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# Charge and Solvent Effects on the Redox Behavior of Vanadyl Salen-Crown Complexes

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**ABSTRACT.** The incorporation of charged functionalities proximal to a redox active transition metal center is an attractive strategy for modulating redox behavior, installing electric fields, and potentially enhancing catalysis. Vanadyl salen (salen = *N,N'*-ethylenebis(salicylideneaminato)) complexes functionalized with a crown ether containing a 1+ ( $\text{Na}^+$ ,  $\text{K}^+$ ), 2+ ( $\text{Ba}^{2+}$ ), or 3+ ( $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Nd}^{3+}$ ) cation were synthesized and their electrochemical behavior investigated by cyclic voltammetry in both polar (acetonitrile and dimethylformamide) and non-polar (dichloromethane) solvents. The vanadium(V/IV) reduction potential shifted anodically (>900 mV in acetonitrile and >700 mV in dichloromethane) with increasing cation charge as compared to complexes lacking the proximal cation. The redox behavior of the parent salen and 3,3-methoxy substituted salen (salen-OMe) vanadyl complexes was also investigated and compared to the crown-containing complexes. For (salen-OMe)V(O), a weak association of triflate salt at the vanadium(IV) oxidation state was observed through cyclic voltammetry titration studies. The reduction potential for all vanadyl crown complexes measured in dimethylformamide was

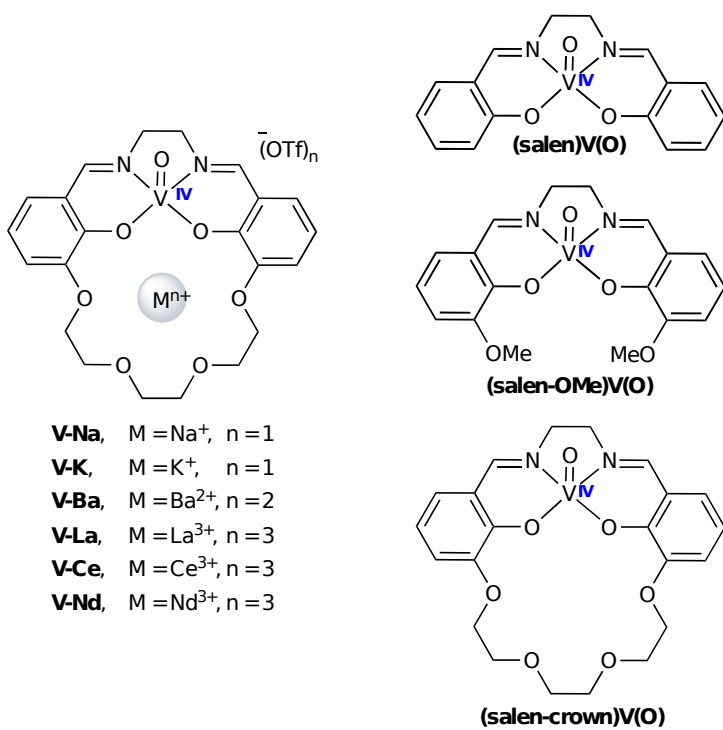
insensitive to cation charge magnitude. Titration studies of dimethylformamide into acetonitrile resulted in cathodic shifting of the vanadium(V/IV) reduction potential with increasing concentration of dimethylformamide. Binding constants of dimethylformamide ( $K_{\text{DMF}}$ ) for the series of crown complexes shows increased binding affinity in the order of **V-La**>**V-Ba**>**V-K**>**(salen)V(O)**, indicating an enhancement of Lewis acid/base interaction with increase of cation charge. This study demonstrates the non-innocent role of solvent coordination on redox behavior and considerations for electric field quenching.

## INTRODUCTION.

Vanadium complexes in the 4+ and 5+ oxidation states are highly attractive due to their activity for a variety of oxidation reactions.<sup>1-3</sup> Vanadyl (V=O) complexes dominate the chemistry of vanadium due to their stability and this has led to many applications ranging from catalysis,<sup>4-11</sup> electrochemistry,<sup>12-14</sup> bioinorganic chemistry,<sup>15,16</sup> and molecular magnetism.<sup>17-22</sup> Salen (salen = *N,N'*-ethylenebis(salicylideneaminato)) vanadyl complexes are interesting models of vanadium containing enzyme active sites and have shown activity for the oxygen reduction reaction (ORR)<sup>29</sup> and autoxidation of alkenes.<sup>30</sup> Given the rich oxidation chemistry of salen vanadyl complexes, tuning the electrochemistry and redox behavior is attractive and a potential strategy for controlling reactivity at very oxidizing potentials. Further, it is important to understand solvent effects on the redox behavior, as this may determine reactivity profiles and stability of the vanadyl ion. Proximal non-redox active Lewis acidic metals can result in large shifts in redox potentials and enhancement of reactivity.<sup>31-35</sup> Increasing the magnitude of charge of a positively charged ion or substituent typically results in an anodic shift, or more positive shift, of reduction

potential. Investigations on the impact of charge effects on homogeneous transition metal complexes are important for understanding electron transfer processes, spectroscopic properties, and impact on catalytic activity. Given the stability of the salen vanadyl (V/IV) redox couple and its role in reactions involving vanadium complexes, we investigated salen-crown vanadyl complexes containing various non-redox active cations to tune the redox behavior. Solvent effects in both polar and non-polar solvents were investigated to explore how both charge and solvent impact electron transfer, reorganization, and coordination around the vanadyl center. Understanding solvent effects when charge is present is also critical for ion-pairing, solvent screening, and coordination as it relates to reactivity.<sup>36</sup> Gaining a better understanding of the interplay of charge effects, solvent interactions, and redox behavior at vanadyl complexes informs how these characteristics may influence reactivity.

