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$[Co_2(ppca)_2(H_2O)(V_4O_{12})_{0.5}]$: A Framework Material Exhibiting Reversible Shrinkage and Expansion through a Single-Crystal-to-Single-Crystal Transformation Involving a Change in the Cobalt Coordination Environment**

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It is well known that many materials undergo structural phase transitions as a function of temperature, and that different atomic arrangements are stable in different temperature ranges. Although some of these phase transitions are irreversible, the original structure generally re-forms readily upon returning to the initial temperature. This process is fundamentally different from that observed for a small and rather unique category of organic–inorganic framework materials that exhibit so-called "dynamic structural changes".[1] In these materials, temperature changes lead to the reversible removal of guest molecules which is often accompanied by large atomic motion and significant changes in the framework structures.[1b,c] Importantly, the original framework structure is not restored by a temperature change, but rather by the reabsorption of the guest molecules.[2] As structural changes upon loss of guest-molecules are typically induced by heating of a porous three-dimensional framework, significant thermal stability, both in the presence and absence of guest molecules, is a necessity.

Dynamic structural changes induced by the removal/reabsorption of guest molecules are rare, and even less common are those structural changes that are caused by the removal/addition of ligands from the framework itself. Such changes in metal coordination environment can lead to changes in physical properties, for example, color, and could potentially lead to their use in sensing devices.[1,2]

Herein, we describe the synthesis and structural characterization of a new, mixed-metal 3D porous coordination polymer: $[\{[Co_2(ppca)_2(H_2O)(V_4O_{12})_{0.5}]\cdot 3.62\,H_2O\}_n]$ (**1**, ppca = 4-(pyridin-4-yl)pyridine-2-carboxylic acid; Scheme 1),

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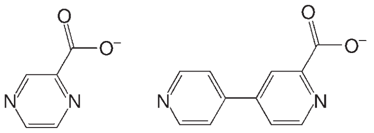
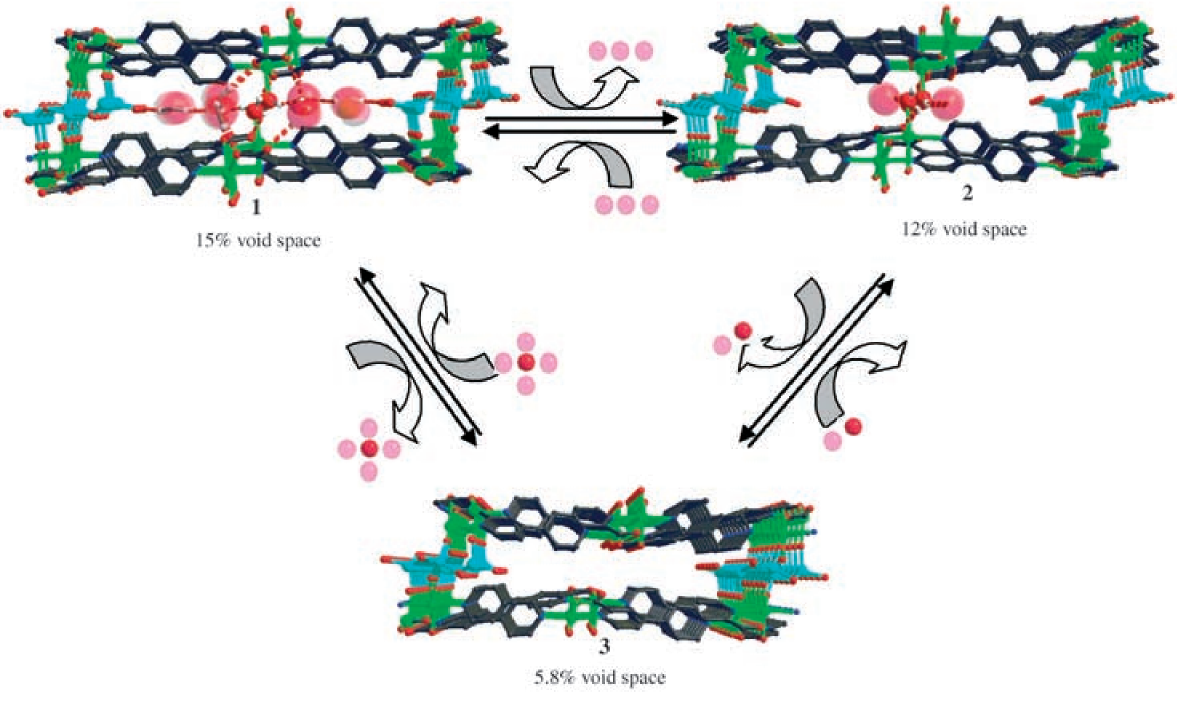


