New Macrocyclic Complexes of Titanium(IV): Synthesis, Reactivity, and X-Ray Crystal Structure of the Trigonal Prismatic Ti($C_{22}H_{22}N_4$)Cl₂, and Synthesis and Reactivity of its Peroxo, Disulphido, and Pyrocatecholato Derivatives

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The new macrocyclic complex of titanium(IV), Ti(C₂₂H₂₂N₄)Cl₂ 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 $C_{22}H_{22}N_4^{2-}$ 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 TiLCl₂.

field effects for this d⁰ 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 TiCl₄ with LH₂ under basic conditions (see Scheme 1) results in the formation of molecular TiLCl₂. This moisture-sensitive complex yields an equilibrium mixture of the oxotitanium(IV) species, TiL=O, and the μ -oxo-bridged species, [TiL=O-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 TiLCl₂ complex with H_2O_2 generates the very stable, orange, crystalline peroxo complex, TiLO₂. Oxygen atom transfer from TiLO₂ to Ph₃P to form Ph₃PO and to FeL to form FeL-O-FeL occurs readily. The stability of the peroxo complex suggested the possibility of the isolation of the analogous disulphido complex. Reaction of TiLO or TiLCl₂ with S₈ under reducing conditions generates TiLS₂. The reaction of this disulphido complex with Ph₃P generates the corresponding TiLS complex and Ph₃PS. We believe this is the first report of sulphido and disulphido complexes of Ti^{TV}, 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 TiCl₂ 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 $2 \cdot 410(1)$ Å and the Ti-N distance $2 \cdot 042(4)$ Å. The displacement of Ti^{IV} from the N₄ coordination plane, $0 \cdot 91$ 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, Ti($C_{22}H_{22}N_4$)Cl₂ Et₃NHCl, and belonged to the triclinic space group, $P\overline{1}$ 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.



system, a type of complex not possible with most other rigid macrocylic 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 CO_3^{2-} complex from TiLO and CO_2 was a reasonable possibility. Reaction of TiLO with CO_2 took place under only 2 a⁺m of pressure and below 0 °C, to yield a bright orange product. The nature of this product is surprising for two reasons: (i) CO_2 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 CO_3^{2-} ions or other known CO_2 adducts.³ The full character-

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

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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References

- 1 V. L. Goedken, J. J. Pluth, S.-M. Peng, and B. Bursten, J. Am. Chem. Soc., 1976, 98, 8014.
- 2 M. C. Weiss, B. Bursten, S.-M. Peng, and V. L. Goedken, J. Am. Chem. Soc., 1976, 98, 8021.
- 3 G. Fachinetti, C. Floriani, A. Chiesi-Villa, and C. Guastini, J. Am. Chem. Soc., 1979, 101, 1767, and references cited therein.