

Synthesis and characterisation of tris(2,4-dinitrophenoxo)monooxovanadium(V) and its complex salts

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The monooxovanadium(V) complex of composition $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$ (I) was synthesized by the reaction of VOCl_3 with $\text{Me}_3\text{SiOC}_6\text{H}_3(\text{NO}_2)_{2-2,4}$ in toluene and characterised by elemental analyses, molar conductance, and IR, ^1H - and ^{13}C -NMR, and mass spectral studies. The reactions of (I) with alkali metal 2,4-dinitrophenoxides $[\text{MOC}_6\text{H}_3(\text{NO}_2)_{2-2,4}]$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) yield complex salts of composition $\text{M}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$ authenticated by physicochemical and IR spectral studies. Thermal behaviour of complexes was studied by TG and DTA techniques. The molecular modelling calculations of the parent complex and its complex salts were performed to visualise the probable geometry around vanadium metal, which, coupled with spectroscopic evidence, suggests a distorted tetrahedral and a trigonal-bipyramidal geometry for respective complexes.

Key Words: 2,4-Dinitrophenol, monooxovanadium(V) complex, complex salts, spectroscopic studies, thermal studies

Introduction

There has been continuous interest over the years in the use of phenols as ligands since these cannot only be modified in steric bulk by substitution but incorporation of electron withdrawing or electron donating substituents at the phenolic ring can offer an enormous structural variety of complex and cluster species. The substituted

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phenols have been reported to form complexes with main group elements, transition metals, lanthanides, and actinides and their potential applications as antioxidants, surfactants etc. are well documented.¹⁻⁸ Of the transition metals, the chemistry of vanadium has drawn considerable attention owing to the promising applications of vanadium complexes as catalysts,⁹ in organic synthesis,¹⁰ material sciences,¹¹ and biological activities as insulin mimetic,^{12,13} anticancer,¹⁴ antitumour,¹⁵ and antimicrobial agents.¹⁶ For vanadium, the chemistry of oxovanadium(IV) and (V) ions of the type VO^{2+} , VO^{3+} , VO_2^{2+} , and $\text{V}_2\text{O}_3^{4+}$ with a variety of ligands has widely been studied.^{17,18} The VO^{3+} ion, in particular because of its hard acidic nature, is known to exhibit rich chemistry with oxygen and nitrogen donor ligands. Of these, vanadium phenolates have been reported to display capabilities of dinitrogen fixation¹⁹⁻²¹ and considerable significance for polymerization,²² oxidation,²³ and potential shape-selective transformations.²⁴ Literature on vanadium aryloxides reveals that reports on vanadium nitrophenolates²⁵⁻²⁹ are scarce. As a part of our continuing studies on phenolate chemistry of vanadium³⁰⁻³² herein we report the synthesis and structural characterisation of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4})_3]$ derived from 2,4-dinitrophenol (Figure 1). The reactions of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-2,4})_3]$ with alkali metal salts of 2,4-dinitrophenol afforded the formation of complex salts.

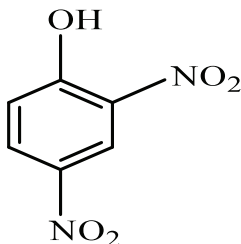


Figure 1. Structure of 2,4-dinitrophenol.

Experimental

Materials and physical measurements

All the solvents used were of A.R. grade and were dried by standard methods. Vanadyl trichloride (VOCl_3) (Aldrich) was used as procured. 2,4-Dinitrophenol (Merck) was recrystallised from chloroform and was then warmed to 100 °C. The purity of the phenol was checked by melting point 112-114 °C (obs) (lit. mp 112-115 °C)

The analysis of carbon, hydrogen, and nitrogen was performed on a Carlo-Erba 1108 elemental analyser. Vanadium in complexes was determined gravimetrically as V_2O_5 . The conductivity measurements in methanol were made using a Harco digital conductivity bridge. FTIR spectra of the complexes were collected on a Nicolet-5700 FTIR spectrophotometer (4000-200 cm^{-1}) as KBr pellets and nujol mull in CsI optics. ¹H- and ¹³C-NMR spectra of the complex were recorded on a Bruker AVANCE II 400 Spectrometer using TMS as an internal standard and $(\text{CD}_3)_2\text{SO}$ as solvent. The FAB mass spectrum was recorded at room temperature 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. 3-Nitrobenzylalcohol (NBA) was used as the matrix. The molecular model calculations using Hyper-Chem.7.5 (student version) were performed to visualise the probable geometry acquired by the complexes by applying MM^+ force field with the Polak-Ribiere algorithm and RMS gradient 0.01 Kcal/mol.

The molecular dynamic simulation was done up to 727 °C (relaxation time ps). Thermograms (TGA and DTA curves) of complexes were recorded on a Shimadzu DT-60 thermal analyser. The thermal studies were carried out by heating the sample in a platinum crucible in air and a heating rate of 20 °C/min was employed. The thermocouple used was Pt/Pt-Rh 10% with a temperature range of 20-1200 °C.

Preparation of complexes

[Me₃Si(OC₆H₃(NO₂)_{2-2,4})]

To a solution of 2,4-dinitrophenol (2.0 g, 10.8 mmol) in toluene was added a solution of Me₃SiCl [1.37 mL, (d = 0.86 g/mL) 1.18 g, 10.8 mmol] taken in the same solvent. The reaction mixture was refluxed for 20 h when a light yellow viscous liquid was obtained. This solution was used for carrying out the reaction with VOCl₃ for the synthesis of the title complex.

M[OC₆H₃(NO₂)_{2-2,4}] (M = Li, Na, K)

Lithium, sodium, and potassium 2,4-dinitrophenoxides were prepared by the reaction of an ethanolic solution of lithium hydroxide (0.1296 g, 5.4 mmol)/sodium hydroxide (0.2175 g, 5.4 mmol)/potassium hydroxide (0.3049 g, 5.4 mmol) with 2,4-dinitrophenol (1 g, 5.4 mmol) in ethanol in separate experiments. It was then stirred overnight at room temperature when deep yellow solids separated out. These were filtered, washed 2-3 times with ethanol, and dried at room temperature.

