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γ-Tris-(2,4-pentanedionato)aluminum(III)

By Bruce W. McClelland*

The University of Tennessee–Oak Ridge Graduate School of Biomedical Sciences, and Biology Division, Oak Ridge National Laboratory,† *Oak Ridge, Tennessee* 37830, *U.S.A.*

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Abstract. $C_{15}H_{21}AlO_6$; orthorhombic, $Pna2_1$, $a=15·699$ (3), $b=32·546$ (7), $c=13·369$ (2) Å; $Z=16$; $D_m=1·25$ (1) (by flotation), $D_x=1·261$ g cm $^{-3}$. Pale yellow transparent eight-sided prisms were obtained from commercially available material (Aldrich Chemical Co. Inc.). The α and γ forms differ primarily in the relative orientations of the molecules. The average molecular structure is not significantly different from that observed in the α form.

Introduction. Crystals were grown by the method of Shkol'nikova (1960). Observed systematic absences $0kl$ for $k+l$ odd and $h0l$ for h odd are consistent with the assignment of $Pna2_1$ as the space group made by Shkol'nikova (1960) on the basis of systematic absences and piezoelectric measurements.‡ Cell parameters were obtained by applying the method of least squares to angle data measured for seven reflections in the range $35° < 2\theta < 38°$ (Mo $K\alpha_1$ radiation, $\lambda = 0·70926$ Å) on an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). A crystal $0·37 \times 0·43 \times 0·70$ mm was mounted with the longest dimension (the **a** direction) nearly parallel to the φ axis of the diffractometer. Intensities of reflections with $2\theta \leq 48°$ were measured with the $\theta/2\theta$ step-scan technique using niobium-filtered Mo $K\bar{\alpha}$ radiation ($\lambda=0·7107$ Å). Since a large fraction of the higher-order reflections were weak, only those reflections in the range $33·5° < 2\theta \leq 48°$ were measured for which a sampling of peak and background counts indicated that the measurement would be significant (*i.e.* net count $\geq 3\sigma_{\text{count}}$, where σ_{count} is the standard deviation from counting statistics). The intensities of three reference reflections monitored during data collection decreased by 2% or less. Lorentz–polarization factors were applied. Since the crystal was quasi-cylindrical, and since $\mu\bar{R}=0·06$, absorption effects were negligible. The intensities of 3704 of a possible 5659 independent reflections were measured, and 3284 had $F_o^2 > 3\sigma(F_o^2)$ [where $\sigma(F_o^2)$ was estimated as given below].

Trial sets of phases were obtained using program *TANFORM* (A. C. Larson's modification of M. Drew's program *PHASEM*). An E map calculated with the use of program *FORDAPER* of A. Zalkin, modified by G. Brunton, from the most consistent trial set revealed the positions of 16 atoms, including the four aluminum atoms. The remaining 72 nonhydrogen atoms were found in two subsequent three-dimensional Fourier syntheses. The trial structure was refined by the full-matrix least-squares method [program *XFLS*-3, a modification of program *ORFLS* of Busing, Martin & Levy (1962)], in which the minimized function was $\sum w(F_o^2 - F_c^2)^2$, with weights w equal to the reciprocals of the variances $\sigma^2(F_o^2)$ estimated from

$$\sigma^2(F_o^2) = (0·03F_o^2)^2 + K^2\sigma^2_{\text{count}}/(\text{Lp})^2.$$

Here K is the (least-squares) scale constant, and Lp is the Lorentz-polarization factor. Refinement was with isotropic thermal parameters for all atoms and included an isotropic extinction parameter g (Zachariasen, 1967; Coppens & Hamilton, 1970) [final value 0·4 (1)]. The final value for $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ was 0·092 based on all reflections with $F_o^2 > 3\sigma(F_o^2)$ and 0·102 based on all measured reflections. The scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and oxygen and those of Veenendaal, MacGillavry, Stam, Potters & Römgens (1959) for aluminum(III).

