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Preliminary communication

The Crystal and Molecular Structure of Cyclopentadienylzinc methyl, $Zn(C_5H_5)Me$

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Summary

In the crystal, cyclopentadienylzinc methyl, $Zn(C_5H_5)Me$, adopts a puckered $-Zn(C_5H_5)Zn(C_5H_5)Zn(C_5H_5)-$ chain structure in which the bridging cyclopentadienyl groups co-ordinate di- or tri-hapto to the bridged zinc atoms, apparently functioning as five-electron ligands.

Although much attention has been paid to the structural characterisation of cyclopentadienyl derivatives of beryllium[1-10] and magnesium,[10-17] and the cyclopentadienyl-mercury compound, $Ph_3PC_5H_4HgI_2$, has been the subject of a recent crystallographic study,[18] the cyclopentadienyl chemistry of the intervening Group II metals, zinc and cadmium, has by contrast been little studied apart from a few brief synthetic and spectroscopic investigations.[19-22] In the case of zinc, this neglect is surprising, because cyclopentadienyl ligands can act as probes of the capacity of metals to take part in multicentre bonding involving carbon, and zinc is located in the Periodic Table on the fringe of that small group of metals that readily form electron deficient alkyl bridges.[23] The capacity of zinc to take part in multicentre bonding to carbon has not to our knowledge been demonstrated by any definitive structural studies to date, although it has been inferred from several studies, e.g. of the degree of association of bis(phenylethynyl)zinc,[24] of the rates of alkyl group exchange reactions of zinc alkyls,[25] of the spontaneous cyclisation reactions of 5-hexen-1-yl derivatives,[26] and of the spectra and reactions of other alkenylzinc compounds[27-29] and of $Zn(SbF_6)_2$-arene-SO_2 systems.[30]

During a study of cyclopentadienylzinc compounds $Zn(C_5H_5)R$ ($R = C_5H_5$, Me, Et, allyl, Bu^t, neopentyl, CPh_3, C≡CPh or Cl) we found that the compound $Zn(C_5H_5)Me$ crystallised in a form suitable for X-ray crystallographic study. Readily prepared from methylzinc iodide and sodium cyclopentadienide in THF, it forms colourless needle-shaped crystals, m.p. 155-158°, which sublime under vacuum with gentle warming. It is insoluble in hexane, but dissolves readily in tetrahydrofuran, and less readily in toluene or benzene, in which it is present as the monomer $Zn(C_5H_5)Me$ (by cryoscopy). The infrared and ^1H n.m.r. spectra of its solutions are consistent with $\underline{h}^5$-coordination of the cyclopentadienyl groups in a symmetric top, C_{5v}, skeletal structure (<u>cf</u>. $Be(C_5H_5)Me$ in the gas phase[1,7]), such as would be appropriate to allow full use of the metal's valence shell atomic orbitals, the cyclopentadienyl ligands functioning as five-electron ligands.

The cyclopentadienyl groups still appear to function as five-electron ligands in crystalline $Zn(C_5H_5)Me$, though in a bridging capacity. Cyclopentadienylzinc methyl crystallises with an orthorhombic cell, with a = 894.4(2) pm, b = 704.4(2) pm, c = 947.6(2) pm, $D_m = 1.59$ g.cm^{-3}, z = 4, $D_c = 1.60$ g.cm^{-3}, $\mu = 38.6$ cm^{-1} for Mo-K_α radiation. The space group is Cmcm or $Cmc2_1$.

The intensities of the hkl and $\bar{h}$kl reflections were measured on a Hilger and Watts four-circle diffractometer, using Zr-filtered Mo-K_α radiation and a 2θ-ω scan. The data were corrected for Lorentz and polarisation effects and for absorption. After averaging, a total of 250 reflections were classed as observed having net counts $\geqslant 2.5\sigma$.