Scheme 1. Structure of 2-pyrazinecarboxylate (left) and the much longer 4-(pyridin-4-yl)pyridine-2-carboxylic acid (ppca) (right).

which undergoes two distinct, reversible single-crystal-to-single-crystal transformations (Scheme 2). The first involves a volume change owing to the reversible removal of guest solvent molecules from the pores of the framework, where shrinkage occurs upon dehydration and reexpansion occurs upon reintroduction of the guests. The second process involves an unusual change in the coordination number of the cobalt center, from 6 (octahedral) to 5 (trigonal bipyramidal), with a concomitant color change.

Our group has previously explored heterometallic coordination polymers with the pyrazinecarboxylate ligand,[3] (Scheme 1) as the simultaneous presence of two different metals can give rise to increased structural diversity and, potentially, to unusual physical properties resulting from the synergistic interaction of two different metal centers.[4] The pyrazinecarboxylate ligand and its substituted derivatives have proven to be extremely versatile for the construction of mixed-metal framework structures because of their ability to engage in several different coordination modes.[3,5] In framework structures synthesized from pyrazinecarboxylate-based ligands, however, the cavity dimensions are limited by the length of the pyrazine ring. Consequently, to increase the cavity dimensions, we recently synthesized a new ligand, 4-(pyridin-4-yl)pyridine-2-carboxylic acid (Hppca) (Scheme 1),[6] which is significantly longer than the pyrazinecarboxylate ligand, but maintains the same number, type, and arrangement of Lewis basic sites. Molecular modeling showed that the terminal N–N separation is about 7.10 Å in Hppca in contrast to 2.75 Å in pyrazinecarboxylate-based ligands. This extension of pyrazinecarboxylate chemistry allows the synthesis of frameworks with larger cavities than those observed in the pyrazinecarboxylate-based framework structures. Consequently, we are exploring the use of this ligand in the preparation of new mixed-metal systems, and herein we report an interesting new framework structure in which cobalt atoms are linked into a 2D array by ppca and cross-linked into a 3D array by vanadium-oxo units. It is well known that vanadium oxide groups are often engaged in the cross-linking of structural components and that they can promote the formation of unique structural geometries.[7] Whereas the coordination modes of the cobalt and the vanadium in this structure are fairly typical for these elements, surprising is the observation of dynamic structural changes that take place upon the thermal removal of both noncoordinated and coordinated water molecules, the process of which is highlighted herein.

The hydrothermal reaction of Hppca, $Co(NO_3)_2{\cdot}6\,H_2O$, and NH_4VO_3 in a 1:1:1 ratio at 160 °C for 48 h yielded small, red, block-shaped crystals of the title compound. Structural analysis of **1** by single-crystal X-ray diffraction revealed that the vanadium centers are part of 1D mixed-metal chains, in which $\{V_4O_{12}\}$ cyclic units bridge neighboring 2D Co/ppca metal–organic layers to form a 3D open framework. The structure contains two crystallographically independent cobalt atoms, Co1 and Co2, which are both found in pseudooctahedral coordination environments. Co1 is coordinated to two oxygen atoms from two different $\{V_4O_{12}\}$ units and to three different ppca ligands; Co2 is likewise coordi-



Scheme 2. The reversible single-crystal-to-single-crystal transformations between **1**, **2**, and **3**; noncoordinated and coordinated H_2O molecules are shown as large opaque and large solid, red spheres, respectively. Hydrogen bonds are indicated by dotted red lines.

nated to three different ppca ligands, but to only one oxygen from one $\{V_4O_{12}\}$ unit, leaving the sixth coordination site occupied by a water molecule (Figure 1).

