

Modular Inorganic Polyoxometalate Frameworks Showing Emergent Properties: Redox Alloys**

Johannes Thiel, Chris Ritchie, Haralampos N. Miras, Carsten Streb, Scott G. Mitchell, Thomas Boyd, M. Nieves Corella Ochoa, Mali H. Rosnes, Jim McIver, De-Liang Long, and Leroy Cronin*

The targeted synthesis of new extended modular frameworks exhibiting specific properties is a principal challenge of modern chemistry research.^[1–3] Many inorganic frameworks^[4,5] and metal–organic frameworks (MOFs)^[6,7] have been reported, but the fine manipulation of their electronic properties remains challenging.^[8] One such approach could be the development of molecular alloys, analogous to metal alloys, yet this idea has rarely been applied, and three dimensional (3D) framework alloys based upon molecular building blocks have not yet been fully realized. Conceptually, the design of 3D framework alloys could be achieved if the components of two isostructural frameworks “A” and “B” could be mixed at the molecular level (in any proportion) forming a crystal of AB units, perfectly arranged, so the AB alloy is also isostructural to frameworks A and B.^[9] The potential applications of such an approach are highly appealing, since the combination of coordination-compound-based building blocks, exhibiting different electronic properties, could allow the targeted tuning of frameworks with properties intermediate between A and B; and even the realization of “emergent” or unexpected properties for the alloy.

In an attempt to develop an approach to this goal, we opted to use polyoxometalate (POM) building blocks, which are early-transition-metal oxide clusters that are well-known for the versatility of their physical and chemical properties.^[10] Their applications cover a wide area of chemical research including, but not limited to, catalysis,^[11] molecular magnetism,^[12] and medicine.^[13] However, more importantly in the current context, they exhibit a very diverse and susceptible redox chemistry and therewith offer the prospect to fine-tune their electronic properties.^[14]

Recently, we reported the first examples of isostructural framework compounds based purely on polyoxometalate clusters,^[15] in which the electronic fine-tuning of the building blocks has been taken into account. Furthermore, these

materials were the first POMs to undergo genuine reversible single-crystal to single-crystal (SC-SC) redox reactions whereby the oxidation state of the material changed.^[16] The networks consist of manganese-substituted α -Keggin-type tungsten oxide clusters, which are fused by multiple Mn–O linkages (see Figure 1) and are of the general formula

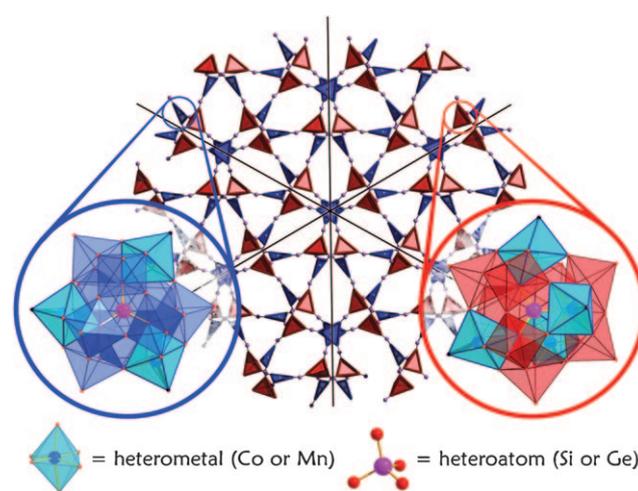


Figure 1. Representation of the “Keggin-net” structure $(C_4H_{10}NO)_m[W_{72}M^{II/III}_{12}X_7O_{268}]$ (where $M = Co^{II}$ or Mn^{III} ; $X = Si$ or Ge) constructed from two types of transition-metal-substituted α -Keggin clusters: 4-connected (red) and 3-connected (blue). The overall structure is represented by linked 3- and 4-connected polyhedra with the oxygen linkers (pink spheres) and the structure of the 3- and 4-connected Keggin-nodes shown in blue and red inserts, respectively. Inserts: The “modular” or interchangeable components are shown as cyan polyhedra (the octahedrally coordinate heterometal center) and pink balls (the tetrahedrally coordinate heteroatom center). Heterometal (Mn or Co): cyan; W: red, and blue octahedra; O: small red spheres; heteroatom (Si or Ge): pink spheres.

