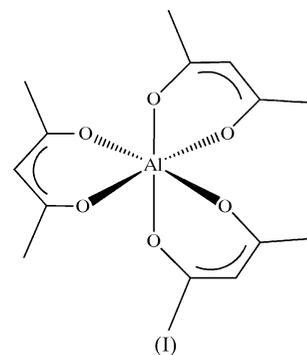
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The crystal structure of the title compound, $[\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3]$, has been investigated by a multi-temperature measurement to provide information on thermal vibrations and disorder in the structure. At 110 K, the structure of a new δ polymorph could be determined. A disorder–order phase transition takes place between 150 and 110 K and is *klassengleich*. The unit-cell volume increases by a factor of three and the diffraction pattern shows weak supercell reflections.

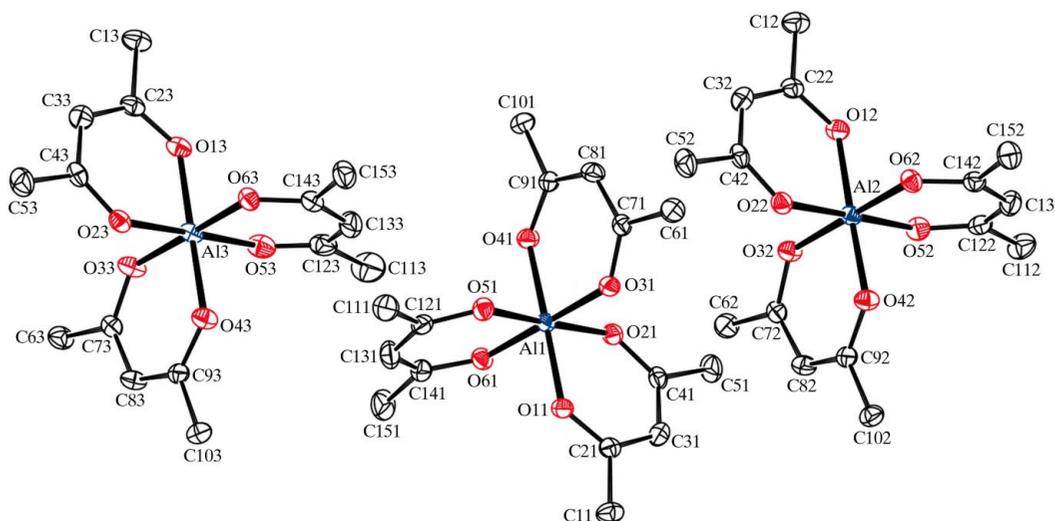
Comment

The crystal structures of trivalent metal acetylacetonate complexes can be grouped into several isomorphous series [an overview is given by Sabolović *et al.* (2004)]. According to an old nomenclature by Astbury & Gilbert (1926), the α polymorph crystallizes in the monoclinic crystal system with space group $P2_1/c$. The β and γ polymorphs crystallize in the

orthorhombic crystal system with space groups $Pbca$ and $Pna2_1$, respectively. Two different polymorphs of $\text{Al}(\text{acac})_3$ (acac is acetylacetonate or 2,4-pentanedionate) have been investigated previously, namely the α and γ polymorphs. Both polymorphs can occur in the same crystallization batch. All previous crystallographic studies of the α polymorph were carried out at room temperature, according to a search of the Cambridge Structural Database (Version 5.28 of November 2006; Allen, 2002). Recently, we redetermined the crystal structure of the γ polymorph at 110 K, which contains four independent molecules (von Chrzanowski *et al.*, 2006). In the course of our studies on $\text{Al}(\text{acac})_3$, we have now redetermined the crystal structure of α - $\text{Al}(\text{acac})_3$, (I), by a multi-temperature measurement at 240, (Ia), 210, (Ib), 180, (Ic), 150, (Id), and 110 K, (Ie), in order to investigate the behavior of atoms C11 and C15, which showed anomalous displacement parameters/disorder in the known studies of α polymorphs (Morosin, 1965; Diaz-Acosta *et al.*, 2001; Fackler & Avdeef, 1974). At a temperature of 110 K, we found a new δ polymorph, (Ie), which is a superstructure of the α polymorph. The phase transition occurs between 150 and 110 K.



