Cobalt and Vanadium Trimetaphosphate Polyanions: Synthesis, Characterization and Electrochemical Evaluation for Non-Aqueous Redox-Flow Battery Applications

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ABSTRACT: An electrochemical cell consisting of cobalt ([Co(III)(P$_3$O$_9$)$_2$]$^{3−}$) and vanadium ([V(III)/(P$_3$O$_9$)$_2$]$^{3−/4−}$) bistrimetaphosphate complexes as catholyte and anolyte species, respectively, was constructed with a cell voltage of 2.4 V and Coulombic efficiencies exceeding 90% for up to 100 total cycles. The [Co(P$_3$O$_9$)$_2$]$^{4−}$ (1) and [V(P$_3$O$_9$)$_2$]$^{3−}$ (2) complexes have favorable properties for flow-battery applications that include reversible redox chemistry, high stability toward electrochemical cycling, and high solubility in MeCN (1.09 ± 0.02 M, [PPN][1]·2MeCN; 0.77 ± 0.06 M, [PPN][2]·DME). The [PPN][1]·2MeCN and [PPN][2]·DME salts were isolated as crystalline solids in 82 and 68% yields, respectively, and characterized by $^31$P NMR, UV-vis, ESI-MS(−), and IR spectroscopy. The [PPN][1]·2MeCN salt was also structurally characterized, crystallizing in the monoclinic P2$_1$/c space group. Treatment of 1 with [p-BrC$_6$H$_4$I$_2$]$^+$ allowed for isolation of the one-electron oxidized spin-crossover complex, [Co(P$_3$O$_9$)$_2$]$^{5−}$ (3), which is the active catholyte species generated during cell charging. The presence of a spin-crossover complex is a feature of the present system that may enable voltage window variation as a function of temperature. The success of the 1-2 cell provides a promising entry point to a potential future class of transition-metal metaphosphate-based all-inorganic non-aqueous redox-flow battery electrolytes.

Redox-flow battery (RFB) technologies have gained widespread interest as promising solutions for renewable and efficient grid-scale energy storage. RFBs offer many advantages over traditional redox storage solutions such as solid-electrode batteries due to their relatively low cost, high efficiency, high scalability, modularity, and longer lifetimes. Aqueous vanadium-based RFBs are the current state-of-the-art, and have successfully demonstrated reliable electrochemical performance at the commercial level. Despite their immense success, aqueous RFBs suffer from several disadvantages that include low energy density (~50 WhL$^{-1}$), limited operational temperatures (0–100 °C), and a narrow electrochemical window (1.2 V). To overcome these challenges, recent research is shifting to non-aqueous RFBs (NARFBs). NARFBs expand the operational voltage window from 1.2 V (water) to much wider electrochemical windows exceeding 5 V depending on the organic solvent employed. NARFBs also offer the potential to work outside of the typical operating temperature of water. However, traditional NARFBs that employ transition-metal complex electrolytes supported by organic ligands (dithiolate, cyclopentadienyl, bipyridine, acetylacetone) suffer from numerous drawbacks such as low cyclability, high production cost, high flammability, limited electrochemical stability, and cross-contamination between the anolyte and catholyte compartments; these drawbacks have thus far prevented wide-scale adoption of NARFBs.

