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Synthesis, spectroscopic and structural characterisation of vanadium(IV) and oxovanadium(IV) complexes with arsenic donor ligands

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ABSTRACT

The reaction of $o-C_6H_4(AsMe_2)_2$ with VCl₄ in anhydrous CCl₄ produces orange eight-coordinate [VCl₄{ $o-C_6H_4(AsMe_2)_2$ }], whilst in CH₂Cl₂ the product is the brown, six-coordinate [VCl₄{ $o-C_6H_4(AsMe_2)_2$ }]. In dilute CH₂Cl₂ solution slow decomposition occurs to form the V^{III} complex [V₂Cl₆{ $(o-C_6H_4(AsMe_2)_2)_2$]. Six-coordination is also found in [VCl₄{MeC(CH₂AsMe₂)₃] and [VCl₄{Et₃As₂]. Hydrolysis of these complexes occurs readily to form vanadyl (VO²⁺) species, pure samples of which are obtained by reaction of [VOCl₂(thf)₂(H₂O)] with the arsines to form green [VOCl₂($o-C_6H_4(AsMe_2)_2$]], [VOCl₂{MeC(CH₂As-Me₂)₃](H₂O)] and [VOCl₂(Et₃As₂]. Green [VOCl₂($o-C_6H_4(PMe_2)_2$]] is formed from [VOCl₂(thf)₂(H₂O)] and the ligand. The [VOCl₂{ $(o-C_6H_4(PMe_2)_2$]] decomposes in the solution open to air to form the diphosphine dioxide complex [VO₂($a-C_6H_4(AsMe_2)_2$], [VOCl₄($a-C_6H_4(AsMe_2)_2$]] or [VOCl₄($a-C_6H_4(AsMe_2)_2$]] contain the novel arsenic(V) cation [$o-C_6H_4(AsMe_2Cl)(\mu-O)(AsMe_2)_2$]]. X-ray crystal structures are reported for [V₂Cl₆($o-C_6H_4(AsMe_2)_2$], [VO(H₂O){ $(o-C_6H_4(POMe_2)_2)_2$][2. [$o-C_6H_4(AsMe_2Cl)(\mu-O)(AsMe_2)$]Cl·[VO(H₂O)₃Cl₂] and powder neutron diffraction data for [VCl₄($o-C_6H_4(AsMe_2)_2$].

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1. Introduction

The coordination chemistry of vanadium is the most complicated of any 3d element, covering seven formal oxidation states $(V^{V} \text{ to } V^{-1})$ [1,2]. Compounds in the higher oxidation states, V^{V} and V^{IV} are dominated by V=O species, labile in solution and relatively easily reduced. Not surprisingly, complexes of the higher oxidation states with neutral soft donor ligands are few, and where obtained are highly reactive, moisture sensitive and very easily reduced. Thus we have recently shown that both series of oxovanadium(V) halides, VO_2X and VOX_3 (X = F or Cl) are immediately reduced by phosphine or arsine ligands although very unstable thioether adducts of VOX₃ can be isolated [3-6]. Vanadium tetrachloride is an unstable liquid which slowly loses chlorine at ambient temperatures forming VCl₃, solid VBr₄ exists only below -23 °C, and VI_4 is unknown [1], hence the coordination chemistry of V^{IV} halides is limited to adducts of VCl₄. Although early work [7] reported VCl₄ was reduced by PPh₃, subsequent studies of a range of PR₃ (and AsR₃) adducts relying heavily upon EPR data reported trans-[VCl₄(ER₃)₂] complexes and Nb and Ta analogues [8-10]. Detailed re-examination of the vanadium systems [11,12] found no evidence for $[VCl_4(PR_3)_2]$, and identified the products as containing V^{III} such as $[VCl_4(PR_3)_2]^-$ or as phosphine oxide adducts, and possibly small amounts of [VOCl₂(PR₃)₂]. There are no authenticated phosphine complexes of vanadium(IV) chloride. A small number of di- and tri-arsine adducts of VCl₄ were reported over 30 years ago [13-15], often included as minor parts in works focused on the Ti^{IV} systems. We have recently reported detailed characterisation of dithioether and diselenoether complexes [VCl4(dichalcogenoether)] and [{VOCl₂(dithioether)}₄] [6,16]. Many diphosphine and diarsine ligands (L-L) form six-coordinate complexes, $[TiX_4(L-L)]$ with TiX₄ (X = Cl or Br), and with very strong σ -donors with small steric requirements such as $o-C_6H_4(EMe_2)_2$ (E = P or As) or Me₂P(CH₂)₂PMe₂, eight-coordination is achievable in the dodecahedral [TiX₄(L-L)₂] [18-22]. Eight coordination is also known for Zr, Hf and Nb complexes of the diarsine [23-25]. However, in contrast to vanadium, Group 4 metals show little tendency to form M=O species, and oxo-derivatives of these metals normally contain M-O-M bridges [1]. Here we report an investigation of corresponding arsenic ligand complexes and some reactions with $o-C_6H_4(PMe_2)_2$.

2. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin–Elmer 983G or Spectrum 100 spectrometers over the range 4000–200 cm⁻¹. ¹H NMR spectra were recorded



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from CDCl₃ solutions using a Bruker AV300 spectrometer. UV/visible spectra were recorded from CH₂Cl₂ solutions or as solid samples diluted with BaSO₄ using the diffuse reflectance attachment of a Perkin-Elmer Lambda 19 spectrometer. Magnetic measurements were made on powdered samples at 25 °C using a Johnson-Matthey Magnetic Susceptibility Balance. Microanalyses on new complexes were undertaken by Medac Ltd. Preparations were undertaken using standard Schlenk and glove box techniques under a N₂ atmosphere, and rigorous exclusion of moisture is necessary to obtain pure complexes. Solvents were dried by distillation from CaH₂ (CH₂Cl₂ or CCl₄) or Na/benzophenone ketyl (hexane, thf and diethyl ether). A fresh bottle of VCl₄ (Aldrich) was used as received. The ligands o-C₆H₄(PMe₂)₂, o-C₆H₄(AsMe₂)₂, MeC-(CH₂AsMe₂)₃ and Ph₂As(CH₂)₂AsPh₂ were made by literature methods [26-28], as was [VOCl₂(thf)₂(H₂O)] [29,30]. Et₃As was obtained from Strem.

2.1. $[VCl_4 \{ o - C_6 H_4 (AsMe_2)_2 \}_2]$

o-C₆H₄(AsMe₂)₂ (0.64 g, 2.5 mmol) was dissolved in anhydrous CCl₄ (10 mL) and VCl₄ (0.19 g, 1.0 mmol) was added dropwise via a syringe to the vigorously stirred solution, resulting in immediate formation of an orange precipitate. The mixture was stirred for 1 h then filtered and the orange solid rinsed with CCl₄ (5 mL) and dried *in vacuo*. Yield: 0.71 g, 92%. *Anal*. Calc. for C₂₀H₃₂As₄Cl₄V (764.9): C, 31.4; H, 4.2. Found: C, 31.0; H, 4.2%. IR (Nujol mull)/cm⁻¹: 325, 317 ν (VCl). UV–Vis E_{max} (CH₂Cl₂)/cm⁻¹: 14 200, 19 800(sh), 23 800, 26 000; (MeCN) 14 400, 20 400, 24 050. E_{max}(diffuse reflectance)/cm⁻¹: 13 260, 20 600(sh), 24 400. μ = 1.82 $\mu_{\rm B}$.

