

contact distance. The alternation of these types of polar and non-polar regions is also found in  $\beta$ -methyl maltoside (Chu & Jeffrey, 1967) and  $\beta$ -methyl xyloside (Brown, Cox & Llewellyn, 1966).

The thermal ellipsoid parameters given in Table 2 show that the oxygen atoms appear to have higher thermal vibration amplitudes perpendicular to their C-O bonds than along them. This phenomenon was also observed in  $\beta$ -methyl maltoside (Chu & Jeffrey, 1967), sorbose (Kim & Rosenstein, 1967), and arabinose (Kim & Jeffrey, 1967). As in  $\beta$ -methyl maltoside, the methyl group has high thermal motion consistent with its van der Waals environment.

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## The Crystal and Molecular Structure of Trimeric Bis(acetylacetonato) zinc (II)

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Bis(acetylacetonato)zinc(II),  $Zn(AcAc)_2$ , may be sublimed to give white monoclinic crystals containing the trimer,  $[Zn(AcAc)_2]_3$ . The unit cell dimensions are  $a=18.63$ ,  $b=8.437$ ,  $c=12.20$  Å,  $\beta=112.68^\circ$ ; measured density,  $1.41$  g.cm $^{-3}$ ; calculated density for  $Z=2$ ,  $1.45$  g.cm $^{-3}$ . Space group:  $C2$ . The structure was solved, including hydrogen atoms and refined by least squares to a conventional residual of 2.6% using 1835 non-zero reflections measured with a counter diffractometer. The trimer contains a central octahedrally coordinated zinc atom, lying on the crystallographic twofold axis, and two terminal pentacoordinated zinc atoms. The coordination geometry about the terminal zinc atoms is closer to a trigonal bipyramidal than to a square pyramidal arrangement. Both the octahedron and the trigonal bipyramids show considerable distortions from their ideal geometries, with mean angular deviations of  $8.2^\circ$  and  $5.3^\circ$  respectively. Each terminal zinc atom is connected to the central one by two shared oxygen atoms, one at an axial and the other at an equatorial position of the trigonal bipyramid. The absolute configuration of the trimer for the crystal studied was determined by considering the anomalous dispersion of the zinc atoms.

#### Introduction

The fact that bis-( $\beta$ -ketoenolato)metal(II) compounds of the first transition series metals (except copper) are coordinately unsaturated when monomeric, and thus

either oligomerize or add donor ligands, is now well known. For the nickel (Bullen, Mason & Pauling, 1965) and cobalt (Cotton & Elder, 1965, 1966; Cotton & Eiss, 1968) acetylacetonates, there are extensive X-ray crystallographic data available, while for others there

are the results of solution equilibrium studies (Graddon, 1962; Graddon & Mockler, 1964; Buckingham, Gorges & Henry, 1967). Inhibition of oligomerization by the presence of bulky substituents on the chelate rings is also well documented both by studies of solutions (Cotton & Fackler, 1961; Fackler & Cotton, 1961; Cotton & Soderberg, 1964) and X-ray work (Cotton & Wood, 1964; Cotton & Wise, 1966).

The structural nature of bis(acetylacetonato)zinc(II) has remained uncertain. Bullen, Mason & Pauling (1965) reported the unit-cell constants and observed density for the compound and from these data calculated that there were 12  $\text{Zn}(\text{AcAc})_2$  formula units in the monoclinic unit cell. This, they proposed, was consistent with a trimeric formulation in the crystal, despite lack of any evidence for association in non-polar solvents (Graddon, 1962). Preliminary investigations in this laboratory indicated the possible space groups  $C2$ ,  $Cm$  or  $C2/m$ , with a unit cell one-half the volume reported by Bullen, Mason & Pauling (1965), owing to their selection of a non-standard face-centered unit cell.

Since the ligand arrangement in  $[\text{Ni}(\text{AcAc})_2]_3$  permits no  $C_2$  axis or mirror plane in the molecule, an identical structure for  $[\text{Zn}(\text{AcAc})_2]_3$  could be ruled out from symmetry considerations. Consequently a structure determination was undertaken to establish whether the compound is really trinuclear in the crystalline state and to obtain structural details. A preliminary report of this work has been published (Bennett, Cotton, Eiss & Elder, 1967).

### Procedure

#### Collection and reduction of data

$[\text{Zn}(\text{AcAc})_2]_3$  was prepared by the method of Rudolph & Henry (1964). Single crystals were grown by sublimation in a drying pistol\* at  $100^\circ\text{C}$  and 0.01 torr. The product had a melting point of  $129^\circ$ , in agreement with the value reported by Rudolph & Henry (1964) and lower than the value of  $152^\circ$  reported by Graddon & Weedon (1963). A suitable crystal approximately  $0.1 \times 0.1 \times 0.3$  mm was selected and mounted along the crystallographic  $b$  axis in a thin-walled Lindemann glass capillary, which was sealed and placed on a eucentric goniometer head. The crystal was found to be monoclinic, with the systematic absences  $h+k \neq 2n$  for all  $hkl$  indicating the possible space groups  $C2$ ,  $Cm$  or  $C2/m$ . Unit-cell parameters, measured on the precession camera and refined on the General Electric XRD-5 manual diffractometer with  $\text{Cu } K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) were  $a = 18.63 \pm 0.01$ ,  $b = 8.437 \pm 0.005$ ,  $c = 12.20 \pm 0.01 \text{ \AA}$ ,  $\beta = 112.68 \pm 0.03^\circ$ ,  $V = 1769 \text{ \AA}^3$ . The density, measured by flotation, was  $1.41 \pm 0.01 \text{ g.cm}^{-3}$  compared with  $1.45 \text{ g.cm}^{-3}$  calculated assuming two trimeric molecules per unit cell. The 1931 reflections in the sphere  $\sin \theta/\lambda \leq 0.62$  were

