

on the Ni^{2+} are neutral, does not show this distortion. The distances are 2.07, 2.02, 2.04 Å and 2.04, 2.03, 2.05 Å for the three independent distances around the two different Ni ions, the distance to the water given last in each trio.

The $\text{Mg}(\text{DPP})_2$ complex differs from the other octahedral complexes in that the solvent molecules are *cis* to one another on the coordination octahedron (Fig. 1). The solvent molecules are all *trans* to one another in the other monomeric complexes. The *cis* arrangement is not required by the space-group symmetry, which could just as easily accommodate the *trans* configuration, but, while all the other distorted octahedra could be described as tetragonally distorted, the octahedron in $\text{Mg}(\text{DPP})_2(\text{DMF})_2$ cannot.

Bullen explains the distortion of the $\text{Co}(\text{AA})_2(\text{H}_2\text{O})_2$ octahedron in terms of combination of the available *d* orbitals of the Co. The same explanation could hold for the Ni complex as well, but not for the magnesium complexes, since Mg^{2+} has no available *d* orbitals. Morosin concludes in his paper that the effect is due to packing forces rather than electronic ones since the diaquo Mg complex shows the same distortion as the Co and Ni complexes. The appearance of the same effect in $\text{Mg}(\text{DPP})_2(\text{DMF})_2$ and in other structures noted above, where the packing and coordination environments are radically different, as well as the absence of any effect in the octahedral nickel acetylacetonate perchlorate complex, leads us to suspect that the effect is primarily electrostatic in origin, with secondary contributions from *d*-orbital hybridization and packing.

We thank Mrs Helena Ruben for her advice and assistance concerning many details of this work.

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Investigations of Alkaline-Earth β -Diketone Complexes. II. The Crystal and Molecular Structure of Bis-(1,3-diphenyl-1,3-propanedionato)calcium Hemioethanolate*

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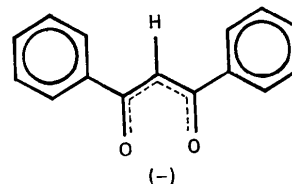
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(Received 29 September 1972; accepted 14 February 1973)

Bis-(1,3-diphenyl-1,3-propanedionato)calcium hemioethanolate, $\text{Ca}[(\text{C}_6\text{H}_5\text{CO})_2\text{CH}]_2(\text{C}_2\text{H}_5\text{OH})_{1/2}$, crystallizes in space group $P\bar{1}$ with $a = 15.247$ (1), $b = 13.555$ (1), $c = 14.097$ (1) Å, $\alpha = 74.64$ (1), $\beta = 95.97$ (1), $\gamma = 113.59$ (1)°, $Z = 4$, at 23°C. The density calculated for two units of empirical formula $\text{Ca}_2\text{C}_{62}\text{H}_{50}\text{O}_9$ in the unit cell is $d_c = 1.32$ g cm⁻³. The structure was solved by direct methods and refined to a conventional *R* value of 0.040 for 4503 reflections collected by counter methods. The complex consists of a centrosymmetric cluster containing four calcium atoms, two with six oxygen neighbors each and two with seven.

Introduction

Alkaline-earth metal cations form complexes with the anion of 1,3-diphenyl-1,3-propanedione:



* Work performed under the auspices of the U.S. Atomic Energy Commission.

Table 1 (cont.)

