

## Deoxovanadium(IV) Complexes of the Dibenzotetramethyltetra-aza[14]-annulene Ligand: Formation of Products containing Thioxo-, $\mu$ -Nitrido-, and Oxidatively Coupled Ligands

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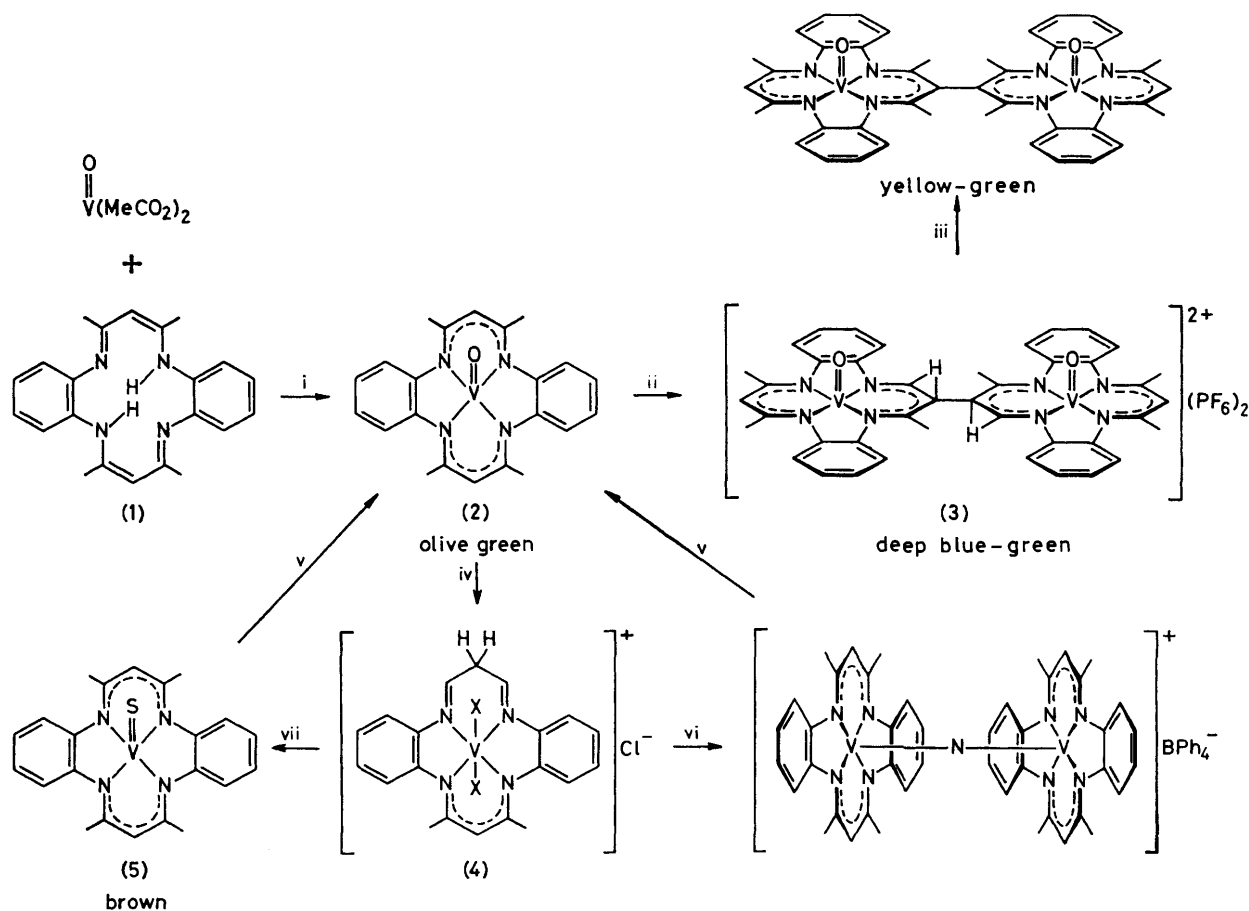
**Summary** Deoxygenation of the oxovanadium(IV) complex,  $V(C_{22}H_{22}N_4)O$ , with anhydrous HCl yields  $V(C_{22}H_{22}N_4)Cl_2 \cdot HCl$  from which a thioxo-complex,  $V(C_{22}H_{22}N_4)S$ , is obtained by reaction with  $H_2S$ , and a  $\mu$ -nitrido-complex  $[V(C_{22}H_{22}N_4)-N-V(C_{22}H_{22}N_4)]^+$  is obtained by reaction with ammonia; a ligand-coupled dimer of  $V(C_{22}H_{22}N_4)O$  is obtained by reaction with mild oxidants.

