Unusual Minicyclic Macrocyclic Sandwich Complex of Titanium(III) containing Cyclopentadienyl and Tetramethyldibenzocyclotetradecane ($C_{22}H_{22}N_4{}^{2-}$) Ligands

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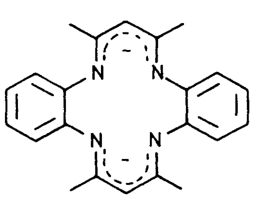
$Ti(C_{22}H_{22}N_4)(C_5H_5)$, obtained from the reaction of $Ti(C_{22}H_{22}N_4)Cl_2$ with NaC_5H_5, consists of a minicyclic ($C_5H_5{}^-$) and a tetra-aza macrocyclic ($C_{22}H_{22}N_4{}^{2-}$) component bound to Ti^{III} in a new type of sandwich complex the structure of which has been determined by *X*-ray crystallography.

Aside from porphyrin and phthalocyanine ligands few studies of titanium with tetra-aza macrocyclic ligands have been published. Previously we demonstrated the unusual structure of $Ti(C_{22}H_{22}N_4)Cl_2$ (*cis*-chloride with an unusually large displacement of the Ti from the N_4 plane, 0.91 Å) and a consequent rich reaction chemistry.[1] The existence of well characterized $(C_5H_5)_2TiCl_2$ and $(\eta^5\text{-}C_5H_5)_2Ti(\sigma\text{-}C_5H_5)_2$ complexes[2] suggested the possibility of an analogous σ-bonded organometallic derivative of the macrocyclic complex, $Ti(C_{22}H_{22}N_4)(\sigma\text{-}C_5H_5)_2$.

We report that the reaction of $Ti(C_{22}H_{22}N_4)Cl_2$ with NaC_5H_5 in tetrahydrofuran (THF) results rather in the reduction of Ti^{IV} to Ti^{III} and the formation of $Ti(C_{22}H_{22}N_4)(C_5H_5)$. New absorptions in the i.r. spectrum at 805 and 789 cm^{-1} suggested a π-bonded $\eta^5\text{-}C_5H_5$ ligand[3] rather than a $\sigma\text{-}C_5H_5$ as might be predicted based on the commonality of co-ordination numbers with square-pyramidal complexes of the type Ti(macrocyclic)X, macrocycle = porphyrin, phthalocyaine, or $C_{22}H_{22}N_4{}^{2-}$. The title compound is air stable, unlike the analogous halide complexes of this and porphyrin and phthalocyanine ligands.



$C_{22}H_{22}N_4{}^{2-}$

The crystal structure (Figure 1) confirms the unusual $Ti(N_4)(\eta^5\text{-}C_5H_5)$ structure.† The Ti^{III} is equivalently bound to the four nitrogen atoms of the $C_{22}H_{22}N_4{}^{2-}$ ligand with the π-bonded $\eta^5\text{-}C_5H_5$ parallel to the N_4 plane forming a minicycle–macrocycle sandwich compound. Rather than specifying the co-ordination number of the complex, it is more useful to think of it as a pseudo-five-co-ordinate complex so enabling comparison of its parameters with those of Ti(L)X (X = halide or oxygen donor). The salient structural data are summarized as follows. (i) The average Ti–N distance is 2.127(4) Å. (ii) The displacement of the Ti^{III} from the N_4 donor plane is unusually large, 0.900 Å, and virtually identical to that of $Ti(C_{22}H_{22}N_4)Cl_2$. This large displacement of Ti from the N_4 plane facilitates $\eta^5\text{-}C_5H_5{}^-$ bonding for two reasons: (a)

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† *Crystal data:* Crystals of $Ti(C_{22}H_{22}N_4)(C_5H_5)$ were grown from tetrahydrofuran and are brown, orthorhombic, space group *Pbca*, a = 8.725(5), b = 17.785(5), c = 25.519(19) Å, Z = 8, U = 4425(7) $Å^3$. The $C_5H_5{}^-$ was disordered, but the disorder was resolved assuming two orientations of the $C_5H_5{}^-$ ligand and refining the ten carbon atoms at 0.5 multiplicity. Refinement of all non-hydrogen atoms with anisotropic thermal parameters and with hydrogen atoms included at fixed positions converged to R = 6.7%, R_w = 7.9% for 2936 independent reflections with $F \geqslant 2\sigma(F)$ out of 5910 unique data collected. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

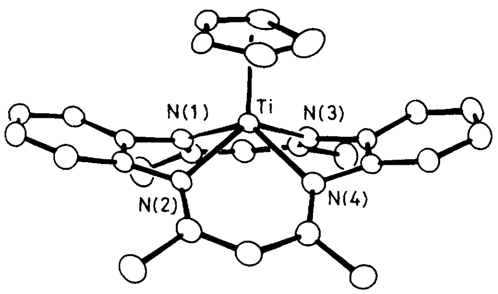

Figure 1. ORTEP plot of Ti($C_{22}H_{22}N_4$)(η^5-C_5H_5) illustrating the displacement of Ti^{III} from the N_4 plane and the pseudocoplanarity of the $C_{22}H_{22}N_4{}^{2-}$ and η^5-$C_5H_5{}^-$ ligands. Only one orientation of the disordered η^5-$C_5H_5{}^-$ ring is shown for clarity.

it prevents undue steric repulsions between the N_4 donor atoms and the η^5-$C_5H_5{}^-$ ring and (b) the Ti^{III} is left somewhat 'naked' and the soft, electron-rich $C_5H_5{}^-$ ligand fulfills its special electronic needs. (iii) The average Ti–C distance is 2.381 Å and the Ti^{III} is 2.067 Å from the C_5 plane. This distance is similar to the Ti(η^5-C_5H_5) distance in $TiCl_3$(η^5-C_5H_5),[4] 2.04 Å, and Ti(Cl_2)(C_5H_5)$_2$, 2.06 Å.[5]

E.s.r. measurements for a toluene glass at −178 °C yielded anisotropic spectra as expected for an $S = 1/2$, $I = 0$ system with the exception that a rhombic rather than the expected tetragonal environment was indicated. This is attributed to substantial differences in the 'bite' of the distances of the five-membered *vs.* six-membered chelate rings, 2.585(5) Å *vs.* 2.851(5) Å. Analyses of the spectrum lead to the d orbital ordering being $d_{x^2-y^2} > d_{z^2} > d_{xz} > d_{yz} > d_{xy}$. Spectra taken at 10 °C exhibited an isotropic nine-line spectrum produced from the interaction of the unpaired electron with four equivalent nitrogen atoms. The hyperfine coupling constants, $a_N = 2.03$ and $a_{Ti} = 13.1$ G,‡ are smaller than for related five-co-ordinate square-pyramidal complexes and reflect the large displacement of the Ti from the N_4 plane and the increased delocalization of the unpaired electron on to the $C_5H_5{}^-$ ring. For example, $a_N = 2.2$—2.5 G for a variety of five-co-ordinate Ti^{III} porphyrin complexes.[6] The value of $a_{Ti} = 17.4$ G for Ti($C_{22}H_{22}N_4$)Cl also reflects the effects of the delocalization on the $C_5H_5{}^-$ ring.

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‡ 1 G = 10^{-4} T.