Solid State Structure of Bis(pentamethylcyclopentadienyl)barium, $(Me_5C_5)_2Ba$; the First *X*-Ray Crystal Structure of an Organobarium Complex

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The single crystal *X*-ray analysis of bis(pentamethylcyclopentadienyl)barium, $(Me_5C_5)_2Ba$, at 118 K reveals a novel structure in which monomeric bent metallocenes with average Ba–C distances of 298.7(18) pm and ring centroid–Ba–ring centroid angles of 131° are grouped in 'quasi-polymeric' chains with the shortest intermolecular Ba–C(methyl) distance being 334.9(5) pm.

Recent studies of several bis(pentamethylcyclopentadienyl)-alkaline earth and -lanthanide complexes in the solid state (M = Sm, Eu)[1] and in the gas phase (M = Yb, Ca, Sr, Ba)[2] have revealed unexpected geometries for these nominally 'ionic' compounds. All the complexes exhibit bent structures with ring centroid–metal–ring centroid angles in the range 140—158°, and not the parallel ring geometries anticipated from basic electrostatic or molecular orbital considerations.[3] As none of these species has been studied in detail in both the solid and vapour states, the possible structural consequences

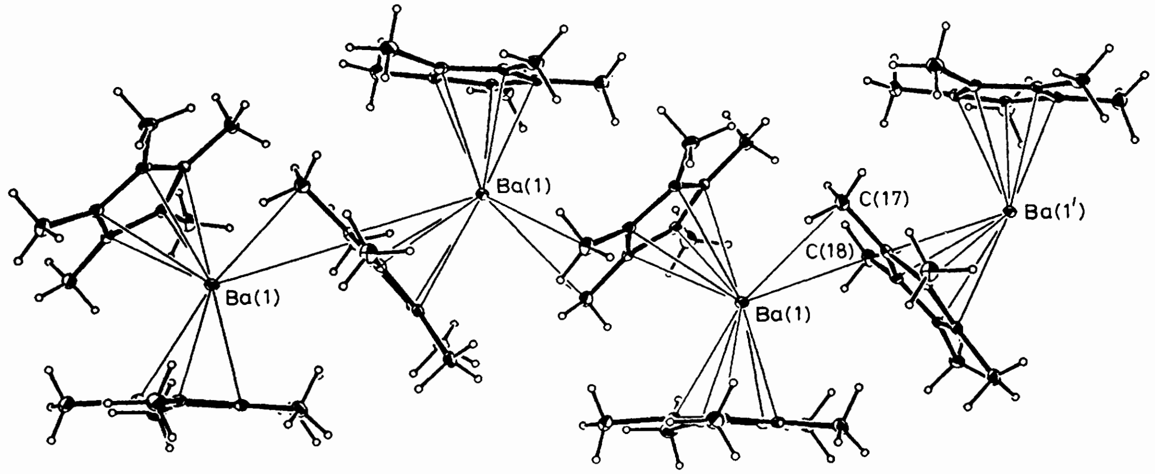

Figure 1. ORTEP view of one chain of $(Me_5C_5)_2Ba$ molecules. The lines indicate the shortest intermolecular Ba–methyl contacts. Distances (pm): Ba(1)–C(17) 339.5(5), Ba(1)–C(18) 345.7(6), Ba(1)–Ba(1') 633.0.

of crystal packing effects and gas phase thermal averaging effects are difficult to assess. In particular, gas electron diffraction (g.e.d.) studies yield structures which may be bent for statistical reasons, and thus equilibrium geometries with parallel rings have not been ruled out for $(Me_5C_5)_2Ca$, $(Me_5C_5)_2Sr$, and $(Me_5C_5)_2Ba$.[2]

In order to facilitate comparisons both with the gas phase results and with the solid-state lanthanide structures, we elected to study the structure of bis(pentamethylcyclopentadienyl)barium in its crystalline form. With the largest metal centre of the three alkaline earths, the barium complex should be the most susceptible to interactions in the solid state.

The disolvate $(Me_5C_5)_2Ba(thf)_2$ (thf = tetrahydrofuran) was prepared from the reaction of $(Me_5C_5)K$ and BaI_2 in thf.[4] Although the 'toluene-reflux method' can be used to produce the thf-free complex,[5] small quantities (0.5 g) of the complex are readily desolvated in a single 190 °C sublimation under a dynamic vacuum of 10^{-6} torr. The white sublimate will dissolve in toluene, from which colourless crystals can be grown. The structure of the complex was determined by single crystal *X*-ray crystallography, a view of which is presented in Figure 1.† It represents the first reported solid state structure of an organobarium complex.

