

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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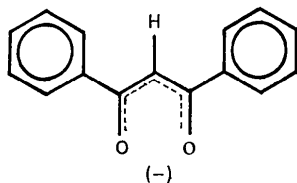
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(Received 29 September 1972; accepted 14 February 1973)

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

- #### References
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891-1898.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390-397.
 HOLLANDER, F. J., TEMPLETON, D. H. & ZALKIN, A. (1973*a*). *Acta Cryst.* **B29**, 1289-1295.
 HOLLANDER, F. J., TEMPLETON, D. H. & ZALKIN, A. (1973*b*). *Acta Cryst.* **B29**, 1303-1308.
 LONG, R. E. (1965). Ph.D. Thesis, Univ. of California, Los Angeles, California.
 PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
 ZALKIN, A., TEMPLETON, D. H. & KARRAKER, D. G. (1969). *Inorg. Chem.* **8**, 2680-2684.

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.

observed. This solution was added to an ethanolic solution of 1,3-diphenyl-1,3-propanedione (HDPP), and a strong aqueous $\text{NH}_3/\text{NH}_4\text{Cl}$, pH 10, buffer was added to the mixture. A whitish precipitate [probably either $\text{Sr}(\text{NO}_3)_2$ or HDPP] immediately formed, and the mixture was refluxed for an hour with stirring. Heating caused the precipitate to dissolve, and cooling yielded a very pale yellow crystalline precipitate which was filtered and dried in air.

Attempts to recrystallize the compound generally yielded a viscous oil, but finally a few crystals were obtained by very slow evaporation of an ethanol solution containing a small amount of acetone. Only one of these was good enough for crystallographic study.

This crystal, a thin plate of approximate dimensions $0.03 \times 0.17 \times 0.32$ mm, was affixed to a glass fiber. Precession photographs indicated a triclinic unit cell. The crystal was mounted on a Picker/Nuclear four-circle automatic diffractometer. Twelve reflections in the range $20^\circ \leq 2\theta \leq 25^\circ$ were carefully centered in χ , ω and 2θ using Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$). The cell dimensions determined from these angles by least squares were $a = 13.715$, $b = 14.189$, $c = 16.050 \text{ \AA}$, $\alpha = 107.60$, $\beta = 90.21$, $\gamma = 113.19^\circ$. The cell dimensions were determined again by the same method after collection of intensity data and were found to have changed by as much as five standard deviations. The second set of cell parameters, $a = 13.759(10)$, $b = 14.182(9)$, $c = 16.031(9) \text{ \AA}$, $\alpha = 107.57(3)$, $\beta = 90.36(3)$, $\gamma = 113.07(3)^\circ$ at 23°C , where the standard deviations are those estimated by least-squares methods, were used throughout the structure analysis. We estimate respectively 0.05, 0.01, 0.02 \AA , 0.30, 0.2, and 0.2° as standard deviations which reflect the variation of parameters during the experiment. The calculated density for $Z = 4$ is 1.38 g cm^{-3} . The density was not measured directly for lack of sufficient material. A preliminary survey revealed a rapid fall-off of intensity with increasing 2θ , there being few appreciable intensities beyond $2\theta = 25^\circ$ and none beyond $2\theta = 30^\circ$.

Intensities were measured by a θ - 2θ scan technique

with graphite monochromatized ($2\theta_m = 11.80^\circ$) Mo $K\alpha$ radiation. Peaks were scanned 0.7° below the predicted $K\alpha_1$ position to 0.7° above the predicted $K\alpha_2$ position at a scan speed of $1^\circ/\text{min}$. Backgrounds were counted for 10 sec at positions offset 0.3° from each end of the scan ranges (all angles 2θ). All reflections $+h, \pm k, \pm l$ with $2\theta < 30^\circ$ ($\sin \theta/\lambda < 0.370$) were measured. Two reflections, the 300 and the $1\bar{3}0$, were measured after each 100 reflections to monitor crystal decay and alignment. During the experiment the intensity of $1\bar{3}0$ decreased steadily to 84% of its original value, while that of 300 showed random variations of $\pm 10\%$ around a similar decrease. In addition to the standards, 2369 reflections were measured, of which 684 had $I < \sigma(I)$. Intensities and their standard deviations, as well as the weights for least squares, were calculated as previously described (Hollander, Templeton & Zalkin, 1973*b*) except that $p = 0.05$ was used. Programs used in the structure analysis are listed in the same place.

