Crystal Structure of *catena*-Di-μ-acetylacetonato-cadmium(II)

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The crystal structure of the title compound has been determined from single crystal *X*-ray diffractometer data, and refined by full-matrix least-squares R 0·042 for 1105 observed reflections. Crystals are monoclinic, space group $P2_1/a$, a = 18·832(8), b = 7·012(3), c = 8·531(3) Å, β = 96·08(3)°, Z = 4. The structure is comprised of linear chains of cadmium atoms spaced at 3·768(2) and 3·718(2) Å; the cadmium atoms are bridged by one oxygen atom from each ligand [Cd–O 2·288—2·353(4) Å] the remaining two co-ordination sites about the six-co-ordinate cadmium being occupied by the other two non-bridging oxygen atoms [Cd–O 2·221, 2·250(4) Å].

THIS paper describes the structure determination of cadmium acetylacetonate which was prepared as described in the literature and recrystallized from ethanol.[1]

EXPERIMENTAL

An approximately square prismatic crystal 0·35 × 0·33 × 0·12 (a) mm with b and c as face diagonals was used for data collection. Unit-cell dimensions were obtained by a least-squares fit of 15 reflections with 2θ *ca.* 30° centred in the counter aperture of a Syntex $P\bar{1}$ diffractometer. A unique data set in the range $2\theta < 100°$ was collected by a conventional 2θ—θ scan giving 1140 reflections of which 1105 with $I > 2\sigma(I)$ were considered observed and used in

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[1] M. Hassanein and I. F. Hewaidy, *Z. anorg. Chem.*, 1970, **373**, 81.

TABLE 1

Atomic positional and thermal (× 10³ Å²) parameters, with least squares estimated standard deviations in parentheses. A decimal point precedes (*x*, *y*, *z*)

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{18}	U_{23}
Cd	51222(2)	25186(5)	07489(5)	20·1(5)	13·2(6)	28·3(5)	1·3(2)	7·4(4)	2·9(2)
Ligand (1)									
O(11)	6163(2)	3208(7)	2181(5)	23(2)	24(3)	57(3)	9(2)	−7(2)	−5(3)
O(21)	5692(2)	−0434(5)	0656(4)	21(2)	17(2)	31(3)	2(2)	0(2)	3(2)
C(11)	7342(4)	328(1)	336(1)	44(5)	34(5)	80(6)	5(4)	−19(4)	−18(5)
C(21)	6724(5)	2261(9)	239(1)	28(5)	38(5)	44(5)	−14(3)	7(4)	1(3)
C(31)	6852(3)	0434(9)	1801(7)	21(3)	19(4)	38(4)	−2(3)	−2(3)	−4(3)
C(41)	6366(3)	−0783(9)	0994(7)	22(3)	25(4)	32(4)	7(3)	10(3)	9(3)
C(51)	6628(5)	−2683(9)	043(1)	44(6)	37(6)	62(7)	8(3)	0(5)	−10(4)
Ligand (2)									
O(12)	4702(2)	1857(7)	3022(5)	53(3)	18(2)	36(3)	3(3)	21(2)	6(2)
O(22)	4626(2)	5480(5)	1237(4)	29(2)	16(2)	27(2)	1(2)	10(2)	1(2)
C(12)	4232(5)	191(1)	5478(9)	71(6)	38(4)	31(5)	−3(5)	10(4)	22(4)
C(22)	4396(4)	291(1)	395(1)	24(4)	38(4)	37(5)	−12(4)	12(3)	7(4)
C(32)	4136(3)	4727(9)	3656(9)	34(4)	14(3)	37(4)	5(3)	8(3)	7(3)
C(42)	4234(3)	5900(9)	2375(7)	24(3)	22(4)	32(4)	−3(3)	6(3)	−2(3)
C(52)	3876(5)	783(1)	228(1)	61(6)	30(4)	62(6)	18(4)	22(5)	14(4)

the structure solution and refinement after correction for absorption.

Crystal Data.—$C_{10}H_{14}CdO_4$, $M = 310·6$, Monoclinic, $a = 18·832(8)$, $b = 7·012(3)$, $c = 8·531(3)$ Å, $\beta = 96·08(3)°$, $U = 1120·1(8)$ Å³, $D_m = 1·83$, $Z = 4$, $D_c = 1·84$ g cm⁻³, $F(000) = 616$. Cu-K_α radiation (monochromatic), $\lambda = 1·5418$ Å, $\mu = 161·6$ cm⁻¹. Space group $P2_1/a$ (No. 14, C^5_{2h}).