The transformation matrix from the high-temperature α polymorph to the low-temperature δ polymorph is $(10\bar{1}/0\bar{1}0/\bar{2}0\bar{1})$. The determinant of this matrix is 3 and thus the volume is increased by a factor of three. The space group remains $P2_1/c$ and the phase transition is therefore *klassengleich*. In the

**Figure 1**

Displacement ellipsoid plot and atomic numbering scheme of the three independent molecules in the asymmetric unit of δ polymorph (Ie). Ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

asymmetric unit of the δ polymorph, there are three independent molecules (Fig. 1). All molecules have an approximate non-crystallographic D_3 symmetry, with r.m.s. deviations between 0.127 and 0.176 Å from ideal symmetry (Pilati & Forni, 1998). The molecules occupy pseudo-special positions with centers of gravity at (0.27, 0.23, 0.26), (0.40, 0.78, 0.07) and (0.06, 0.75, 0.40). All three molecules have essentially the same geometry, as can be seen in a quaternion fit (Fig. 2a). This quaternion fit (Mackay, 1984) considers only the molecular structures, but does not take the crystal packing into account. The packing effects can be seen by the application of the transformation matrix to the α polymorph on the atomic coordinates of the δ polymorph. The result of this operation can be seen in Fig. 2(b). Two of the acac ligands have only very small deviations after this averaging, while the third ligand (C11x–C15x) is severely affected by the packing. The latter ligand corresponds to the ligand with large displacement parameters in the α polymorph. We therefore consider this phase transition as a disorder–order phase transition.

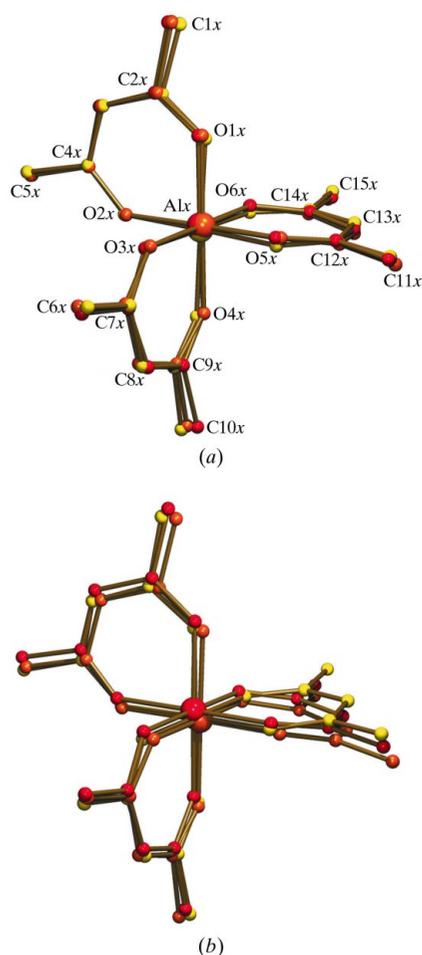


Figure 2
(a) Quaternion fit of the three independent molecules of (Ie). (b) Transformation of the three independent molecules of (Ie) into an average structure using the transformation matrix between the δ and the α polymorph. [In the electronic version of the paper, yellow atoms represent molecule 1 ($x = 1$), red atoms molecule 2 ($x = 2$) and orange atoms molecule 3 ($x = 3$).]