The final values of the atomic parameters and their estimated standard deviations are given in Table 1.†

Discussion. Crystals of the γ form of tris-(2,4-pentanedionato)aluminum(III), hereafter γ-Al(acac)$_3$, grow only occasionally among crystals of the more familiar α form of Al(acac)$_3$, the structure of which has been determined previously (Johnson, 1972; Hon & Pfluger, 1973). While other tris-(2,4-pentanedionato)metal(III) complexes are known to crystallize in the γ form [Astbury (1926) and references therein], an X-ray determination of a γ-form structure has not been reported.

The asymmetric unit of γ-Al(acac)$_3$ was found to consist of two each of the left- and right-handed enantiomorphs of the optically active Al(acac)$_3$ molecule,

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* Postdoctoral Investigator supported by subcontract No. 3322 from the Biology Division of Oak Ridge National Laboratory to the University of Tennessee. Present address: Math-Science Department, Central Oregon Community College, Bend, Oregon 97701, U.S.A.

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‡ There appear to be two errors in Shkol'nikova's (1960) paper: the b and c axes are interchanged, and the space group is given as $Pna2$. From the context, the latter error clearly is a misprint.

† A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31111 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

in accordance with the presumption that γ-Al(acac)$_3$ is a racemate.

The (unweighted) mean values of the chemically equivalent structural parameters are given in Fig. 1. Each value differs by less than $1{\cdot}2S$ (where S is the estimated standard deviation of the sample, also given in Fig. 1)* from the corresponding value in the Al(acac)$_3$ molecule as studied in the α form (Johnson, 1972; Hon & Pfluger, 1973). If hydrogen atoms were included in the present study, it is expected that the parameter values would be brought into generally closer agreement with those of Johnson (1972) and Hon & Pfluger (1973).

Fig. 2 (*a*) shows a projection onto (001) of the eight molecules which are centered near $z=\frac{1}{4}$. The positions for the remaining eight molecules in the unit cell are related to these by the 2_1 axes parallel to **c**.

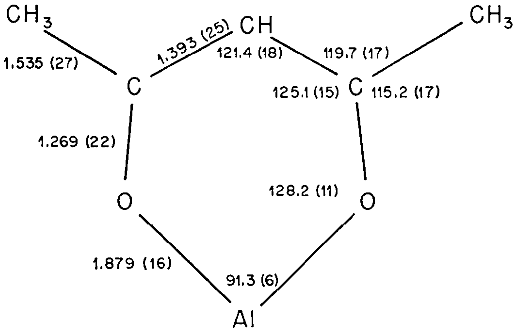

Fig. 1. Mean bond distances (Å) and angles (°) in γ-tris-(2,4-pentanedionato)aluminum(III). The values in parentheses are those of S, the estimated standard deviation of the sample.

Table 1. *Fractional coordinates* ($\times 10^4$) *and thermal parameters* (Å$^2\times 10$)

