

Synthesis and characterisation of vanadium(III) complexes of biphenylphenols

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The vanadium(III) complexes of composition $[VCl_{3-n}(OAr^{1,2})_n \cdot (THF)_2]$ ($OAr^1 = 2$ -phenylphenoxo and $OAr^2 = 4$ -phenylphenoxo, THF = tetrahydrofuran; $n = 1 \rightarrow 3$) were prepared by in situ reaction of $VCl_3 \cdot (THF)_3$ with sodium salt of respective phenols in tetrahydrofuran. The complexes were characterised by elemental analysis, molar conductance, FTIR, UV-Vis, and FAB-mass spectral and magnetic studies. The thermal behaviour of some of the complexes was studied by TG-DTA. The dinuclear phenoxy bridged octahedral structures for the complexes were inferred from the spectral and magnetic studies.

Key Words: Vanadium(III) complexes, biphenylphenols, magnetic study, electronic spectra, mass spectra

Introduction

An ever-increasing research interest in the coordination chemistry of vanadium has been aroused not only due to its exhibiting a range of oxidation states from +5 to -1 but also from the fascinating structural novelties and complexities exhibited by vanadium complexes and their immense biological,^{1,2} industrial,^{3,4} and medicinal applications.^{5,6} For vanadium, +4 oxidation state is the most stable while lower oxidation states are strongly reducing and are stable only at low temperatures. The coordination chemistry and reactivity of low-valent vanadium, +3, are known to display interesting reactivity behaviour, such as the capability of dinitrogen fixation,⁷⁻⁹ in particular, with anionic oxygen donors. Moreover, biological oxygen carriers, which transport and store dioxygen, are characterised by their ability to bind O_2 reversibly, generally through a low-valent metal atom such as iron(II) in haemoglobin or myoglobin¹⁰ or vanadium(III) or (IV) in haemovanadin¹¹ (a protein found in the 1.5-2N H_2SO_4 solution existing in the vacuoles of Ascidiidae blood cells). Vanadium(III,

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IV, and V) complexes have been reported to have found use for the treatment of diabetes and cancer.^{12–15} Polynuclear vanadium(III) complexes isolated from organic solvents or neat carboxylic acid solutions exhibit interesting structures, and spectroscopic and magnetic properties.^{16–24} Dimeric, trimeric, tetranuclear, octanuclear, and decanuclear vanadium(III)/carboxylates have been described. Vanadium(III) complexes are known to produce interesting magnetic properties,^{18–22,26–31} spin-frustration effects,³² and single-molecular magnetic behaviour.^{19,25}

Compared to the voluminous reports on vanadium complexes in higher oxidation states vanadium(IV) and (V), those on vanadium(III) complexes are rather scarce perhaps because of the limited spectral techniques available for their characterisation and their air-sensitive nature. Nevertheless, interest in advancing low-valent vanadium chemistry has also been due to their biological role in organisms such as tunicates.^{33–35} Vanadium(III) and (IV) complexes with tris(2-thiolatoethyl)amine, bis(2-thiolatoethyl)ether,³⁶ 1,2-bis(2-pyridinecarboxamide)benzene,³⁷ and 2-tetrahydrofuran³⁸ have been reported. Vanadium(III) complexes of salicylaldehyde semicarbazones,³⁹ di-2-pyridylketone oxime,⁴⁰ arylthiol,⁴¹ and carboxylates⁴² have been described. Scattered reports describe the phenolate chemistry of vanadium in the +2 and +3 oxidation states. The synthesis and crystal structures of $[(\mu\text{-O-2,6-ArMe}_2)(\text{O-2,6-ArMe}_2)\text{V}^{III}]_2\cdot\text{thf}$ from the reaction of $[\text{V}(\text{dmb})_2]_2\cdot(\text{thf})$ (dmb = dimethoxyphenyl) with 2,6-dimethylphenol have been reported.⁴³ Homoleptic 4 and 6-coordinate vanadium(III) phenolate complexes have been reported.⁴⁴ The synthesis and characterization of 3,5-di-tert-butylcatecholate complexes of vanadium(V), (IV) and (III) have been described.⁴⁵ In continuation of our interest^{46–48} in exploring the chemistry of vanadium in different oxidation states with a variety of substituted phenols, the present work describes an initiative to study the chemistry of lower valent vanadium(III) using biphenylphenols viz. 2-phenylphenol of biological relevance and 4-phenylphenol.