collected on the counter diffractometer with  $\text{Cu } K\alpha$  radiation, filtered by nickel foil, using a moving-crystal moving-counter technique, with a  $2\theta$  scan width of  $2.66^\circ$ . The diffractometer settings were computed from the unit-cell dimensions with use of a program written by Shoemaker (1962). Each peak was given two 40-second scans and the peak intensity ( $P$ ) was the average of these. Two 20-second counts, one at each end of the  $2\theta$  scan range, were added to give the background ( $B$ ). Two reflections were immediately discarded because their maximum counting rate exceeded the linear response range of the detector. All reflections having a background equal to or greater than the peak were assigned an intensity,  $I$ , equal to five counts. The 94 reflections having  $\sigma/I \geq 0.5$  [where  $\sigma/I = (P+B)^{1/2}/I$ ] were discarded because of poor counting statistics. The intensities of the remaining 1835 reflections were corrected for Lorentz and polarization effects. The crystal dimensions were very carefully measured and the faces parallel to  $\mathbf{b}$  were identified as  $(\bar{2}01)$ ,  $(100)$ ,  $(001)$  and  $(401)$ . Equations for the plane faces were calculated, assuming the caps to be  $(010)$  and slight variations (up to 10%) in the parameters for these equations were permitted to give optimum agreement between the calculated and observed absorption curves for the  $0k0$  reflections, obtained by rotation about the  $\varphi$  axis at  $\chi = 90^\circ$ . An absorption correction was then applied, using the equations thus derived for the plane faces of the crystal.

#### Solution and refinement of the structure

The zinc atoms were located on the map of the Patterson function (Sly, Shoemaker & Van den Hende, 1962) at  $(0.155, 0, 0.217)$  and  $(0, 0.120, 0)$ , uniquely determining the space group as  $C2$ . (Since the origin of this space group is arbitrary with respect to the  $y$  axis, the  $xz$  plane was selected along the line connecting the two terminal zinc atoms.) A Fourier map (Sly, Shoemaker & Van den Hende, 1962), phased on the zinc atoms, was used to locate all oxygen atoms and showed distorted octahedral coordination about the central zinc atom and pentacoordination about the terminal zinc atoms. A second Fourier map, phased on zinc and oxygen atoms, showed the positions of all carbon atoms. At this point the residual,  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ , was 0.22.

Five cycles of full-matrix least-squares refinement (Prewitt, 1962, 1966) of positional parameters and isotropic temperature factors [ $B_i$  in the expression  $\exp(-B_i \sin^2 \theta/\lambda^2)$ ], using the atomic scattering factors compiled by Ibers (1962), reduced  $R_1$  to 0.08. An anomalous dispersion correction, using values for  $f'$  and  $f''$  given by Cromer (1965), was followed by two further cycles of refinement. Three subsequent cycles permitted all atoms to refine anisotropically, using an expression for temperature parameters having the form  $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$ . A tentative weighting scheme, based on the Cruickshank (1965) criterion that  $\omega \Delta^2$  should be a constant, was

\* The crystals produced in a conventional sublimator under these conditions were too small for X-ray examination, but the geometry of the drying pistol proved suitable for growth of larger crystals.



the choice was not prejudiced by the weighting scheme, two quite different weighting schemes were used. An empirical weighting scheme, *A*, was selected as follows: The reflections were sorted in order of increasing  $|F_o|$  and were divided into groups of 50. For each group an average value of  $|F_o|$  and an average value of  $\Delta^2$  (or  $||F_o| - |F_c||^2$ ) were calculated. A set of values of  $\sigma$  (or  $1/\sqrt{\omega}$ ) were then selected, giving a constant value of  $\omega\Delta^2$ : for  $|F_o| \leq 12$ ,  $\sigma = \sqrt{-0.32|F_o| + 5.24}$ ; for  $12 < |F_o|$

$\leq 32$ ,  $\sigma = 1.18$ ; for  $|F_o| > 32$ ,  $\sigma = \sqrt{0.132|F_o| - 2.82}$ . An experimental weighting scheme, *B*, after Doedens & Ibers (1967), was based on the standard deviation of corrected intensities:  $\sigma(I) = [P + B + (pI)^2]^{1/2}$ , where *p*, an uncertainty factor, was assigned a value of 0.04. The standard deviation of the square of the structure factor,  $\sigma(F^2)$ , was then  $\sigma(I)$  corrected for the Lorentz, polarization and absorption factors. The weighting scheme selected was then  $\sigma = \sigma(F^2)/2F$ .

Table 2. Atom parameters for  $[\text{Zn}(\text{AcAc})_2]_3$ 

The estimated standard deviations occurring in the last recorded decimal place of each parameter are given in parentheses. For form of Debye-Waller factor, see text.