The structure (Fig. 1), which was solved by the heavy atom method,

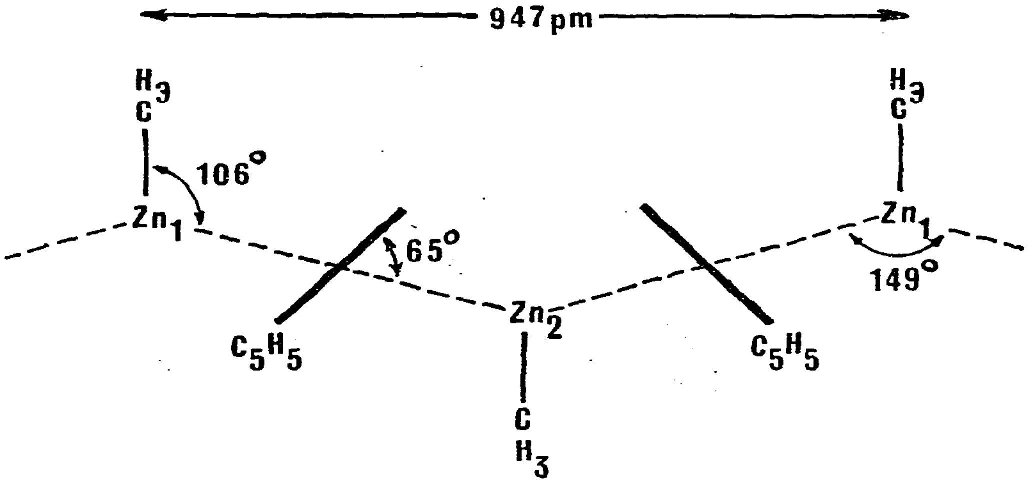

Fig. 1. The puckered chain structure of $Zn(C_5H_5)Me$, showing the inclination of the C_5H_5 planes to the Zn------Zn vectors.

consists of puckered chains of zinc atoms, each with a methyl group attached, linked by bridging cyclopentadienyl groups inclined at an angle of 65° to the metal-metal vectors. Some uncertainty remains concerning the orientation of the cyclopentadienyl groups within the ring planes. An attempt to solve the structure in the non-centric space group $Cmc2_1$ resulted in electron density maps which showed small peaks between the cyclopentadienyl carbon atoms, suggesting that these groups were disordered and that the structure was centrosymmetric. In the centric space group Cmcm, two orientations of the cyclopentadienyl groups are possible, namely (i) where they lie across the mirror planes at $x = 0$ and ½ (see Fig. 2(i)), and (ii) where they are situated about 2-fold axes normal to these mirror planes (Fig. 2(ii)). Anisotropic temperature factors were used for the zinc and methyl carbon atoms, isotropic factors were used for the cyclopentadienyl carbon atoms, and calculated positions were used for the cyclopentadienyl hydrogen atoms. The R factors were 0.057 and 0.059 for the two orientations. For each orientation, an electron density difference map showed very small peaks at the positions of atoms in the other orientation. The composite arrangement, with the cyclopentadienyl atoms placed at sites corresponding to both orientations, gave an R value

