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Redox-Active Coordination Polymers from Esterified Hexavanadate Units and Divalent Metal Cations

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The redox-active bis(pyridyl)-capped hexavanadate $[V_6O_{13}\{(OCH_2)_3C(4\text{-}CONHC_5H_4N)\}_2]^{2-}$ (**1**) reacts with divalent first-row transition-metal cations (Mn^{II}, Co^{II}, Ni^{II}, or Zn^{II}) to yield crystalline linear zwitterionic coordination polymers (**1**M). The zwitterionic coordination chains are connected to each other by hydrogen bonds to form a 3D network. Microporous channels are formed along the packing axes of the 2D networks. All four compounds exhibit almost identical cell parameters, space group ($P\bar{1}$) and crystal morphology. The materials have been characterized by X-ray crystallography, ^1H and ^{51}V NMR, IR, UV/Vis, elemental analysis, and TGA. All compounds **1**M are reversibly reduced by chemical reductants such as phenylhydrazine and $NaBH_4$ in CCl_4 in which the hexavanadates are insoluble.

Introduction

Supramolecular coordination chemistry as a means to construct sophisticated solid materials has been a topic of intense research.[1] Recently, coordination polymers based on organic polyoxometalate (POM) derivatives and metal ions have attracted increasing attention because of the extensive and diverse properties of POMs.[2] In coordination polymers, POM units are generally formed under hydrothermal conditions, so it is difficult to relate the final structure and composition to the starting materials.[3] There are examples of applying preformed complete[4] or lacunary POMs[5] as ligands to metal ions to construct coordination polymers. However, the coordination modes of the POM oxo groups in the coordination polymers are complex and not defensibly predictable. By using pre-formed organic POM derivatives with a well-defined coordination mode as linking ligands, one can expect to design the morphologies and properties of the products from an understanding of the geometrical possibilities from the building units. Recently, coordination polymers using pre-formed organic POM derivatives have been reported. The first supramolecular coordination network materials[6] with pre-formed organic POM derivatives were reported by Stein et al. using organic POM derivatives with aniline moieties, $[W_6O_{25}H(AsC_6H_4\text{-}4\text{-}NH_2)_2]^{5-}$ and $[Mo_{12}O_{46}(AsC_6H_4\text{-}NH_2)_4]^{4-}$. In these materials, both the aniline moieties and POM oxo groups are coordinated to transition-metal ions. Stein et al. reported another coordination network assembled with Cu^{II}, (4,4′-bipyridyl)ethylene, and a preformed POM derivative, $[Mo_{12}O_{46}(AsC_6H_4NH_2)_4]^{4-}$.[7] In the network, the POM derivative behaves as a non-coordinating anion. Presumably because of the weak coordinating ability of the aniline, the coordination modes of the POM building units are complicated. More recently, Hasenknopf et al. reported the assembly of the polyoxomolybdate $[MnMo_6O_{18}\{(OCH_2)_3CNHCO(4\text{-}C_5H_4N)\}_2]^{3-}$ and $[PdCl_2(PhCN)_2]$, that yields a transparent and birefringent gel.[8] The design and construction of materials based on a redox-active building block with a pre-defined coordination mode and transformation into a crystalline coordination material would constitute an advance.

Here we report the preparation of a pyridine-terminated bis(trialkoxo)hexavanadate complex, $[V_6O_{13}\{(OCH_2)_3C(4\text{-}CONHC_5H_4N)\}_2]^{2-}$ (**1**), and the assembly of **1** with divalent transition-metal cations, M = Mn^{II}, Co^{II}, Ni^{II}, or Zn^{II}, to form POM-based coordination polymers. We are interested in the hexavanadate units esterified in a linear fashion with two chelating triols, $[V_6O_{13}\{(OCH_2)_3CR\}_2]^{2-}$, because the alkoxy groups of the chelating (triester)V_3 units are quite stable to hydrolysis,[9] and bis(triester)V_6 units can be extensively and reversibly reduced.[10] Unfortunately, the terminal R groups on the triester "caps" of the compounds reported to date, R = CH_3, CH_2CH_3, NO_2, and CH_2OH, bind metal ions poorly if at all.[10,11] Complex **1** can be viewed as a tunable, redox-active analogue of organic linking molecules such as 4,4′-bipyridine. A larger goal of this study, which we document, is the reversible reduction of POM-based open-framework coordination networks, and in particular oxidative regeneration (re-oxidation) by air. The latter phenomenon typically implies the ability of the POM-based