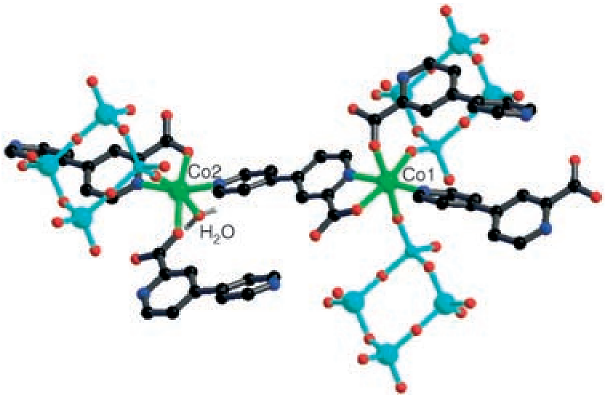


Figure 1. View of the coordination environments of the two crystallographically independent cobalt centers and the ligand coordination mode of **1**. Co: green; V: cyan; O: red; C: black; N: blue; H: white.

As shown in Figure 1, each ppca ligand is coordinated to one cobalt atom in a bidentate fashion through one carboxylate oxygen atom and the adjacent nitrogen atom of the ring. The second nitrogen atom of the ligand is coordinated to a second cobalt atom, and the remaining carboxylate oxygen atom further coordinates to a third cobalt atom in a monodentate fashion in the *syn,anti* carboxy mode. Thus, each ppca ligand functions in a μ_3-bridging mode that leads to 2D layers with the composition $[\{Co_2(ppca)_2(H_2O)\}_\infty]$ (Figure 2a).

The VO_3^- anion of the ammonium vanadate reagent is the source of the tetrahedral vanadium in the present structure. Vanadium is found in complex **1** as $\{V_4O_{12}\}$ units, which bridge the 2D metal–organic layers described above, and in doing so, become an integral part of 1D inorganic $[\{Co_4(V_4O_{12})\}_\infty]$ chains (Figure 2b). When one considers the connectivity between the 2D metal–organic layers and the 1D mixed-metal chains, the overall structure is best described as a 3D porous organic–inorganic framework containing rectangular channels of approximate dimensions 5.2 × 22.3 Å^2 (atom-to-atom) running parallel to the *c* axis (Figure 3) and 5.6 × 11.3 Å^2 along the *a* axis (see Supporting Information). These channels constitute 15% of the crystal volume[8] and are much larger than those found in similar complexes constructed from the simple pyrazinecarboxylate ligand.[6b,c] The channels are filled by guest water molecules that participate in a collective, well-ordered hydrogen-bonded network involving water molecules, carboxylate oxygen atoms, and the vanadium oxide units of the framework (see Supporting Information).

It is a well-known phenomenon that guest solvent molecules located in cavities or channels can often be removed from the framework structure without causing framework collapse and, furthermore, that they can sometimes also be reinserted. To explore this possibility, single crystals of the present cobalt–vanadium framework were heated to different temperatures. These crystals were then analyzed by single-crystal X-ray diffraction. Heating the single crystals to 150 °C for 1 day yielded $[\{[Co_2(ppca)_2(H_2O)(V_4O_{12})_{0.5}]\cdot 0.55\,H_2O\}_n]$ (**2**) (see Supporting Information). The structure determination of **2** revealed that the crystal system and space group remain the same as those of **1**, but that approximately three water molecules had been removed from the pores per formula unit. The remaining water molecules are located near Co2, where they form hydrogen bonds to the coordinated water ligand (see Supporting Information). These hydrogen bonds appear to impart the noncoordinated water molecules with enhanced thermal stability. The removal of the three water molecules of hydration is accompanied by a slight decrease in cell volume (from 1411 to 1336 Å^3) and in

