

New tetradentate Schiff bases, their oxovanadium(IV) complexes, and some complexes of bidentate Schiff bases with vanadium(III)

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Abstract—New vanadyl(IV) complexes of tetradentate Schiff-base dianions containing one, two or three carbon atoms between the two iminato-nitrogen atoms are described. The compounds are either mononuclear or polymeric, as shown by the value of v(V=O), and depending upon the Schiff-base dianion. There is no evidence for electron delocalization along the polymeric chains. Some vanadium(III) complexes of bidentate Schiff-base monoanions have also been isolated; the crystal structure of $[VO(2-OC_6H_4CHNH)_2]$ and preliminary data on the structure of $[V(Prhap)_3] \cdot$ toluene $[HPrhap = 2-HOC_6H_4C(Me)NCH_2CH_2Me]$ are reported. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: vanadium; Schiff bases; low oxidation states; complexes; X-ray structures; preparations.

We have recently described [1,2] preparations and structures of cations consisting of vanadium-oxygen chains, all containing the tetradentate $(salen)^{2-}$, $(OC_6H_4CH:NCH_2CH_2N:CHC_6H_4O)^{2-}$. We have now extended the scope of these reactions to oxovanadium(IV) complexes with similar Schiff base ligands. In the course of this work we have prepared several new Schiff bases and their oxovanadium(IV) complexes which present several features of interest. We have also attempted, without much success, to reduce vanadyl(IV) and dichlorovanadium(IV) complexes of tetradentate Schiff base anions to vanadium-(III) complexes, but we succeeded in preparing vanadium(III) complexes of bidentate Schiff-base monoanions, using sodium or lithium reduction.

RESULTS AND DISCUSSION

Complexes of vanadium(IV) and tetradentate Schiffbase dianions

Most of the tetradentate Schiff bases described here have either ethylene ($-CH_2CH_2-$) or 2,2-dimethyl-(trimethylene) ($-CH_2CMe_2CH_2-$) bridges between their two nitrogen atoms. Metal complexes derived from these two types of Schiff base will have five- or six-membered central chelate rings, respectively. All the Schiff bases used are detailed in Table 1. The new vanadyl(IV) complexes are listed in Table 2.

Ethylene-bridged complexes

Oxovanadium(IV) complexes with ethylene bridges may be divided into two classes. A typical example of

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		Table 1. New ar	nd known Schiff bases				;
Amine	Aldehyde/ketone	Abbreviated sym	bols and formula	Yield%	С%	₩%	N%
NH ₂ CH ₂ CH ₂ NH ₂ NH ₂ CH ₂ CH ₂ NH ₂	2-OH-4,6-(M¢O) ₂ C,H ₂ CHO 2-OH-5-CIC,H ₂ CHO	H ₂ {(MeO) ₄ salen} H ₂ Cl ₂ salen	$C_{20}H_{24}N_2O_6$ $C_{11}H_{11}CI_5N_5O_5$	51 89	60.8(61.9) 57 4(57 6)	6.4(6.2) 4.1(4.2)	7.0(7.2) 8.2(8.3)
NH ₂ CH ₂ CH ₂ NH ₂	2-OH-5-BrC ₆ H ₃ CHO	H ₂ Br ₂ salen	$C_{16}H_{14}Br_2N_2O_2$	92	45.4(45.1)	3.1(3.3)	6.2(6.6)
NH ₂ CH ₂ CH ₂ NH ₂	2-OH-3,5-Cl ₂ C ₆ H ₂ CHO	H ₂ Cl ₄ salen	$C_{16}H_{12}Cl_4N_2O_2$	87	53.7(53.6)	3.9(3.9)	15.6(15.6)
NH ₂ CH ₂ CH ₂ NH ₂	2-OH-3,5-Br ₂ C ₆ H ₂ CHO	H_2Br_4 salen	C ₁₆ H ₁₂ Br ₄ N ₂ O ₂	16	47.3(47.3)	2.7(3.0)	6.6(6.9)
NH ₂ CH ₂ CH ₂ NH ₂	2-OH-5-NO ₂ C ₆ H ₃ CHO	H ₂ {(NO ₂) ₂ salen}	C ₁₆ H ₁₄ N ₄ O ₆	80	32.4(32.9)	1.9(2.1)	4.5(4.8)
NH ₂ CH ₂ CH ₂ NH ₂	2-OH-C ₆ H ₄ COMe	H_2 hapen"	$C_{18}H_{20}N_2O_2$	95	73.0(73.0)	6.8(6.8)	9.5(9.5)
NH ₂ CHMeCH ₂ NH ₂	2-OH-C,H4CHO	H ₂ sal-1,2-pn ⁴	$C_{17}H_{19}N_2O_2$	68	72.0(72.3)	(6.4)	
NH ₂ CH ₂ CMe ₂ CH ₂ NH ₂	2-OH-3-MeOC ₆ H ₃ CHO	H ₂ {(MeO) ₂ salnptn}	$C_{21}H_{26}N_2O_4$	45	68.4(68.1)	7.0(7.0)	7.6(7.6)
NH ₂ CH ₂ CMe ₂ CH ₂ NH ₂	2-OH-C ₁₀ H ₆ CHO	H_2 nalnptn	$C_{27}H_{26}N_2O_2$	20	78.5(79.0)	6.3(6.3)	6.9(6.8)
NH ₂ CH ₂ CMe ₂ CH ₂ NH ₂	2-OH-C ₆ H₄COMe	H ₂ hapntn	$C_{21}H_{26}N_2O_2$	58	74.5(74.5)	8.1(7.6)	8.4(8.2)
NH ₂ CH ₂ CH ₂ CH ₂ NH ₂	2-0H-4,6-(MeO) ₂ C ₆ H ₂ CHO	$H_2\{(MeO)_4 salpn\}$	$C_{21}H_{26}N_2O_6$	48	62.6(62.7)	6.6(6.5)	7.2(7.0)
NH2CH2CH2CH2NH4	2-OH-C ₆ H ₄ COMe	H_2 happn	$C_{19}H_{22}N_2O_2$	56	72.6(73.5)	6.9(7.1)	8.8(9.0)
NH ₂ CH ₂ NH ₂	2-OH-C ₆ H ₄ CHO	H ₂ salmn	$C_{15}H_{14}N_2O_2$	62	70.7(70.9)	5.5(5.5)	10.9(11.0)
NH,	2-OH-C ₆ H ₄ CHO	Hydrosalicylamide	C ₂ H ₁₈ N ₂ O ₃	72	72.4(72.8)	5.2(5.2)	8.1(8.1)
NH ₂ CH ₂ C ₆ H ₅	2-OH-C ₆ H ₄ CHO	Hbzsal"	C ₁₄ H ₁₃ NO	95	79.4(79.6)	6.1(6.2)	6.6(6.6)
NH ₂ CH ₂ C ₆ H ₅	2-OH-C ₆ H ₄ COCH ₃	Hbzhap	C ₁₅ H ₁₅ NO	93	80.0(80.0)	6.7(6.7)	6.2(6.2)
NH₂C ₆ H₄Me-4	2-OH-C ₆ H ₄ COCH ₃	HMebzhap	C ₁₆ H ₁₇ NO	89	80.3(80.3)	7.2(7.2)	5.9(5.9)
NH ₂ CH ₂ CH ₂ CH ₃	2-OH-C ₉ H ₄ COCH ₃	HPrhap	C ₁₁ H ₁₆ NO	94	74.5(74.5)	8.7(8.5)	7.9(7.9)