[VO(OC₆H₃(NO₂)_{2-2,4})₃]

To a solution of VOCl₃ (1.0296 mL, 1.88 g, 10.84 mmol) in toluene (30 mL), a toluene solution containing three equivalent of [Me₃Si(OC₆H₃(NO₂)_{2-2,4})] (32.5 mmol) was added. The reaction mixture was refluxed for 25 h, to ensure the completion of the reaction. The Me₃SiCl formed during the reaction as a by-product and the excess solvent were distilled off and the concentrate was then repeatedly treated with petroleum ether, until a dark green solid was obtained. It was recrystallised from ethanol and dried in vacuo. Yield (5.33 g, 80%).

NMR(δ , ppm); ¹H, 8.72 (d, 3H, J_{m-m}=2.8 Hz), 8.33, 8.35 (dd, 3H, J_{m-m}=2.8 Hz, J_{m-o}=9.2 Hz), 7.32 (dd, 3H, J_{m-o}=9.2 Hz); ¹³C, 157.62 C-1, 135.88 C-2, 121.67 C-3, 138.34 C-4, 129.16 C-5, 119.81 C-6.

Reactions of VO(OC₆H₃(NO₂)_{2-2,4})₃ with alkali metal 2,4-dinitrophenoxides [M(OC₆H₃(NO₂)_{2-2,4})] (M = Li, Na, K)

To VO(OC₆H₃(NO₂)_{2-2,4})₃ (0.5 g, 1.62 mmol) dissolved in ethanol was added an equimolar amount of Li[OC₆H₃(NO₂)_{2-2,4}] (0.1542 g, 1.62 mmol)/Na[OC₆H₃(NO₂)_{2-2,4}] (0.167 g, 1.62 mmol)/K[OC₆H₃(NO₂)_{2-2,4}] (0.1802 g, 1.62 mmol) in ethanol in separate experiments. The reaction mixture was stirred for 5-6 h followed by reflux for another 5-6 h during which the colour changed from greenish to yellowish-green. The resultant solution was concentrated by distilling off the excess solvent and was dried under vacuum by successive addition of petroleum ether.

Results and discussion

The direct reaction of VOCl_3 with 3 equivalents of 2,4-dinitrophenol in toluene results in low yield of the desired product. Hence, in an alternative method, the reaction of VOCl_3 with trimethylsilyl derivative of 2,4-dinitrophenol in 1:3 molar ratio in toluene afforded the quantitative formation of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_3]$ (80%) in conformity with elemental analyses (Table 1) according to the following equation:

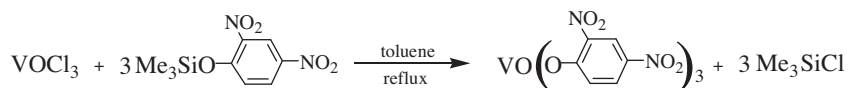


Table 1. Analytical data of monooxovanadium (V) complexes.

Complex (Molecular formula) [Formula weight]	Colour	Decom. temp. (°C)	Elemental analysis % Found (Calc.)				Λ_m in CH_3OH ($\text{S cm}^2 \text{mol}^{-1}$)
			V	C	H	N	
$[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_3]$ ($\text{VC}_{18}\text{H}_9\text{N}_6\text{O}_{16}$) [616]	Dark green	104	8.26 (8.27)	35.20 (35.06)	1.45 (1.46)	14.20 (14.0)	4.63
$\text{Li}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_4]$ ($\text{VLiC}_{24}\text{H}_{12}\text{N}_8\text{O}_{21}$) [806]	Light green	93	6.28 (6.32)	35.56 (35.7)	1.32 (1.48)	13.78 (13.89)	31.5
$\text{Na}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_4]$ ($\text{VNaC}_{24}\text{H}_{12}\text{N}_8\text{O}_{21}$) [822]	Green	117	6.27 (6.20)	34.84 (35.0)	1.39 (1.45)	13.56 (13.62)	19.98
$\text{K}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_4]$ ($\text{VKC}_{24}\text{H}_{12}\text{N}_8\text{O}_{21}$) [838]	Green	117	6.01 (6.08)	34.28 (34.36)	1.38 (1.43)	13.31 (13.36)	10.83

The complex is dark green and is soluble in most of the common non-polar organic solvents. It is also soluble in methanol and dimethylsulphoxide. The molar conductance value of millimolar solution of the complex in methanol ($4.63 \text{ S cm}^2 \text{ mol}^{-1}$) suggests its non-ionic nature.

FT-IR spectra. A comparison of the IR spectra of the complex (Table 2) with that of free 2,4-dinitrophenol showed the absence of an absorption band occurring at $\sim 3200 \text{ cm}^{-1}$ due to the phenolic $\nu(\text{OH})$ mode in 2,4-dinitrophenol. The most important band observed at $\sim 1255 \text{ cm}^{-1}$ in 2,4-dinitrophenol due to $\nu(\text{C-O})$ mode is found to appear at $\sim 1257 \text{ cm}^{-1}$ in the complex, which may be rationalised as characteristic of bonding of phenolic oxygen of 2,4-dinitrophenol with the vanadyl group. The bonding from phenolic oxygen to vanadium has further been indicated by the appearance of entirely new bands in the $580\text{-}520 \text{ cm}^{-1}$ region ascribed to $\nu(\text{V-O})$ mode.¹⁸ The absorption band due to $\nu(\text{V=O})$ mode appeared at 985 cm^{-1} in

[VO(OC₆H₃(NO₂)_{2-2,4})₃] relative to that reported to occur at 1035 cm⁻¹³³ in VOCl₃ and in the 1020-960 cm⁻¹ region in a number of vanadyl salts and complexes.³⁴ A lowering in $\nu(\text{V}=\text{O})$ mode may be attributed to a weakening of the V=O bond from terminal oxo oxygen $p\pi \rightarrow$ vanadium $d\pi$ donation upon complexation with phenoxide ion. The bands occurring in 1545-1520 cm⁻¹ and 1345-1332 cm⁻¹ regions attributed to $\nu_{asym}(\text{NO}_2)$ and $\nu_{sym}(\text{NO}_2)$ modes in 2,4-dinitrophenol in line with previous reports on nitro compounds³⁵⁻³⁸ appeared at ~ 1541 , ~ 1347 , and ~ 1333 cm⁻¹ in the complex. These observations indicate that the -NO₂ group is not involved in bonding to vanadium metal. Hence, a monodentate nature of 2,4-dinitrophenol is suggested.