2.2. $[VCl_4\{o-C_6H_4(AsMe_2)_2\}]$

o-C₆H₄(AsMe₂)₂ (0.51 g, 1.8 mmol) was dissolved in anhydrous CH₂Cl₂ (10 mL) and VCl₄ (0.38 g, 2.0 mmol) was added via a syringe to the vigorously stirred solution. A dark red solution formed. The mixture was stirred for 1 h, concentrated and the brown solid was filtered off and dried *in vacuo*. Yield 0.27 g, 56%. *Anal.* Calc. for C₁₀H₁₆As₂Cl₄V (478.8): C, 25.1; H, 3.4. Found: C, 25.2; H, 3.6%. IR (Nujol mull)/cm⁻¹: 356, 346 *v*(VCl). UV–Vis E_{max} (CH₂Cl₂)/cm⁻¹: 15 100, 19 300(sh), 22 700. E_{max} (diffuse reflectance)/cm⁻¹: 13 600, 20 800, 24 500, 26 800. μ = 1.75 μ_B.

2.3. [VCl₄{MeC(CH₂AsMe₂)₃}]

(*NB. This reaction is extremely moisture sensitive and the reaction mixture turns green with trace moisture*). MeC(CH₂AsMe₂)₃ (0.76 g, 2.0 mmol) was dissolved in anhydrous CCl₄ (10 mL) and VCl₄ (0.38 g, 2.0 mmol) syringed in, producing an immediate brown precipitate. The mixture was stirred for 1 h, and then the precipitate filtered off, rinsed with CCl₄ (5 mL) and dried *in vacuo*. Yield 0.56 g, 49%. *Anal.* Calc. for C₁₁H₂₇As₃Cl₄V (576.8): C, 22.9; H, 4.7. Found: C, 22.3; H, 3.8%. IR (Nujol mull)/cm⁻¹: 368, 349, 332, 323 ν (VCl). UV–Vis E_{max} (diffuse reflectance)/cm⁻¹: 13 300, 19 200, 24 270, 26 040(sh). μ = 1.75 μ _B. The same product was obtained using CH₂Cl₂ as solvent.

2.4. [VCl₄(Et₃As)₂]

Et₃As (0.32 g, 2.0 mmol) was dissolved in anhydrous CH_2CI_2 (10 mL) and the solution cooled to -30 °C; VCI_4 (0.19 g, 1.0 mmol) in CH_2CI_2 (5 mL) was added dropwise via a syringe to the vigorously stirred solution, which was allowed to warm to room temperature with stirring. After 5 min. the dark red-brown precipitate was filtered off, and dried *in vacuo*. Yield 0.25 g, 48%. The dark red-brown powder slowly becomes paler on storage. *Anal.* Calc. for $C_{12}H_{30}As_2CI_4V$ (517.0): C, 27.9; H, 5.8. Found: C, 28.0; H,

5.9%. IR (Nujol mull)/cm⁻¹: 358 (br) v(VCl). UV–Vis. E_{max} (diffuse reflectance)/cm⁻¹: 12 800, 17 900, 27 100. μ = 1.90 μ_{B} .

2.5. $[V_2Cl_6\{o-C_6H_4(AsMe_2)_2\}_2]$

VCl₄ (0.19 g, 1.0 mmol) was dissolved in anhydrous CH₂Cl₂ (40 mL) and the solution was carefully layered with a solution of $o-C_6H_4(AsMe_2)_2$ (0.25 g, 0.9 mmol) in anhydrous CH₂Cl₂ (50 mL). The mixture was stoppered and left at room temperature for two weeks. Initially a brown solution developed, and then this deposited a precipitate and some crystals. After two weeks the solid was filtered off and dried to yield a pink-brown powder. Yield 0.12 g, 30%. *Anal.* Calc. for C₂₀H₃₂As₄Cl₆V₂ (886.8): C, 27.1; H, 3.6. Found: C, 27.9; H, 3.6%. IR (Nujol mull)/cm⁻¹: 340 (br), 270(sh) ν (VCl). UV–Vis. E_{max} (diffuse reflectance)/cm⁻¹: 12 010, 19 500(sh), 27 800. μ = 2.80 μ_B .

2.6. [VCl₃{MeC(CH₂AsMe₂)₃}]

A solution of VCl₄ (0.19 g, 1.0 mmol) in anhydrous CH₂Cl₂ (40 mL) was layered with a solution of MeC(CH₂AsMe₂)₃ (0.38 g, 1.0 mmol) in anhydrous CH₂Cl₂ (60 mL) and stoppered. After one week at room temperature a pink-brown precipitate was formed, which was filtered off and dried *in vacuo*. Yield: 0.23 g, 42%. *Anal*: Calc. for C₁₁H₂₇As₃Cl₃V (541.4): C, 24.1; H, 5.0. Found: C, 24.2; H, 4.3%. IR (Nujol mull)/cm⁻¹: 345, 330 v(VCl). UV–Vis. E_{max} (diffuse reflectance)/cm⁻¹: 13 900(w), 18 200, 28 600. μ = 2.71 µ_B.

2.7. $[VOCl_2\{MeC(CH_2AsMe_2)_3\}(H_2O)]$

Powdered [VOCl₂(thf)₂(H₂O)] (0.30 g, 1.0 mmol) was suspended in CH₂Cl₂ (15 mL) and the triarsine (0.38 g, 1.0 mmol) added. Upon stirring, a deep green solution rapidly formed, and after 1 h the solvent was removed *in vacuo* and the dull green solid was rinsed with CH₂Cl₂ (2 mL) and dried *in vacuo*. Yield: 0.48 g, 88%. *Anal*. Calc. for C₁₁H₂₉As₃Cl₂O₂V (540.0): C, 24.5; H, 5.4. Found: C, 24.7; H, 5.3%. IR (Nujol mull)/cm⁻¹: 3400, 1620 (H₂O), 982(s) v(VO), 357(sh), 334 v(VCl). UV–Vis. E_{max} (diffuse reflectance)/cm⁻¹: 12 000(sh), 14 300, 22 940, 27 470. μ = 1.80 μ_{B} .

2.8. $[VOCl_2\{o-C_6H_4(AsMe_2)_2\}]$

[VOCl₂(thf)₂(H₂O)] (0.30 g, 1.0 mmol) was suspended in CH₂Cl₂ (15 mL) and o-C₆H₄(AsMe₂)₂ (0.57 g, 2.0 mmol) added. The blue solid rapidly dissolved on stirring to form a deep green solution, and after 1 h the solvent was concentrated to ~5 mL *in vacuo* and then refrigerated overnight. The dull green precipitate was filtered off, rinsed with *n*-hexane (5 mL) and dried *in vacuo*. Yield: 0.29 g, 69%. *Anal.* Calc. for C₁₀H₁₆As₂Cl₂OV (429.9): C, 28.3; H, 3.8. Found: C, 28.1; H, 3.0%. IR (Nujol mull)/cm⁻¹: 973(s) v(VO), 340(br) v(VCl). UV–Vis E_{max} (CH₂Cl₂)/cm⁻¹ ($\varepsilon_{mol}/dm^3 mol^{-1} cm^{-1}$): 15 150 (100), 17 850(sh), 22 980(sh ~150), 27 000(sh ~350), 29 500 (1500). E_{max} (diffuse reflectance)/cm⁻¹: 13 900, 14 900(sh), 24 300, 28 000. $\mu = 1.69 \mu_{B}$.