	x	y	z	B		x	y	z	B
Al(*A*)	3439 (3)	2486 (1)	2500 (0)	36 (1)	Al(*C*)	1299 (3)	2535 (1)	7488 (5)	33 (1)
O(1*A*)	2720 (6)	2161 (3)	1660 (9)	44 (2)	O(1*C*)	1759 (6)	2117 (3)	6678 (9)	44 (2)
O(2*A*)	3758 (6)	2020 (3)	3219 (9)	43 (2)	O(2*C*)	642 (6)	2152 (3)	8238 (9)	43 (2)
C(1*A*)	2145 (11)	1602 (5)	739 (15)	61 (4)	C(1*C*)	2027 (11)	1475 (5)	5836 (15)	65 (4)
C(2*A*)	2726 (9)	1779 (4)	1575 (12)	41 (3)	C(2*C*)	1559 (9)	1731 (4)	6665 (12)	42 (3)
C(3*A*)	3166 (10)	1488 (5)	2192 (14)	59 (4)	C(3*C*)	1023 (9)	1553 (5)	7343 (13)	49 (3)
C(4*A*)	3650 (10)	1637 (5)	2994 (14)	53 (4)	C(4*C*)	616 (10)	1769 (5)	8087 (14)	47 (3)
C(5*A*)	4122 (10)	1338 (5)	3658 (14)	62 (4)	C(5*C*)	99 (11)	1528 (5)	8877 (15)	65 (4)
O(3*A*)	4335 (6)	2396 (3)	1596 (8)	38 (2)	O(3*C*)	1969 (6)	2907 (3)	6773 (9)	38 (2)
O(4*A*)	4128 (6)	2813 (3)	3302 (9)	42 (2)	O(4*C*)	2160 (6)	2464 (3)	8439 (8)	39 (2)
C(6*A*)	5668 (10)	2406 (5)	769 (14)	55 (4)	C(6*C*)	3177 (11)	3235 (5)	6039 (15)	65 (4)
C(7*A*)	5090 (10)	2533 (5)	1607 (13)	45 (3)	C(7*C*)	2751 (9)	2967 (4)	6862 (13)	42 (3)
C(8*A*)	5407 (10)	2781 (5)	2376 (13)	51 (4)	C(8*C*)	3283 (10)	2820 (5)	7627 (13)	49 (3)
C(9*A*)	4900 (10)	2900 (5)	3171 (14)	52 (4)	C(9*C*)	2942 (9)	2589 (4)	8393 (13)	44 (3)
C(10*A*)	5281 (11)	3175 (6)	4033 (16)	67 (5)	C(10*C*)	3500 (11)	2453 (6)	9275 (15)	64 (5)
O(5*A*)	3109 (6)	2935 (3)	1699 (9)	40 (2)	O(5*C*)	411 (6)	2595 (3)	6544 (9)	44 (2)
O(6*A*)	2542 (6)	2584 (3)	3385 (9)	48 (2)	O(6*C*)	859 (6)	2953 (3)	8285 (8)	40 (2)
C(11*A*)	2340 (11)	3478 (5)	968 (16)	67 (5)	C(11*C*)	−821 (10)	2805 (5)	5682 (14)	55 (4)
C(12*A*)	2468 (10)	3164 (5)	1798 (14)	51 (4)	C(12*C*)	−213 (9)	2842 (4)	6553 (13)	41 (3)
C(13*A*)	1914 (10)	3157 (5)	2633 (15)	58 (4)	C(13*C*)	−353 (9)	3134 (5)	7302 (14)	51 (4)
C(14*A*)	1979 (10)	2864 (5)	3361 (13)	47 (3)	C(14*C*)	199 (10)	3166 (5)	8112 (14)	50 (4)
C(15*A*)	1361 (11)	2880 (5)	4269 (15)	62 (4)	C(15*C*)	−3 (11)	3503 (5)	8929 (16)	69 (5)