Table 2. FT-IR spectral data of monooxovanadium (V) complexes.

Complex	Bands (cm ⁻¹)
[VO(OC ₆ H ₃ (NO ₂) _{2-2,4}) ₃]	3109 m, 1627 s, 1601 s, 1562 w, 1541 s, 1480 m, s, 1347 s, 1333 s, 1257 s, 1186 s, 1148 m, 1138 m, 1109 s, 1083 m, 1066 s, 985 s, 928 w, 917 s, 851 s, 838 s, 820 w, 788 m, 744 s, 715 s, 692 m, 641 s, 578 m, 523 m, 427 m.
Li[VO(OC ₆ H ₃ (NO ₂) _{2-2,4}) ₄]	3110 m, 3065 m, 2960 m, 2930 m, 1635 s, 1557 s, 1541 s, 1475 m, 1435 s, 1342 s, 1252 s, 1185 m, 1138 s, 1109 s, 965 s, 916 s, 835 s, 792 s, 746 s, 715 s, 682 m, 512 s, 425 m.
Na[VO(OC ₆ H ₃ (NO ₂) _{2-2,4}) ₄]	3100 m, 2924 m, 1829 m, 1634 s, 1561 s, 1541 s, 1433 s, 1342 s, 1280 s, 1184 m, 1139 s, 1109 s, 968 s, 914 s, 835 s, 789 s, 744 s, 712 s, 686 m, 637 m, 518 s, 427 m.
K[VO(OC ₆ H ₃ (NO ₂) _{2-2,4}) ₄]	3115 m, 3069 m, 2965 m, 2931 m, 2845 m, 1627 s, 1600 s, 1556 s, 1535 s, 1530 s, 1478 m, 1457 w, 1437 s, 1345 s, 1333 s, 1258 s, 1188 s, 1151 m, 1138 s, 1109 s, 1059 m, 971 w, 957 w, 929 w, 916 s, 850 s, 835 s, 795 s, 767 m, 746 s, 717 s, 683 m, 672 m, 641 s, 576 s, 547 m, 513 s, 429 m.

¹H-NMR spectra. The ¹H-NMR spectra of free 2,4-dinitrophenol are known to display signals at δ 4.65, 7.35, 9.1, and 8.5 ppm attributed to the presence of phenolic -OH group, ortho, meta proton (m) having adjacent -NO₂ groups at 2 & 4-positions of the ring and other meta proton (m') having 4 -NO₂ substituent as its immediate neighbour, respectively. The ¹H-NMR spectra of the complex did not display any signal at δ 4.65 ppm, confirming the deprotonation of the phenolic proton. The aromatic protons gave resonances at δ 7.32, δ 8.72 ppm and δ 8.33, 8.35 ppm, respectively. The upfield shifts observed for the different types of protons in the complex may be ascribed to the shielding of o, m, and m' protons resulting from the possible drift of electron density from the vanadyl group (V=O) onto the aromatic ring through phenolic oxygen (Figures 2a and 2b). The shielding experienced by the protons may be considered to be governed by the structural features also.

¹³C-NMR spectra. The information obtained from ¹H-NMR spectra of complex was further supported by its ¹³C-NMR spectra. The ¹³C-NMR spectrum of 2,4-dinitrophenol is known to exhibit 6 distinct resonances due to aromatic carbons of the phenolic ring in the δ 117.5-158.5 ppm range. The C-1, C-2, and C-4 bearing -OH and -NO₂ substituents respectively displayed less intense signals at δ 158.5, 136.5, and 141.9 ppm, respectively,

while C-3, C-5, and C-6 showed intense signals at δ 120.1, 131.1, and 117.5 ppm, respectively. The spectrum of the complex showed 6 distinct signals indicating their nonequivalent nature. Furthermore, it was noteworthy that moderate to significant upfield shifts were observed for C-1, C-2, C-4, and C-5, which may be ascribed to the hyperconjugation effect. On the other hand, the downfield shifts observed for C-3 and C-6 of the magnitude $-\Delta = \delta$ 1.57 ppm and δ 2.31 ppm, respectively, may be attributed to the fact that the substituents (-OH and NO₂ groups) show an influence beyond the carbon to which the substituent is directly attached; hence, these carbons are deshielded (Figure 3). Nevertheless, the role of the vanadyl group (V=O) cannot be excluded for displaying such behaviour.