OBSERVED STRUCTURE FACTORS FOR C₄₀H₂₂O₁₂ · 1/2 C₂₈H₂₀O₈ (CONTINUED)
PAGE 3

h	k	l	F _o	h	k	l	F _o	h	k	l	F _o	h	k	l	F _o
1	0	0	100	1	0	0	100	1	0	0	100	1	0	0	100
1	1	0	115	1	1	0	115	1	1	0	115	1	1	0	115
1	2	0	130	1	2	0	130	1	2	0	130	1	2	0	130
1	3	0	145	1	3	0	145	1	3	0	145	1	3	0	145
1	4	0	160	1	4	0	160	1	4	0	160	1	4	0	160
1	5	0	175	1	5	0	175	1	5	0	175	1	5	0	175
1	6	0	190	1	6	0	190	1	6	0	190	1	6	0	190
1	7	0	205	1	7	0	205	1	7	0	205	1	7	0	205
1	8	0	220	1	8	0	220	1	8	0	220	1	8	0	220
1	9	0	235	1	9	0	235	1	9	0	235	1	9	0	235
1	10	0	250	1	10	0	250	1	10	0	250	1	10	0	250
1	11	0	265	1	11	0	265	1	11	0	265	1	11	0	265
1	12	0	280	1	12	0	280	1	12	0	280	1	12	0	280
1	13	0	295	1	13	0	295	1	13	0	295	1	13	0	295
1	14	0	310	1	14	0	310	1	14	0	310	1	14	0	310
1	15	0	325	1	15	0	325	1	15	0	325	1	15	0	325
1	16	0	340	1	16	0	340	1	16	0	340	1	16	0	340
1	17	0	355	1	17	0	355	1	17	0	355	1	17	0	355
1	18	0	370	1	18	0	370	1	18	0	370	1	18	0	370
1	19	0	385	1	19	0	385	1	19	0	385	1	19	0	385
1	20	0	400	1	20	0	400	1	20	0	400	1	20	0	400
1	21	0	415	1	21	0	415	1	21	0	415	1	21	0	415
1	22	0	430	1	22	0	430	1	22	0	430	1	22	0	430
1	23	0	445	1	23	0	445	1	23	0	445	1	23	0	445
1	24	0	460	1	24	0	460	1	24	0	460	1	24	0	460
1	25	0	475	1	25	0	475	1	25	0	475	1	25	0	475
1	26	0	490	1	26	0	490	1	26	0	490	1	26	0	490
1	27	0	505	1	27	0	505	1	27	0	505	1	27	0	505
1	28	0	520	1	28	0	520	1	28	0	520	1	28	0	520
1	29	0	535	1	29	0	535	1	29	0	535	1	29	0	535
1	30	0	550	1	30	0	550	1	30	0	550	1	30	0	550
1	31	0	565	1	31	0	565	1	31	0	565	1	31	0	565
1	32	0	580	1	32	0	580	1	32	0	580	1	32	0	580
1	33	0	595	1	33	0	595	1	33	0	595	1	33	0	595
1	34	0	610	1	34	0	610	1	34	0	610	1	34	0	610
1	35	0	625	1	35	0	625	1	35	0	625	1	35	0	625
1	36	0	640	1	36	0	640	1	36	0	640	1	36	0	640
1	37	0	655	1	37	0	655	1	37	0	655	1	37	0	655
1	38	0	670	1	38	0	670	1	38	0	670	1	38	0	670
1	39	0	685	1	39	0	685	1	39	0	685	1	39	0	685
1	40	0	700	1	40	0	700	1	40	0	700	1	40	0	700
1	41	0	715	1	41	0	715	1	41	0	715	1	41	0	715
1	42	0	730	1	42	0	730	1	42	0	730	1	42	0	730
1	43	0	745	1	43	0	745	1	43	0	745	1	43	0	745
1	44	0	760	1	44	0	760	1	44	0	760	1	44	0	760
1	45	0	775	1	45	0	775	1	45	0	775	1	45	0	775
1	46	0	790	1	46	0	790	1	46	0	790	1	46	0	790
1	47	0	805	1	47	0	805	1	47	0	805	1	47	0	805
1	48	0	820	1	48	0	820	1	48	0	820	1	48	0	820
1	49	0	835	1	49	0	835	1	49	0	835	1	49	0	835
1	50	0	850	1	50	0	850	1	50	0	850	1	50	0	850
1	51	0	865	1	51	0	865	1	51	0	865	1	51	0	865
1	52	0	880	1	52	0	880	1	52	0	880	1	52	0	880
1	53	0	895	1	53	0	895	1	53	0	895	1	53	0	895
1	54	0	910	1	54	0	910	1	54	0	910	1	54	0	910
1	55	0	925	1	55	0	925	1	55	0	925	1	55	0	925
1	56	0	940	1	56	0	940	1	56	0	940	1	56	0	940
1	57	0	955	1	57	0	955	1	57	0	955	1	57	0	955
1	58	0	970	1	58	0	970	1	58	0	970	1	58	0	970
1	59	0	985	1	59	0	985	1	59	0	985	1	59	0	985
1	60	0	1000	1	60	0	1000	1	60	0	1000	1	60	0	1000

