Eight-co-ordinated Zirconium(IV) Schiff-base Compounds: an *X*-Ray Study

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Summary The crystal structure of tetrakis-(*N*-ethylsalicylaldiminato)zirconium(IV) contains eight-co-ordinated (dodecahedral) tetrachelated zirconium in the unusual S_4 configuration with remarkably long Zr–N bond lengths; n.m.r. evidence suggests that the *N*-isopropyl derivative is also eight-co-ordinate whereas the *N*-t-butyl derivative involves a lower co-ordination of the zirconium.

THE *X*-ray structure determination of tetrakis-(*N*-ethylsalicylaldiminato)titanium(IV) (I; M = Ti, R = Et) revealed a distorted *cis*-octahedral configuration with two bidentate and two unidentate ligands co-ordinated through the oxygen atoms.[1] In view of the surprising unidentacy of two of the ligands in this complex, we have now prepared and examined some zirconium analogues (I; M = Zr) for comparison.

The complexes were obtained by treatment of zirconium tetrakisdimethylamide with the appropriate aldimine in non-aqueous solution (satisfactory elemental analyses were obtained).

$$\mathrm{M(NMe_2)_4 + 4HOC_6H_4CH\!:\!NR \rightarrow M(OC_6H_4CH\!:\!NR)_4 + 4HNMe_2}.$$

$$\text{(I)};\ \mathrm{M = Ti,\ R = Me,\ Et,\ Pr^i,\ Bu^t}$$

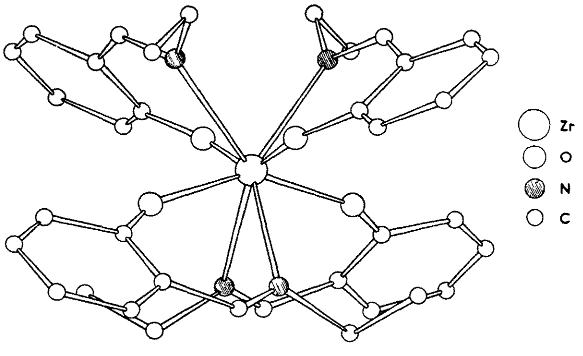
$$\mathrm{M = Zr,\ R = Et,\ Pr^i,\ Bu^t}.$$

The n.m.r. spectra of (I; M = Zr, R = Et, $\mathrm{Pr^i}$) in solution ($CDCl_3$ and CS_2) broadened only slightly at low temperatures, whereas the methyl, methylene, and methine protons of the titanium complexes split into double peaks at low temperature due to slowing down of intramolecular exchange between bidentate and unidentate ligands. This suggested that the zirconium complexes were eight-co-ordinated with four equivalent bidentate ligands. A single-crystal *X*-ray structure determination has confirmed this and revealed an interesting configuration for the tetrachelated molecule.

A tetragonal crystal of $C_{36}H_{40}N_4O_4Zr$ gave $a = b = 10{\cdot}285$ Å; $c = 31{\cdot}55$ Å; $Z = 4$; $D_m = 1{\cdot}35$; $D_c = 1{\cdot}36$ g/cm³; with space group $I4_1/a$-(C_{4h}^6). The intensities of 836 independent non-zero reflections were recorded with a General Electric XRD6 diffractometer using Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å). No absorption corrections were applied. The presence of only four molecules in the unit cell required the zirconium atom to be in a special position on a $\bar{4}$-(S_4) axis. The positions of the light atoms (except hydrogen) were determined from the first electron-density synthesis phased on zirconium. Full-matrix least-squares refinement has reduced the *R*-factor to 0·078 and refinement is being continued. The structure viewed down the *b* axis is shown in the Figure.

The preference of the zirconium atom for a dodecahedral eight-co-ordination is not unusual.[2] However, in previously known dodecahedral structures with chelate ligands the D_{2d} isomer has predominated (chelation along the *m* edges, following the notation of Hoard and Silverton[3]). Recently, $\mathrm{NH_4[Pr(TTA)_4],H_2O}$ (TTA = thenoyltrifluoroacetylacetonate) and $\mathrm{Cs[Y(HFA)_4]}$ (HFA = hexafluoroacetylacetonate)[4] were found to adopt the D_2 isomer configuration (chelation along the *g* edges). The zirconium complex (I; M = Zr, R = Et) is also chelated along the *g* edges of the dodecahedron, but it is the first known compound exhibiting the S_4 configuration. The shape of the dodecahedron is specified by the parameters[3]: Zr–N, 2·539 ± 0·009 Å; Zr–O, 2·055 ± 0·007 Å; Zr–N/Zr–O, 1·236; θ_{N}, 34·6 ± 0·2°; θ_{O}, 73·3 ± 0·5°; where θ_{N}, θ_{O} are the angles between the Zr–N, Zr–O bonds and the S_4 axis,[2] respectively (*cf.* the hard-sphere model of the dodecahedron[3] which has equal bond lengths M–A and M–B with θ_{A}, θ_{B} values of 36·85 and 69·46° respectively).

Of particular interest are the very long Zr–N bond length (0·36 Å longer than the sum of the covalent radii for Zr and N[5]) and the short Zr–O bond length (usually 2·15—2·55 Å in 8-co-ordinated complexes[2]) together with the fact that the nitrogens occupy A positions in the dodecahedron and the oxygens take the B positions. The bite of the chelate rings (2·78 ± 0·01 Å) is normal for this type of ligand[2] and the rings are slightly folded about a line through the oxygen and nitrogen atoms. It therefore seems that the Zr–N bonding is rather weak. Besides possible steric factors there appear to be electronic factors which favour Zr–O bonding at the expense of Zr–N. Thus the negatively charged oxygens should prefer the B-positions to minimise Coulombic repulsion and they could also act as π-donors, with the zirconium using its vacant d_{xy} orbital[6] and thereby achieving an 18-electron configuration. The imino nitrogen atoms are poor π-donors and they occupy the A-positions which are less favourable for π-bonding to the d_{xy} orbital.[6]



FIGURE

Packing considerations within the crystal and the solution n.m.r. results suggest that the *N*-isopropyl complex (I; M = Zr, R = $\mathrm{Pr^i}$) is probably of similar structure to the *N*-ethyl derivative (I; M = Zr, R = Et) but that the *N*-t-butyl complex (I; M = Zr, R = $\mathrm{Bu^t}$) probably is not eight co-ordinate.

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