Experimental

All the solvents used were of A.R. grade and were dried by standard methods. 2- and 4-phenylphenols (Merck) were recrystallized from benzene and the purity was checked by their sharp melting points (57 and 168 °C, respectively). $\text{VCl}_3\cdot(\text{THF})_3$ was used as received.

Physical measurements

Vanadium in complexes was determined gravimetrically as V_2O_5 while chlorine was determined by Volhard's method. Elemental analyses were performed on Carlo-Erba 1108 Elemental Analyzer. The conductivity measurements in nitrobenzene were made on an Elico Conductivity Bridge type CM-82T. The room temperature magnetic moments of the vanadium(III) complexes were studied by Guoy's method. Corrections were applied for diamagnetism calculated from Pascal's constants. Effective magnetic moments were calculated as $\mu_{eff} = 2.828 (\chi_v \text{ T})^{1/2}$, where χ_v is the magnetic susceptibility per vanadium. FTIR spectra of complexes were collected on a Nicolet-Avatar 5700 spectrophotometer (4000–200 cm^{-1}) as KBr pellets and Nujol mull in CsI optics. UV-Vis spectra were recorded on a CARY 100 BIO UV-Vis spectrophotometer. The FAB mass spectra were recorded on a JEOL SX 102/DA-600 mass spectrometer/data system using Ar/Xe (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV. m-Nitrobenzylalcohol (NBA) was used as the matrix. Thermograms were

recorded on simultaneous TG-DTA SHIMADZU DT-60 thermal analyzer. The analytical constants were as follows: heating rate, 20 °C min⁻¹, reference, Al₂O₃; thermocouple, Pt/Pt-Rh 10%; and atmosphere, air.

Preparation of sodium salts of 2- and 4-phenylphenols

To a solution of 2- and 4-phenylphenols (1.98 g, 0.011 mol) in tetrahydrofuran was added an equimolar amount of sodium hydride (0.28 g, 0.011 mol) in small instalments with continuous stirring at room temperature in separate experiments. The addition resulted in an immediate evolution of hydrogen gas. The resulting solution was then stirred at room temperature for 6-7 h. The sodium salt thus obtained was used in situ for further reactions.

Synthesis of [VCl_{3-n}(OAr^{1,2})_n·(THF)₂] (where OAr¹ = OC₆H₄-C₆H₅-2 and OAr² = OC₆H₄-C₆H₅-4; n = 1 → 3)

In a typical reaction, for the preparation of complex of composition [VCl₂(OAr^{1,2})·(THF)₂], to a solution of VCl₃·(THF)₃ (0.98 g, 0.0026 mol) in dry tetrahydrofuran was added an equimolar solution of sodium salt of 2- and 4-phenylphenols (0.51 g, 0.0026 mol) in the same solvent in separate experiments under nitrogen atmosphere. The reaction mixture was stirred for 7-8 h. The stirring resulted in the separation of a white solid, identified as sodium chloride. It was then removed by vacuum filtration. The filtrate was concentrated under vacuum. The concentrate was then treated with petroleum ether when a solid was obtained. It was dried under vacuum.

VCl₂(OC₆H₄-C₆H₅-2)·(THF)₂, Dichlorodioxacyclopentane(2-phenylphenoxide)vanadium (III), yield, 0.88 g (65%), Anal. C₂₀H₂₅Cl₂O₃V (435.25). Found C 55.56, H 6.24, Cl 16.59, V 12.02, calc. C, 55.19; H, 5.79; Cl, 16.29; V, 11.70 (%). μ_{eff} 2.3 B. M.

ν (cm⁻¹) 3069, 3017, 2959, 2926, 2843, 2364, 2062, 1620, 1588, 1560, 1478, 1455, 1449, 1432, 1380, 1324, 1264, 1218, 1175, 1099, 1062, 1016, 935, 917, 880, 830, 803, 757, 732, 699, 668, 645, 610, 564, 518, 493, 443, 378, 327, λ_{max} (nm); 730, 660, 577, 520, 482.