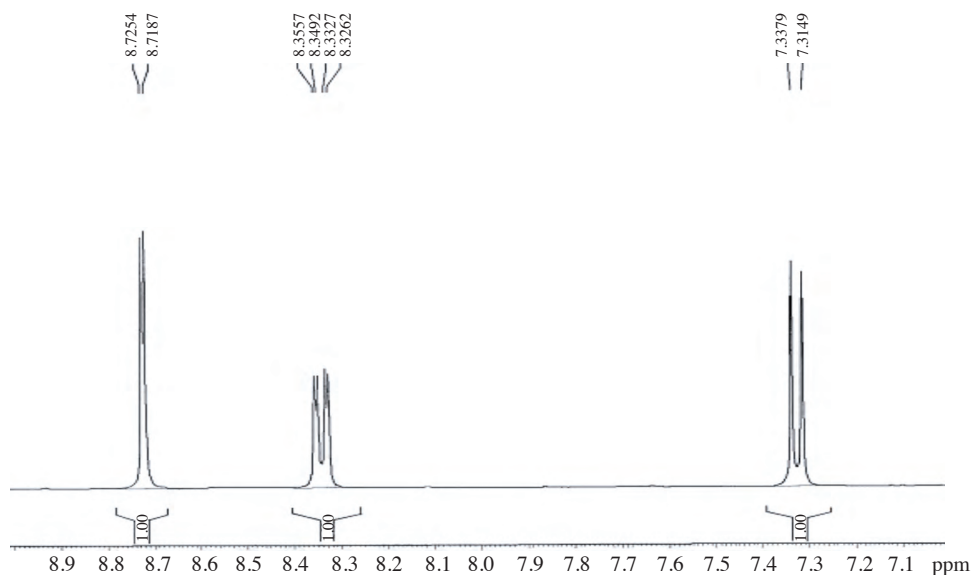


Figure 2a. ¹H-NMR spectra of VO{OC₆H₃(NO₂)₂}₃.

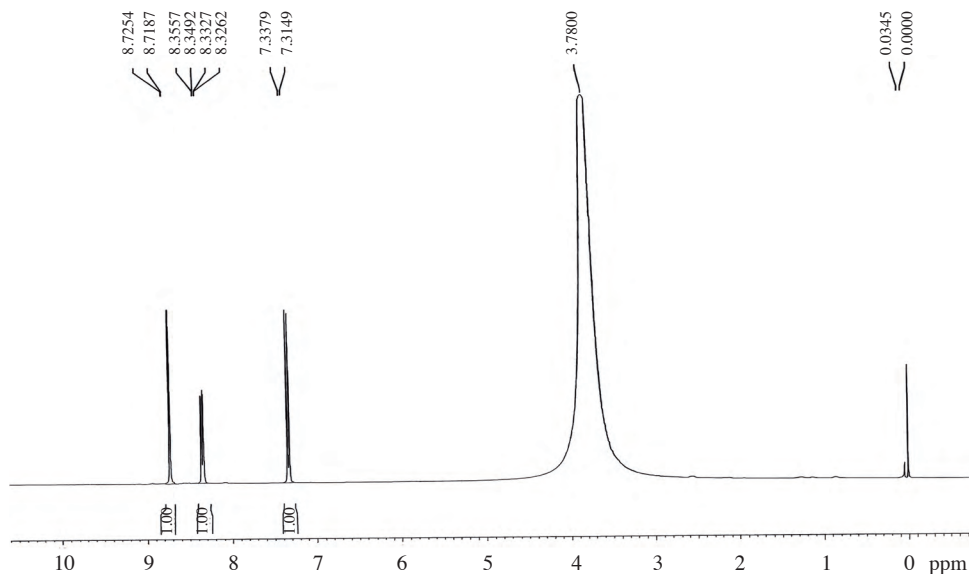


Figure 2b. ¹H-NMR spectra of VO(OC₆H₃(NO₂)_{2-2,4})₃.

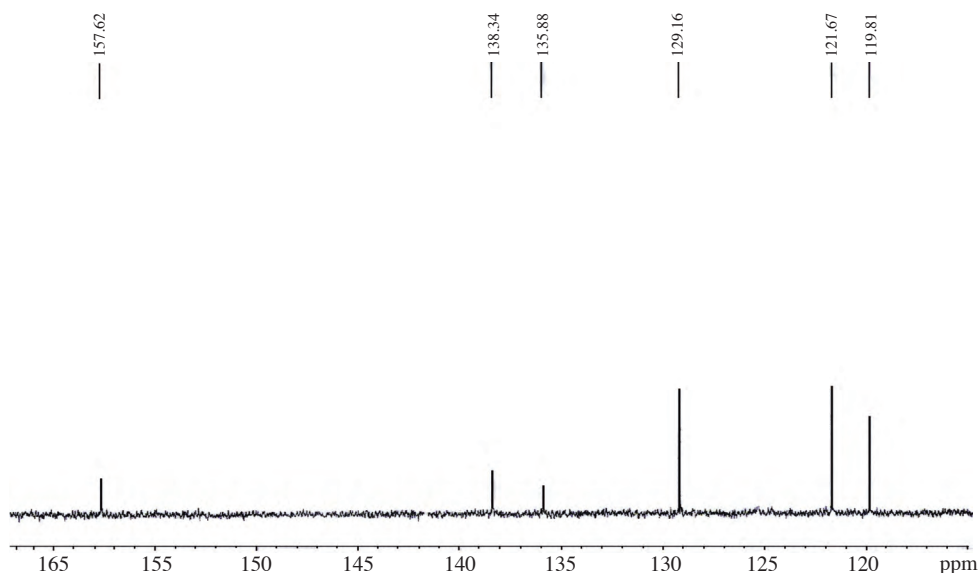

Figure 3. ^{13}C -NMR spectra of $\text{VO}\{\text{OC}_6\text{H}_3(\text{NO}_2)_2\}_3$.

Table 3. Mass spectral data of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$.