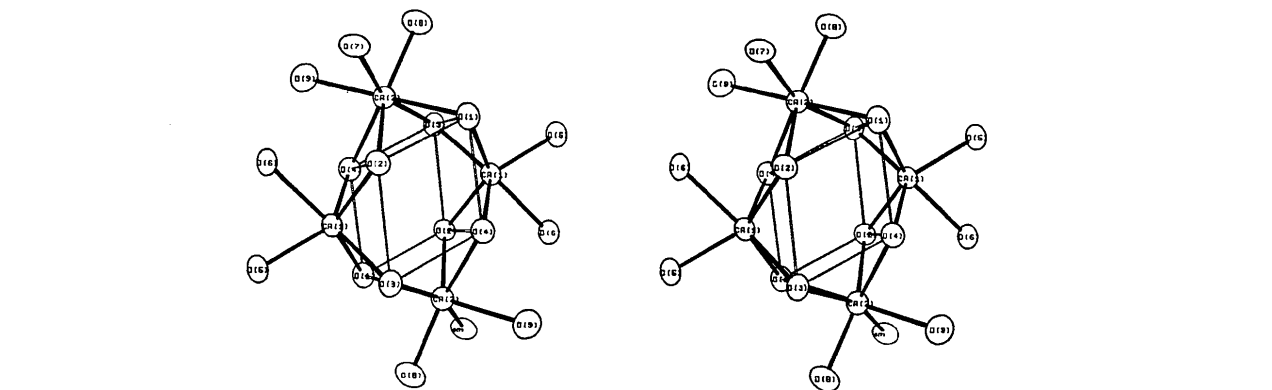


Fig. 1. Stereoscopic view of the neighbors of the Ca ions. The center of symmetry at $0, \frac{1}{2}, \frac{1}{2}$ is in the center of the cluster. Thermal ellipsoids have been scaled to include 50% probability.

were obtained by slow evaporation of a warm chloroform solution.

The crystals were mounted on glass fibers. Precession photographs indicated a triclinic unit cell, and yielded preliminary cell dimensions. Another crystal was mounted on a Picker/Nuclear four-circle automatic diffractometer. Twelve high-angle reflections were carefully centered using monochromatized Cu $K\alpha_1$ radiation ($\lambda = 1.54051 \text{ \AA}$) at 23°C . The cell dimensions, determined by refining the 2θ measurements, were $a = 15.247(1)$, $b = 13.555(1)$, $c = 14.097(3) \text{ \AA}$, $\alpha = 74.64(1)$, $\beta = 95.97(1)$, $\gamma = 113.59(1)^\circ$. The calculated density of the compound based on a cell volume of 2576 \AA^3 , and the formula $\text{Ca}(\text{DPP})_2$, is $d_c = 0.314Z$. Attempts to measure the density failed because a solution could not be found which neither dissolved the crystals nor caused them to decompose, but observations indicated that the most reasonable value of Z was 4. This assumption was confirmed by the refinement of the structure, and the density based on the actual composition is $d_c = 1.32 \text{ g cm}^{-3}$.

A more or less spherical crystal approximately 0.12 mm in radius was used for data collection with monochromatized ($2\theta_m = 26.42^\circ$) Cu $K\alpha$ radiation and a θ - 2θ scan technique. The peaks were scanned at a rate of $1^\circ/\text{min}$ from 1.0° below the calculated $K\alpha_1$ position to 1.0° above the calculated $K\alpha_2$ position. Backgrounds were counted for 10 sec at positions offset by 0.5° from each end of the scan (all angles 2θ). The hemisphere of data $+h, \pm k, \pm l$ was collected for $2\theta = 0$ - 100° ($\sin \theta/\lambda < 0.500$). Three reflections, 400, 030 and 003, were measured after each 100 reflections to monitor crystal decay. In the entire experiment 5824 reflections were measured, including remeasurements in connection with the decay correction. The standards showed a gradual fall in relative intensity from 1.00 to 0.942 over the first 3973 reflections, then a sharp drop to a relative intensity of 0.820 between reflections 3973 and 3974 that was caused by a malfunction in the equipment. The exact location of the change was determined

by remeasuring the reflections in that region. The data were processed as previously described (Hollander, Templeton & Zalkin, 1973a) to give 5294 unique re-

Table 3. Final parameters for hydrogen atoms

Parameters without standard deviations were not refined. The form of the temperature factor is $T = \exp(-B \sin^2 \theta/\lambda^2)$.