An absorption correction ($\mu = 21.2 \text{ cm}^{-1}$) was calculated by the method of Gaussian integration. The correction factors ranged from 1.07 to 1.41. The data were corrected for the linear crystal decay and Lorentz and polarization effects. Those reflections measured more than once were averaged to give 2204 unique reflections, of which 1561 had $F^2 > \sigma(F^2)$.

The atomic scattering factors of Doyle & Turner (1968) were used for neutral strontium, carbon and oxygen, together with the real and imaginary dispersion corrections of Cromer & Liberman (1970).

Structure determination and refinement

The positions of two independent Sr atoms were found with a three-dimensional Patterson map, and least-squares refinement gave $R_1 = \sum |AF| / \sum |F_o| = 0.36$. A Fourier map phased by these atoms revealed 38 additional atoms which refined by least squares to $R_1 = 0.27$. Another Fourier map revealed the other 30 atoms of the DPP ligands and another peak, designated O(9), which

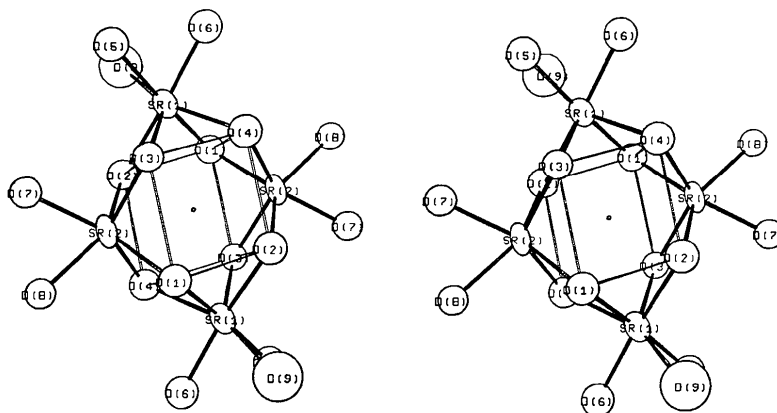


Fig. 1. Stereoscopic view of the coordination around the Sr atoms. The center of symmetry at 0,0,0 is indicated. Thermal ellipsoids have been scaled to include 50% probability.

Table 2. *Final coordinates and thermal parameters*

In this and following tables the standard deviation of the least significant digit(s) is given in parentheses. The form of the temperature factor (B in units of \AA^2) is $T = \exp[-0.25 (B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ for anisotropic and $T = \exp(-B \sin^2 \theta/\lambda^2)$ for isotropic thermal parameters. The coordinates of the Sr atoms are multiplied by 10^4 , those of the other atoms by 10^3 .

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sr(1)	2003 (3)	-410 (2)	449 (2)	7.4 (3)	4.5 (2)	4.4 (2)	3.1 (2)	0.4 (2)	0.5 (2)
Sr(2)	158 (3)	1118 (2)	1623 (2)	7.4 (3)	4.2 (2)	2.6 (2)	2.5 (2)	0.6 (2)	0.0 (1)

Table 2 (cont.)

