

Synthesis and Thermal Average Gas Phase Molecular Structures of Bis(pentamethylcyclopentadienyl)-strontium and -barium; the First Organo-strontium and -barium Structures

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The thermal average gas phase molecular structures of bis(pentamethylcyclopentadienyl)-strontium, $\text{Sr}(\text{C}_5\text{Me}_5)_2$, and -barium, $\text{Ba}(\text{C}_5\text{Me}_5)_2$, are best described as bent sandwich structures where the mean Sr–C and Ba–C bond distances are 275.0(8) and 289.8(17) pm and the ring centroid–metal–ring centroid angles are 149(3)° and 148(6)° respectively.

Bis(cyclopentadienyl) compounds of the group 2 metals have been known for several years.¹ $\text{Be}(\text{C}_5\text{H}_5)_2$ has a structure with one ring η^5 bonded and the other ring η^1 or η^3 bonded to the Be atom in both the gas² and crystalline³ phase. $\text{Mg}(\text{C}_5\text{H}_5)_2$ has a ferrocene-like structure with parallel rings η^5 bonded to Mg in both the gas⁴ and crystalline⁵ phase. $\text{Ca}(\text{C}_5\text{H}_5)_2$ is polymeric in the crystalline phase,⁶ and the compound is not volatile enough to be investigated by gas phase electron diffraction (g.e.d.). Introduction of methyl groups on the cyclopentadienyl ring has previously been used to prevent polymerisation and increase the vapour pressure of a compound.⁷ The fully methylated compound, $\text{Ca}(\text{C}_5\text{Me}_5)_2$, has been successfully investigated by g.e.d. recently.⁸ $\text{Sr}(\text{C}_5\text{H}_5)_2$ and $\text{Ba}(\text{C}_5\text{H}_5)_2$ are, because of the high temperatures needed to sublime the two compounds (360–440 °C and 420–460 °C, respectively) and the similarity of their i.r. spectra¹ with that of the calcium analogue, expected to be polymers in the crystalline phase. We have synthesized $\text{Sr}(\text{C}_5\text{Me}_5)_2$ and $\text{Ba}(\text{C}_5\text{Me}_5)_2$ from SrI_2 or BaI_2 and NaC_5Me_5 in diethyl ether

(Sr) or tetrahydrofuran (thf) (Ba). The co-ordination complexes $(\text{Me}_5\text{C}_5)_2\text{Sr}(\text{OEt}_2)$ and $(\text{Me}_5\text{C}_5)_2\text{Ba}(\text{thf})_2$ were made base-free by the 'toluene-reflux method' as previously described.⁹ Both compounds give monomeric molecular ions in the mass spectrometer and He-I and He-II photoelectron spectroscopic studies show that no significant decomposition occurs in the gas phase.⁹ We present here the thermal average gas phase structures of $\text{Sr}(\text{C}_5\text{Me}_5)_2$ (**1**) and $\text{Ba}(\text{C}_5\text{Me}_5)_2$ (**2**) as determined by g.e.d. These are, as far as we know, the first structures of organometallic strontium and barium compounds (*i.e.* with direct Sr–C or Ba–C bonding).

The g.e.d. data were recorded on Balzers Eldigraph KDG-2 with nozzle and reservoir temperatures of approximately 200 °C and 270 °C for (**1**) and (**2**), respectively. The temperatures correspond to vapour pressures of about 1 torr, which is sufficient when a torus-shaped nozzle¹⁰ is used. We used the

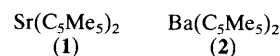


Table 1. The most important thermal average geometrical parameters and root mean square amplitudes of vibration (*l*-values) for $\text{Ca}(\text{C}_5\text{Me}_5)_2$, $\text{Sr}(\text{C}_5\text{Me}_5)_2$, and $\text{Ba}(\text{C}_5\text{Me}_5)_2$. The uncertainties listed are the least-square standard deviations multiplied by a factor of three to compensate for systematic errors and errors introduced by the assumptions.

	$\text{Ca}(\text{C}_5\text{Me}_5)_2^a$		$\text{Sr}(\text{C}_5\text{Me}_5)_2$		$\text{Ba}(\text{C}_5\text{Me}_5)_2$	
	r_d/pm	l/pm	r_d/pm	l/pm	r_d/pm	l/pm
Distances						
d^b	231.2(6)	—	246.9(6)	—	263.1(6)	—
M–C						
Mean	260.9(6)	9.9(11)	275.0(8)	10.5(7)	289.8(17)	14.8(16)
Range	255–267	—	269.6–280.4	—	284.0–295.0	—
C(1)–C(2)	142.7(3)	5.2(5)	142.8(3)	4.7 ^d	142.9(4)	4.7 ^d
C(1)–C(11)	150.6(4)	5.7(5)	150.6(4)	5.2 ^d	151.1(5)	5.2 ^d
C–H	110.7(4)	8.3(5)	110.1(5)	8.4(6)	110.5(6)	8.5(7)
Angles						
α	154(3)°	—	149(3)°	—	148(6)°	—
θ	–1.4(9)°	—	–2.9(15)°	—	–3(3)°	—
$\angle \text{C}_5, \text{C}_5^c$	20(2)°	—	25(3)°	—	26(6)°	—

^a Values taken from ref. 8. ^b The metal–ring centroid distance. ^c The angle between the ring planes. ^d Fixed values.

