Crystal Structure of Potassium Tris(acetylacetonato)cadmate(II) Monohydrate

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The crystal structure of the title compound has been determined from single-crystal *X*-ray diffractometer data by the heavy-atom method, and refined to *R* 0·071 (1997 observed reflections) by block-diagonal least-squares. Crystals are monoclinic, $P2_1/a$, $a = 16{\cdot}46(1)$, $b = 14{\cdot}051(6)$, $c = 8{\cdot}404(3)$ Å, $\beta = 101{\cdot}60(3)°$, $Z = 4$. The structure is comprised of discrete potassium cations and $[Cd(C_5H_7O_2)_3]^-$ anions, in which the metal atom is co-ordinated by the three ligands, with Cd–O 2·247(7)—2·325(9) Å, in a very good approximation to trigonal prismatic stereochemistry. The potassium environment is comprised of five of the six ligand oxygen atoms and the water molecule, with K–O 2·622(11)—2·802(8) Å.

IN contrast to the tris(acetylacetonato)metal(III) derivatives, little interest has been shown in the chemistry of the salts of the tris(acetylacetonato)metallate(II) ions which are formed with a wider range of metal atoms. In conjunction with our recent work on the structure determination of cadmium acetylacetonate,[1] we have determined the crystal structure of potassium tris(acetylacetonato)cadmate(II), monohydrate, prepared by the method used for the sodium analogue.[2] The potassium salt was used since it gave more satisfactory crystals (from methanol, monoclinic needles, elongated along *c*).

EXPERIMENTAL

A needle section 0·15 × 0·15 × 0·30 mm was used for data collection; unit-cell dimensions were obtained by a least-squares fit of 15 reflections with 2θ *ca.* 25° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set in the range $2\theta < 50°$, collected by conventional 2θ—θ scan, yielded 2278 independent reflections of which 1997, having $I > 2\sigma(I)$ were considered observed and used in the structure solution. During data collection, the crystal decrepitated badly in the *X*-ray beam, the intensity of the standards at the end of the run (high *h*) being only *ca.* 0·70 of the initial intensity. The data accordingly was reduced to a common scale based on the standards used for monitoring the run; although desirable, no absorption correction was applied because of the difficulty of approximating the changing shape of the crystal.

Crystal Data.—$C_{15}H_{23}CdKO_7$, $M = 466{\cdot}9$, Monoclinic, $a = 16{\cdot}46(1)$, $b = 14{\cdot}051(6)$, $c = 8{\cdot}404(3)$ Å, $\beta = 101{\cdot}60(3)°$, $U = 1904(1)$ Å^3, $D_m = 1{\cdot}63(1)$, $Z = 4$, $D_c = 1{\cdot}63$ g cm^{-3}, $F(000) = 944$. Monochromatic Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å. Space group $P2_1/a$ (No. 14, C_{2h}^5). Neutral atom scattering factors,[3] those for cadmium and potassium corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[4]

The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least-squares, the parameters of the metal and oxygen atoms being refined as a single matrix in the final stages in order to approximate to a full matrix procedure. Anisotropic thermal parameters were 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, because their positions were indistinct in a final difference map, and they contributed relatively little to the scattering. In the final refinement cycle, no parameter shift was $>0{\cdot}2\sigma$ and refinement terminated at *R* 0·071, and R' 0·068 $[R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$. The weighting scheme used was of the form $w = (\sigma|F_o| + n|F_o|^2)^{-1}$, where $n = 5 \times 10^{-4}$ was found to be appropriate.

Data processing was carried out by use of a local adaptation of the *X*-Ray '72 system on a CDC 6200 machine at this University.[5]

Structure factor tables are given in Supplementary Publication No. SUP 21264 (10 pp., 1 microfiche).† Final positional and thermal parameters are listed in Table 1, bond distances and angles in Table 2, and details of ligand planes in Table 3.

DISCUSSION

The structure is comprised of discrete potassium cations and tris(acetylacetonato)cadmate anions, the

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† For details, see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1974, Index issue.

[1] E. N. Maslen, T. M. Greaney, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1975, 400.

[2] F. P. Dwyer and A. M. Sargeson, *Proc. Roy. Soc. New South Wales*, 1956, **40**, 29.