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) The Cd environment			
Cd–O(11)	2·250(4)	O(11)–Cd–O(21^{I})	153·3(2)
Cd–O(21)	2·336(4)	O(11)–Cd–O(22^{II})	91·9(2)
Cd–O(12)	2·221(5)	O(21)–Cd–O(12)	93·0(2)
Cd–O(22)	2·332(4)	O(21)–Cd–O(22)	171·4(2)
Cd–O(21^{I})	2·353(4)	O(21)–Cd–O(21^{I})	73·0(1)
Cd–O(22^{II})	2·288(4)	O(21)–Cd–O(22^{II})	112·7(1)
		O(12)–Cd–O(22)	81·0(2)
O(11)–Cd–O(21)	80·4(2)	O(12)–Cd–O(21^{I})	92·4(2)
O(11)–Cd–O(12)	86·7(2)	O(12)–Cd–O(22^{II})	153·7(2)
O(11)–Cd–O(22)	93·1(2)	O(22)–Cd–O(21^{I})	113·1(1)
O(21^{I})–Cd–O(22^{II})	100·3(1)	O(22)–Cd–O(22^{II})	72·8(1)
Cd · · · Cd^{I}	3·768(2)	Cd · · · Cd^{II}	3·718(2)
Cd–O(21)–Cd^{I}	107·0(1)	Cd–O(22)–Cd^{II}	107·2(2)
(*b*) The ligands: values for ligand (2) follow those for ligand (1)			
O(1)–C(2)	1·245(9), 1·265(9)	Cd–O(1)–C(2)	129·9(5), 130·9(5)
C(2)–C(1)	1·53(1), 1·54(1)	O(1)–C(2)–C(1)	114·3(6), 114·3(6)
C(2)–C(3)	1·405(9), 1·381(9)	O(1)–C(2)–C(3)	127·4(7), 126·8(7)
C(3)–C(4)	1·380(8), 1·394(9)	C(1)–C(2)–C(3)	118·2(7), 118·4(7)
C(4)–C(5)	1·52(1), 1·51(1)	C(2)–C(3)–C(4)	127·8(6), 127·9(7)
C(4)–O(2)	1·296(7), 1·313(7)	C(3)–C(4)–C(5)	118·8(6), 118·2(6)
O(1) · · · O(2)	2·960(6), 2·958(6)	O(3)–C(4)–O(2)	125·2(6), 125·4(5)
		C(5)–C(4)–O(2)	116·0(6), 116·3(6)
		C(4)–O(2)–Cd	127·0(4), 126·7(4)
Cd–O(21^{I})–C(41^{I})	124·5(4)	Cd–O(22^{II})–C(42^{II})	126·0(4)

Roman numeral superscripts denote the following transformations of the asymmetric unit, *x*, *y*, *z*:

I $1 - x, \bar{y}, \bar{z}$ II $1 - x, 1 - y, \bar{z}$

The structure was solved by the heavy-atom method; final refinement stages were by full-matrix least-squares, anisotropic thermal parameters for all non-hydrogen atoms being of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. No hydrogen atoms were included in the refinement since they were indistinct in a final difference map and contributed relatively little to the scattering. In the final refinement cycle, no parameter shift exceeded $0·2\sigma$, and refinement terminated at R 0·042 and R' 0·075 [$R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$]. The weighting scheme used was of the form $w = (\sigma^2|F_o| + n|F_o|^2)^{-1}$, a value of $n = 3 \times 10^{-4}$ being found appropriate.

Data processing was carried out by use of a local adaptation of the ' *X*-Ray '72 ' system [2] on a CDC 6200. Scattering factors used were for the neutral atoms,[3] that for cadmium being corrected for anomalous dispersion ($\Delta f', \Delta f''$).[4] Structure-factor Tables are given in Supplementary Publication No. SUP 21180 (7 pp., 1 microfiche).* Final atom positional and thermal parameters are listed in Table 1, bond distances and angles in Table 2.

DISCUSSION

Among the wide variety of co-ordination types found in the complexes of the acetylacetonate ligand, the bisacetylacetonatometal(II) derivatives are particularly notable for their diversity; the present structure adds yet another novel example within the series. The complex is comprised of infinite parallel chains parallel to *b*, the cadmium atoms being bridged by pairs of oxygen bridges from each of two independent ligands (1) and (2); within each of the ligands one of the oxygen atoms [O(1)] co-ordinates simply to the cadmium atom, being *cis* to its analogue for the other ligand, while the other oxygen [O(2)] the pairs of cadmium atoms (Figure 1).

The cadmium environment is octahedral, to a first approximation, and is composed of four bridging-ligand and the *cis* pair of non-bridging ligand oxygen atoms,

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[2] ' *X*-Ray ' System, version of June 1972, Technical Report, TR 192 of the Computer Science Centre, University of Maryland, U.S.A.