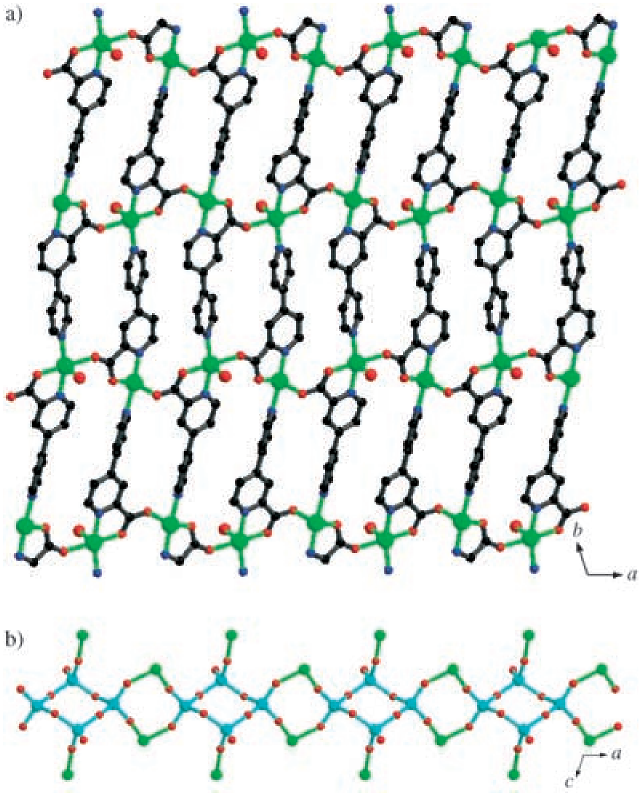


Figure 2. a) 2D metal–organic layer of composition $[\{Co_2(ppca)_2(H_2O)\}_\infty]$; b) 1D inorganic chains of composition $[\{Co_4(V_4O_{12})\}_\infty]$. Co: green; V: cyan; C: black; O: red.

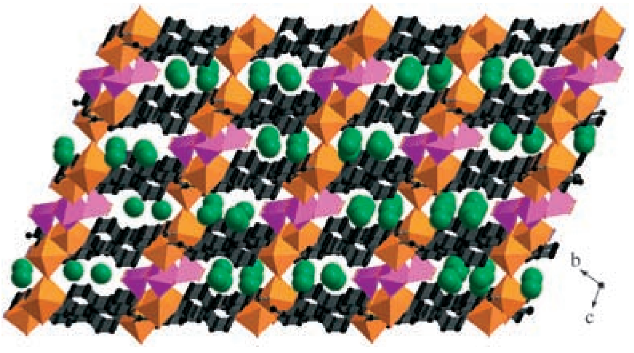


Figure 3. View of the 3D porous organic–inorganic framework with rectangular channels filled with guest water molecules. The guest water molecules are shown as large green spheres; Co octahedra: orange; V tetrahedra: pink.

the volumes of the channels (from 15 to 12 % of the total crystal volume).[8]

Immersion of crystals of **2** in water results in complete rehydration and re-formation of the original structure, including the hydrogen-bonding network observed in the original structure of **1** (see Supporting Information). The unit-cell volume of the rehydrated framework material was determined to be 1409.5(1) Å^3, and the channels again constitute 15 % of the total crystal volume.[8] The reintroduction of guest water molecules also occurs spontaneously when crystals of **2** are exposed to air; they take less than 1 week to become fully saturated, and the process demonstrates that the removal and reinsertion of the guest water molecules is completely reversible.