The ADDSYM routine of the program *PLATON* (Spek, 2003) indicates pseudo-translational symmetry for the δ polymorph. This pseudo-translational symmetry can also be seen in the X-ray intensities. Reflections with $h + 2l = 3n$ correspond to the subcell and are much stronger than the other reflections. Nevertheless, the weak supercell reflections are clearly present and prevent a transformation to the subcell (Fig. 3). The strongest superstructure reflection is (220) with $I/\sigma(I)$ of 157.29. The average $I/\sigma(I)$ of the subcell reflections is 44.43, while the supercell reflections have an average $I/\sigma(I)$ of 13.60. A test on pseudo-translational symmetry based on normalized structure factors from measured data (Casarano *et al.*, 1985), as implemented in the program *SIR97* (Altomare *et al.*, 1999), results in a value of 70% for the mean fractional scattering power of the electron density for reflections with $h \pm 1l = 3n$ and with $h + 2l = 3n$. The corresponding $\langle E^{*2} \rangle$ value for these reflections is 2.409.

Despite the pseudo-translational symmetry, a full-matrix least-squares refinement with *SHELXL97* (Sheldrick, 1997) can be performed with default refinement parameters and without restraints or constraints. No correlation matrix elements were larger than 0.5. The weighting scheme for the refinement was optimized by *SHELXL97* based on all 11 232 unique reflections and results in a goodness-of-fit of 1.046. The corresponding goodness-of-fit for the 3741 strong subcell

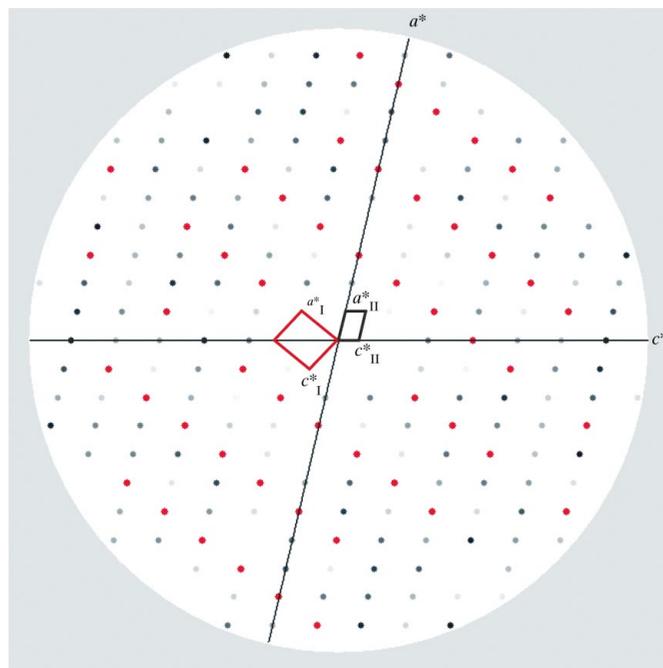


Figure 3
Simulated precession photograph of δ polymorph (Ie) using the reflection file of the refinement (Barbour, 1999), showing the h_0l plane. Intensities are drawn on a logarithmic scale. Dark dots (red in the electronic version of the paper) represent strong reflections of the subcell; light dots represent weak reflections of the supercell. (The base vectors of the reciprocal subcell are drawn with red lines in the electronic version, and those of the supercell with gray lines.) The transformation matrix used to generate the subcell is $\begin{pmatrix} 1/3 & 0 & 1/3 \\ 0 & 1/3 & 0 \\ 1/3 & 0 & 1/3 \end{pmatrix}$.

reflections without re-refinement and with the same weighting scheme is 1.418, and for the 7491 weak supercell reflections 0.881. Obviously, the weighted sigmas of the subcell reflections

are underestimated and those of the supercell reflections overestimated in the refinement. A manual correction of the sigmas based on normal probability plots for subcell and

