X-Ray Crystal Structure of Tetrakis(8-quinolinolato)zirconium(IV), A Dodecahedral $M(AB)_4$ System

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Summary The structure of the title compound confirms previous suggestions that the stereochemistry of dodecahedral transition-metal complexes of the type $M(AB)_4$ is dependent upon the electronic configuration of the metal ion.

IN 1960 a stereochemical rule applying to the geometry of eight-co-ordinate, dodecahedral d^1 and d^2 transition metal complexes was proposed by Orgel.[1] Further development of Orgel's idea to include d^0 complexes[2–4] suggests that dodecahedral molecules of the type $M(AB)_4$ are expected to have structures in which the ligands are sorted into the appropriate A and B co-ordination sites[5] according to their relative π-donor–acceptor capabilities and the electronic configuration of the transition-metal ion. The structures of $[MeNC)_4Mo(CN)_4]$,[6] $[W(Brquin)_4]$[3] (Brquin = 5-bromoquinolin-8-olate), and [Zr(nes)$_4$][4] (nes = N-ethylsalicylaldiminate) tend to support this proposal although the stereochemistry of the former two complexes may be determined by steric rather than electronic interactions. While the structure of [TiCl$_4$(diars)$_2$] conforms to Orgel's rule, stereoisomers having arsenic atoms in the B co-ordination sites are unlikely because the 'bite' of the diarsine ligand is too short to span the longest (b) edge of a dodecahedron.[2] The structures of complexes whose only essential difference is the electronic configuration of the metal ion could be used to test Orgel's hypothesis. Following work by Bonds, *et al.*[3] on the structure of [W(Brquin)$_4$] and predictions concerning the structure of the zirconium(IV) analogue, we have prepared the complex [Zr(quin)$_4$] (quin = quinolin-8-olate) and determined its structure by X-ray diffraction. (Use of the identical ligand is unnecessary for our purpose since the bromine atom is unimportant in relation to the stereochemistry of the tungsten complex.) *Crystal data:* Zr(C$_9$H$_6$NO)$_4$,3 toluene, M = 944·26, orthorhombic, space group $Fddd$, a = 14·186 (4), b = 27·720 (9), c = 21·371 (6) Å, D_m = 1·45 g cm^{-3}, Z = 8, D_c = 1·49 g cm^{-3}. The structure has at present been refined to R = 0·108 for the 1077 observed reflections measured with an automated diffractometer using Co-K_α radiation.†

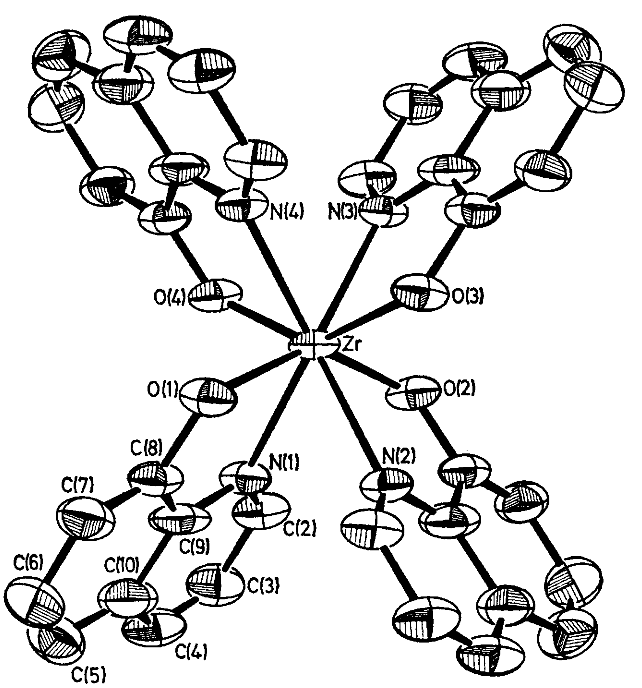

FIGURE. A view of the [Zr(C$_9$H$_6$NO)$_4$] molecule along the twofold axis which passes through the Zr atom and the midpoint of the dodecahedral b edge defined by oxygen atoms O(1) and O(3).

The zirconium atom occupies special position 8a at the intersection of three twofold axes. The complex (Figure) adopts a dodecahedral geometry in which the bidentate 8-quinolinolato ligands span the g edges of a D_{2d} dodecahedron to give the D_2 *gggg* stereoisomer, in agreement with the prediction of Bonds, *et al.*[3] The interpenetrating ABBA trapezoids are nearly perpendicular (85·3°), with the metal atom and the atoms which define an individual trapezoid being planar to within 0·03 Å. The most important feature of the structure is the occupancy of the A and B co-ordination positions. In the d^2 [W(Brquin)$_4$] complex (D_{2d} *mmmm* stereoisomer), the π-donor phenolic oxygen atoms occupy the A sites, while the π-acceptor quinolinolate nitrogen atoms occupy the B sites. However, in the d^0 [Zr(quin)$_4$] complex, the reverse site occupancy is observed since the π-donor oxygen atoms are now able to be accommodated at the B sites adjacent to the vacant $d_{x^2-y^2}$ metal orbital. The dimensions of the co-ordination polyhedra of [Zr(quin)$_4$] and [W(Brquin)$_4$] are summarized in the Table. Major differences are seen in the lengths of the a and m edges owing to the different site occupancies and ligand wrapping patterns in the two complexes. The a edges are longer in the zirconium complex because the bonds to the A sites (Zr–N and W–O) differ by more than 0·3 Å. The m edges in the zirconium complex are not constrained by the bite of the ligand and are thus some 0·23 Å longer than in the tungsten complex.

TABLE. Dimensions (Å) of the co-ordination polyhedra

Bond	[Zr(quin)$_4$][a]	[W(Brquin)$_4$][b]
M–O	2·106(6)[c]	2·065[d]
M–N	2·405(8)	2·198[d]
Edge[e]		
a	2·810(10)	2·330[d]
b	3·146[d]	3·224[d]
m	2·738(11)	2·501[d]
g	2·717[d]	2·653[d]

[a] This work. [b] Ref. 3. [c] Figures in parentheses are standard deviations in the last significant figure. [d] Mean values. [e] Edges are labelled according to Hoard and Silverton.[5]

The structures of [Zr(quin)$_4$] and [W(Brquin)$_4$] provide definitive proof that the choice of stereoisomer for a dodecahedral molecule can be controlled by the electronic configuration of the transition metal ion. In the absence of unreasonable steric interactions, Orgel's hypothesis appears to be a useful guide to the stereochemistry of eight-co-ordinate d^0 and d^2 transition metal complexes.

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† Two of the toluene molecules have been located, and these are disordered with respect to a crystallographic twofold axis. The remaining toluene molecule, probably badly disordered, has not yet been located.

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