2.9. $[VOCl_2\{o-C_6H_4(PMe_2)_2\}]$

This compound was prepared similarly to the diarsine analogue as a bright green powder. Yield: 55%. *Anal.* Calc. for C₁₀H₁₆Cl₂OP₂V (336.0): C, 35.7; H, 4.8. Found: C, 36.2; H, 5.2%. IR (Nujol mull)/ cm⁻¹: 970(s) v(VO), 348(s) v(VCl). UV–Vis E_{max} (CH₂Cl₂)/cm⁻¹: 16 550 (80), 24 580 (130), 30 120 (4700); E_{max} (diffuse reflectance)/cm⁻¹: 12 500(sh), 15 600, 25 000, 28 500(sh). μ = 1.70 μ_{B} . 1632

2.10. $[VOCl_2(Et_3As)_2]$

 $[VOCl_2(thf)_2(H_2O)]$ (0.30 g, 1.0 mmol) was suspended in CH_2Cl_2 (15 mL) and Et₃As (0.35 g, 2.1 mmol) added. The blue solid slowly dissolved on stirring to form a dull green solution. The solution was concentrated to \sim 4 mL and refrigerated overnight. The dull green precipitate was filtered off, rinsed with *n*-hexane (5 mL) and dried in vacuo. Yield: 0.22 g, 47%. Anal. Calc. for C12H30As2Cl2OV.1/2CH2Cl2 (504.5): C, 29.7; H, 6.2. Found: C, 29.8; H, 5.9%. IR (Nujol)/cm⁻¹: 979(s) v(VO), 340(br), 310(sh) v(VCl). UV-Vis. E_{max} (diffuse reflectance)/cm⁻¹: 12 000, 15 000 (sh), 26 300.

2.11. Reaction of VCl₄ with $o-C_6H_4(PMe_2)_2$

A solution of $o-C_6H_4(PMe_2)_2$ (0.20 g, 1.0 mmol) in anhydrous CH₂Cl₂ (10 mL) was frozen solid in liq. N₂ and a solution of VCl₄ (0.47 g, 3.0 mmol) in CH₂Cl₂ (10 mL) added via a syringe, and the mixture allowed to warm. On melting a very dark red solution formed immediately, and after 30 min this was concentrated in vacuo to 10 mL and the red-brown solid filtered off and dried in vacuo. Yield: 0.20 g. Anal. Calc. for C₁₀H₁₆Cl₈P₂V (527.8): C, 22.6; H, 3.0. Found: C, 23.3; H, 4.1%. IR (Nujol mull)/cm⁻¹: 360-300 (vbr) v(VCl). UV-Vis (diffuse reflectance)/cm⁻¹: 15 300(sh), 21 400, 29 000. The initial reaction solution exhibits a broad ³¹P{¹H} NMR resonance at δ = 91.

The above product (0.1 g) was dissolved in thf (20 mL) and the solution was stirred while open to air, when the initial dark solution paled, changing colour through brown, yellow, green and finally pale blue. After 24 h. the solution was concentrated to \sim 10 mL and refrigerated for one week when it produced a small number of pale blue crystals, which were used for the X-ray study. Concentration of the mother liquor produced a blue powder. Anal. Calc. for C₂₀H₃₆Cl₂O₇P₄V: C, 37.9; H, 5.6. Found: C, 38.4; H, 6.3%. IR (Nujol mull)/cm⁻¹: 3400(vbr) v(OH), 1640 δ (HOH), 1181(m), 1145(s), 1098(vs) v(PO), 995(s) v(VO). UV–Vis E_{max} (CH₂Cl₂)/cm⁻¹ $(\varepsilon_{\text{mol}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$: 11 630(15), 20 830(12), 26 040(2100).

Table 1	
Crystallograph	ic data. ^a

2.12. Reaction of $[VCl_4\{o-C_6H_4(AsMe_2)_2\}_2]$ in thf with moist air

 $[VCl_4 \{o-C_6H_4(AsMe_2)_2\}_2]$ (0.1 g) was suspended in thf (20 mL) and the solution was stirred in air. The solid dissolved to give a dark solution which changed to green and then blue over a few hours. After 12 h, concentration of the solution to a small volume gave a blue powder, which was filtered off, rinsed with diethyl ether (5 mL) and dried. Yield 0.03 g. IR (Nujol mull)/cm⁻¹: 990 v(VO). UV–Vis E_{max} (Me₂CO)/cm⁻¹: 12 500(sh), 14 900, 26 800. Similar products were obtained starting with [VCl₄{o-C₆H₄- $(AsMe_2)_2$ or $[VOCl_2\{o-C_6H_4(AsMe_2)_2\}]$. Concentration of the synthesis solutions to a small volume (5 mL) and refrigeration gave blue crystals on several occasions, most diffracted too poorly for an X-ray structure analysis, but in two cases the structures were determined (see Section 3.5).

2.13. X-ray crystallography and powder neutron diffraction

Crystallographic parameters are given in Table 1. Crystals were isolated from the reaction mixtures usually following a period of refrigeration as described above. Data collections were carried out using a Bruker-Nonius Kappa CCD diffractometer fitted with monochromated (graphite or confocal mirrors) Mo Ka radiation $(\lambda = 0.71073 \text{ Å})$. Crystals were held at 120 K in a nitrogen gas stream. Structure solutions were straightforward [31-33] and comments about some of the refinement details follow. H atoms bonded to carbon were introduced in calculated positions using the default C-H distance. Hydrogen atoms bonded to oxygen were convincingly located in the later difference maps having both a reasonable geometry and being high-up in the difference electron density map peak listing. In addition, these H atoms formed hydrogen bonds of the type O-H-O or O-H-Cl. These O-bonded H atoms were refined with a fixed U_{iso} and inclusion of DFIX commands on the O-H distance.