Bis(pentamethylcyclopentadienyl)barium crystallizes with two crystallographically independent but essentially identical molecules in the unit cell, and like the gas phase structure, displays a bent metallocene geometry.[6] Several key structural parameters are significantly different in the solid state and gas phase complexes, however. Notably, the average Ba–C distance of 298.7(18) pm observed in the crystal is 9 pm greater than that found in the g.e.d.-determined structure of the metallocene, but corresponds closely to that expected from the sum of the ionic radii of six-co-ordinate Ba^{2+} (135 pm)[7] and the $C_5Me_5^-$ anion (164 pm).[8] In addition, the ring centroid–Ba–ring centroid angle of 131° found in the solid is 17° more acute than that observed in the gas phase, and is the smallest such angle yet observed in any $(Me_5C_5)_2M$ complex lacking co-ligands.

Although the rings display normal C–C(ring) and C–C(methyl) distances averaging 142(2) and 150(2) pm, respectively, and are clearly bound in a pentahapto fashion to the metal centres, the organobarium structure is not as stereochemically 'regular' as that of $(Me_5C_5)_2Sm$ or the isostructural $(Me_5C_5)_2Eu$. The individual Ba–C distances within a complex vary by as much as 15.9 pm, compared to a range of only 4 pm in the samarium analogue. Likewise, the Ba–ring centroid distances differ by 5.7 and 7.6 pm in the two independent $(Me_5C_5)_2Ba$ complexes, although by only 0.6 pm in $(Me_5C_5)_2Sm$.

These structural distortions may be associated with the relatively close packing of the complexes in the solid state. Individual $(Me_5C_5)_2Ba$ units can be identified in the lattice, but they are grouped together to form 'quasi-polymeric' chains (see Figure 1). Within the chains, the shortest intermolecular Ba–C(methyl) distances are 334.9(5) and 339.5(5) pm; considering that the radius of Ba^{2+} is *ca.* 20 pm larger than that of Sm^{2+},[7] these distances are effectively closer than the analogous distance of 322 pm found in $(Me_5C_5)_2Sm$. Similarly, the difference between the longest intramolecular and shortest intermolecular Ba–C distance is 27.5 pm, which is less than the corresponding distance of 40.5 pm found in $(Me_5C_5)_2Sm$. Those cyclopentadienyl rings involved in the shortest intermolecular Ba–C(methyl) contacts are also those which display the longest intramolecular Ba–C and Ba–ring centroid distances, strengthening the evidence for solid state interactions. There are, however, no intermolecular Ba–H_3(C) distances closer than 298 pm.

The close proximity of the complexes in crystalline $(Me_5C_5)_2Ba$ thus causes its structure to lie between that of the discrete $(Me_5C_5)_2Ln$ complexes and a truly polymeric pentamethylcyclopentadienyl species such as $(Me_5C_5)Tl$.[9] Since the bending observed in the solid state is greater than that in the gas phase, packing effects may serve to augment bending which is already present for electronic reasons.

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† *Crystal data* for $(Me_5C_5)_2Ba$: $C_{20}H_{30}Ba$, monoclinic, space group $P2_1/n$, $a = 18.043(4)$, $b = 11.830(2)$, $c = 18.206(4)$ Å, $\beta = 105.67(1)°$, $U = 3741.79$ Å^3, $Z = 8$, $D_c = 1.448$ g cm^{-3}. Data were collected on a Picker four-circle goniostat at 118 K using graphite monochromated Mo-K_α radiation. Continuous θ–2θ scans with fixed backgrounds were used to collect a total of 7027 intensities (4883 unique) in the range $6 < 2\theta < 45°$, of which 4482 had $F > 2.33\sigma(F)$. Data were reduced to a unique set of intensities and associated sigmas in the usual manner. The structure was solved with a combination of direct methods (MULTAN78) and Fourier techniques. All hydrogen atoms were clearly visible in a difference Fourier synthesis phased on the non-hydrogen parameters. The hydrogen atoms were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. $R = 0.0295$, $R_w = 0.0323$. A final difference Fourier was featureless, with the largest peak being 0.45 e Å^{-3}. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.