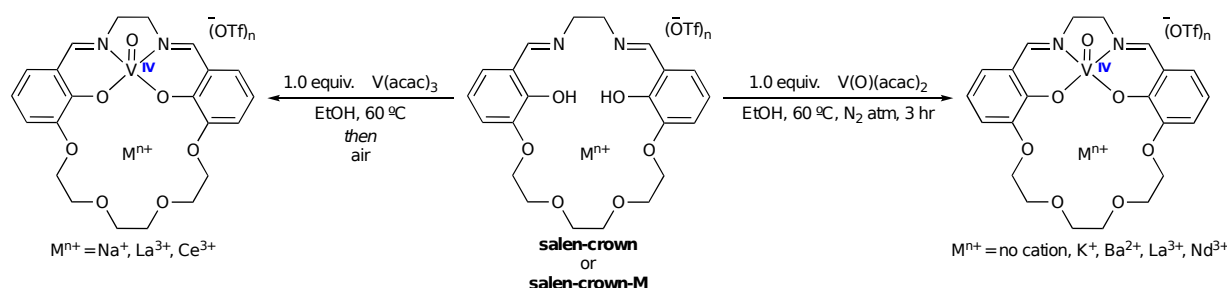
**Chart 1.** Vanadyl complexes investigated in this study.

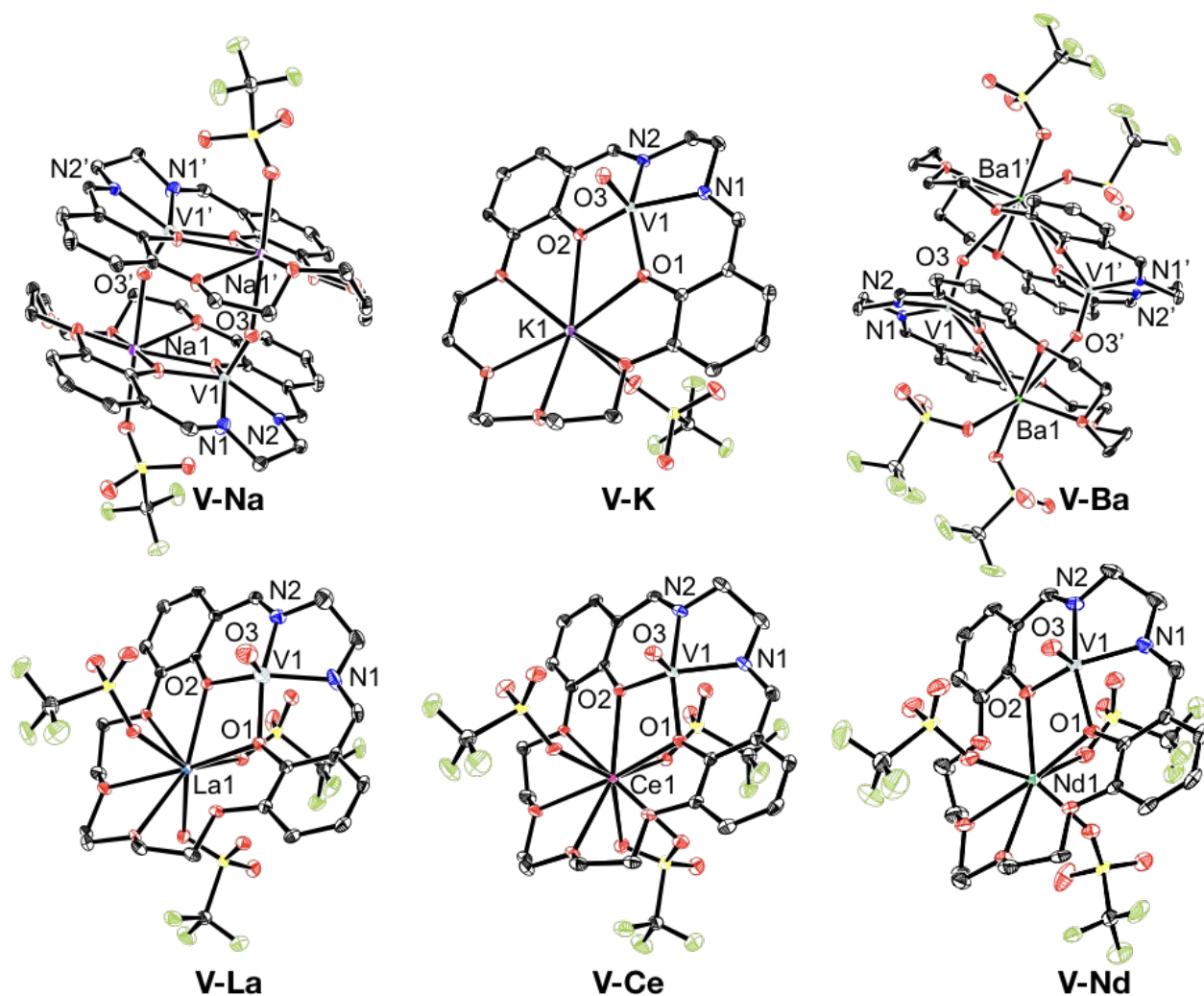


RESULTS AND DISCUSSION.

**Synthesis and structural characterization.** Complexes **(salen)V(O)** and **(salen-OMe)V(O)**<sup>37</sup> as well as the **salen-crown**<sup>38</sup> and **salen-crown-M**<sup>31-33,39</sup> (M = Na<sup>+</sup>, K<sup>+</sup>, Ba<sup>2+</sup>) ligands have been previously reported and were prepared accordingly. **Salen-crown-Ln** ligands (Ln = La, Ce, Nd) were prepared through metalation of **salen-crown** with the respective Ln(OTf)<sub>3</sub> salt in a 1:1 mixture of CHCl<sub>3</sub> and MeOH. The corresponding vanadyl complexes were then achieved through metalation of the desired **salen-crown-M** ligand with V(acac)<sub>3</sub> (acac = acetylacetonate) in EtOH followed by exposure to air. Alternatively, the desired vanadyl complexes could be obtained directly through metalation of the **salen-crown-M** ligand with vanadyl acetylacetonate (V(O)(acac)<sub>2</sub>) (Scheme 1). Single crystals suitable for X-ray diffraction of the vanadyl complexes (**V-Na**, **V-K**, **V-Ba**, **V-La**, **V-Ce**, **V-Nd**) were obtained following slow diffusion of diethyl ether into concentrated MeCN solutions at room temperature (Figure 1). The empty crown vanadyl complex (**(salen-crown)V(O)**) could not be crystallized due to its insolubility in MeCN.