Al(*B*)	3711 (3)	5008 (1)	2262 (5)	37 (1)	Al(*D*)	1476 (3)	4988 (1)	7243 (4)	36 (1)
O(1*B*)	4237 (6)	4537 (3)	1763 (9)	48 (2)	O(1*D*)	915 (6)	4622 (3)	6382 (9)	42 (2)
O(2*B*)	3096 (6)	4695 (3)	3225 (9)	48 (2)	O(2*D*)	2056 (6)	4546 (3)	7835 (9)	42 (2)
C(1*B*)	4667 (10)	3837 (5)	1449 (14)	60 (4)	C(1*D*)	393 (11)	4027 (5)	5562 (13)	55 (4)
C(2*B*)	4154 (10)	4159 (5)	2033 (13)	49 (4)	C(2*D*)	928 (9)	4230 (4)	6366 (13)	44 (3)
C(3*B*)	3624 (9)	4029 (4)	2834 (13)	45 (3)	C(3*D*)	1418 (10)	3982 (5)	7036 (14)	61 (4)
C(4*B*)	3140 (9)	4301 (4)	3374 (12)	41 (3)	C(4*D*)	1930 (9)	4160 (5)	7741 (13)	45 (3)
C(5*B*)	2531 (11)	4160 (5)	4178 (14)	53 (4)	C(5*D*)	2434 (11)	3887 (5)	8424 (14)	60 (4)
O(3*B*)	4304 (6)	5331 (3)	1330 (9)	42 (2)	O(3*D*)	2338 (6)	5050 (3)	6255 (8)	41 (2)
O(4*B*)	4596 (6)	5068 (3)	3199 (9)	41 (2)	O(4*D*)	2037 (6)	5338 (3)	8118 (9)	42 (2)
C(6*B*)	5282 (11)	5761 (5)	507 (15)	64 (5)	C(6*D*)	3571 (10)	5255 (5)	5393 (14)	56 (4)
C(7*B*)	5018 (9)	5517 (4)	1473 (13)	44 (3)	C(7*D*)	3008 (9)	5252 (4)	6315 (13)	40 (3)
C(8*B*)	5502 (9)	5505 (5)	2300 (13)	49 (3)	C(8*D*)	3286 (10)	5483 (5)	7155 (14)	52 (4)
C(9*B*)	5270 (9)	5276 (4)	3136 (13)	40 (3)	C(9*D*)	2763 (9)	5505 (5)	8024 (13)	45 (3)
C(10*B*)	5844 (11)	5282 (5)	4029 (14)	58 (4)	C(10*D*)	3060 (12)	5760 (6)	8927 (15)	66 (4)
O(5*B*)	2823 (7)	4945 (3)	1306 (10)	52 (3)	O(5*D*)	880 (6)	5427 (3)	6659 (9)	42 (2)
O(6*B*)	3186 (6)	5475 (3)	2801 (8)	42 (2)	O(6*D*)	614 (6)	4910 (3)	8185 (9)	43 (2)
C(11*B*)	1543 (13)	5009 (6)	411 (17)	81 (6)	C(11*D*)	−145 (12)	5907 (6)	6139 (17)	71 (5)
C(12*B*)	2154 (10)	5127 (5)	1265 (14)	50 (4)	C(12*D*)	144 (10)	5549 (5)	6835 (14)	53 (4)
C(13*B*)	1933 (10)	5462 (5)	1887 (14)	57 (4)	C(13*D*)	−373 (10)	5392 (5)	7592 (15)	55 (4)
C(14*B*)	2439 (10)	5614 (5)	2610 (14)	49 (3)	C(14*D*)	−125 (9)	5078 (4)	8233 (14)	44 (3)
C(15*B*)	2142 (11)	5974 (5)	3284 (16)	68 (5)	C(15*D*)	−709 (10)	4924 (5)	9032 (15)	59 (4)