Powder X-ray diffraction data were collected using a Siemens D5000 diffractometer with Cu Ka1 radiation. Samples were

Compound	$eq:cl_cl_cl_cl_cl_cl_cl_cl_cl_cl_cl_cl_cl_c$	$\label{eq:VO(H_2O)} \begin{split} & [VO(H_2O)\{o\text{-}C_6H_4(P(O)\text{-}\\ Me_2)_2\}_2]Cl_2\cdot 3H_2O \end{split}$	[VOCl ₂ (MeCN) ₂ (H ₂ O)]	[<i>o</i> -C ₆ H ₄ (AsMe ₂ Cl)(μ-O)- (AsMe ₂)][VO(H ₂ O) ₃ Cl ₂] Cl·H ₂ O
Formula	C20.8H33.6AS4Cl7.6V2	C20H40Cl2O9P4V	C4H8Cl2N2O2V	C10H24AS2Cl4O6V
Formula weight	954.66	670.24	237.96	582.87
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	<i>P</i> bca (#61)	$P2_1/c$ (#14)	P1 (#2)	$P2_1/c$ (#14)
a (Å)	14.383(3)	11.374(2)	5.4137(10)	7.8680(10)
b (Å)	15.503(3)	14.269(3)	7.4724(15)	8.6091(10)
c (Å)	15.688(4)	19.474(3)	11.963(3)	31.333(4)
α (°)	90	90	89.313(15)	90
β(°)	90	106.997(10)	80.920(10)	95.171(10)
γ (°)	90	90	76.887(10)	90
U (Å ³⁾	3498.2(13)	3022.7(10)	465.28(16)	2113.7(5)
Z	4	4	2	4
μ (Mo K α) (mm ⁻¹)	4.882	0.760	1.595	4.102
F(000)	1862	1396	238	1156
Total number of reflections	20 212	26 765	8107	21 572
Unique reflections	3981	6872	2111	4757
Rint	0.085	0.069	0.033	0.041
Number of parameters, restraints	171, 2	358, 8	108, 2	236, 9
Goodness-of-fit (GOF) on F ²	1.175	1.148	1.078	1.080
Resid. electron density (e $Å^{-3}$)	-0.77 to +1.05	-0.59 to +0.55	-0.45 to +0.42	-0.54 to +0.54
$R_1^{b} [I_0 > 2\sigma(I_0)]$	0.064	0.062	0.029	0.035
R_1 (all data)	0.119	0.108	0.032	0.043
$wR_2^{b} [I_o > 2\sigma(I_o)]$	0.104	0.109	0.073	0.070
wR_2 (all data)	0.125	0.130	0.076	0.075
wR_2 (all data)	0.125	0.130	0.076	0.075

^a Common items: temperature = 120 K; wavelength (Mo Kα) = 0.71073 Å; θ (max) = 27.5°. ^b $R_1 = \Sigma || F_o| - |F_c||/\Sigma |F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.



Fig. 1. Fit to the PND pattern of $[VCl_4{o-C_6H_4(AsMe_2)_2}]$. Allowed reflections are shown by tick marks, the data points by crosses and the modelled intensity by the upper continuous line. The lower continuous line shows the difference between the measured and modelled patterns.

mounted under N_2 in an air-tight holder. Structure refinements were carried out using the GSAS package [34,35].

The powder neutron diffraction (PND) pattern of [VCl₄{o- $C_6H_4(AsMe_2)_2$ was collected over 2 h on a powdered sample (300 mg) mounted in a 6 mm vanadium can, using the GEM diffractometer at ISIS. The highest resolution data banks (banks 5 and 6) contained very broad peaks that were unsuitable for structure refinement. However a series of peaks in banks 3 and 4 did seem suitable, albeit with a high, curving background. The data were refined using the atom positions of $[TiCl_4[o-C_6H_4(PMe_2)_2]_2]$ as a starting point. It was not found to be possible to refine carbon and hydrogen positions independently and hence the methyl groups and phenyl rings were maintained in their known geometries using a series of soft constraints. These were then allowed to refine along with the As and Cl positions, and thermal parameters for all atoms except V. V scatters very weakly ($b_{coh} = -0.38 \text{ fm}$) but this is not problematic as it is located on a special position (0,0,0). The refined pattern from bank 3 is shown in Fig. 1. (R_{wp} = 25.9%, R_p = 19.8%), and full details are available as Supplementary material.



Scheme 1. Synthesis of VCl₄ and VOCl₂ complexes with tertiary arsines.

3. Results and discussion

3.1. VCl₄ complexes

See Scheme 1. The reaction of VCl_4 with $o-C_6H_4(AsMe_2)_2$ in anhydrous CCl₄, irrespective of the reactant ratios used, gave orange $[VCl_4{o-C_6H_4(AsMe_2)_2}]$ as reported [13,17], contrasting with the corresponding Ti^{IV} system where 1:1 or 1:2 complexes can be isolated depending upon the conditions [17-21]. The driving force appears to be the insolubility of the 2:1 complex in CCl₄. However, by reaction of VCl₄ and o-C₆H₄(AsMe₂)₂ in a 1:0.9 molar ratio using CH₂Cl₂ as solvent, we have obtained the hitherto unknown brown $[VCl_4{o-C_6H_4(AsMe_2)_2}]$. Both complexes are poorly soluble in CH₂Cl₂ and hydrolytically unstable in solution or in the solid state, turning green. The magnetic moments of 1.7–1.8 $\mu_{\rm B}$ (Section 2) are typical of d¹ V^{IV} [36]. Solution UV–Vis spectra were difficult to obtain due to very poor solubility and moisture sensitivity, but the diffuse reflectance spectra show broad features at $\sim 14~000$ and \sim 20 000 cm⁻¹, which are only slightly different in energy maxima between the two complexes, an effect also observed for the corresponding Ti^{IV} species [21]. The assignment of these features follows from the spectra of the d⁰ titanium analogues which show $\sigma(As) \rightarrow Ti(d)$ and $\pi(Cl) \rightarrow Ti(d)$ at ~21 000 and ~28 000 cm⁻¹ respectively, reflecting the difference in donor atom orbital energies [21]. In the more easily reduced V^{IV} systems, the bands have shifted to lower energy, but the \sim 6–7 000 cm⁻¹ difference between them remains. Thus the assignment of the lower energy band as $\sigma(As) \rightarrow V(3d)$ and the higher energy feature as $\pi(Cl) \rightarrow V(3d)$ is secure. The $\pi(Cl) \rightarrow V(3d)$ bands are also of similar energy to the corresponding features in the thio- and seleno-ether adducts [6,16]. The two complexes are readily distinguished by the frequencies of the V-Cl stretching modes in the far-IR spectra. The six-coordinate [VCl₄{o-C₆H₄(AsMe₂)₂}] shows very broad v(VCl) \sim 360–340 cm⁻¹ (theory C_{2v}, 2a₁ + b₁ + b₂), whilst in the eightcoordinate $[VCl_4{o-C_6H_4(AsMe_2)_2}_2]$ the corresponding bands are at 325, 315 cm⁻¹ (theory D_{2d}, b₂ + e), again replicating the trends in the titanium systems [21]. Many attempts to obtain crystals of either complex were unsuccessful, the complexes are slightly soluble in chlorocarbons and upon standing, these solutions deposit V^{III} complexes due to reduction (see Section 3.2), whilst donor solvents including MeCN, thf or MeNO₂ bring about more rapid reduction and/or displacement of the diarsine.

