Preparation and Properties of Tetrachloro-oxo-vanadates(IV) and Vanadium(IV) Oxide Dichloride Adducts: The Existence of Two Isomers of Pyridinium Tetrachloro-oxo-vanadate(IV)

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Complexes of the type $VOCl_2L_n$ (L = monodentate or bidentate neutral ligand; n = 1, 2 or 3) and $A_2[VOCl_4]$ (A = monopositive cation) have been well known for many years [1–5]: there are approximately fifty known compounds of the first class, and thirteen of the second class. Despite the large number of compounds which have been reported (in a correspondingly large number of publications), there is a dearth of reliable spectroscopic data upon these complexes. Nor has there been reported a reliable general synthetic route to these complexes, in the absence of hydroxylic solvents. The methods for preparing the adducts, $VOCl_2L_n$, include the controlled hydrolysis of vanadium(IV) chloride adducts [6, 7], controlled oxidation of vanadium(III) chloride adducts [8, 9], reaction of the ligand with aqueous $VOCl_2$ [10, 11], reaction of the ligand with $VOCl_3$ [12, 13], and reaction of the ligand with $VOCl_2(MeOH)_3$ in methanol [14]. The methods for preparing $A_2[VOCl_4]$ complexes include the reaction of $VOCl_2(diox)_2$ (diox = 1,4-dioxan) with ACl in liquid sulphur dioxide [15, 16], thermal decomposition or dehydration of hydrates or ethanenitrile adducts [15–19], reaction of $VOCl_2(MeCN)_2(diox)_{0.5}$ with ACl in ethanenitrile [15, 16] and direct reaction between $VOCl_2$ and ACl in trichloromethane [20]. We report here a general synthetic procedure for $VOCl_2L_n$ and $A_2[VOCl_4]$ complexes, which gives reproducible results and no solvolysis or thermolysis problems.

The reaction between $VOCl_2$ and ethanenitrile has been reported to give the complex $VOCl_2(CH_3CN)_{2.5}$ [21]. Ethanenitrile complexes of vanadium are commonly non-stoicheiometric [22–25], but we find that this product is more accurately described as $VOCl_2(CH_3CN)_2$. This complex is extremely simple to prepare on a large scale (~ 100 g), and is therefore a convenient starting material for general synthetic work. Solution of $VOCl_2(MeCN)_2$ in tetrahydrofuran

(thf) or ethanenitrile will undergo ligand displacement according to:

$$VOCl_2(MeCN)_2 \xrightarrow[\text{thf or } CH_3CN]{L} VOCl_2L_n$$

$$VOCl_2(MeCN)_2 \xrightarrow[CH_3CN]{ACl} A_2[VOCl_4]$$
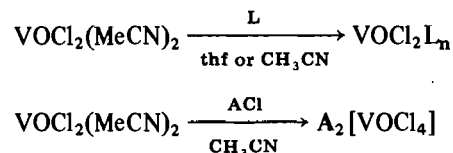
Complexes prepared by these routes** include $VOCl_2L_3$ (L = py, dpso, dmso)***, $VOCl_2L_2$ (L = hmpa, Ph_3PO, py, Ph_3P, tmu, tmtu, Ph_2MeP, $PhMe_2P$)***, $VOCl_2L$ (L = cyc_3P, dppm, dppe)*** and $A_2[VOCl_4]$ (A = pyH, Me_4N, Et_4N, Ph_4As)***. It is of especial interest to note that this method is successful for the synthesis of phosphine adducts. Previous published [26] attempts to synthesise phosphine adducts of $VOCl_2$ and VCl_4 have failed [27–33]. Attempts to prepare adducts of $AsPh_3$ and $SbPh_3$ were unsuccessful, however.

Despite the large number of complexes of the type $VOCl_2L_n$ and $A_2[VOCl_4]$ which have been reported, the V–Cl stretching frequencies have only been assigned for $VOCl_2(NMe_3)_2$ [34], $VOCl_2(dipy)$ and $VOCl_2(phen)$ [7]. The structures of $VOCl_2(NMe_3)_2$ [12] and $VOCl_2(tmu)_2$ [35] have been determined by X-ray crystallography, and are of type I (based upon a trigonal bipyramid) and type II (based upon a square pyramid), respectively:
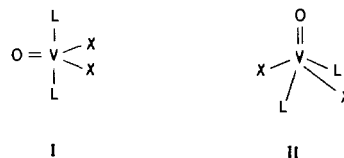
As found for the analogous bromide complexes [27], structure (I) should give two strong i.r. active bands, and structure (II) should give one strong i.r. active band. The Table classifies the complexes of empirical formula $VOCl_2L_2$ and $A_2[VOCl_4]$ according to their observed i.r. spectra. The complexes of type (I) are found to have higher ν(V–Cl) frequencies than those of type (II). This is also consistent with the known structural data {for $VOCl_2(NMe_3)_2$, $\bar{r}$(V–Cl) = 0.225

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TABLE. I.r. Data.