	x	y	z	$B(\text{\AA}^2)$
H(01)	-.134(2)	.150(3)	.777(2)	3.8(7)
H(02)	-.222(2)	-.028(2)	.869(2)	4.4(8)
H(03)	-.211(2)	-.182(3)	.827(2)	5.8(9)
H(04)	-.108(2)	-.145(3)	.702(2)	5.4(9)
H(05)	-.028(2)	.024(3)	.611(2)	5.3(9)
H(6)	.093(2)	.199(2)	.589(2)	3.1(7)
H(07)	.159(2)	.231(3)	.439(2)	3.9(7)
H(08)	.293(2)	.255(3)	.356(2)	5.9(9)
H(09)	.428(3)	.425(3)	.347(3)	7.4(11)
H(10)	.432(3)	.546(3)	.434(2)	5.5(10)
H(11)	.303(2)	.524(3)	.516(2)	4.9(8)
H(12)	.242(3)	.620(3)	.253(3)	7.0(10)
H(13)	.365(4)	.667(5)	.150(4)	12.3(18)
H(14)	.362(3)	.540(4)	.056(3)	9.0(13)
H(15)	.226(3)	.388(3)	.057(3)	6.5(11)
H(16)	.104(3)	.336(4)	.162(3)	9.2(13)
H(17)	.020(2)	.290(3)	.283(2)	4.4(8)
H(18)	-.078(3)	.135(4)	.297(3)	9.4(14)
H(19)	-.185(3)	-.043(4)	.335(3)	9.3(14)
H(20)	-.292(2)	-.116(3)	.455(2)	4.0(7)
H(21)	-.296(3)	.003(3)	.554(3)	7.6(11)
H(22)	-.206(3)	.179(4)	.506(3)	8.8(13)
H(23)	.679(3)	.137(3)	.809(2)	5.1(9)
H(24)	.596(2)	.000(3)	.939(3)	5.0(9)
H(25)	.429(3)	-.116(3)	.925(3)	5.6(9)
H(26)	.363(3)	-.094(3)	.774(3)	6.4(11)
H(27)	.440(2)	.037(3)	.643(3)	5.3(10)
H(28)	.518(2)	.167(2)	.520(2)	3.1(7)
H(29)	.473(2)	.130(3)	.571(2)	3.9(8)
H(30)	.386(3)	.151(3)	.238(2)	6.1(9)
H(31)	.440(3)	.339(3)	.126(3)	5.9(10)
H(32)	.569(3)	.477(3)	.156(3)	7.8(13)
H(33)	.653(2)	.454(2)	.301(2)	3.2(7)
H(34)	-.288(2)	.703(2)	.299(2)	1.9(7)
H(35)	-.416(3)	.737(3)	.307(3)	7.5(12)
H(36)	-.475(3)	.796(3)	.157(3)	6.3(11)
H(37)	-.419(3)	.796(3)	.007(3)	7.4(11)
H(38)	-.291(2)	.751(2)	.016(2)	3.8(8)
H(39)	-.127(2)	.798(2)	.050(2)	2.6(7)
H(40)	-.023(2)	.915(3)	-.058(2)	4.9(8)
H(41)	.102(3)	1.039(3)	-.159(3)	7.4(11)
H(42)	.249(3)	1.004(3)	-.142(3)	7.5(12)
H(43)	.262(3)	.962(3)	-.023(3)	7.6(13)
H(44)	.136(2)	.743(2)	.070(2)	3.1(7)
H(45)	.779(5)	.375(6)	.281(5)	15.6(28)
H(46)	.717(3)	.312(4)	.136(3)	10.6(14)
H(47)	.7497	.4344	.1232	12.000
H(48)	.8860	.3438	.113	14.000
H(49)	.930(4)	.469(5)	.089(5)	15.000
H(50)	.841(4)	.394(4)	.015(4)	12.8(16)

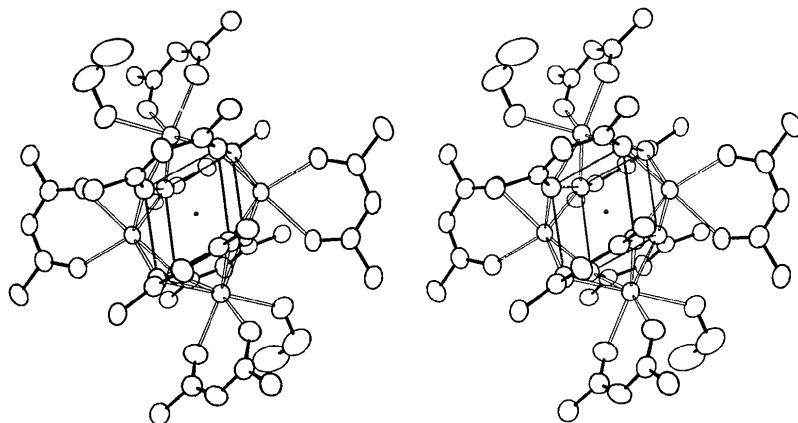


Fig. 2. Stereoscopic view of the complex cluster. Hydrogen atoms and phenyl carbon atoms that are not attached directly to the diketone have been omitted. View direction and scaling of the thermal ellipsoids are the same as in Fig. 1.

flections of which 4504 had $F^2 > \sigma(F^2)$. No correction was made for absorption. With $\mu = 23 \text{ cm}^{-1}$, a 33% variation in diameters would result in a 15% variation in transmission factors, and the crystal is believed to have been more nearly spherical than that.