$(C_4H_{10}NO)_{40}[W_{72}Mn^{III}_{12}X_7O_{268}]$ ($X = Si$ or Ge heteroatom). Embedded in the framework are two types of α -Keggin anions acting as either 3-connected or 4-connected building blocks resulting in the cubic germanium nitride like network structure.^[17]

Herein we show that it is possible to develop fully modular redox frameworks based upon the structural type, $(C_4H_{10}NO)_m[W_{72}M^{II/III}_{12}X_7O_{268}]$ by changing both the linking heterometal ions, M, and the heteroatoms, X. As such, the linking metal ion can be either $Mn^{II/III}$ or $Co^{II/III}$ and the heteroatoms can be Si^{IV} or Ge^{IV} so that four pure frameworks

[*] J. Thiel, Dr. C. Ritchie, Dr. H. N. Miras, Dr. C. Streb, S. G. Mitchell, T. Boyd, M. N. Corella Ochoa, M. H. Rosnes, J. McIver, Dr. D.-L. Long, Prof. L. Cronin
WestCHEM, School of Chemistry, The University of Glasgow
Glasgow G12 8QQ (UK)
Fax: (+44) 141-330-4888
E-mail: l.cronin@chem.gla.ac.uk
Homepage: <http://www.croninlab.com>

[**] This work was supported by the ESPRC, the Leverhulme Trust, WestCHEM, and the University of Glasgow.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201002672>.

can be synthesized by one-pot syntheses: $(\text{Mn}^{\text{III}}\text{Si}) = \mathbf{1a}$, $(\text{Mn}^{\text{III}}\text{Ge}) = \mathbf{2a}$, $(\text{Co}^{\text{II}}\text{Si}) = \mathbf{3a}$, and $(\text{Co}^{\text{II}}\text{Ge}) = \mathbf{4a}$; and four more compounds can be accessed by post-synthetic modification (reduction for the Mn-based compounds and oxidation for the Co-based ones): $(\text{Mn}^{\text{II}}\text{Si}) = \mathbf{1b}$, $(\text{Mn}^{\text{II}}\text{Ge}) = \mathbf{2b}$, $(\text{Co}^{\text{III}}\text{Si}) = \mathbf{3b}$, and $(\text{Co}^{\text{III}}\text{Ge}) = \mathbf{4b}$. In addition, substituted transition-metal ion mixtures ($\text{Co}^{\text{II}}/\text{Mn}^{\text{III}}$) of the frameworks can be synthesized, yielding “alloy” framework materials of formula $[(\text{Mn}^{\text{III}})_x(\text{Co}^{\text{II}})_{12-x}\text{Si}_y\text{Ge}_{7-y}]$ (**5**; see Figure 1). We show that these “alloy” materials are synthetically accessible solid mixtures containing the different heterometals blended at the molecular level (i.e. not mixtures of discrete single crystals with the average composition of a mixture) and, additionally, these materials show distinctive physical properties as a result of their “alloy-like” nature when compared to the “native” compounds, **1a/b–4a/b**.

It is important in the context of this work to note that the reaction conditions for the previously synthesized Mn-based framework compounds **1a** and **2a**,^[15,16] were used as the starting point to incorporate Co into the system to produce compounds **3–5**, that is, they crystallized under near-identical conditions from aqueous morpholine-buffered media over a period of 1–2 months as tetrahedral crystals in greater than 10% yield. To elucidate the structural details and the exact composition the compounds have been fully characterized by IR, UV/Vis, and flame atomic absorption spectroscopy (FAAS), elemental analysis, redox titrations, and extensive single-crystal X-ray crystallographic investigations. Importantly, the combination of these techniques shows that the mixed-metal frameworks **5** are, in fact, intrinsic mixtures, rather than crystal mixtures of distinct transition-metal-substituted frameworks (see Figure 2 and see Supporting Information for further details).