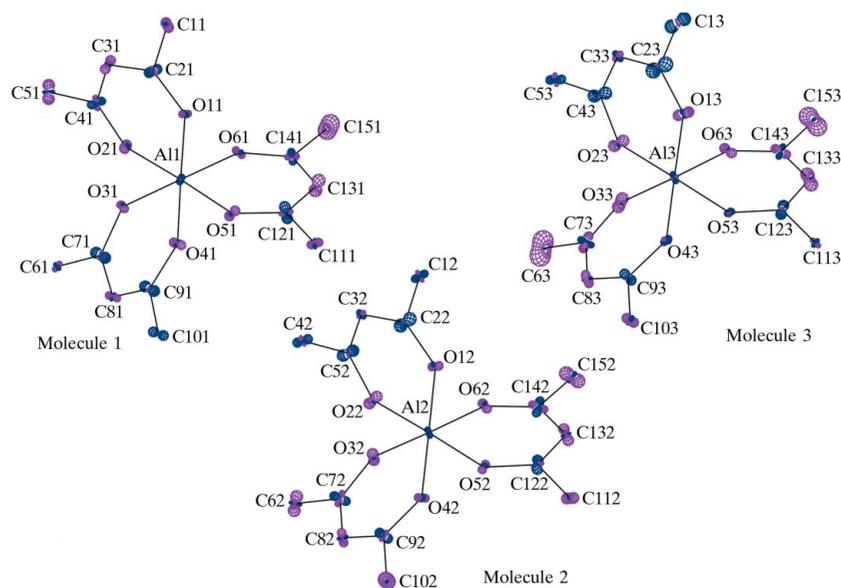


Figure 4

Peanut plot (Hummel *et al.*, 1990) of (*Ie*) showing the difference between the measured displacement parameters and the parameters obtained by three independent rigid-body analyses using the program *THMA11* (Schomaker & Trueblood, 1998). A scale factor of 3.08 was used for the r.m.s. surfaces. Darker spheres (blue in the electronic version of the paper) indicate positive differences and lighter spheres (purple in the electronic version) negative differences. All molecules are drawn independently in the same orientation and do not represent the crystal packing.

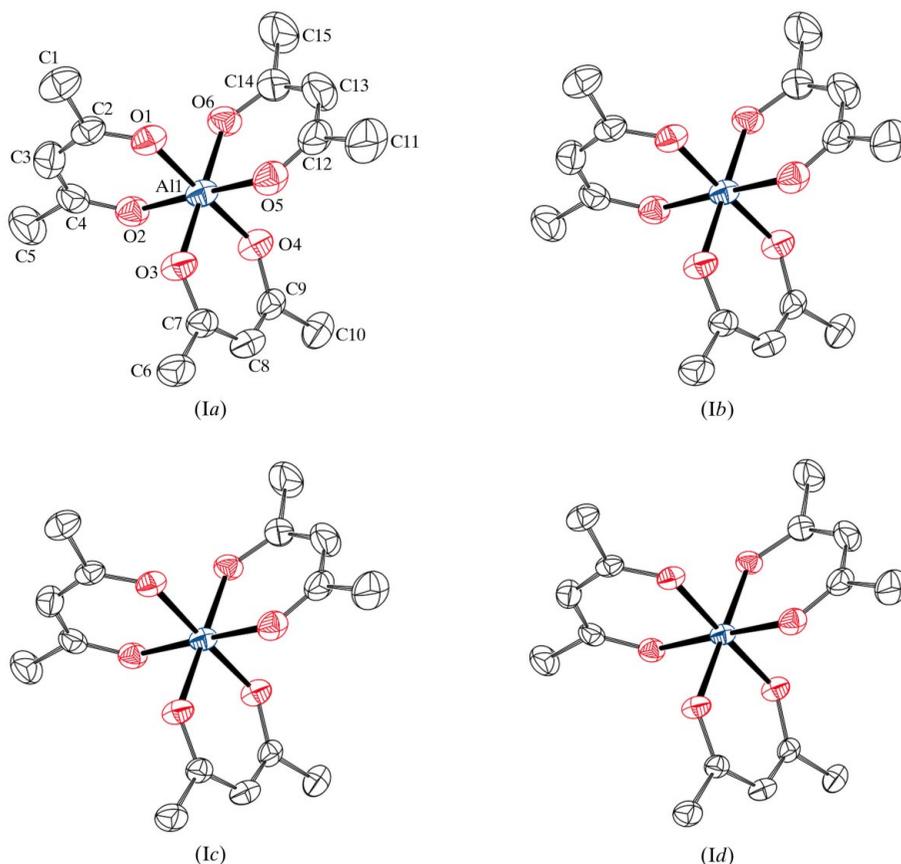


Figure 5

Displacement ellipsoid plots and atomic numbering scheme of (*Ia*)–(*Id*). Ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. All plots are drawn in the same orientation and have the same labeling scheme.

supercell reflections did not change the outcome of the refinement.