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Formulae		Yield%	C%	Analyses" H%	%N	Colour	v(V==0) (cm ⁻¹)	$\mu_{ m eff}/\mu_{ m B}$
[VO(salen)] • MeOH	C ₁₇ H ₁₈ N ₂ O ₄ V	81	55.3(55.9)	4.7(4.9)	7.7(7.7)	Green	972	1.80
[VO(salen)] [3] ⁴	C ₁₆ H ₁₄ N ₂ O ₃	87	57.6(57.7)	4.2(4.2)	8.4(8.4)	Green	277	1.83
[VO{(MeO) ₂ salen}] [18] ^b	$C_{19}H_{18}N_2O_5V$	92	53.3(55.0)	4.7(4.6)	8.3(7.1)	Green	978	1.85
[VO(nalen)] [19] ⁶	$C_{24}H_{18}N_2O_3V$	89	67.1(66.6)	3.7(4.1)	6.0(6.4)	Green	984	1.77
[VO{(MeO) ₄ salen}]	$C_{20}H_{22}N_2O_7V$	76	53.3(53.0)	4.9(4.9)	6.3(6.2)	Green	983	1.83
[VO(Cl ₂ salen)]	$C_{16}H_{12}Cl_2N_2O_3V$	85	47.9(47.8)	2.8(3.0)	6.8(7.0)	Green	980	1.80
[VO(Br ₂ salen)]	$C_{16}H_{12}Br_2N_2O_3V$	60	39.3(39.1)	2.2(2.4)	5.3(5.7)	Green	980	1.86
[VO(Cl ₄ salen)]	$C_{16}H_{10}Cl_4N_2O_3V$	91	41.4(40.8)	2.3(2.1)	5.8(6.0)	Red	881	1.81
[VO(Cl ₄ salen)]	$C_{16}H_{10}Cl_4N_2O_3V$	90	40.9(40.8)	1.9(2.1)	5.8(6.0)	Green	992	1.65
[VO(Br ₄ salen)]	$\mathbf{C}_{16}\mathbf{H}_{10}\mathbf{Br_4N_2O_3V}$	90	29.6(29.6)	1.5(1.5)	4.2(4.3)	Orange	880	1.74
[VO{(NO ₂) ₂ salen}]	$C_{16}H_{12}N_4O_7V$	78	45.1(45.3)	3.0(2.8)	13.0(13.2)	Red	879	1.75
[VO(salnptn)] [11] ^h	$C_{19}H_{20}N_2O_3$	59	60.4(60.8)	5.3(5.3)	7.2(7.5)	Orange	868	1.83
[VO(sal-1,2-pn)]	$C_{17}H_{16}N_2O_3V$	62	58.1(58.8)	4.5(4.6)	7.9(8.1)	Green	776	1.77
[VO(hapen)]	$C_{18}H_{18}N_2O_3V$	83	59.3(59.8)	4.9(5.0)	7.6(7.8)	Green	126	1.77
[VO{(MeO) ₂ salnptn}]	$C_{21}H_{24}N_2O_5V$		57.2(57.9)	5.5(5.5)	6.3(6.4)	Brown	858	2.07
[VO(nalnptn)]	$C_{27}H_{24}N_2O_5V$	77	67.2(68.2)	4.5(5.1)	5.9(5.9)	Yellow	877	1.71
[VO{(MeO)₄salpn}]	$C_{21}H_{24}N_2O_7V$	82	54.5(54.0)	5.1(5.1)	6.0(6.0)	Yellow	860	1.88
[VO(salmn)] · MeOH	$C_{16}H_{16}N_2O_4V$	40	54.3(54.7)	4.1(4.6)	7.8(8.0)	Yellow	986	1.73
[VO(OC ₆ H ₄ CHNH) ₂]	$C_{i4}H_{i2}N_2O_3V$	62	55.0(54.7)	4.1(3.9)	9.2(9.1)	Green	186	1.73

Table 2. Schiff base complexes of vanadyl(IV)

" Required values in parentheses. ^b These have been previously reported in the given references, but all the data are from our preparations. ^c No deviation from ideal behaviour down to 87 K.