**Scheme 1.** Synthesis of vanadyl complexes.





**Figure 1.** Solid-state molecular structures of vanadyl complexes at 50% probability ellipsoids. Hydrogen atoms omitted for clarity. See Table 1 for selected bond metrics.

In the solid state, **V-Na** and **V-Ba** complexes exist as dimers where the oxo ligand bridges between the vanadium and cation, M (M = Na<sup>+</sup> or Ba<sup>2+</sup>). The bond lengths of the V–O bonds vary minimally across the series for the solid state monomeric or dimeric species (Table 1). Direct binding of a Lewis acid to an oxometal fragment has been shown to result in significant elongation of the M–O bond.<sup>40–42</sup> However, for the crown complexes, we do not observe significant elongation of the V–O bonds with the cation bound in the crown-ether tether.

All complexes exhibit distorted square pyramidal geometry with  $\tau_5$  values ranging between 0.01 and 0.14. The vanadium atom is displaced toward the apical oxygen atom away from the basal plane (defined by the Schiff base  $N_2O_2$  atoms) in all complexes. The neodymium compound had significant distortion in the crystal structure (say something more here).

**Table 1.** Summary of structural, spectroscopic, and electrochemical parameters of vanadyl complexes.

Complex	V–Oxido Bond (Å)	V–M distance (Å)	Cation M radius (Å) <sup>a</sup>	$\tau_5$	Displacement of V from basal plane ( $N_2O_2$ ) (Å)
(salen)V(O) <sup>b</sup>	1.590(1)	–	–	0.18	0.589
(salen-OMe)V(O) <sup>c</sup>	1.590(3)	–	–	0.13	0.589
V-Na	1.5986(15)	3.4850(10)	1.02	0.01	0.518
V-K	1.6025(10)	3.8076(4)	1.38	0.14	0.613
V-Ba	1.6059(11)	3.7983(3)	1.35	0.12	0.610
V-La	1.600(3)	3.5980(7)	1.03	0.12	0.492
V-Ce	1.588(2)	3.6100(6)	1.01	0.10	0.485
V-Nd	1.586(3)	3.59569(17)	0.98	0.10	0.492

<sup>a</sup> Values from ref. <sup>43</sup>. <sup>b</sup> Values from ref. <sup>44</sup>. <sup>c</sup> Values from ref. <sup>45</sup>.

### Solution state magnetic moment measurements and electron paramagnetic resonance

#### spectroscopy.

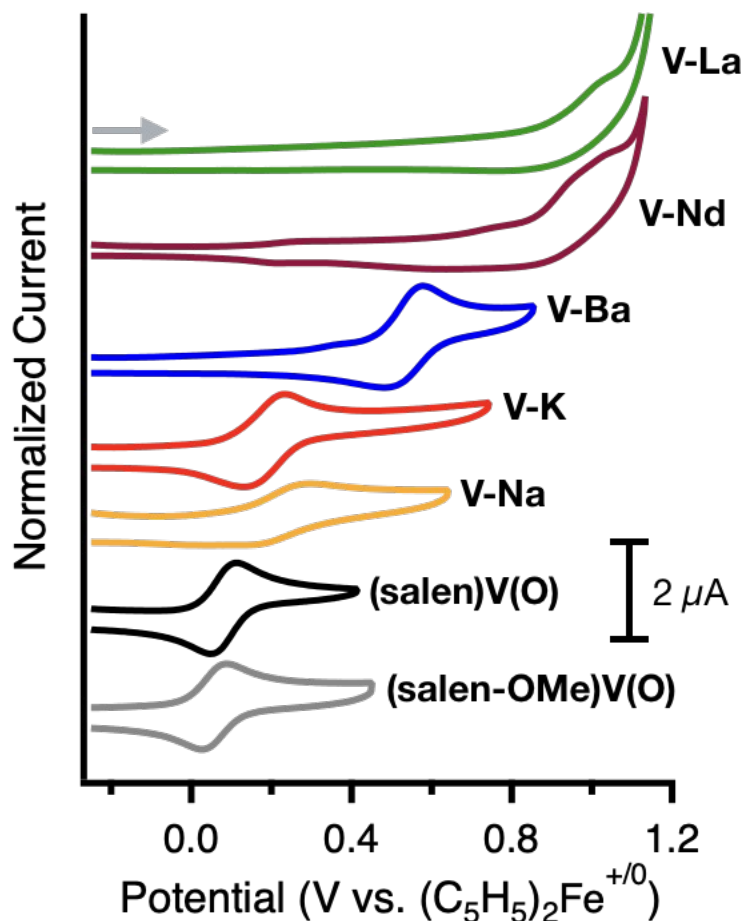
The solution state magnetic moments of the heterobimetallic complexes were measured by Evans method in MeCN at 23 °C. [insert conclusions here.] Electron paramagnetic resonance (EPR) spectra were collected at 77 K in 1:1 MeCN/toluene solutions. The spectra support a vanadium-centered  $S = 1/2$  assignment with average  $g$  values  $\sim 1.98$  for the series of heterobimetallic complexes and exhibit the expected eight-line hyperfine splitting due to the  $I =$



$7/2$   $^{51}\text{V}$  (99.75% natural abundance) nucleus (See SI Figure SX, Table SX). No spin coupling between the vanadium center and  $\text{Ce}^{3+}$  or  $\text{Nd}^{3+}$  was observed for **V-Ce** or **V-Nd**, respectively. The EPR spectra exhibit axially symmetric spectra consistent with those typical for related square pyramidal oxovanadium(IV) complexes.<sup>46,47</sup>