In view of the instability of $[VCl_4 \{o-C_6H_4(AsMe_2)_2\}_2]$, the structure analysis using powder diffraction was attempted. An X-ray powder diffraction pattern showed a series of broad peaks that resembled patterns generated from the single crystal X-ray structure of $[TiCl_4{o-C_6H_4(PMe_2)_2}]$ [21,24]. A Le Bail fit to this pattern in space group I-42m showed a reasonable fit with lattice parameters of a = 9.27 and c = 16.29 Å and Rietveld refinement using the atom positions from [TiCl₄{o-C₆H₄(PMe₂)₂]₂] gave a respectable fit, though the errors on the heavy atom (Cl, As) positions were large and the carbon positions could not be refined. The high incoherent scattering cross-section of hydrogen has meant that neutron diffraction is little used in the determination of structures containing organic substituents. Recent work has shown that by using high flux diffractometers this is becoming less of a problem, as the intensity of peaks above the incoherent background can be significant [37]. On this basis a PND experiment was attempted. The structure obtained from the PND data is shown in Fig. 2 and full structural details are available as Supplementary material. The errors in the atom positions are, of course, larger than those that would be expected from a single crystal X-ray study. As expected with such a high incoherent scattering background, the thermal parameters are also unrealistic. However, the data are clearly good enough to demonstrate that $[VCl_4 \{0-C_6H_4(AsMe_2)_2\}_2]$ is isostructural with $[MX_4\{o-C_6H_4(EMe_2)_2\}_2]$ (M = Ti, Zr, Hf etc,



Fig. 2. The structure of $[VCl_4\{o-C_6H_4(AsMe_2)_2\}_2]$ derived from analysis of the PND data showing the atom labelling scheme. Hydrogen positions are omitted for clarity. Selected bond lengths (Å) and angles (°): V1–Cl1 2.52(2); V1–As1 2.61(5); As1–C1 1.96(4); As1–C2 1.99(4); minimum As1–V1–As1 78.7(24); Cl1–V1–Cl1 96.12(25); Cl1–V1–As1 69.7(12).

X = Cl or Br) and to draw some conclusions from the bond lengths. The V–Cl distance of 2.52(2) Å compares well with those reported in [TiCl₄{o-C₆H₄(AsMe₂)₂}] (2.46(2) Å) and [TiCl₄{o-C₆H₄-(PMe₂)₂}] (2.501(3) Å), whilst the V–As distance of 2.61(5) Å may be compared with those in [TiX₄{o-C₆H₄(AsMe₂)₂}] (X = Cl 2.71(2) Å; X = Br 2.733(1) Å) [17,21,22]. The diarsine ligand architecture is also satisfactorily generated by the PND data fit. Comparisons with the bond lengths and angles in [V₂Cl₆{o-C₆H₄(AsMe₂)₂}] (Section 3.2 below) are also possible, and suggest that the three major differences *viz* – change in metal oxidation state and coordination number, and also the absence of directly *trans* ligands in the dodecahedral complex (and hence no equivalent to the *trans* influences clearly seen in the V^{III} complex) largely cancel out.

The reaction of VCl₄ with Et₃As in CH₂Cl₂ or CCl₄ is noticeably exothermic at ambient temperatures and work-up of the reactions affords materials which range in colour from dark red-brown to pale pink, indicating variable amounts of reduction. However, if the reactions are conducted at low temperature ($-30 \degree C in CH_2Cl_2$), followed by brief warming to room temperature, and rapid isolation of the solid, the product is the dark red-brown [VCl₄(Et₃As)₂]. The single strong symmetrical band in the far-IR (ν (VCl)) at 358 cm⁻¹ suggests it is the *trans* isomer (theory e_u). The reaction of the softer and weaker donor arylarsines, Ph₃As or Ph₂As(CH₂)₂AsPh₂ with VCl₄ in CH₂Cl₂ solution at 0 °C, gave products containing substantial amounts of V^{III}.

The triarsine MeC(CH₂AsMe₂)₃ reacts with VCl₄ in either CH₂Cl₂ or CCl₄ to form brown [VCl₄(κ^2 -MeC(CH₂AsMe₂)₃]; the reaction is extremely sensitive to moisture, generating a green vanadyl complex unless rigorous exclusion of moisture is achieved. The original study [14] proposed that this complex and the [TiX₄{MeC-(CH₂AsMe₂)₃] analogues were seven-coordinate, but for the titanium systems, variable temperature NMR studies showed the arsenic ligand to be bound as a bidentate, although undergoing rapid exchange of the free and bound –AsMe₂ groups in solution at ambient temperatures, and this was confirmed by the crystal structure of [TiBr₄{ κ^2 -MeC(CH₂AsMe₂)₃] [21]. The formulation of the vanadium complex as [VCl₄{ κ^2 -MeC(CH₂AsMe₂)₃] follows by analogy, and is supported by the far-IR spectrum which shows V–Cl stretches in the region typical of six-coordinate complexes.

3.2. VCl₃ complexes

During many attempts to prepare crystals of the VCl₄ complexes, a dilute solution of VCl₄ in anhydrous CH₂Cl₂ was layered with a CH₂Cl₂ solution of the o-C₆H₄(AsMe₂)₂. On standing at room



Fig. 3. Structure of $[V_2Cl_6[o-C_6H_4(AsMe_2)_2]_2]\cdot nCH_2Cl_2$ with the atom numbering scheme adopted. The dimer is centrosymmetric. Ellipsoids are drawn at the 50% probability level and H atoms and the solvate molecule are omitted for clarity. Symmetry operation: a = 1 - x, -y, 1 - z.

temperature, a brown-pink powder slowly separated, along with some red-brown crystals. The structure of the latter revealed them to be $[V_2Cl_6{o-C_6H_4(AsMe_2)_2}_2]$ (Fig. 3, Table 2), a centrosymmetric dimer with an edge-shared bi-octahedral geometry. The vanadium is in a distorted six-coordinate environment with a chelating diarsine, two short terminal chlorines (2.285(2), 2.292(2) Å) and longer bridging chlorines (2.398(2), 2.471(2)Å) with the longest bond trans to chlorine. This is the first structure of a V^{III} arsine, the closest analogue being [V₂Cl₆(PMe₃)₄] [11], also an edge-sharing dimer, but with two PMe₃ ligands *cis* on one vanadium and the second PMe₃ pair trans on the other. The complex is paramagnetic with μ = 2.80 $\mu_{\rm B}$, consistent with a d² ion, and the UV–Vis spectrum shows weak d-d absorption bands in the visible region (12010, 19 500(sh)), with the first intense (charge transfer) band in the near UV (27 000 cm⁻¹), a typical V^{III} spectrum [37] and clearly very different from those of $[VCl_4 \{o-C_6H_4(AsMe_2)_2\}_x]$ (x = 1, 2) above. A dilute CH₂Cl₂ solution of VCl₄ layered with a CH₂Cl₂ solution of MeC(CH₂AsMe₂)₃, also deposited a pink-brown powder over two weeks, which was identified as (fac) [VCl₃{ κ^3 -MeC(CH₂AsMe₂)₃] (Section 2.6). This complex has previously been obtained directly from [VCl₃(thf)₃] and MeC(CH₂AsMe₂)₃ [14].

3.3. Vanadyl (VOCl₂) complexes

Hydrolysis of V^{IV} complexes commonly produces vanadyl species, although only in certain cases does this yield clean products, e.g. [VOCl₂(L–L)] (L–L = 2,2'-bipyridyl, 1,10-phenanthroline) [39], as further hydrolysis often occurs displacing the neutral ligands. The original reports of VCl₄–arsine complexes [12–15] mentioned exposure to moisture producing green vanadyl complexes, but only for two triarsines, MeC(CH₂AsMe₂)₃ and MeAs(o-C₆H₄AsMe₂)₂ were the products described [14]. Reaction of VOCl₃ with o-C₆H₄(AsMe₂)₂ in CH₂Cl₂ also gives a green product, but a pure com-

Table 2						
Selected bond	lengths (Å) ar	nd angles (°) for [$V_2Cl_6\{0-C_6H\}$	$(AsMe_2)_2$	nCH2Cl2.

