Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2020

Site-Selective Halogenation of Mixed-valent Vanadium Oxide Clusters

Michela L. Maiola,[a] Brittney E. Petel,[a] William W. Brennessel,[a] Ellen M. Matson*[a]

[a]Department of Chemistry, University of Rochester, Rochester, New York 14627, United States
Corresponding author email: matson@chem.rochester.edu

Supporting Information Table of Contents:

^{1}H NMR yields: Yields for **4-$V_6O_6Cl^0$** and for **1-$V_6O_6Cl^{1-}$** via the chlorination of $[V_6O_7(OC_2H_5)_{12}]^{2-}$ with $TiCl_3(thf)_3$ were obtained by ^{1}H NMR yields by integration against a known amount of internal standard, pyridine.

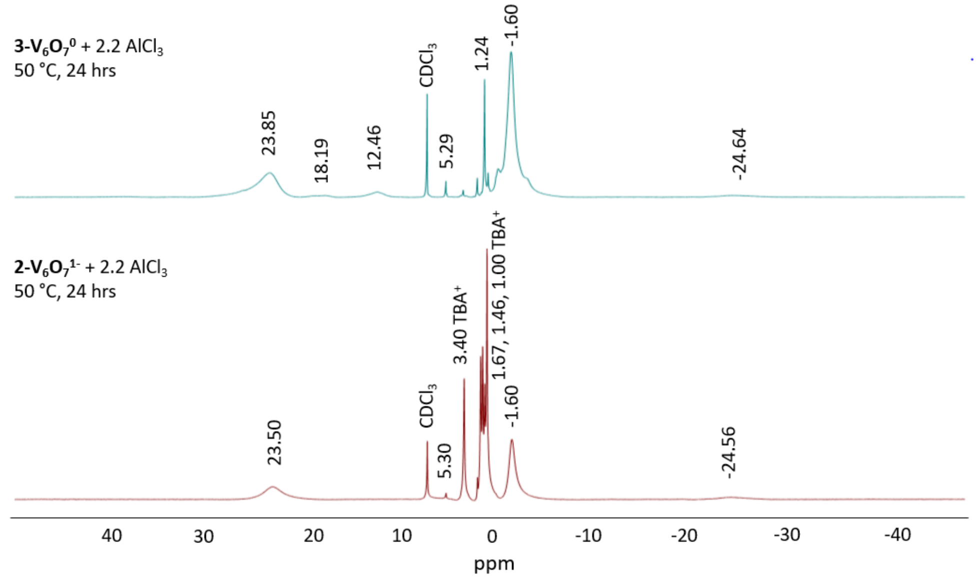

Figure S1. ^{1}H NMR spectra of $AlCl_3$ reactions with $[V_6O_7(OC_2H_5)_{12}]^{1-}$ (**2-$V_6O_7^{1-}$**, bottom, red) and $V_6O_7(OC_2H_5)_{12}$ (**3-$V_6O_7^{0}$**, top, blue) at 50 ºC for 24 hours in $CDCl_3$. Resonances labeled as "TBA" correspond to the tetrabutylammonium counter ion of the starting material, **2-$V_6O_7^{1-}$**.