**Cyclic voltammetry.** Cyclic voltammetry of **(salen)V(O)** (Figure 2, black trace) and **(salen-OMe)V(O)** (Figure 2, gray trace) in acetonitrile (dielectric of 37.5) show reversible reductions corresponding to the V(V/IV) reduction at 0.090 and 0.066 V vs  $(\text{C}_5\text{H}_5)_2\text{Fe}^{+/0}$ , respectively, consistent with previously reported values.<sup>48</sup> The electrochemical properties of **V-M** ( $\text{M}^{n+} = \text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Nd}^{3+}$ ,  $\text{La}^{3+}$ ) were also measured in acetonitrile (Figure 2 and SI Figure SX) and values for the V(V/IV)  $E_{1/2}$  are listed in Table 2. The V(V/IV) redox event for **V-Na**, **V-K**, and **V-Ba** is reversible and shifts anodically with increase of cation charge, consistent with the effect of incorporating charge with related heterobimetallic complexes previously investigated by our group.<sup>31-35</sup> The vanadium(V/IV) reduction potential for the monocations (**V-Na** and **V-K**) shifts 90-130 mV more positive than **(salen)V(O)** and 114-164 mV more positive than **(salen-OMe)V(O)**. For the dication, **V-Ba**, the vanadium(V/IV) reduction potential shifts 440 mV positive of **(salen)V(O)** and 464 mV positive of **(salen-OMe)V(O)**. The cyclic voltammograms of **V-La** and **V-Nd** showed an irreversible oxidation event ( $E_{\text{pa}}$ ) at 1.1 and 1.09 V vs  $(\text{C}_5\text{H}_5)_2\text{Fe}^{+/0}$ , respectively, indicating chemical instability of the vanadium(V) oxo for these complexes in MeCN. Attempts to isolate the lanthanum containing vanadium(V) oxo complex following chemical oxidation of **V-La** with  $\text{NOBF}_4$  were unsuccessful. Differential pulse voltammetry of **V-La** showed an additional oxidation feature directly following the V(IV/V) oxidation ( $>1.3$  V vs  $\text{Fc}^{+/0}$ ) tentatively assigned as formation of the V(V)-phenoxy radical, which may contribute to

the observed electrochemical and chemical instability in isolating this species at such oxidizing potentials (See SI Figure SX).



**Figure 2.** Cyclic voltammograms of (salen)V(O), (salen-OMe)V(O), and V-M (M = Na<sup>+</sup>, K<sup>+</sup>, Ba<sup>2+</sup>, Nd<sup>3+</sup>, and La<sup>3+</sup>) (0.5 mM) in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in MeCN under N<sub>2</sub>. Scan rate is 100 mV/s. Decamethylferrocene was used as internal reference and all potentials are reported vs. the (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sup>+0</sup> redox couple.

**Table 2.** Summary of electrochemical data for vanadyl complexes.

Complex	$E_{1/2}$ V(V/IV) (V), MeCN <sup>a</sup>	$E_{1/2}$ V(V/IV) (V), DCM <sup>a</sup>	$E_{1/2}$ V(V/IV) (V), DMF <sup>a</sup>	$pK_a$ of M(OH <sub>2</sub> )	$\log(K_{\text{DMF}})$

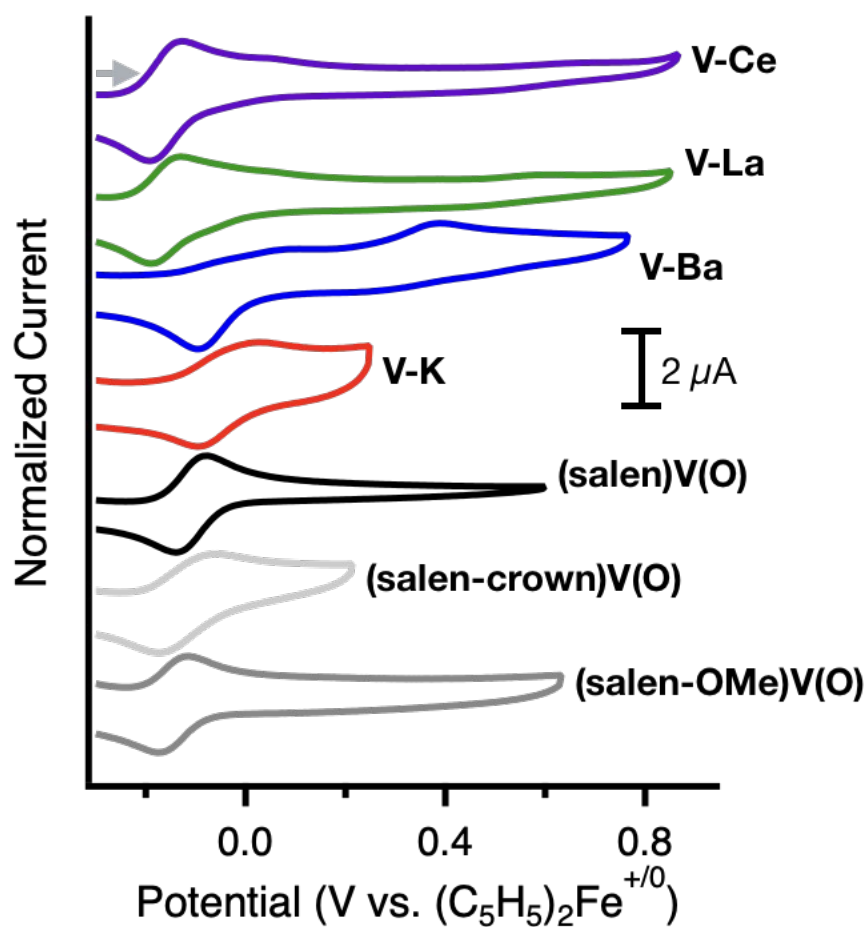
				(aq.) <sup>b</sup>	
<b>(salen)V(O)</b>	0.090	0.045	-0.10	--	1.75
<b>(salen-OMe)V(O)</b>	0.066	--	-0.13	--	--
<b>(salen-crown)V(O)</b>	--	--	-0.12	--	--
<b>V-Na</b>	0.23	0.195	-0.050	14.8	--
<b>V-K</b>	0.18	--	-0.036	16.3	1.90
<b>V-Ba</b>	0.53	0.41	0.39, -0.11 <sup>c</sup>	13.4	3.67
<b>V-La</b>	1.1 <sup>d</sup>	0.78 <sup>d</sup>	-0.16	9.06	7.42
<b>V-Ce</b>	--	--	-0.16	9.3	--
<b>V-Nd</b>	1.09 <sup>d</sup>	--	--	8.4	--