Next, to investigate the removal of all noncoordinated and coordinated water molecules, single crystals of **1** were heated to 300 °C for 2 h. The effects of heating were again analyzed by single-crystal X-ray diffraction. The structure determination of $[\{Co_2(ppca)_2(V_4O_{12})_{0.5}\}_n]$ (**3**) confirmed the complete removal of the guest water molecules as well as the removal of the water molecule coordinated to Co2 (see Supporting Information). Although the crystal system and space group remain unchanged, the 3D framework is significantly changed from that of **1** or **2** in that the Co2 center in **3** is now only five-coordinate and has changed from an octahedral (as in **1** or **2**) to a trigonal bipyramidal coordination environment (Figure 4). Accompanying this change in the cobalt coordination environment is a color change from red to brown (Figure 5). Whereas **3** remains almost isostructural with **1** or **2**, the 2D metal–organic layer in **3** has the composition $[\{Co_2(ppca)_2\}_\infty]$, rather than $[\{Co_2(ppca)_2(H_2O)\}_\infty]$. More importantly, however, the unit-cell volume is decreased further and the channels only retain one-third of their original volume, now constituting only 5.8 % of the total crystal volume.[8]

Brief immersion of **3** into water or exposure to air for several days completely reverses the structural change, and the original material, **1**, including the coordinated water molecule, is reconstituted (see Supporting Information). Thus the rehydration process is accompanied by return of the original color (Figure 5). A crystallographic investigation determined that the structure of the reconstituted **3** is the same as that of **1** (see Supporting Information).

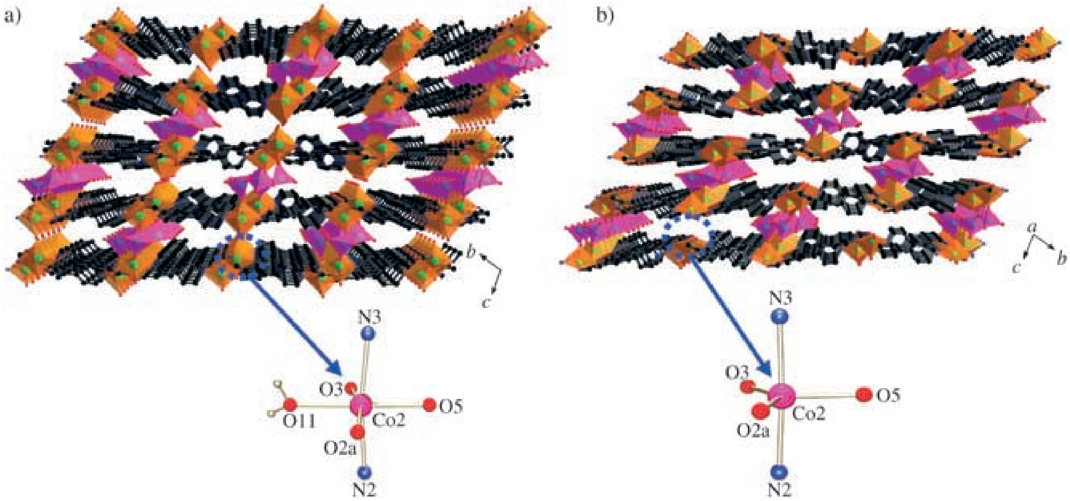


Figure 4. a) View of the $[\{Co_2(ppca)_2(H_2O)(V_4O_{12})_{0.5}\}_n]$ framework containing hydrated Co2 in an octahedral coordination environment; b) view of the dehydrated $[\{Co_2(ppca)_2(V_4O_{12})_{0.5}\}_n]$ framework containing Co2 in a trigonal-bipyramidal coordination environment.

