

New Macrocyclic Complexes of Titanium(IV): Synthesis, Reactivity, and X-Ray Crystal Structure of the Trigonal Prismatic $\text{Ti}(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{Cl}_2$, and Synthesis and Reactivity of its Peroxo, Disulphido, and Pyrocatecholato Derivatives

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The new macrocyclic complex of titanium(IV), $\text{Ti}(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{Cl}_2$ has been shown by X-ray crystallography to have a trigonal prismatic co-ordination geometry; the synthesis and reactivities of the peroxo, disulphido, and pyrocatecholato derivatives are discussed.

The conjugated $\text{C}_{22}\text{H}_{22}\text{N}_4^{2-}$ ligand (L), although flexible because of possible rotation about the N-C bonds of the *o*-phenylenediamine moiety, is constrained such that the four N atoms are confined to a plane. Because the unstrained nitrogen-to-centre distance, 1.92 Å,¹ is shorter than

preferred for most first-row metal-to-nitrogen distances, in complexes with this ligand these metals are displaced from the N_4 donor plane, by up to 0.70 Å for the Mn^{II} complex.² Investigation of the chemistry of the Ti^{IV} complexes of this ligand has been initiated because (i) of the absence of crystal-

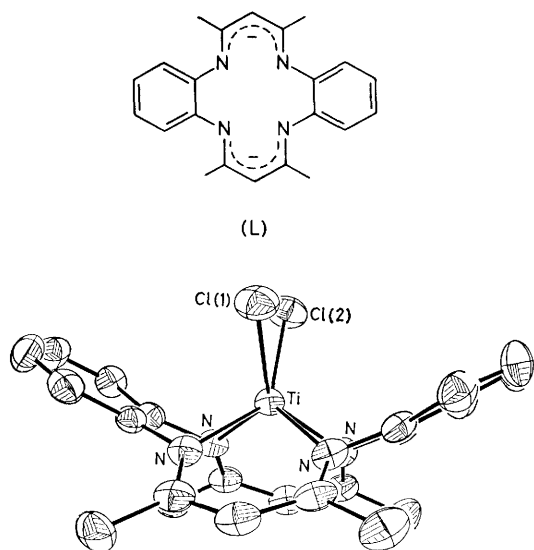


Figure 1. X-Ray structure of the complex TiLCl_2 .

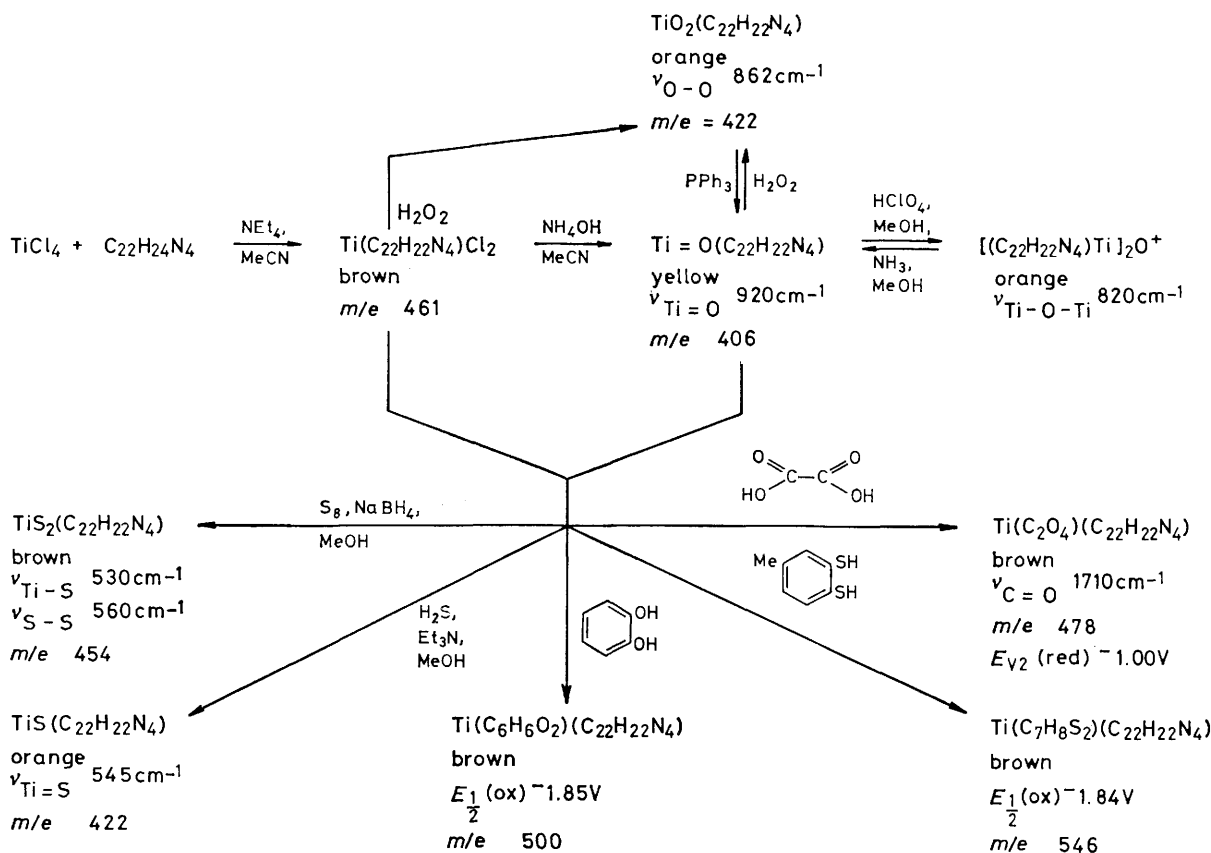
field effects for this d^0 system, (ii) oxidation states as high as +4 have not been previously observed for this ligand, and (iii) the affinity of Ti^{IV} for side-bonded peroxo ligands may have application as oxygen atom transfer agents for organic substrates.