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material to catalyze air-based oxidations, an area of considerable interest in context with removal of pollutants, decontamination of toxic agents, environmental remediation, and green chemistry.[12–14]

Results and Discussion

The triol derivative $(HOCH_2)_3CNHCO(4\text{-}C_5H_4N)$ was prepared by the reaction of $(HOCH_2)_3CNH_2$ and isonicotinoyl chloride hydrochloride, $(4\text{-}C_5H_4N)COCl{\cdot}HCl$, in DMA under N_2 in the presence of K_2CO_3 at 60 °C for 72 h. The bis(pyridyl)-capped hexavanadate **1** was prepared by the reaction of $(HOCH_2)_3CNHCO(4\text{-}C_5H_4N)$ with $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$[15] in DMA under N_2 at 80 °C for 60 h, a modification of the method used by Zubieta and co-workers for the $\text{-}CH_3$, $\text{-}CH_2CH_3$, $\text{-}NO_2$, and $\text{-}CH_2OH$ derivatives,[10] and characterized by various spectroscopic methods and X-ray crystallography. Coordination polymers, $[M(DMF)_2(H_2O)_2(V_6O_{13}\{(OCH_2)_3CCONH(4\text{-}C_5H_4N)\}_2)]_n$ (M = Mn, Co, Ni, or Zn), were synthesized in 70–80% yield, by adding the appropriate transition-metal ion, dissolved either in methanol or in acetonitrile, to the stock solution of **1** in DMF and storing the solution at room temperature for 4–7 d. Regardless of the molar ratio of metal ion/**1**, zwitterionic (1:1 = divalent metal ion/**1**) compounds were obtained. In the case of **1**Ni and **1**Zn, single crystals suitable for X-ray diffraction were obtained by carefully layering the stock solution of **1** with a solution of the metal ion. In the case of **1**Mn and **1**Co, the formation of the product was relatively slow, so dilute solutions of each metal ion and the solution of **1** were mixed and the resulting solution was left undisturbed at room temperature for 4 d to afford single crystals suitable for X-ray diffraction.

All four coordination polymers **1**M (M = Mn, Co, Ni, or Zn) are nearly isostructural and exhibit almost identical unit cell parameters, space group ($P\bar{1}$) and crystal morphology. The metal atom, M, is in a symmetry-unique position in all four coordination polymers. This d-electron-containing metal center is located in a crystallographic inversion center and is six-coordinate with 2 DMF, 2 water, and 2 pyridine ligands all *trans* to each other (Figure 1). The divalent transition-metal ions and the pyridine-terminated triesterified polyoxovanadates form one-dimensional (1D) coordination chains. Interestingly, the 1D coordination chains are connected to each other by weak hydrogen bonds involving C–H moieties of the pyridine units to form microporous channels. Four different types of hydrogen bonds connect the 1D chains in a direction nearly parallel to the crystallographic *c* axis to form a two-dimensional (2D) network (Figure 2): (1) a relatively strong hydrogen bond between a coordinated water molecule and a bridging oxo group of the POM (O–O distance ca. 2.7 Å), weak hydrogen bonds between either pyridine hydrogen atoms and (2) bridging oxo groups of the POM (O–O distance ca. 3.3 Å) or (3) a terminal oxo group of the POM (O–O distance ca. 3.7 Å), and (4) hydrogen bonds between pyridine hydrogen atoms and carbonyl oxygen atoms of amide units (N–O distance ca. 3.7 Å). The 2D networks, in turn, are linked to each other in a direction nearly parallel to the crystallographic *a* axis by hydrogen bonds between a methyl hydrogen atom of the coordinated DMF molecule and a terminal oxo group (O–O distance ca. 3.4 Å) of the POM. Microporous channels are formed along the crystallographic *c* axis of the 2D networks (Figure 3).