5-coordinate (Type I)		5-coordinate (Type II)		6-coordinate	
Complex	$\nu(V-Cl)/cm^{-1}$	Complex	$\nu(V-Cl)/cm^{-1}$	Complex	$\nu(V-Cl)/cm^{-1}$
$VOCl_2(Ph_3P)_2$	412, 356	$VOCl_2(dppm)^a$	394	$VOCl_2(py)_3$	356, 313
$VOCl_2(Ph_2MeP)_2$	409, 360	$VOCl_2(hmpa)_2$	385	$VOCl_2(dmso)_3$	353, 321
$VOCl_2(NMe_3)_2$	404, 383 [34]	$VOCl_2(Ph_3PO)_2$	384	$VOCl_2(dpso)_3$	312, 282
$(pyH)_2[VOCl_4]$ (blue)	399, 356	$VOCl_2(tmu)_2$	375		
		$VOCl_2(py)_2$	373		
		$VOCl_2(tmtu)_2$	372		
		$VOCl_2(bipy)^a$	371 [7]		
		$VOCl_2(phen)^a$	366 [7]		
		$(Ph_4As)_2[VOCl_4]$	346		
		$(pyH)_2[VOCl_4]$ (green)	345		
		$(Et_4N)_2[VOCl_4]$	344		
		$(Me_4N)_2[VOCl_4]$	344		

^{a}These complexes have a *cis* structure.
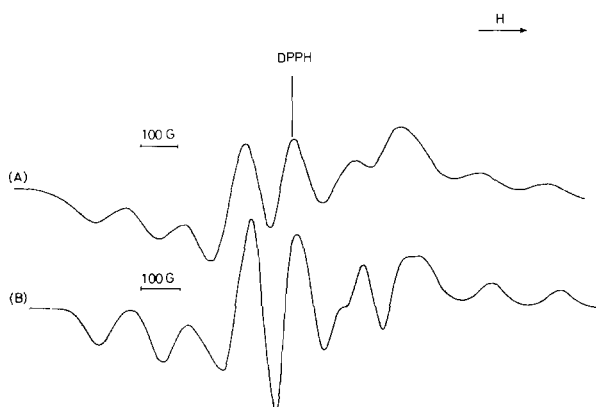

Fig. 1. Ambient temperature e.p.r. spectra of (A) powdered $VOCl_2(PPh_3)_2$, (B) powdered $VOCl_2(PPh_3O)_2$.

nm [12]; for $VOCl_2(tmu)_2$, $\bar{r}(V-Cl) = 0.234$ nm [35]}. Both classes of five coordinate complex, $VOCl_2L_2$, as anticipated [36, 37], exhibit higher $\nu(V-Cl)$ frequencies than the six-coordinate complexes of type $VOCl_2L_3$ (see Table).

At room temperature, the reaction between $(pyH)Cl$ and $VOCl_2(MeCN)_2$ in MeCN gives the expected green complex, $(pyH)_2[VOCl_4]$, which exhibits similar spectroscopic (electronic and infrared) properties to other known $A_2[VOCl_4]$ salts, including $(Et_4N)_2[VOCl_4]$ (isomorphous with $(Et_4N)_2[TiOCl_4]$, which contains a C_{4v} anion [38]). At -30 °C, however, a blue compound of identical empirical formulation is formed, which exhibits a different diffuse reflectance spectrum, and shows an infrared spectrum typical of a type (I) complex {*cf.* the green form, which is typical of type (II)}. For $(Et_4N)_2[VOBr_4]$, $[VOBr_4]^{2-}$ is known to undergo a reversible, temperature dependent ($C_{2v} \rightleftharpoons C_{4v}$)

transformation [22], the C_{4v} form being the form stable at room temperature, and the only isomer isolated. It would appear that $(pyH)_2[VOCl_4]$ is undergoing a similar reversible transformation. Both forms can be isolated as crystalline solids, but the blue form is stable at room temperature for only a few days.