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^4$	$\beta_{12} \times 10^4$	$\beta_{13} \times 10^4$	$\beta_{23} \times 10^4$
Zn(1)	0.15626 (3)	0.0	0.22034 (4)	26.1 (2)	115.6 (8)	56.9 (4)	4.2 (3)	5.8 (2)	8.1 (5)
Zn(2)	0.0	-0.11600 (9)	0.0	19.6 (2)	99.7 (10)	61.5 (5)	0.0	13.7 (3)	0.0
O(11)	0.26545 (17)	-0.07922 (46)	0.30061 (25)	35.9 (11)	219.6 (67)	75.5 (25)	26.8 (22)	11.6 (13)	44.7 (33)
O(12)	0.13257 (17)	-0.06203 (45)	0.35851 (25)	34.5 (10)	256.8 (73)	64.9 (23)	1.8 (21)	10.0 (13)	27.8 (31)
O(21)	0.18672 (15)	0.22487 (34)	0.20571 (25)	27.6 (10)	121.0 (44)	84.8 (25)	-2.0 (17)	10.3 (13)	2.3 (27)
O(22)	0.03948 (14)	0.06726 (30)	0.13460 (22)	23.8 (8)	100.8 (37)	64.9 (21)	3.7 (14)	8.9 (11)	-7.7 (22)
O(31)	0.12235 (12)	-0.11635 (37)	0.06041 (20)	21.1 (7)	124.5 (38)	60.9 (19)	2.6 (17)	14.9 (9)	-2.3 (27)
O(32)	-0.00024 (16)	-0.26516 (35)	-0.12908 (24)	33.0 (10)	126.2 (43)	73.9 (23)	-10.2 (18)	21.9 (13)	-14.2 (27)
C(11)	0.37728 (33)	-0.20034 (102)	0.43827 (56)	45.8 (22)	384.3 (175)	132.6 (62)	53.2 (53)	12.5 (30)	93.6 (88)
C(12)	0.29315 (26)	-0.15067 (60)	0.39893 (40)	37.9 (16)	165.7 (84)	80.2 (37)	12.8 (29)	1.1 (19)	9.2 (44)
C(13)	0.25403 (29)	-0.18275 (63)	0.47196 (38)	45.9 (18)	178.9 (79)	70.8 (37)	2.0 (33)	4.7 (21)	26.5 (44)
C(14)	0.17826 (26)	-0.13781 (67)	0.44908 (37)	43.1 (17)	215.2 (95)	63.9 (31)	-20.6 (35)	10.7 (18)	8.2 (47)
C(15)	0.14442 (34)	-0.18230 (109)	0.54021 (48)	51.4 (23)	467.4 (209)	85.9 (45)	-28.6 (58)	21.2 (26)	53.4 (80)
C(21)	0.18194 (28)	0.50468 (71)	0.21210 (46)	44.0 (18)	124.6 (61)	138.9 (50)	-10.0 (38)	25.3 (25)	1.6 (62)
C(22)	0.14386 (23)	0.34611 (46)	0.19562 (34)	34.6 (14)	104.8 (57)	67.6 (30)	1.7 (23)	13.1 (16)	1.0 (32)
C(23)	0.06363 (24)	0.34022 (49)	0.17054 (39)	36.3 (15)	108.7 (58)	93.3 (37)	10.8 (24)	16.1 (19)	-18.5 (37)
C(24)	0.01631 (22)	0.20925 (48)	0.14169 (35)	27.9 (13)	125.0 (64)	66.1 (30)	14.3 (23)	12.1 (16)	-10.5 (33)
C(25)	-0.06929 (24)	0.22675 (62)	0.11504 (45)	28.7 (15)	183.2 (83)	121.3 (47)	14.7 (29)	20.0 (21)	-36.9 (52)
C(31)	0.24341 (23)	-0.09610 (90)	0.04005 (43)	24.5 (13)	341.9 (130)	113.4 (45)	-61.6 (38)	27.3 (20)	-4.9 (70)
C(32)	0.16038 (19)	-0.14690 (47)	-0.00660 (33)	24.4 (11)	137.5 (66)	76.9 (30)	11.3 (22)	20.7 (15)	12.1 (35)
C(33)	0.12850 (23)	-0.21938 (56)	-0.11484 (36)	34.8 (14)	166.7 (72)	79.8 (33)	8.3 (27)	29.6 (18)	-3.5 (41)
C(34)	0.05134 (23)	-0.27392 (50)	-0.17068 (34)	38.0 (15)	116.6 (57)	69.7 (31)	3.6 (24)	24.5 (18)	1.1 (35)
C(35)	0.02887 (32)	-0.35162 (71)	-0.29131 (40)	64.8 (24)	216.6 (100)	74.3 (37)	-21.4 (41)	34.6 (25)	-25.4 (51)

		<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
C(11)	H(1)	0.391	-0.291	0.508
	H(2)	0.389	-0.248	0.363
	H(3)	0.415	-0.096	0.474
C(13)	H(1)	0.284	-0.247	0.555
C(15)	H(1)	0.114	-0.077	0.554
	H(2)	0.104	-0.280	0.506
	H(3)	0.190	-0.218	0.625
C(21)	H(1)	0.245	0.488	0.237
	H(2)	0.158	0.573	0.130
	H(3)	0.173	0.570	0.284
C(23)	H(1)	0.036	0.452	0.175
C(25)	H(1)	-0.087	0.141	0.167
	H(2)	-0.081	0.348	0.137
	H(3)	-0.102	0.204	0.019
C(31)	H(1)	0.272	-0.152	-0.014
	H(2)	0.245	0.033	0.032
	H(3)	0.273	-0.132	0.133
C(33)	H(1)	0.167	-0.235	-0.163
C(35)	H(1)	0.081	-0.404	-0.299
	H(2)	-0.014	-0.444	-0.301
	H(3)	0.004	-0.261	-0.360

Each of the four possible combinations of atomic coordinates and weighting schemes reached convergence after two cycles of refinement, with no parameter shifting by more than one estimated standard deviation. The values of  $R_1$  and  $R_2 = \{\sum \omega |F_o| - |F_c|^2 / \sum \omega |F_o|^2\}^{1/2}$ , obtained were as follows:

Enantiomer: Weighting scheme:	$x, y, z$		$x, \bar{y}, z$	
	<i>A</i>	<i>B</i>	<i>A</i>	<i>B</i>
$R_1$	3.40%	3.46%	3.30%	3.36%
$R_2$	5.25%	5.93%	5.17%	5.86%

For either enantiomer the two weighting schemes gave parameters which agreed in every case to within one estimated standard deviation; the parameters for the two enantiomers differed significantly, but not enough to make it possible to choose between the two on the basis of bond lengths and bond angles. However, Hamilton's *R* factor test (Hamilton, 1965), assuming one degree of freedom, permitted selection of the  $x, \bar{y}, z$  enantiomer with a confidence of 99.5%.

A difference Fourier map clearly indicated all 21 hydrogen atoms as peaks of approximately  $0.25 \text{ e.}\text{\AA}^{-3}$ . The standard deviation in electron density, estimated by the formula of Cruickshank (1949), was  $0.03 \text{ e.}\text{\AA}^{-3}$ . The positions selected from the difference Fourier map generally gave reasonable distances and angles, but some peaks were broad and selection of a 'maximum' was relatively arbitrary. It was therefore decided to assign hydrogen positions in accordance with C-H bond lengths and bond angles considered to be reasonable and typical for the type of hydrogen atom concerned and at the same time in satisfactory accord with the difference Fourier map. Isotropic temperature factors selected for hydrogen atoms were 6.5 for methyl hydrogen atoms and 5.5 for ring hydrogen atoms.