V1-Cl1	2.285(2)	V1–Cl3a	2.471(2)
V1-Cl2	2.292(2)	V1–As1	2.557(1)
V1-Cl3	2.398(2)	V1–As2	2.646(1)
Cl1-V1-Cl2	$\begin{array}{c} 101.39(8)\\ 94.19(8)\\ 164.11(8)\\ 88.00(6)\\ 89.39(6)\\ 94.31(6)\\ 77.59(4) \end{array}$	Cl1-V1-Cl3a	94.86(8)
Cl1-V1-Cl3		Cl3-V1-Cl3a	84.66(7)
Cl2-V1-Cl3		V1-Cl3-V1a	95.34(7)
Cl1-V1-As1		Cl1-V1-As2	165.38(7)
Cl2-V1-As1		Cl2-V1-As2	81.18(6)
Cl3-V1-As1		Cl3-V1-As2	84.53(6)
As1-V1-As2		Cl3a-V1-As2	99.51(6)

Symmetry operation: a = 1 - x, -y, 1 - z.

plex has not been isolated [3]. We find that although vanadyl complexes are formed during hydrolysis, this does not constitute a clean synthesis (see Section 3.4 below). We have recently shown that [{VOCl₂(dithioether)}₄] can be prepared from reaction of VCl₄ with the siloxane (Me₃Si)₂O in CH₂Cl₂/MeCN solution, followed by addition of the dithioether [6], but our attempts to apply this route to the arsenic ligands failed. The product obtained was a diarsine-free, pale-green powder, identified as $[VOCl_2(MeCN)_x]$. The failure is apparently due to the ability of the nitrile solvent to displace the diarsine from the hard V^{IV} centre, and was confirmed when attempts to grow crystals from an MeCN solution of $[VOCl_2{o-C_6H_4(AsMe_2)_2}]$ (made as described below) yielded green crystals of [VOCl₂(MeCN)₂(H₂O)] (confirmed by a crystal structure determination); the water is presumably adventitious. The structure (Fig. 4) shows an octahedral vanadium centre coordinated to two *cis* chlorines, two *cis* nitriles with a V=0 unit *trans* to H_2O . The relationship of this green complex to the reported [40] blue [VOCl₂(MeCN)₂(H₂O)] is unclear; the IR spectra are different $(v(CN) = 2320, 2300 \text{ cm}^{-1} v(VO) = 990 \text{ cm}^{-1} \text{ (blue)}, v(CN) = 2311,$ 2285 cm⁻¹ v(VO) = 980 cm⁻¹ (green)); presumably they are geometric isomers.

However, we found that addition of $o-C_6H_4(AsMe_2)_2$ MeC- $(CH_2AsMe_2)_3$ or Et₃As to a suspension of $[VOCl_2(thf)_2(H_2O)]$ [29,30] in CH₂Cl₂ resulted in formation of deep green solutions, which on concentration yielded dull green powders, [VOCl2- $\{0-C_6H_4(AsMe_2)_2\}$, $[VOCl_2\{MeC(CH_2AsMe_2)_3\}(H_2O)]$ and $[VOCl_2-C_6H_4(AsMe_2)_2]$ (Et₃As)₂] respectively (see Scheme 1). A similar reaction using $o-C_6H_4(PMe_2)_2$ gave bright green [VOCl₂{ $o-C_6H_4(PMe_2)_2$ }]. Despite the presence of one water molecule in the vanadium reagent, anhydrous compounds are readily obtained (see also Ref. [40] for similar observations). All the vanadyl complexes hydrolyse in air, but much more slowly than the VCl₄ adducts, and slowly decolourise even in the solid state over a few weeks due to reduction. The $[VOCl_2{o-C_6H_4(EMe_2)_2}]$ show strong IR active v(VO) stretches at 970 (E = P) and 973 (E = As) cm⁻¹, typical of V^{IV}=O bonds, v(VCl) at \sim 340–350 cm⁻¹, and are paramagnetic ($\mu \sim 1.8 \mu_B$) as expected. The diffuse reflectance UV-Vis spectra are very different to those of [VCl₄(ligand)] discussed above, exhibiting several weak bands in



Fig. 4. Structure of $[VOCl_2(MeCN)_2(H_2O)]$ with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level with H atoms given a common arbitrary size. Selected bond lengths (Å) and angles (°): V1–O1 1.593(2); V1–O2 2.232(2); V1–N1 2.116(2); V1–N2 2.124(2); V1–C11 2.3615(7); V1–C12 2.3523(7); O1–V1–N1 95.04(7); O1–V1–N2 93.21(7); N1–V1–N2 83.84(6); N1–V1–O2 80.06(6); N2–V1–O2 82.48(6); O1–V1–C12 100.93(5); N2–V1–C12 90.46(5); O2–V1–C12 83.68(4); O1–V1–C11 97.07(5); N1–V1–C11 89.36(5); C11–V1–C12 93.38(2).

the visible region, assigned as d-d transitions of the vanadyl unit, and intense features in the near UV due to charge transfer transitions [38]. The effect of an M=O unit in shifting the $L \rightarrow M$ charge transfer bands to higher energy, due to the effects of M–O π -bonding on the d-orbital energies is well established in many systems [38]. The solution spectra of the two complexes are significantly different in CH₂Cl₂ solution, suggesting a change in coordination number – probably five-coordinate, square pyramidal monomers in solution, which associate into "octahedral" chains or rings with V=0...V links in the solids. Unfortunately, although green crystals of the $[VOCl_2\{o-C_6H_4(AsMe_2)_2\}]$ have been obtained on several occasions, these have proved poorly diffracting and hence a crystal structure has not been obtained. The [VOCl₂{MeC(CH₂AsMe₂)₃}-(H₂O)] is rather different in that all samples show the presence of significant amounts of water in the IR spectra, in addition to a v(VO) stretch at 982 and v(VCI) at 357, 334 cm⁻¹. The Me–As ligand rocking modes in the region $925-800 \text{ cm}^{-1}$ are very similar to those in $[VCl_4{\kappa^2-MeC(CH_2AsMe_2)_3}]$, and we tentatively formulate the complex as six-coordinate $[VOCl_2{\kappa^2-MeC(CH_2AsMe_2)_3} (H_2O)$], with the water probably coordinating trans to V=0.

A small number of VOCl₂ adducts of phosphines have been reported previously, including the structurally authenticated $[VOCl_2(PPh_3)_2]$ - a trigonal bipyramid with axial phosphines [12], $[VOCl_2\{P(SiMe_3)_3\}_2]$ [41], and (*fac*) octahedral $[VOCl_2\{[12]ane-P_3Et_3\}]$ [42].



Fig. 5. Structure of the cation in $[VO(H_2O)\{o-C_6H_4(P(O)Me_2)_2\}_2]Cl_2\cdot 3H_2O$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms bonded to C are omitted for clarity.