Ionic species	m/z (relative abundance)
$[\text{VO}\{\text{OC}_6\text{H}_3(\text{NO}_2)_2\}_3+3\text{H}]^+$	619(8%)
$[\text{VO}\{\text{OC}_6\text{H}_3(\text{NO}_2)_2\}_2(\text{OC}_6\text{H}_3(\text{NO}_2)(\text{NO})+\text{H})^+]$	601(10%)
$[\text{VO}\{\text{OC}_6\text{H}_3(\text{NO}_2)_2\}_2(\text{OC}_6\text{H}_5)-2\text{H}]^+$	524(35%)
$[\text{V}\{\text{OC}_6\text{H}_3(\text{NO}_2)_2\}\{\text{OC}_6\text{H}_3(\text{NO})_2\}(\text{OC}_6\text{H}_4(\text{NO})-\text{H})^+]$	506(30%)
$[\text{VO}\{\text{OC}_6\text{H}_3(\text{NO}_2)_2\}\{\text{OC}_6\text{H}_3(\text{NO})_2\}(\text{OC}_6\text{H}_5)-2\text{H}]^+$	492(20%)
$[\text{VO}\{\text{OC}_6\text{H}_3(\text{NO}_2)(\text{NO})\}(\text{OC}_6\text{H}_4(\text{NO}) (\text{OC}_6\text{H}_5))^+]$	449(38%)
$[\text{VO}\{\text{OC}_6\text{H}_3(\text{NO}_2)_2\}_2(\text{OC}_6\text{H}_4(\text{NO}_2)+3\text{H})^+]$	391(60%)
$[\text{VO}\{\text{OC}_6\text{H}_3(\text{NO}_2)\}(\text{OC}_6\text{H}_4(\text{NO})-\text{H})^+]$	339(10%)
$[\text{V}\{\text{OC}_6\text{H}_3(\text{NO}_2)_2\}(\text{OC}_6\text{H}_5)+2\text{H}]^+$	329(42%)
$[\text{V}\{\text{OC}_6\text{H}_4(\text{NO}_2)\}(\text{OC}_6\text{H}_5)-\text{H}]^+$	279(15%)
$[\text{VO}\{\text{OC}_6\text{H}_3(\text{NO})_2\}]^+$	218(25%)
$[\text{VO}\{\text{OC}_6\text{H}_4\text{NO}_2\}-\text{H}]^+$	203(20%)
$[\text{OC}_6\text{H}_3(\text{NO}_2)(\text{NO})-2\text{H}]^+$	165(30%)
$[\text{OC}_6\text{H}_4(\text{NO}_2)-2\text{H}]^+$	136 (100%)
$[\text{OC}_6\text{H}_4(\text{NO})-2\text{H}]^+$	120(40%)
$[\text{OC}_6\text{H}_3(\text{NO}_2)(\text{NO})-2\text{H}]^+$	107(50%)

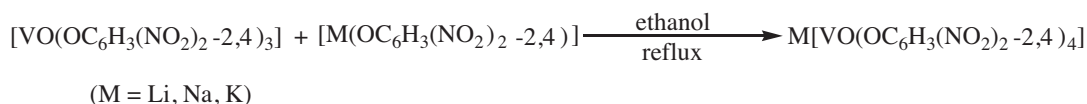
Mass spectra. The FAB-mass spectrum of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$ was obtained and the most abundant fragment ions^{39,40} are given in Table 3. The most intense peak at m/z 136 (100%) corresponding to $[\text{OC}_6\text{H}_3(\text{NO}_2)-\text{H}]^+$ seems to have been formed by cleavage of the C-NO₂ bond. The relative abundance of the molecular ion peak is quite small. The intense peaks that appeared at m/z 165, 120, and 107 assigned to

$[\text{OC}_6\text{H}_3(\text{NO}_2)(\text{NO})\text{-}2\text{H}]^+$, $[\text{OC}_6\text{H}_3(\text{NO})\text{-H}]^+$, and $[\text{C}_6\text{H}_5(\text{NO})]^+$ fragment ions correspond to the fragments of the coordinated phenolic ligand only. The fragment ions corresponding to vanadium and vanadyl species were assigned.

Reactions of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$ with alkali metal 2,4-dinitrophenoxides

$[\text{M}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})]$ (M = Li, Na, K)

The interaction of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$ with alkali metal phenoxides led to the formation of complex salts according to the equation:



in conformity with their elemental analyses (Table 1). The molar conductance values of complex salts in 10^{-3} M solution in methanol are higher (31.5, 19.98, 10.83 S $\text{cm}^2 \text{mol}^{-1}$) than that of the parent complex. These observations suggest that the coordination of alkali metal phenoxides with parent complex promotes ionisation, thereby depicting their slightly electrolytic behaviour.

The infrared spectra of complex salts (Table 2) showed that the bands due to $\nu(\text{CH})$ mode appeared at the same wave numbers as in parent complex except for a slight broadening of these bands upon complexation. The bands due to $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{O})$ modes occurring in the $1638\text{-}1450 \text{ cm}^{-1}$ region and at 1257 cm^{-1} respectively in parent complex shifted towards higher wave numbers in complex salts. This may possibly be attributed to the fact that the anions of the type $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_4]^-$ carrying negative charge restrict the drainage of electron density from the ring to the metal.

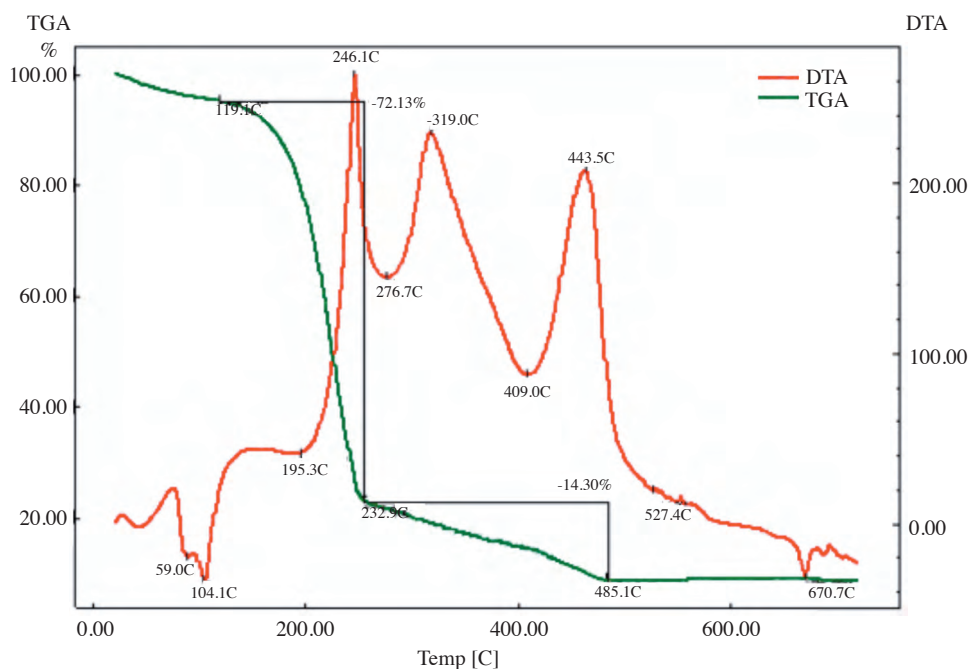
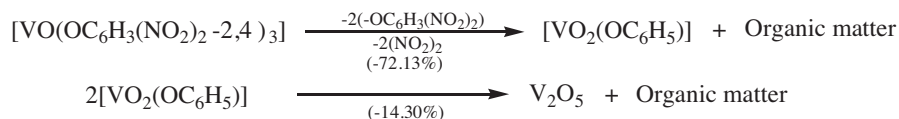


Figure 4. TGA/DTA curve of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$.

