Acta Cryst. (1974). B30, 1364

Tris(acetylacetonato)gallium(III)

By K. Dymock and Gus J. Palenik

Center for Molecular Structures, Department of Chemistry, University of Florida, Gainesville, Florida 32611, *U.S.A.*

(*Received* 13 *December* 1973; *accepted* 5 *February* 1974)

Abstract. Tris(acetylacetonato)gallium(III), $C_{15}H_{21}O_6Ga$, M.W. 367·05, monoclinic, $P2_1/c$, $a=14·003$ (4), $b=7·588$ (2), $c=16·491$ (3) Å, $\beta=99·00$ (2)°; $U=1720·2$ (7) Å^3; $d_{\text{meas}}=1·41$, $d_{\text{calc}}=1·417$ g cm^{-3} for $Z=4$; μ(Cu $K\alpha$)$=25·7$ cm^{-1}. The compound was prepared by the reaction of $GaCl_3$ with sodium acetylacetonate. Large, plate-like, orange crystals were grown from methanol. The final R was 0·060 for 1872 observed reflections used in the analysis. The 6 oxygen atoms of the three ligands form a nearly ideal octahedron around the gallium atom. The average Ga–O bond length is 1·952 (6) Å, with an average ligand bite of 2·802 Å.

Introduction. Preliminary precession photographs indicated monoclinic symmetry. The systematic absences $h0l$: $l=2n+1$ and $0k0$: $k=2n+1$ indicated the space group $P2_1/c$ (C^5_{2h}). A well formed, plate-like crystal with dimensions 0·28 × 0·23 × 0·12 mm was used for the intensity measurements. The unit-cell dimensions and intensity data were measured using Cu $K\alpha$ radiation and a Syntex $P\bar{1}$ diffractometer. A least-squares fit of the 2θ, ω, χ and φ values for 15 reflections gave the above cell dimensions. A variable-speed (1 to 24° min^{-1} depending on the intensity) θ–2θ scan technique was used in measuring all the independent reflections up to a limit of $2\theta=110°$ (Cu radiation). The scan range was from 1° below the α_1 peak to 1° above the α_2 peak; background counts were taken at each end of the range. The intensity, I, was equal to the scan rate [total scan counts–(background counts/background to scan ratio)], with $\sigma(I)$ equal to [total scan counts + (background count/background to scan ratio)^2]$^{1/2}$. The 1872 reflections with $I>1·25\ \sigma(I)$ were used in the analysis. The intensity data were reduced to a set of observed structure amplitudes on an arbitrary scale by application of the Lorentz-polarization corrections; no absorption corrections were necessary [μ(Cu $K\alpha$)$=25·7$ cm^{-1}].

The structure was solved by the heavy-atom method although the compound was isomorphous with Cr(acac)$_3$, in which acac is acetylacetonato (Morosin, 1965). Least-squares refinement using isotropic thermal parameters reduced $R(=\sum||F_o|-|F_c||/\sum|F_o|)$ to 0·14 and then, with anisotropic thermal parameters, to 0·060. The two reflections 002 and 110 which obviously suffered from extinction were given zero weight in the refinement. The quantity minimized in the calculations was $\sum w(|F_o|-|F_c|)^2$, where $w=F_o^2/a^2$ if $|F_o|<a$, $w=1$ if $a\le|F_o|\le b$ and $w=b^2/F_o^2$ if $|F_o|\ge b$, where $a=12·0$ and $b=48·0$. Scattering factors were taken from Hanson, Herman, Lea & Skillman (1964). All calculations were carried out on an IBM 370/165 computer with programs written or modified by one of us (G.J.P.). The final parameters are listed in Table 1* with the distances and angles given in Table 2. The thermal parameters for C(6), C(7) and C(8) were particularly large; however, this ligand also had anomalous thermal parameters in the isomorphous Cr(acac)$_3$ (Morosin, 1965), Al(acac)$_3$ and Co(acac)$_3$ (Hon & Pfluger, 1973), and Ru(acac)$_3$ (Chao, Sime & Sime, 1973) structures. However, Morosin (1965) concluded that these large thermal parameters were 'real' since X-ray photographs at low temperatures showed no diffuse spots.

