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UNSATURATED ORGANOMETALLIC COMPOUNDS OF THE MAIN GROUP ELEMENTS. DICYCLOPENTADIENYLCALCIUM

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Summary

Dicyclopentadienylcalcium, $(C_5H_5)_2Ca$, has been isolated and characterized by mass spectroscopic and single X-ray crystallographic diffraction studies. The mass spectrum of $(C_5H_5)_2Ca$ shows some surprising similarities to the mass spectra of $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ni$ in that the molecular ions, $(C_5H_5)Ca^+$, $(C_5H_5)_2Ca^+$ and $(C_5H_5)_3Ca_2^+$, are all present. Crystals of both $(C_5H_5)_2Ca \cdot (THF)_2$ and $(C_5H_5)_2Ca$ were prepared by the reaction of calcium metal with cyclopentadiene in THF. $(C_5H_5)_2Ca$ crystallizes as parallelopipeds in the space group $C2/c$ with $a = 13.922(3)$, $b = 8.641(2)$ and $c = 15.374(4)$ Å; β 112.25(1)°; $\rho_{calc} = 1.321$ g cm^{-3} for $Z = 8$. X-ray data to $2\theta = 60°$ (Mo-K_α radiation) were collected with a Picker Facs 1-Diffractometer. All atoms, including hydrogen atoms, were refined by full matrix least squares to final discrepancy factors of $R_F = 0.034$ and $R_{wF} = 0.036$ for 2489 reflections. The coordination sphere about the calcium atom consists of two h^5-C_5H_5 rings, one h^3-C_5H_5 ring and one h^1-C_5H_5 ring. Three of the rings are disposed about the calcium atom in a roughly trigonal manner. The fourth (h^1-C_5H_5) ring is positioned so that a line from its calcium atom to the closest carbon atom is approximately perpendicular to the plane formed by the centroids of the other three rings. Ca—C distances are 2.75(1) Å (h^5-C_5H_5); 2.85(1) Å (h^5-C_5H_5); 2.701(1); 2.789(2) and 2.951(2)Å (h^3-C_5H_5) and 3.100(2) Å (h^1-C_5H_5). The structure is the first example of a cyclopentadienyl compound with the h^5-C_5H_5, h^5-C_5H_5, h^3-C_5H_5, h^1-C_5H_5 configuration.

Introduction

Organocalcium compounds can most easily be prepared in liquid ammonia in which the calcium metal is soluble. Unfortunately, the products obtained in such reactions are insoluble solids of varying compositions and not easily studied

[1]. As a result, the organic chemistry of calcium is poorly developed and relatively few alkyl- and aryl-calcium compounds have been prepared and characterized [2]. One of the few well-characterized organocalcium compounds prepared and isolated by a modification of this technique was dicyclopentadienylcalcium which was first made by Ziegler and coworkers [3] by the reaction of calcium carbide with cyclopentadiene in liquid ammonia. Another cleaner synthetic method involves the superficial amalgamation of calcium metal with a few atomic per cent of mercury which enhances the reactivity of the calcium [4, 5]. This "activated" calcium has been found to react with certain aromatic hydrocarbons in tetrahydrofuran [5]. $(C_5H_5)_2Ca$, prepared by the reaction of calcium metal in THF (not activated by Hg) [6] contains two solvent molecules which can be removed by heating under high vacuum. The unsolvated $(C_5H_5)_2Ca$ was found to crystallize in a space group different than $(C_5H_5)_2Mg$ and $(C_5H_5)_2Fe$.

The infrared spectrum of $(C_5H_5)_2Ca$ in solution [7] shows four strong bands at 3049, 1499, 1006, and 760 cm^{-1} which are attributed to the four infrared active modes of the $C_5H_5^-$ anion. In addition, there are bands near 630, 663, and 1235 cm^{-1} which have been proposed as being due to a weak coupling of the two rings through a covalent bonding component [7]. In the solid state, the infrared spectrum of $(C_5H_5)_2Ca$ gives the following bands: 3049m, 1590m, 1433w, 1362m, 1199w, 1006s, 889, 778vs, 750vs [6], 662w, 625m [8]. The bands at 3049, 1433, 1006, 778, and 750 cm^{-1} can again be assigned to the vibrations of the $C_5H_5^-$ anion. However, the band at 1499 cm^{-1} is now weaker and has been shifted to 1433 cm^{-1}. Similar shifts have been interpreted as a decrease in the ionic bonding [7]. The weak band at 1199 cm^{-1} which did not appear in the solution spectrum usually is absent for ionic compounds containing the $C_5H_5^-$ anion [7] and the presence of this band would also imply some degree of covalent bonding in the compound if the infrared arguments are accepted. Weak coupling of ring frequencies has been used to explain the band at 1362 cm^{-1}. The bands 662 and 625 cm^{-1} are again assigned to weak coupling between rings.