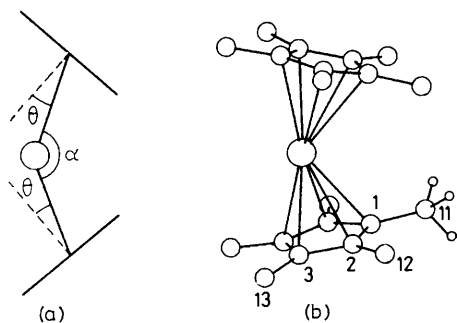


Figure 1. (a) Definitions of the bend angle, α , and the tilt angle, θ . θ as shown is defined as positive. (b) The thermal average molecular structure of $\text{Sr}(\text{C}_5\text{Me}_5)_2$ in the gas phase. Most of the hydrogen atoms are omitted for clarity.

Table 2. Structural trends of the alkaline earth bis(pentamethylcyclopentadienyl)-, di-iodo-, and difluoro-compounds. Numbers are thermal average bend angles in degrees from gas phase electron diffraction studies, while letters in parentheses are results from gas phase molecular beam electron deflection studies; lin. = linear.

M	$\text{M}(\text{C}_5\text{Me}_5)_2$	MI_2	MF_2
Mg	180 ^a	(lin.) ^d	(lin.) ^d
Ca	154(3) ^b	148 ^e (lin.) ^f	(bent) ^f
Sr	149(3) ^c	144 ^e (lin.) ^f	(bent) ^f
Ba	148(6) ^c	137.6(9) ^g (bent) ^f	(bent) ^f

^a Fixed value from ref. 8. ^b Ref. 8. ^c This study. ^d Ref. 16. ^e Ref. 12. ^f Ref. 17. ^g Ref. 13; the angle was 148.0(9)° when shrinkage effects were corrected for.

data from $s = 15$ to 260 nm^{-1} for both compounds. The data were processed by standard procedures.¹¹

The molecular model is shown in Figure 1. It was assumed that the C_5Me_5 ligands have C_{5v} symmetry, and that the C–Me fragments have C_{3v} symmetry with the hydrogen atoms fixed in positions with two pointed towards and one pointed away from the metal atom as shown in Figure 1. The best fit was obtained when the rings had a staggered conformation. The molecules then have C_s symmetry, where the mirror plane is defined by the metal atom and the C(1)–C(11) bond. With these assumptions the molecular geometry is described by eight independent geometrical parameters; the bond distances C–C(in ring), C–C(Me), C–H, the angle between the C_5 ring plane and the C–C(Me) bond, the valence angle CCH, the bend angle α , the tilt angle θ , and the metal–ring centroid distance d (see Figure 1). In addition to these eight geometrical parameters, 12 (Sr) and 11 (Ba) root mean square amplitudes of vibrations (l -values) were refined by least squares fit of a theoretical intensity curve to the experimental curves.

The most important geometrical parameters and l -values for (1), (2), and for comparison $\text{Ca}(\text{C}_5\text{Me}_5)_2$, are listed in Table 1. The estimated standard deviations noted in parentheses are the least squares standard deviations multiplied by a factor of three to compensate for the errors introduced by the assumptions and systematic errors. The tilt angles, θ , of $-2.9(15)^\circ$ and $-3(3)^\circ$ show that in both compounds the rings are near to η^5 bonded to the metal. A distortion from η^5 bonded rings towards η^3 or η^1 bonds correspond to tilt angles with absolute values of approximately 18° and $\geq 28^\circ$ respectively. Such models can therefore be ruled out. It must be emphasized that the structures are *thermal average* structures that have not been corrected for shrinkage effects. Such corrections are expected to make the bend angles larger, and

the equilibrium structures may be regular sandwich structures (i.e. $\alpha = 180^\circ$ and $\theta = 0^\circ$). In the latter case the molecules must undergo large amplitude motion, and the energy needed to bend the molecule 20° must be less than 2 kJ mol^{-1} .⁸

The structural feature of general chemical interest in the alkaline earth permethylmetallocenes in the gas phase is the change in thermal average structure from magnesium to barium; $\text{Mg}(\text{C}_5\text{Me}_5)_2$ has D_{5d} or D_{5h} idealized symmetry⁸ and the Ca,⁸ Sr, and Ba analogues have idealized C_{2v} symmetry. These structural features parallel the average structures found for the alkaline earth dihalides, assuming that the centroid of the C_5Me_5 -ring occupies one co-ordination site. CaI_2 , SrI_2 , and BaI_2 have been investigated by g.e.d. ($1100\text{--}1300^\circ\text{C}$),^{12,13} see Table 2. The average metal–iodine bond distances are 286(2) (Ca), 300(2) (Sr), and 314.3(4) pm (Ba). No g.e.d. data are available for MgI_2 . The reasons for the structural trends are presumably related. Two different models have been proposed to account for the geometry of the alkaline earth dihalides: a molecular orbital model based upon the inclusion of d-orbitals into a Walsh correlation diagram,¹⁴ and a polarized-ion model which analyses the attractive and repulsive forces on the basis of Coulomb's law as if the bonds were purely ionic.¹⁵

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