The atomic scattering factors of Doyle & Turner (1968) were used for Ca^{2+} , O and C, along with the real and imaginary dispersion terms of Cromer & Liberman (1970). The spherical scattering factors of Stewart, Davidson & Simpson (1965) were used for the hydrogen atoms.

The method of calculation of $\sigma(F)$ and the weights in least squares, a few other experimental details, and the computer programs used are given in the preceding paper (Hollander *et al.*, 1973a). The factor p , used to reduce the weight of strong reflections, was 0.0 through most of the refinement but 0.05 in the last cycles.

Structure determination and refinement

We assumed that the space group is $P\bar{1}$, and this assumption is confirmed by the solution and successful refinement of the structure. Phases were assigned to the 333 E values (normalized structure factors) greater than 2.00 using Long's (1965) program. After some difficulty, an E map was obtained which revealed two large peaks and a number of smaller peaks in configurations identifiable as portions of DPP molecules. Positional and isotropic thermal parameters for the 41 atoms found on the E -map were then refined by full-matrix least-squares analysis. Two cycles of refinement brought $R_1 = \sum |\Delta F| / \sum |F_o|$ to 0.41, and the generated signs of the F 's were used to phase a Fourier map. This map showed 69 peaks and one shoulder in chemically reasonable positions for the expected formulation of $\text{Ca}(\text{DPP})_2$ with two Ca atoms in the asymmetric unit. The seventy atoms were refined with isotropic temperature parameters for three cycles, and for three additional cycles in which the two Ca atoms and eight O atoms were allowed anisotropic thermal parameters, to $R_1 = 0.21$. A difference Fourier showed three major peaks with heights of 6, 3 and $3 \text{ e} \text{ \AA}^{-3}$, and no other peaks as high as $1 \text{ e} \text{ \AA}^{-3}$. The three peaks were close together, and the largest peak was 2.41 \AA from Ca(1). We correctly assumed that the peaks represented an ethanol molecule coordinated to the Ca. The atoms of the ethanol molecule were included in the least squares with isotropic thermal parameters, together with the calculated positions of the 44 hydrogen atoms on the DPP ligands. Each hydrogen atom was given an isotropic thermal parameter equal to the average thermal parameter of the ring it was bound to, and neither its position nor thermal parameter was allowed to change. The ethanol atoms refined well, and R_1 was reduced to 0.09.

For further refinement the atoms were divided into blocks because of computer limitations. With non-hydrogen atoms anisotropic and hydrogen atoms isotropic, refinement in three blocks reduced R_1 to 0.048.

Availability of a larger computer allowed further refinement in two blocks, the first containing the two 'inner' DPP molecules and the second containing the two 'outer' DPP molecules and the ethanol. The overall scale factor and the two Ca atoms were refined with each block.

Certain H atoms behaved poorly and some of their parameters were fixed to allow convergence (see Table 3). Two final cycles of each block brought the shifts of all parameters to less than 20% of their standard deviations and most to less than 10%. The final R_1 was 0.040 for 4503 reflections, and $R_2 = [\sum w(\Delta F)^2 / \sum w F_o^2]^{1/2}$ was 0.043. The standard deviation of an observation of unit weight was 1.14. Examination of the data revealed no evidence of secondary extinction effects. A Fourier synthesis of ΔF showed no peak larger than $0.3 \text{ e} \text{ \AA}^{-3}$.

The observed structure factors, their standard deviations and the differences between observed and calculated structure factors are given in Table 1. The final parameters of the atoms are given in Tables 2 and 3.

Results and discussion

The complex consists of clusters of composition $[\text{Ca}_2(\text{DPP})_4(\text{C}_2\text{H}_5\text{OH})_2]$ around the crystallographic in-