Discussion. The gallium derivative was studied as part of a broad program devoted to the chemistry of gallium. The crystals of Ga(acac)$_3$ are isomorphous with Cr(acac)$_3$ (Morosin, 1965), Rh(acac)$_3$ (Morrow & Par-

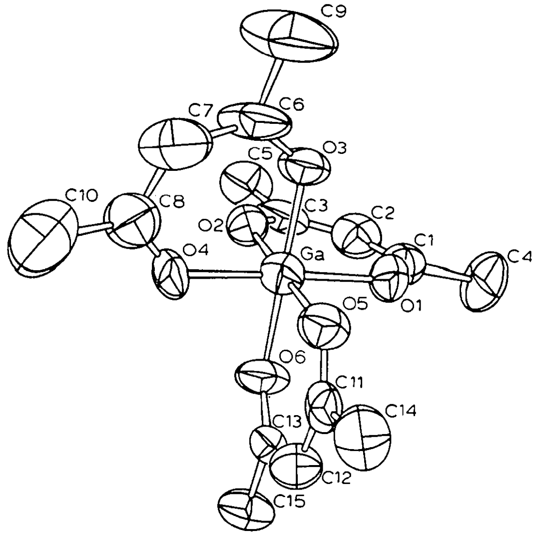

Fig. 1. An *ORTEP* drawing of tris(acetylacetonato)gallium (III) showing the atomic numbering and thermal ellipsoids.

---

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30363 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Final positional and thermal parameters for tris(acetylacetonato)gallium*(III)

The parameters are × 10^4 except for those of gallium which are × 10^5. The thermal parameters are of the form:

$$\exp\{-[\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl]\}.$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ga	26242 (7)	26678 (13)	2949 (5)	678 (6)	2335 (23)	322 (4)	−424 (21)	132 (7)	43 (16)
O(1)	1355 (4)	1894 (7)	−263 (3)	49 (3)	236 (13)	41 (2)	−47 (11)	−1 (5)	−1 (9)
O(2)	2429 (4)	5011 (7)	−189 (3)	82 (4)	220 (12)	38 (3)	−79 (12)	9 (5)	22 (9)
O(3)	3201 (4)	1881 (8)	−649 (3)	60 (4)	352 (16)	31 (2)	−6 (12)	20 (5)	4 (9)
O(4)	3867 (5)	3419 (9)	888 (3)	79 (5)	359 (17)	36 (3)	−125 (15)	−33 (5)	26 (10)
O(5)	2817 (4)	292 (7)	751 (3)	80 (4)	218 (12)	36 (2)	2 (11)	17 (5)	8 (9)
O(6)	2035 (4)	3465 (7)	1242 (3)	104 (5)	208 (12)	32 (2)	−2 (12)	45 (5)	13 (9)
C(1)	716 (6)	2930 (13)	−629 (5)	53 (5)	293 (24)	38 (4)	−20 (19)	31 (7)	−47 (15)
C(2)	813 (7)	4694 (13)	−805 (5)	69 (6)	247 (23)	52 (4)	27 (20)	17 (8)	−8 (16)
C(3)	1665 (8)	5640 (12)	−604 (5)	98 (8)	230 (20)	24 (3)	17 (21)	24 (8)	−12 (13)
C(4)	−277(6)	2023 (15)	−913 (7)	48 (6)	433 (33)	84 (6)	−65 (22)	13 (9)	−21 (22)
C(5)	1714 (8)	7515 (13)	−895 (6)	153 (10)	175 (19)	55 (4)	−15 (24)	35 (10)	31 (16)
C(6)	4087 (8)	1876 (20)	−694 (6)	78 (7)	774 (51)	37 (4)	97 (32)	30 (9)	74 (23)
C(7)	4817 (7)	2409 (30)	−78 (7)	56 (7)	1286 (88)	55 (6)	−82 (47)	−6 (10)	102 (42)
C(8)	4668 (8)	3185 (20)	676 (6)	65 (7)	755 (52)	47 (5)	−170 (32)	−44 (10)	125 (25)
C(9)	4342 (10)	1099 (27)	−1495 (7)	107 (10)	1184 (83)	57 (6)	320 (47)	58 (12)	−28 (36)
C(10)	5517 (10)	3797 (29)	1290 (8)	106 (10)	1265 (95)	69 (7)	−432 (52)	−93 (14)	172 (41)
C(11)	2653 (5)	−222 (11)	1458 (5)	43 (5)	222 (19)	41 (4)	−52 (15)	−26 (7)	15 (14)
C(12)	2261 (6)	824 (12)	2020 (5)	72 (6)	210 (20)	38 (4)	−12 (17)	10 (8)	31 (14)
C(13)	1980 (5)	2560 (12)	1878 (4)	58 (5)	269 (21)	27 (3)	−55 (19)	7 (6)	−14 (15)
C(14)	2905 (6)	−2130 (11)	1659 (5)	84 (6)	193 (19)	54 (4)	15 (18)	−20 (8)	50 (14)
C(15)	1532 (7)	3553 (13)	2542 (5)	108 (8)	324 (25)	41 (4)	42 (22)	51 (9)	−18 (16)