Two cycles of refinement were now executed in which all parameters were varied for Zn, O and C atoms. Hydrogen atom parameters were not varied, but the hydrogen atoms were shifted after each cycle by an amount equal to the shift of the carbon atom to which they were bonded. A final weighting scheme, selected in the same manner as weighting scheme *A* but with new values of  $\Delta^2$ , was as follows: For  $|F_o| \leq 10$ ,  $\sigma = \sqrt{-0.175|F_o| + 3.0}$ ; for  $10 < |F_o| \leq 55$ ,  $\sigma = 1.12$ ; for  $|F_o| > 55$ ,  $\sigma = \sqrt{0.0964|F_o| - 4.05}$ . (The range for  $\Delta^2 = \text{constant}$  is seen to be more than doubled by inclusion of hydrogen atoms.) Two final cycles of refinement followed. The last cycle, for which no parameter shifted by more than one-fifth of an estimated standard deviation, gave values of  $R_1$  and  $R_2$  of 0.026 and 0.039 respectively. A final difference Fourier map showed no electron density greater than  $0.3 \text{ e.}\text{\AA}^{-3}$ . Calculation of the structure factors of reflections rejected because of poor counting statistics gave no  $|F_c|$  greater than 2.5 times the minimum observable magnitude. The final value of the function  $\sqrt{\sum \omega |F_o| - |F_c|^2 / (m-n)}$ , 0.927, where  $n$  is the number of parameters varied and  $m$  is the number of reflections included in the refinement,

is close enough to the expected value of unity to suggest that the weights are approximately on an absolute scale.

## Results

The absolute amplitudes of the observed and calculated structure factors for the reflections used in refinement are listed in Table 1. Final positional parameters for all atoms are given in Table 2, using the numbering system indicated in Fig. 1. Table 3 lists the positional parameters for non-hydrogen atoms with respect to an orthogonal coordinate system having  $y$  coincident with the crystallographic  $b$  axis and  $z$  coincident with the  $c^*$  (reciprocal  $c$ ) axis. A right-handed coordinate system was selected for both the monoclinic cell and the orthogonal axes.

Table 3. Orthogonal coordinates of all non-hydrogen atoms

	<i>X</i>	<i>Y</i>	<i>Z</i>
Zn(1)	1.87467	0.0	2.48034
Zn(2)	0.0	-0.97873	0.0
O(11)	3.53115	-0.66838	3.38389
O(12)	0.78340	-0.52339	4.03561
O(21)	2.51082	1.89722	2.31562
O(22)	0.10237	0.56745	1.51509
O(31)	1.99509	-0.98169	0.68006
O(32)	0.60270	-2.23719	-1.45305
C(11)	4.96700	-1.69030	4.93347
C(12)	3.58483	-1.27117	4.49063
C(13)	2.51247	-1.54185	5.31272
C(14)	1.20851	-1.16272	5.05512
C(15)	0.14929	-1.53810	6.08089
C(21)	2.39176	4.25796	2.38753
C(22)	1.75988	2.92013	2.20199
C(23)	0.38316	2.87044	1.91971
C(24)	-0.36263	1.76547	1.59498
C(25)	-1.83213	1.91312	1.29501
C(31)	4.34637	-0.81079	0.45087
C(32)	3.01888	-1.23936	-0.07433
C(33)	2.93417	-1.85094	-1.29270
C(34)	1.75936	-2.31107	-1.92132
C(35)	1.90824	-2.96664	-3.27920

Figs. 2 and 3 are views of the unit cell, observed along the  $b$  and  $c^*$  axes respectively.† Table 4 gives bond lengths and angles within the ligand rings; Table 5 gives the bond lengths and angles for bonds involving zinc and oxygen atoms. The Zn(1)-Zn(2) distance is  $3.259 \pm 0.001 \text{ \AA}$  and the Zn-Zn-Zn angle is  $145.05^\circ \pm 0.03^\circ$ .

## Discussion

Bond distances within the ligand rings are essentially the same as the values listed in Lingafelter & Braun's (1966) survey of previously reported structures of monomeric acetylacetonato complexes. The bonds be-

† The molecules of  $[\text{Zn}(\text{AcAc})_2]_3$  differ from the drawing in the preliminary communication with respect to: (1) reflection in the  $xz$  plane, and (2) a correction in the orientation of the ligand ring number three.

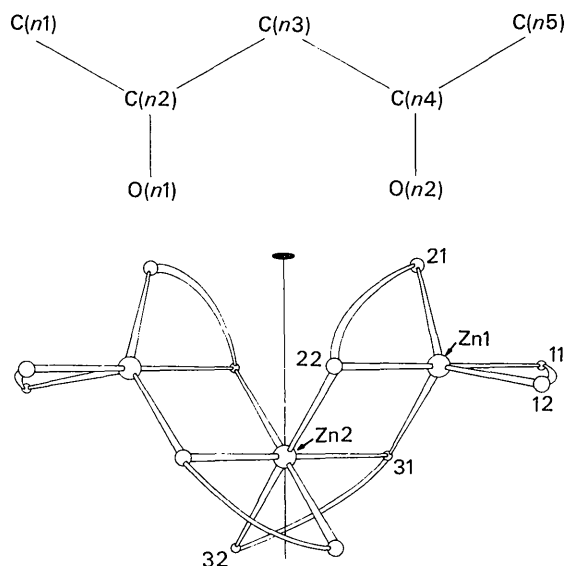


Fig. 1. (a) A sketch showing the numbering scheme for atoms in the chelate rings. The subscript  $n$  ( $= 1, 2, 3$ ) is a running index identifying the rings. (b) Numbering scheme for the oxygen atoms. The two oxygen atoms of the  $n$ th ring are identified as  $O(n1)$  and  $O(n2)$ .

tween the methyl carbon atoms and the carbonyl carbon atoms have an average which is slightly but significantly shorter ( $0.02 \text{ \AA}$ ) than the literature average, but no individual C-C bond distance is significantly less than the range of reported values. The bond angles are somewhat more variable (up to  $2^\circ$ ), presumably owing to intramolecular crowding and/or crystal packing forces.