Table 4. Distances (\AA) in the coordination cluster

Ca(1)-O(1)	2.353 (2)	O(2)-O(4)	2.995 (3)†
Ca(1)-O(2)	2.333 (2)	O(3)-O(4)	2.804 (3)*†
Ca(1)-O(3)	2.358 (2)	O(1)-O(5)	3.410†
Ca(1)-O(4)	2.353 (2)	O(1)-O(8)	3.111
Ca(1)-O(5)	2.256 (2)	O(2)-O(4)	3.333 (3)
Ca(1)-O(6)	2.395 (2)	O(2)-O(6)	3.010
Ca(2)-O(1)	2.416 (2)	O(2)-O(7)	2.999
Ca(2)-O(2)	2.411 (2)	O(3)-O(5)	3.526
Ca(2)-O(3)	2.436 (2)	O(3)-O(8)	3.205
Ca(2)-O(4)	2.508 (2)	O(4)-O(6)	2.943
Ca(2)-O(7)	2.308 (2)	O(4)-O(9)	2.851
Ca(2)-O(8)	2.266 (2)	O(5)-O(6)	2.801 (3)*
Ca(2)-O(9)	2.408 (2)	O(6)-O(9)	2.941 (4)
O(1)-O(2)	2.772 (3)*†	O(7)-O(8)	2.803 (3)*
O(1)-O(3)	2.807 (3)†	O(7)-O(9)	3.054 (3)
O(1)-O(4)	3.037 (3)†	O(8)-O(9)	3.491 (4)
O(2)-O(3)	3.102 (3)†		

* 'Bite' of the ligand.

† Edges of central parallelepiped.

‡ Absence of a standard deviation indicates that atoms were refined in two different blocks of least-squares. Standard deviations are probably the same as others, $\pm 0.003 \text{ \AA}$.

Table 5. Angles ($^\circ$) between planes of phenyl rings and diketone moieties

DPP	Phenyl 1 to diketone	Phenyl 2 to diketone	Phenyl 1 to Phenyl 2
1	21.1	31.0	33.8
2	13.4	7.8	16.1
3	5.6	34.0	28.6
4	36.6	12.9	47.6

Table 6. Bond distances (Å)

DPP(1)		DPP(2)	
C(1)—C(2)	1.379 (5)	C(16)—C(17)	1.385 (6)
C(2)—C(3)	1.376 (5)	C(17)—C(18)	1.350 (7)
C(3)—C(4)	1.367 (5)	C(18)—C(19)	1.367 (7)
C(4)—C(5)	1.391 (5)	C(19)—C(20)	1.378 (6)
C(5)—C(6)	1.388 (4)	C(20)—C(21)	1.379 (5)
C(6)—C(1)	1.381 (4)	C(21)—C(16)	1.364 (5)
C(6)—C(7)	1.496 (4)	C(21)—C(22)	1.500 (4)
C(7)—O(1)	1.285 (3)	C(22)—O(3)	1.280 (3)
C(7)—C(8)	1.387 (4)	C(22)—C(23)	1.391 (4)
C(8)—C(9)	1.397 (4)	C(23)—C(24)	1.403 (4)
C(9)—O(2)	1.283 (3)	C(24)—O(4)	1.277 (3)
C(9)—C(10)	1.496 (4)	C(24)—C(25)	1.502 (4)
C(10)—C(11)	1.377 (4)	C(25)—C(26)	1.379 (5)
C(11)—C(12)	1.368 (5)	C(26)—C(27)	1.384 (6)
C(12)—C(13)	1.365 (6)	C(27)—C(28)	1.349 (6)
C(13)—C(14)	1.368 (6)	C(28)—C(29)	1.348 (5)
C(14)—C(15)	1.387 (5)	C(29)—C(30)	1.373 (5)
C(15)—C(10)	1.386 (4)	C(30)—C(25)	1.368 (5)
C(1)—H(1)	0.92 (3)	C(16)—H(12)	0.97 (4)
C(2)—H(2)	0.95 (3)	C(17)—H(13)	0.92 (5)
C(3)—H(3)	0.97 (3)	C(18)—H(14)	0.90 (5)
C(4)—H(4)	0.92 (3)	C(19)—H(15)	0.93 (4)
C(5)—H(5)	0.95 (3)	C(20)—H(16)	1.00 (4)
C(8)—H(6)	0.93 (3)	C(23)—H(17)	0.95 (3)
C(11)—H(7)	1.00 (3)	C(26)—H(18)	0.95 (4)
C(12)—H(8)	1.01 (4)	C(27)—H(19)	0.86 (4)
C(13)—H(9)	0.91 (4)	C(28)—H(20)	0.94 (3)
C(14)—H(10)	0.88 (3)	C(29)—H(21)	1.00 (4)
C(15)—H(11)	0.94 (3)	C(30)—H(22)	0.90 (4)
DPP(3)		DPP(4)	
C(31)—C(32)	1.389 (5)	C(46)—C(47)	1.384 (5)
C(32)—C(33)	1.367 (6)	C(47)—C(48)	1.373 (5)
C(33)—C(34)	1.364 (6)	C(48)—C(49)	1.365 (6)
C(34)—C(35)	1.378 (5)	C(49)—C(50)	1.373 (5)
C(35)—C(36)	1.393 (5)	C(50)—C(51)	1.373 (4)
C(36)—C(31)	1.381 (5)	C(51)—C(46)	1.373 (5)
C(36)—C(37)	1.506 (4)	C(51)—C(52)	1.507 (4)
C(37)—O(5)	1.272 (3)	C(52)—O(7)	1.263 (3)
C(37)—C(38)	1.399 (4)	C(52)—C(53)	1.393 (4)
C(38)—C(39)	1.399 (4)	C(53)—C(54)	1.395 (4)
C(39)—O(6)	1.262 (3)	C(54)—O(8)	1.261 (3)
C(39)—C(40)	1.502 (4)	C(54)—C(55)	1.506 (4)
C(40)—C(41)	1.381 (4)	C(55)—C(56)	1.372 (5)
C(41)—C(42)	1.386 (6)	C(56)—C(57)	1.383 (5)
C(42)—C(43)	1.354 (6)	C(57)—C(58)	1.353 (6)
C(43)—C(44)	1.374 (6)	C(58)—C(59)	1.365 (6)
C(44)—C(45)	1.388 (5)	C(59)—C(60)	1.380 (5)
C(45)—C(40)	1.382 (5)	C(60)—C(55)	1.383 (5)
C(31)—H(23)	0.98 (3)	C(46)—H(34)	0.79 (3)
C(32)—H(24)	0.93 (3)	C(47)—H(35)	0.94 (4)
C(33)—H(25)	0.97 (4)	C(48)—H(36)	0.84 (4)
C(34)—H(26)	0.92 (4)	C(49)—H(37)	0.98 (4)
C(35)—H(27)	0.92 (3)	C(50)—H(38)	0.94 (3)
C(38)—H(28)	0.93 (3)	C(53)—H(39)	0.85 (3)
C(41)—H(29)	0.94 (3)	C(56)—H(40)	1.01 (3)
C(42)—H(30)	0.99 (4)	C(57)—H(41)	1.01 (4)
C(43)—H(31)	0.88 (4)	C(58)—H(42)	0.92 (4)
C(44)—H(32)	0.92 (4)	C(59)—H(43)	0.92 (4)
C(45)—H(33)	0.96 (3)	C(60)—H(44)	0.87 (3)
Ethanol			
O(9)—C(61)	1.390 (5)		
C(61)—C(62)	1.464 (7)		
O(9)—H(45)	0.68 (6)		
C(61)—H(46)	1.12 (5)		
C(61)—H(47)*	1.00		
C(62)—H(48)*	1.00		
C(62)—H(49)	1.04 (6)		
C(62)—H(50)	1.09 (6)		