VCl₂(OC₆H₄-C₆H₅-4)·(THF)₂, Dichlorodioxacyclopentane(4-phenylphenoxide)vanadium (III), yield 0.95 g (70%), C₂₀H₂₅Cl₂O₃V, (435.25), Found C 55.35, H 5.93, Cl 16.60, V 11.46, calc. C, 55.19; H, 5.79; Cl, 16.29; V, 11.70 (%), μ_{eff} 2.2 B. M. ν (cm⁻¹) 3080, 2618, 2471, 2446, 2421, 2367, 2347, 2271, 2243, 2147, 2065, 2017, 1964, 1896, 1834, 1823, 1752, 1642, 1580, 1490, 1456, 1431, 1411, 1370, 1352, 1308, 1295, 1278, 1176, 1133, 1090, 1081, 1054, 1002, 988, 926, 907, 885, 846, 835, 768, 754, 732, 723, 715, 683, 666, 650, 631, 602, 530, 521, 498, 486, 478, 465, 443, 432, 424, 399, 348, 335, 325, 291, 271, 266, 253, 242, 236, λ_{max} (nm); 731, 650, 580, 515, 484.

A similar procedure was adopted for the synthesis of [VCl(OAr^{1,2})₂·(THF)₂] and [V(OAr^{1,2})₃·(THF)₂] complexes by the reaction of VCl₃·(THF)₃ (0.99 g, 0.0026 mol) with 2 and 3 equivalents (1.02 g, 0.0053 mol/1.53 g, 0.0080 mol) of sodium salts of 2- and 4-phenylphenols in separate experiments whereupon dark green to black solids were formed. It is pertinent to mention here that, despite our efforts, the complex [V(OC₆H₄-C₆H₅-4)₃·THF₂] could not be isolated due to its highly hygroscopic nature.

VCl(OC₆H₄-C₆H₅-2)₂·(THF)₂, Chlorodioxacyclopentane(di-2-phenylphenoxide)vanadium

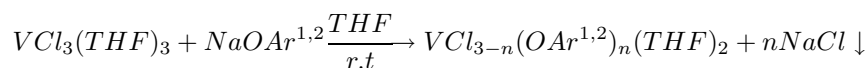
(III), yield 1.07 g (63%) C₃₂H₃₄ClO₄V (569.00), Found C 67.21, H 6.39, Cl 6.55, V 8.02, calc. C, 67.55; H, 6.02; Cl, 6.23; V, 8.95 (%). μ_{eff} 2.1 B. M. ν (cm⁻¹) 2364, 1620, 1559, 1465, 1397, 1322, 1270, 1221, 1172, 1125, 1062, 990, 888, 825, 761, 699, 545, 391, 333, λ_{max} (nm); 732, 695, 582, 500, 483.

V(OC₆H₄-C₆H₅-2)₃·(THF)₂, Dioxacyclopentane(tri-2-phenylphenoxide)vanadium(III), yield 1.24 g (60%) C₄₄H₄₃O₅V (702.75) found C 75.62, H 6.84, V 6.70, calc. C, 75.20; H, 6.17; V, 7.25 (%). μ_{eff} 2.0 B. M. ν (cm⁻¹) 2962, 2918, 2855, 1620, 1563, 1472, 1420, 1391, 1322, 1262, 1166, 1098, 1045, 1015, 890, 871, 832, 749, 692, 611, 524, 489, 397, λ_{max} (nm); 734, 700, 579, 510, 485.

VCl(OC₆H₄-C₆H₅-4)₂·(THF)₂, Chlorodioxacyclopentane(di-4-phenylphenoxide)vanadium(III), yield 1.11 g (65%) C₃₂H₃₄ClO₄V (569.00), Found C 66.02, H 6.26, Cl 5.78, V 9.21, calc C, 67.55; H, 6.02; Cl, 6.23; V, 8.95 (%). μ_{eff} 2.0 B. M. ν (cm⁻¹) 2932, 2857, 2363, 1942, 1653, 1790, 1600, 1557, 1495, 1451, 1418, 1267, 1069, 1052, 984, 889, 825, 745, 636, 512, 580, 475, 389, λ_{max} (nm); 735, 690, 586, 500, 486.