New tetradentate Schiff bases

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the first class is [VO(salen)], which forms green crystals, is fairly soluble in solvents such as acetonitrile and dichloromethane, has v(V=0) in its solid-state IR spectrum at 980 cm⁻¹ and is monomeric in the solid state [3,4]. The class also includes a complex with a ligand derived from ethylenediamine and 2hydroxybenzophenone, which has v(V=0) at 981 cm^{-1} [5]. The only difference from the salen complex is that the CH=N motif is replaced by CPh=N. However, an analogous complex made in the same way with a ligand derived from ethylenediamine and 2hydroxy-5-chlorobenzophenone is gold, not green, relatively insoluble and has v(V=0) at 881 cm⁻¹. This is representative of the second class, with v(V=O) ca 100 cm^{-1} to lower frequency compared with the first. These are all apparently polymeric in the solid state, forming chains $\cdots V = O \rightarrow V = O \rightarrow \cdots$. The shift of ca 100 cm⁻¹ in v(V=O) between apparently similar compounds is also found in the chemistry of vanadyl(IV) complexes with bidentate and tridentate ligands and at least one compound is known which exists in both forms with different crystal shapes [6]. The two forms are apparently isomers.

If we assume that the green vanadyl(IV) complexes are all square pyramidal and five-coordinate, as in [VO(salen)] [3], the difference between the v(V=O)values can easily be rationalized [7] in terms of the infinite chain polymerization of the orange or gold compounds in the solid state. No structural studies showing such polymeric chains in ethylene-bridged complexes (except [1] for the cation [V(salen)-OV(salen)O]⁺ with v(V=O) at 880 cm⁻¹) have been reported, although [VO{OC₆H₄CH:N(CH₂)₃-N:CHC₆H₄O}] has a chain structure and a low value of v(V=O) [7].

The reason for the changeover from "normal" v(V=0) values at 980 cm⁻¹ "low" values at 880 cm⁻¹ must be in part electronic, because substitutions in the phenyl rings should not influence sterically the geometry round the vanadium atom [5]. The electronic effects of aromatic substituents might most simply be assessed using the pK_A values of the related 3- and 4-substituted benzoic acids; pK_A values in acetonitrile (the solvent most frequently used in this work) include 20.7 for benzoic acid, 19.5 for 3-bromobenzoic acid, 19.2 for 3-nitrobenzoic acid and 18.7 for 3,5-dichlorobenzoic acid [8].

We have therefore made $[VO\{(MeO)_4salen\}]$, $[VO(Cl_2salen)]$, $[VO(Br_2salen)]$, $[VO(Cl_4salen)]$, $[VO(Br_4salen)]$ and $[VO\{(NO_2)_2salen\}]$ using Schiff bases prepared from ethylenediamine and 4,6-dimethoxysalicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 3,5dibromosalicylaldehyde and 5-nitrosalicylaldehyde, 3,5dibromosalicylaldehyde and 5-nitrosalicylaldehyde, respectively. The first three form green crystals with higher v(V=O), the last two form insoluble powders with low v(V=O). The sixth complex, derived from Cl_4 salen is unique among tetradentate Schiff base derivatives in being apparently obtainable in both polymeric and monomeric forms, although we were unable to confirm this by X-ray structure analysis. The green solid, $v(V=O) = 991 \text{ cm}^{-1}$, was isolated from acetonitrile after heating the preparative reaction mixture in acetonitrile for 20 min at reflux. Upon prolonged exposure to acetonitrile solution or upon exposure to solvents such as diethyl ether, acetone, dichloromethane and methanol, or even upon heating the solid *in vacuo*, the green form changes to the orange form, with $v(V=O) = 868 \text{ cm}^{-1}$. We believe that the only other example of such isomerism is the complex bis[(*N*-(4-chlorophenyl)salicylideneaminato) oxovanadium(IV)] [6,7].

The data seem to suggest that within a given class of compound (monomeric or polynuclear) some lowering of v(V=O) is favoured by electron-withdrawing substituents such as chloro, bromo and nitro. The known [VO{(MeO)₂salen}] has a high v(V=O) and is presumably monomeric. There are no intermediate values of v(V=O), which suggests a sudden switch in structure induced by the electronic effects of the substituents and the change between monomeric and polymeric structures seems a reasonable explanation.

However, this may not be in the whole story. Kuska and Yang [5] studied a series of analogous complexes based on the Schiff base 4,5-R¹R²C₆H₂(OH)CPh=N- $CH_2CH_2 - N = CPhC_6H_2(OH)R^1R^2 - 4.5$. They plotted v(V=0) against the Hammett σ factors for R¹ and R², and showed that v(V=O) increases with the electronwithdrawing power of the substituents within the "high-frequency" group, which is observed for: $R^{1} = H, R^{2} = Cl; R^{1} = CH_{3}, R^{2} = Cl; R^{1} = R^{2} = H$ and $R^1 = H$, $R^2 = CH_3$ in solution in CHCl₃. However, in Nujol mulls, the first two compounds are in the "low-frequency" group. Our data, within the "high-frequency" and "low-frequency" groups, show that electron-withdrawing substituents have no consistent effect on v(V=O), but the overall effect, as with Kuska and Yang, is hardly significant and certainly not comparable with the effect of polymerization on v(V=0). However, the observations do imply that steric effects have a secondary influence. The fact that heavily substituted aromatic rings and bridges other than ethylene tend to favour polymerization hints at a crystal-packing effect. However, the low solubility of the polymeric compounds has prevented sensible solution studies.

The magnetic moments of all the complexes are close to the spin-only values for vanadium(IV) complexes. As the unpaired electron is believed to be in an orbital orthogonal to the V=O axis [9], it should not be affected by polymerization along V-O--V-O chains. The effective magnetic moment of $[VO\{(NO_2)_2 salen\}]$ exhibits normal Curie-Weiss behaviour down to 87 K.

2,2-Dimethyl(trimethylene)-bridged complexes

Alone among compounds of formula $[VO(OC_6H_4 CH : N(CH_2)_nN : CHC_6H_4O)]$ (*n* = 2–10) the complex

with n = 3 has a "low" v(V=O) [4] and that with n = 4 shows two values of v(V=O). The X-ray structure for n = 3 shows that this material is polymeric [7]. This may be a consequence of distortions in the coordination sphere of the vanadium atom upon lengthening the bridge rather than electronic factors, since there are no substituents on phenyl rings.

