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4-methoxyphenoxo complexes of monooxovanadium(V) and their reactions with cyanoanilines and cyanopyridines

Neeraj Sharma*, Anoop K. Sood, S. S. Bhatt and S. C. Chaudhry

Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla-171005, India

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Abstract—The new 4-methoxyphenoxomonooxovanadium(V) complexes with the general formulae $[VOCl_{3-x}(OC_6H_4OMe\text{-}4)_x]$ (where $x = 1 \rightarrow 3$) have been conveniently synthesized in good yields using $VOCl_3$ and the trimethylsilyl derivative of 4-methoxyphenol, $Me_3SiOC_6H_4OMe$-4 as reactants in CCl_4. The complexes were characterized by chemical analyses, conductively measurements, IR, ^{1}H NMR, electronic spectra and thermal studies. Coordination compounds of the parent complexes with cyanoanilines and cyanopyridines have been prepared and studied. Tentative stereochemistries are assigned in each case. © 1997 Elsevier Science Ltd

Keywords: 4-methoxyphenol; monooxovanadium(V); cyanoanilines; cyanopyridines; IR; NMR.

In recent years, vanadium phenolate chemistry [1,2] has witnessed an accelerating interest not only due to the fact that the hard phenolate ligands known to behave as excellent ancillary ligands [3,4], stabilize the highest available oxidation state of vanadium incorporating VO^{3+} moiety preferentially [5] but also because of their implications in a variety of biomolecules [6]. Furthermore, vanadium phenolates have emerged as catalysts for polymerisation and oxidation [7] and potential shape selective transformations [8]. Although several novel vanadium phenolates have been reported to be characterised in the form of multidentate hetero-ligand chelates [1,9] with special emphasis on their relevance in biological systems, yet it has been felt that an understanding of the biological significance and physiology of vanadium seems to rest in part, on the knowledge of coordination chemistry of vanadium. It is in this context that our main interest has centred around the synthesis of new vanadium aryloxides which is likely to establish a symbiotic relationship between the biochemistry and coordination chemistry of vanadium. As a part of our ongoing studies [10,11] of monooxovanadium(V) complexes with a variety of phenols having different substituents which by their electronic and steric effects may show significant influences on the structure and reactivity at metal centre, we now report the synthesis and characterisation of new 4-methoxyphenoxo complexes of monooxovanadium(V). Further, the reaction of these parent complexes with some cyanoanilines and cyanopyridines have also been carried out to explore the coordination behaviour of such ligands.

EXPERIMENTAL

$VOCl_3$ (Aldrich) was used without further purification. 4-Methoxyphenol was recrystallized from benzene and the purity was checked by its m.p. (55°C). Solvents were made anhydrous before use by standard methods. $4\text{-}MeOC_6H_4SiMe_3$ was prepared by the reaction of Me_3SiCl with $4\text{-}MeOC_6H_4OH$ in the presence of Et_3N. 2- and 3-Cyanopyridines (Aldrich) were purified prior to their use by recrystallization from 95% ethanol and were checked by sharp melting points and IR spectral data. 3- and 4-Cyanoanilines (Aldrich) were used as procured.

Vanadium was estimated as V_2O_5 after decomposing the complexes with a mixture of conc. HNO_3 and H_2SO_4 followed by heating at 600°C for 1–2 h and chlorine by Volhard's method. Carbon and hydrogen were determined using a Carlo Erba 1106 elemental

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* Author to whom correspondence should be addressed.

analyzer. The IR spectra were recorded in KBr and Nujol mulls on a Beckman IR 4250 spectrophotometer and ^{1}H NMR spectra on a Jeol JNM PMX60SI spectrometer using $CDCl_3$ as solvent. Electronic spectra were recorded on Beckman DU-6 spectrophotometer using CH_3CN and CH_3OH as solvents. Thermograms were recorded on a SHIMADZU Thermal Analyzer DT-40. Molecular weights were determined cryoscopically in nitrobenzene using a Beckmann thermometer while conductance measurements in the same solvent were made on an Elico Conductivity Bridge CM Type 82T using a 10^{-3} M solution at 25°C.