The phase transition from the high-temperature α phase to the low-temperature δ phase breaks the translational symmetry for the C11–C15 acac ligand (see above). Nevertheless, the anisotropy of some methyl groups is still rather large, but this now concerns also methyl groups of other acac ligands. Indeed, rigid-body analyses (Schomaker & Trueblood, 1998) for the three molecules result in relatively high agreement factors of $R = 0.156\text{--}0.187$ ($R = \{\sum[(U_{\text{obs}} - U_{\text{calc}})^2] / \sum(U_{\text{obs}}^2)\}^{1/2}$). Difference plots (Hummel *et al.*, 1990) between the observed displacement parameters and the rigid-body models (Fig. 4) make the large internal motions of the methyl groups visible. These internal motions are also reflected in a relatively large variation of the bond lengths. For example, the Al–O distances range between 1.8704 (9) and 1.8924 (9) Å (Table 1). The corresponding Al–O distances in the γ polymorph (von Chrzanowski *et al.*, 2006) are 1.8728 (13)–1.8947 (12) Å and show a similar variation. Because Al^{III} does not express Jahn–Teller distortions, this variation can only be explained by internal thermal motion. The thermal motion also explains why the Al–O distances of the crystal structure determinations are shorter than the value of 1.9159 Å obtained from quantum chemical calculations (Diaz-Acosta *et al.*, 2001).

As expected, a temperature-dependent measurement of the α polymorph shows a decreasing thermal motion with decreasing temperature (Fig. 5). The eigenvalues of translation T_i and libration L_i tensors obtained from rigid-body analyses (PLATON; Spek, 2003) show that this decrease is

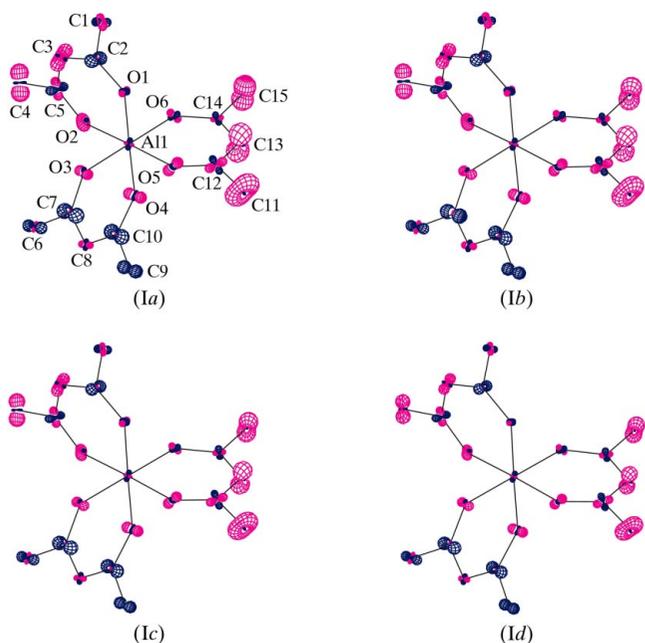


Figure 7 Peanut plots of (Ia)–(Id) showing the difference between the measured displacement parameters and the parameters obtained by rigid-body analyses using the program THMA11 (Schomaker & Trueblood, 1998). A scale factor of 3.08 was used for the r.m.s. surfaces. (The color scheme is the same as that in Fig. 4.)