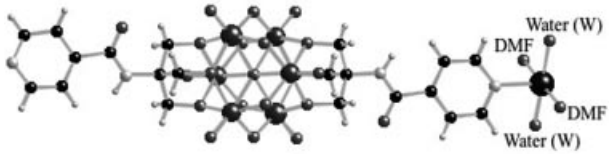

Figure 1. Structure of the repeating coordination unit of **1**Co. Selected distances [Å] and angles [°]: Co–O(DMF) 2.065(3), Co–O(W) 2.067(2), Co–N(pyridine) 2.157(2); O(DMF)–Co–O(W) 88.91(10), O(DMF)–Co–N(pyridine) 86.69(11), O(W)–Co–N(pyridine) 90.84(10).

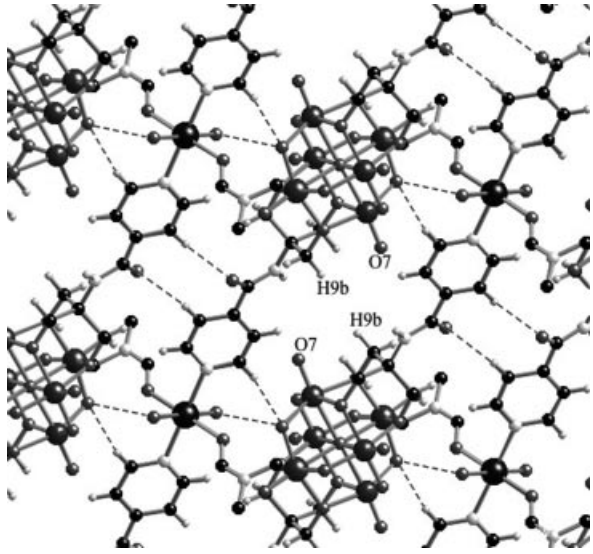

Figure 2. View parallel to the *a* axis. DMF molecules and some hydrogen atoms are omitted for clarity. Longest dimension (O7–O7) 5.54 Å, shortest dimension (H9b–H9b) 2.76 Å.

Bond valence sum (BVS) calculations[16] confirm that all six symmetry-distinct vanadium atoms in the hexavanadate unit are in the +5 oxidation state (values 5.0–5.1). The infrared and UV/Vis spectroscopic data are also consistent with vanadium(V).[17]

All the product polymers are slightly soluble (0.04–0.2 mM in the repeating unit) in polar aprotic solvents such as DMSO, DMF and CH_3CN and insoluble in non-coordinating solvents such as dichloroethane and chloroform. Both the ^1H and ^{51}V NMR spectra of **1**Zn and **1**Mn (see Figures S1 and S2 in the Supporting Information) clearly show that only the signals for the monomer are observed, and that these signals have effectively identical chemical shifts to that for **1** only. Expectedly, the ^1H NMR spectra of the polymers with paramagnetic centers (**1**M; M = Mn, Co, or Ni) exhibit broader signals than those of **1**Zn. Dissolution clearly involves dissociation of the pyridine–metal coordination bond in **1**M. The slow kinetics of formation/

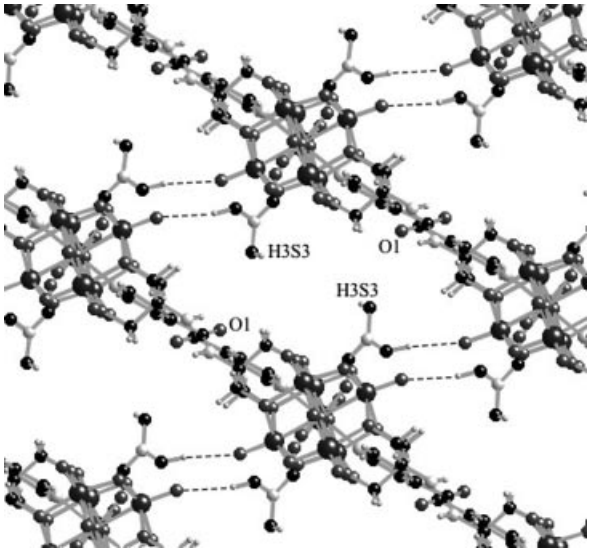

Figure 3. View parallel to the crystallographic *c* axis. Longest dimension (O1–O1) 8.89 Å, shortest dimension (H3S1–H3S1) 4.27 Å. Channel-filling DMF molecules and some hydrogen atoms are omitted for clarity.