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

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

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

TABLE 1

Atomic positional parameters ($\times 10^5$ for Cd; $\times 10^4$ for others) and thermal parameters ($\times 10^3$ Å^2), with least-squares estimated standard deviations in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	28090(6)	45024(5)	46536(9)	33(1)	28(1)	32(1)	0(1)	9(0)	1(0)
Ligand (1)									
O(1)	1450(5)	5034(6)	3860(10)	40(6)	44(5)	76(6)	−4(5)	5(5)	−7(4)
O(2)	2243(5)	3325(5)	2984(10)	35(6)	44(5)	50(4)	1(5)	5(4)	−11(4)
C(1)	0013(9)	5199(9)	2723(16)	41(9)	71(10)	84(9)	35(9)	15(8)	19(8)
C(2)	0843(8)	4682(7)	2924(13)	41(9)	28(6)	60(7)	−12(7)	19(7)	15(5)
C(3)	0838(8)	3843(8)	1988(14)	47(9)	47(7)	57(7)	15(8)	19(7)	8(6)
C(4)	1535(8)	3241(8)	2063(11)	56(9)	45(6)	29(5)	−26(8)	14(6)	1(5)
C(5)	1427(9)	2365(9)	0907(15)	67(11)	43(7)	73(8)	−6(9)	17(9)	−26(7)
Ligand (2)									
O(1)	2573(6)	5098(5)	7073(7)	65(7)	44(4)	25(4)	15(5)	21(4)	6(3)
O(2)	3368(6)	3323(5)	6352(7)	64(7)	38(4)	27(4)	3(5)	8(4)	1(3)
C(1)	2332(9)	5241(9)	9755(14)	78(12)	67(8)	40(6)	9(10)	34(7)	−9(6)
C(2)	2688(7)	4732(7)	8438(11)	38(8)	35(6)	31(5)	−20(7)	7(6)	−6(4)
C(3)	3109(8)	3862(8)	8924(13)	54(10)	30(6)	44(6)	−1(8)	9(7)	3(5)
C(4)	3402(8)	3223(8)	7856(13)	34(8)	32(6)	51(6)	−9(7)	5(6)	0(5)
C(5)	3831(10)	2327(9)	8602(14)	77(12)	48(7)	66(8)	43(9)	14(9)	30(7)
Ligand (3)									
O(1)	3099(5)	6042(5)	4205(9)	40(6)	29(4)	63(5)	−18(5)	32(5)	−2(4)
O(2)	3921(5)	4314(5)	3404(8)	40(6)	33(4)	40(4)	10(4)	18(4)	−2(3)
C(1)	3749(9)	7515(8)	3728(13)	69(11)	28(6)	60(7)	−21(8)	20(8)	3(5)
C(2)	3686(8)	6407(7)	3688(12)	52(9)	28(5)	39(6)	−24(7)	4(6)	5(5)
C(3)	4318(7)	5928(8)	3108(12)	35(8)	49(7)	39(6)	9(8)	22(6)	−1(5)
C(4)	4413(8)	4939(8)	2997(12)	41(8)	41(8)	33(5)	−12(8)	0(6)	10(5)
C(5)	5137(8)	4540(9)	2299(14)	40(9)	68(8)	61(7)	38(9)	33(7)	2(7)
Water molecule									
O(4)	4324(6)	2404(6)	3155(12)	62(8)	45(5)	119(7)	−2(6)	42(7)	1(6)
Cation									
K	3109(2)	1725(2)	4415(3)	55(3)	32(2)	54(2)	−7(2)	20(2)	−1(1)

latter possessing the expected pseudo-three-fold symmetry. Figure 1 shows that the cadmium and potassium atoms alternate to form a zig-zag chain parallel to *b*, with the potassium ion approaching the complex anion along the three-fold axis so that O(11$^{\mathrm{I}}$), O(12$^{\mathrm{I}}$), and O(13$^{\mathrm{I}}$) participate in its co-ordination sphere; the other end of the next anion is approached rather more obliquely so that, while O(21) and O(22) also participate, the sixth co-ordination position is occupied by the water molecule O(4). Although the six potassium–oxygen contacts are similar in magnitude, ranging from 2·62 to 2·80 Å, the angular geometry about the potassium is quite irregular, the angles at the potassium subtended by adjacent oxygen atoms varying between 64·4 and 113·3°. The water oxygen O(4) has no contact <3·5 Å to any oxygen other than the adjacent O(21) and O(22) in the potassium co-ordination sphere, and presumably is not significantly hydrogen-bonded to other entities.