Based on the infrared spectrum of $(C_5H_5)_2Ca$, it seems reasonable to conclude that, in solution, $(C_5H_5)_2Ca$ is primarily held together by electrostatic interactions. In the solid state, however, unsolvated $(C_5H_5)_2Ca$ apparently shows a significant increase in the interaction between the cyclopentadienyl rings and the calcium atom. With the hope of learning more about the bonding and stereochemical features of $(C_5H_5)_2Ca$ in the solid state, the structural and mass spectroscopic properties of $(C_5H_5)_2Ca$, dicyclopentadienylcalcium, were investigated.

Experimental

A. Synthesis

The method of Fischer [6] was used to prepare the unsolvated dicyclopentadienylcalcium compound. Freshly distilled cyclopentadiene, 5 ml (0.06 mole), and 1 g (0.025 mole) of finely rasped calcium metal were added to 100 ml of dry tetrahydrofuran (THF) and refluxed under nitrogen for two hours. The solution was then cooled and taken into a helium filled dry box and filtered, yielding a white powder. Recrystallization of the powder from THF gave large colorless crystals of the disolvated $(C_5H_5)_2Ca \cdot 2THF$. The recrystallized product was heated in a tube under vacuum to 100°C and the solvent removed. The tube was then sealed under vacuum and placed in a sand bath at 265°C. Small very clear colorless crystals sublimed on the walls of the tube. The crystals were cleaved to a proper shape and size for X-ray analysis.

B. Mass spectroscopic characterization

The sample was placed in a gold crucible in the dry box and then taken to the instrument room in a sealed vial. The crucible containing the sample was quickly transferred to the probe of the mass spectrometer and evacuated. Using this method, decomposition of the air sensitive sample was minimized.

C. X-ray analysis

1. Data collection and reduction

Because $(C_5H_5)_2Ca$ is sensitive to oxygen and water, the mounting of the crystals and the sealing of the crystals in glass-walled capillaries was carried out in an argon filled dry box. A crystal suitable for X-ray analysis, a parallelopiped with approximate dimensions 0.3 × 0.3 × 0.5 mm, was obtained by cleaving a longer crystal which was grown by sublimation. Preliminary precession photographs showed the crystals to be monoclinic with systematic absences on hkl for $h + k = 2n + 1$ and on $h0l$ for $l = 2n + 1$. These absences indicate the two indistinguishable space groups $C2/c$ and Cc. The crystal was mounted so that the rotation axis was coincident with the c^* axis.

Thirty reflections were carefully centered on a Picker four-circle diffractometer and used in a least squares refinement of the lattice parameters (T 23°C, $\lambda = 0.71069$ Å). The cell constants obtained were: $a = 13.922(3)$, $b = 8.641(2)$, $c = 15.374(4)$ Å, and β 112.25(1)°. Due to the reactivity of the crystals with the halogenated hydrocarbons used for the density measurements by the flotation method, an accurate density measurement could not be obtained. However, a crude density measurement showed the density to be between 1.3 and 1.4 g cm^{-1}. A density of 1.3213 g cm^{-3} was calculated assuming eight asymmetric units of $(C_5H_5)_2Ca$ per unit cell.