crystallization as well as solubilization of all compounds **1**M precluded quantification of the dissociation equilibrium constants: K = [soluble monomer]. Dynamic light scattering (DLS) was attempted in order to corroborate the findings but the low solubility of dissociated monomers precluded acquisition of acceptable data.[18]

Thermogravimetric analysis (TGA) shows that the polymers **1**M are thermally less stable than the monomeric hexavanadate **1**. The polymers lose 20–30% of their total weight from 30 to 160 °C which correlates with the loss of the DMF molecules in the pores and the two DMF molecules coordinated to the metal ion in each formula unit. The differential scanning calorimetry (DSC) data supports the implications of TGA data. The IR spectra of **1**Zn at different temperatures were obtained to confirm the stability of the compound (see Figure S5).

The phase purity of the bulk material was evaluated by X-ray powder diffraction pattern (XRPD). The measured XRPD pattern matches well with that of the calculated one from the single crystal data (see Figure S6). Unfortunately, XRPD data of all compounds **1**M dried under vacuum (10^{-2} Torr for 2 d) indicated loss of crystallinity, consistent with the complete loss of framework structure upon the evacuation of the channel-occupying solvent molecules.

All compounds **1**M are reversibly reduced by chemical reductants such as phenylhydrazine and $NaBH_4$ in tetrachloromethane in which the compounds **1**M are insoluble. Reduction by $NaBH_4$ is much slower than that by phenylhydrazine. The reduced compounds **1**M are reoxidized without decomposition by any of the following: O_2, Br_2, Ce^{IV}, and $S_2O_8^{2-}$ (reoxidation by O_2 is very slow but accelerated in the presence of HCl vapor). The reduction and reoxidation of the hexavanadate unit can be easily detected from the distinctive change in color (red in fully oxidized state and blue in reduced species) and by the characteristic ν_{V-O-V} stretch for the fully oxidized hexavanadate unit at 790–810 cm^{-1} that shifts to a lower energy (750 cm^{-1}) upon reduction. The shift to a lower frequency upon reduction is consistent with protonation. Zubieta and co-workers documented longer V–O distances relative to those of fully oxidized hexavanadate units and protonated oxygen atoms by BVS calculations in the X-ray structure of the reduced forms of tris(alkoxo)hexavanadates.[19] The number of reduced vanadium atoms in the bis(triester)hexavanadate unit reproducibly determined by titration with Br_2 averages 2.5.

Conclusions

In conclusion, we have prepared a new class of POM-based supramolecular materials composed of the linear pyridine-terminated redox-active esterified hexavanadate units and divalent transition-metal cations (Mn^{II}, Co^{II}, Ni^{II}, or Zn^{II}). The terminal linking groups on the triester "cap" of the bis(triester)V_6 units, the metal composition of the POM units and the linking cations should all be independently variable affording a fairly diverse family of redox-active open-framework materials.

Experimental Section

General Methods and Materials: All chemicals were obtained from Aldrich. Dimethylacetamide (DMA) was dried with molecular sieves (3 Å) before use. Other chemicals were used as received. ^1H and ^{13}C NMR spectra were recorded either with a Varian INOVA 400 MHz instrument or a Mercury 300 MHz instrument. ^{51}V NMR spectra were recorded with a Varian Unity 600 MHz instrument. ^1H and ^{13}C NMR spectra were referenced to the deuterated solvent itself, and chemical shifts are reported relative to $(CH_3)_4Si$. ^{51}V NMR spectra were referenced externally by the sample replacement method to a 10 mM solution of $H_4PVMo_{11}O_{40}$ in 0.60 M NaCl (δ = –533.6 ppm relative to neat $VOCl_3$), and chemical shifts are reported relative to $VOCl_3$. IR spectra were recorded with a Nicolet 510 FT-IR instrument. Electronic absorption spectra were collected with a Hewlett-Packard 8452A UV/Vis spectrophotometer. Thermal gravimetric analyses (TGA) were performed with an ISI TGA 1000 instrument under N_2 flow from 25 to 400 °C at a rate of 10 °C/min. Differential scanning calorimetry (DSC) data were recorded with an ISI DSC 100 instrument under N_2 flow from 25 to 400 °C at a rate of 10 °C/min. Elemental analyses for C, H, and N were conducted by Atlantic Microlab, Norcross, GA, and elemental analyses for all other elements were conducted either by Desert Analytics, Tucson, AZ or by Kanti Lab Ltd., Mississauga, Ontario.