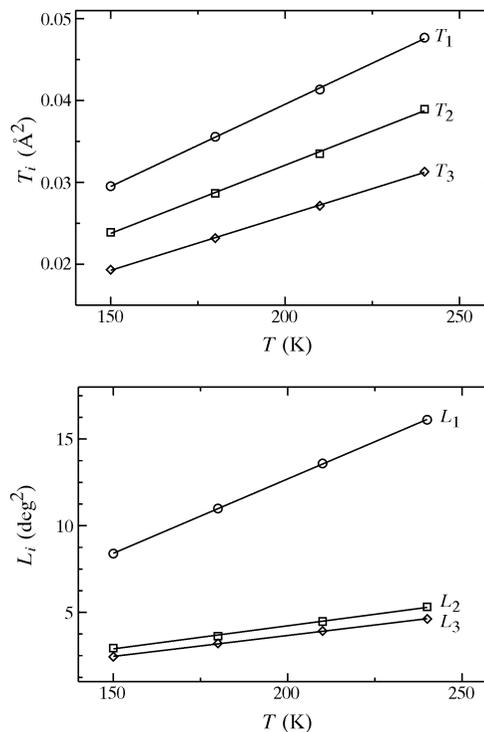


Figure 6 Eigenvalues of translation T_i (top) and libration L_i (bottom) tensors from rigid-body analyses (PLATON; Spek, 2003) as a function of temperature.

linear (Fig. 6). In the whole temperature range, the agreement factors are rather high ($R = 0.155\text{--}0.167$). The corresponding internal motion is visualized by difference plots (Hummel *et al.*, 1990) between the observed displacement parameters and the rigid-body models for (Ia)–(Id) (Fig. 7). The non-rigid behaviour is mainly expressed by only one acac ligand (C11–C15). This is the same ligand that breaks the translational symmetry in the δ phase. Quantum chemical calculations have proven the presence of out-of-plane deformations in isolated Al(acac)₃ molecules (Diaz-Acosta *et al.*, 2001). However, from the observed phase transition, we assume that the anisotropy of C11–C15 is a property of the crystal packing.

Experimental

Crystals were obtained by slow evaporation of a solution of the commercially available material (Aldrich) in ethyl acetate at room temperature. In the batch, plate- and needle-shaped crystals were present. For data collection, a plate-shaped crystal was selected.

Determination (Ia), at 240 K

Crystal data

[Al(C₅H₇O₂)₃]
 $M_r = 324.30$
 Monoclinic, $P2_1/c$
 $a = 13.9140$ (7) Å
 $b = 7.50076$ (17) Å
 $c = 16.2547$ (6) Å
 $\beta = 98.806$ (2)°
 $V = 1676.44$ (11) Å³

$Z = 4$
 $D_x = 1.285$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.14$ mm⁻¹
 $T = 240$ (2) K
 Hexagonal prism, colorless
 $0.42 \times 0.39 \times 0.18$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.67, T_{\max} = 0.97$

29848 measured reflections
 3870 independent reflections
 3065 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.124$
 $S = 1.08$
 3870 reflections
 205 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.4307P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

Determination (1b), at 210 K

Crystal data

$[\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3]$
 $M_r = 324.30$
 Monoclinic, $P2_1/c$
 $a = 13.8640 (6) \text{ \AA}$
 $b = 7.4755 (3) \text{ \AA}$
 $c = 16.2080 (11) \text{ \AA}$
 $\beta = 98.821 (2)^\circ$
 $V = 1659.94 (15) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.298 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.15 \text{ mm}^{-1}$
 $T = 210 (2) \text{ K}$
 Hexagonal prism, colorless
 $0.42 \times 0.39 \times 0.18 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.70, T_{\max} = 0.97$

29627 measured reflections
 3823 independent reflections
 3133 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.114$
 $S = 1.07$
 3823 reflections
 205 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 0.4987P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Determination (1c), at 180 K