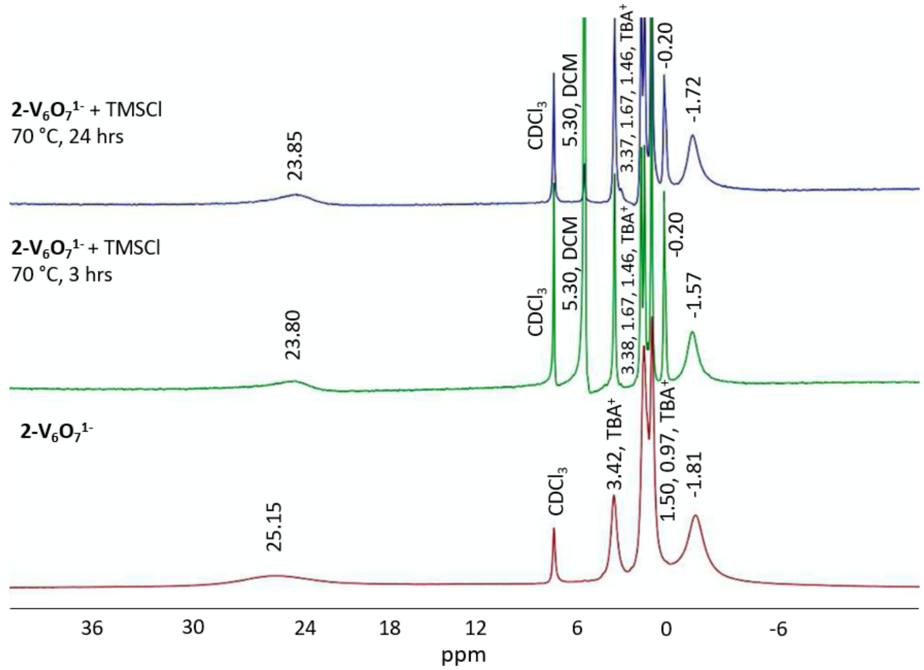

Figure S2. ^{1}H NMR spectra of $[V_6O_7(OC_2H_5)_{12}]^{1-}$ (**2-$V_6O_7^{1-}$**, bottom, red) and TMSCl reactions with $[V_6O_7(OC_2H_5)_{12}]^{1-}$ (**2-$V_6O_7^{1-}$**) at 70 ºC for 3 hours (middle, green) and at 70 ºC for 24 hours (top, blue) in $CDCl_3$. Resonances labeled as "TBA" correspond to the tetrabutylammonium counter ion of the starting material, **2-$V_6O_7^{1-}$**. Resonances labeled as DCM correspond to dichloromethane.

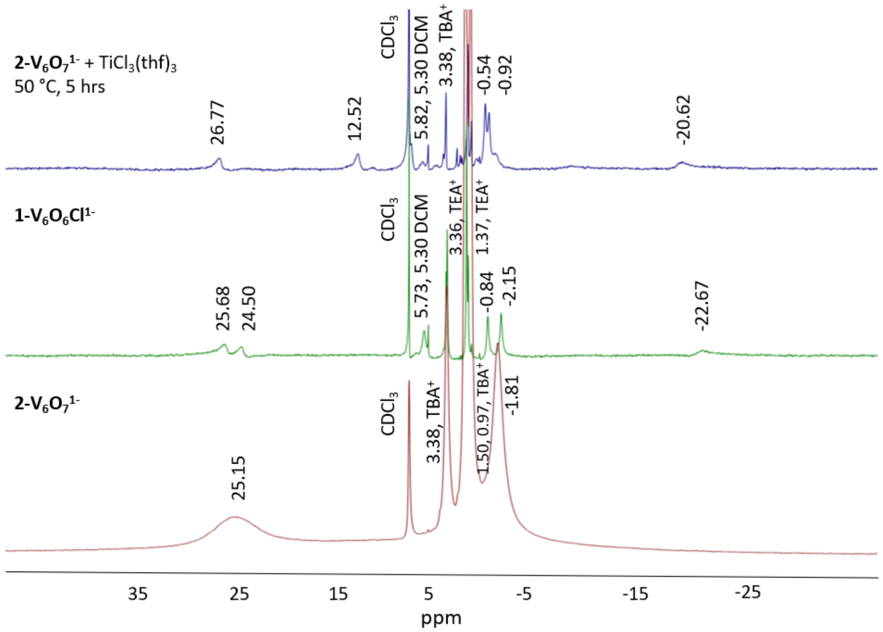

Figure S3. ^{1}H NMR spectra of $[V_6O_7(OC_2H_5)_{12}]^{1-}$ (**2-$V_6O_7^{1-}$**, bottom, red), $[V_6O_6Cl(OC_2H_5)_{12}]^{1-}$ (**1-$V_6O_6Cl^{1-}$**, middle, green), and the reaction of $TiCl_3(thf)_3$ with **2-$V_6O_7^{1-}$** at 50 °C for 5 hours in $CDCl_3$. Resonances labeled as "TBA" correspond to the tetrabutylammonium counter ion of the starting material, **2-$V_6O_7^{1-}$**, while signals labeled as "TEA" correspond to the tetraethylammonium cation of the independently synthesized sample of **1-$V_6O_6Cl^{1-}$**. Resonances labeled as DCM correspond to dichloromethane.