Preparation of $(HOCH_2)_3CNHCO(4\text{-}C_5H_4N)$: A solid mixture of K_2CO_3 (6.08 g, 44.0 mmol) and $(HOCH_2)_3CNH_2$ (2.42 g, 20.0 mmol) was added to a solution of isonicotinoyl chloride hydrochloride, $(4\text{-}C_5H_4N)COCl{\cdot}HCl$ (3.81 g, 21.4 mmol) in 30 mL of DMA under N_2. The resulting yellow solution and K_2CO_3 pellets were stirred under N_2 at 60 °C for 72 h. During the reaction, a decrease of the amount of K_2CO_3 pellets and the formation of a fine powder was observed. After the reaction batch was cooled to room temperature, the fine powder was filtered with a fine fritted glass filter. Acetone (150 mL) was added to the filtrate. After 1 d, the resulting crystalline material (needle morphology; isonicotinic acid, confirmed by ^1H NMR and IR) was filtered off, and the fil-

trate was concentrated to about 25 mL. Acetone (100 mL) was added to the concentrated solution. After 1 d, the resulting crystalline material was filtered off, and the filtrate was concentrated under vacuum to about 4 mL. To this concentrate was added 20 mL of acetone. After 1 d, a crystalline solid was obtained (2.8 g, 62%). The product was used for further reaction without additional purification. [Note 1: A small amount of isonicotinic acid (2–5% based on the integration of the ^{1}H NMR spectrum of the product) observed in the product could be removed by repeated (2–3 times) crystallization in DMA/acetone. Note 2: When the product was used for further reaction without additional purification, the impurity was successfully removed during the crystallization of the subsequent material, **1**.] ^{1}H NMR ([D$_6$]DMSO): δ = 3.68 (d, 12 H), 4.67 (t, 6 H), 7.49 (s, 1 H), 7.69 (d, 2 H), 8.69 (d, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 60.47 ($HOCH_2$), 63.78 (CNH), 122.16 (β-Py), 143.02 (γ-Py), 150.66 (α-Py), 166.19 (CO) ppm. $C_{10}H_{14}N_2O_4$ (226.23): calcd. C 53.09, H 6.23, N 12.38; found C 52.58, H 6.13, N 12.13. IR (KBr, 400–4000 cm^{-1}): $\tilde{\nu}$ = 3422 (s, br.), 3261 (w), 3097 (w), 3028 (w), 2920 (m), 2849 (w), 1733 (w), 1641 (s), 1607 (w), 1581(m), 1552 (m), 1493 (w), 1453 (w), 1418 (w), 1374 (w), 1054 (m), 1024 (m), 962 (w), 895 (w), 845 (w), 757 (w), 700 (m) cm^{-1}.