We report here syntheses of several dimethyl (trimethylene)-bridged complexes which also contain six-membered central chelate rings, with a geometry about the vanadium atom similar to that of trimethylene-bridged complexes. All these complexes, i.e. [VO(salnptn)], [VO{(MeO)₂salnptn}], [VO(nalnptn)] and [VO{(MeO)₄salpn}] from 2,2-dimethylpropane-1,3-diamine and salicylaldehyde, 3-methoxysalicylaldehyde and 2-hydroxy-1-naphthaldehyde, respectively, and from 4,6-dimethoxysalicyaldehyde and propane-1,3-diamine show a "low" v(V=O) value and are presumably polymeric. This was confirmed for [VO(salnptn)] by an X-ray study [10]. Unlike its trimethylene-bridged analogue, the dimethyl(trimethylene) derivative [VO(salnptn)] is soluble in common organic solvents and several protonation, oxidation and reduction reactions of it have been carried out. Details of these reactions are being published separately. The effective magnetic moment of [VO (salnptn)] was found to be virtually independent of field and temperature from 293 K down to 87 K and the compound exhibits normal Curie-Weiss behaviour. Even though the compound is apparently polymeric, there is no indication of electron delocalization, consistent with the unpaired electron being in the d_{xy} orbital and orthogonal to the V—O chain.

Yields of dimethyl(trimethylate)-bridged complexes were usually considerably smaller than those of ethylene-bridged complexes made by the same route. The attempted synthesis of $[VO(OC_6H_4CMe:NCH_2$ $CMe_2CH_2N:CMeC_6H_4O)]$ and of its trimethylenebridged analogue from $[VO(acac)_2]$ and the Schiff base failed altogether, while the synthesis of its ethylene-bridged analogue by the same route proceeded in good yield.

Methylene-bridged complexes

A Schiff base with a methylene bridge would be accessible from methylenediamine if this existed. A compound derived from this Schiff base with molybdenum, but synthesized from hexamethylenetetramine, salicylaldehyde and, presumably, traces of water, has recently been reported [11]. Unexpectedly, the tetradentate Schiff base is dinucleating. We have, however, prepared HOC₆H₄ CH:NCH₂N:CHC₆H₄OH (H₂salmn) for the first time by reaction of salicylaldehyde, methylenediamine dihydrochlorine and triethylamine.

Treatment of H_2 salmn with $[VO(acac)_2]$ or with $VOSO_4$ under various conditions gave products which could not be characterized. However, treatment of

H₂salmn with [{VO(OMe)(acac)}₂] under very mild conditions gave a yellow powder, soluble in dichloromethane and acetonitrile, analysing for [VO (salmn)] · MeOH with an IR band at 986 cm⁻¹ characteristic of a terminal v(V=O) and a magnetic moment of 1.73 BM. Due to the colour it seems unlikely that this is the simple monomer of its empirical formula and a crystal structure analysis is needed to elucidate its nature.

Attempted synthesis compounds of vanadium(II) with tetradentate Schiff-base dianions

Attempts were made to prepare vanadium(II) complexes of $(hapen)^{2-}$ and $(happn)^{2-}$ by reaction of the sodium or lithium salts of the Schiff bases with $VCl_2(thf)_2$ [12], $VBr_2(MeOH)(thf)$ [13] or $[VCl_2(py)_4]$ [14]. In no case was an unequivocal vanadium(II) product obtained. Attempts were also made to reduce the vanadium(IV) complexes [VCl₂(hapen)] and [VCl₂(sal-1,2-pn)] with sodium sand. These dihalides were prepared from the corresponding vanadyl species by standard routes. This method was also unsuccessful, although in the latter case a vanadium(III) complex, $[{VCl(sal-1,2-pn)}_2]$, was obtained and characterized. All these halo-compounds are detailed in Table 3. This formulation is based upon the usual analytical and spectroscopic data and analogy with $[{VCl(salen)}_2]$, which has been suggested to be dinuclear [15].

Compounds of vanadium(IV) with bidentate Schiff-base monoanions

Schiff bases are made in 1 : 1 reactions between aldehydes and primary amines.

$$ArCHO + RNH_2 \longrightarrow ArCH : NR$$

However, when R = H (i.e. with ammonia), three molecules of aromatic aldehyde react with two molecules of ammonia giving hydroamides, whereas aliphatic aldehydes yield polymers (aldol condensation) and/or aldehyde-ammonias.

$$ArCHO + 2NH_3 \longrightarrow ArCH : NCHArN : CHAr$$

 H
 $AlkCHO + NH_3 \longrightarrow AlkC \longrightarrow OH$
 NH_2

We made hydrosalicylamide (Ar = C₆H₄OH), from salicylaldehyde and ammonia, to react with VOSO₄. We hoped to obtain an analogue of [VO(salmn)] substituted in the methylene bridge by a $--C_6H_4OH$ group, but we isolated green crystals analysing as $C_{14}H_{12}N_2O_3V$ with a strong IR band at 980 cm⁻¹, ν (V=O), and sharp bands at 3360 and 3240 cm⁻¹ ν (NH). We assign the structure [VO(OC₆H₄ CH:NH)₂] to this compound; it contains a sali-

Form	nulae	Yield%	C%	Analyses" H%	N%	Colour	μ _{eff} /μ _B 295 K
[VCl ₂ (sal-1.2-pn)]	C ₁₇ H ₁₄ Cl ₂ N ₂ O ₂ V	86	50.8(50.8)	4.0(4.0)	7.1(7.0)	Blue	1.72
$[VBr_2(sal-1,2-pn)]$	$C_{17}H_{16}Br_2N_2O_2V$	74	41.1(41.6)	3.3(3.3)	5.7(5.7)	Blue	1.79
[Vl ₂ (sal-1,2-pn)]	C ₁₇ H ₁₆ I ₂ N ₂ O ₂ V	18	33.9(34.9)	2.8(2.8)	4.7(4.8)	Tan	1.87
$[{VCl(sal-1,2-pn)}_2]$	$C_{34}H_{32}Cl_2N_4O_4V_2$		56.2(55.8)	6.1(4.1)	8.5(7.7)	Dark red	
$[VCl_2(hapen)] \cdot 2H_2O$	$C_{18}H_{22}Cl_2N_2O_4V$	71	47.4(47.8)	4.3(4.9)	6.7(6.2)	Blue	
[VBr ₂ (hapen)]	$C_{18}H_{18}Br_2N_2O_2V$	59	45.1(42.8)	3.7(3.6)	6.2(5.4)	Blue	

Table 3. Halo complexes of vanadium(III) and vanadium(IV)

"Analytical figures in parentheses are calculated values.

cylideneiminato-ligand whose free acid (salicylaldeimine, $HOC_6H_4CH:NH$) is unknown, and it is the previously unreported parent compound of all oxovanadium(IV) bis(bidentate) Schiff base complexes.