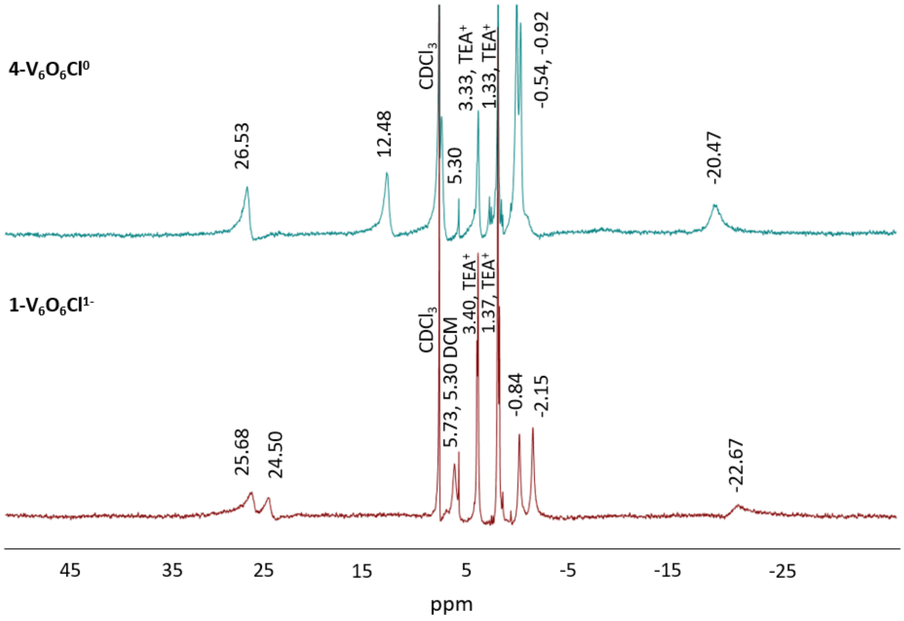

Figure S4. ^{1}H NMR spectra of $[V_6O_6Cl(OC_2H_5)_{12}]^{1-}$ (**1-$V_6O_6Cl^{1-}$**, bottom, red) and $[V_6O_6Cl(OC_2H_5)_{12}]^0$ (**4-$V_6O_6Cl^0$**, top, blue) in $CDCl_3$. Resonances labeled as "TBA" correspond to the tetrabutylammonium counter ion of the starting material, **2-$V_6O_7^{1-}$**, while signals labeled as "TEA" correspond to the tetraethylammonium cation of the independently synthesized sample of **1-$V_6O_6Cl^{1-}$**. Resonances labeled as DCM correspond to dichloromethane.

Table S1. Crystallographic Parameters of **4-$V_6O_6Cl^0$**, **6-V_6O_6OTf**, and **5-$V_6O_6Cl^+$**.

Molecule	4-$V_6O_6Cl^0$	6-V_6O_6OTf	5-$V_6O_6Cl^+$
Empirical formula	$C_{24}H_{60}ClO_{18}V_6$	$C_{25}H_{60}F_3O_{21}SV_6$	$C_{28}H_{70}Cl_6O_{26}V_6W_3$
Formula weight	977.82	1091.43	1892.73
CCDC	1990064	1990063	1990062
Temperature	223.00(10) K	100.00(10) K	100.00(10) K
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	I2/m	P-1	P-1
Unit cell dimensions	a = 10.7617(7) Å b = 17.7653(9) Å c = 10.9667(7) Å $\alpha = 90^o$ $\beta = 107.866(7)^o$ $\gamma = 90^o$	a = 10.7375(2) Å b = 11.6187(3) Å c = 19.2768(4) Å $\alpha = 83.447(2)^o$ $\beta = 77.638(2)^o$ $\gamma = 64.530(2)^o$	a = 10.7819(4) Å b = 15.5823(4) Å c = 16.9994(5) Å $\alpha = 81.532(2)^o$ $\beta = 87.046(3)^o$ $\gamma = 83.092(3)^o$
Volume	1995.5(2) Å_3	2120.16(9) Å_3	2802.71(15) Å_3
Z	2	2	2
Reflections collected	2173	35608	48081
Independent reflections	2173	8882 [R(int) = 0.0763]	11712 [R(int) = 0.1213]
Goodness-of-fit on F2	1.040	1.044	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0712, wR2 = 0.2043	R1 = 0.0732, wR2 = 0.2077	R1 = 0.1002, wR2 = 0.2861

Comments on Disorder in Complex 5-$V_6O_6Cl^+$. Three ethoxy ligands of the vanadium cluster are modeled as disordered over two positions each: O10-C7-C8, 0.51(3):0.49(3), O14-C15-C16, 0.60(3):0.40(3), O17-C21-C22, 0.52(3):0.48(3). A major portion of the tungsten cluster was modeled as disordered over two positions (0.740(1):0.260(1)). An additional methyl group of an ethoxy ligand on this cluster was also modeled as disordered over two positions 0.77(6):0.23(6)).