Two types of Zn-O bond length were observed; bonds from zinc atoms to bridging oxygen atoms average  $2.00 \text{ \AA}$  and bonds from zinc atoms to non-bridging oxygen atoms average  $2.10 \text{ \AA}$ . The former value is in very good agreement with the average value of  $2.01 \pm 0.02$  for the Zn-O bond lengths in  $\text{Zn}(\text{AcAc})_2 \cdot \text{H}_2\text{O}$  (Montgomery & Lingafelter, 1963). All Zn-O distances but one [ $\text{Zn}(1)-\text{O}(12)$ ] are significantly longer than  $1.962 \pm 0.007 \text{ \AA}$  reported for the tetrahedrally bonded zinc atom of bis(dipivaloylmethanido)zinc(II) (Cotton & Wood, 1964).

The  $\text{ZnO}_5$  skeleton of  $\text{Zn}(\text{AcAc})_2 \cdot \text{H}_2\text{O}$  was reported (Montgomery & Lingafelter, 1963) to be approximately square pyramidal, slightly distorted toward a trigonal bipyramid (average angular deviations from ideal:  $2.9^\circ$  for square pyramid,  $10.5^\circ$  for trigonal bipyramid).

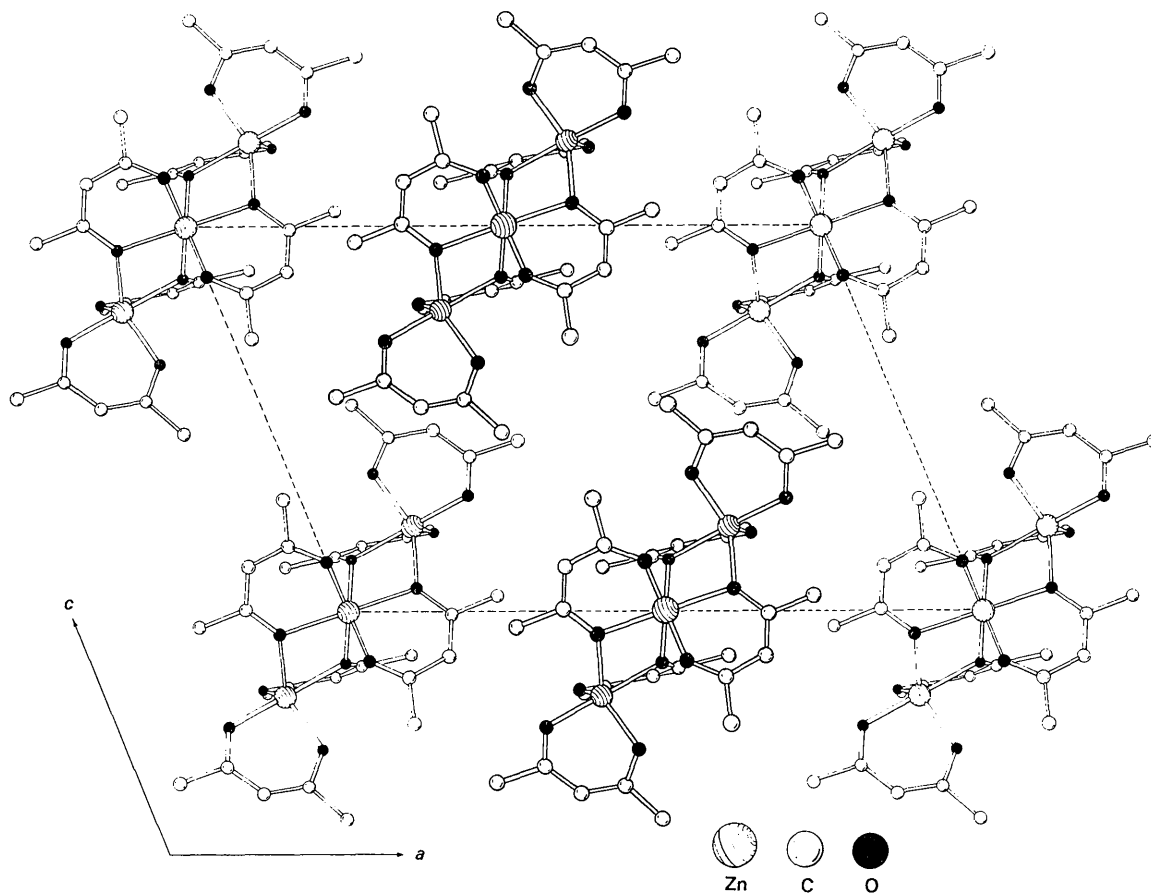


Fig. 2. Projection of the  $[\text{Zn}(\text{AcAc})_2]_3$  structure along the  $b$  axis. The packing arrangement of the molecules gives rise to a well-developed (201) face (see text).

As shown in Table 6, the terminal zinc atoms in  $[\text{Zn}(\text{AcAc})_2]_3$  are again generally intermediate between these extremes, but closer to a trigonal bipyramid\* (mean deviation  $5.3^\circ$ , versus  $12.3^\circ$  for a square pyramid). Both the terminal five-coordinate zinc atom and the central six-coordinate zinc atom (mean angular deviation from ideal octahedron,  $8.2^\circ$ ) have considerable angular distortion. This is in agreement with the distortion observed in the other polymeric acetylacetonato complexes and is probably due to intramolecular crowding and to restrictions imposed by the internal geometry of the ligand, since intermolecular crystal packing forces would not be expected to have such large effects on the inner coordination sphere.

Fig. 2 shows the tendency of the trinuclear molecules to become aligned in the unit cell, accounting for the well-developed  $(\bar{2}01)$  face and the tendency for selection of the corresponding face-centered unit cell.

Intermolecular contacts less than  $4 \text{ \AA}$  (Table 7) can all be regarded as normal van der Waals contacts. Table 8 lists direction cosines for the best planes through the OCCO ring systems; Table 8 gives deviations of the ligand atoms and of the zinc atoms from these planes. As in  $[\text{Co}(\text{AcAc})_2]_3\text{H}_2\text{O}$  (Cotton & Eiss, 1968) and other structures (Cotton & Wood, 1964; Lingafelter & Braun, 1966), the out-of-plane distance of the metal atom varies widely, from less than  $0.1 \text{ \AA}$  to more than  $1.0 \text{ \AA}$ , but again this does not have an apparent correlation with the M-O bond lengths.