Results and discussion

The vanadium(III) complexes of biphenylphenols were prepared in fairly good yields (60%-70%) by the reaction of VCl₃(THF)₃ and sodium salts of 2- and 4-phenylphenols in tetrahydrofuran at room temperature under nitrogen atmosphere. The analytical data of the complexes conform to the proposed stoichiometric formulations (Scheme 1).

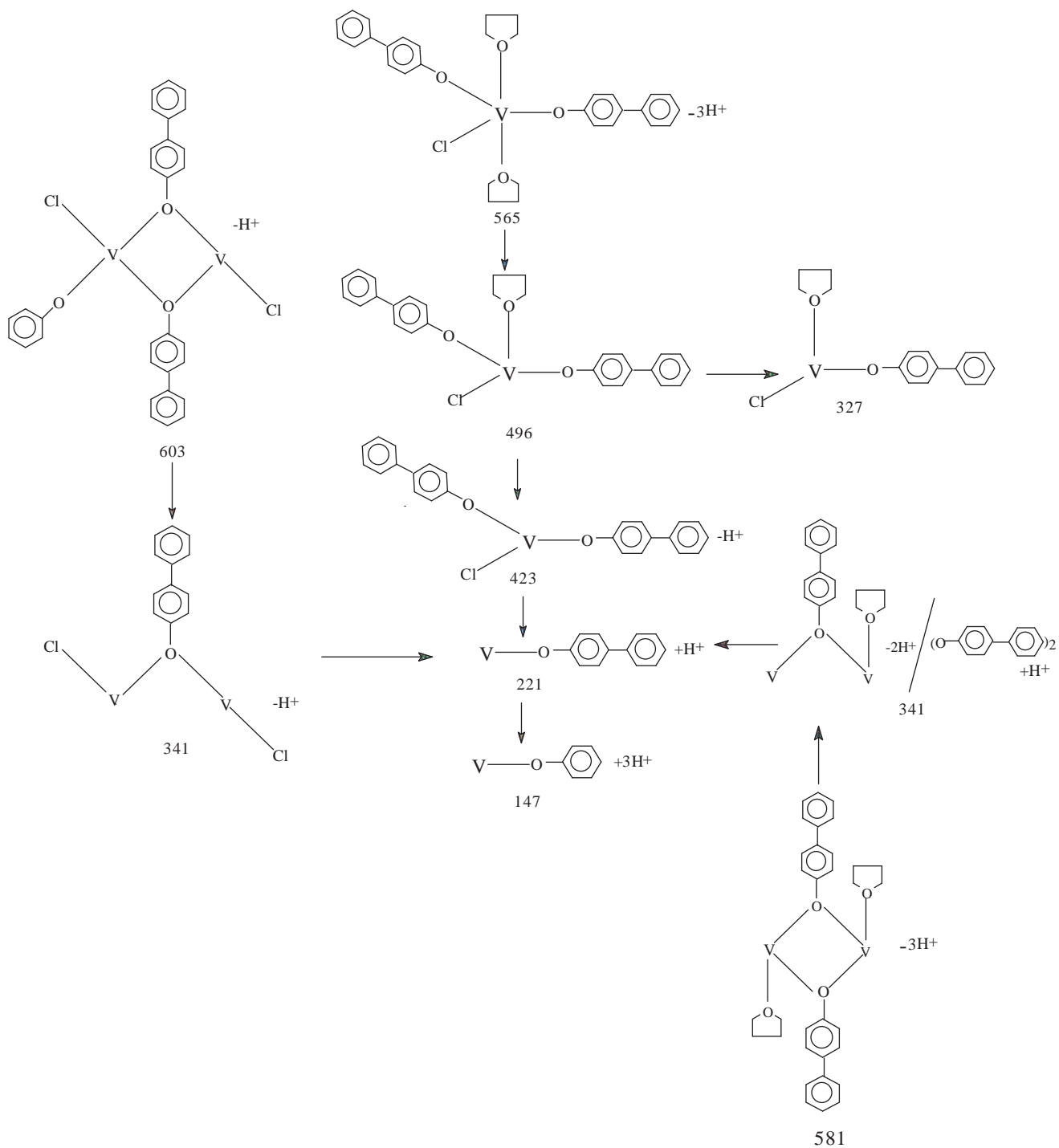


(where $OAr^1 = OC_6H_4 - C_6H_4 - 2$; $OAr^2 = OC_6H_4 - C_6H_4 - 4$; $n = 1 \rightarrow 3$)

The complexes are green to black. They are soluble in common organic solvents. The molar conductance values of millimolar solution of the complexes in nitrobenzene ranging from 0.18-2.5 S cm² mol⁻¹ show that all the complexes are non-ionic.

IR spectra

The formation of the complexes was ascertained from a comparison of the i.r. spectra of complexes with that of 2-phenyl and 4-phenylphenols scanned in the 4000-200 cm⁻¹ region. The absorption bands occurring at 3653 cm⁻¹ and 3393 cm⁻¹ due to the phenolic ν OH mode in 2-phenyl and 4-phenylphenols were found to be absent in complexes, thereby suggesting the