For each disordered moiety, analogous bond lengths and angles between the two defined positions were restrained to be similar. Anisotropic displacement parameters for proximal atoms were constrained to be equivalent and/or restrained to be similar.

The larger-than-expected residual peaks and holes in the difference Fourier map that appear near the heavy tungsten atoms may be related to absorption correction errors. A face-indexing absorption correction of the tiny nearly-cubic crystal reduced the absolute value of the residuals very slightly over spherical and empirical absorption corrections. The crystal was cracked, however, with a 85:15 component mass ratio. No non-merohedral twin modeling was successful, likely since the reflections of the two components could not be resolved well. To date no better crystals have been found for analysis.

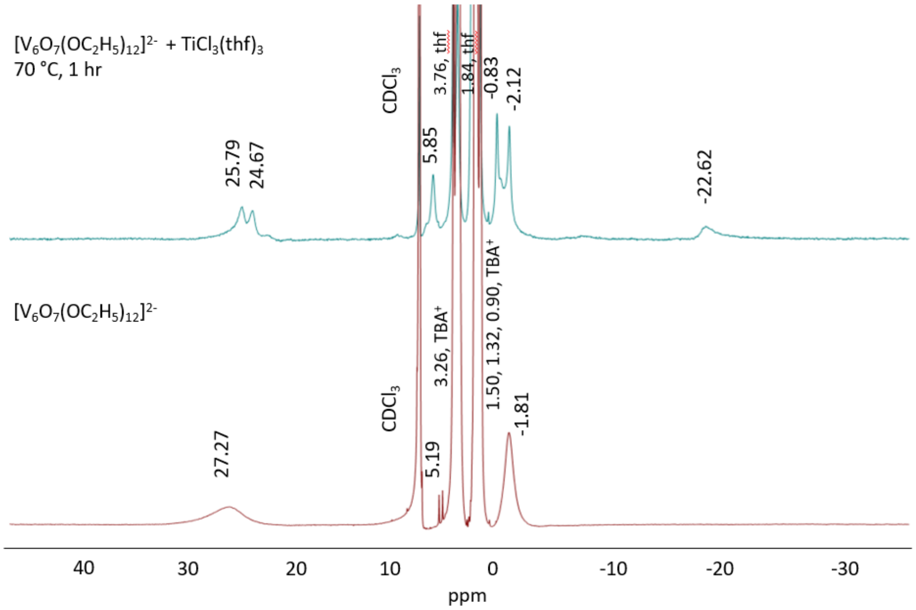

Figure S5. ^{1}H NMR spectra of $[V_6O_7(OC_2H_5)_{12}]^{2-}$ (bottom, red) and the reaction of $TiCl_3(thf)_3$ with $[V_6O_7(OC_2H_5)_{12}]^{2-}$ (top, blue) at 70°C for 1 hour in $CDCl_3$. Resonances labeled as "TBA" correspond to the tetrabutylammonium counter ion of the starting material, **2-$V_6O_7^{1-}$**. Signals labeled as "thf" correspond to tetrahydrofuran.