Diffraction data were obtained on a fully automated Picker four-circle diffractometer equipped with a highly oriented graphite single crystal monochromator using Mo-K_α radiation. The data were measured using the $\theta - 2\theta$ scan technique with a scan rate of 1.0° min^{-1} and a scan width of 2.0°. Stationary crystal-stationary counter background counts of 10 seconds were taken at the beginning and at the end of each scan. A take-off angle of 1.5° was used which provided approximately 80% of the intensity of a typically large peak. Pulse height analyzer settings of 3.0 and 8.0 for the lower and upper level discriminators respectively were used. Several ω scans showed the typical full peak width at half height to be less than 0.20° indicating that the mosaicity was acceptably low for data collection. Copper foil attenuators whose attenuation factors were known were automatically inserted in front of the counter aperture whenever the counting rate exceeded 10000 counts per second in order to eliminate saturation of the counter circuit. Three standard peaks were monitored every sixty reflections to insure crystal and counter stability. A C-centering reject subroutine was added to the regular data collection program in order to skip systematic absent reflections and speed up data collection.

A full form of data ($\bar{h}kl$ and hkl) was measured to $2\theta_{max}$ 60° giving 2872 reflections of which 2489 were unique. The intensities were corrected for background, and Lorentz-polarization effects. Structure factor amplitudes were calculated using a local program GORDO. Due to the size of the linear absorption coefficient ($\mu = 6.32\ \text{cm}^{-1}$), an absorption correction was made with the program ORABS [9]. Of the unique data, 957 reflections were considered observed using the criteria $I_{obs} \geqslant 3\ \sigma_c(I)$ where $\sigma_c = [T_c + 0.25(t_c/t_b)^2(B_1 + B_2)]^{1/2}$ and T_c = total counts, t_c = time spent counting the intensity peak, t_b = time spent counting background, and B_1 and B_2 are background intensities. All the data were used in the refinement.

2. *Solution and refinement of the structure*

The solution of the structure was obtained by the heavy-atom Patterson method, using the 957 reflections with $I_{obs} \geqslant 3\sigma_c$. The coordinates for the calcium atom were obtained from a Patterson map generated from the observed structure factors using the space group $C2/c$ which was indicated by an $N(Z)$ test [10]. Successive Fourier maps revealed well-defined positions for two five-membered rings and what appeared to be a "six-membered" ring. After several cycles of refinement of positional and thermal parameters, the refinement converged at an R factor of 0.155.

Refinement was then tried in the space group Cc with the "six-membered" ring left out. A difference Fourier calculation based on the Cc space group refinement revealed the omitted ring in the same location and in the same six-membered configuration as previously found in the refinement in the space group $C2/c$. The "six-membered" ring was then assumed to be a disordered five-membered ring and two carbon atoms were substituted for each of four positions of the "six-membered" ring which had electron density in the shape of a dumbbell. All ten carbon atoms were given weights of one-half and isotropic thermal parameters of 4.0. In addition, each hydrogen atom was placed at the theoretically calculated position 1.00 Å from its parent carbon atom [11] and given the fixed isotropic thermal parameter of 3.5. Introduction of the disordered model for the third ring and the inclusion of the hydrogen atoms in the refinement dropped the R factor to 0.119.

Up to this point in the refinement, unit weights were used. In the remainder of the refinement, all 2489 unique reflections were used with counting statistical weights as defined below and with all negative F_{obs} set equal to zero.

$$\sigma(F) = \frac{F}{2I}\left[T_c + 0.25\left(\frac{t_c}{t_b}\right)^2 (B_1 + B_2) + (KI)^2\right]^{1/2},\ K = 0.02$$

After converting to anisotropic temperature factors for the non-hydrogen atoms and after four cycles of full anisotropic refinement of the non-hydrogen atoms and one cycle each of refinement on the hydrogen atom positions and isotropic temperature factors the R factor converged at 0.037. Because of difficulty in the refinement of the disordered five-membered ring, the positional parameters in this ring were refined separately from the anisotropic temperature parameters in the last cycles of full anisotropic refinement of the non-hydrogen atoms. After several more cycles, the refinement converged at the R factors:

TABLE 1

POSITIONAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN $(C_5H_5)_2Ca$

Atoms	x	y	z
Ca	0.30414(3)	0.41915(3)	0.15043(3)
C(1)	0.2376(1)	0.7191(2)	0.1414(1)
C(2)	0.2446(1)	0.6655(2)	0.2297(1)
C(3)	0.1662(1)	0.5563(2)	0.2143(1)
C(4)	0.1110(1)	0.5442(2)	0.1182(1)
C(5)	0.1549(1)	0.6446(2)	0.0736(1)
C(6)	0.5	0.3237(3)	0.25
C(7)	0.4828(1)	0.4145(3)	0.3140(1)
C(8)	0.4900(2)	0.5654(3)	0.2904(2)
C(9)	0.2992(36)	0.1459(14)	0.0449(10)
C(10)	0.3437(16)	0.2520(27)	0.0042(14)
C(11)	0.2646(38)	0.3575(11)	−0.0402(6)
C(12)	0.1757(21)	0.3133(66)	−0.0323(23)
C(13)	0.1956(29)	0.1794(52)	0.0215(26)

$$R_1 = \Sigma(F_o - F_c)/\Sigma F_o = 0.034 \text{ and } R_2 = (\Sigma w(F_o - F_c)^2/\Sigma w F_o^2)^{1/2} = 0.036$$

The estimated standard deviation of an observation of unit weight was 1.73. A final difference Fourier map showed a maximum peak of 0.456 e Å^{-3}. A test of the counting statistics weighting scheme showed no systematic variation of $w(F_o - F_c)^2$ with the magnitude of the structure factors or with increasing $\sin\theta/\lambda$. The scattering factors used in refinement for C and Ca were taken from the compilation of Hanson et al. [12] and those for hydrogen are the best spherical form factors of Stewart et al. [13]. Real and imaginary dispersion corrections were made for the calcium atom [14]. All refinement was carried out on an XDS Sigma 5 computer.

The final positional and thermal parameters for the non-hydrogen atoms

TABLE 2

ANISOTROPIC THERMAL PARAMETERS FOR THE NON-HYDROGEN ATOMS IN $(C_5H_5)_2Ca$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	0.0028(0)	0.0092(0)	0.0027(0)	0.0009(0)	0.0005(0)	−0.0014(0)
C(1)	0.0071(1)	0.0090(2)	0.0055(1)	0.0005(1)	0.0032(1)	−0.0000(1)
C(2)	0.0044(1)	0.0115(2)	0.0034(1)	0.0022(1)	0.0007(1)	−0.0016(1)
C(3)	0.0054(1)	0.0107(3)	0.0044(1)	0.0026(1)	0.0026(1)	0.0007(1)
C(4)	0.0037(1)	0.0127(3)	0.0052(1)	0.0015(1)	0.0010(1)	−0.0022(1)
C(5)	0.0075(1)	0.0139(3)	0.0029(1)	0.0047(2)	0.0010(1)	0.0002(1)
C(6)	0.0026(1)	0.0131(4)	0.0094(2)	0.0000(0)	0.0004(1)	0.0000(0)
C(7)	0.0028(1)	0.0391(7)	0.0038(1)	0.0007(2)	0.0009(1)	0.0032(2)
C(8)	0.0038(1)	0.0217(4)	0.0118(2)	0.0009(2)	0.0006(1)	−0.0098(2)
C(9)	0.0094(18)	0.0096(10)	0.0024(2)	0.0018(9)	0.0007(6)	−0.0002(4)
C(10)	0.0030(6)	0.0205(14)	0.0030(4)	0.0010(8)	0.0008(3)	−0.0037(6)
C(11)	0.0080(12)	0.0093(7)	0.0027(2)	0.0007(13)	0.0005(6)	−0.0009(4)
C(12)	0.0043(9)	0.0330(57)	0.0047(11)	0.0060(22)	−0.0008(6)	−0.0089(17)
C(13)	0.0048(7)	0.0296(49)	0.0060(9)	−0.0065(13)	0.0040(7)	−0.0089(16)

[a] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE 3

POSITIONAL PARAMETERS AND ISOTROPIC THERMAL PARAMETERS FOR THE HYDROGEN ATOMS IN $(C_5H_5)_2Ca$

Atom	x	y	z	B^a
H(1)	0.2811	0.7870	0.1294	4.56
H(2)	0.3009	0.6884	0.2912	4.39
H(3)	0.1512	0.5068	0.2592	3.85
H(4)	0.0529	0.4783	0.0907	5.34
H(5)	0.1351	0.6627	0.0097	5.41
H(6)	0.5000	0.2151	0.2500	8.08
H(7)	0.4691	0.3856	0.3606	7.12
H(8)	0.4889	0.6444	0.3232	8.32
H(9)	0.3448	0.0669	0.0805	3.45
H(10)	0.4100	0.2550	0.0100	1.99
H(11)	0.2847	0.4364	−0.0743	6.30
H(12)	0.1070	0.3541	−0.0494	8.09
H(13)	0.1523	0.1166	0.0394	7.93

[a] The hydrogen atoms were given isotropic thermal parameters of the form $\exp[-B(\sin^2\theta/\lambda^2)]$.

are contained in Tables 1 and 2 respectively. Table 3 gives the hydrogen atom positions and thermal parameters. Tables 4 and 5 give the interatomic distances and angles. A list of the observed and calculated structure factor amplitudes is available*.