The program VIBELL (Shoemaker & Srivastava, 1963) was used to calculate equivalent isotropic temperature factors (listed in Table 9) and the magnitudes and directions for the axes of the ellipsoids of thermal vibration for  $[\text{Zn}(\text{AcAc})_2]_3$ . The equivalent isotropic temperature factors seem reasonable and are in fair agreement with the values reported (Cotton & Eiss, 1968) for  $[\text{Co}(\text{AcAc})_2]_3\text{H}_2\text{O}$ . The somewhat higher magnitudes for  $[\text{Zn}(\text{AcAc})_2]_3$  were anticipated, in view of the very high volatility of  $[\text{Zn}(\text{AcAc})_2]_3$  which, unlike the polymeric acetylacetonato complexes of  $\text{Cr}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Fe}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$  and  $\text{Ni}^{\text{II}}$ , sublimes in vacuum at  $50^\circ\text{C}$ . In addition the relative magnitudes of the equivalent isotropic temperature factors for the carbon atoms in each ring are in the expected order - highest for methyl carbon atoms and lowest for carbonyl carbon atoms. The major vibration axis for all oxygen atoms is roughly (within  $20^\circ$ ) perpendicular to the Zn-O and C-O bonds in which they participate. All ring atoms have minor axes of vibration which lie roughly (within  $25^\circ$ ) in the plane of the ligand molecule.

\* The exact value for the mean deviation from the ideal angles for a square pyramid depends on the selection of the model used; Gillespie's (1963) criterion (used in Table 6) that electrostatic repulsion should be minimized when the angle between the apical and basal ligand atoms is  $100^\circ$ , gives the reported mean deviation of  $12.3^\circ$ . The empirical model chosen by Montgomery & Lingafelter (1963) assumes all Zn-O distances to equal their mean value and the base of the ideal pyramid to lie on the best plane through the four basal atoms, and gives a mean deviation of  $12.5^\circ$ .

Table 4. Bond lengths and angles within the ligand rings

Figures in parentheses are the estimated standard deviations occurring in the last recorded decimal place of each parameter. Literature average values are from Lingafelter & Braun's compilation.

Ring	$\text{C}(n1)-\text{C}(n2)$ ; $\text{C}(n4)-\text{C}(n5)$	$\text{C}(n2)-\text{C}(n3)$ ; $\text{C}(n3)-\text{C}(n4)$	$\text{C}(n2)-\text{O}(n1)$ ; $\text{C}(n4)-\text{O}(n2)$
1	1.511 (7); 1.522 (7)	1.378 (6); 1.382 (7)	1.261 (5); 1.276 (5)
2	1.491 (5); 1.507 (6)	1.406 (6); 1.372 (5)	1.274 (4); 1.288 (4)
3	1.490 (5); 1.515 (6)	1.366 (5); 1.410 (6)	1.298 (4); 1.250 (5)
Average	1.506 (2)	1.386 (2)	1.274 (2)
Literature average	1.524 (3)	1.390 (3)	1.274 (3)
Ring	$\text{C}(n1)-\text{C}(n2)-\text{C}(n3)$ ; $\text{C}(n3)-\text{C}(n4)-\text{C}(n5)$	$\text{C}(n1)-\text{C}(n2)-\text{O}(n1)$ ; $\text{O}(n2)-\text{C}(n4)-\text{C}(n5)$	$\text{O}(n1)-\text{C}(n2)-\text{C}(n3)$ ; $\text{C}(n3)-\text{C}(n4)-\text{O}(n2)$
1	118.9 (5); 117.6 (5)	115.4 (5); 115.5 (4)	125.7 (4); 126.9 (5)
2	118.1 (4); 119.9 (4)	117.4 (4); 115.5 (4)	124.5 (4); 124.6 (4)
3	119.9 (4); 117.3 (4)	116.2 (3); 116.9 (4)	124.0 (3); 125.8 (4)
Average	118.6 (2)	116.1 (2)	125.2 (2)
Literature average	119.8 (3)	114.8 (2)	125.3 (3)
Ring	$\text{C}(n2)-\text{C}(n3)-\text{C}(n4)$		
1	124.7 (4)		
2	127.5 (4)		
3	126.6 (4)		
Average	126.3 (2)		
Literature average	124.0 (3)		

$[\text{Zn}(\text{AcAc})_2]_3$  is the first compound in which the occurrence of both five- and six-coordinate zinc atoms has been reported. The tendency for both five- and six-

coordination, but preference for five-coordination, in the derivatives of  $\text{Zn}(\text{AcAc})_2$  is apparent from an examination of the reported base adducts; the stable

Table 5. Bond distances and angles involving zinc and oxygen atoms

Figures in parentheses are the estimated standard deviations occurring in the last recorded decimal place of each parameter.

Zn(1)–O(11)	2.002 (3)		
Zn(1)–O(12)	1.971 (3)		
Zn(1)–O(21)	2.008 (3)		
Zn(1)–O(22)	2.096 (2)		
Zn(1)–O(31)	2.054 (2)		
Zn(2)–O(22)	2.167 (2)		
Zn(2)–O(31)	2.108 (2)		
Zn(2)–O(32)	2.015 (3)		
O(11)–Zn(1)–O(12)	90.8 (1)	O(22)–Zn(1)–O(31)	74.4 (1)
O(11)–Zn(1)–O(21)	95.2 (1)	O(22)–Zn(2)–O(32)	159.4 (1)
O(11)–Zn(1)–O(22)	176.2 (1)	O(22)–Zn(2)–O(22)**	89.0 (1)
O(11)–Zn(1)–O(31)	100.8 (1)	O(22)–Zn(2)–O(31)**	105.7 (1)
O(12)–Zn—O(21)	119.4 (1)	O(22)–Zn(2)–O(32)**	87.5 (1)
O(12)–Zn(1)–O(22)	88.1 (1)	O(31)–Zn(2)–O(32)	87.1 (1)
O(12)–Zn(1)–O(31)	126.7 (1)	O(31)–Zn(2)–O(31)**	180.0 (1)
O(21)–Zn(1)–O(22)	88.5 (1)	O(31)–Zn(2)–O(32)**	92.8 (1)
O(21)–Zn(1)–O(31)	111.2 (1)	O(32)–Zn(2)–O(32)**	102.7 (1)
O(22)–Zn(1)–O(31)	77.0 (1)		

\*\* An oxygen atom with two asterisks,  $O_{mn}^{**}$ , is related to the atom  $O_{mn}$  by the twofold axis of rotation.