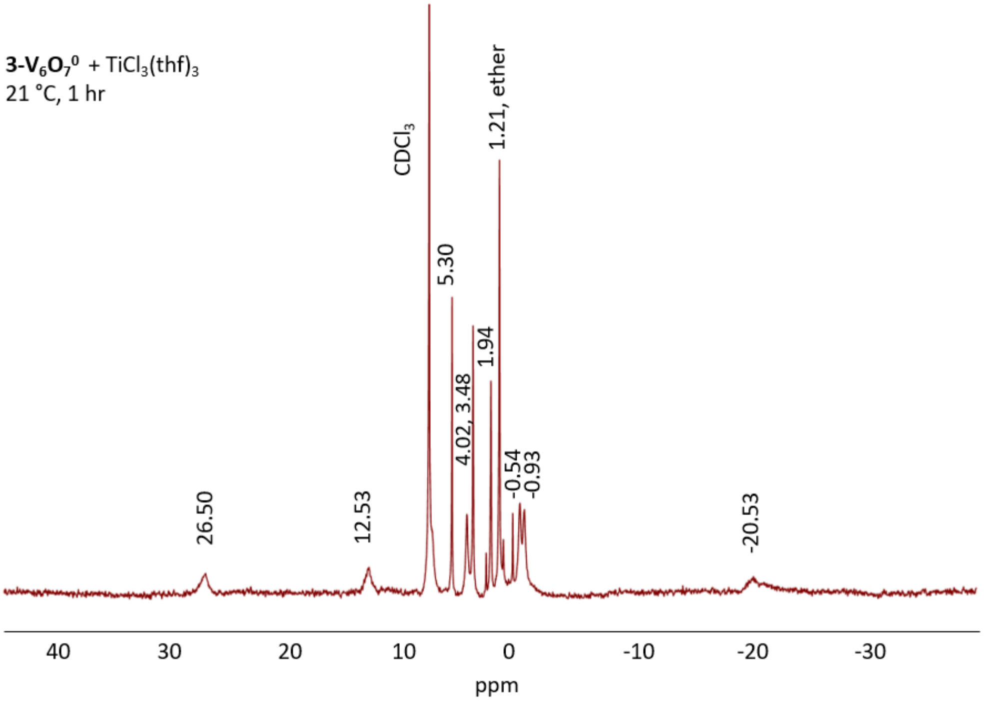

Figure S6. ^{1}H NMR spectra of the reaction of $TiCl_3(thf)_3$ with $V_6O_7(OC_2H_5)_{12}$ (**3-$V_6O_7^0$**) at 21 ºC for 1 hour in $CDCl_3$. Diamagnetic region has been labeled indicating organic solvent impurities (e.g. diethyl ether, dichloromethane).

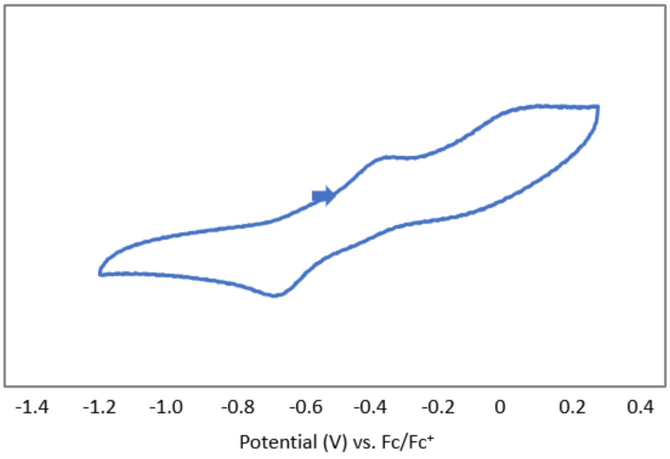

Figure S7. Cyclic voltammogram of $TiCl_3(thf)_3$ collected in dichloromethane with 0.1 M $[^nBu_4N][PF_6]$ as the supporting electrolyte.

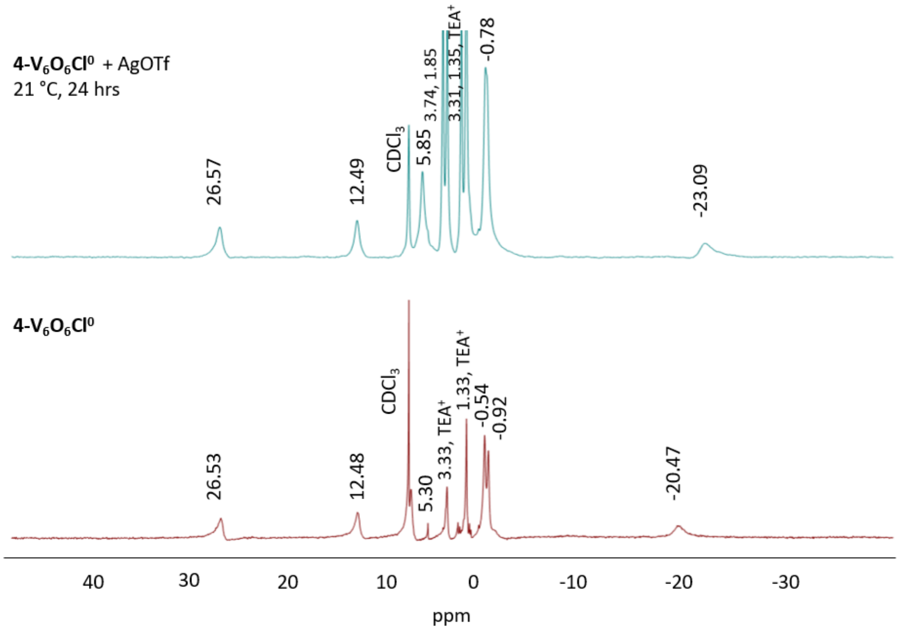

Figure S8. ^{1}H NMR spectra of $V_6O_6Cl(OC_2H_5)_{12}$ (**4-$V_6O_6Cl^0$**, bottom, red) and the reaction of AgOTf with **4-$V_6O_6Cl^0$** (top, blue) at 21 °C for 24 hours in $CDCl_3$. Resonances labeled as "TEA" correspond to residual tetraethylammonium salts from independent synthesis.

