

Preliminary communication

THE X-RAY STRUCTURE OF THE h^5 -CYCLOPENTADIENYLTRIS-(TROPOLONATO)ZIRCONIUM(IV) 1:1 DICHLOROMETHANE SOLVATE

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Summary

X-ray structure analysis has shown that h^5 -cyclopentadienyltris(tropolonato)zirconium(IV) may be regarded as seven-coordinate with a slightly distorted pentagonal bipyramidal geometry; the h^5 -cyclopentadienyl group occupies an axial position.

Frazer and Newton reported the synthesis of cyclopentadienyl complexes of the type $(h^5-C_5H_5)Zr(ke)_2$ by the reaction of dichloro- h^5 -cyclopentadienylzirconium(IV) with diketones (keH) [1]. However with tropolone (TH), further substitution always occurred so that only the tris-chelate complex $h^5-C_5H_5Zr^{IV}T_3$ was obtained. This observation is consistent with the tendency of tropolone to form complexes of high coordination number. The structure of the tropolone complex has been determined from crystals obtained by recrystallisation from dichloromethane.

Crystals of $C_{26}H_{20}O_6Zr \cdot CH_2Cl_2$ are triclinic, spacegroup $P\bar{1}$, a 9.83, b 12.44, c 13.88 Å, α 103.7, β 94.2, γ 128.4°, V 1236 Å³; D_o 1.59, D_c 1.62 g cm⁻³, Z = 2. Eight small crystals, which decomposed slowly in the X-ray beam, were used to collect 3453 visually estimated reflections using Cu- K_α radiation. Block diagonal least-squares refinement of all non-hydrogen atomic positional and anisotropic thermal parameters reduced the discrepancy index R to 0.095. The molecular geometry is shown in Fig.1; estimated standard deviations in the bond lengths average Zr—O, Zr—C, C—O 0.01 Å, C—C 0.02 Å. The tropolonato ligand bond lengths given are the mean values for chemically equivalent bonds of the three tropolonato ligands. There appear to be two hydrogen bonds between the dichloromethane and the complex (O(1)—H(1) 2.27 and O(5)—H(2) 2.30 Å).

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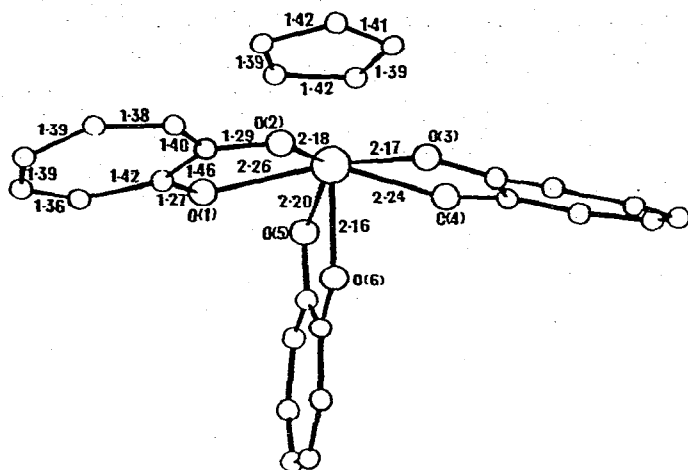


Fig.1. The structure of h^5 -cyclopentadienyltris(tropolonato)zirconium(IV); bond lengths in Å.

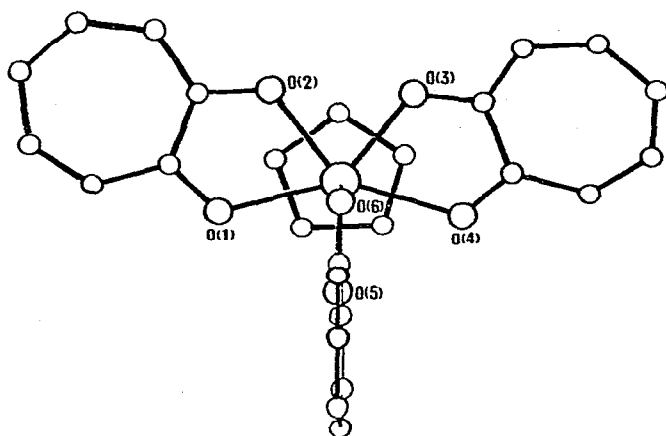


Fig.2. The molecular structure projected onto the plane of the cyclopentadienyl ligand.

The coordination geometry of the zirconium atom may be regarded as distorted pentagonal bipyramidal with the h^5 -cyclopentadienyl group occupying one axial site (Zr—C 2.52–2.59 Å), the other six positions being occupied by tropolonato-oxygen atoms. The five carbon atoms of the cyclopentadienyl group are in a staggered conformation relative to the equatorial oxygen atoms (Fig.2). The zirconium atom is 0.40 Å above the equatorial plane towards the cyclopentadienyl group. The geometry is comparable to that of the h^5 -cyclopentadienyltris(hexafluoroacetylacetonato)zirconium(IV) complex, reported by Elder [2], but with some significant differences caused by the smaller bite of the tropolonato ligand (mean tropolonato O—O 2.52 Å). The five equatorial oxygen atoms of the $C_5H_5ZrT_3$ complex are nearly coplanar (maximum deviation 0.11 Å) as are those in the hexafluoroacetylacetonato complex. However it is of interest that in the tropolonato complex the near planarity of the equatorial oxygen atoms is achieved by the Zr—O(6)

axial bond being distorted 5.9° away from the ideal position. This distortion can be seen in Fig. 2.

References

- 1 M.J. Frazer and W.E. Newton, *Inorg. Chem.*, 10 (1971) 2137.
- 2 M. Elder, *Inorg. Chem.*, 8 (1969) 2103.