Deoxygenation of Vanadyl Schiff's Base Complexes: Conversion of Oxocation Complexes into Halogeno-derivatives

By MARCO PASQUALI,† AFRÂNIO TORRES-FILHO,‡ and CARLO FLORIANI*†

(†*Istituto di Chimica Generale ed Inorganica, Università di Pisa,* 56100 *Pisa, Italy;* ‡*Instituto de Quimica, Universidade Federal da Bahia,* 40000 *Salvador, Bahia, Brazil*)

Summary Deoxygenation of vanadyl Schiff's base complexes by $SOCl_2$ gave the corresponding dichloro-derivatives of vanadium(IV).

THE chemistry of vanadium(IV) is dominated by the stable VO^{2+} ion,[1] which forms a wide variety of complexes, with the VO^{2+} entity maintaining a discrete existence in each complex.[2] Six-co-ordinate complexes of the simple V^{4+} ion are rare, especially with chelating ligands.[3]

We report a route for converting the VO^{2+} unit into the more reactive $VCl_2{}^{2+}$ unit, which can be used to transform many of the existent vanadyl complexes into the corresponding dichlorovanadium(IV) six-co-ordinate complexes, and may be useful for oxygen substitution in other oxocationic complexes.

There is a large amount of data on vanadyl Schiff's base complexes containing tetradentate[4] or bidentate Schiff's base ligand.[5] Most of the oxovanadium(IV) Schiff base complexes are monomeric, $\nu_{V=O}$ *ca.* 960 cm^{-1},[2] except for *NN'*-propylenebis(salicylideneiminato)oxovanadium(IV)[6] and its derivatives,[4] which can be envisaged as having polymerised through the V=O unit. We have studied the electronic and/or steric conditions under which polymerisation of vanadyl complexes can occur. The only two examples of polymeric complexes seem to be those containing *N*-phenyl-*p*-chloro- and *N*-phenyl-*p*-nitro-(salicylaldimine) as ligands, which show an anomalously low V=O stretching frequency at 885 (*p*-Cl) and 875 cm^{-1} (*p*-NO_2), and this seems to be diagnostic of a polymeric form *via* V–O–V interaction.[4]

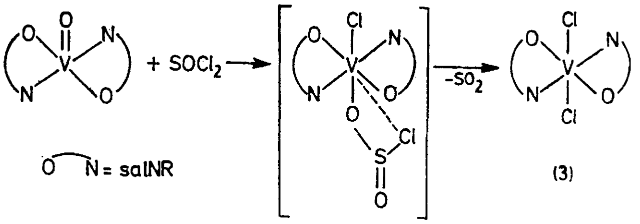
Treating a benzene solution of bis-*N*-n-butyl(salicylideneiminato)oxovanadium(IV), (I) [$VO(salNR)_2$; R = Bu^n] with a stoicheiometric amount of $SOCl_2$ at room temperature gave green-blue crystals of bis-*N*-n-butyl(salicylideneiminato)dichlorovanadium(IV), (II), quantitatively (reaction 1). In reactions under similar conditions with other vanadyl complexes with bidentate ligands, R = $PhCH_2$, Ph, *p*-ClC_6H_4, the dichloro-derivatives may sometimes include benzene which can be lost by heating or recrystallisation from acetone. The resulting dichloro-complexes were identified *via* analysis, magnetic moment (μ_{eff} 1·7—1·8 B.M. at 292 K for all the complexes), and i.r. spectra.

$$\underset{\text{(I)}}{[VO(salNBu^n)_2]} + SOCl_2 \rightarrow \underset{\text{(II)}}{[VCl_2(salNBu^n)_2]} + SO_2 \qquad (1)$$

The bis(acetylacetonato)oxovanadium(IV) complex [$VO(acac)_2$], treated in similar way with $SOCl_2$, gave [$VCl_2(acac)_2$], prepared previously by reaction of the diketone with [VCl_4] in anhydrous benzene.[3] In this way the relatively unreactive VO^{2+} unit can be converted into the very reactive $VCl_2{}^{2+}$. The [$VCl_2(salNR)_2$] complexes can be used as precursors to other substituted complexes and organovanadium(IV) compounds in which the V–C bond can be stabilized by the Schiff's base ligands.[7] The Cl ligands exchange rapidly with other anionic ligands such as SCN^-.[8]

Treating a benzene suspension of *NN'*-ethylenebis(salicylideneiminato)oxovanadium(IV), (III), with $SOCl_2$ at 40 °C for 1 h gave deep blue crystals of the dichloro-derivative, [$V(salen)Cl_2$], (IV), which was identified *via* analysis magnetic (1·72 BM at 292 K), and i.r. data, and shown to be identical to a sample of [$V(salen)Cl_2$] obtained by reaction (2). Similar deoxygenation of *NN'*-*o*-phenylenebis(salicylideneiminato)oxovanadium(IV) gave the corresponding dichloro-derivative. When the ligand around VO^{2+} is a relatively rigid tetradentate one the reaction with $SOCl_2$ seems to be more difficult. This was confirmed by the absence of reaction between vanadylphthalocyanine and $SOCl_2$, even under drastic conditions (excess of $SOCl_2$ in boiling benzene).

$$[VCl_4] + salenH_2 \longrightarrow \underset{\text{(IV)}}{[VCl_2(salen)]} + 2HCl \qquad (2)$$



These results may be of interest with regard to the rôle of $SOCl_2$ in the deoxygenation.[9] The presence of flexible ligands around the metal allows a multicentre, concerted attack by $SOCl_2$ and decomposition of the intermediates formed. A completely closed-ring equatorial ligand, such as the phthalocyanine, may hinder $SOCl_2$ attack and the opening of the V=O double bond (reaction 3).

Transfer of oxygen from an oxotransition metal compound or, *vice-versa*, deoxygenation of an organic substrate by transition metal complexes may be useful synthetically. Satisfactory elemental analytical data were obtained for all the compounds reported.

We thank C.N.R. (Rome) for support and Professor A. Celso Spinola Costa for encouragement.

(*Received, 4th April* 1975; *Com.* 388.)

---

[1] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972, p. 825.
[2] J. Selbin, *Chem. Rev.*, 1965, **65**, 153; *Coordination Chem. Rev.*, 1966, **1**, 293.
[3] R. B. VonDreele and R. C. Fay, *J. Amer. Chem. Soc.*, 1972, **94**, 7935 and refs. therein.
[4] R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, 1974, **13**, 587 and refs therein.
[5] Y. Kuge and S. Yamada, *Bull. Chem. Soc. Japan*, 1972, **45**, 799.
[6] M. Mathew, A. J. Carty, and G. J. Palenik, *J. Amer. Chem. Soc.*, 1970, **92**, 3197.
[7] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1971, 3665.
[8] M. Pasquali and C. Floriani, to be published.
[9] J. March, 'Advanced Organic Chemistry: Reactions, Mechanisms and Structure,' McGraw-Hill, New York, 1968, p. 268.