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

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Summary Deoxygenation of vanadyl Schiff’s base complexes by SOCl₂ gave the corresponding dichloro-derivatives of vanadium(IV).

The chemistry of vanadium(IV) is dominated by the stable VO²⁺ ion, which forms a wide variety of complexes, with the VO²⁺ entity maintaining a discrete existence in each complex. Six-co-ordinate complexes of the simple V⁴⁺ ion are rare, especially with chelating ligands.

We report a route for converting the VO²⁺ unit into the more reactive VCl₂²⁺ 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 or bidentate Schiff’s base ligand. Most of the oxovanadium(IV) Schiff base complexes are monomeric, νv=O ca. 960 cm⁻¹, except for NN’-propylenebis(salicylideneiminato)oxovanadium(IV) and its derivatives, 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-NO₂), and this seems to be diagnostic of a polymeric form via V=O-V interaction.
Treating a benzene solution of bis-N-n-butyl(salicylideneiminato)oxovanadium(IV), (I) \([\text{VO(salNBu}_2\text{)}]_2\), with a stoichiometric 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, \(R = \text{PhCH}_2, \text{Ph, p-ClC}_6\text{H}_4\), 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 (\(\mu_{\text{eff}} 1.7-1.8\) B.M. at 292 K for all the complexes), and i.r. spectra.

The bis(acetylacetonato)oxovanadium(IV) complex \([\text{VO(acac)}]_2\), treated in similar way with SOCl\(_2\), gave \([\text{VCl}_2(\text{acac})]_2\), prepared previously by reaction of the diketone with \([\text{VCl}_4]\) in anhydrous benzene.\(^3\) In this way the relatively unreactive VO\(^{4+}\) unit can be converted into the very reactive VCL\(_2\)\(^+\). The \([\text{VCl}_4(salNR)]_2\) 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, \([\text{V(salen)Cl}_2]\), (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 \([\text{V(salen)Cl}_2]\) obtained by reaction (2). Similar deoxygenation of NN'-o-phenylenebis(salicylideneiminato)oxovanadium(IV) gave the corresponding dichloro-derivative. When the ligand around VO\(^{4+}\) is a relatively rigid tetradentate one the reaction with SOCl\(_4\) seems to be more difficult. This was confirmed by the absence of reaction between vanadylphthalocyanine and SOCl\(_4\), even under drastic conditions (excess of SOCl\(_4\) in boiling benzene).

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\begin{align*}
\text{[VCl}_4\text{] + salenH}_2 & \longrightarrow \text{[VCl}_4\text{(salen)]} + 2\text{HCl} \\
\text{(IV)}
\end{align*}
\]

These results may be of interest with regard to the rôle of SOCl\(_4\) in the deoxygenation.\(^6\) The presence of flexible ligands around the metal allows a multicentre, concerted attack by SOCl\(_4\) and decomposition of the intermediates formed. A completely closed-ring equatorial ligand, such as the phthalocyanine, may hinder SOCl\(_4\) 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.

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\(^7\) C. Floriani and F. Calderazzo, \(J. Chem. Soc., (A), 1971, 3665.\)

\(^8\) M. Pasquali and C. Floriani, to be published.