<sup>a</sup> Reduction potentials referenced to (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sup>+0</sup> couple. <sup>b</sup> Values from ref. . <sup>c</sup> The redox events are irreversible, so in lieu of reporting a  $E_{1/2}$ , the values reported here correspond to  $E_{pa}$  and  $E_{pc}$  potentials, for the irreversible oxidation and reduction events, respectively. <sup>d</sup> The redox event is irreversible, so the reported potentials correspond to an  $E_{pa}$  for the irreversible oxidation to the V(V) species.

To further investigate the effect of solvent on the electrochemical behavior of the vanadyl complexes, cyclic voltammetry was also performed in dichloromethane (dielectric of 8.93) and dimethylformamide (dielectric of 36.7). Cyclic voltammograms of **V-K**, **V-Ba**, and **V-La** measured in dichloromethane exhibited similar positive shifts for the vanadium(V/IV) couple with increase of cation charge. The vanadium(V/IV) couple for **V-K** and **V-Ba** appeared reversible, but **V-La** showed an irreversible oxidation, similar to its behavior in MeCN. However, all three complexes were sparingly soluble in DCM. Still, shifts of 150 mV (**V-K**), 365 mV (**V-Ba**) and 735 mV (**V-La**) more positive than **(salen)V(O)** were observed (see SI Figure SX).

The electrochemical behavior in dimethylformamide was markedly different than that observed in either MeCN or DCM. The vanadium(V/IV) redox couple was insensitive to cation

bound in the crown, only varying 124 mV across the series (Figure 3). Say something about excluding the possibility of the cation falling out here. Titration studies of adding excess equivalents of triflate salt to solutions of either V-Ka, V-Ba, or V-La did not produce any changes in the CV (See SI). The effect of anion dissociation in DMF was also explored as a reasoning for the lack of positive redox shift for V-La by cyclic voltammetry. However, comparing reduction potentials of [V-La][OTf]<sub>3</sub> and [V-La][Cl]<sub>3</sub> in DMF with 0.1 M TBABPh<sub>4</sub> electrolyte showed no real difference (SI Figure SX). It is expected that the chloride anion could be more strongly coordinating than triflate. However, the similar reduction potentials indicate that another interaction must be responsible for the lack of positive shift in DMF.



**Figure 3.** Cyclic voltammograms of **(salen)V(O)**, **(salen-OMe)V(O)**, **(salen-crown)V(O)**, and **V-M** ( $M = K^+, Ba^{2+}, La^{3+}, Ce^{3+}$ ) (0.5 mM) in 0.1 M TBAPF<sub>6</sub> in DMF under N<sub>2</sub>. Scan rate is 100 mV/s. Decamethylferrocene was used as internal reference and all potentials are reported vs. the (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sup>+0</sup> redox couple.

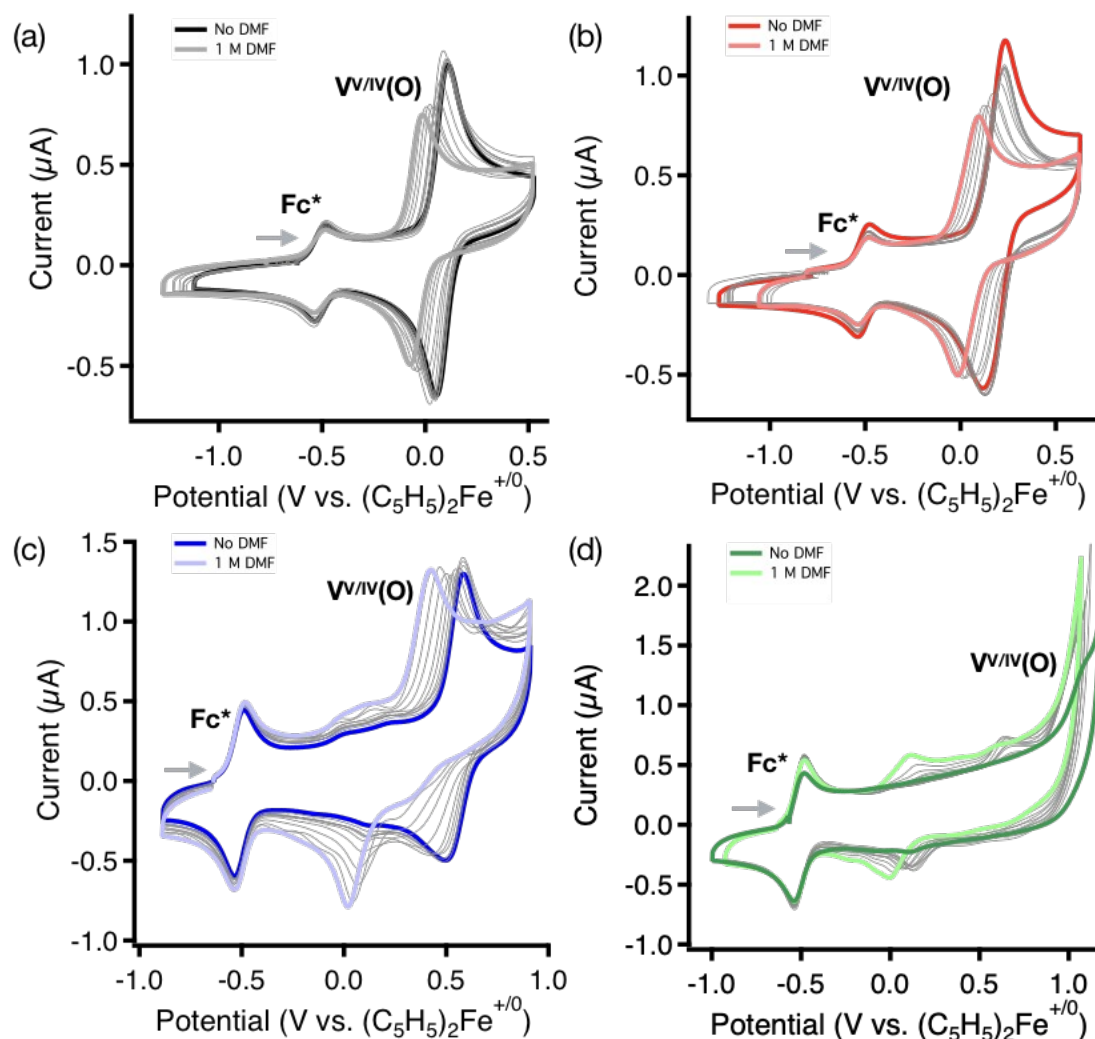
Square pyramidal salen vanadium oxo complexes possess an empty coordination site trans to the oxo group, and previous studies have investigated association of weakly binding anions at this position.<sup>49-51</sup> Additionally, dimeric or oligomeric chains with V-O-V-O linkages have been observed.<sup>52-55</sup> Upon oxidation, the more electron deficient vanadium(V) should prefer to be six-coordinate instead of five and thus more likely to bind coordinating solvents or Lewis bases at the axial position.<sup>56</sup> Previous electrochemical studies on salen vanadium oxo complexes in polar versus non-polar solvents shows that solvent and electrolyte interactions can greatly impact the redox behavior<sup>48</sup> and catalytic oxidation reactivity.<sup>37,57-59</sup> The cyclic voltammogram of **V-Ba** in DMF suggests chemical reactivity on the CV timescale. Describe CV of barium complex. Talk about solvent dielectric and solvent screening of charge/electric field?<sup>60</sup> The differences in the cyclic voltammograms of the vanadium complexes in MeCN versus DMF cannot be explained by dielectric constant because the values are similar (37.5 and 36.7, respectively). Instead, a better descriptor would be to consider the differences in Lewis basicity of the solvents. Gutman donor number.<sup>61,62</sup>