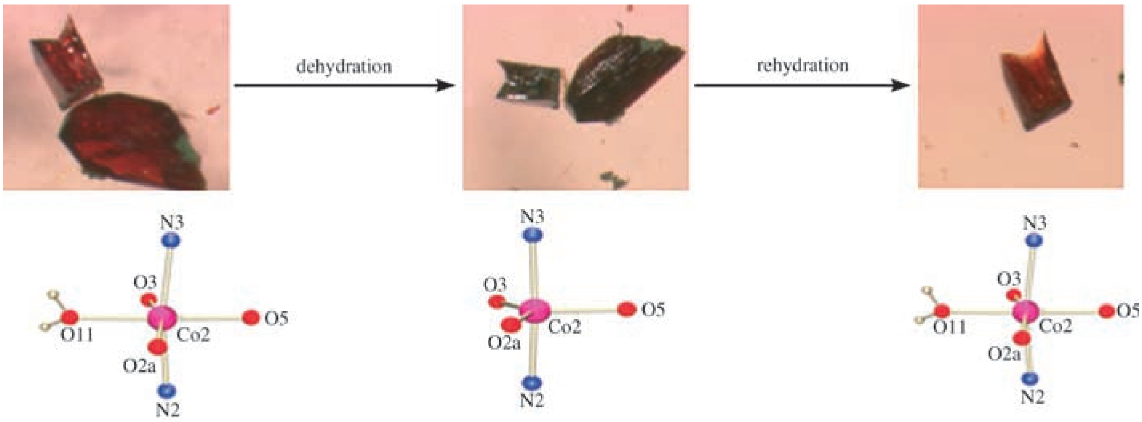


Figure 5. Pictorial representation of the dehydration and rehydration processes. The red crystal turns brown upon dehydration and change of the cobalt coordination environment from octahedral to trigonal bipyramidal. The crystal changes back to the original red color upon rehydration and returns to the original octahedral cobalt coordination environment.

A closer analysis of the structure of **3** suggests a possible cause for such a large decrease in volume upon complete dehydration. The removal of the coordinated water molecule from Co2 removes a quasi-pillaring between the channel walls (Figure 4), hence allowing a shear motion to bring the channel walls closer together. Thus, whereas the removal of the guest water molecules leads to a small decrease in volume, similar to what has been observed in other framework materials,[9] it is the removal of the coordinated water molecules that initiates the more substantial channel "collapse".

In summary, we have successfully synthesized a vanadium oxide bridged, mixed-metal 3D porous framework by using the new ligand ppca. The framework undergoes a dynamic structural change initiated by the removal of both non-coordinated and coordinated water molecules. The most significant structural change involves an unusual transformation of the local Co2 coordination environment, permitting unusual shrinkage and expansion in a single-crystal-to-single-crystal dehydration/rehydration process. Clearly, the existence of the five-coordinate cobalt center suggests a series of follow-up experiments to determine if the religation is possible with, for example, ammonia, rather than water. Such experiments will be performed in the near future.

Experimental Section

1: Hppca (0.2 mmol), $Co(NO_3)_2\cdot 6H_2O$ (0.2 mmol), and NH_4VO_3 (0.2 mmol) were mixed in an aqueous solution (12 mL). The mixture was stirred at room temperature for about 1 h, and then placed in a 45-mL teflon-lined autoclave and heated at 160 °C for 2 days. Red crystals of **1** formed and were manually isolated, washed with water, and dried in air (9.4 mg, 12 %). The structural consistency and phase purity of the product was checked by comparison of the observed X-ray diffraction pattern with that calculated from the single-crystal structural data (see Supporting Information). Single-crystal X-ray crystallography was carried out on a Bruker SMART APEX CCD diffractometer system.[10]

1: $C_{22}H_{23.25}Co_2N_4O_{14.62}V_2$, $M = 797.42$, triclinic, space group $P\bar{1}$, $a = 9.7957(5)$, $b = 11.3068(6)$, $c = 14.1357(8)$ Å, $\alpha = 101.755(1)$, $\beta = 104.449(1)$, $\gamma = 104.087(1)°$, $V = 1411.0(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.877$ g cm^{-3}, $T = 150(1)$ K, $F(000) = 800$, $\mu(Mo_{K\alpha}) = 1.877$ mm^{-1}, red block crystal, 16047 reflections measured, 5759 unique ($R_{int} = 0.0417$), 432 parameters, $R_1 = 0.0320$ ($I > 2\sigma(I)$), $wR_2 = 0.0743$ (all data), GOF = 0.957.