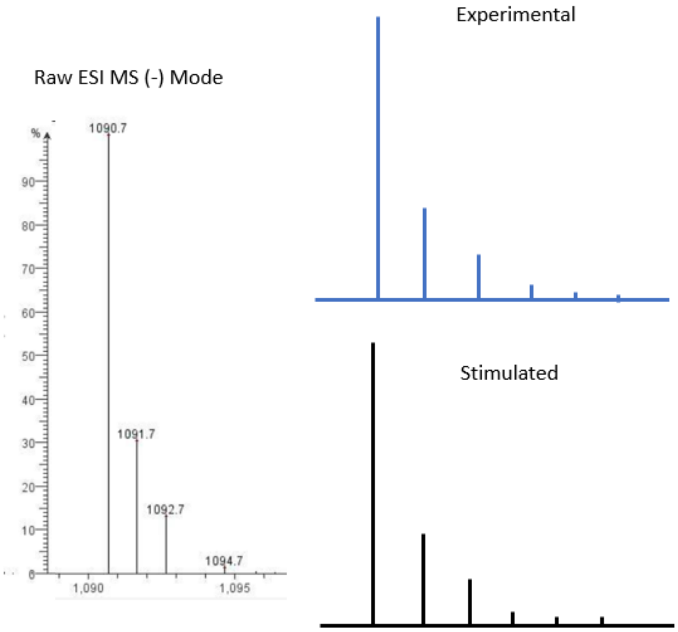

Figure S9. ESI-MS (-)ve of **6-V_6O_6OTf** (m/z = 1091 amu; $[V_6O_6(OC_2H_5)_{12}]OTf$).

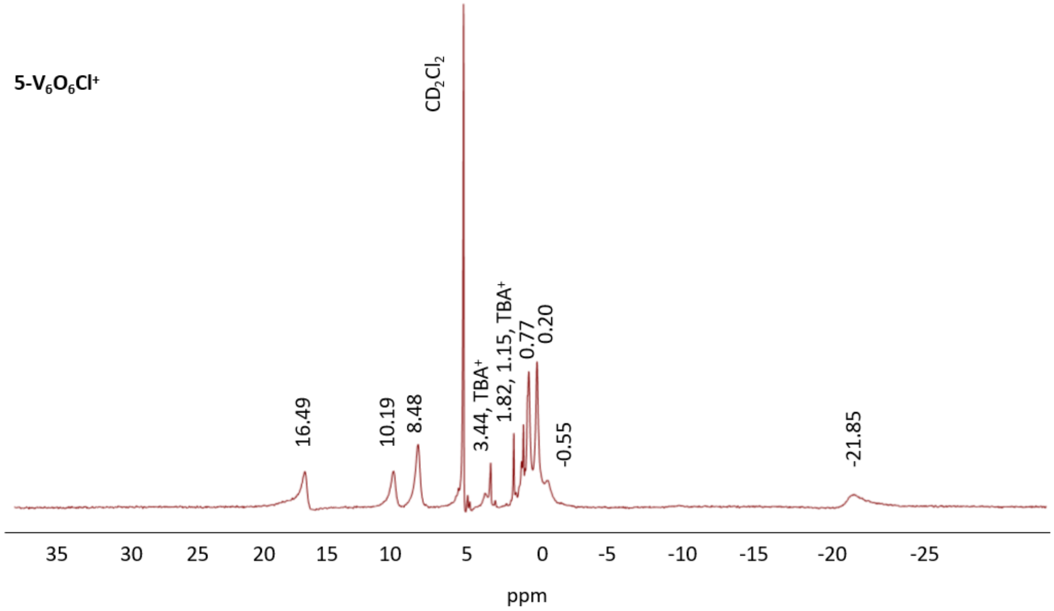

Figure S10. ^{1}H NMR spectra of $[V_6O_6Cl(OC_2H_5)_{12}]^{1+}$ (**5-$V_6O_6Cl^+$**) in CD_2Cl_2 synthesized by the reaction of WCl_6 with $V_6O_7(OC_2H_5)_{12}$ (**3-$V_6O_7^0$**). Resonances labeled as "TBA" correspond to the tetrabutylammonium counter ion of the starting material, **2-$V_6O_7^{1-}$**.