To explore the interaction with DMF, cyclic voltammograms of the vanadyl complexes, **(salen)V(O)**, **V-K**, **V-Ba**, and **V-La**, were taken at different concentration of DMF in MeCN. In all cases, the vanadium(V/IV) reduction potential shifted cathodically with increasing concentrations of DMF (Figure 4). Further, for **V-La**, the redox couple became reversible at

concentrations of 0.1 M DMF and above. This cathodic shifting can be explained by DMF binding at the axial position, thus increasing electron density at the metal center and making it easier to oxidize from vanadium(IV) to (V). Binding constants for DMF ( $K_{\text{DMF}}$ ) can be calculated using an adaptation of the Nernst equation (eq 1), where a plot of  $E_{1/2}$  vs  $\log[\text{DMF}]$  gives a linear relationship.<sup>63,64</sup>

$$\Delta E_{1/2} = q \frac{0.0592}{n} \log[\text{DMF}] + \frac{0.0592}{n} \log(K_{\text{DMF}}) \quad (1)$$

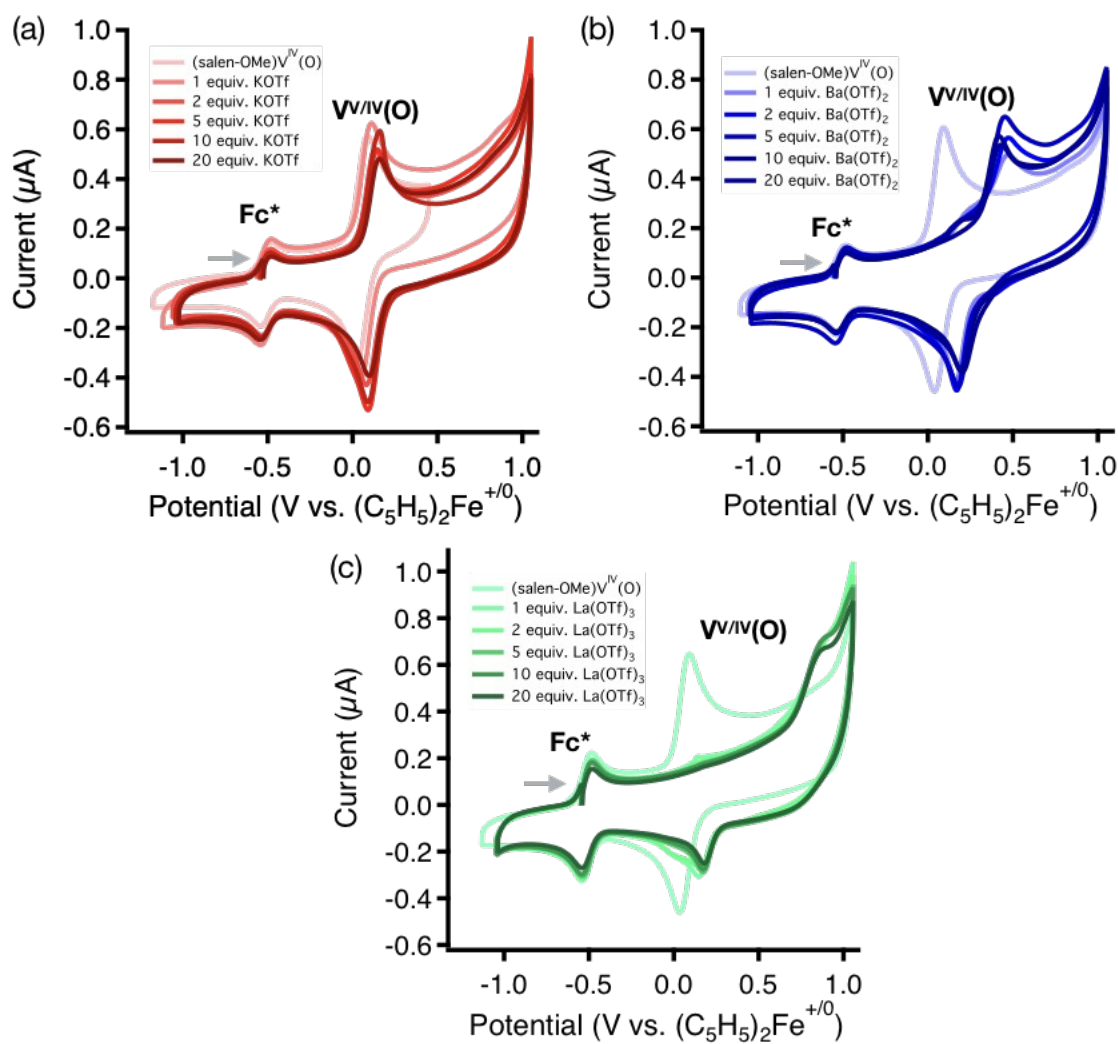
In eq 1,  $q$  is the number of DMF molecules bound and  $n$  refers to the number of electrons involved in the redox event. For the one electron oxidation of vanadium(IV) to vanadium(V), the value of  $K_{\text{DMF}}$  increases as cation charge increases (Table 2). Further, the slope obtained from these data can be used to determine the number of DMF molecules bound. In the case of **(salen)V(O)**, there should be only one empty coordination site for DMF and the slope value of 0.05 V/decade is consistent with the binding of one molecule of DMF (See SI Figure SX). For the **V-M** complexes, the Lewis acidic metal cation provides an additional binding site. A similar analysis of the slopes for **V-K**, **V-Ba**, and **V-La** suggests that more than one molecule of DMF could be binding ( $q > 1$ ) (See SI). Therefore, binding of multiple molecules at these complexes cannot be ruled out.