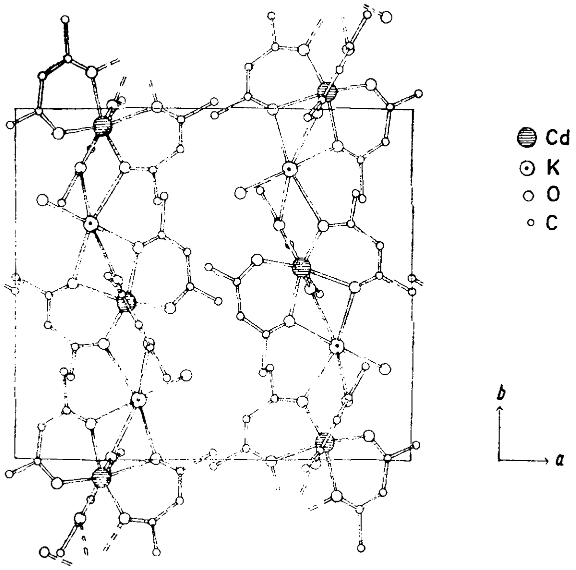

FIGURE 1 Unit cell contents viewed down *c**

By the use of a repulsion model, it has been shown that in tris(bidentate) complexes, the gross geometry is determined by the ligand 'normalized bite,' defined as the ratio of the chelating distance of the ligand to the metal–ligand distance.[6] Depending on whether this bite is large (*e.g.* 1·414) or small (*e.g.* 1·0), it is found that the parameter θ, describing the twist of the top triangle with respect to the bottom triangle of the D_3 geometry, ranges from 30° for the octahedron to 0° for the trigonal prism; for intermediate cases the *b*–θ relationship is described by a smooth curve which is a good fit to all previously determined structures with the exception of the tris(dithiolato)metal(III) derivatives.[7]

In the present structure, the normalized bite of the ligand is 1·28 and a value of 23° would be predicted for θ. In fact, the observed value of θ is 0° and the stereochemistry about the metal is obviously highly anomalous by the foregoing considerations, being a trigonal prism slightly distorted by the variations in the Cd–O distances which vary between 2·247 and 2·325 Å. Inspection of

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[6] D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1561.

[7] Ref. 6, Table 1 and references *t*, *u*, *v* therein.

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses

(*a*) K environment

K–O(21)	2·801(8)	K–O(11$^{\mathrm{I}}$)	2·802(8)
K–O(22)	2·756(7)	K–O(12$^{\mathrm{I}}$)	2·736(8)
K–O(4)	2·622(11)	K–O(13$^{\mathrm{I}}$)	2·674(9)

O(21)–K–O(22)	66·7(2)	O(22)–K–O(13$^{\mathrm{I}}$)	94·4(3)
O(21)–K–O(4)	84·2(3)	O(4)–K–O(11$^{\mathrm{I}}$)	112·2(9)
O(21)–K–O(11$^{\mathrm{I}}$)	163·6(3)	O(4)–K–O(12$^{\mathrm{I}}$)	113·3(3)
O(21)–K–O(12$^{\mathrm{I}}$)	110·3(2)	O(4)–K–O(13$^{\mathrm{I}}$)	178·1(3)
O(21)–K–O(13$^{\mathrm{I}}$)	96·6(3)	O(11$^{\mathrm{I}}$)–K–O(12$^{\mathrm{I}}$)	64·4(2)
O(22)–K–O(4)	84·4(3)	O(11$^{\mathrm{I}}$)–K–O(13$^{\mathrm{I}}$)	67·0(3)
O(22)–K–O(11$^{\mathrm{I}}$)	113·1(2)	O(12$^{\mathrm{I}}$)–K–O(13$^{\mathrm{I}}$)	68·0(2)
O(22)–K–O(12$^{\mathrm{I}}$)	162·0(3)		