Preparation of complexes [$VOCl_2(OC_6H_4OMe\text{-}4$], [$VOCl(OC_6H_4OMe\text{-}4)_2$] *and* [$VO(OC_6H_4OMe\text{-}4)_3$]

A typical reaction procedure is as follows: $VOCl_3$ (1 mmol) in dry CCl_4 (50 cm^3) was reacted with 1 mmol, 2 mmol and 3 mmol of $Me_3SiOC_6H_4OMe\text{-}4$ in separate experiments. The reaction mixtures which immediately turned purple were stirred for 4–5 h followed by heating under reflux for 2–3 h to ensure completion of the reaction when the colour of the mixture solution changed from purple to black. The by-product, Me_3SiCl formed in the reaction and excess solvent were distilled off and the resulting concentrated solution was at first kept overnight and was then treated with petroleum ether. The precipitated black complexes were filtered, washed with petroleum ether and dried *in vacuo*.

Preparation of cyanoaniline (CNAn) and cyanopyridine (CNpy) adducts

A solution of the parent complexes $VOCl(OC_6H_4OMe\text{-}4)_2$ and $VO(OC_6H_4OMe\text{-}4)_3$ in benzene was treated with methanolic solution of 2- and 3-cyanoanilines and 3- and 4-cyanopyridines in separate experiments. The contents were first stirred for 3–4 h at room temperature and then refluxed when a colour change of the mixture solution and the appearance of black to brown solids was observed. These were washed with chloroform and dried *in vacuo*.

RESULTS AND DISCUSSION

The interaction of $VOCl_3$ with appropriate amounts of trimethylsilyl-4-methoxyphenoxide in CCl_4 affords the corresponding complexes in good yield accompanied by the formation of Me_3SiCl as follows:

$$VOCl_3 + xMe_3SiOC_6H_4OMe\text{-}4$$

$$\xrightarrow[\text{reflux}]{CCl_4} VOCl_{3-x}(OC_6H_4OMe\text{-}4)_x + xMe_3SiCl$$

(where $x = 1 \rightarrow 3$)

The elemental analyses of the complexes agreed well with the proposed stoichiometry. The complexes are moisture sensitive black solids but are stable in a dry atmosphere. They are fairly soluble in common organic solvents. The molar conductances of the millimolar solutions of these complexes in nitrobenzene are too low to be attributed to an electrolyte while the cryoscopic molecular weight determinations in the same solvent indicate that the complexes are monomers.

The formation of new monooxovanadium(V) complexes has been further inferred from the significant changes observed in the principal IR spectral bands *viz.* ν(V=O) and ν(V—Cl) of $VOCl_3$; ν(C—O) of the phenoxide ion of the reactants and the appearance of new bands due to ν(V—O) stretching upon complex formation. Due to well known [12] better π-donor character of aryloxide ligands compared to alkoxide and halide ions, the successive replacement of chloride ion by 4-methoxyphenoxide ion has revealed a shift in the ν(V=O) mode to lower wavenumbers by 60–80 cm^{-1}compared to that observed in $VOCl_3$ at 1035 cm^{-1} [13] and in the region 960–1020 cm^{-1} in a number of vanadyl salts and complexes [14]. The ν(V=O) for the complexes $VOCl_2(OC_6H_4OMe\text{-}4)$ (**1**), $VOCl(OC_6H_4OMe\text{-}4)_2$ (**2**) and $VO(OC_6H_4OMe\text{-}4)_3$ (**3**) has been observed at 960, 965 and 972 cm^{-1} respectively. This lowering in ν(V=O) may be understood to have arisen from the decreased terminal oxo oxygen $p\pi \rightarrow$ vanadium $d\pi$ interactions due to the increased electron density around vanadium due to electron release from the ring to the metal atom. This observation is further substantiated by the fact that $\nu(C_{ring}$—O) observed at 1185 cm^{-1} in pure $Me_3Si\text{-}OC_6OMe\text{-}4$ is lowered to 1085, 1090 and 1100 cm^{-1} in **1**, **2** and **3**, respectively. The appearance of new bands around 790 and 710 cm^{-1} has been assigned to ν_{asym} and ν_{sym} (V—O) modes. Apparently, these observations suggest a considerable contribution from a structure of the type ring C$\cdots$O$\cdots$M resulting from the drainage of electron density from the ring to metal. Further sharp bands around 535 cm^{-1} in $VOCl_2(OC_6H_4OMe\text{-}4)$ and $VOCl(OC_6H_4OMe\text{-}4)_2$ have been assigned to ν(V—Cl) mode.