Herein, we report a new approach to NARFB electrolyte design through the use of redox-active cyclic phosphate metal complexes. This work presents trimetaphosphate ([P$_3$O$_9$]$^{3−}$) anions as all-inorganic supporting ligands for cobalt and vanadium ions (Figure 1, B; [PPN][Co(P$_3$O$_9$)$_2$]·2MeCN, [PPN][1]·2MeCN; [PPN][V(P$_3$O$_9$)$_2$]·DME, [PPN][2]·DME), in which the redox-active metal center’s coordination sphere is completed entirely by a pair of metaphosphate rings. The electrochemical inertness of the redox inactive cyclic phosphates (IP$_3$H$^{n+}$), coupled with their low cost, low toxicity, and flame-retardant nature render them promising building blocks for flow-battery chemistries. When 1 and 2 were paired as catholyte and anolyte species, respectively, the resulting dual-active-species electrochemical cell displayed a total cell voltage of 2.4 V. The chelating nature of the metaphosphate ring aids in disfavoring ligand dissociation, and the lack of C–H bonds provides oxidative stability to the redox-active species that increases the cell’s lifetime when compared with the cycle lifetimes of other NARFB candidate systems. The transition-metal complexes are also polyanionic in all charge states that are relevant to cycling of the RFB, a property that minimizes crossover of active species through membrane separators. Additionally, the solubilities of the metaphosphate complexes in polar organic media are enhanced when compared with solubilities of other transition metal complex electrolytes due to the highly lipophilic PPN$^+$ (PPN$^+$ = bis(triphenyolphosphate)(iminium) cations). The cation, however, is a variable component of the current system. The PPN$^+$ cation was chosen for the present study on the basis of our previous work, but other cations could be selected to optimize properties including solubility and cost.

We have previously shown that monohydrated trimetaphosphate ([P$_3$O$_9$H$^{2−}$]) is capable of effecting ligand exchange through protonolysis of acetylacetone (acac) from [OTi(acac)$_2$]$_2$ to generate the terminal titanyl trimetraphosphate complex, [OTiP$_3$O$_9$(acac)]$^{2−}$. Employing this strategy of protolytic ligand replacement, salts of complexes [Co(P$_3$O$_9$)$_2$]$^{4−}$ (1) and [V(P$_3$O$_9$)$_2$]$^{3−}$ (2) were prepared through treatment of [PPN][Co(P$_3$O$_9$)$_2$] (2 equiv) with Co(acac)$_2$ or V(acac)$_3$ (1 equiv), respectively (Equation 1). Acetylacetone (acacH), the byproduct formed through protonation, is easily separable from the transition-metal metaphosphate complexes, making the preparation of the PPN$^+$ salts of 1 and 2 convenient and straightforward. Preparation of [PPN][V(P$_3$O$_9$)$_2$]·DME, however, requires three equivalents

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**Figure 1.** A: Cyclic voltammograms of 2 mM MeCN solutions of \([\text{PPN}]_2[\text{P}_3\text{O}_9\text{H}]_2\) (blue) and \([\text{PPN}]_2[\text{DME}]\) (gray) scanned at 100 mV/s and referenced vs. \(\text{Fc/Fc}^+\). Working electrode: glassy carbon, pseudo-reference electrode: \(\text{Ag/Ag}^+\), counter electrode: Pt wire. Arrows indicate scan direction. B: Schematic representation of an H-cell used for charge-discharge studies with molecular structure drawings of \([\text{Co}(\text{P}_3\text{O}_9\text{H})_2]^{4+/3-}\) (anolyte, left), and \([\text{V}(\text{P}_3\text{O}_9\text{H})_2]^{3+/4-}\) (anolyte, right). Typical experiments were run at 5 mM \([\text{PPN}]_2[\text{I}]\) 2MeCN and \([\text{PPN}]_2[\text{DME}]\) concentrations in a 0.5 M MeCN solution of \([\text{TBA}]_2[\text{PF}_6]\) with a Neosepta® anion-selective membrane separating each compartment, and carbon paper electrodes.