deprotonation of phenolic oxygen. The absorption bands due to ν (C-O) mode occurring in 1327-1269 cm⁻¹ and 1335-1199 cm⁻¹ regions⁴⁹⁻⁵¹ in uncoordinated 2-phenyl and 4-phenylphenol respectively were observed to move to lower wave numbers and appeared in 1221-1165 cm⁻¹ and 1230-1175 cm⁻¹ regions in the respective complexes, and were ascribed to the ν_{c-o} mode of the phenolic group compared to those occurring in the 1340-1270 cm⁻¹ region in phenols. This negative shift of ν_{c-o} mode in the complexes suggested bonding through phenolic oxygen. The bands that appeared in the 580-490 cm⁻¹ region were assigned to ν (V-O) mode.^{52,53} The chloro complexes [VCl_{3-n}(OAr^{1,2})_n] exhibited bands at \sim 390 cm⁻¹ due to ν (V-Cl) mode.⁵⁴ The occurrence of bands in 834-760 cm⁻¹ region assigned to ν (V-O-V) mode suggests the dimeric nature of the complexes. The bands occurring in 1060-1040 and 890-880 cm⁻¹ regions



Scheme 1

in complexes were assigned to that of the coordinated tetrahydrofuran to vanadium metal compared to these bands occurring at 1048 and 880 cm^{-1} in free tetrahydrofuran molecule.