In the ^{1}H NMR spectrum of the complexes the absence of a signal at δ 5.77 due to the phenolic -OH proton in free 4-methoxyphenol confirms deprotonation of this group. The complexes $VOCl_2(OC_6H_4OMe\text{-}4)$ (**1**), $VOCl(OC_6H_4OMe\text{-}4)_2$ (**2**) and $VO(OC_6H_4OMe\text{-}4)_3$ displayed two resonances in each case *viz* δ 6.98 (s, 4H, aromatic) and δ 3.95 (s, 3H, -OMe); δ 6.92 (s, 4H, aromatic) and δ 3.82 (s, 3H, -OMe) and δ 6.8 (s, 4H aromatic) and δ 3.83 (s, 3H, -OMe), respectively attributed to aromatic and method protons. These resonances clearly indicate that there is a significant downfield shift compared to free phenol resonances at δ 6.62 (*o*- and *m*-aromatic H) and δ 3.60 (-OMe) and that of $Me_3SiOC_6H_4OMe\text{-}4$ at δ 6.7 (*o*- and *m*-aromatic H) and δ 3.81 (-OMe). These shifts may be ascribed to the deshielding of these protons due to a drainage of electron density from aromatic nucleus to the metal atom (ArO—V). These observations are substantiated by a similar explanation offered by Clark and coworkers [15] and Chisholm [12] for the downfield shifts observed in the tantalum(V) complexes with different substituted phenols.

The UV–vis spectra of the complexes have been examined in the region 200–700 nm. The 10^{-3} mol dm^{-3} solutions of the complexes $VOCl_2(OC_6H_4OMe\text{-}4)$ (**1**) and $VO(OC_6H_4OMe\text{-}4)_3$ (**3**) in acetonitrile displayed intense bands at 600 nm and 576 nm, respectively. The optical spectrum of the complex $VOCl(OC_6H_4OMe\text{-}4)_2$ (**2**) was however recorded in CH_3CN+CH_3OH mixture solution as the complex was not completely soluble in CH_3CN. It exhibited an absorption band at 325 nm.

It is pertinent to mention here that all of the complexes studied in the present work are black solids of vanadium(V), a d^0 species. For such complexes thus no *d*—*d* bands are expected or observed. However complexes with VO^{3+} bound to phenolic groups are known to display intense absorption bands in the visible region. The visible absorption band is assigned to be a ligand-to-metal charge transfer transition (LMCT) from the oxygen $p\pi$-orbital of phenolate → vanadium(V) $d\pi^*$. Such transition are characteristic of phenolate or catecholate coordination to all reducible metal ions [16,17]. Intense charge transfer spectra is known to be observed for the monooxovanadium(V) phenolates [18,19]. Thus the results presented herein for complexes (**1**) and (**3**) are in agreement with these earlier observations. It appears that intense charge transfer spectra observed in the 570–610 nm range for the complexes are a hallmark of VO^{3+} phenolates.

The observance of an absorption band at shorter wave lengths (blue shift) 325 nm for **2** may be described as a consequence of the solvent effect which is quite large indeed. It can safely be said that the solvent has the effect of raising the LMCT energy into the UV region of the spectrum.

Thermal investigations of all the three complexes have revealed similar decomposition patterns. The decompositions which begin around 90°C are complete in the range 550–600°C. Single stage continuous weight loss of 64.8, 71.5 and 77.45% against theoretical percentages 65.13, 73.85 and 79.12 for **1**, **2** and **3**, respectively has been rationalized in terms of decomposition of the complexes to yield V_2O_5 as the end product. No definite intermediate is indicated from thermal studies.

Based upon the above data, a distorted tetrahedral structure may be proposed for the 4-methoxyphenoxo complexes of monooxovanadium(V) in accordance with earlier reports for the similar complexes.