TABLE 4

INTERATOMIC DISTANCES (Å) FOR THE NON-HYDROGEN ATOMS IN $(C_5H_5)_2Ca$

Atoms	Distance	Atoms	Distance
Ca—C(1)	2.739(2)[a]	Ca—C(12)	2.848(10)
Ca—C(2)	2.734(2)	Ca—C(12)′	2.792(13)
Ca—C(2)′	3.100(2)	Ca—C(13)	2.869(9)
Ca—C(3)	2.737(2)	Ca—C(13)′	2.778(13)
Ca—C(4)	2.763(2)	C(1)—C(2)	1.403(2)
Ca—C(5)	2.766(2)	C(2)—C(3)	1.393(2)
Ca—C(6)	2.701(1)	C(3)—C(4)	1.388(2)
Ca—C(7)	2.789(2)	C(4)—C(5)	1.383(3)
Ca—C(7)′	2.805(2)	C(5)—C(1)	1.384(3)
Ca—C(8)	2.951(2)	C(6)—C(7)	1.349(3)
Ca—C(8)′	2.943(2)	C(7)—C(8)	1.367(3)
Ca—C(9)	2.850(16)	C(8)—C(8)′	1.372(5)
Ca—C(9)′	2.851(18)	C(9)—C(10)	1.381(23)
Ca—C(10)	2.893(11)	C(10)—C(11)	1.394(15)
Ca—C(10)′	2.892(15)	C(11)—C(12)	1.344(16)
Ca—C(11)	2.819(12)	C(12)—C(13)	1.388(16)
Ca—C(11)′	2.876(10)	C(13)—C(9)	1.379(16)

[a] Errors in the lattice parameters are included in the estimated standard deviations

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* The table of structure factors has been deposited as NAPS Document No. 02437, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46th Street, New York, New York 10017. A copy may be secured by citing the document and remitting $ 1.50 for microfiche or $ 5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

TABLE 5

BOND ANGLES (DEG) FOR THE NON-HYDROGEN ATOMS IN $(C_5H_5)_2Ca$

Atoms	Angle
C(2)—C(1)—C(5)	107.9(2)[a]
C(1)—C(2)—C(3)	107.2(1)
C(2)—C(3)—C(4)	108.3(2)
C(3)—C(4)—C(5)	108.0(2)
C(4)—C(5)—C(1)	108.5(2)
C(7)—C(6)—C(7)′	108.8(3)
C(6)—C(7)—C(8)	108.1(2)
C(7)—C(8)—C(8)′	107.5(1)
C(10)—C(9)—C(13)	110.3(12)
C(9)—C(10)—C(11)	104.5(14)
C(10)—C(11)—C(12)	110.7(15)
C(11)—C(12)—C(13)	108.0(8)
C(12)—C(13)—C(9)	106.4(7)

[a] Errors in the lattice parameters are included in the estimated standard deviations

Discussion

The mass spectrum of $(C_5H_5)_2Ca$ (Table 6) provides some interesting facts. As in most π-cyclopentadienyl compounds, the molecular ion is of high abundance [15]. Even when the electron impact energy is increased from 10 to 70 eV, the molecular ions $(C_5H_5)_2Ca^+$ and the $(C_5H_5)Ca^+$ ion are still found in high abundance. From this, one can conclude that there must be a rather strong interaction between the metal and the rings. The peaks at 210 and 275 are assigned to the $(C_5H_5)_2Ca_2^+$ and $(C_5H_5)_3Ca_2^+$ ions respectively. Such ions have also been found in the low eV mass spectrum of ferrocene and nickelocene [16], but not for $(C_5H_5)_2Mg$ and $(C_5H_5)_2Mn$. They are attributed to the reaction between the $(C_5H_5)Ca^+$ ion and a neutral $(C_5H_5)_2Ca$ molecule.