(*b*) Cd environment

Cd–O(11)	2·325(9)	Cd–O(22)	2·258(7)
Cd–O(21)	2·247(7)	Cd–O(13)	2·264(7)
Cd–O(12)	2·303(7)	Cd–O(23)	2·302(8)

O(11)–Cd–O(21)	78·7(3)	O(21)–Cd–O(23)	84·2(3)
O(11)–Cd–O(12)	79·2(3)	O(12)–Cd–O(22)	80·1(3)
O(11)–Cd–O(22)	131·5(3)	O(12)–Cd–O(13)	83·0(3)
O(11)–Cd–O(13)	82·4(3)	O(12)–Cd–O(23)	137·4(3)
O(11)–Cd–O(23)	135·5(3)	O(22)–Cd–O(13)	137·2(3)
O(21)–Cd–O(12)	134·2(3)	O(22)–Cd–O(23)	86·8(3)
O(21)–Cd–O(22)	85·4(3)	O(13)–Cd–O(23)	79·6(3)
O(21)–Cd–O(13)	132·4(3)		

Cd–O(11)–K$^{\mathrm{II}}$	89·4(3)	Cd–O(22)–K	103·3(2)
Cd–O(21)–K	102·2(3)	Cd–O(13)–K$^{\mathrm{II}}$	94·0(3)
Cd–O(12)–K$^{\mathrm{II}}$	91·5(2)		

(*c*) The ligands [in order, ligands (1)—(3)]

	(1)	(2)	(3)
O(1)–C(2)	1·24(1)	1·24(1)	1·25(1)
C(2)–C(1)	1·53(2)	1·53(2)	1·56(1)
C(2)–C(3)	1·42(2)	1·42(2)	1·41(2)
C(3)–C(4)	14·2(2)	1·42(2)	1·40(2)
C(4)–C(5)	1·56(2)	1·52(2)	1·54(2)
C(4)–O(2)	1·27(1)	1·26(1)	1·29(1)
O(1) · · · O(2)	2·90(1)	2·94(1)	2·92(1)

	(1)	(2)	(3)
Cd–O(1)–C(2)	131·0(8)	130·3(7)	130·9(7)
O(1)–C(2)–C(1)	117·8(9)	117·8(10)	117·1(11)
O(1)–C(2)–C(3)	126·7(11)	126·8(10)	127·1(10)
C(1)–C(2)–C(3)	115·5(10)	115·4(9)	115·8(11)
C(2)–C(3)–C(4)	123·9(10)	124·6(9)	126·7(11)
C(3)–C(4)–C(5)	117·0(10)	116·9(10)	119·4(11)
C(3)–C(4)–O(2)	127·4(10)	127·6(10)	125·0(12)
C(5)–C(4)–O(2)	115·5(11)	115·4(10)	115·5(10)
C(4)–O(2)–Cd	131·7(7)	130·2(7)	130·1(7)

Roman numeral superscripts refer to the following equivalent positions, relative to the reference molecule at *x*, *y*, *z*:

I $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$ II $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$

the cell diagram suggests that the anomaly may result from the intimate interaction of the rather small cation with the five of the six ligand oxygen atoms in the immediate co-ordination geometry of the cadmium. Structure determinations of complex species with small ions of opposite charge embedded in a lattice with a limited quantity of solvent are rare. Of four species formally similar to the present example [*i.e.* $K_x(ML_3)_y,zH_2O$] reported recently,[8] $K[Sn(HCO_2)_3]$ does not contain bidentate ligands,[8a] in $K[As(o\text{-}C_6H_4O_2)_3],1\frac{1}{2}H_2O$ the potassium co-ordination sphere does not closely correlate with that of the other metal, being considerably occupied by water,[8b] and in $Ag[Fe(C_5H_7O_2)_3][ClO_4],H_2O$ the cation (silver) is itself bonded to the ligand also in an unusual way;[8c] $K_3[Co(HN{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH)_3]$, the only comparable example,[8d] does not have the intimate association between the cation and the metal environment found in the present case, the less electronegative atoms of the ligand being bonded to the metal. This is also true of the structure of the only other $[M(acac)_3]^-$ derivative whose structure has been determined, trisilver dinitratotris(acetylacetonato)niccolate(II) monohydrate.[9] {The structure of the $[Co(acac)_3]^-$ species has been determined as the salt of the $[Bu_4N]^+$ cation;[10] both these Ni$^{\mathrm{II}}$ and Co$^{\mathrm{II}}$ derivatives appear to have normal geometries.} †