Preparation of [(*n*-$C_4H_9)_4N]_2[V_6O_{13}\{(CH_2O)_3CNHCO(4$-$C_5H_4N)\}_2]$·1.8DMF {[(*n*-$C_4H_9)_4N]_2$1·1.8DMF}: The bis(pyridyl)-capped hexavanadate **1** was prepared by a modification of the method reported by Zubieta and co-workers.[10] DMA (62 mL) was transferred to the solid mixture of $(HOCH_2)_3CNHCO(4$-$C_5H_4N)$ (1.21 g, 5.40 mmol) and $[(n$-$C_4H_9)_4N]_2[H_3V_{10}O_{28}]$ (3.01 g, 1.80 mmol). An orange solution resulted and the flask was wrapped with aluminum foil to protect the solution from potential photoreduction; stirring was continued under N_2 at 80–90 °C for 60 h. After the reaction batch was cooled to room temperature, the resulting deep reddish brown solution was filtered with a fine fritted glass filter. The filtrate was added to 180 mL of diethyl ether in ca. 1-mL portions using a Pasteur pipette. The dark brown precipitate was filtered and washed with diethyl ether. The pure product was obtained by repeated (normally two) crystallization [dimethylformamide (DMF)/acetonitrile/ether = 2:1:6]. After filteration and washing with diethyl ether, the resulting crystalline product was dried under vacuum at room temperature for 1 d. The yield (2.1 g, 45%) was calculated based on the amount of vanadium. The amount of the solvent in the crystal was confirmed by TGA. ^{1}H NMR ([D$_6$]DMSO): δ = 0.92 (t, 24 H), 1.30 (sext, 16 H), 1.55 (quint, 16 H), 3.15 (t, 16 H), 5.27 (d, 12 H), 7.69 (d, 4 H), 8.05 (s, 2 H), 8.67 (d, 4 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 14.20, 19.89, 23.75, 53.92 (CNH), 58.17, 82.71 ($HOCH_2$), 122.35 (β-Py), 142.66 (γ-Py), 150.61 (α-Py), 166.49 (CO) ppm. ^{51}V NMR ([D$_6$]DMSO): δ = –494.9 ppm. $C_{57.4}H_{106.6}N_{7.8}O_{22.8}V_6$ (**1**·1.8DMF, 1576.73): calcd. C 43.71, H 6.82, N 6.93, V 19.40; found C 43.61, H 6.80, N 6.95, V 19.49. UV/Vis (DMF): λ_{max} (ε) = 360 (6000 M^{-1} cm^{-1}) nm. IR (KBr, 400–4000 cm^{-1}): $\tilde{\nu}$ = 3345 (m, br.), 3272 (w), 2962 (m), 2934 (m, sh), 2876 (m), 1730 (w), 1669 (s), 1597 (w), 1540 (m), 1486 (m), 1407 (w), 1384 (w), 1322 (m), 1280 (w), 1188 (w), 1153 (w), 1102 (s),1050 (s), 953(s), 811 (s), 798 (m), 723 (s), 639 (m), 583 (m), 515 (w), 460 (w), 417 (m) cm^{-1}.

Preparation of Coordination Polymers

General Preparation: A 10.2 mM stock solution of **1** was used for the preparation of the polymers. The stock solution was prepared by dissolving 1.60 g (1.02 mmol) of **1** in 100 mL of DMF. Coordination polymers were synthesized by adding the appropriate transition-metal ions dissolved either in methanol or in acetonitrile to the stock solution of **1** (yield 70–80%). In the case of **1**Ni and **1**Zn, single crystals suitable for X-ray diffraction study were obtained by careful layering of a stock solution of **1** with the solution of each metal ion. In the case of **1**Mn and with **1**Co, dilute solutions of each metal ion and a solution of **1** were mixed, and the resulting solution was left undisturbed at room temperature for several days. Single crystals suitable for X-ray diffraction analysis were produced. Samples for elemental analysis were dried under vacuum for 2 d. The crystalline materials appeared to lose crystallinity when dried (the crystals lose luster when dried).

Preparation of $[Co(H_2O)_2(DMF)_2(V_6O_{13}\{(CH_2O)_3CNHCO(4$-$C_5H_4N)\}_2)]_n$ (1Co): A solution of $Co(NO_3)_2$ (5.2 mM) in acetonitrile and a stock solution of **1** (diluted from 10.2 mM to 5.1 mM) were mixed and left undisturbed for several days to form crystals suitable for X-ray diffraction. $C_{38.6}H_{69.4}CoN_{10.3}O_{29.2}V_6$ (**1**Co·4.2DMF, 1509.61): calcd. C 30.72, H 4.64, Co 3.91, N 9.47, V 20.27; found C 30.18, H 4.75, Co 4.01, N 9.44, V 19.5. The amount of solvent was consistent with the TGA data. IR (KBr, 400–4000 cm^{-1}): $\tilde{\nu}$ = 3399 (m, br.), 3261 (m), 2928 (m), 2860 (w), 1653 (s), 1543 (m), 1495 (w), 1438 (w), 1417 (w), 1386 (m), 1324 (w), 1283 (w), 1255 (w), 1101 (m), 1049 (m), 957 (s), 810 (m), 800 (m),720 (m), 622 (w), 618 (w), 583 (w), 417 (m) cm^{-1}.