The coordination sphere around the calcium atom, shown in Fig. 1, consists of two h^5-C_5H_5 groups (rings A and C), one h^3-C_5H_5 group (ring B), and one h^1-C_5H_5 group (ring A′). Ring B lies on a two-fold axis and ring C is disordered about an inversion center. Only one half of the disorder is shown for clarity. The overall crystal structure, shown in Fig. 2, consists of calcium atoms which are linked together by three crystallographically unique bridging cyclopenta-

TABLE 6

MASS SPECTRUM OF $(C_5H_5)_2Ca$ AT 280°C

Mass	I/Sum (%), 10 eV	I/Sum (%), 70 eV	Assignment
40	0.51	11.11	Ca^+
65	1.99	3.41	$C_5H_5^+$
105	38.88	43.18	$(C_5H_5)Ca^+$
170	40.76	17.35	$(C_5H_5)_2Ca^+$
210	< 0.03		$(C_5H_5)_2Ca_2^+$
275	< 0.1	< 0.05	$(C_5H_5)_3Ca_2^+$

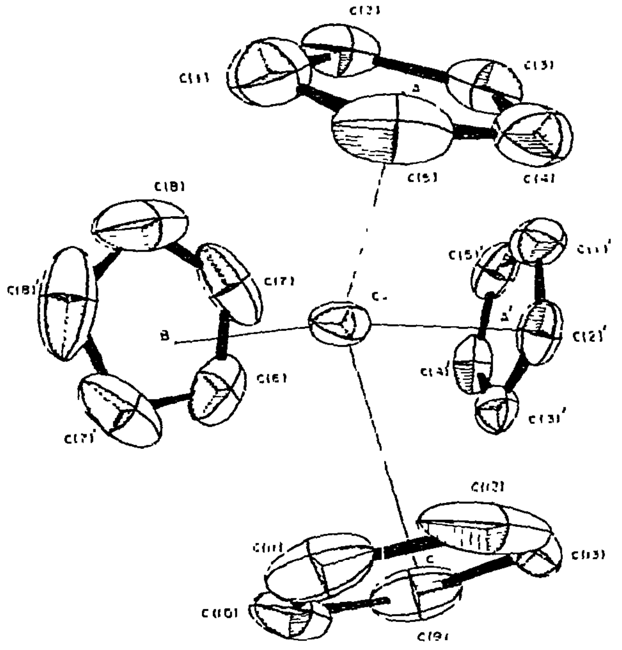

Fig. 1. The molecular geometry of $(C_5H_5)_2Ca$

dienyl rings. Three of the rings in the calcium atom coordination sphere (A, B and C) are disposed about the calcium atom in a roughly trigonal manner. The angles subtended at the calcium atom by the centroids of the rings are 117.8, 117.5, and 118.9° for the centroid A—Ca—centroid B, centroid A—Ca—centroid C, and centroid B—Ca—centroid C angles respectively. The fourth ring (A')