	x	y	z	B
O(1)	178 (1)	16 (2)	-88 (1)	5.9 (5)
O(2)	183 (1)	139 (2)	89 (1)	6.3 (5)
C(01)	241 (3)	3 (3)	-247 (2)	8.7 (10)
C(02)	263 (3)	5 (3)	-335 (3)	12.3 (12)
C(03)	286 (3)	101 (4)	-355 (3)	12.8 (13)
C(04)	326 (3)	205 (4)	-293 (3)	13.3 (13)
C(05)	298 (3)	203 (3)	-203 (2)	10.1 (11)
C(06)	265 (3)	110 (3)	-185 (2)	8.4 (10)
C(07)	234 (2)	113 (3)	-94 (2)	7.2 (9)
C(08)	274 (2)	211 (2)	-23 (2)	5.0 (7)
C(09)	240 (2)	218 (2)	62 (2)	5.5 (8)
C(10)	275 (2)	331 (2)	126 (2)	5.8 (8)
C(11)	293 (2)	416 (2)	94 (2)	5.4 (8)
C(12)	334 (2)	529 (2)	163 (2)	6.7 (8)
C(13)	342 (2)	537 (3)	250 (2)	7.8 (9)
C(14)	322 (2)	449 (3)	275 (2)	7.0 (9)
C(15)	289 (2)	341 (2)	215 (2)	6.6 (8)
O(3)	-35 (1)	66 (1)	-125 (1)	5.0 (5)
O(4)	-27 (1)	189 (2)	55 (1)	6.4 (5)
C(16)	-28 (3)	68 (3)	-293 (2)	8.4 (9)
C(17)	-13 (3)	70 (3)	-383 (3)	11.6 (12)
C(18)	43 (3)	165 (4)	-399 (3)	12.5 (13)
C(19)	98 (3)	261 (3)	-326 (3)	11.9 (12)
C(20)	82 (3)	256 (3)	-237 (2)	9.7 (11)
C(21)	20 (3)	163 (3)	-226 (2)	7.2 (9)
C(22)	2 (2)	159 (3)	-138 (2)	6.7 (9)
C(23)	17 (2)	256 (2)	-66 (2)	4.2 (7)
C(24)	4 (2)	265 (2)	22 (2)	5.8 (8)
C(25)	24 (2)	379 (2)	89 (2)	5.4 (8)
C(26)	79 (2)	472 (3)	61 (2)	6.9 (8)
C(27)	104 (2)	576 (2)	128 (2)	7.3 (9)
C(28)	70 (3)	583 (3)	212 (2)	8.4 (10)
C(29)	20 (3)	487 (3)	234 (2)	9.0 (10)
C(30)	-3 (2)	381 (3)	168 (2)	7.4 (9)
O(5)	260 (1)	-78 (1)	171 (1)	6.5 (5)
O(6)	259 (1)	-187 (1)	-10 (1)	6.7 (5)
C(31)	257 (3)	-113 (3)	325 (2)	9.7 (10)
C(32)	270 (3)	-112 (3)	420 (3)	12.4 (12)
C(33)	361 (3)	-126 (3)	443 (2)	10.6 (11)
C(34)	434 (3)	-139 (3)	392 (3)	13.4 (14)
C(35)	428 (3)	-135 (3)	300 (2)	10.6 (11)
C(36)	336 (3)	-125 (2)	281 (2)	6.5 (8)
C(37)	311 (2)	-129 (2)	185 (2)	6.0 (8)
C(38)	344 (2)	-199 (2)	118 (2)	6.2 (8)
C(39)	315 (2)	-221 (2)	26 (2)	5.7 (8)
C(40)	337 (3)	-318 (2)	-39 (2)	6.1 (8)
C(41)	425 (3)	-337 (3)	-15 (2)	8.5 (10)
C(42)	440 (3)	-423 (3)	-80 (3)	10.7 (11)
C(43)	376 (3)	-478 (3)	-157 (2)	9.2 (10)
C(44)	290 (3)	-461 (3)	-186 (2)	8.8 (9)
C(45)	271 (3)	-364 (3)	-118 (3)	10.1 (10)
O(7)	129 (1)	177 (1)	302 (1)	5.6 (5)
O(8)	-48 (1)	219 (1)	283 (1)	5.0 (5)
C(46)	301 (3)	199 (3)	409 (2)	8.9 (10)
C(47)	399 (3)	232 (3)	463 (2)	9.6 (10)
C(48)	442 (3)	329 (3)	537 (2)	10.0 (11)
C(49)	387 (3)	390 (3)	555 (2)	10.7 (11)
C(50)	285 (3)	369 (3)	511 (2)	9.0 (10)
C(51)	252 (2)	268 (3)	434 (2)	5.6 (8)