TABLE 3

Equations of least-squares planes through the ligands in form $pX + qY + rZ = s$ where X, Y, Z are coordinates in Å such that $X = ax + cz\cos\beta$, $Y = by$, and $Z = cz\sin\beta$. σ/Å Is the estimated standard deviation of the defining atoms from the plane. Deviations (Å) of relevant atoms from the plane are given in square brackets

	10^4p	10^4q	10^4r	s	$10^2\sigma$
Ligand (1)	4250	5337	−7311	2·121	5
[O(11) 0·07, O(21) −0·07, C(11) −0·05, C(21) 0·01, C(31) 0·01, C(41) −0·01, C(51) 0·04, Cd 0·08]					
Ligand (2)	8485	4774	2285	7·278	5
[O(12) 0·05, O(22) −0·06, C(12) −0·07, C(22) 0·03, C(32) 0·05, C(42) −0·01, C(52) 0·02, Cd −0·13]					
Ligand (3)	3800	−0253	9246	4·663	1
[O(13) −0·01, O(23) 0·01, C(13) 0·01, C(23) −0·01, C(33) −0·01, C(43) 0·01, C(53) −0·01, Cd 0·18]					

Angles (°) between planes: (1)–(2) 63·4, (1)–(3) 58·1, (2)–(3) 58·6

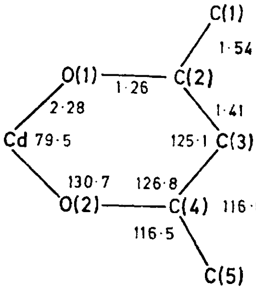

FIGURE 2 Mean geometry (distances in Å, angles in °) of the ligand systems and associated cadmium atom, together with the atom numbering system in the ligands

The metal–oxygen distances of the present complex anion lie within the usual range; the ligand geometry is effectively C_{2v} in symmetry, unlike $[Cd(acac)_2]$ in which there is a pronounced distortion due to one of the oxygen

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† *Note added in proof*: A recent report[11] of the crystal structure of $Rb_2[Na(hfac)_3]$ (hfac$^-$ = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) also describes the occurrence of three acetylacetonate-type ligands involved in trigonal prismatic co-ordination about the central metal atom. As in the present case, an intimate interaction occurs between the ligand donor atoms of the complex anion and the adjacent cations.

[8] (*a*) A. Jelen and O. Lindqvist, *Acta Chem. Scand.*, 1969, **23**, 3071; (*b*) A. Kobayashi, T. Ho, F. Marumo, and V. Saito, *Acta Cryst.*, 1972, **B28**, 3446; (*c*) L. R. Nassimbeni and M. M. Thackeray, *Acta Cryst.*, 1974, **B30**, 1072; (*d*) P. J. M. W. L. Birker, J. M. M. Smits, J. J. Bour, and P. T. Beurskens, *Rec. Trav. chim.*, 1973, **92**, 1240.

[9] W. H. Watson and C. T. Lin, *Inorg. Chem.*, 1966, **5**, 1074.

[10] B. Granoff, *Diss. Abs.*, 1967, **B27**, 4341.

[11] D. E. Fenton, C. Nave, and M. R. Truter, *J.C.S. Dalton*, 1973, 2188.

atoms being bridging. Mean ligand geometry is shown in Figure 2.

The present result suggests a number of interesting possibilities. If it can be shown by structure determination of other salts of the type M[Cd(acac)$_3$],H$_2$O that the cation is a dominant electrostatic influence in determining the effective D_{3h} symmetry about the cadmium, then it should be possible to extend the present work to complexes of the unfilled *d*-shell transition-metal(II) ions. It may then be possible to obtain a unique series of tris-(acetylacetonato)metallate(II) anions with the novel symmetry and so determine the properties of the consequent unusual electronic ground-state behaviour.

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