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The Preparation and Crystal and Molecular Structure of Diethylammonium Tris(tetraphenyldisiloxanediolato) Zirconate(IV)

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The chemistry of organosiloxanes has received much attention in recent years, not only on account of their inherent academic interest but also in view of the industrial and pharmacological uses of certain groups of compound within this class. Considerable attention has also been focussed on metallo–organosiloxanes-systems in which organosiloxane species are bonded to other metal atoms. Although earlier reports indicated that very stable molecular compounds could be prepared in which titanium atoms had been incorporated into siloxane rings [1] and that metal-containing polymeric species could be prepared [2], no structural confirmation has yet been obtained. The only organosiloxane type ligands which have featured in structural work are the triorganosiloxanes [3], and in most cases the compounds can be considered to be special types of alkoxide derivatives.

Accordingly, as part of our general study of organosiloxanes and related compounds, we are examining the reactions of organosilanols with various metal-containing species. Here we report the preparation and structure of a novel zirconium organosiloxane.

The compound was obtained in very low yield by the reaction of tetrakisdiethylaminozirconium and diphenylsilanediol in THF. Recrystallization from diethyl ether gave colourless crystals (M.p. >360) suitable for X-ray study. (Found: C, 64.80; H, 5.80; N, 1.85%. Calc for $[C_{72}H_{60}O_9Si_6Zr]$ $(C_4H_{12}N)_2$: C, 65.05; H, 5.69; N, 1.89%.)

The crystals are monoclinic, space group P2/n, with a = 15.185(2), b = 15.416(4), c = 16.667(2) Å, β = 93.62(1)°, D_m = 1.22, D_c = 1.26 Mg m^{-3} and Z = 2. The structure was solved and refined by standard procedures using 4170 observed intensities collected on a Nonius CAD4 automatic diffractometer in a manner described previously [4]. With all non-hydrogen atoms assigned anisotropic temperature factor coefficients, the current R value is 0.0501.

The structure analysis revealed that the compound was the diethylammonium salt of the tris(tetraphenyldisiloxanediolato)zirconium anion, in which the ligand is derived from the condensation of two

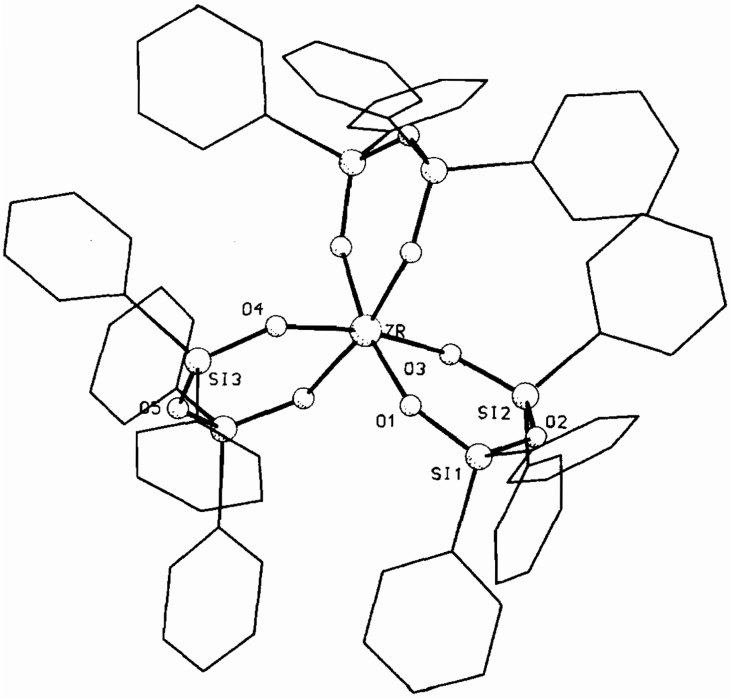

Fig. 1. Structure of tris(tetraphenyldisiloxanediolato)zirconium anion.

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diphenylsilanediol molecules. That is not surprising in view of the basic nature of the reaction medium arising from the release of diethylamine and indeed, the bulk of the product in the reaction is a white, amorphous, probably polymeric material.

The anion has a tris-chelate, distorted octahedral structure with C_2 molecular symmetry coincident with a crystallographic two-fold axis (Fig. 1). The distortions from ideal octahedral ZrO_6 co-ordination are interesting in that they are almost entirely of the octahedral → prismatic twist type. The bite of the diolato ligand is large (O···O = 2.85, 2.88 Å) giving rise to chelate O–Zr–O angles of 85.6 and 85.9°. This situation probably arises as a result of the flexibility of the Si–O–Si and Si–O–Zr linkages in the rings, where the relevant angles are ~132 and 139° respectively. The octahedral → trigonal prismatic twist angle, defined as the projection angle between the two triangular faces linked by each of the chelate ligands, averages to 46.9°. The ratio of the average ligand bite to Zr–O bond length is 1.37 and this yields a modified octahedral twist angle of 56° on the basis of Keperts' calculations [5] on the minimisation of interligand repulsions. Thus we have an indication of a 9° distortion towards trigonal prismatic geometry. This is quite small and parallels results obtained for the tris(benzene-2-dithiolate)-zirconate(IV) ion [6] where the corresponding angle is 12°. Whether this small distortion is meaningful in terms of the preferred stereochemistry at zirconium is debateable, although it is worth commenting that the presence of the phenyl rings on the silicon atoms would certainly favour the antiprismatic (*i.e.* octahedral) over the prismatic co-ordination.

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