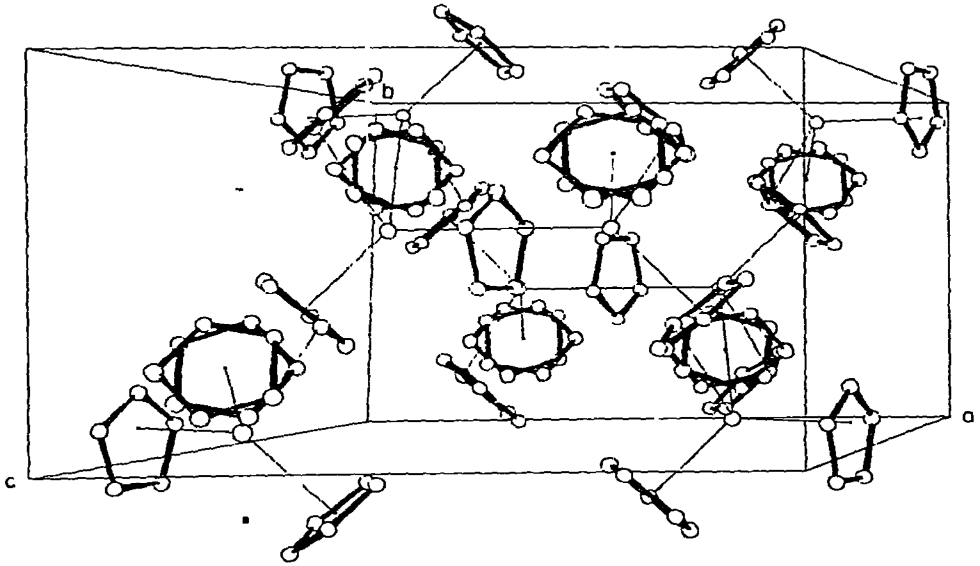

Fig. 2. The ab projection of the unit cell of $(C_5H_5)_2Ca$.

TABLE 7

BEST WEIGHTED LEAST-SQUARES PLANES FOR $(C_5H_5)_2Ca$

Plane	Atoms in Plane	Equation of Plane[a,b]
1	C(1), C(2), C(3) C(4), C(5)	$0.6865x - 0.7257y - 0.0466z + 2.9019 = 0$
2	C(6), C(7), C(7) C(8), C(8)'	$-0.8321x - 0.0000y - 0.5546z + 6.5541 = 0$
3	C(9), C(10), C(11) C(12), C(13)	$0.0647x - 0.5514y - 0.8317z + 0.9550 = 0$
4	centroids of rings A, B, and C	$0.4573x + 0.6627y - 0.5931z - 3.0232 = 0$

Deviations of Atoms from Planes (Å)

Atom	Plane 1	Atom	Plane 2	Atom	Plane 3	Atom	Plane 4
C(1)	0.005(2)	C(6)	−0.000(2)	C(9)	−0.019(14)	Ca	−0.356(1)
C(2)	−0.004(2)	C(7)	0.004(2)	C(10)	0.012(21)		
C(3)	0.003(2)	C(7)'	−0.004(2)	C(11)	−0.019(10)		
C(4)	−0.001(2)	C(8)	−0.008(3)	C(12)	0.014(42)		
C(5)	−0.003(2)	C(8)'	0.008(3)	C(13)	0.013(40)		
Ca	2.480(1)	Ca	2.573(1)	Ca	−2.604(1)		

[a] The orthogonal unit cell vectors x, y, z are related to the monoclinic vectors a, b, c as follows: $(x, y, z) = (a + c\cos\beta, b, c\sin\beta)$. [b] The weight of each atom is inversely proportional to the mean variance of the positional parameters for that atom.

which is symmetry related to ring A is positioned so that a line from the calcium atom to the C(2)' carbon atom of the ring is approximately perpendicular to the plane formed by the centroids of the other three rings. All the rings are found to be planar (Table 7).

Ring A has essentially equivalent carbon—carbon bond lengths and angles with an average C—C distance of 1.39 Å and an average C—C—C angle of 108.0°. The average carbon—calcium distance for ring A is 2.75 Å with the calcium atom 2.48 Å from the plane of the ring and approximately equidistant to all carbon atoms in the ring. This calcium—carbon atom distance does not fit the general trend found for transition metal π-cyclopentadienyl complexes. Similar to the case of iron and cobalt, the calcium—carbon atom distance is shorter than that predicted by the method of Johnson et al. [17] (2.9 Å).

Ring C also has nearly equivalent bond lengths and angles with an average C—C distance of 1.38 Å and an average C—C—C angle of 108.0°. The average calcium—carbon atom distance for ring C of 2.85 Å is longer than the corresponding distance for ring A with the calcium atom again approximately equidistant from all carbon atoms in the ring. The calcium atom is 2.60 Å from the plane of the ring. The longer calcium—carbon distances in ring C are expected since ring C is equally associated with two calcium atoms whereas ring A is much more closely associated with one calcium atom than with another.

The Ca—C(6), Ca—C(7) and Ca—C(8) distances of 2.701(1), 2.789(2), and 2.951(2)Å respectively point out the *trihapto* character of ring B. The equivalent C(6)—C(7)′ and C(6)—C(7) bond lengths are 1.349(3)Å while the C(7)—C(8) [equivalent to C(7)′—C(8)′] and C(8)—C(8)′ bond lengths are 1.367(3) and 1.372(5) Å respectively. The C—C—C angles are all nearly equivalent with an average value of 108.0°. Ring A′, which is equivalent to ring A but is unique with respect to a particular calcium atom coordination site, also appears to interact with the calcium atom. The closest approach of the calcium atom is to C(2)′ which is 3.100(2) Å. All the other carbon atoms in this ring appear to be too far away for significant interaction with the calcium atom.