Table 4. Thermal data of monooxovanadium (V) complexes.

Complex	Initial decomp. temp. (°C)	Stages of decomp.	TGA data			DTA data	
			Decomp. range (°C)	% Wt. loss	Decomp. products	Peak temp. (%)	Peak nature
[VO(OC ₆ H ₃ (NO ₂) ₂ -2,4)] ₃	119.18	2	119.18-255.96	72.13	[VO ₂ (OC ₆ H ₃)]	104.12	Endo
			255.96-485.14	14.30	V ₂ O ₅	246.19	Exo
						319.05	Exo
						468.32	Exo
Li[VO(OC ₆ H ₃ (NO ₂) ₂ -2,4)]	71.46	3	71.46-106.25	13.026	Li[VO(OC ₆ H ₃ (NO ₂) ₂)](OC ₆ H ₅)	92.99	Endo
			106.25-185.76	5.951	Li[VO(OC ₆ H ₃ (NO ₂) ₂)(OC ₆ H ₄ NO ₂)(OC ₆ H ₅)]	310.70	Exo
			185.76-314.49	72.959	VO ₂		(v. shp)
Na[VO(OC ₆ H ₃ (NO ₂) ₂ -2,4)] ₄	123.68	3	123.68-223.58	49.144	Na[VO(OC ₆ H ₃ (NO ₂) ₂)(OC ₆ H ₄ NO ₂)	116.81	Endo (shp)
			223.58-339.91	15.944	Na[VO ₂ (OC ₆ H ₃ (NO ₂) ₂)]	224.91	Exo
						305.71	Exo
					NaVO ₃	580.22	Exo (broad)
K[VO(OC ₆ H ₃ (NO ₂) ₂ -2,4)] ₄	105.24	3	105.24-207.9	53.92	K[VO(OC ₆ H ₃ (NO ₂) ₂)(OC ₆ H ₅)	116.64	Endo (shp)
			207.9-343.10	18.88	K[VO ₂ (OC ₆ H ₃)]	225.65	Exo
						301.28	Exo
					KVO ₃	560.27	Endo (Fble)

Thermal studies. Thermal data inferred from TGA-DTA curves of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2,4})_3]$ and its complex salts are collected in Table 4. The TGA curve of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2,4})_3]$ (Figure 4) shows it to be thermally stable up to 119 °C, beyond which the complex decomposes in 2 distinct steps. The observed percentage weight losses account for the probable formation of $[\text{VO}_2(\text{OC}_6\text{H}_5)]$ as the likely intermediate and of V_2O_5 as the ultimate residue according to the equations:



The thermal decompositions of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2,4})_3]$ are accompanied by both exothermic and endothermic peaks in the DTA curve. Thermal decomposition behaviour of the complex salts $\text{Li}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2,4})_4]$, $\text{Na}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2,4})_4]$, and $\text{K}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2,4})_4]$ studied in air are given in Figures 5-7. The TG curve of $\text{Li}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2,4})_4]$ shows it to decompose in 3 steps. Based upon % weight losses, the likely proposition of intermediates and ultimate product of decomposition may be represented as:

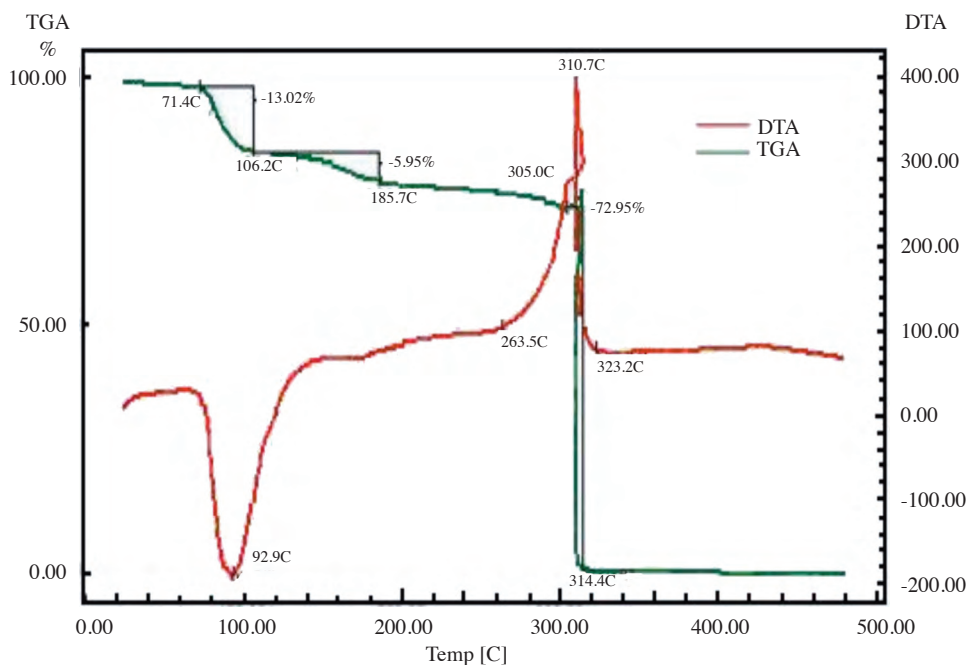
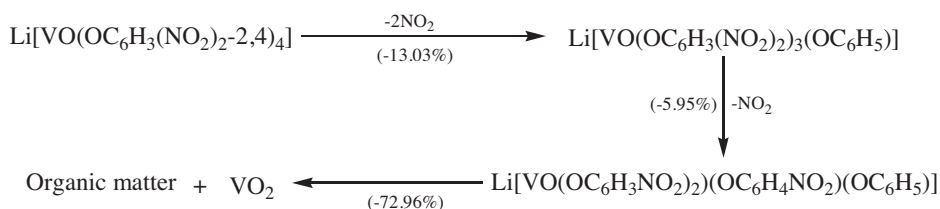


Figure 5. TGA/DTA curve of $\text{Li}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2,4})_4]$.