Table 3	
Selected bond lengths (Å) and angles (°) for	$[VO(H_2O){o-C_6H_4(P(O)Me_2)_2}_2]Cl_2 \cdot 3H_2O$

V1-01	2.119(3)	V1-04	1.992(3)
V1-02	2.037(3)	V1-05	1.601(3)
V1-03	2.009(3)	V1-06	2.045(3)
P1-01	1.510(3)	P3-03	1.518(3)
P2-02	1.518(3)	P4-04	1.518(3)
02-V1-01	81.82(10)	06-V1-02	90.59(12)
03-V1-01	82.40(11)	04-V1-03	87.33(11)
04-V1-01	87.07(11)	05-V1-03	97.44(13)
06-V1-01	81.04(11)	06-V1-03	92.49(12)
04-V1-02	86.27(11)	05-V1-04	100.12(14)
05-V1-02	98.92(13)	06-V1-05	91.78(14)

3.4. Reactions with $o-C_6H_4(PMe_2)_2$

The reaction in a 1:1 or 1:2 molar ratio of VCl₄: $o-C_6H_4(PMe_2)_2$ in CCl₄ or CH₂Cl₂ at ambient temperatures gave dark solutions, which on standing deposited unidentified intractable mixtures of black, red and yellow powders (*cf.* the VCl₄–PMe₃ reaction [11]). The reaction of $o-C_6H_4(PMe_2)_2$ in CH₂Cl₂ with excess (threefold) of VCl₄ at low temperatures produced a very dark solution which had a single, broad ³¹P{¹H}NMR resonance at δ = 91, which is in the range [43] observed for chlorophosphonium(V) derivatives. A dark red-brown, very moisture sensitive solid was deposited on standing, which was tentatively identified as [$o-C_6H_4(PMe_2Cl)_2$]-[V^{IV}Cl₆] from the microanalysis, its IR and UV–Vis spectra. The red-brown solid is insoluble in chlorocarbons, and is decomposed by donor solvents.

When this solid was dissolved in thf and the solution stirred in air for 24 h, the colour changed from red-brown, through yellow to green and finally blue. Work-up of this blue solution yielded pale blue crystals which the X-ray structure analysis (Fig. 5, Table 3)





identified as a cationic vanadyl (V^{IV}) complex of the diphosphine dioxide [VO(H₂O){ $o-C_6H_4(P(O)Me_2)_2$]_2]Cl₂·3H₂O, formed through a sequence of hydrolysis and oxidation reactions. The vanadium is six-coordinate, bonded to one V=O (1.601(3) Å), two chelating diphosphine dioxides (V-O = 1.992(2)-2.119(3) Å) which are disposed *cis* with chelate angles (87.3(1) and 81.8(1)°). The coordination sphere is completed by a water molecule (the H's were readily identified in the electron density map) with V-OH₂ = 2.045(3) Å. The V=O is slightly longer than that in the square pyramidal [VO-Cl₂(OPPh₃)₂] (1.584(5) Å) [44]. The IR spectrum shows a strong V=O stretch at 995 cm⁻¹ and several PO stretches, while the UV-Vis spectrum shows weak d–d transitions in the visible region and the onset of charge transfer bands > ~25 000 cm⁻¹, typical of vanadyl complexes containing oxygen donor ligands [38].

3.5. Hydrolysis of V^{IV} arsine complexes

Comparison of the IR and UV–Vis spectra of $[VOCl_2]\kappa^2$ -MeC– $(CH_2AsMe_2)_3$ (H_2O) (above), with those obtained from the green solids made by reacting VCl₄ and MeC(CH₂AsMe₂)₃ in "laboratory grade" CCl₄ without taking any precautions to exclude moisture, and also by exposing solid $[VCl_4[\kappa^2-MeC(CH_2ASMe_2)_3]]$ briefly to air, exhibit similar features, showing that [VOCl₂{MeC(CH₂As- $Me_2_3(H_2O)$ is a significant component of the products. However, the products are not obtained in a pure state by hydrolysis, and prolonged exposure to air resulted in blue oils. The [VCl₄{o- $C_6H_4(AsMe_2)_2_n$] (*n* = 1 or 2) also become green in moist air and eventually blue oils result. When either $[VCl_4\{o-C_6H_4(AsMe_2)_2\}_n]$ (n = 1 or 2) are stirred in thf solution exposed to air, the initial brown solutions turn green and then blue, and removal of the solvent, followed by washing the sticky blue residues with diethyl ether affords blue powders which are, on the basis of their IR spectra, assigned as VOCl₂ with water or thf as co-ligands, and do not contain any arsenic ligands. Blue crystals have been obtained on several occasions from the reaction solutions, but mostly gave very weak diffraction patterns. In one case the structure of a deep blue crystal (Fig. 6) showed it to contain co-crystallised oxidised/halogenated diarsine cation $[o-C_6H_4(AsMe_2Cl)(\mu-O)(AsMe_2)]^+$ and cis- $[VOCl_2(H_2O)_3]$. The latter is a distorted octahedral molecule with cis chlorines, a short V=O (1.588(2)Å) and three facially bound water molecules with the longest V-OH₂ trans to the vanadyl unit. Although $[VOCl_2 xH_2O]$ (x usually unspecified) is a well known starting material [1] and there are several structurally authenticated adducts of $[VOCl_2(H_2O)_2]$, this seems to be the first structural characterisation of the tris(aquo) species The bond lengths are all slightly longer than in the five-coordinate [VOCl₂(H₂O)₂]·2Et₂O (which also has trans Cl's) [30] or $[VOCl_2(H_2O)_2 \cdot L]$ (L = 15-crown-5 or 18-crown-6) [45,46], and the nearest analogue is mer-cis-[VOCl₂(MeOH)₃] [30]. The previously unknown organoarsenic(V) cation, $[o-C_6H_4(AsMe_2Cl)(\mu-O)AsMe_2]^+Cl^-$, is formally derived by oxidation/chlorination from the diarsine ligand and contains an asymmetric As-O-As bridge, and surprisingly one arsenic carries a bonded chlorine, whilst for the other the charge is balanced by a chloride ion in the lattice. A blue crystal from a different batch showed the same organoarsenic cation, but in this case the vanadium was present as [VOCl₄]²⁻ anions.¹ The differing final products for the hydrolysis/oxidation in the diarsine and diphosphine systems reflect the much greater ease of oxidation of the phosphorus centres to phosphine oxide, whilst the arsenic is much less readily oxidised, and the As-Cl bonds are more resistant to hydrolysis.

4. Conclusions

The formation of tertiary arsine adducts of VCl₄ has been confirmed, contrasting with the discredited reports of phosphine analogues. Adducts of VCl₃ have also been prepared as reduction products of the same reactions, including the first structurally authenticated V^{III} arsine $[V_2Cl_6\{o-C_6H_4(AsMe_2)_2\}_2]$. Hydrolysis of the V^{IV} complexes proceeds via vanadyl-arsine complexes, which can be obtained pure by reaction of [VOCl₂(thf)₂(H₂O)] with the ligands. In contrast, the very strongly coordinating diphosphine, o- $C_6H_4(PMe_2)_2$, instantly reduces VCl₄ even at low temperatures. The different behaviour of the phosphine and arsine ligands reflects the stronger reducing power of the former. However, the vanadyl diphosphine complex [VOCl₂{o-C₆H₄(PMe₂)₂}], is readily obtained showing the stability conferred upon the V^{IV} centre by the V=O linkage. The V^{IV} complexes undergo complex decomposition in thf solution exposed to air, the final products being identified in the case of the diphosphine as a vanadyl diphosphine dioxide, $[VO(H_2O){o-C_6H_4(P(O)Me_2)_2}_2]Cl_2$, whereas $[VCl_4{o-C_6H_4(P(O)Me_2)_2}_2]Cl_2$ $C_6H_4(AsMe_2)_2_x$] decompose with chlorination of the arsenic ligand to the cation [o-C₆H₄(AsMe₂Cl)(µ-O)(AsMe₂)]⁺, and cis-[VOCl₂- $(H_2O)_3$] is also produced.