X-ray studies of similar complexes $[VO(OC_6H_4 CH:NR)_2]$ [16] ($R \neq H$) show that the two N donor atoms take *trans* positions to one another to minimize interactions between their R groups. In our compound where R = H these interactions would be small and there seems no reason why these two atoms should not be *cis* to one another, with one N—H group above and one below the plane formed by the N₂O₂ atom donor set, as happens to the methylene groups in [VO(salen)]. This would result in two slightly different N—H stretching frequencies. In fact, the NH groups are indeed *trans*, but different. An X-ray structure analysis has clarified the situation. The structure is shown in Fig. 1 and selected bond lengths and angles are in Table 4. The vanadium atom is five-coordinate with the expected square pyramidal pattern, similar to that in [VO(salen)] [3], the vanadyl oxygen O(3) is in the apical position and the two bidentate ligands form the base plane. However, whereas in [VO(salen)] the two halves are related by pseudo-mirror plane symmetry, here the two ligands are related by a pseudo-two-fold symmetry axis along the V—O(3) bond. The difference in the two imido groups, at opposite corners of the square base plane, arises from their contacts with adjacent molecules; H(29) forms a good hydrogen bond with the vanadyl oxygen atom of the next molecule down the *a* axis (thus linking the molecules in infinite chains parallel to this axis); in contrast, H(19) has no close neighbours.

Dimensions around the V atom are as expected. The V—O(3) vanadyl distance is short, at 1.589(4) Å. The two V—O distances in the base plane are virtually identical, as are the two V—N distances. All the distances are very similar to those found in [VO(salen)].



Fig. 1. Representation of the molecular structure of [VO(OC₆H₄CHNH)₂] showing the single intermolecular hydrogen bond.

(a) About the V atom			
V—O(11)	1.919(4)	V—N(29)	2.058(6)
V—N(19)	2.056(6)	VO(3)	1.589(4)
V—O(21)	1.917(4)		
O(11)—V—N(19)	86.2(2)	O(21)VN(29)	86.4(2)
O(11)V-O(21)	139.2(2)	O(11)—V—O(3)	111.6(2)
N(19) - V - O(21)	84.6(2)	N(19)-V-O(3)	102.4(3)
O(11) - V - N(29)	83.7(2)	O(21)—V—O(3)	109.2(2)
N(19)—V—N(29)	152.3(2)	N(29)—V—O(3)	105.3(2)
(b) In the OC_6H_4CHNH ligands			
O(11)—C(12)	1.323(7)	O(21)—C(22)	1.322(7)
C(12) - C(13)	1.407(9)	C(22)—C(23)	1.399(9)
C(12)—C(17)	1.403(9)	C(22)—C(27)	1.417(10)
C(13)—C(14)	1.381(10)	C(23)—C(24)	1.382(9)
C(14)—C(15)	1.384(12)	C(24)—C(25)	1.389(11)
C(15)—C(16)	1.365(11)	C(25)—C(26)	1.362(10)
C(16)—C(17)	1.406(8)	C(26)—C(27)	1.420(9)
C(17)C(18)	1.428(9)	C(27)—C(28)	1.427(9)
C(18)—N(19)	1.281(9)	C(28)—N(29)	1.281(8)
N(19)—H(19)	0.82(8)	N(29)—H(29)	0.94(9)
V—O(11)—C(12)	129.2(4)	V—O(21)—C(22)	130.9(4)
O(11)-C(12)-C(13)	118.3(6)	O(21)—C(22)—C(23)	118.6(6)
O(11)—C(12)—C(17)	124.0(5)	O(21) - C(22) - C(27)	123.0(6)
C(13) - C(12) - C(17)	117.7(6)	C(23)—C(22)—C(27)	118.4(6)
C(12) - C(13) - C(14)	121.0(8)	C(22) - C(23) - C(24)	121.2(7)
C(13) - C(14) - C(15)	120.9(7)	C(23) - C(24) - C(25)	120.5(7)
C(14) - C(15) - C(16)	119.2(6)	C(24)—C(25)—C(26)	119.8(6)
C(15) - C(16) - C(17)	121.4(7)	C(25)—C(26)—C(27)	121.3(7)
C(12) - C(17) - C(16)	119.8(6)	C(22) - C(27) - C(26)	118.8(6)
C(12) - C(17) - C(18)	121.4(5)	C(22) - C(27) - C(28)	121.7(6)
C(16) - C(17) - C(18)	118.7(6)	C(26) - C(27) - C(28)	119.4(6)
C(17) - C(18) - N(19)	125.4(6)	C(27)-C(28)-N(29)	125.1(6)
VN(19)C(18)	126.4(5)	V—N(29)—C(28)	128.0(5)
V—N(19)—H(19)	127(5)	V—N(29)—H(29)	113(5)
C(18) - N(19) - H(19)	105(5)	C(28)—N(29)—H(29)	119(5)
(c) In the hydrogen bond			
$N(29) \cdots O(3')$	3.145(8)	N(29) - H(29) - O(3')	146(7)
H(29)···O(3')	2.32(10)		

Table 4. Molecular dimensions in [VO(OC₆H₄CHNH)₂]. Bond lengths are in Å, angles in (°), e.s.d.s are in parentheses

N.B. O(3') is at x - 1, y, z.