The identity of A as the bistrimetaphosphate cobalt(II) complex was confirmed by an X-ray diffraction study (Section S12). The solid-state structure of B displays the cobalt(II) ion within an all-oxygen octahedral coordination environment provided by the two \([\text{P}_3\text{O}_9\text{H}]^{3-}\) rings with a Co–O$_{avg}$ distance of 2.108(9) Å (Figure S64). An X-ray diffraction study of \([\text{PPN}]_2[\text{DME}]\) was not conducted as the solid-state structure of \([\text{NEt}_4]^3+\) [P(3,4)] has been reported previously. \(^{22}\)

Complex 1 is characterized by a \(^{31}\)P NMR resonance located at $\delta$ 616.7 ppm ($\Delta \nu_{1/2} = 466$ Hz, MeCN, 25 °C, Figure S1) that is assigned to the phosphorus atoms of the \([\text{P}_3\text{O}_9\text{H}]^{3-}\) ligand. This signal is shifted significantly downfield from that of monohydronitratetraphosphate ($\delta$ -22.5 ppm, MeCN) \(^{24}\) due to the influence imparted by the paramagnetic Co(II) $d^7$ metal center. Consistent with the presence of a high-spin Co(II) ion, complex 1 displays an $S = 3/2$ electronic configuration at 25 °C in D$_2$O, as determined by the Evans method ($\mu_{\text{eff}} = 4.10$ $\mu_\text{B}$). \(^{26}\) The electronic spectrum of 1 measured in MeCN (Figure S6, Figure S7) is characterized by absorptions located at $\lambda_{\text{max}}$ 487 (sh), 540 ($\epsilon = 5$ M$^{-1}$ cm$^{-1}$), and 1135 ($\epsilon = 1$ M$^{-1}$ cm$^{-1}$), which are assigned to the $A_{2g}(F) \rightarrow T_{1g}(F), A_{2g}(F) \rightarrow T_{1g}(F)$, and $T_{2g}(F) \rightarrow T_{1g}(F)$ transitions, respectively, based on the spectral features observed for other octahedral high-spin cobalt(II) complexes. \(^{27,28,29}\)

The $^{31}$P NMR spectrum of complex 2, recorded in acetonitrile, features a broad ($\Delta \nu_{1/2} = 3100$ Hz, Figure S8) singlet located at $\delta$ 1680 ppm that is assigned to the three equivalent phosphorus atoms of each \([\text{P}_3\text{O}_9\text{H}]^{3-}\) ligand. Complex 2 features absorptions located at $\lambda_{\text{max}}$ 449 ($\epsilon = 10$ M$^{-1}$ cm$^{-1}$), and 666 ($\epsilon = 4$ M$^{-1}$ cm$^{-1}$) in the visible region of the electromagnetic spectrum that are assigned to the $3T_{d}(P) \rightarrow 3T_{1g}$ and $3T_{2g} \rightarrow 3T_{1g}$ transitions, respectively (Figure S13). These bands compare well with the absorptions observed for similar octahedral vanadium(III) complexes supported by weak-field ligands. \(^{31}\) The magnetic moment for 2 ($\mu_{\text{eff}} = 2.99$ $\mu_\text{B}$), as measured by the Evans method \(^{25}\) (CD$_2$CN, 25 °C), is consistent with a triplet $d^5$ electronic configuration.

The \([\text{PPN}]_2[\text{I}]\) 2MeCN and \([\text{PPN}]_2[\text{DME}]\) DME salts have electrochemical and solubility properties that are attractive for NARFB applications. The solubilities of both salts in MeCN were determined using UV-vis spectroscopy. Acetonitrile is the optimal polar-organic solvent choice for the \([\text{PPN}]_2[\text{I}]\) 2MeCN and \([\text{PPN}]_2[\text{DME}]\) DME electrolytes as it is a commonly used solvent for NARFB applications on the basis of its wide electrochemical window (ca. 5 V) and low viscosity. \(^{32}\) The solubilities of \([\text{PPN}]_2[\text{I}]\) 2MeCN and \([\text{PPN}]_2[\text{DME}]\) DME in MeCN were determined to be 1.09 ± 0.02 and 0.77 ± 0.06 M, respectively. These solubilities compare favorably with those of other transition-metal complexes of acid for protonation of all three acac ligands of V(acac)$_3$. Two equivalents are provided by \([\text{PPN}]_2[\text{P}_3\text{O}_9\text{H}]_2\), and the third is provided by addition of one equivalent of \(\rho\text{-CF}_3\text{C}_6\text{H}_4\text{COOH}\). The \(\rho\text{-CF}_3\text{C}_6\text{H}_4\text{COOH}\) reagent was chosen as an appropriate acid for protonation of acac from V(acac)$_3$ based on $pK_a$ values, \(^{24}\) and due to the formation of the \([\text{PPN}]_2[\text{CF}_3\text{C}_6\text{H}_4\text{COO}]\) byproduct, which is easily separated away from \([\text{PPN}]_2[\text{DME}]\) by thorough washing of the isolated material with THF. Both \([\text{PPN}]_2[\text{I}]\) 2MeCN and \([\text{PPN}]_2[\text{DME}]\) were crystallized from MeCN/DME solvent mixtures, and isolated as crystalline solids in 82 and 68% yields, respectively.