Firstly, the heterometal atoms, that is, manganese ions found in the archetypal “Keggin-Net” compounds $\{\text{Mn}^{\text{III}}\text{Si}\}$ **1** and $\{\text{Mn}^{\text{III}}\text{Ge}\}$ **2** can be replaced for cobalt through a minor modification of the synthetic procedure, thereby giving access to two further compounds of the composition $(\text{C}_4\text{H}_{10}\text{NO})_{46}[\text{W}_{72}\text{Co}^{\text{II}}_{12}\text{X}_7(\text{OH})_6\text{O}_{262}]$ ($\text{X} = \text{Si}$ ($\text{Co}^{\text{II}}\text{Si}$) or Ge ($\text{Co}^{\text{II}}\text{Ge}$)), compounds **3a** and **4a** respectively. Contrary to the archetypal frameworks (those containing Mn^{III}),^[15,16] the “native” oxidation state of the heterometal in compounds **3a** and **4a** is Co^{II} . This opens the door to the possibility of performing comparative investigations on the redox behavior of the Mn- and Co-based “Keggin-Nets” by single-crystal to single-crystal (SC-SC) transformations. Comparison of the redox behavior between the “native” Mn- and Co-frameworks is straightforward since the Co frameworks, **3** and **4**, require oxidation of $\text{Co}^{\text{II}}\text{X}$ to $\text{Co}^{\text{III}}\text{X}$; while the Mn versions, **1** and **2**, require reduction of $\text{Mn}^{\text{III}}\text{X}$ to $\text{Mn}^{\text{II}}\text{X}$.

Structurally, the 3-connected and 4-connected α -Keggin-cluster-type building blocks arrange in an ABA'B' packing mode (see Figure 1). The framework is topologically identical to that of cubic germanium nitride network which also crystallizes in the space group *I-43d*. This material has the formula Ge_3N_4 , with the germanium atoms acting as 4-connected nodes and the nitrogen atoms as 3-connected nodes.^[17] In **3** and **4**, the 3-connected Keggin building block, which is horizontally situated in the first layer A, can be

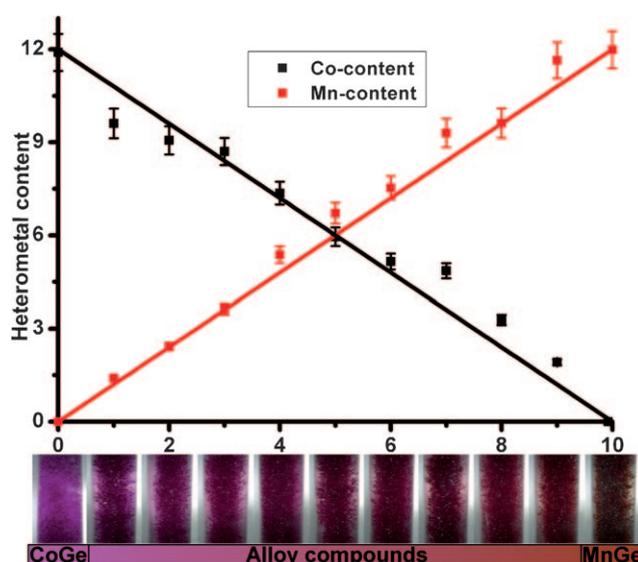


Figure 2. Graph showing the number of heterometal atoms (Co and Mn) per formula unit of framework alloy $[(\text{Mn}^{\text{III}})_x(\text{Co}^{\text{II/III}})_{12-x}\text{Ge}_7]$ (**5**) found by FAAS, plotted against the relative ratio of Co/Mn (10:0 → 0:10) as used in the synthetic procedure. Below the x-axis are pictures of single crystals of “native” compounds $\text{Co}^{\text{II}}\text{Ge}$ (**4a**; far left) and $\text{Mn}^{\text{III}}\text{Ge}$ (**2a**; far right) and the molecular alloys of **5** with a Co/Mn ratio 9:1 to 1:9, illustrating the color variance from purple to brown. The solid red and black lines in the graph represent the general trend in Mn and Co content, respectively.

considered as the center of the layer. It is linked to three 4-connected units which then link into the next layer, B. Only 3-connected Keggin clusters can be found in this layer, but unlike those in the previous plane, they are tilted by approximately 70.5° . In this conformation, these units form a link between the layers A and A', while A' is the mirror image of A. The mirror planes are orthogonal to the layers running diagonally through the silicon centers of the 3-connected building blocks. These mirror planes also transform the B-plane to B' which consequently builds the link between A' and A. Further, morpholinium cations, which have a templating effect during the synthesis and act as a pH buffer, can be identified by elemental analysis as disordered counterions in the pores of the negatively charged framework material.