Reactions with 2- *and* 3-*cyanoanilines* (*CNAn*)

The reaction of $VOCl(OC_6H_4OMe\text{-}4)_2$ with 2- and 3-cyanoanilines (CNAn) affords the formation of isolable addition compounds of compositions $VOCl(OC_6H_4OMe\text{-}4)_2$. 2CNAn which are similar to the adducts formed by $VOCl_3$ of the type $VOCl_3 \cdot 2L$ [22]. All of these adducts are intensely coloured solids which decompose rather quickly upon exposure to the moist atmosphere. However, they can be stored at room temperature for an extended period under anhydrous conditions. The molar conductance values (0.85–1.86 ohm^{-1} cm^2 $mole^{-1}$) of the millimolar solutions of these adducts in nitrobenzene are too low to be attributed to electrolytic nature.

Information on the structure of these adducts has been obtained from their IR spectra as it plays a key role in deciding the bonding modes of the ligands. The cyanoanilines having two potential donor sites ($-NH_2$ and -CN) might behave as monodentate or bidentate depending upon whether the coordination takes place through the amino group or the nitrile group or both. The principal bands of such ligands which are expected to undergo significant changes are those due to ν(CN) mode present at about 2240 cm^{-1} and the νNH asymmetric and symmetric modes observed at around 3440 and 3360 cm^{-1} in uncoordinate cyanoanilines and these changes can be used to establish the site of coordination. Coordination through nitrogen of the nitrile group is known to result in an increase in νCN [23] modes while coordination through nitrogen of $-NH_2$ group leads to a characteristic negative shift. In case, there is observed a decrease in νCN modes, it is generally interpreted as resulting from the coordination of cyano group through its triple bond [24,25].

In the IR spectra of the adducts of composition $VOCl(OC_6H_4OMe\text{-}4)_2 \cdot 2CNAn$, isolated in the present studies, the position of bands due to $\nu_{asym}NH$ and $\nu_{sym}NH$ vibrations have been found to remain almost unaltered while there is a significant shift of νCN modes towards higher wave numbers. These observations suggest that nitrogen of the amino group is not involved in coordination to the metal while the nitrile gets coordinated to the metal through its nitrogen and thereby indicates the monodentate nature of cyanoanilines in these adducts. Interestingly, these findings contrast markedly with those found for coordination compounds formed by copper(II) chloride and bromide with these ligands wherein a bonding through nitrogen of $-NH_2$ group had been proposed [26]. A reasonable explanation for our observations in the oxovanadium(V) aryloxide adducts showing coordination through nitrogen of nitrile group and not amino group is provided in terms of inherent electron withdrawing property of nitrile group from the ring through resonance which thereby reduces the donor character of amino group in the cyanoanilines.

The other most significant change observed in the parent complex on adduct formation is in the V=O stretch. The band present at 960 cm^{-1} assigned to ν(V=O) in parent aryloxide, is lowered by about 30–35 cm^{-1}. This lowering may be attributed to the basic strength of the cyanoanilines. Greater basic strength

Table 1. Analytical data of the 4-methoxyphenoxo oxovanadium(V) complexes and adducts with cyanoanilines and cyanopyridines

Complex (empirical formula)	Colour	M.p. (°C)	Elemental analysis % found (calcd) V	Cl	C	H	Molar conductance in $PhNO_2$ Ω^{-1} cm^2 mole^{-1}	Molecular weight in $PhNO_2$ found (calcd)	Yield (%)
1. $VOCl_2(OC_6H_4OMe\text{-}4)$ $VC_7H_7Cl_2O_3$	Black	188^s	19.2 (19.5)	24.7 (24.2)	32.5 (32.2)	2.2 (2.6)	2.4	273 (261)	67
2. $VOCl(OC_6H_4OMe\text{-}4)_2$ $VC_{14}H_{14}ClO_5$	Black	120–123^s	14.6 (14.6)	10.4 (10.2)	47.9 (48.3)	4.4 (4.1)	2.1	364 (348)	61
3. $VO(OC_6H_4OMe\text{-}4)_3$ $VC_{21}H_{21}O_7$	Black	High (> 260)	11.7 (11.7)	—	57.4 (57.8)	4.7 (4.8)	1.7	454 (436)	72
4. $VOCl(OC_6H_4OMe\text{-}4)_2 \cdot 2CNAn\text{-}2$ $VC_{28}H_{26}ClO_5N_4$	Dark brown	160	9.1 (8.7)	6.6 (6.1)	57.2 (57.5)	4.6 (4.5)	1.3	—	83
5. $VOCl(OC_6H_4OMe\text{-}4)_2 \cdot 2CNAn\text{-}3$ $VC_{28}H_{26}ClO_5N_4$	Black	170	9.1 (8.7)	6.4 (6.0)	57.1 (57.5)	4.7 (4.5)	1.38	—	79
6. $VO(OC_6H_4OMe\text{-}4)_3 \cdot 2Cpy\text{-}3$ $VC_{33}H_{29}O_7N_4$	Black	High (> 260)	7.5 (7.9)	— —	61.9 (61.4)	4.4 (4.5)	1.2	—	73
7. $VO(OC_6H_4OMe\text{-}4)_3 \cdot 2CNpy\text{-}4$ $VC_{33}H_{29}O_7N_4$	Black	High (> 260)	7.3 (7.9)	—	61.3 (61.4)	4.5 (4.5)	—	—	75