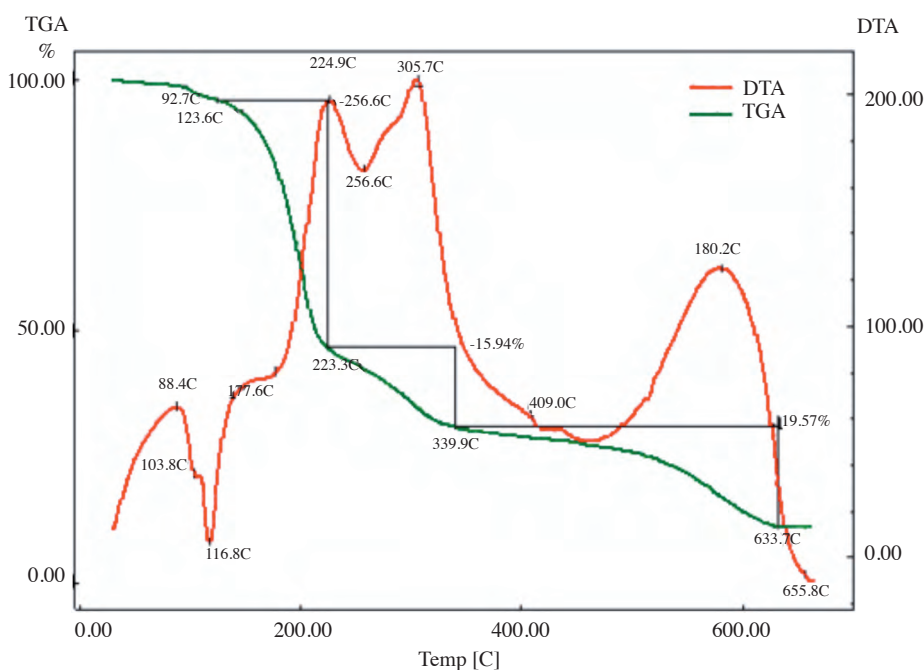
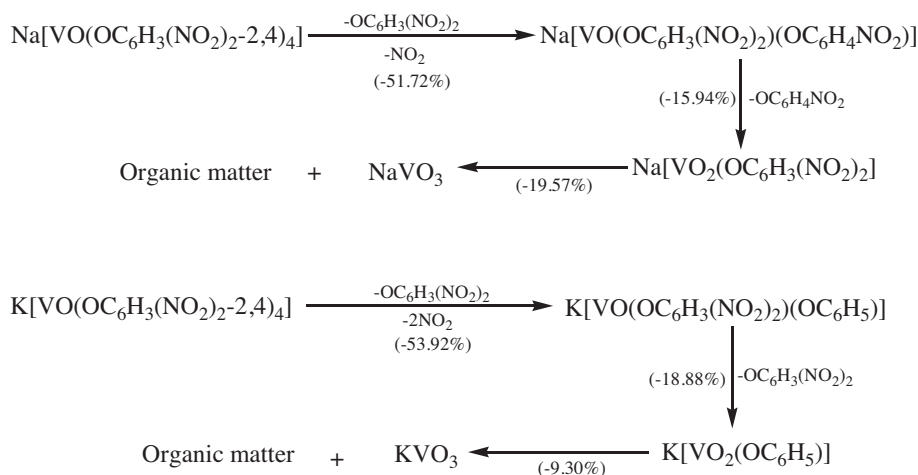


Figure 6. TGA/DTA curve of $\text{Na}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_4]$.

Strikingly, a sharp exotherm at 310.70°C along with a slight explosion and rapid weight loss observed in the DTA curve of $\text{Li}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_4]$ bears a close resemblance to the characteristic features of high energy materials such as TNT (trinitrotoluene), HMX or octagon (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetranitramine), and RDX or hexogen (hexahydro-1,3,5-trinitro-5-triazine or cyclotrimethylene trinitramine). This observation is indicative of the promising potential of lithium-vanadium complex salt as explosive material.

The TG curves of $\text{Na}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_4]$ and $\text{K}[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_2\text{-}2,4)_4]$ also show 3-step decompositions. However, based upon percentage weight losses, the decomposition schemes may be rationalised as:



where in NaVO_3 and KVO_3 are formed as final decomposition products.