The geometry found for dicyclopentadienylcalcium (atomic radius = 1.97 Å) fits into a trend in the coordination number and manner of coordination that has developed among cyclopentadienylmetal complexes. This trend basically parallels the change in the size of the atomic radius of the metal atom. Iron, with one of the smallest atomic radii of 1.26 Å, forms the familiar ferrocene [18] in which the iron atom has a coordination sphere consisting of two h^5-C_5H_5 groups. Titanium, with an atomic radius of 1.47 Å, forms complexes consisting of two h^5-C_5H_5 groups which are bent back so that additional groups can coordinate. In tricyclopentadienyltitanium [19] the two h^5-C_5H_5 groups are bent such that the centroid—metal—centroid angle is 133°. This allows for the third cyclopentadienyl group to act as a three-electron ligand. In tetracyclopentadienyltitanium [20] the two h^5-C_5H_5 groups are bent with the formation of a 130° angle. This permits the coordination of the two remaining rings although only in a *monohapto* manner. Tricyclopentadienylscandium [21] is similar to tetracyclopentadienyltitanium with two h^5-C_5H_5 and two h^1-C_5H_5 groups. The increased size of the atomic radius of scandium of 1.62 Å has resulted in the preferred coordination number of four even though the coordination of three cyclopentadienyl rings in much the same manner as in tricyclopentadienyltitanium would be expected. If the atomic radius is increased further, one would expect either an increase in the coordination number or an increase in the interaction of C_5H_5 rings with the metal atom. In dicyclopentadienylcalcium the coordination number is still four but as discussed above there is an increased metal ring interaction with two h^5-C_5H_5 groups, one h^3-C_5H_5 group and one h^1-C_5H_5 group in the coordination sphere. Thus it seems that there are two primary factors which contribute to the geometry around the metal atom in cyclopentadienylmetal complexes: (1) steric interactions which are directly dependent on the size of the metal atom radius, and (2) maximum interaction between the metal atom and the cyclopentadienyl groups either by metal orbital—ligand orbital overlap, electrostatic interaction, or a combination of both.

The covalent contribution to the bonding in bent di-π-cyclopentadienyltransition metal compounds may be explained in terms of a model recently suggested by Green and coworkers [22] and based on an earlier model [23] used to explain the bonding in di-π-cyclopentadienyl dihydrides. This model, however, is based on a molecular orbital treatment [23] which indicates that for values of the angle between the metal ring axes in the range 135-180° the metal—ring bond strength is little changed. Therefore, such a model would not apply to compounds involving trigonally arranged cyclopentadienyl groups such as $(C_5H_5)_2Ca$.

The covalent contribution to the bonding in $(C_5H_5)_2Ca$ is expected to be similar to that proposed for rare earth cyclopentadienides [24, 25] in which the ligands are trigonally disposed about the metal atom as in triindenylsamarium [26]. Although the bonding in both cases is predominantly ionic in character, some covalent bonding may exist. The possible valence configurations which can form covalent bonds in a trigonal configuration are sp^2, dp^2, sd^2 and d^3 hybridizations [27]. The 4*s*, 4*p*, and 3*d* orbitals of calcium are of suitable size and energy for forming covalent metal—ligand bonds. In the case of $(C_5H_5)_2Ca$, two of the three trigonal orbitals would be directed toward the centers of the h^5-C_5H_5 groups with the third orbital pointing toward the allylic portions of the h^3-C_5H_5 group. Trigonal hybridization of the orbitals in the *x* and *y* planes allows those orbitals in the *z* direction to interact with the fourth ring in the calcium coordination sphere. This view is supported by the fact that the Ca atom has been pulled approximately 0.4 Å out of the plane formed by the centroids of the trigonally dispersed rings (Table 7) toward the fourth ring. This same model, which results in unhybridized *z*-orbitals, has been used to explain the unexpected strong Lewis acidity of most tricyclopentadienyllanthanide complexes and the ready formation of many surprisingly stable adducts.

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