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plex electrolytes, and exceed the operational concentration of V(acac)₃ (ca. 50 mM) by a factor of approximately twenty. The lower solubility of [PPN]₃[CoII(P₃O₉)₂]·2MeCN when compared with that of [PPN]₃[CoII(P₃O₉)₂]·2MeCN can be explained by the fact that complex 2 is trianionic and therefore is accompanied by three lipophilic PPN⁺ cations when compared with the four associated with 1.

In MeCN, 1 features a reversible oxidation located at E₁/₂ = +0.550 V vs. Fe/C₇Fe⁺ that is assigned to the CoII/III couple, and 2 exhibits a reversible reduction at E₁/₂ = −1.865 V vs. Fe/C₇Fe⁺ attributed to the VIII/II couple (Figure 1, A). Based on their combined reversible redox events, complexes 1 and 2 were paired to construct a cell with a theoretical voltage of 2.4 V in which 1 serves as the catholyte and cycles between Co(II) and Co(III) oxidation states, and 2 serves as the anolyte, cycling between V(III) and V(II) oxidation states. Within this system, both metal complexes undergo one electron redox events, and alternate between tri- and tetraanionic species (Figure 1, B).

Such a two-compartment static H-cell was assembled to assess the charge-discharge characteristics of 1 and 2 in MeCN (Section S8). The H-cell is commonly used to approximate the conditions of a flow system and allows for the use of small volumes of electrolyte solutions. The catholyte and anolyte compartments of the cell contained 5 mM MeCN solutions of 1 and 2, respectively, and Teflon coated stirbars were used in each reservoir to effect efficient mixing. The cell was run with [TBA][PF₆] supporting electrolyte, and the two compartments were separated with a Neosepta® (ASTOM, Japan) membrane (Figure 1, B). The Neosepta® membrane is an anion-exchange membrane with monovalent permeability, allowing for the transport of [PF₆]⁻ anions with minimal permeation of the redox-active multiply charged metal metaphosphate species, [Co(P₃O₉)₂]³⁺/³⁻, and [V(P₃O₉)₂]³⁻/²⁻. Electrodes constructed of high-surface-area carbon (with 1 cm² active areas) were used in each compartment of the cell. Galvanostatic cycling of the cell was performed at 80% state of charge (SOC), and the cell was charged and discharged at currents of 0.210 mA (C/2.5) and 0.0525 mA (C/10), respectively (Figure 2, top). Voltage cutoffs (0.5–3.1 V vs. Ag/Ag⁺) were selected on the basis of the cyclic voltammograms of each complex to ensure that only the desired redox couples were accessed.