**Figure 4.** Cyclic voltammetry of (a) (salen)V(O), (b) V-K, (c) V-Ba, (d) V-La with titration of DMF. Scan rate at 100 mV/s in MeCN and 0.1 M TBAPF<sub>6</sub> electrolyte. Redox feature at  $E_{1/2} = -0.51$  V is decamethylferrocene (Fc\*) used as internal standard.

The interaction of the Lewis acidic metal with the methoxy substituted complex, (salen-OMe)V(O), was also explored. Interactions with salen vanadium oxo complexes with Rare Earth metals<sup>65</sup> and Group 14 and 15 Lewis acids<sup>45</sup> have been observed before. Two different sites of interaction are possible – through the oxo group or through the methoxy substituents, more akin to the salen-crown complexes. A more electrophilic vanadium oxo center would disfavor

association through the oxo unit. Cyclic voltammograms of **(salen-OMe)V(O)** were taken at different concentrations of  $M(\text{OTf})_n$  salt ( $M^{n+} = \text{K}^+, \text{Ba}^{2+}, \text{La}^{3+}$ ) in MeCN (Figure 5). An anodic shift of the vanadium(IV/V) oxidation feature was observed for all salts with increasing equivalents added. However, the potential for the return wave, reduction of the vanadium(V) back to vanadium(IV), was shifted anodically by a smaller amount (Table 3). The asymmetry observed in the magnitude of the shift at the two redox features may be attributed to charge repulsion between the cationic vanadium(V) and the Lewis acidic metal, leading to a weaker association.





**Figure 5.** Cyclic voltammetry of (salen-OMe)V(O) with titration of (a) KOTf, (b) Ba(OTf)<sub>2</sub>, or (c) La(OTf)<sub>3</sub> salts. Scan rate at 100 mV/s in MeCN and 0.1 M TBAPF<sub>6</sub> electrolyte. Redox feature at  $E_{1/2} = -0.51$  V is decamethyl ferrocene (Fc\*) used as internal standard.

**Table 3.** Summary of redox potential shifts from tritration of (salen-OMe)V(O) with triflate salts.<sup>a</sup>

Equiv. salt added	K(OTf) <sub>2</sub>		Ba(OTf) <sub>2</sub>		La(OTf) <sub>3</sub>	
	$\Delta E_{pa}$ (V)	$\Delta E_{pc}$ (V)	$\Delta E_{pa}$ (V)	$\Delta E_{pc}$ (V)	$\Delta E_{pa}$ (V)	$\Delta E_{pc}$ (V)
<b>1</b>	0.020	0.014	0.367	0.122	0.794	0.114
<b>2</b>	0.025	0.030	0.369	0.125	0.794	0.119
<b>5</b>	0.045	0.051	0.374	0.141	0.804	0.136
<b>10</b>	0.058	0.058	0.331	0.158	0.794	0.142
<b>20</b>	0.082	0.069	0.321	0.163	0.794	0.144

**Electronic and vibrational spectroscopy.** The UV-visible spectra of the V-M complexes were explored in both MeCN and DMF (See SI for full spectra). There are two major absorption bands observed for all complexes, with an intense band at ~360 nm corresponding to a mixed  $\pi-\pi^*/$ charge transfer (CT) transition and a weaker band at ~580 nm corresponding to V(IV) d-d transitions.<sup>56</sup> A slight red shift was observed in DMF for the  $\pi-\pi^*$  band that was more pronounced for complexes containing a cation, and this shift may be due to stabilization by DMF coordination.

The solid-state infrared spectra show that the V=O stretching frequency increases by 32 cm<sup>-1</sup> and the imine C=N bond frequency increases by 42 cm<sup>-1</sup> over the series of complexes. Plotting

the vibrational data against the  $E_{1/2}$  data collected in different solvents show that a positive linear Stark effect is present in MeCN and DCM, however in DMF no positive correlation is observed, consistent with DMF coordination (Figure SX). Table 4 lists a summary of UV-visible and vibrational spectroscopy.