Table 2 (cont.)

	x	y	z	B
C(52)	148 (3)	251 (2)	387 (2)	6.8 (9)
C(53)	73 (3)	286 (2)	414 (2)	5.8 (8)
C(54)	-16 (3)	271 (2)	370 (2)	6.0 (8)
C(55)	-105 (3)	309 (2)	404 (2)	7.9 (10)
C(56)	-87 (3)	351 (3)	502 (2)	9.7 (10)
C(57)	-168 (4)	391 (3)	537 (2)	11.0 (12)
C(58)	-248 (3)	387 (2)	488 (2)	8.3 (9)
C(59)	-258 (3)	347 (3)	395 (3)	12.2 (12)
C(60)	-177 (3)	311 (2)	358 (2)	8.2 (10)
O(9)	404 (2)	82 (2)	75 (2)	13.4 (8)
C(61)	479 (4)	104 (4)	134 (3)	13.7 (14)
C(62)	565 (4)	75 (4)	141 (3)	16.1 (15)
C(63)	476 (3)	203 (3)	214 (3)	14.7 (13)

was assumed, in analogy to the Ca complex (Hollander, Templeton & Zalkin, 1973a), to be the oxygen atom of an ethanol molecule. Three cycles of least squares on these atoms, all refined with isotropic thermal parameters brought R_1 to 0.14. With Sr atoms given anisotropic thermal parameters, R_1 was reduced to 0.094, but a satisfactory description was not achieved for an ethanol molecule in the vicinity of O(9), either ordered or disordered.

A difference Fourier map, with the atoms of 'ethanol' omitted, showed a triangular area of electron density with a peak at each corner and high density at the center. Further attempts to fit a disordered ethanol model, consisting of six half-atoms, yielded thermal parameters which were the lowest in the structure. It was then realized that the triangular region of electron density could also be fitted by an acetone molecule. Inclusion of these atoms in four cycles of refinement brought R_1 to 0.088, $R_2 = (\sum w(\Delta F)^2 / \sum w F_0^2)^{1/2}$ to 0.072, the standard deviation of an observation of unit weight to 1.47, and each shift to less than 10% of its standard deviation. The thermal parameters of all of the acetone atoms were in keeping with those of the rest of the structure, and the refinement was considered complete. A difference Fourier map showed no peaks greater than 0.6 e \AA^{-3} . No attempt was made to refine hydrogen atoms.

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

Results and discussion

This structure was determined with data of low resolution (few reflections with $d < 1.6 \text{ \AA}$), and as a result the

refinement was slow and the bond distances not very accurate. The circumstances resemble those existing in some studies of very large molecules such as proteins. We were slow to recognize the acetone molecule, but it may be encouraging to others who work with data of marginal resolution that we could distinguish acetone from ethanol and that the bond distances are reasonably consistent.

The complex consists of clusters of composition $[\text{Sr}_2(\text{DPP})_4(\text{CH}_3)_2\text{CO}]_2$ around the center of symmetry at 0,0,0. The 3.42 Å distance between C(26) and C(26) across the center of symmetry at $0, \frac{1}{2}, 0$ is the only one shorter than 3.50 Å between atoms in different clusters, disregarding hydrogen atoms.

The contacts of the strontium and oxygen atoms (Fig. 1 and Table 3) exhibit the same topology as is found in the calcium complex (preceding paper), but the central parallelepiped is much more nearly rectangular. The most acute dihedral angle is 83° , while in the calcium compound it is 69° . The distances from Sr to the bridging oxygen atoms average 2.55 Å with no significant difference between the two kinds of Sr atoms. The distances from the Sr atoms to the unshared oxygens average to 2.44 Å, indicating the expected tighter bonding to the unshared ligands, and the Sr(1) to O(9) distance is 2.60 Å, in keeping with the fact that the acetone is uncharged and thus not as tightly bound as the negative DPP ligands.