It is possible to perform SC-SC redox transformations on $\text{Co}^{\text{II}}\text{Si}$ (compound **3a**) and $\text{Co}^{\text{II}}\text{Ge}$ (compound **4a**) by oxidation of the Co centers ($\text{Co}^{\text{II}}\text{X} \rightarrow \text{Co}^{\text{III}}\text{X}$) with complete retention of the integrity of the framework. For this process, fresh crystals of the compounds were dispersed in methanol and treated with a vast excess of selective oxidizing agent, *meta*-chloroperoxybenzoic acid, *m*-CPBA (see Supporting Information). During this process, the color of the crystals changes from purple to brown after a few seconds. The color remained stable only if the crystals were retained in a methanolic solution containing an excess of oxidant. Single-crystal X-ray diffraction structural analyses of the oxidized compounds showed a contraction of the unit cell dimensions while maintaining the overall structural features. For the Si versions, the unit cell volume contraction was 3.8%, whereas

the Ge compound showed a decrease of 2.5%. Upon leaving the crystals dispersed in methanol (without excess oxidant) for a prolonged time, their color changes back from brown to purple again indicative of their instability in the higher oxidation state. In addition, the oxidation state change has been confirmed by solid state UV/Vis spectroscopy, which showed a significant absorption band at 703 nm for oxidized **3** and **4** corresponding to the transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ for octahedrally coordinated Co^{III} centers (see the Supporting Information for further details).

After perfecting the syntheses for the four isostructural compounds **1a–4a** ($\text{Mn}^{\text{III}}\text{Si}$, $\text{Mn}^{\text{III}}\text{Ge}$, $\text{Co}^{\text{II}}\text{Si}$, and $\text{Co}^{\text{II}}\text{Ge}$), it seemed obvious to pursue the idea of synthesizing a molecular alloy based on polyoxometalates. Theoretically, two parts of the structure can be regarded as modular components that are easily interchangeable; the heteroatom in the center of the Keggin clusters which can be either Si or Ge, and the heterometal that is involved in the bond formation between the building blocks and that can either be Mn^{III} or Co^{II} in the native state; both can have their oxidation state switched.

As the materials with different heteroatoms, X, only display a minor variance in the kinetics of redox switchability and no observable difference in their electronic behavior, molecular alloys using the heterometals, M, as the exchangeable building blocks offered a more attractive route. The most feasible approach to synthesizing these new compounds was found by preparing solutions for the crystallization of the pure compounds and then mixing solutions of M^1 and M^2 in the appropriate ratios. The ratios were not altered stoichiometrically, but in relative 10% steps, leading to a total of nine single-crystal molecular alloys. Owing to the much higher yield in the crystallization of the frameworks with Ge-centered Keggin clusters, we discuss herein in detail these compounds: nine molecular alloys of formula $[(\text{Mn}^{\text{III}})_x(\text{Co}^{\text{II}})_{12-x}\text{Ge}_7]$ (**5**) synthesized with different Mn/Co ratios (see Figure 2).

Single crystals of the frameworks prepared by heterometal mixing are visually easily identifiable because of the purple-to-brown color gradient observed going from (Co/Mn ratio of 9:1 to 1:9; see Figure 2 and Supporting Information). Further quantitative confirmation of these molecular alloys was gathered by performing solid state UV/Vis measurements on the different molecular alloys (Co/Mn 9:1 to 1:9) of **5** (see Figure 3), as well as crystallographic studies (Supporting Information; Table S3). These showed an increased intensity for the absorption band at around 480 nm (${}^5E_g \rightarrow {}^5T_{2g}$ in Mn^{III}) and a decrease at that around 560 nm (${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$ Co^{II}) with increasing Mn/Co ratio. Importantly, none of the solid state UV/Vis spectra showed any presence of Co^{III} ions thus indicating that no oxidation of Co^{II} to Co^{III} occurs during the synthetic procedure and that all the alloy mixtures of **5** contained mixed-valence heterometals: Co^{II} and Mn^{III} . Furthermore, FAAS unambiguously confirmed the heterometal content per formula unit to vary linearly for the 10% Co/Mn mixing steps. The graph in Figure 2 and data contained within the Supporting Information illustrate this finding.