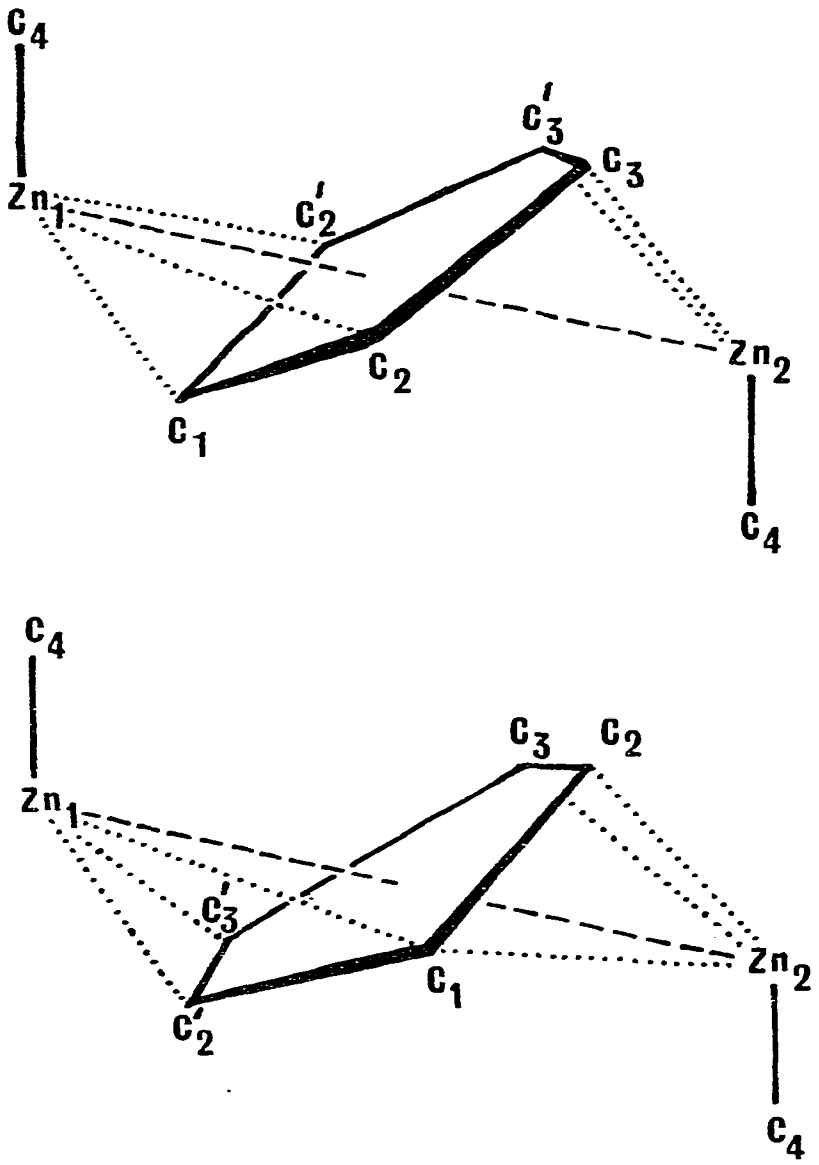

Fig. 2. Alternative possible orientations of the C_5H_5 groups with respect to the bridged ZnMe units.*

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* For clarity, neither Fig. 2(i) nor Fig. 2(ii) shows the additional C_5H_5 ring required for a centrosymmetric structure.

Table. Interatomic distances (pm) for orientations (i) and (ii)

	(i)	(ii)		(i)	(ii)
Zn----Zn	491	491	Zn_2-C_2	281	225
Zn_1-C_1	222	274	Zn_2-C_3	231	241
Zn_1-C_2	265	314	Zn_2-C_4	197	195
Zn_1-C_3	311	298	C_1-C_2	144	139
Zn_1-C_4	197	195	C_2-C_3	139	135
Zn_2-C_1	312	274	C_3-C'_3	138	147

Mean e.s.d.'s: Zn–C, 1.3 pm; C–C, 2 pm

of 0.055. From the R values, orientation (i) appears marginally preferable to (ii), but it would seem more realistic to describe the structure in terms of highly disordered or rotating cyclopentadienyl groups.

Whatever its orientation, each cyclopentadienyl ring clearly bridges two metal atoms located perpendicularly above (Zn_1) and below (Zn_2) diametrically opposed points on its circumference, and on average may be regarded as contributing 2½ electrons to each metal atom. For example, for orientation (i), atoms C_1, C_2 and C'_2 appear to be bonded to Zn_1, and C_3 and C'_3 to Zn_2 (key interatomic distances and angles are given with the figures). Orientation (ii) places C'_2 and C'_3 clearly bonded to Zn_1, C_2 and C_3 likewise bonded to Zn_2, and atom C_1 equidistant from (but less strongly bonded to) Zn_1 and Zn_2. These bonding interactions are indicated by the dotted lines in Fig. 2. All other possible orientations of the cyclopentadienyl rings must lie between (i) and (ii).

Each zinc atom is thus surrounded by a distorted trigonal arrangement of three ligands which provide the total of six electrons needed to fill the metal's valence shell: a methyl group functioning as a 1-electron ligand, and two cyclopentadienyl groups, of hapticities in the range 2-3, contributing five electrons between them.

This $-M(C_5H_5)M(C_5H_5)M(C_5H_5)-$ chain structure of $Zn(C_5H_5)Me$ may be compared with those of $In(C_5H_5)$,[31] $Tl(C_5H_5)$,[31] $Pb(C_5H_5)_2$,[32] $Ga(C_5H_5)Me_2$[33] and

$Na(C_5H_5)(TMED)$.[34] All these chains are puckered, the degree of puckering reflecting the spatial requirements of the terminal substituents[32–34] or 'lone-pair' electrons[31,32] on the metal atoms. The type of bridging found in $Zn(C_5H_5)Me$ is intermediate between that found in $Na(C_5H_5)$-TMED[34] (in which the metal atoms lie above and below the ring plane, on the ring 5-fold axis) and $Ga(C_5H_5)Me_2$[33] (in which the bridged metal atoms lie respectively vertically above and vertically below points outside the C_5 ring – the ring bonds monohapto to each of the bridged gallium atoms). Displacement of the metal atoms from the 5-fold axis towards the ring perimeter is also a feature of crystalline $Be(C_5H_5)_2$,[4,5] $Ca(C_5H_5)_2$[35] and $Al(C_5H_5)Me_2$.[36,37]

Our finding that $Zn(C_5H_5)Me$ polymerises through bridging cyclopentadienyl groups, like the mixed cyclopentadienyl(methyl) derivatives of aluminium[36,37] and gallium,[33] raises the question of whether its magnesium analogue, $Mg(C_5H_5)Me$, does likewise. Cyclopentadienylmagnesium methyl has been prepared in unsolvated form[38,39] and, on the basis of its infrared spectrum, was considered to have a methyl-bridged structure in the solid.[39]

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