Preparation of $[Mn(H_2O)_2(DMF)_2(V_6O_{13}\{(CH_2O)_3CNHCO(4$-$C_5H_4N)\}_2)]_n$ (1Mn): Complex **1**Mn was prepared according to the same procedure as described above for **1**Co except using $Mn(NO_3)_2$·xH$_2$O (x = 4–6) (in calculations x was taken as 6) in methanol as a metal source instead of $Co(NO_3)_2$·6H$_2$O in acetonitrile. $C_{33.8}H_{58.2}MnN_{8.6}O_{27.6}V_6$ (**1**Mn·2.6DMF, 1387.26): calcd. C 29.25, H 4.23, Mn 3.96, N 8.68, V 22.04; found C 28.68, H 4.33, Mn 4.25, N 8.55, V 21.6. The amount of solvent was consistent with the TGA data. IR (KBr, 400–4000 cm^{-1}): $\tilde{\nu}$ = 3251 (m, br.), 3060 (w), 2929 (w), 2867 (w), 1654 (s), 1545 (m), 1496 (w), 1438 (w), 1417 (w), 1387 (w), 1323 (w), 1284 (w), 1255 (w), 1187 (w), 1101 (m), 1050 (s), 958 (s), 809 (s), 795 (m), 718 (s), 641 (m), 586 (w), 515 (w), 420 (m) cm^{-1}.

Preparation of $[Ni(H_2O)_2(DMF)_2(V_6O_{13}\{(CH_2O)_3CNHCO(4$-$C_5H_4N)\}_2)]_n$ (1Ni): Single crystals suitable for X-ray diffraction were prepared by a solution diffusion method as follows. DMF (1.0 mL) was layered on top of 1.0 mL of a stock solution of **1** (10.2 mM) in a 5-mL test tube. To the layered DMF solution, 1.5 mL of a solution of $Ni(NO_3)_2$·6H$_2$O in acetonitrile (6.6 mM) was carefully added. After several days, single crystals suitable for X-ray diffraction were obtained. $C_{32.6}H_{55.4}N_{8.2}NiO_{27.2}V_6$ (**1**Ni·2.2DMF, 1361.78): calcd. C 28.75, H 4.10, N 8.44, Ni 4.26, V 22.47; found C 28.15, H 4.22, N 8.23, Ni 4.11, V 21.91. The amount of solvent was consistent with the TGA data. IR (KBr, 400–4000 cm^{-1}): $\tilde{\nu}$ = 3423 (m, br.), 2929 (w), 2863 (w), 1650 (s), 1541 (m), 1495 (w), 1436 (w), 1417 (w), 1384 (w), 1325 (w), 1282 (w), 1101(m), 1049(m), 958(s), 811(m), 723(m), 645 (w), 586 (w), 555 (w), 417(m) cm^{-1}.

Preparation of $[Zn(H_2O)_2(DMF)_2(V_6O_{13}\{(CH_2O)_3CNHCO(4$-$C_5H_4N)\}_2)]_n$ (1Zn): Single crystals suitable for X-ray diffraction were prepared according to the same method described for the crystallization of **1**Ni. $C_{31.4}H_{53.6}N_{7.8}O_{26.8}V_6Zn$ (**1**Zn·1.8DMF, 1340.25): calcd. C 28.16, H 4.04, N 8.16, V 22.84, Zn 4.78; found C 28.51, H 3.80, N 8.16, V 20.9, Zn 4.5. The amount of solvent was consistent with the TGA data. IR (KBr, 400–4000 cm^{-1}): $\tilde{\nu}$ = 3418 (s, br.), 3026 (w), 2921 (w), 2866 (w), 1733 (w), 1655 (s), 1539 (m), 1494 (w), 1451 (w), 1420 (w), 1385 (w), 1327 (w), 1282 (w), 1100 (m), 1066 (m), 1047 (s), 960 (s), 810 (s), 792 (s), 699 (s), 646 (m), 584 (w), 569 (w), 420 (m) cm^{-1}.