Complexes of vanadium(II) and vanadium(III) with bidentate Schiff-base anions

An attempt to prepare a vanadium(II) complex from VCl₂(thf)₂ and the sodium salt of the Schiff base formed from 2-hydroxyacetophenone and *n*-propylamine, Na(Prhap), gave, instead of [V(Prhap)₂], [V(Prhap)₃] (see Experimental). This has been characterized as an octahedral vanadium(III) complex with a tris(chelate) structure by a single-crystal X-ray determination. The resolution obtained was finally only to R = 0.10 and therefore serves only to confirm the essential octahedral structure nature of the material (Fig. 2). We include experimental details below only for the record and do not propose to discuss the structure further. Since considerable care was taken to exclude adventitious oxygen during this work, the oxidation of vanadium(II) to vanadium(III) might have been due to the Schiff base. However, reactions of saturated compounds, such as $[VCl_2(py)_4]$, with heavily substituted bidentate Schiff base anions, in the hope that the pyridine would block otherwise reactive sites, gave only poorly characterized blue materials. We cannot claim to have prepared with certainty any vanadium(II) compounds.

The vanadium(III) complexes (Table 5) presumably all have a structure similar to that of $[V(Prhap)_3]$. Their effective magnetic moments are close to the spin-only value at room temperature (2.83 μ_B), and they decrease considerably with temperature. This is the usual behaviour of mononuclear, distorted,



Fig. 2. Structure of the vanadium complex in $[V(Prhap)_3] \cdot C_7H_8$. Thermal ellipsoids are drawn at 50% probability.

octahedral six-coordinate vanadium(III) complexes [17].

EXPERIMENTAL

Reactions involving vanadium complexes were carried out using standard Schlenk techniques in dried solvents under N2. C,H,N analyses were carried out at the Universities of Sussex and Surrey, or by Butterworth Microanalytical Laboratories. IR spectra were obtained using a Perkin-Elmer 883 spectrometer and magnetic moments at 20°C were determined by the Faraday method using Hg[Co(CNS)₄] as standard and making diamagnetic corrections using Pascal's constants. Variable-temperature magnetic moments on two compounds were made on a Gouy balance. Aldehydes, amines, VOSO₄ and [VO(OC-MeCHCOMe)₂], and [VO(acac)₂] were purchased from Aldrich or Lancaster Synthesis. [VCl₂(py)₄] [14], VCl₂(thf)₂ [12] and VBr₂(MeOH)(thf) [13] were prepared by literature methods.

Schiff bases (Table 1) were generally prepared by mixing boiling methanol solutions of aldehydes and amines and their vanadium compounds (Table 2) by ligand exchange with $[VO(acac)_2]$, as described [3]. All exceptions to this are given below. Analyses, yields, colours, V—O stretching frequencies v(V=O) and magnetic moments (μ_B) are given in the Tables.

Ethylene-N,N'-*bis(salicylideneiminato)oxovanadium* (IV)-*methanol*(1/1)

The Schiff base H₂salen (0.53 g, 2 mmol) and $[VO(acac)_2]$ (0.53 g, 2.0 mmol) were dissolved in dichloromethane (20 cm³) and methanol (20 cm³) was added. After 24 h the volume was slowly reduced *in vacuo* to ~10 cm³, when green crystals (0.59 g, 81%) were formed, washed with methanol and diethyl ether and dried *in vacuo*.

Methylene-N,N'-bis(salicylideneimine)

Methylenediamine bishydrochloride (3.0 g, 25 mmol) dissolved in methanol (40 cm³) was cooled to -60° C. Salicylaldehyde (6.1 g, 50 mmol) and triethylamine (10 cm³, ~75 mmol) were added and the solution allowed to warm with stirring overnight, giving a light yellow crystalline precipitate which was filtered off, washed with diethyl ether and dried in air, yield 4.0 g, 62%.

Methylene-N,N'-*bis(salicylideneiminato)oxovanadium* (IV)-*methanol*(1/1)

The Schiff base H₂salen (0.51 g, 2 mmol) and $[{VO(OMe)(acac)}_2]$ (0.78 g, 2 mmol) were dissolved in dichloromethane (20 cm³) and methanol (20 cm³) was added. The volume was reduced *in vacuo* after 24

h to $\sim 10 \text{ cm}^3$ when a yellow powder precipitated. This was filtered off and dried *in vacuo*; yield 0.31 g, 44%.

Hydrosalicylamide

Ammonia (2.0 M in methanol, 20 cm³, 40 mmol) was added to salicylaldehyde (7.3 g, 60 mmol) giving a yellow solid. The mixture was warmed briefly to 60° C when all dissolved to give a clear solution and then allowed to cool giving yellow crystals (5.0 g, 72%).

Oxobis(salicylideneiminato)vanadium(IV)

 $VOSO_4 \cdot H_2O$ (0.9 g, 5 mmol), hydrosalicylamide (1.8 g, 5 mmol) and methylamine (2 cm³, 15 mmol) were heated under reflux in aqueous ethanol (1 : 1, 50 cm³) for 1 h giving a green solid which was filtered off, washed with water, ethanol and diethyl ether and recrystallized from acetonitrile (100 cm³).

Tris(2-phenolato-N-benzylacetophenoneimine)vanadium(III)

Toluene (150 cm³) was added to Hbzhap (3.44 g, 15.27 mmol) under nitrogen forming a clear yellow solution. This was cooled in an ice-bath and LiMe (11.0 cm³, 1.4 M solution in diethyl ether) was syringed in forming a red solution after much effervescence. After stirring for 5 min, $[VCl_3(MeCN)_3]$ (1.43 g, 5.10 mmol) was added producing a mixed suspension of the green starting material and the white lithium salt Li(bzhap), but on stirring a deep red solution formed and the $[VCl_3(MeCN)_3]$ slowly dissolved. The mixture was heated under reflux for 3 h, allowed to cool and then the white precipitate (LiCl) was filtered off and the deep red solution was reduced slightly in volume. Flame red microcrystals separated, which were filtered off and dried *in vacuo*.