Table 2. *Bond lengths* (Å) *and angles* (°) *in tris(acetylacetonato)gallium*(III)

Ga—O(1)	1·956 (5)	O(1)—C(1)	1·267 (10)
Ga—O(2)	1·949 (5)	C(1)—C(4)	1·561 (13)
Ga—O(3)	1·947 (5)	C(1)—C(2)	1·381 (14)
Ga—O(4)	1·941 (7)	C(2)—C(3)	1·388 (14)
Ga—O(5)	1·954 (5)	C(3)—C(5)	1·505 (13)
Ga—O(6)	1·964 (6)	C(3)—O(2)	1·267 (11)
O(1)-O(2)	2·792 (8)	O(3)—C(6)	1·254 (13)
O(1)-O(3)	2·755 (8)	C(6)—C(9)	1·532 (17)
O(1)-O(5)	2·715 (8)	C(6)—C(7)	1·381 (17)
O(1)-O(6)	2·769 (7)	C(7)—C(8)	1·412 (18)
O(2)-O(3)	2·763 (8)	C(8)—C(10)	1·506 (18)
O(2)-O(4)	2·742 (9)	C(8)—O(4)	1·239 (14)
O(2)-O(6)	2·754 (7)	O(5)—C(11)	1·277 (10)
O(3)-O(4)	2·800 (8)	C(11)-C(14)	1·514 (12)
O(3)-O(5)	2·719 (7)	C(11)-C(12)	1·392 (12)
O(4)-O(5)	2·781 (9)	C(12)-C(13)	1·384 (13)
O(4)-O(6)	2·717 (9)	C(13)-C(15)	1·535 (12)
O(5)-O(6)	2·814 (8)	C(13)-O(6)	1·260 (9)
O(1)-Ga—O(2)	91·3 (2)	C(2)—C(3)—O(2)	123·7 (8)
O(1)-Ga—O(3)	89·8 (2)	C(3)—O(2)—Ga	128·0 (6)
O(1)-Ga—O(4)	177·8 (2)	Ga—O(3)—C(6)	125·8 (7)
O(1)-Ga—O(5)	88·0 (2)	O(3)—C(6)—C(7)	125·6 (12)
O(1)-Ga—O(6)	89·9 (2)	O(3)—C(6)—C(9)	114·7 (11)
O(2)-Ga—O(3)	90·4 (2)	C(9)—C(6)—C(7)	119·6 (12)
O(2)-Ga—O(4)	89·7 (3)	C(6)—C(7)—C(8)	124·6 (14)
O(2)-Ga—O(5)	178·5 (2)	C(7)—C(8)—O(4)	124·8 (12)
O(2)-Ga—O(6)	89·5 (2)	C(7)—C(8)—C(10)	120·3 (12)
O(3)-Ga—O(4)	92·2 (3)	C(10)-C(8)—O(4)	115·0 (11)
O(3)-Ga—O(5)	88·4 (2)	C(8)—O(4)—Ga	126·7 (7)
O(3)-Ga—O(6)	179·7 (2)	Ga—O(5)—C(11)	126·5 (5)
O(4)-Ga—O(5)	91·1 (2)	O(5)—C(11)-C(12)	124·8 (7)
O(4)-Ga—O(6)	88·2 (3)	O(5)—C(11)-C(14)	114·9 (7)
O(5)-Ga—O(6)	91·8 (2)	C(14)-C(11)-C(12)	120·3 (7)
Ga—O(1)-C(1)	124·0 (5)	C(11)-C(12)-C(13)	124·3 (8)
O(1)-C(1)-C(4)	114·0 (7)	C(12)-C(13)-O(6)	127·2 (8)
C(4)-C(1)-C(2)	118·2 (8)	C(12)-C(13)-C(15)	119·0 (7)
C(1)-C(2)-C(3)	124·1 (9)	C(15)-C(13)-O(6)	113·8 (7)
C(2)-C(3)-C(5)	119·6 (8)	C(13)-O(6)—Ga	125·0 (5)
C(5)-C(3)-O(2)	116·7 (8)		

ker, 1973) and Co(acac)$_3$ and Al(acac)$_3$ (Hon & Pfluger, 1973).