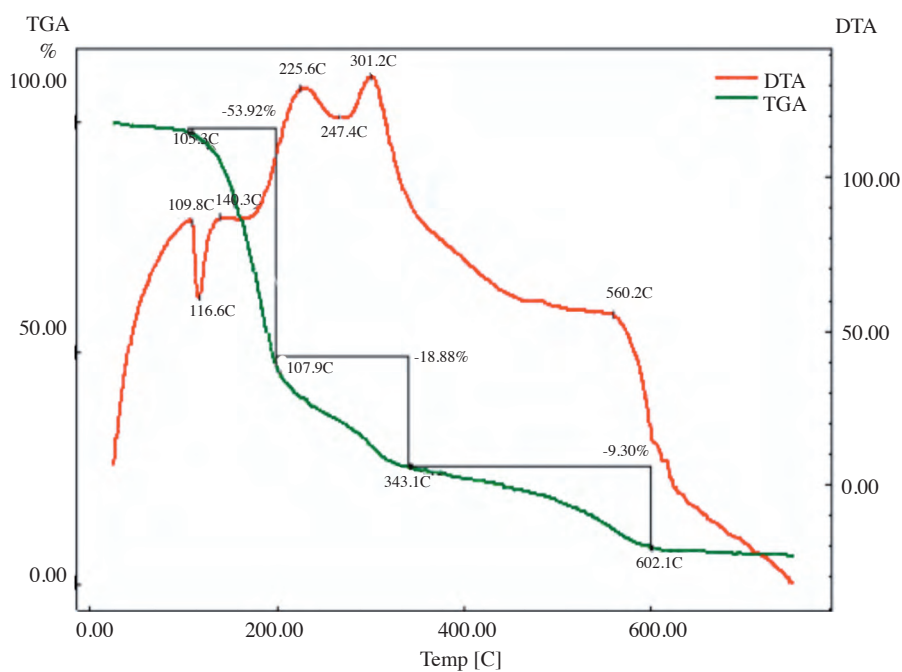


Figure 7. TGA/DTA curve of $K[VO(OC_6H_3(NO_2)_2-2,4)_4]$.

Molecular modelling. The molecular mechanical adjustments for energy optimisation from strained structures to the likely geometry of parent complex and its complex salts were made. The molecular mechanics were repeated 5 to 6 times to ensure that the structure with minimised energy is attained, which is assumed to be closer to the stable geometry. The perspective structures for complexes are presented in Figures 8 and

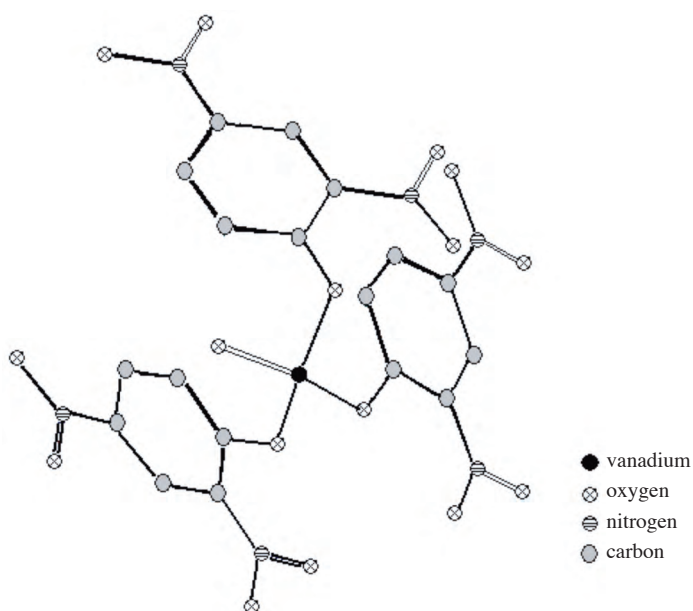


Figure 8. Structure of $[VO(OC_6H_3(NO_2)_2-2,4)_3]$.

9. From molecular modelling calculations coupled with analytical and IR, ^1H -, ^{13}C -NMR, and mass spectral data, for $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$ a distorted tetrahedral geometry may tentatively be proposed. Based upon limited analytical and IR spectral data in hand on complex salts, a trigonal-bipyramidal environment around vanadium may be suggested.

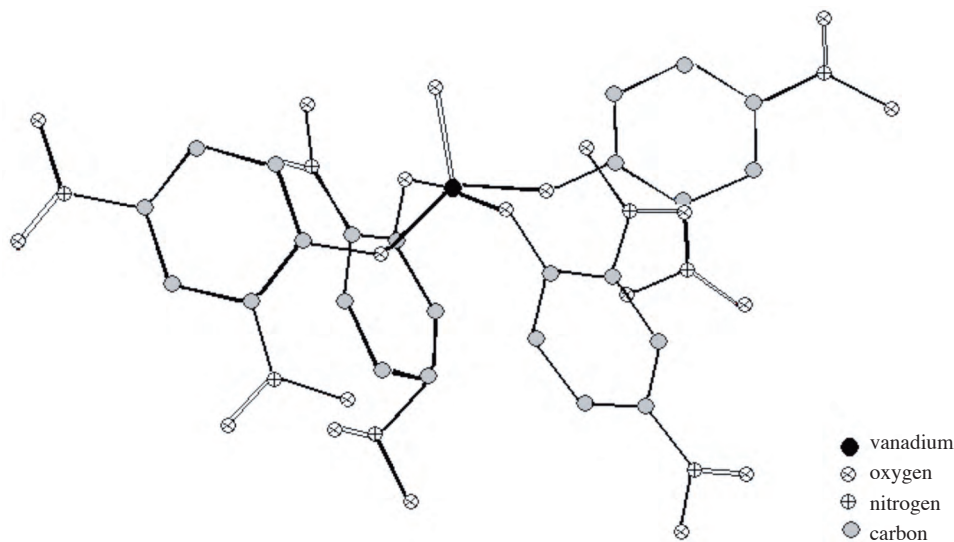


Figure 9. Structure of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_4]^-$.

Conclusions

The present study demonstrates that for the quantitative synthesis of the title complex $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$ the use of $[\text{Me}_3\text{Si}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})]$ facilitates the replacement of 3 chloride ions by 2,4-dinitrophenoxide ion from VOCl_3 . The reaction of $[\text{VO}(\text{OC}_6\text{H}_3(\text{NO}_2)_{2-2,4})_3]$ with alkali metal 2,4-dinitrophenoxides affords the formation of complex salts. A study on thermal decomposition behaviour of the parent complex showed the formation of V_2O_5 as the ultimate decomposition product, while complex salts derived from lithium, sodium, and potassium 2,4-dinitrophenoxides yielded VO_2 , NaVO_3 , and KVO_3 as the final residue of respective complexes. Thermal behaviour shown by complex salt derived from lithium is different from that of sodium and potassium analogues in terms of percentage weight losses and nature of the TG curve, suggesting its potential as an explosive material.

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