Table 3. Distances (Å) in the coordination cluster (See Fig. 1)

Sr(1)–O(1)	2.54 (2)	O(2)–O(3)	3.05 (3)*
Sr(1)–O(2)	2.54 (2)	O(2)–O(4)	3.30 (3)*
Sr(1)–O(3)	2.57 (2)	O(3)–O(4)	2.86 (2)*†
Sr(1)–O(4)	2.58 (2)	O(1)–O(8)	3.61 (3)
Sr(1)–O(5)	2.46 (2)	O(1)–O(9)	3.67 (3)
Sr(1)–O(6)	2.43 (2)	O(2)–O(7)	3.42 (3)
Sr(1)–O(9)	2.60 (3)	O(2)–O(9)	3.43 (3)
Sr(2)–O(1)	2.59 (2)	O(3)–O(5)	3.27 (3)
Sr(2)–O(2)	2.53 (2)	O(3)–O(7)	3.48 (2)
Sr(2)–O(3)	2.53 (2)	O(4)–O(6)	3.26 (3)
Sr(2)–O(4)	2.47 (2)	O(4)–O(8)	3.58 (3)
Sr(2)–O(7)	2.42 (2)	O(5)–O(6)	2.85 (2)†
Sr(2)–O(8)	2.47 (2)	O(5)–O(9)	3.18 (3)
O(1)–O(2)	2.83 (2)*†	O(6)–O(9)	3.36 (3)
O(1)–O(3)	3.37 (2)*	O(7)–O(8)	2.76 (2)†
O(1)–O(4)	3.04 (3)*		

* Edge of the central oxygen parallelepiped.

† Bite of the ligand.

The phenyl rings and diketone moieties are planar within experimental error. The angles between these planes, designated as in the preceding paper, are listed in Table 4. Bond distances are given in Table 5. The average C–C distance in the phenyl groups of 1.41 Å is close to the results obtained for other phenyl examples when hydrogen has been omitted from the calculation and the other average distances, C–O = 1.28 Å, C–C (diketone) = 1.40 Å, C(phenyl)–C(diketone) = 1.53 Å, are in reasonable agreement with other values for this

ligand (Williams, 1966; Hollander, Templeton & Zalkin, 1973a, b).

Table 4. 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	16.0	27.2	14.6
2	19.6	10.4	18.4
3	32.8	25.3	45.0
4	22.8	14.8	37.1

Table 5. Intra-molecular distances (Å)