This gallium structure provides an example of a spherical d^{10} ion coordinated to three acetylacetonates. These data are important in explaining the variation of ligand bite with the metal–oxygen distance. Hon & Pfluger (1973) discussed the variation of bite with M–O distance and found, with the exception of Al, a linear correlation for the Co, Mn, Cr, V and Fe cases. However, the addition of the Ga(III), Sc(III) (Anderson, Neuman & Melson, 1973) and Rh(III) (Morrow & Parker, 1973) data makes the linear relationship much poorer. In fact, the Rh(III) case deviates approximately as much as the Al complex. Although this observation suggests that only the trivalent ions of a given row such as Sc–Ga will have a linear correllation between bite and M–O distance, the fit is poor even in the Sc–Ga series. Hon & Pfluger (1973) have suggested that Al(III) is anomalous because of the greater ionic character in the Al–O bond but this explanation does not appear completely valid. If one assumes that the acidity of the hexaequo ions reflects ionic character in the M–O bond, then the Ga(III) case should also be anomalous since the K_a's for the $M(H_2O)_6^{3+}$ species are $3{\cdot}5\times10^{-3}$ for Ga and $1{\cdot}12\times10^{-5}$ for Al (Cotton & Wilkinson, 1964). Furthermore, simple geometrical arguments would predict that in order to maintain approximately octahedral geometry about the metal (*i.e.* O–M–O about 90°), the bite must vary with M–O distance in approximately the observed manner. One can conclude that since the ligand bite will depend on several different factors, such as the M–O distance, the O···O nonbonded contacts, the electron distribution in the metal ion, and the relative ease of deformation of the acetylacetone ion, a simple correlation between bite and M–O distance probably does not exist. Nevertheless, the fundamental questions regarding chemical bonding which are raised by this series of compounds deserve further study.

We wish to thank the U.S. Public Health Service for financial support through Grant CA-12390 and the Northeast Regional Data Center at the University of Florida for a grant of computer time.

References

ANDERSON, T. J., NEUMAN, M. A. & MELSON, G. A. (1973). *Inorg. Chem.* **12**, 927–930.

CHAO, G. K., SIME, R. L. & SIME, R. J. (1973). *Acta Cryst.* **B29**, 2845–2849.

COTTON, F. A. & WILKINSON, G. (1966). *Advanced Inorganic Chemistry*, 2nd ed., p. 437. New York: Interscience.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

HON, P. K. & PFLUGER, C. E. (1973). *J. Coord. Chem.* **3**, 67–76.

MOROSIN, B. (1965). *Acta Cryst.* **19**, 131–137.

MORROW, J. C. & PARKER, E. B. JR (1973). *Acta Cryst.* **B29**, 1145–1146.

Acta Cryst. (1974). **B30**, 1366

1,3-Dichloroacetone

BY ALEX MEHLSEN SØRENSEN

Chemical Laboratory C, The Royal Danish School of Pharmacy, DK-2100 Copenhagen Ø, Denmark

(*Received* 31 *December* 1973; *accepted* 17 *January* 1974)

Abstract. 1,3-Dichloroacetone, $(CH_2Cl)_2CO$, monoclinic, $P2_1/c$, $a=14{\cdot}635(6)$, $b=5{\cdot}261(4)$, $c=16{\cdot}426(9)$ Å, $\beta=124{\cdot}08(4)°$, $Z=8$, $D_m=1{\cdot}62$ (flotation in KI solution), $D_x=1{\cdot}62$ g cm^{-3}. The two crystallographically independent molecules are, within the accuracy of the determination, identical. In each molecule the atoms Cl–C–C(O)–C–Cl are coplanar, the conformation of the atoms Cl–C–C=O being synperiplanar. No short intermolecular contacts exist.

Introduction. X-ray intensities were collected on a Nonius three-circle automatic diffractometer. Details of the data collection were as follows. Radiation: crystal-monochromated Mo $K\alpha$, $\lambda=0{\cdot}71069$ Å; measuring technique: moving-crystal–stationary-detector with scan speed 1·2° min^{-1} in the θ range 2·5–21°; the crystal ($0{\cdot}46\times0{\cdot}40\times0{\cdot}38$ mm) was mounted in a glass capillary and oriented with **b** parallel to the φ axis of the goniostat; 1235 independent reflexions were measured having $|F_{\rm rel}|$ values in the range 0 to 150; 894 reflexions with $|F_{\rm rel}|>3$ were used in the least-squares refinement. μ (Mo $K\alpha$) is 10·9 cm^{-1}, and no absorption correction was applied.

The structure was solved by a symbolic addition procedure (Dewar, 1968). Full-matrix least-squares refinement of the non-hydrogen atoms resulted in $R=0{\cdot}13$ and a subsequent difference map revealed the eight hydrogen atoms. Further least-squares refinement of positional parameters for all atoms and anisotropic temperature parameters for the non-hydrogen atoms led to a final R of 0·04. The quantity minimized was $\sum w(|F_o|-|F_c|)^2$ with a weighting scheme $w=(6{\cdot}0+|F_o|$