Reaction of TiCl_4 with LH_2 under basic conditions (see Scheme 1) results in the formation of molecular TiLCl_2 . This moisture-sensitive complex yields an equilibrium mixture of the oxotitanium(IV) species, $\text{TiL}=\text{O}$, and the μ -oxo-bridged species, $[\text{TiL}-\text{O}-\text{TiL}]^{2+}$, in solvents containing small amounts of water. Either species can be isolated, depend-

ing upon the reaction conditions. Reaction of either the TiLO or the TiLCl_2 complex with H_2O_2 generates the very stable, orange, crystalline peroxo complex, TiLO_2 . Oxygen atom transfer from TiLO_2 to Ph_3P to form Ph_3PO and to FeL to form $\text{FeL}-\text{O}-\text{FeL}$ occurs readily. The stability of the peroxo complex suggested the possibility of the isolation of the analogous disulphido complex. Reaction of TiLO or TiLCl_2 with S_8 under reducing conditions generates TiLS_2 . The reaction of this disulphido complex with Ph_3P generates the corresponding TiLS complex and Ph_3PS . We believe this is the first report of sulphido and disulphido complexes of Ti^{IV} , which are analogues of the titanyl and titanium(IV) peroxo species. The interconversion of these compounds is illustrated in Scheme 1.

The crystal structure† of the TiCl_2 complex revealed the unexpected *cis*-geometry of the Cl ligands and the trigonal prismatic co-ordination geometry (see Figure 1). The average Ti-Cl distance is 2.410(1) Å and the Ti-N distance 2.042(4) Å. The displacement of Ti^{IV} from the N_4 co-ordination plane, 0.91 Å, is the largest observed for this ligand and accounts for the availability of *cis*-co-ordination sites. The availability of *cis*-co-ordination sites suggested the accessibility of bidentate chelate complexes with the TiL

† Crystals of the complex were isolated as the triethylammonium chloride double salt, $\text{Ti}(\text{C}_{22}\text{H}_{22}\text{N}_4)\text{Cl}_2 \cdot \text{Et}_3\text{NHCl}$, and belonged to the triclinic space group, $P\bar{1}$ with $a = 10.502(4)$, $b = 11.808(5)$, $c = 12.751(6)$ Å, $\alpha = 95.54(4)$, $\beta = 106.20(6)$, $\gamma = 92.797(5)$, $Z = 2$. 3714 reflections were collected on a Nicolet P3 automated diffractometer. The structure was refined using 2415 reflections to a conventional R value of 4.8% and a weighted R value of 5.37%. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 1

system, a type of complex not possible with most other rigid macrocyclic ligands. The O atom of TiLO is sufficiently basic that it is readily displaced by chelates such as pyrocatechol, 2-mercaptophenol, 3,4-dimercaptotoluene, and oxalic acid to form the corresponding pyrocatecholate and oxalato complexes. These complexes have been examined *via* cyclic voltammetry; the reversible redox potentials are listed in Scheme 1.

The instability of the Ti=O bond relative to the V^{IV}=O bond, and the stability of bidentate chelates, suggested that formation of a bidentate CO₃²⁻ complex from TiLO and CO₂ was a reasonable possibility. Reaction of TiLO with CO₂ took place under only 2 atm of pressure and below 0 °C, to yield a bright orange product. The nature of this product is surprising for two reasons: (i) CO₂ is readily lost, even from the solid state to regenerate TiLO and (ii) the new i.r. absorptions were not identifiable as belonging to co-ordinated CO₃²⁻ ions or other known CO₂ adducts.³ The full character-

ization of this unusual complex must await a low-temperature X-ray structure determination.

A number of features of the chemistry associated with the Ti^{IV}L system are unusual. Among these are the trigonal prismatic co-ordination geometry, the unusual affinity for sulphur derivatives and the unusual stability of the resultant complexes, and the reversible reaction observed with carbon dioxide. Full electrochemical and X-ray structural investigations of these complexes will be published elsewhere.

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