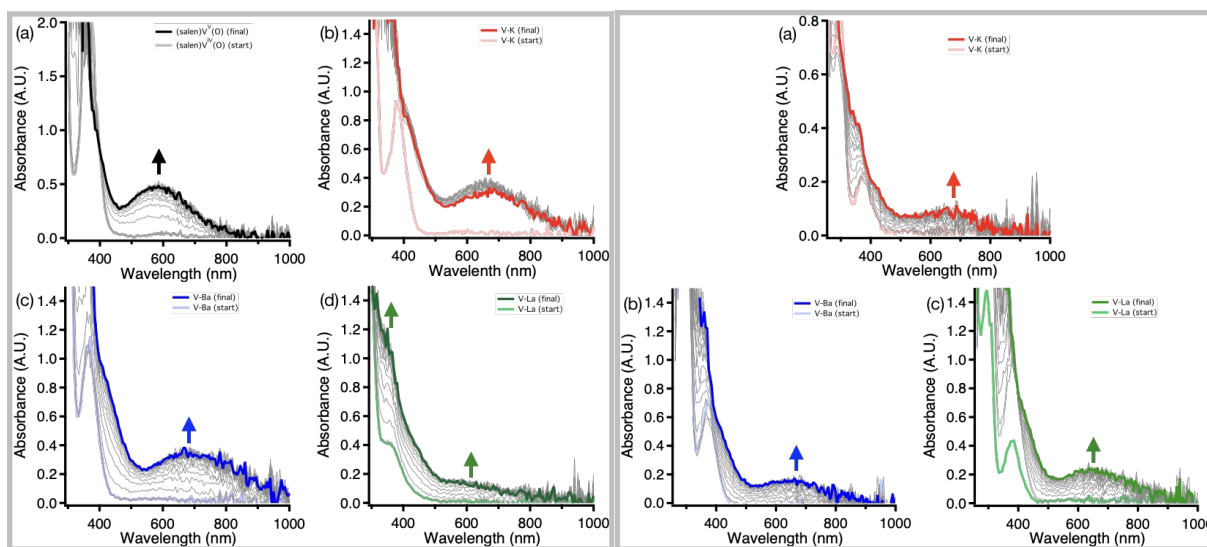
**Table 4.** Summary of electronic absorbance and vibrational spectroscopy.

Complex	MeCN	DMF	$\nu(\text{V}=\text{O})$ ( $\text{cm}^{-1}$ )	$\nu(\text{C}=\text{N})$ ( $\text{cm}^{-1}$ )
	$\lambda/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )	$\lambda/\text{nm}$ ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ )		
(salen)V(O)	365 (9600), 590 (210)	363 (6075), 587 (123) <sup>a</sup>	968	1531
(salen-OMe)V(O)	360 (5600), 600 (200)	--	976	1522
(salen-crown)V(O)	--	376 (3400), 598 (110)	979	1525
V-Na	374 (2500), 592 (60)	378 (2990), 594 (70)	986	1554
V-K	374 (23,500), 584 (160)	376 (3900), 572 (90)	987	1553
V-Ba	366 (4400), 588 (70)	382 (5600), 578 (110)	989	1557
V-La	354 (4000), 610 (60)	378 (6300), 602 (170)	998	1563
V-Ce	354 (3900), 604 (170)	380 (9300), 592 (280)	1000	1564
V-Nd	346 (4700), 596 (180)	386 (3100), 598 (80)	994	1530

<sup>a</sup> Values from ref <sup>66</sup>.

Spectroelectrochemical UV-vis studies were also used to further investigate the stability of the vanadium complexes following oxidation in both MeCN and DMF. A controlled potential

electrolysis  $\sim 200$  mV positive of the V(V/IV) reduction potential was applied in 0.2 M TBAPF<sub>6</sub> solutions and UV-Vis spectra were collected at 1 second intervals during electrolysis. In MeCN, (salen)V(O), V-K, V-Ba all showed the growth of a broad absorbance peak between 600-800 nm corresponding to the growth of a charge transfer band associated with formation of the V(V) species. Electrolysis of V-La did not result in growth of an absorbance peak indicating formation of the V(V) complexes, further supporting the instability and inaccessibility of the V(V) complex for the lanthanum containing complex. In DMF, however, the growth of the charge transfer band was observed for V-K, V-Ba, and V-La, indicating that bound DMF may be providing stabilization of the V(V) form in line with the reversibility observed for the V(V/IV) redox coupling in DMF solutions.



**Figure 6.** Spectroelectrochemical UV-Vis of vanadium complexes. Left: in MeCN with 0.2 M TBAPF<sub>6</sub> electrolyte. (a) (salen)V(O), (b) V-K, (c) V-Ba, (d) V-La. Right: in DMF with 0.2 M TBAPF<sub>6</sub> electrolyte. (a) V-K, (b) V-Ba, (c) V-La.

## CONCLUSIONS

These studies indicate that solvation effects and ability of DMF to act as a Lewis base can effectively quench electrostatic charge effects on reduction potentials. Cyclic voltammetry and UV-Vis confirmed that DMF can act as a ligand and the binding constant increases as the cation charge increases and the metal center becomes more electron. In acetonitrile, incorporation of charge leads to a shift in reduction potential for the vanadium(V/IV) couple by >900 mV. However, in DMF the reduction potential only shifts by 124 mV across the series of complexes investigated.

We have also demonstrated that addition of exogenous triflate salt to (salen-OMe)V(O) in MeCN produces a positive shift in the V(V/IV) reduction potential, but charge repulsion upon oxidation to V(V) results in cation dissociation and a loss of reversibility by cyclic voltammetry. The impact of these studies shows that electrostatic effects are solvent and coordination environment dependent and inform future work on considering these interactions to avoid electric field quenching and improve catalyst design.

## ASSOCIATED CONTENT

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