THE chemistry of vanadyl complexes has been largely ignored because of the inertness of the  $V=O^{2+}$  bond ( $t_{1/2}$  for O-exchange with bulk water is *ca.* 400 min)<sup>1</sup> and the unusually high bond energy of  $V=O^{2+}$  (atomization energy = 140 kcal/mol).<sup>2</sup> We have now synthesised oxovanadium(IV) complexes of (1), deoxygenated the  $V^{IV}$  centre, and used the highly charged  $V^{IV}$  centre as a site to polarize and activate substrate molecules.

Reaction of  $VO(MeCO_2)_2$  with (1) (see the Scheme) yields (2). This compound, although exhibiting a reversible one-

electron oxidation wave at +0.245 V *vs.* standard calomel electrode (S.C.E.) (cyclic voltammetry) with 0.1 M electrolyte, reacts irreversibly with chemical oxidants such as  $O_2$ ,  $Ag^+$ ,  $Ce^{IV}$ , or  $I_2$  to yield deep blue-green solutions from which  $PF_6^-$  or  $ClO_4^-$  salts can be isolated. Physical evidence suggests an oxidatively coupled species (3) *via* C- $\gamma$  of the pentanedi-iminato-chelate rings, similar to oxidatively coupled species characterized for the  $Ni^{II}$  complex of this ligand.<sup>3</sup> Reaction of (3) with  $NEt_3$  yields a complex with properties very similar (electronic spectra,  $\nu_{V=O}$  stretch, *etc.*) to those of (2) but for which mass spectral data implicate a dimer ( $m/e = 818$ ).

Reaction of (2) with anhydrous HCl deoxygenates the  $V^{IV}$  complex, forming (4) with C- $\gamma$  of one of the pentanedi-iminato-rings protonated (*i.e.* spectra show two C=N imine bonds). Unlike many of the other dihalogeno-vanadium complexes with bi- or tetra-dentate Schiff base ligands,<sup>4</sup> even freshly prepared (4) is only sparingly soluble in all



SCHEME. i, toluene, reflux, 18 h, ii,  $[O]$ ,  $PF_6^-$ , iii, base ( $NEt_3$ ), iv, HCl, MeCN, v,  $H_2O$ , vi,  $NH_3$ ,  $BPh_4^-$ , vii,  $H_2S$ , pyridine.

solvents tested, making characterization difficult. Treatment of this complex with H<sub>2</sub>S and base yields the thioxo-analogue of (2), (5) ( $\nu_{\text{V-S}}$  545 cm<sup>-1</sup>). As expected, this complex is extremely unstable with respect to hydrolysis, regenerating (2).

Reaction of (4) with NH<sub>3</sub> in MeCN produces a deep red solution from which [V(C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>)-N-V(C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>)]BPh<sub>4</sub> [ $E_{1/2}(\text{ox}) = -0.863$  V vs. S.C.E. with 0.1 M electrolyte] crystallizes on addition of NaBPh<sub>4</sub>. Consistent with this formulation is the absence of an N-H stretch in the i.r. spectrum and a new absorption at 890 cm<sup>-1</sup> assignable to a V-N stretch. Hydrolysis of this complex to (2) and NH<sub>3</sub> is relatively slow, requiring several minutes in a 1:1 mixture of MeCN:H<sub>2</sub>O. The sole precedent for a  $\mu$ -nitrido-bridge among the first-row transition metal complexes is found in the very well characterized, mixed valence complex [FeTPP-N-FeTPP]<sup>+</sup> (TPP = tetraphenylporphyrin).<sup>5</sup>

The e.s.r. spectral parameters of (4) and (5) (Table) are consistent with those expected on substitution of an oxo-group by two chloride ligands<sup>6</sup> or a thioxo-group,<sup>7</sup> respectively. Room temperature solution spectra and low-temperature (-130 °C) glassy spectra at X-band frequencies were obtained for all these species in a toluene-acetonitrile

TABLE. Spin-Hamiltonian parameters for selected vanadium(IV) complexes.

	(2)	(4)	(5)
$\langle g \rangle$	1.973	1.960	1.9703
$g_{\parallel}$	1.9587	1.9534	1.9607
$g_{\perp}$	1.9805	1.9636	1.9751
$\langle A \rangle$	96.09	74.76	81.16
$A_{\parallel}$	161.98	180.60	143.35
$A_{\perp}$	63.15	21.85	50.04

(50:50) mixture. The averaged solution values for the  $\langle g \rangle$  tensors and the nuclear hyperfine interaction,  $\langle A \rangle$ , tensors of both species are appreciably reduced compared with the values for (2). These reductions clearly represent a relative decrease of charge on the central vanadium(IV) ion and increased covalency in the metal-axial ligand bonds. The large decrease in  $g_{\perp}$  observed for (4) may be an indication of *cis*-co-ordination of the halide ligands. A decrease in  $g_{\parallel}$  with *trans*-geometry and decreases in  $g_{\perp}$  with *cis*-co-ordination have been noted in the e.s.r. spectra of other dihalogeno-vanadium(IV) complexes.<sup>6</sup>

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