Preliminary ion-exchange experiments performed on the single crystals of compounds **1a** to **4a**, and alloys of **5** were designed to probe the electronic properties of the materials

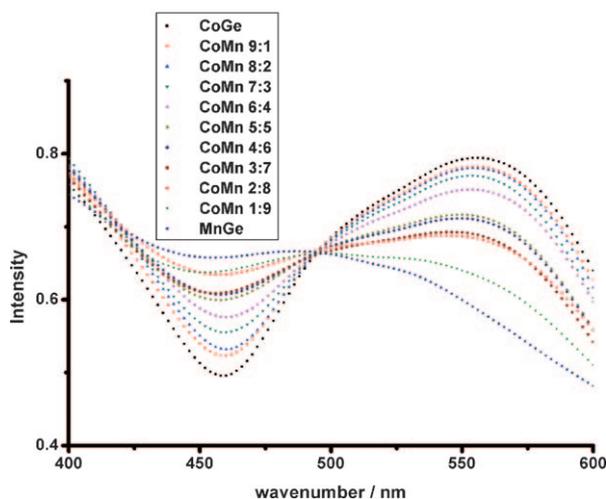


Figure 3. Graph showing the solid-state diffuse reflectance UV/Vis spectra recorded from single crystals of “native” compounds $\text{Co}^{\text{II}}\text{Ge}$ (**4a**) and $\text{Mn}^{\text{III}}\text{Ge}$ (**2a**) and the molecular alloys (Co/Mn ratio 9:1 to 1:9) of **5**.

and how they varied with respect to the heterometal and anionic charge on the framework. In this respect, NMR spectroscopy was used as an indirect method of quantifying how the electronic effect of the Ge-centered alloy frameworks **5** varied in comparison to the “native” framework materials **2** and **4**, as described in the Supporting Information. Initial results indicate that the alloy compounds are different to the pure Mn and Co based compounds, but in-depth analysis is precluded because the diffusion effects appear to dominate on the timescale of the experiments much more than the intrinsic electronic differences. Instead we did initial cyclic voltammetry (CV) experiments on the pure compounds based upon Co and Mn, and also on the 50:50 alloy compound (Figure 4). These showed two waves tentatively assigned to redox processes at the tungsten centers where the first

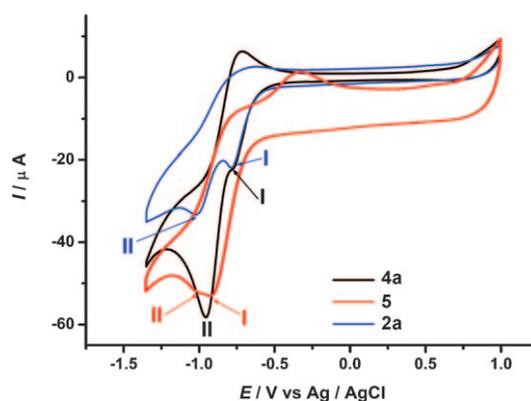


Figure 4. Graph showing the overlaid voltammograms of the “native” compounds $\text{Co}^{\text{II}}\text{Ge}$ (**4a**) and $\text{Mn}^{\text{III}}\text{Ge}$ (**2a**) in comparison with the (50:50) alloy material with a Co/Mn ratio of 5:5 (**5**). Although the second reduction wave (II) for the alloy lies at -0.97 V, which is what is expected for the intermediate value between the Co and Mn, the alloy compound has a first reduction wave (I) of -0.893 V, far removed from the intermediate value of -0.76 V.

reduction wave for the Co and Mn nets **4a** and **2a** were similar (-0.755 V and -0.760 V) while the value for the 50:50 mixture was -0.893 V, whereas the second reduction lies in the expected intermediate range (Supporting Information, Table S1). Therefore the alloy compound appears to be more difficult to be reduced in comparison with parent pure materials. This is a surprising result since a value for the alloy that is intermediate between the extremes would be expected, whereas a totally different set of electronic/redox properties in the alloy compared to the “pure” environment is indicated by this study.

In conclusion, we have synthesized two new members, $\text{Co}^{\text{II/III}}\text{Si}$ (**3**) and $\text{Co}^{\text{II/III}}\text{Ge}$ (**4**), of the “Keggin Net” family of extended modular frameworks. Importantly, the introduction of the cobalt heterometal has changed the redox activity of these materials. The linking heterometal Co^{II} centers can be oxidized to unstable Co^{III} in a reversible single-crystal–single-crystal transformation in which the framework integrity of the material is completely retained. The reversible nature of the reaction coupled with the retention of the framework structure should allow for ease of application in oxidation catalysis. Furthermore, the concept of molecular alloys has been presented for the first time in the context of 3D inorganic frameworks and is demonstrated by a series of linked mixed Co/Mn polyoxometalate networks, thus opening up another route to discover new electronically interesting materials with emergent physical properties.