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Appendix A. Supplementary material

CCDC 757918, 757919, 757920, 757921, and 757922 contain the supplementary crystallographic data for compounds. These data can be obtained free of charge via http://www.ccdc.cam.ac. uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.02.003.

References

- F.A. Cotton, G. Wilkinson, M. Bochmann, C.A. Murillo, Advanced Inorganic Chemistry, Wiley, NY, 1998.
- [2] C. Crans, J.J. Smee, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol 4, Elsevier, Oxford, 2004. Chapter 4.
- [3] C.D. Beard, R.J. Barrie, J. Evans, W. Levason, G. Reid, M.D. Spicer, Eur. J. Inorg. Chem. (2006) 4391.
- [4] M.F. Davis, W. Levason, J. Paterson, G. Reid, M. Webster, Eur. J. Inorg. Chem. (2008) 802.
- [5] M.F. Davis, M. Jura, A. Leung, W. Levason, B. Littlefield, G. Reid, M. Webster, Dalton Trans. (2008) 6265.
- [6] A.L. Hector, W. Levason, A.J. Middleton, G. Reid, M. Webster, Eur. J. Inorg. Chem. (2007) 3655.
- [7] B.E. Bridgeland, G.W.A. Fowles, R.A. Walton, J. Inorg. Nucl. Chem. 27 (1965) 383.
- [8] G. Labauze, E. Samuel, J. Livage, Inorg. Chem. 19 (1980) 1384.
- [9] E. Samuel, G. Labauze, J. Livage, Nouv. J. Chim. 1 (1977) 93.
- [10] J. Zah-Leto, E. Samuel, J. Livage, Inorg. Chem. 27 (1988) 2233.
- [11] F.A. Cotton, J. Lu, T. Ren, Inorg. Chim. Acta 215 (1994) 47.
 [12] F.A. Cotton, J. Lu, Inorg. Chem. 34 (1995) 2639.
- [13] R.J.H. Clark, J. Chem. Soc. (1965) 5699.
- [14] R.J.H. Clark, M.L. Greenfield, R.S. Nyholm, J. Chem. Soc., A (1966) 1254.
- [15] D.L. Kepert, K.R. Trigwell, J. Chem. Soc., Dalton Trans. (1975) 1903.
- [16] A.L. Hector, M. Jura, W. Levason, S.D. Reid, G. Reid, New J. Chem. 33 (2009) 641.
- [17] R.J.H. Clark, J. Lewis, R.S. Nyholm, J. Chem. Soc. (1962) 2460.
- [18] F.A. Cotton, J.H. Matonic, C.A. Murillo, M.A. Petrukhina, Inorg. Chim. Acta 267 (1998) 173.
- [19] F.A. Cotton, C.A. Murillo, M.A. Petrukhina, J. Organomet. Chem. 573 (1999) 78.
- [20] R.J.H. Clark, R.H.U. Negrotti, R.S. Nyholm, Chem. Commun. (1966) 486.
- [21] R. Hart, W. Levason, B. Patel, G. Reid, Eur. J. Inorg. Chem. (2001) 2927
- [22] W. Levason, M.L. Matthews, B. Patel, G. Reid, M. Webster, Polyhedron 23 (2004) 605.

¹ [*o*-C₆H₄(AsMe₂Cl)(μ-O)(AsMe₂)]₂[VOCl₄]. C₂₀H₃₂As₄Cl₆O₃V, RMM = 883.78, monoclinic, space group P2₁/*n*, Z=2, *T* = 120 K. Cell dimensions: *a* = 8.2495(10), *b* = 8.6904(10), *c* = 22.132(4) Å, *β* = 98.254(10)°, *U* = 1570.3(4) Å³. λ = 0.71073 Å, 18 278 reflections measured, 3 596 unique reflections, *R*_{int} = 0.033. *R*₁ [*I*₀ > 2*σ*(*I*₀)] = 0.030, *wR*₂ (all data) = 0.065.

- [23] F.A. Cotton, P.A. Kibala, W.A. Wojtczac, Acta Crystallogr., Sect. C 47 (1991) 89.
- [24] W. Levason, M.L. Matthews, B. Patel, G. Reid, M. Webster, Dalton Trans. (2004) 3305.
- [25] D.L. Kepert, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1981) 652.
- [26] R.D. Feltham, A. Kasenally, R.S. Nyholm, J. Organomet. Chem. 7 (1967) 285.
- [27] E.P. Kyba, S.T. Liu, R.L. Harris, Organometallics 2 (1983) 1877.
- [28] A. Tzschach, W. Lunge, Chem. Ber. 95 (1962) 1360.
- [29] H.J. Seifert, J. Uebach, Z. Anorg. Allgem. Chem. 479 (1981) 32.
- [30] D. Papoutsakis, A.S. Ichimura, V.G. Young Jr., J.E. Jackson, D.G. Nocera, Dalton Trans. (2004) 224.
- [31] G.M. Sheldrick, SHELXS 97 Programme for Crystal Structure Solution, University of Göttingen, Germany, 1997.
- [32] G.M. Sheldrick, SHELXL 97 Programme for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [33] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876.
- [34] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 2004.

- [35] B.H. Toby, J. Appl. Crystallogr. 34 (2001) 210.
- [36] B.N. Figgis, J. Lewis, Prog. Inorg. Chem. 6 (1967) 56.
 [37] M.T. Weller, P.F. Henry, V.P. Ting, C.C. Wilson, Chem. Commun. (2009) 2973. [38] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, Amsterdam,
- 1984. [39] R.J.H. Clark, J. Chem. Soc. (1963) 1377.
- [40] S. Bristow, S.C.M. McAvilley, W. Clegg, D. Collison, Polyhedron 8 (1989) 87.
- [41] W. Plass, W. Schwarz, Z. Anorg. Allgem. Chem. 622 (1996) 1756.
- [42] R.J. Baker, P.C. Davies, P.G. Edwards, R.D. Farley, S.S. Liyanage, D.M. Murphy, B. Young, Eur. J. Inorg. Chem. (2002) 1975.
- [43] S.M. Godfrey, I. Mushtaq, R.G. Pritchard, J. Chem. Soc., Dalton Trans. (1999) 1319.
- [44] M.R. Caira, B.J. Gellatly, Acta Crystallogr., Sect. B 36 (1980) 1198.
- [45] V.S. Sergienko, V.K. Borzunov, Koord. Khim. 17 (1991) 1072. CSD refcode: CAYMIY01.
- [46] N. Azuma, T. Ozawa, K. Ishizu, Polyhedron 13 (1994) 1715.