DPP(1)		DPP(2)	
C(01)–C(02)	1.45 (4)	C(16)–C(17)	1.47 (4)
C(02)–C(03)	1.41 (4)	C(17)–C(18)	1.38 (4)
C(03)–C(04)	1.39 (5)	C(18)–C(19)	1.42 (4)
C(04)–C(05)	1.51 (4)	C(19)–C(20)	1.45 (4)
C(05)–C(06)	1.34 (4)	C(20)–C(21)	1.33 (4)
C(06)–C(01)	1.44 (4)	C(21)–C(16)	1.34 (3)
C(06)–C(07)	1.51 (3)	C(21)–C(22)	1.45 (3)
C(07)–O(1)	1.32 (3)	C(22)–O(3)	1.31 (3)
C(07)–C(08)	1.41 (3)	C(22)–C(23)	1.44 (3)
C(08)–C(09)	1.43 (3)	C(23)–C(24)	1.40 (3)
C(09)–O(2)	1.29 (3)	C(24)–O(4)	1.28 (3)
C(09)–C(10)	1.50 (3)	C(24)–C(25)	1.56 (3)
C(10)–C(11)	1.38 (3)	C(25)–C(26)	1.45 (3)
C(11)–C(12)	1.53 (3)	C(26)–C(27)	1.44 (3)
C(12)–C(13)	1.36 (3)	C(27)–C(28)	1.41 (3)
C(13)–C(14)	1.35 (3)	C(28)–C(29)	1.43 (4)
C(14)–C(15)	1.43 (3)	C(29)–C(30)	1.46 (4)
C(15)–C(10)	1.40 (3)	C(30)–C(25)	1.32 (3)
DPP(3)		DPP(4)	
C(31)–C(32)	1.54 (4)	C(46)–C(47)	1.43 (4)
C(32)–C(33)	1.40 (4)	C(47)–C(48)	1.42 (4)
C(33)–C(34)	1.34 (4)	C(48)–C(49)	1.33 (4)
C(34)–C(35)	1.51 (4)	C(49)–C(50)	1.44 (4)
C(35)–C(36)	1.36 (4)	C(50)–C(51)	1.48 (3)
C(36)–C(31)	1.34 (4)	C(51)–C(46)	1.36 (3)
C(36)–C(37)	1.55 (3)	C(51)–C(52)	1.51 (3)
C(37)–O(5)	1.25 (3)	C(52)–O(7)	1.39 (3)
C(37)–C(38)	1.44 (3)	C(52)–C(53)	1.34 (3)
C(38)–C(39)	1.42 (3)	C(53)–C(54)	1.32 (3)
C(39)–O(6)	1.27 (3)	C(54)–O(8)	1.33 (3)
C(39)–C(40)	1.61 (3)	C(54)–C(55)	1.57 (4)
C(40)–C(41)	1.40 (4)	C(55)–C(56)	1.48 (4)
C(41)–C(42)	1.44 (4)	C(56)–C(57)	1.47 (4)
C(42)–C(43)	1.33 (4)	C(57)–C(58)	1.32 (4)
C(43)–C(44)	1.39 (4)	C(58)–C(59)	1.41 (4)
C(44)–C(45)	1.59 (4)	C(59)–C(60)	1.46 (4)
C(45)–C(40)	1.37 (3)	C(60)–C(55)	1.26 (4)
Acetone			
O(9)–C(61)	1.28 (4)		
C(61)–C(62)	1.42 (5)		
C(61)–C(63)	1.60 (5)		

Since the ionic radius of Sr^{2+} is greater than that of Ca^{2+} , it is not unreasonable that a larger molecule, acetone, would replace the ethanol which is found in the Ca complex. However, it is not obvious why the preference should be so specific that crystallization was not achieved with ethanol, and that acetone replaced ethanol when the latter was in great excess. Nor is it obvious why the packing is not more nearly isomorphous.

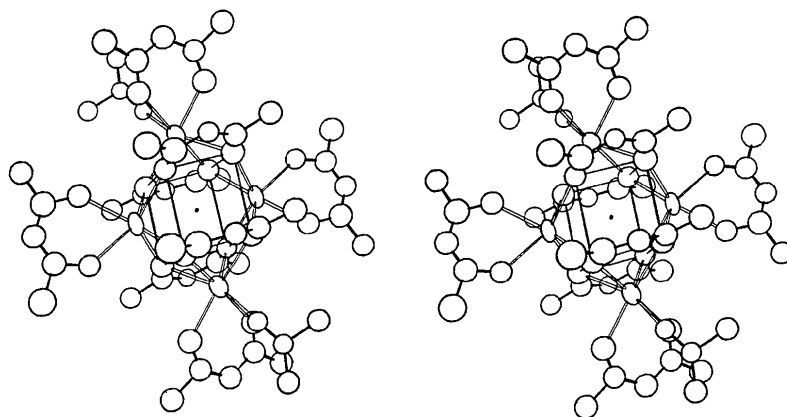


Fig. 2. Stereoscopic view of the complex cluster. Phenyl carbon atoms except for those attached directly to the diketone have been omitted and the acetone atoms have been given artificial thermal parameters for clarity. View direction and scaling of the thermal ellipsoids are the same as in Fig. 1.