Tris(2 - phenolato - N - 4 - methylbenzylacetophenoneim-ine)vanadium(III)

To an ice-cold solution of the Schiff base HMebzhap (3.40 g, 14.2 mmol) in toluene (100 cm³), LiMe (10.2 cm³, 14.2 mmol, 1.4 M solution in diethyl ether) was added. Much efferverscence occurred and the yellow solution became dark red, but upon complete addition of the LiMe a white precipitate formed with a pale orange solution. Then [VCl₃(MeCN)₃] (1.33 g, 4.73 mmol) was added and the mixture heated under reflux for 1 h. The red-brown microcrystals which appeared from the deep red solution on cooling were filtered off on a sintered disc and extracted with the mother liquor. A white solid (LiCl) remained on the sinter and the red filtrate was held at -15° C. Very little solid precipitated, so the solution was taken to

					Analy	yses"				μ_{eff}	$\mu_{\rm B}$	
Formulae		Yield%	Ŭ	%	Η	%	Ž	0	Colour	293 K	89 K	θ (K)
[V(bzhap) ₃]	C ₄₅ H ₄₂ N ₃ O ₃ V		74.8	(74.8)	5.8	(5.9)	5.2	(5.8)	Flame red	2.97	2.69	20
$[V(Mebzhap)_3]$ —LCl (2/1)	$C_{48}H_{48}Cl_{1/2}Ll_{1/2}N_{3}O_{3}V$	47	73.3	(73.3)	6.4	(6.2)	5.4	(5.3)	Red-brown	2.93	2.74	18
[V(bzsal),]LiCl (4/1)	$C_{42}H_{36}Cl_2Li_2N_3O_3V$		72.0	(6.17)	5.3	(5.2)	6.1	(0.0)	Red			
[V(Prhap) ₃] · C ₇ H ₈	$C_{40}H_{34}N_3O_3V$	ļ	71.5	(71.5)	7.6	(7.5)	6.4	(6.3)	Red	2.93	2.63	30
" Required values in parentheses.												

dryness and the red-brown solid washed with and finally suspended in diethyl ether. The solid was filtered off and dried *in vacuo*. The analyses suggest that some LiCl is associated with the complex.

Tris(salicylaldehydatobenzylimine)vanadium(III)

The Schiff base Hbzsal (3.35 g, 15.9 mmol) was dissolved in toluene (100 cm³) to give a clear yellow solution. This was cooled in solid CO₂ ice/acetone and LiMe (11.4 cm³, 47.6 mmol, 1.4 M solution in diethyl ether) added slowly, forming a white precipitate in an opaque solution. On warming to room temperature and after much effervescence the colour of the solution had changed to pink but the white precipitate remained. [VCl₃(MeCN)₃] (1.33 g, 4.73 mmol) was added and the suspension stirred overnight. Next day a red precipitate had formed; this was filtered off and extracted from the sintered disc by the mother liquor. The red product which appeared on cooling was filtered off and dried *in vacuo*.

Tris(2-*phenolato*-N-n-*propylacetophenoneimine*)*vanadium*(III)-*toluene*(1/1)

Na(Prhap) was prepared by the careful addition of sodium hydride (2.21 g, 92.1 mmol) to a solution of HPrhap (16.1 g, 90.8 mmol) in thf (70 cm³). The white product which precipitated after much effervescence was filtered off and dried *in vacuo*.

To a yellow solution of Na(Prhap) (1.85 g) in thf (100 cm³) was added the vanadium(II) species $VBr_2(MeOH)(thf)$ (0.93 g, 2.62 mmol). On stirring, a red solution formed almost immediately and stirring was continued at room temperature overnight. The white solid (NaCl) which precipitated was filtered off and the deep red filtrate was concentrated to dryness yielding a dark red product.

Toluene (70 cm³) was added to give a deep red solution. A little toluene was pumped off until some solid began to form. Then the mixture was left to stand at room temperature for ca 3 weeks during which time bright red crystals appeared. They were filtered off and dried *in vacuo*. The crystals changed to green on exposure to air.

Halocomplexes of vanadium(III) and vanadium(IV)

Dichloro[propan-1,2-diyl-N,N'-bis(salicylideneiminato)]vanadium(IV) The HCl gas used in this preparation was prepared by the careful dropwise addition of concentrated H_2SO_4 to concentrated HCl. The vanadyl derivative [VO(sal-1,2-pn)] (2.01 g, 5.79 mmol) was dissolved in acetonitrile (50 cm³) forming a green solution. The HCl gas was bubbled through this solution, which changed rapidly from green to deep blue, for *ca* 30 min. The deep blue microcrystalline solid which formed on standing at 4°C overnight was filtered off, washed with methanol and dried in a vacuum desiccator.

Dibromo[propan-1,2-diyl-N,N'-bis(salicylideneimiato)]vanadium(IV). The HBr gas used in this preparation was generated from bromine and tetralin. The HBr gas was bubbled through a green acetonitrile of [VO(sal-1,2-pn)] (0.5 g, 1.4 mmol) which became blue-purple within 5 min. The gas was bubbled through the reaction mixture for a further 25 min. The deep blue solid which formed on standing at 4°C overnight was filtered off, washed with methanol and dried in a vacuum desiccator.

Diiodo[propan-1,2-diyl-N,N'-bis(salicylideneiminato)]vanadium(IV). A flask containing [VO(sal-1,2pn)] (1.74 g, 5.01 mmol) was evacuated, dinitrogen was admitted and the solid dissolved in freshly distilled dichloromethane (100 cm³), forming a green solution. Trimethylsilyl iodide (1.43 cm³, 10.0 mmol) was added forming a brown-black solution with the rapid precipitation, on stirring, of a tan solid. This was filtered off and dried *in vacuo*.