Magnetic studies

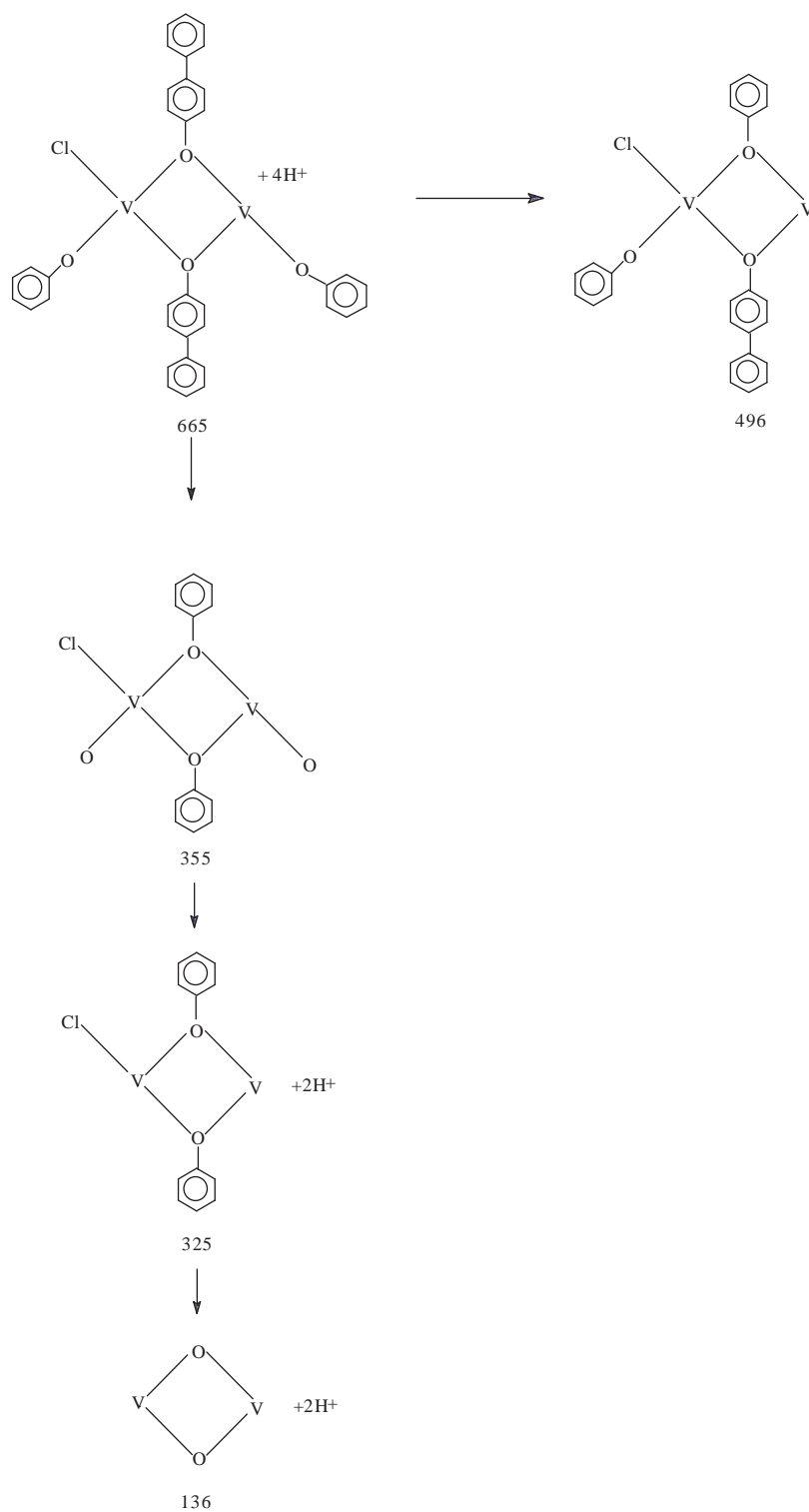
The room temperature solid state magnetic moment of complexes $[\text{VCl}_{3-n}(\text{OAr}^{1,2})_n \cdot (\text{THF})_2]$ of magnitude 2.0-2.3 μ_{eff} per vanadium suggest weak antiferromagnetic coupling between the vanadium(III) atoms⁵⁵⁻⁵⁷ through phenoxy bridging. The observed deviation from a spin-only value of 2.83 μ_{eff} for V^{3+} (d^2 system) may be ascribed to a ligand mediated superexchange mechanism as is shown by dinuclear V(III) tris(aryloxy) $[(\mu\text{-O-2,6-ArMe}_2)(\text{O-2,6-ArMe}_2)_2\text{V}]_2 \cdot \text{thf} \cdot \text{C}_7\text{H}_8^{43}$ and dinuclear tris(2,2,2-trichloroethoxy) and (2,2,2-trifluoroethoxy) vanadium(III).⁵⁸ These observations, however, differ from the solution magnetic susceptibility data for mononuclear homoleptic 4 and 6-coordinate vanadium(III) phenolate species $[\{\text{V}(\text{OC}_6\text{H}_5)_6\}\text{-Li}(\text{DME})\}_3]$, $[\{\text{V}(\text{DIPP})_4\}\text{-Li}(\text{THF})\}_4]$, and $[\text{Li}(12\text{-crown-4})\{\text{V}(\text{DIPP})_4\}]$ (DME = 1,2-dimethoxyethane, DIPP = 2,6-diisopropylphenolate), which are known to show magnetic moment in the 2.72-2.90 μ_{eff} range,⁴⁴ consistent with a d^2 electronic configuration.