Experimental Section

Synthesis of $(\text{C}_4\text{H}_{10}\text{NO})_{46}[\text{W}_{72}\text{Co}_{12}\text{Si}_7\text{O}_{262}(\text{OH})_6]\cdot 68\text{H}_2\text{O}$ ($\text{Co}^{\text{II}}\text{Si}$, **3a**): Morpholine (9.0 g, 103 mmol) was added to NaCl (1M; 200 mL), and the pH value subsequently adjusted to pH 8.0 by addition of aqueous H_2SO_4 (4.5M). $\text{K}_8[\text{SiW}_{10}\text{O}_{36}]\cdot 12\text{H}_2\text{O}$ (1.486 g, 0.5 mmol) was added to this mixture and stirred vigorously until fully dissolved. The addition of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.253 g, 0.9 mmol) to this mixture resulted in a red solution. Finally H_2O_2 (30 vol%; 2.5 mL) was added to the reaction mixture to assist the self-assembly of the framework. The clear brown solution is left to crystallize. Deep purple tetrahedral crystals form over 1 month. Yield after 2 months 380 mg, 16.02 μmol , 9.92%, based on W. Elemental analysis for $(\text{C}_4\text{H}_{10}\text{NO})_{46}[\text{W}_{72}\text{Co}_{12}\text{Si}_7\text{O}_{262}(\text{OH})_6]\cdot 68\text{H}_2\text{O}$, $\text{C}_{184}\text{H}_{602}\text{Co}_{12}\text{N}_{46}\text{O}_{382}\text{Si}_7\text{W}_{72}$, $M_w = 23\,714$ g mol^{-1} , (%) calcd: C 9.32, H 2.56, N 2.72, Co 2.98, W 55.82; found C 9.34, H 2.51, N 2.60, Co 1.56, W 60.06. FT-IR (KBr) $\tilde{\nu} = 3423$ (br), 2962 (wk), 2932 (wk), 2453 (wk), 1630 (wk), 1582 (m), 1449 (m), 1400 (wk), 1380 (wk), 309 (wk), 1234 (wk), 1192 (wk), 1098 (s), 1041 (wk), 999 (wk), 958 (m), 890 (s), 796 (m), 739 (s), 686 (m), 512 (wk), 479 cm^{-1} (wk). This sample suffers from systematic depression of the Co values arising from interference between the Si, Co, W which accounts for the discrepancy between the measured and calculated values. Potentiometric redox titrations of the solid material using $\text{Ce}^{\text{IV}}(\text{SO}_4)_2$ in sulfuric acid demonstrate that the 12 Co are present, all as Co^{II} .

Synthesis of $(\text{C}_4\text{H}_{10}\text{NO})_{46}[\text{W}_{72}\text{Co}_{12}\text{Ge}_7\text{O}_{262}(\text{OH})_6]\cdot 150\text{H}_2\text{O}$ ($\text{Co}^{\text{II}}\text{Ge}$, **4a**): Morpholine (9.0 g, 103 mmol) was added to NaCl (1M; 200 mL) and the pH value subsequently adjusted to pH 8 by addition of aqueous H_2SO_4 (4.5M). $\text{K}_8[\text{GeW}_{10}\text{O}_{36}]\cdot 6\text{H}_2\text{O}$ (1.455 g, 0.5 mmol) was added to this mixture and stirred vigorously until fully dissolved. The addition of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.253 g, 0.9 mmol) to this mixture resulted in a red solution. Finally H_2O_2 (30 vol%; 2.5 mL) was added to the reaction mixture to assist the self-assembly of the framework. The clear brown solution was left to crystallize. Deep purple tetrahedral crystals formed over 1 month. Yield after 1 month 400 mg, 15.68 μmol , 13.37% based on W. Elemental analysis for

$(\text{C}_4\text{H}_{10}\text{NO})_{46}\text{H}_6[\text{W}_{72}\text{Co}_{12}\text{Ge}_7\text{O}_{268}]\cdot 150\text{H}_2\text{O}$, $\text{C}_{184}\text{H}_{766}\text{Co}_{12}\text{Ge}_7\text{N}_{46}\text{O}_{464}\text{W}_{72}$, $M_w = 25\,501$ g mol^{-1} , (%) calcd: C 8.68, H 3.03, N 2.53, W 51.54, Co 2.70; found C 8.64, H 2.42, N 2.38, W 49.86, Co 2.75, 3419 (br), 2454 (wk), 1629 (m), 1595 (m), 1450 (wk), 1404 (wk), 1382 (wk), 1311 (wk), 1232 (wk), 1190 (wk), 1101 (m), 1037 (wk), 936 (m), 868 (s), 793 (s), 722 (s), 632 (m), 587 (m), 445 cm^{-1} (m).

