# Novel Schiff-base Titanium(IV) Compounds

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*N*-ALKYLSALICYLALDIMINATO-GROUPS normally behave as chelating ligands with transition metals. Interesting special features of these ligands are (i) the control of tetrahedral-square-planar equilibria by the steric effect of the *N*-alkyl group in some bis-chelated derivatives and (ii) dimerization of *N*-methyl derivatives due to oxygen bridging leading to five-co-ordinated bivalent metals (*e.g.* Co, Cu).[1] The discovery of eight-co-ordinated titanium compounds by Clark *et al.*[2] raised the possibility of titanium forming a tetrachelated derivative of an *N*-alkylsalicylaldiminate. We have prepared some tetrakis-derivatives by the following reaction:

$$\mathrm{Ti(NMe_2)_4 + 4\,HOC_6H_4CH{:}NR \rightarrow Ti(OC_6H_4CH{:}NR)_4 + 4HNMe_2}$$

(I); R = Me, Et, Bu$^t$.

The n.m.r. spectrum of (I; R = Et) in solution ($CDCl_3$) showed broadened methylene, methyl, and methine proton resonances at room temperature which at low temperature split into double peaks suggesting an exchange between two types of ligand in equal proportions. This result could be explained by the presence of either an eight-co-ordinated tetra-chelated complex with a configuration containing the ligands in two distinguishable environments or a six-co-ordinated complex containing two bidentate and two unidentate ligands.

A single-crystal *X*-ray structure determination has shown the second alternative to be correct and the compound has the *cis*-unidentate configuration shown in the Figure. Orthorhombic crystals of $C_{36}H_{40}N_4O_4Ti$ gave $a = 10{\cdot}15$, $b = 17{\cdot}01$, $c = 39{\cdot}26$ Å, $Z = 8$, $D_o = 1{\cdot}22$, $D_c = 1{\cdot}26$ g./cc. with space group *Pbca*. Three-dimensional *X*-ray data were collected by the equi-inclination Weissenberg technique using Cu-$K_\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Intensities were estimated visually and 1005 independent reflections were obtained. No absorption corrections were applied. The metal co-ordinates were determined from the Patterson synthesis and the light atoms (except hydrogen) from subsequent Fourier synthesis. The *R*-factor has been reduced to 0·126 and refinement is being continued. The structure viewed down the *b*-axis is shown in the Figure and it contains several interesting features. The preference of titanium(IV) for six-coordination is not surprising but the presence of unidentate aldimine ligands is remarkable. The adoption of the *cis*-unidentate configuration recalls the similar behaviour of Ti(acac)$_2$(OR)$_2$ compounds[3] and this feature together with the *cis*-nitrogen *trans*-oxygen arrangement of the bidentate aldimine groups will be discussed in a later publication. The Ti–N bonds (2·24—2·25 ± 0·03 Å) are considerably longer than Ti–O bonds (1·87—1·91 ± 0·02 Å) and the $TiO_4N_2$ octahedron is considerably distorted (*e.g.* the chelate ring ∠OTiN = 83 ± 1°). It is noteworthy that similar Ti–O and Ti–N bond lengths were found in *cis*-Ti(Oxinate)$_2$Cl$_2$.[4] The n.m.r. spectrum of the *N*-methyl derivative (I; R = Me) suggests that it also contains bis-unidentate bis-bidentate ligands but the *N*-t-butyl derivative (I; R = Bu$^t$) is different and is still being investigated.

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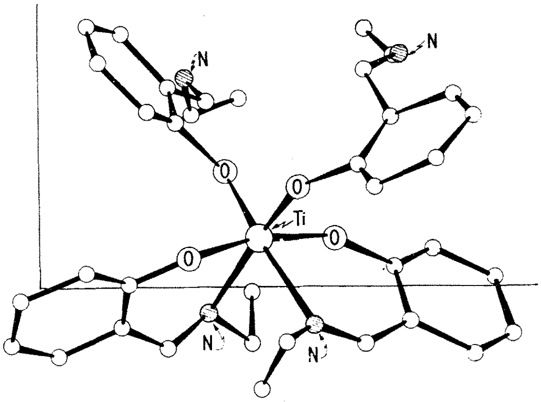

FIGURE

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