* Hydrogen atom restrained to a fixed position in the least squares refinements.

version center at $0, \frac{1}{2}, \frac{1}{2}$. There is only one such cluster per unit cell, and its neighbors are related to it by unit cell translations. There are no contact distances of less than 3.50 Å between the non-hydrogen atoms of different clusters. Interatomic distances within the cluster are given in Table 4.

Each calcium ion has either six or seven oxygen neighbors (Fig. 1). Eight oxygen atoms which are each shared by two calcium ions are at the corners of a slightly distorted parallelepiped in the center of the complex, while the other ten oxygen atoms are neighbors of only one calcium each. Fig. 2 shows the arrangement of the organic ligands in the complex.

The Ca—O distances average 2.37 Å, close to the sum of the crystal radii (Pauling, 1960), 2.39 Å. The range is from 2.256 (2) Å to 2.508 (2) Å. In general these distances are shorter when one or both of the atoms involved have a lower coordination number, but Ca(1)—O(6) = 2.395 Å is an exception.

The DPP(*n*) molecules themselves can be analyzed in terms of three planes each, phenyl 1 and phenyl 2 (1–6 and 10–15; Fig. 3) and the diketone plane (7–9 and O's 1 and 2; Fig. 3). Atoms of the phenyl groups deviate by no more than five standard deviations from the respective plane, and most of them are within three standard deviations. The diketone atoms of DPP(2) and DPP(3) are within six standard deviations of planarity, but the diketone portions of DPP(1) and DPP(4) are significantly twisted and are only planar to 15 standard deviations. The phenyl groups are rotated with respect to the diketone planes by angles ranging from 5.6 to 36.6° (Table 5). One assumes that this rotation is due to packing forces.