The resulting cell displayed a Vcell of 2.4 V, which is consistent with the 2.4 V theoretical maximum voltage of the cell based on the CVs of each complex (Figure 1, A). The observed operating cell voltage of 2.4 V is among the highest we are aware of for the state-of-the-art NARBs involving metal-based redox systems that exhibit high cycling stability. The charge-discharge cycles of the 1-2 cell have high Coulombic efficiencies exceeding 90% for up to 100 cycles (Figure 2, bottom), with minor losses likely due to degradation of the anolyte after prolonged cycling, and small amounts of species crossover through the membrane (Section S8.1.1.). These efficiencies compare favorably with those reported for other NARB candidate systems and are higher than those reported for V(acac)₃ in similar cell designs (ca. 70%, 8,9). The excellent performance of metal metaphosphate polyanions in NARB applications is likely due in part to the high chemical and electrochemical stability of the all-inorganic trimetaphosphate ligands. Additionally, the polyanionic nature of all redox-active species relevant to cycling of the present cell is likely a key factor in the effective utilization of existing membrane technology as it contributes to minimal cross-contamination between the anolyte and catholyte compartments. We have addressed the stability of the anolyte and catholyte species within the context of the H-cell configuration and half-cell cyclability studies (Section S9). Future work will be needed at the full cell level to assess stability benchmarks relevant to an operating flow cell.
be populated to some extent at 25 °C. Solution magnetic susceptibility data of [PPN]$_3$[3-MeCN at 25 °C (Evans method, $\mu_{eff} = 3.32 \mu_B$, Cd$_2$CN) further substantiated contribution from the S = 2 high-spin state. These data in combination with the classification of trimetaphosphate as a weak-field ligand suggest that complex 3 exhibits a low-spin High-spin transition described by the $A_1g (O_2)$ $\leftrightarrow T_2g (O_3)$ states. In fact, many of the cobalt(III) complexes supported by the Kläui ligand exhibit singlet-quintet spin-crossover behavior as well.38-40 There is a large body of literature describing isoelectronic (3d$^8$) octahedral iron(II) spin-crossover complexes.41 and it has been well documented that the spin-state transition proceeds directly from $S = 0$ to $S = 2$, and never through a detectable $S = 1$ state.38

Collection of the $^{31}$P NMR spectrum of 3 at 25, 45, and 75 °C displayed corresponding downfield shifts in the $[P_2O_5]$$^3$- resonance ranging from 2.1 (25 °C) to 17.9 ppm (75 °C) (Figure S21). The solution magnetic susceptibility values also increased from $\mu_{eff} = 3.32$ (25 °C) to 3.74 $\mu_B$ (75 °C); these observations are consistent with thermally-induced spin crossover to a paramagnetic state at elevated temperature.27,42 The spin-crossover behavior is accompanied by a visually-detectable loss of color at low temperature (< 15 °C), and an intensification of the yellow color at elevated temperature (> 50 °C), as shown in Figure 3. These noticeable color changes allowed us to probe the spin-crossover behavior of 3 further through collection of variable-temperature UV-vis data (10-75 °C, Figure 3). The spin equilibrium was modeled by using the absorbance intensities at various temperatures and fitting the data to the Boltzmann distribution, 27,40,42,43 Values of $\Delta H$ and $\Delta S$ were extracted from the UV-vis data and determined to be, 56.02 ± 2.09 kJmol$^{-1}$, and 18.49 ± 2.09 kJmol$^{-1}$, respectively. These data allowed for calculation of the high-spin percentage at any given temperature, where the high-spin S = 2 percentage at 300 K was determined to be 34.0 ± 7.2%.

Electrochemical investigations of the spin-equilibrium phenomenon for spin-crossover complexes reveal that these systems display feature half-wave potentials that are highly temperature dependent.38 The fact that the spin crossover complex 3 is the active catalyze species generated during cell charging offers a unique opportunity to potentially expand the overall cell voltage ($V_{cell}$) of the present 1-2 system based on operating temperature.

Supporting Information Available: Experimental details and characterization data for all complexes including crystallographic data for [PPN]$_3$[Co(P$_3$O$_5$)$_2$]2MeCN. This material is available free of charge via the Internet at http://pubs.acs.org.

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