Electronic spectra

The electronic spectral data of the newly synthesized complexes $[\text{VCl}_{3-n}(\text{OAr}^{1,2})_n(\text{THF})_2]$, recorded in methanol in the 200-900 nm range, display a broad band in the 500-520 nm (19,230-20,000 cm^{-1}) range and a shoulder in the 650-700 nm (14,285-15385 cm^{-1}) range assigned to ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ and ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{T}_{2g}$ transitions respectively, in accordance with an octahedral geometry⁵⁹. Interestingly, low energy intense LMCT transitions in the visible region of the optical spectrum that appeared at 17,055 cm^{-1} (~ 586 nm) and 13,593 cm^{-1} (~ 735 nm) in these complexes are consistent with the trends found in vanadium phenolates. The transitions observed ~ 485 nm have been assigned for an internal CT transition within the $\text{V}^{III}\text{-O-V}^{III}$ moiety^{20,42,60}.

Mass spectra

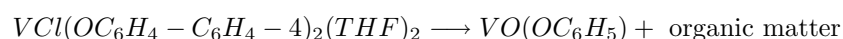
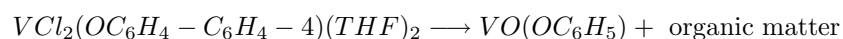
The FAB-mass spectra of a representative vanadium(III) complex, $[\text{VCl}(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4})_2 \cdot (\text{THF})_2]$ (M), were studied (Figure 1). The complex exhibited a molecular ion peak at m/z 565 (14%) corresponding to $[\text{VCl}(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4})_2 \cdot (\text{THF})_2 - 3\text{H}]^+$ $[\text{M} - 3\text{H}]^+$. The fragment ions at 496 (12%) and 423 (14%) corresponded to $[\text{VCl}(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4})_2 \cdot (\text{THF})]^+$ and $[\text{VCl}(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4})_2\text{-H}]^+$, respectively, resulting from the successive removal of THF molecules from the molecular ion. The base peak at m/z 147 (100%) was ascribed to $[\text{V}(\text{OC}_6\text{H}_5) + 3\text{H}]^+$. The other structurally important major fragment ions in the complex are: m/z 401 (25%), $[\text{V}(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4})_2 + 2\text{H}]^+$, 221 (45%) $[\text{V}(\text{OC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4}) + \text{H}]^+$, and 170 (45%) $[\text{HOC}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4}]^+$. The fragmentation pathways including possible structures of ions are given in Scheme 2.



Scheme 2. FAB-induced decomposition pattern for the complex $[VCl(OC_6H_4-C_6H_5-4)_2 \cdot (THF)_2]_2$.

Thermal studies

The thermal behaviour of vanadium(III) 4-phenylphenoxides [$VCl_2(OC_6H_4-C_6H_5-4)$] and [$VCl(OC_6H_4-C_6H_5-4)_2$] was studied by TG-DTA techniques. The complexes showed initial decomposition at 44.29 and 48.52 °C, respectively, after which temperature the complexes underwent decomposition in a single step. The percentage weight losses of 61.09% and 71.26% for the respective complexes accounted strikingly for the formation of $VO(OC_6H_5)$ as the ultimate product of decomposition rather than VO_2 . It is further important to note that the complexes did not display any exothermic or endothermic peak in DTA curves. The scheme of decomposition may be given as:



Conclusion

The new low-valent vanadium(III) complexes of 2- and 4-phenylphenols are accessible from the reaction of $VCl_3(THF)_3$ with sodium salts of the respective phenols. The successful isolation of new vanadium(III) complexes of biphenylphenols described herein is probably as a consequence of the coordinating THF solvent. The investigations of the structures of the complexes by physicochemical, i.e., and electronic spectra and magnetic studies reveal that the coordination environment of the central atom in complexes is distorted octahedral wherein monomeric units are held together by bridging phenoxo groups and 2 tetrahydrofuran molecules are attached to each monomer. Thermal behaviour study of the 2 complexes points to the formation of $VO(OC_6H_5)$ rather VO_2 as the ultimate decomposition product.

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