[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[4] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 7.

the latter being at shorter distances ($2{\cdot}22_1$, $2{\cdot}25_0$ Å) than the former ($2{\cdot}28_8$—$2{\cdot}35_3$ Å). The angular geometry of the octahedron is quite distorted, the angles between adjacent Cd–O bonds ranging from 72·8 to 113·1° and the angles between opposed Cd–O bonds from 153·3 to 171·4°. Examination of this seemingly irregular array of bonds and angles reveals a very good approximation to a two-fold axis within the infinite chain at each cadmium, passing between the pair of non-bridging oxygen atoms. The cadmium–oxygen distances are in no way unusual, since the irregular geometries observed for this metal give rise to a very wide spectrum of values.

In previously determined acetylacetonate structures with similar ligands containing a bridging and a non-bridging oxygen, in no case has the geometry within the ligand been shown to be significantly asymmetric. Although no thermal correction has been applied to the geometry of the present structure, the accuracy and agreement between independent analogous parts of the structure suggests that it is very likely that the ligand is quite asymmetric. Figure 2 shows the mean ligand geometry; within the ligand, no value deviates from the mean of the pair by $>\sigma$, and it is clear that O(1)–C(2) is less than O(2)–C(4) because of the greater involvement of O(2) in bonding to the two metal atoms. Likewise the geometry about O(2) is distorted, C(3)–C(4)–O(2) and Cd–O(2)–C(4) being appreciably diminished in comparison with C(3)–C(2)–O(1) and Cd–O(1)–C(2). Both ligands are tolerably planar (Table 3), the deviation of the cadmium from ligand (1) being appreciably greater than from ligand (2).

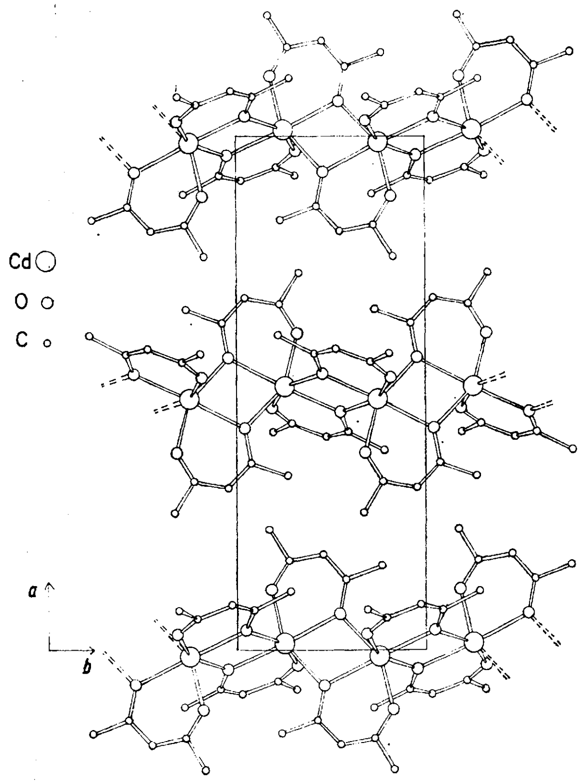

FIGURE 1 Unit-cell contents viewed down c^*

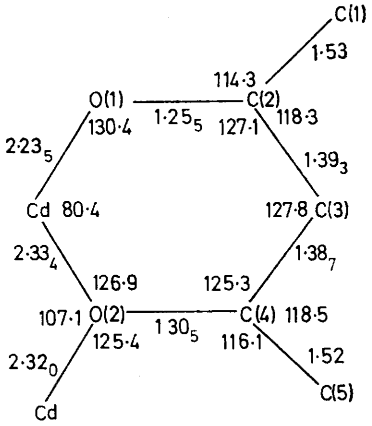

FIGURE 2 The mean geometry of the two ligand systems and the associated cadmium atoms showing the atom numbering system in the ligands

TABLE 3

Equations of least-squares planes through the ligands, expressed in orthogonal (Å) co-ordinates X, Y, Z where $X = ax + cz\cos\beta$, $Y = by$, and $Z = cz\sin\beta$. Deviations (Å) of atoms from planes are given in square brackets; σ is the estimated standard deviation of the defining atoms from the plane

Ligand (1): $-0{\cdot}3298X - 0{\cdot}3988Y + 0{\cdot}8557Z = -2{\cdot}996$

[O(1) $-0{\cdot}08$, O(2) 0·08, C(1) 0·06, C(2) 0, C(3) $-0{\cdot}02$, C(4) 0·01, C(5) $-0{\cdot}04$, Cd $-0{\cdot}32$; σ 0·06]

Ligand (2): $0{\cdot}7921X + 0{\cdot}3645Y + 0{\cdot}4896Z = 8{\cdot}636$

[O(1) $-0{\cdot}11$, O(2) 0·09, C(1) 0·05, C(2) 0·02, C(3) 0, C(4) 0·01 C(5) $-0{\cdot}06$, Cd $-0{\cdot}09$; σ 0·07]

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