Several other β -diketone complexes are known to form polymeric structures. Most of these involve acetylacetonate anion (AA) as the ligand, and the cations share oxygen atoms to achieve octahedral coordination. $\text{Ni}(\text{AA})_2$ forms linear trimers; each Ni atom is octahedrally coordinated and the octahedra share faces (Bullen, Mason & Pauling, 1961). $\text{Co}(\text{AA})_2$ forms a tetrameric chain with octahedra sharing faces between the two Co atoms at each end and sharing an edge between the two central Co atoms (Cotton & Elder, 1965). $\text{Co}(\text{AA})_2(\text{H}_2\text{O})$ dimerizes so that each cobalt can be octahedrally coordinated, and the octahedra share an edge (Cotton & Elder, 1966).

Gerlach & Holm (1969) note that β -diketones with bulky side groups act to suppress polymerization and force the complexes to become monomeric even though octahedral coordination may be lost. For example, the structures of bis-(2,2,6,6-tetramethyl-3,5-heptanedionato)zinc and nickel, $\text{Zn}(\text{DPM})_2$ and $\text{Ni}(\text{DPM})_2$, are monomeric, and the coordination is tetrahedral and planar respectively (Cotton & Wood, 1964; Cotton & Wise, 1966). Various evidence indicates similar structures for the DPM complexes of other divalent transition metals (Gerlach & Holm, 1969).

The magnesium complex with DPP (Hollander, Zalkin & Templeton, 1973*b*) is monomeric, but it achieves octahedral coordination by incorporation of small solvent molecules. With a larger cation, such as calcium or strontium, more bulky side groups can be tolerated in polymers. The dimer of $\text{Pr}(\text{DPM})_3$ (Erasmus & Boeyens, 1970), which involves sharing bulky DPM ligands to achieve sevenfold coordination, is another example. Further, a recent study of the DMP complexes of the alkaline-earth metals by means of vapor-phase diffusion, mass spectroscopy and molecular weight measurements indicates that the Ca, Sr and Ba complexes are polymeric in solution and in the vapor phase, but that the Mg complex is monomeric (Schwarberg, Sievers & Moshier, 1970).

These results suggest that a combination of the bulk of the ligand and the length of the M–O bond is the criterion for whether or not polymerization is favorable. With a short M–O bond length, as with Mg or the divalent first-row transition metals, ligands with side groups as bulky as *t*-butyl (DPM) or phenyl (DPP) are forced too close to one another in the configurations necessary for polymerization. When the M–O distance increases, as for Ca, Sr or Pr(III), then neighboring ligands need not be so close together, and the advantage of sharing ligands to get greater coordination from the negative ions can be realized.

References

- BULLEN, G. J., MASON, R. & PAULING, P. (1961). *Nature, Lond.* **189**, 291–292.
 COTTON, F. A. & ELDER, R. C. (1965). *Inorg. Chem.* **4**, 1145–1151.
 COTTON, F. A. & ELDER, R. C. (1966). *Inorg. Chem.* **5**, 423–429.
 COTTON, F. A. & WISE, J. J. (1966). *Inorg. Chem.* **5**, 1200–1207.
 COTTON, F. A. & WOOD, J. S. (1964). *Inorg. Chem.* **3**, 245–251.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
 DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
 ERASMUS, C. S. & BOEYENS, J. C. A. (1970). *Acta Cryst.* **B26**, 1843–1854.
 GERLACH, D. H. & HOLM, R. H. (1969). *Inorg. Chem.* **8**, 2292–2297.
 HAMMOND, G. S., NONHEBEL, D. C. & WU, C-H. S. (1963). *Inorg. Chem.* **2**, 73–76.
 HOLLANDER, F. J., TEMPLETON, D. H. & ZALKIN, A. (1973*a*). *Acta Cryst.* **B29**, 1295–1303.
 HOLLANDER, F. J., TEMPLETON, D. H. & ZALKIN, A. (1973*b*). *Acta Cryst.* **B29**, 1289–1295.
 SCHWARBERG, J. E., SIEVERS, R. E. & MOSHIER, R. W. (1970). *Anal. Chem.* **42**, 1828–1830.
 WILLIAMS, D. E. (1966). *Acta Cryst.* **21**, 340–349.