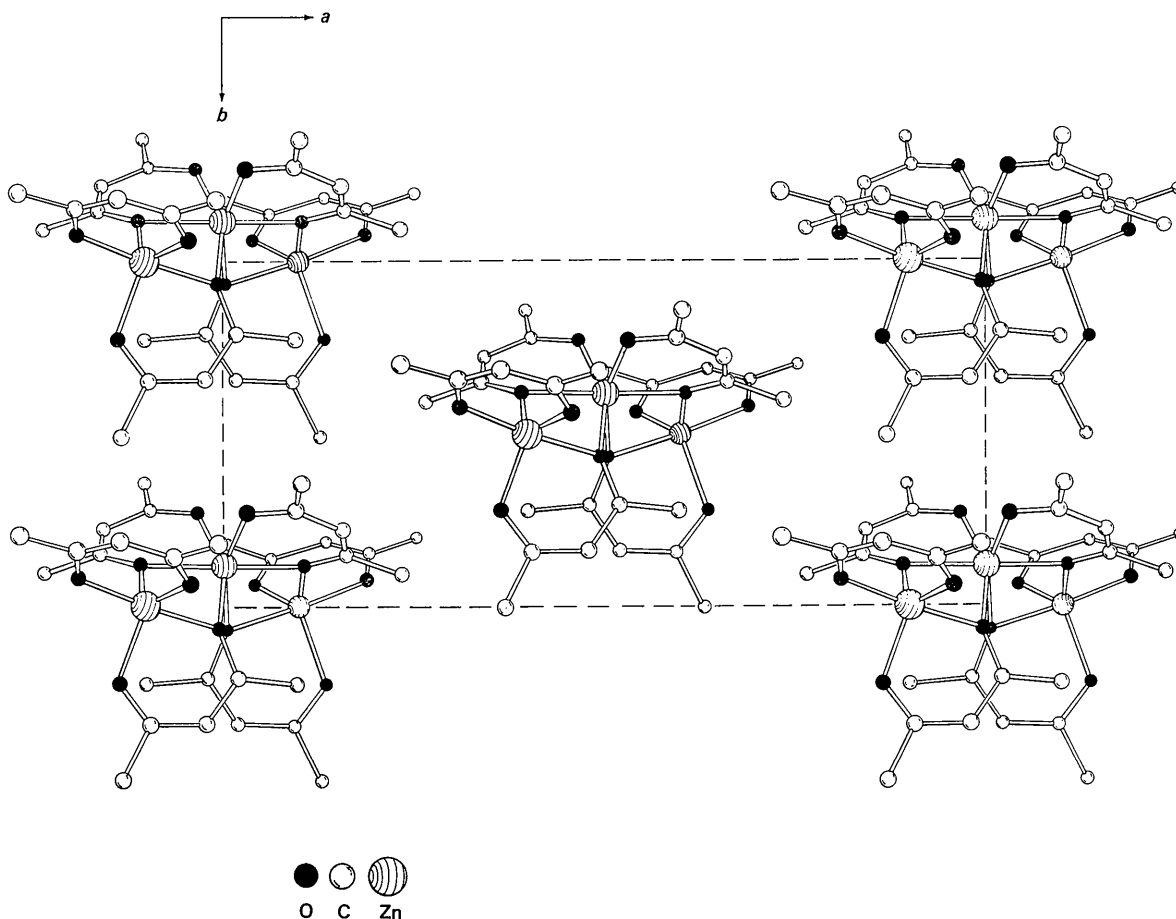


Fig. 3. Projection of the  $[\text{Zn}(\text{AcAc})_2]_3$  structure along the  $c^*$  (reciprocal  $c$ ) axis.



monohydrate,  $\text{Zn}(\text{AcAc})_2\text{H}_2\text{O}$ , is pentacoordinate, though the existence of  $\text{Zn}(\text{AcAc})_2 \cdot 2\text{H}_2\text{O}$  has also been proposed (Lippert & Truter, 1960). For  $\text{NH}_3$  and substituted pyridines,  $\text{Zn}(\text{AcAc})_2\text{B}$  is the more stable ad-

Table 6. Comparison of observed O–Zn(1)–O angles with values for the ideal trigonal bipyramid and square pyramid

Angle	Ideal trigonal bipyramid	Observed	Ideal square pyramid
O(12)–Zn(1)–O(21)	120°	119.4°	100°
O(21)–Zn(1)–O(11)	90	95.2	100
O(21)–Zn(1)–O(22)	90	88.5	100
O(21)–Zn(1)–O(31)	120	111.2	100
O(31)–Zn(1)–O(11)	90	100.8	88.4
O(12)–Zn(1)–O(22)	90	88.1	88.4
O(31)–Zn(1)–O(22)	90	77.0	88.4
O(11)–Zn(1)–O(12)	90	90.8	88.4
O(12)–Zn(1)–O(31)	120	126.7	160
O(11)–Zn(1)–O(22)	180	176.2	160
Average deviation	5.3		12.3

Table 7. Intermolecular contacts less than 4.0 Å in  $[\text{Zn}(\text{AcAc})_2]_3$