X-ray Crystallography: Suitable crystals of **1** and **1**M (M = Mn, Co, Ni, or Zn) were coated with Paratone N oil, suspended on a small fiber loop, and placed in a cooled nitrogen stream at 100 K

of a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite-monochromated Mo-K_α (0.71073 Å) radiation. Redundant data were measured using a series of combinations of φ and ω scans with 10 s frame exposures and 0.3° frame widths. Data collection, indexing, and initial cell refinements were handled using SMART software.[20] Frame integration and final cell refinements were carried out using SAINT software.[21] The final cell parameters were determined from least-squares refinements, and the SADABS program[22] was used to carry out absorption corrections. The structures were solved by direct methods and difference Fourier techniques. All atoms were refined anisotropically, except where noted (see data deposited in the crystal structure data base). The final *R*1 scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography*.[23] Additional details for **1** and **1**Co are provided in Table 1 (see crystallographic details for **1**Mn, **1**Ni, and **1**Zn in the crystal structure data base). CCDC-229734 to -229738 contain the supplementary crystallographic data for the structures reported upon in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data and structure refinement for **1** and **1**Co.

	1	**1**Co
Empirical formula	$C_{61}H_{115}N_9O_{24}V_6$	$C_{41.30}H_{75.70}CoN_{11.10}O_{30.10}V_6$
Formula mass	1664.26	1586.96
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	16.0689(9)	11.6301(7)
b [Å]	15.6178(9)	11.7707(7)
c [Å]	17.2400(1)	13.4852(8)
α [°]	90	91.801(1)
β [°]	115.118 (1)	112.050(1)
γ [°]	90	109.797(1)
V [Å^3]	3917.4(4)	1583.06(16)
Z	2	1
$D_{calcd.}$ [mg/m^3]	1.411	1.646
μ [mm^{-1}]	0.762	1.195
Reflections collected	69186	28163
Independent reflections	14310	11210
R(int)	0.0476	0.0567
GOF on F^2	1.014	1.032
$R1$ [$I > 2\sigma(I)$]	0.0674	0.0780
$wR2$ [$I > 2\sigma(I)$]	0.1920	0.2263

Reduction and Reoxidation of 1M: To **1**M suspended in CCl_4, where **1**M is completely insoluble, either chemical reductant, $NaBH_4$ or phenylhydrazine, was added, and the suspension was stirred for 36 h or 24 h, respectively. The reduction of **1**M can be easily observed from the distinctive change in the color of **1**M (red in fully oxidized state and blue in reduced state). Reduced **1**M was reoxidized in a separate reaction by O_2, Br_2, Ce^{IV}, or $S_2O_8^{2-}$.

Titration of Reduced 1Zn with Br_2: The number of reduced vanadium atoms in the bis(triester)hexavanadate unit was evaluated by titration with Br_2. To phenylhydrazine hydrochloride (104 mg, 0.720 mmol), suspended in 6.0 mL of chloroform, triethylamine (100 mL, 0.720 mmol) was added to obtain a homogeneous solution. Solid **1**Zn (160 mg, 0.120 mmol of repeating unit) was suspended in 10.0 mL of chloroform. To the suspension, the phenylhydrazine solution was added, and the mixture was stirred for 24 h. The initial red solid turned bluish green over the reaction period. The powder was then filtered and washed with methanol (2 × 5 mL) and diethyl ether (2 × 5 mL) and was suspended in 10.0 mL of tetrachloromethane (CCl_4). To this suspension, 0.10 M of Br_2 in CCl_4 was added slowly until the decoloration of Br_2 was no longer observed. The titration gives reproducible values within the experimental error (< 0.1 mL). An average of 3.0 mL of the Br_2 solution was added in the titrations. Therefore, the number of reduced vanadium atoms in the hexavanadate unit averages 2.5.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{51}V NMR of **1**Zn, ^{1}H NMR of **1**Mn, TGA of monomer and **1**Zn, DSC of monomer and **1**Zn, FT-IR of **1**Zn as a function of temperature, simulated and measured powder X-ray diffraction pattern, cyclic voltammetry data of **1** and analogous compounds.

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[18] In any event, the sizes of dissociated monomers, and aggregates of up to ca. 10 or more monomers, at these concentration, are likely below the lower limit for size distribution quantification by DLS. The intensity of light scattering is proportional to the concentration in solution and the cube of the size of the molecule.
[19] IR and crystallographic studies on the reduced forms of tris(alkoxo)hexavanadate units by Zubieta et al. shows that the protonation of the bridging oxo group in the reduced species lengthens the V–O bonds and results in the low energy shift of the ν_{V-O-V} stretch. See ref.[10]
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