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* If the individual examples of each parameter are taken to be equal, the estimated standard deviation of the corresponding mean value (Fig. 1) would be $S/n^{1/2}$, where the number, n, of individual values is 12 or 24. For distances Al–O and C–CH, the correlation resulting from the averaging of bonds having a common atom would reduce the uncertainty in the mean yet a little further.

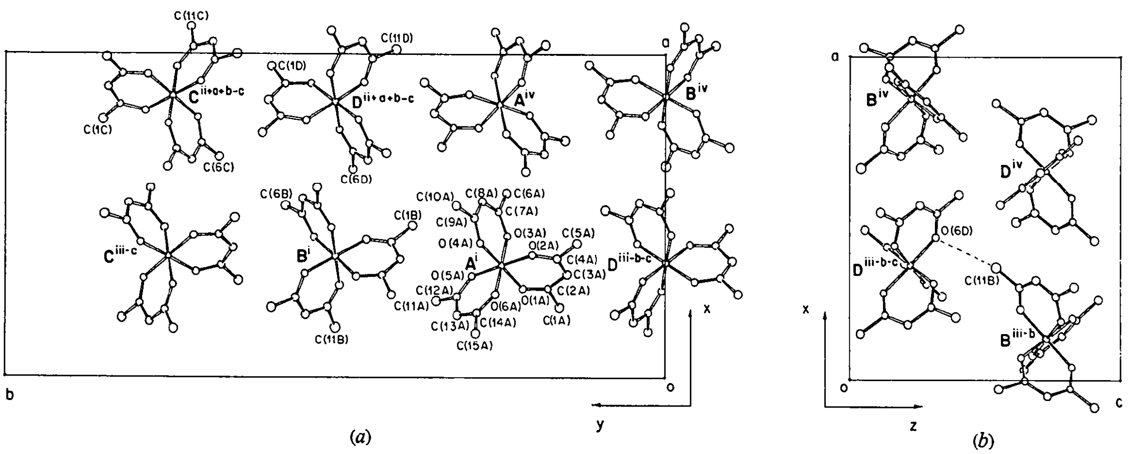

Fig. 2. (*a*) Projection onto (001) of the molecules near $z=\frac{1}{4}$. (*b*) Projection onto (010) of the molecules near $y=0$. For both (*a*) and (*b*), the molecules are related to the corresponding reference molecules in Table 1 by the symmetry operations and lattice vectors given as superscripts, where $\mathrm{i}=x,y,z$; $\mathrm{ii}=-x,-y,\frac{1}{2}+z$; $\mathrm{iii}=\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z$; $\mathrm{iv}=\frac{1}{2}+x,\frac{1}{2}-y,z$. The atom numbering for molecules *B*, C, and *D* follows that shown for molecule *A* in (*a*). The dashed line in (*b*) indicates the shortest intermolecular C···O distance, 3·33 Å. This figure was prepared in part with program *ORTEP* (Johnson, 1965).

The structure possesses extensive pseudosymmetry as follows. There is a pseudo-halving of the unit cell at $y=\frac{1}{2}$. Each half has the pseudo space group *Pcab*, with pseudo-centers at positions with coordinates $0,\frac{1}{8},0$, *etc.* in the true unit cell. Thus, all four molecules in the true asymmetric unit are related by pseudosymmetry. The pseudo *c*-glide plane at $x=\frac{1}{4}$ can be seen in Fig. 2(*b*), which shows the four molecules near $y=0$ projected onto (010).

Several tris-(2,4-pentanedionato)metal(III) complexes crystallize in a form with space group *Pcab*, $a\simeq 15{\cdot}5$, $b\simeq 16{\cdot}7$, $c\simeq 13{\cdot}7$ Å [Anderson, Neuman & Melson (1973) and references therein; McClelland (1974)]. While the aluminum analog of that form has not yet been found, it does have the same space group and approximately the same cell dimensions as the pseudo cell of γ-Al(acac)$_3$. This suggests a possible structural similarity between the two forms, and if unit cells of the two forms are superimposed and appropriately translated, the positions and orientations of the molecules in the two structures indeed approximately coincide.

The α form of Al(acac)$_3$ has a monoclinic unit cell of dimensions $a=13{\cdot}978$, $b=7{\cdot}538$, $c=16{\cdot}310$ Å, with $\beta=98{\cdot}79°$ (Johnson, 1972). Thus, $(a\sin\beta)_\alpha\simeq c_\gamma, b_\alpha\simeq a_\gamma/2$, and $c_\alpha\simeq b_\gamma/2$. When four α unit cells (two deep along y_α and z_α) are superimposed upon a γ unit cell as suggested by the cell dimension similarities and then are translated appropriately, the molecular centers (aluminum atoms) may be brought to coincide within about 0·8 Å along $\mathbf{a}_\gamma(\mathbf{b}_\alpha)$, about 0·3 Å along $\mathbf{b}_\gamma(\mathbf{c}_\alpha)$, and about 0·5 Å along $\mathbf{c}_\gamma(\mathbf{b}_\alpha\times\mathbf{c}_\alpha)$. This coincidence does not extend further, of course, because $\beta_\alpha\neq 90°$, so that in the α crystal there is a 2·1 Å shift of the aluminum atoms along $\mathbf{c}_\alpha$ for each translation $\mathbf{a}_\alpha$. The primary difference between the two forms lies in the relative orientation of the molecules, as Astbury (1926) postulated; in γ-Al(acac)$_3$ the threefold axes of the molecules are aligned approximately parallel to the z_γ axis [Fig. 2(*a*)], while in α-Al(acac)$_3$ the threefold axes are oriented in directions 30° from the y_α axis (which corresponds to the x_γ axis).

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