The e.p.r. spectra of powdered or polycrystalline samples of VOX_2L_2 (X = Cl, Br) and $A_2[VOX_4]$ show anisotropic hyperfine splitting as a function of the steric bulk of L and A. For example, $VOBr_2(py)_2$, $VOCl_2(CH_3CN)_2$, $VOBr_2(thiox)_2$, $VOBr_2(quin)_2$ and $VOBr_2(diox)_2$ give simple single-line first-derivative spectra; $VOX_2(hmpa)_2$, $VOX_2(PPh_3)_2$ and $VOX_2(dpso)_2$ {X = Cl, Br} all show varying degrees of fine structure (*e.g.* Fig. 1); $VOCl_2(Ph_3PO)_2$ shows very well resolved fine structure (Fig. 1). Similarly, $(pyH)_2[VOCl_4]$ has a simple first-derivative e.p.r. spectrum, $(Et_4N)_2[VOCl_4]$ shows some fine
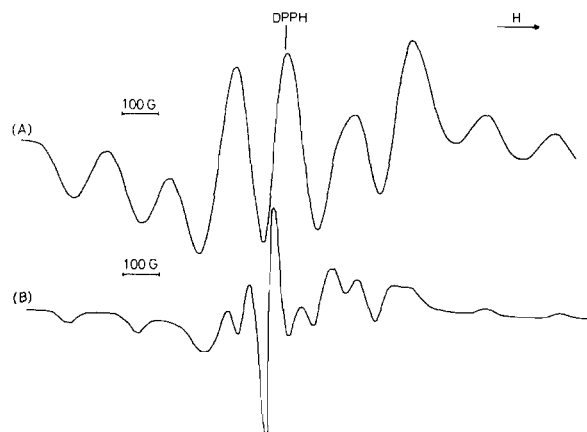

Fig. 2. Ambient temperature e.p.r. spectra of (A) powdered $(Et_4N)_2[VOCl_4]$, (B) powdered $(Ph_4As)_2[VOCl_4]$.
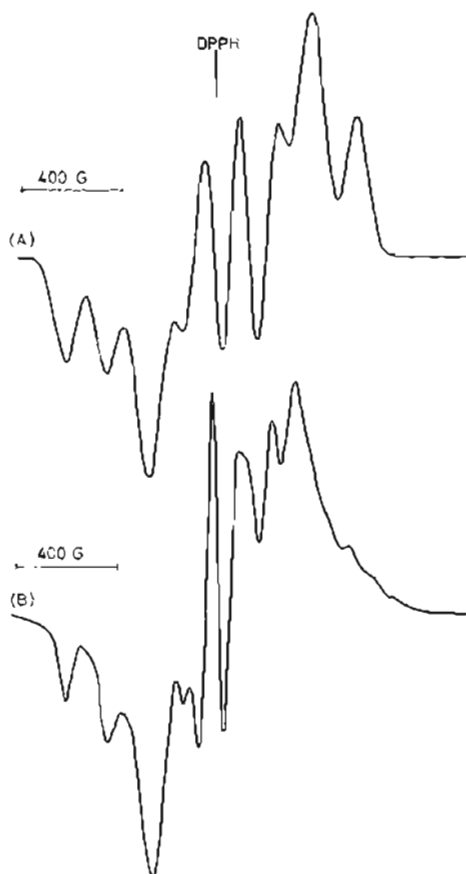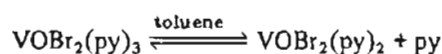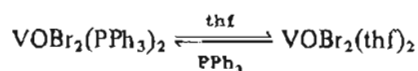
Fig. 3. E.p.r. spectra of $(Et_4N)_2[VOBr_4]$; (A) powdered sample at ambient temperature, (B) frozen solution in ethanenitrile at $-155 °C$.

Full details of the isotropic and anisotropic e.p.r. characterisation of these complexes will be published in the near future. However, it is clear from this study that the electronic spectra of complexes of the type $VOCl_2L_n$ which have been recorded for solutions in coordinating solvents [*e.g.* 7, 13, 31] must be regarded with extreme caution, and that even those recorded in non-coordinating solvents may also be open to doubt in the absence of any other evidence as to the species present in solution.

Acknowledgements

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structure, and $(Ph_4As)[VOCl_4]$ shows fourteen of the theoretical sixteen resonances (see Fig. 2). It has been possible, in many cases, to determine experimentally the values of $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ in the solid state, without requiring single crystals. These values may be compared with those obtained for low temperature glasses in various non-aqueous solvents, to establish whether or not the vanadium(IV) species retains the same structure in solution as in the solid state. For example, Fig. 3 illustrates the comparison between the e.p.r. spectra of a polycrystalline sample of $(Et_4N)_2[VOBr_4]$ and a sample in an ethanenitrile glass.

The e.p.r. spectra of VOX_2L_n complexes in non-aqueous solvents at room temperature provide clear evidence for the occurrence of ligand dissociation and displacement reactions. For example, the following reactions have been shown to occur:

$$VOBr_2(PPh_3)_2 \underset{PPh_3}{\overset{thf}{\rightleftharpoons}} VOBr_2(thf)_2$$

$$VOBr_2(py)_3 \overset{toluene}{\rightleftharpoons} VOBr_2(py)_2 + py$$

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