Atom I	Atom J	Distance	Vector from molecule containing I to molecule containing J*
C(21)	O(11)	3.823	0, 1, 0
C(15)	O(11)	3.910	$-\frac{1}{2}, \frac{1}{2}, 0$
C(11)	O(12)	3.980	$\frac{1}{2}, \frac{1}{2}, 1$
C(31)	O(21)	3.997	$\frac{1}{2}, -\frac{1}{2}, 0$
C(13)	O(21)	3.734	$\frac{1}{2}, \frac{1}{2}, 1$
C(15)	O(21)	3.550	$\frac{1}{2}, \frac{1}{2}, 1$
C(21)	O(31)	3.646	0, 1, 0
C(21)	O(32)	3.689	0, 1, 0
C(23)	O(32)	3.504	0, 1, 0
C(21)	C(12)	3.782	0, 1, 0
C(21)	C(13)	3.940	0, 1, 0
C(21)	C(13)	3.903	$\frac{1}{2}, \frac{1}{2}, 1$
C(22)	C(13)	3.765	$\frac{1}{2}, \frac{1}{2}, 1$
C(35)	C(15)	3.783	0, 0, 1
C(21)	C(15)	3.814	$\frac{1}{2}, \frac{1}{2}, 1$
C(31)	C(21)	3.927	$\frac{1}{2}, \frac{1}{2}, 0$
C(32)	C(21)	3.885	0, 1, 0
C(31)	C(25)	3.576	$\frac{1}{2}, \frac{1}{2}, 0$
C(33)	C(31)	3.867	$\frac{1}{2}, \frac{1}{2}, 0$
C(23)	C(35)	3.723	0, 1, 0

\* In many cases more than one vector is possible between similar sets of atoms related by the  $C_2$  axis. Only one of these possible vectors is listed.

Table 9. Equivalent isotropic temperature parameters for non-hydrogen atoms

	Equivalent B		Equivalent B
Zn(1)	3.30 Å <sup>2</sup>	C(15)	8.03 Å <sup>2</sup>
Zn(2)	2.76	C(21)	5.39
O(11)	4.97	C(22)	3.63
O(12)	5.09	C(23)	4.19
O(21)	3.87	C(24)	3.51
O(22)	3.14	C(25)	5.01
O(31)	3.02	C(31)	5.99
O(32)	3.68	C(32)	3.48
C(11)	8.11	C(33)	4.09
C(12)	4.89	C(34)	3.67
C(13)	5.12	C(35)	5.72
C(14)	5.05		

duct, though 4-methylpyridine also gives  $\text{Zn}(\text{AcAc})_2\text{B}_2$  as a stable product (Graddon & Weedon, 1963). Molecular weight determinations indicate these monobase adducts to be monomeric (and thus presumably five-coordinate) in solution. This is in accordance with the structure of  $\text{Zn}(\text{AcAc})_2\text{H}_2\text{O}$  and with the pentacoordinate terminal zinc atoms in  $[\text{Zn}(\text{AcAc})_2]_3$ ; however, the existence of the central six-coordinate zinc atom in this molecule shows that the difference in stability is not very large. Otherwise a dimeric molecule of five-coordinate zinc atoms similar to bis-(*N*-methylsilylaldiminato)zinc(II) (Orioli, Di Vaira & Sacconi, 1966) would be expected. Other derivatives of  $\text{Zn}(\text{AcAc})_2$  which may involve six-coordinate zinc are  $\text{NaZn}(\text{AcAc})_3$  (Dwyer & Sargeson, 1956), and  $\text{Zn}(\text{AcAc})_3(\text{CH}_3\text{COO})$  (Rudolph & Henry, 1964). The latter may be  $[\text{Zn}(\text{CH}_3\text{COO})][\text{Zn}(\text{AcAc})_3]^-$ , as proposed by Rudolph & Henry (1965), or a polymeric species involving five- and/or six-coordination (for example a dimer of five-coordinate zinc atoms, with a chelating acetate group). This will clearly be an area of interest for future structural investigations.

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Table 8.

(a) Direction cosines for best planes for the chelate rings.

Ring	L	M	N	D
1	0.1566	0.8664	0.4742	1.581
2	-0.2378	-0.1284	0.9628	1.373
3	0.1145	-0.8881	0.4452	1.406

(b) Distance of atoms from ligand plane.

Ring	C(n1)	C(n2)*	C(n3)*	C(n4)*	C(n5)	O(n1)*	O(n2)*	Zn(1)	Zn(2)
1	0.072	0.008	-0.004	-0.002	-0.007	-0.003	0.002	-0.112	—
2	-0.189	-0.046	0.016	0.023	0.064	0.016	-0.011	0.570	-1.247
3	0.013	0.008	-0.001	-0.007	-0.012	-0.003	-0.003	-0.087	-0.536

\* Atoms used to calculate best plane.

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## The Structure of $\text{Li}_9\text{Al}_4$ \*

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$\text{Li}_9\text{Al}_4$  has been found to crystallize in the monoclinic system, and a crystal structure with  $B2/m$  space group symmetry is compatible with observed intensities of X-ray reflections. Precision lattice parameters have been measured as  $a_0 = 19.1551 \pm 0.0005$ ,  $b_0 = 5.4288 \pm 0.0001$ ,  $c_0 = 4.4988 \pm 0.0001$  Å, and  $\gamma_0 = 107.671 \pm 0.002^\circ$  at  $23 \pm 2^\circ\text{C}$ . The unit cell contains two formulae of  $\text{Li}_9\text{Al}_4$ . A discrepancy index of 0.099 was obtained from three-dimensional intensity data with a total of 547 independent reflections. A difference density map at this discrepancy level contained no significant extrema or gradients. Thus, in the specific crystal from which the intensity data were taken there is no indication of a lithium deficiency which would alter the stoichiometry to 'Li<sub>2</sub>Al' as reported in the currently accepted temperature-composition diagram.

### Introduction

The structure of the phase  $\text{Na}_2\text{Tl}$  has recently been determined (Hansen & Smith, 1967) and found to be a new structure type. In a search for isoelectronic

phases which might be isostructural with  $\text{Na}_2\text{Tl}$ , available data (Hansen & Anderko, 1958; Elliott, 1965) on the binary phase relationships between alkali metals and Group III metals were examined. In the lithium-aluminum system one such phase 'Li<sub>2</sub>Al' was reported to form by peritectic reaction between LiAl and liquid (69 at.% Li) at  $522^\circ\text{C}$ ; the published phase diagram is reproduced in Fig. 1. The structure of 'Li<sub>2</sub>Al' has now been investigated and the results are herein reported.

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