Chloro[propan - 1,2 - diyl - N,N' - bis(salicylideneiminato)]vanadium(III). The dark blue crystalline [VCl₂(sal-1,2-pn)] (0.7 g, 1.7 mmol) was added to thf (30 cm³) forming a blue-black suspension in a blue solution. An excess of sodium sand (0.13 g, 5.6 mmol) was added and after stirring the mixture at room temperature for 3 days, a dark red solution and white precipitate resulted. The white solid, presumably NaCl, was filtered off and the filtrate was taken to dryness, yielding a dark red semicrystalline solid.

Dichloro[ethylene - N,N' - bis(acetophenoneiminato)] vanadium(IV). A green solution of [VO(hapen)] (0.5 g, 1.4 mmol) in acetonitrile (50 cm³) was treated with HCl gas. The solution changed rapidly from green to deep blue and gas was bubbled through the reaction mixture for a further 25 min. The deep blue microcrystalline solid which formed on standing at 4°C overnight was filtered off, washed with methanol and dried in a vacuum desiccator.

Dibromo[ethylene - N,N' - bis(acetophenoneiminato)] vanadium(IV). This was made by bubbling HBr gas through an acetonitrile solution (50 cm³) of [VO(hapen)] (0.5 g, 1.4 mmol) until the colour changed from green to a deep blue. On standing at 15° C overnight, a dark grey-blue solid precipitated which was filtered off, washed with methanol and dried in a desiccator.

Crystal structure analysis of [VO(OC₆H₄CHNH)₂]

Crystal data. $C_{14}H_{12}N_2O_3V$, M = 307.2. Orthorhombic, space group $P2_12_12_1$ (no. 19), a = 5.5475(6), b = 11.797(1), c = 20.494(3) Å, Vol. = 1341.1 Å³. Z = 4, $D_c = 1.521$ g cm⁻³, F(000) = 628, μ (Mo- K_z) = 7.2 cm⁻¹, λ (Mo- K_z) = 0.71069 Å.

Crystals are very long, fine, grey needles. One, cut down to $ca 0.36 \times 0.13 \times 0.04$ mm, was mounted on a glass fibre and, after photographic examination, was

transferred to an Enraf–Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (by refinement from the settings of 25 reflections, having θ in the range 10– 12°, each reflection centred in four orientations) and measurement of diffraction intensities (to $\theta_{max} = 25^\circ$).

During processing, the intensity data were corrected for Lorentz-polarization effects and were adjusted to eliminate negative net intensities (by Bayesian statistical methods). There was no deterioration of the crystal during examination. Of the 1410 unique reflections input to the SHELX program system for structure analysis, 1196 had $1 > 2\sigma_1$.

The structure was determined by the heavy atom method and refined by full-matrix least-squares procedures. All the non-hydrogen atoms were allowed anisotropic thermal parameters. The two imido hydrogen atoms were located in difference maps and their coordinates were refined independently; the remaining H atoms were included in idealized positions. The isotropic thermal parameters of all the H atoms were refined freely. Refinement converged with R = 0.060 and $R_g = 0.073$ [20] for all 1410 reflections weighted $w = (\sigma_F^2 + 0.00341 F^2)^{-1}$. In a final difference map, the largest peaks, at *ca* 0.7 e Å⁻³, were around the vanadium atom.

Refinement of the opposite enantiomeric structure produced R and R_g [20] values of 0.064 and 0.077 and slightly higher e.s.d.s throughout. We are confident, therefore, that we are reporting the absolute configuration for that particular crystal.

Scattering factors for neutral atoms were taken from reference [21]. Computer programs used in this analysis have been noted above and in Table 4 of reference [22], and were run on a DEC MicroVAX 3600 machine currently in the Chatt Laboratory.

Crystal structure determination of [V(Prhap)₃] · C₇H₈

Crystal data. $C_{33}H_{42}N_3O_3V \cdot C_7H_8$, M = 671.8. Monoclinic, space group $P2_1/c$ (no. 14), a = 12.434(27), b = 18.418(25), c = 16.529(11) Å, $\beta = 101.16(12)^\circ$, Vol. = 3714 Å³. Z = 4, $D_c = 1.201$ g cm⁻³, F(000) = 1432, $\mu(Mo-K_{\alpha}) = 2.9$ cm⁻¹, T = 295 K. $\lambda(Mo-K_{\alpha}) = 0.71073$ Å.

The intensity data were collected from a crystal with dimensions $1 \times 0.45 \times 0.45$ mm using an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo- K_x radiation. The resulting unit cell, obtained from 25 reflections, had larger than usual errors, probably as a result of the crystal size but also arising from a lack of crystal quality due to the disorder present in the structure. This has been reflected in the relatively high final *R* value (R = 0.10) at the end of the refinement.

The Lorentz-polarization correction was applied to the diffraction intensities. An empirical absorption correction based upon Ψ -scan data gave minimum/maximum corrections of 0.30/0.99, average 0.66, which so badly distorted the intensity data that refinement was impeded. The correction was later ignored and this is justified as the absorption coefficient is only 2.9 cm^{-1} .

The position of the V atom together with four oxygen atoms was obtained from the Patterson map. The usual heavy atom method produced the remainder of the molecule, now identified as [V(Prhap)₃], together with some disordered atoms indicative of a solvent molecule. Convergence was slow, reaching an R value of 0.22 with difficulty. The decision was made at this stage to ignore the empirical absorption corrected data and to use the uncorrected set, when R improved to 0.18. At the same time, effort was expended to establish the exact nature of the solvent molecule and whether it was only a fractional molecule or a full molecule. It was concluded after trial refinements of the occupancy factors that the solvent was that of a full toluene molecule. Hydrogen atoms were also added to the atoms list, but not refined, in calculated positions using $d_{\rm CH} = 1.0$ Å.

Anisotropic refinement of the vanadium complex, the toluene molecule remaining isotropic, allowed *R* to converge to 0.10, $R_w = 0.14$ and S = 1.291 using a weighting scheme $w^{-1} = [\sigma_F^2 + (0.08F)^2 + 8.0]$. The highest peak in the final difference map was 0.55 electrons. The isotropic temperature factors, B_{iso} , of the toluene atoms are very high, ranging from 16 to 34 Å², indicating substantial disorder in the structure.

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