S = sublime.

of the ligand, causes a greater extent of lowering. Similar observations have been made earlier also in $VOCl_3$ complexes with a variety of ligands [27]. Apart from this, the new bands observed in the region 320–360 cm^{-1} have been assigned to $\nu(V—N_{base})$ modes. The bands due to $\nu(V—O_{phenoxo})$ and C—O—V vibrations of the parent oxovanadium(V) aryloxide shift slightly towards higher wave numbers perhaps due to the strengthening of the phenoxovanadium bond with the introduction of the base in accordance with the earlier observations [28].

Reactions with 3- *and* 4-*cyanopyridines* (*CNpy*)

Addition compounds of composition $VO(OC_6H_4OMe\text{-}4)_3$. 2CNpy-3 and $VO(OC_6H_4OMe\text{-}4)_3\cdot$ 2CNpy-4 have been obtained by the reaction of monooxovanadium(V) aryloxide, $VO(OC_6H_4OMe\text{-}4)_3$ with respective cyanopyridines. Stoichiometric composition of the adducts has been established by elemental analysis. All these adducts are coloured solids, stable under anhydrous conditions. They are fairly soluble in methanol, sparingly soluble in chloroform, carbon tetrachloride, dichloromethane and benzene and insoluble in petroleum ether and diethylether. The molar conductance values of 10^{-3}M solutions of these adducts (Table 1) suggest them to be non-ionic in nature.

A careful examination of the IR spectra of the cyanopyridine adducts with $VO(OC_6H_4OMe\text{-}4)_3$ has established unambiguously the coordination sites of the ligand. Four principal bands observed in the region 1410–1580 cm^{-1} in pure cyanopyridines assigned to ν(C—C) and ν(C—N) vibrations and two low frequency bands in the region 960–1082 cm^{-1} have experienced a significant positive shift on adduct formation while the nitrile stretching observed around 2240–2250 cm^{-1} remain unperturbed. These observations suggest that coordination in cyanopyridine takes place from ring nitrogen only and not from the nitrile nitrogen of cyanopyridines, thus suggesting monodentate nature of cyanopyridines in these adducts. Similar observations have been made earlier also in the case of adducts of 4-*t*-butylphenoxides of monooxovanadium(V) with these cyanopyridines [29]. Other important bands due to $V—O_{(phenoxo)}$ and $V—N_{(base)}$ [30] are observed in the same range as in the case of cyanoanilines. A hexacoordinated irregular octahedral configuration around vanadium may thus be proposed for the adducts of 4-methoxyphenoxo complexes of monooxovanadium(V) with the nitrogen bases.

In conclusion, the new 4-methoxyphenoxo complexes with VO^{3+} isolated in the present work are very stable, which is in agreement with the general observation that these types of ligands stabilise the highest available oxidation states and represent new examples of vanadium(V) coordination chemistry. A striking feature of this work is that an interesting contrast to the previous report on the coordination behaviour of cyanoanilines has been observed in the parent complexes indicating coordination through the -CN nitrogen rather than the $-NH_2$ group to the vanadium, which to our knowledge is the first example of this type.

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