Crystal data

$[\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3]$
 $M_r = 324.30$
 Monoclinic, $P2_1/c$
 $a = 13.8385 (7) \text{ \AA}$
 $b = 7.4614 (3) \text{ \AA}$
 $c = 16.1873 (11) \text{ \AA}$
 $\beta = 98.871 (2)^\circ$
 $V = 1651.42 (16) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.304 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.15 \text{ mm}^{-1}$
 $T = 180 (2) \text{ K}$
 Hexagonal prism, colorless
 $0.42 \times 0.39 \times 0.18 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.73, T_{\max} = 0.97$

29482 measured reflections
 3801 independent reflections
 3201 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.103$
 $S = 1.08$
 3801 reflections
 205 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.5412P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Determination (1d), at 150 K

Crystal data

$[\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3]$
 $M_r = 324.30$
 Monoclinic, $P2_1/c$
 $a = 13.7961 (5) \text{ \AA}$
 $b = 7.44012 (17) \text{ \AA}$
 $c = 16.1488 (5) \text{ \AA}$
 $\beta = 98.914 (3)^\circ$
 $V = 1637.57 (9) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.315 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.15 \text{ mm}^{-1}$
 $T = 150 (2) \text{ K}$
 Hexagonal prism, colorless
 $0.42 \times 0.39 \times 0.18 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.74, T_{\max} = 0.98$

29260 measured reflections
 3771 independent reflections
 3248 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.094$
 $S = 1.05$
 3771 reflections
 205 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.6404P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

Determination (1e), at 110 K

Crystal data

$[\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3]$
 $M_r = 324.30$
 Monoclinic, $P2_1/c$
 $a = 22.7424 (11) \text{ \AA}$
 $b = 7.4467 (2) \text{ \AA}$
 $c = 29.6165 (13) \text{ \AA}$
 $\beta = 103.221 (2)^\circ$
 $V = 4882.8 (3) \text{ \AA}^3$

$Z = 12$
 $D_x = 1.323 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.15 \text{ mm}^{-1}$
 $T = 110 (2) \text{ K}$
 Hexagonal prism, colorless
 $0.42 \times 0.39 \times 0.18 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.66, T_{\max} = 0.98$

83926 measured reflections
 11232 independent reflections
 8990 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.111$
 $S = 1.05$
 11232 reflections
 613 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 1.8338P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (\AA) for δ polymorph (1e).

Al1—O51	1.8704 (9)	Al2—O42	1.8853 (10)
Al1—O41	1.8837 (10)	Al2—O22	1.8890 (9)
Al1—O61	1.8847 (9)	Al2—O32	1.8904 (10)
Al1—O21	1.8867 (9)	Al3—O63	1.8735 (10)
Al1—O11	1.8894 (10)	Al3—O13	1.8824 (10)
Al1—O31	1.8924 (9)	Al3—O53	1.8838 (10)
Al2—O62	1.8757 (10)	Al3—O43	1.8857 (10)
Al2—O52	1.8793 (10)	Al3—O33	1.8902 (10)
Al2—O12	1.8848 (10)	Al3—O23	1.8910 (10)

The X-ray intensities of (Ia)–(Ie) were obtained with two different exposure times and rotation angles of 1° . 364 φ and 252 ω scans were measured with an exposure time of 45 s per frame, and 167 φ scans with an exposure time of 9 s per frame. All H atoms were introduced in geometrically idealized positions, refined with a riding model and subsequently confirmed in a difference Fourier map. Their isotropic displacement parameters were constrained, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$ for H atoms of the central CH groups and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

For all determinations, data collection: *COLLECT* (Nonius, 1999); cell refinement: *PEAKREF* (Schreurs, 2005); data reduction: *EVALI4* (Duisenberg *et al.*, 2003) for (Ia), (Ib), (Ic) and (Id), and *EVALI5* (Xian *et al.*, 2006) for (Ie); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) for (Ia) and (Ie); coordinates were taken from (Ia) for (Ib), (Ic) and (Id); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: manual editing of the *SHELXL97* output.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3070). Services for accessing these data are described at the back of the journal.

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