2: $C_{22}H_{17.10}Co_2N_4O_{11.55}V_2$, $M = 742.04$, triclinic, space group $P\bar{1}$, $a = 9.6788(8)$, $b = 10.8844(9)$, $c = 13.925(1)$ Å, $\alpha = 99.698(2)$, $\beta = 106.605(2)$, $\gamma = 101.615(2)°$, $V = 1336.5(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.844$ g cm^{-3}, $T = 150(1)$ K, $F(000) = 739$, $\mu(Mo_{K\alpha}) = 1.966$ mm^{-1}, red block crystal, 11562 reflections measured, 4269 unique ($R_{int} = 0.0458$), 386 parameters, $R_1 = 0.0391$ ($I > 2\sigma(I)$), $wR_2 = 0.0927$ (all data), GOF = 1.075.

1 (reconstituted from **2**): $C_{22}H_{23.26}Co_2N_4O_{14.63}V_2$, $M = 797.53$, triclinic, space group $P\bar{1}$, $a = 9.7941(6)$, $b = 11.2958(7)$, $c = 14.1310(9)$ Å, $\alpha = 101.728(1)$, $\beta = 104.447(1)$, $\gamma = 104.054(1)°$, $V = 1409.5(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.879$ g cm^{-3}, $T = 150(1)$ K, $F(000) = 801$, $\mu(Mo_{K\alpha}) = 1.879$ mm^{-1}, red block crystal, 13392 reflections measured, 5009 unique ($R_{int} = 0.0458$), 432 parameters, $R_1 = 0.0349$ ($I > 2\sigma(I)$), $wR_2 = 0.0821$ (all data), GOF = 0.978.

3: $C_{22}H_{14}Co_2N_4O_{10}V_2$, $M = 714.11$, triclinic, space group $P\bar{1}$, $a = 9.6775(9)$, $b = 10.3376(9)$, $c = 13.7956(13)$ Å, $\alpha = 76.531(2)$, $\beta = 75.321(2)$, $\gamma = 82.387(2)°$, $V = 1294.4(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.832$ g cm^{-3}, $T = 150(1)$ K, $F(000) = 708$, $\mu(Mo_{K\alpha}) = 2.022$ mm^{-1}, brown block crystal, 12073 reflections measured, 4140 unique ($R_{int} = 0.0639$), 361 parameters, $R_1 = 0.0429$ ($I > 2\sigma(I)$), $wR_2 = 0.0873$ (all data), GOF = 1.021.

1 (reconstituted from **3**): $C_{22}H_{22.66}Co_2N_4O_{14.33}V_2$, $M = 792.13$, triclinic, space group $P\bar{1}$, $a = 9.7987(8)$, $b = 11.270(1)$, $c = 14.200(1)$ Å, $\alpha = 101.799(2)$, $\beta = 104.251(2)$, $\gamma = 103.899(2)°$, $V = 1416.3(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.857$ g cm^{-3}, $T = 294(2)$ K, $F(000) = 795$, $\mu(Mo_{K\alpha}) = 1.868$ mm^{-1}, red block crystal, 10344 reflections measured, 4522 unique ($R_{int} = 0.0481$), 401 parameters, $R_1 = 0.0363$ ($I > 2\sigma(F)$), $wR_2 = 0.0750$ (all data), GOF = 0.966.

CCDC-275335 (**1**), -275336 (**2**), -275337 (**1** reconstituted from **2**), -275338 (**3**), and -275339 (**1** reconstituted from **3**) contain the supplementary crystallographic data for 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.

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