Bond distances in the DPP ligands and the ethanol are shown in Table 6. The averages of various types of bond are in reasonable agreement with literature values. There is a statistically (but perhaps not chemically) significant difference in the C—O bond lengths between those involving bridging oxygen atoms and those involving non-bridging oxygens. The average for the former, 1.281 (2) Å, is slightly longer than the average for the latter, 1.264 (3) Å. The phenyl C—C bonds also show a statistically significant variation. The bonds to

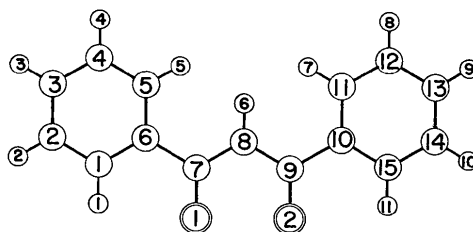


Fig. 3. Generalized numbering system for DPP ligands. Carbons are large single circles, oxygens are large double circles and hydrogens are small single circles. Numbering shown is for DPP(1); for successive DPP molecules add 2 to the oxygen numbers, 15 to the carbon numbers and 11 to the hydrogen numbers.

the *para* carbon average 1.363 (2) Å compared to the averages of the *ortho-meta* bonds [1.382 (2) Å] and the bonds to the carbon adjacent to the diketone [1.379 (3) Å]. The average of all C-H bonds in the DPP molecules is 0.94 Å with a spread of ± 0.09 Å.

The bond angles in the ligands are normal for complexed DPP molecules (Zalkin, Templeton & Karraker, 1969; Hollander, Templeton & Zalkin, 1973*a, b*). The diketone ring is spread, with O-C-C and C-C-C bond angles of about 125°, to give the ligand a bigger 'bite', and the interior angle in the phenyl ring at the juncture to the diketone is reduced from 120° to $\sim 118^\circ$.

The C-O and C-C bond distances in the ethanol appear greatly shortened, probably due to the very large amounts of anisotropic thermal motion (Fig. 2, Table 2).

Acta Cryst. (1973). B29, 1303

Investigations of Alkaline-Earth β -Diketone Complexes. III. The Crystal and Molecular Structure of Bis-(1,3-diphenyl-1,3-propanedionato)strontium Hemiacetate*

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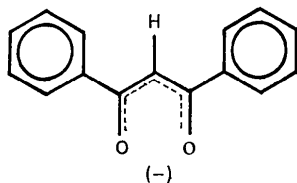
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(Received 29 September 1972; accepted 14 February 1973)

The crystals of bis-(1,3-diphenyl-1,3-propanedionato)strontium hemiacetate are triclinic, space group $P\bar{1}$, with $a = 13.759$ (50), $b = 14.182$ (10), $c = 16.031$ (20) Å, $\alpha = 107.57$ (3), $\beta = 90.36$ (20), $\gamma = 113.07$ (20)° at 23°C. The calculated density for two units of empirical formula $\text{Sr}_2\text{C}_{63}\text{H}_{50}\text{O}_9$ in the unit cell is 1.38 g cm^{-3} . X-ray diffraction measurements were made of 2204 independent reflections from a single crystal by θ - 2θ scans with a scintillation counter and monochromatized Mo $K\alpha$ radiation. The non-hydrogen atoms were found by Fourier methods and refined by least-squares methods to $R = 0.088$ for 1561 reflections with $F^2 > \sigma(F^2)$. Hydrogen atoms were not located. The topology of the complex is similar to that of the corresponding $\text{Ca}(\text{DPP})_2$ hemioacetate, consisting of a centrosymmetric cluster containing four strontium ions, but the packing is such that the two crystals are not isomorphous. These two compounds are compared with other polymeric β -diketone complexes.

Introduction

Alkaline-earth metal cations form complexes with the anion of 1,3-diphenyl-1,3-propanedione:



This paper reports the structure of $\text{Sr}(\text{DPP})_2$ hemiacetate. The complex forms tetrameric polymers of

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the same general configuration as those found for the DPP complex of calcium (Hollander, Templeton & Zalkin, 1973*a*). However, the solvent molecule included in the Sr complex is acetone, rather than the ethanol of the Ca complex and there are differences in the details of the polymer shape. Thus, despite the fact that the general forms of the complexes are similar and the space group ($P\bar{1}$) the same, the structures are not isomorphous and the unit cells cannot be brought into congruence.

Experimental procedure

The complex was synthesized using a modification of the method of Hammond, Nonhebel & Wu (1963). Strontium nitrate was dissolved in a small amount of water, and ethanol added until precipitation was just

* Work done under the auspices of the U.S. Atomic Energy Commission.