Received: May 4, 2010

Published online: July 14, 2010

Keywords: alloys · framework materials · polyoxometalates · redox chemistry

- a) Q. Li, W. Zhang, O. Miljani, C. H. Sue, Y. L. Zhao, L. Liu, C. B. Knobler, J. F. Stoddart, O. M. Yaghi, *Science* **2009**, *325*, 855; b) H. Deng, C. J. Doonan, H. Furukawa, R. B. Ferreira, J. Towne, C. B. Knobler, B. Wang, O. M. Yaghi, *Science* **2010**, *327*, 846.
- S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.
- P. H. Dinolfo, J. T. Hupp, *Chem. Mater.* **2001**, *13*, 3113.
- A. K. Cheetham, G. Férey, T. Loiseau, *Angew. Chem.* **1999**, *111*, 3466; *Angew. Chem. Int. Ed.* **1999**, *38*, 3268.
- M. E. Davis, *Nature* **2002**, *417*, 813.
- M. Eddaoudi, H. L. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391.
- N. W. Ockwig, O. Delgado-Friedrichs, M. O’Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176.
- M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.
- a) O. Kahn, C. J. Martinez, *Science* **1998**, *279*, 44; b) D. Braga, G. Cojazzi, D. Paolucci, F. Grepioni, *Chem. Commun.* **2001**, 803; c) P. Dechambenoit, S. Ferlay, N. Kyritsakas, M. W. Hosseini, *Chem. Commun.* **2009**, 1559.
- D. L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105.
- C. L. Hill, C. M. Prosser-McCartha, *Coord. Chem. Rev.* **1995**, *143*, 407.
- C. Ritchie, A. Ferguson, H. Nojiri, H. N. Miras, Y. F. Song, D. L. Long, E. Burkholder, M. Murrie, P. Kögerler, E. K. Brechin, L. Cronin, *Angew. Chem.* **2008**, *120*, 5691; *Angew. Chem. Int. Ed.* **2008**, *47*, 5609.
- J. T. Rhule, C. L. Hill, D. A. Judd, *Chem. Rev.* **1998**, *98*, 327.
- C. M. Tourné, G. F. Tourné, S. A. Malik, T. J. R. Weakley, *J. Inorg. Nucl. Chem.* **1970**, *32*, 3875.
- C. Ritchie, C. Streb, J. Thiel, S. G. Mitchell, H. N. Miras, D. L. Long, T. Boyd, R. D. Peacock, T. McGlone, L. Cronin, *Angew. Chem.* **2008**, *120*, 6987; *Angew. Chem. Int. Ed.* **2008**, *47*, 6881.
- J. Thiel, C. Ritchie, C. Streb, D. L. Long, L. Cronin, *J. Am. Chem. Soc.* **2009**, *131*, 4180.
- P. Kroll, *J. Solid State Chem.* **2003**, *176*, 530–537.
- Crystallographic data for $\text{Co}^{\text{II}}\text{Si}$ (**3a**): $\text{C}_{184}\text{H}_{602}\text{N}_{46}\text{Co}_{12}\text{O}_{382}\text{Si}_7\text{W}_{72}$, $M_r = 23\,714.11$ g mol^{-1} ; tetrahedral crystal; $0.18 \times 0.16 \times 0.16$ mm^3 ; $T = 150(2)$ K; cubic, space group $I-43d$, $a = 38.6278(4)$ Å, $V = 57\,636.8(10)$ Å³, $Z = 4$, $\rho = 2.731$ g cm^{-3} , $\mu(\text{Cu}_{\text{K}\alpha}) = 29.353$ mm^{-1} , $F(000) = 43\,296$, 15 679 reflections measured, 3731 unique ($R_{\text{int}} = 0.1118$), 320 refined parameters, $R1 = 0.0947$, $wR2 = 0.2507$ (all data). Crystal data were measured on a Gemini Oxford diffractometer using $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54184$ Å) at 150(2) K. Crystallographic data for $\text{Co}^{\text{II}}\text{Ge}$ (**4a**): $\text{C}_{184}\text{H}_{602}\text{N}_{46}\text{Co}_{12}\text{O}_{382}\text{Ge}_7\text{W}_{72}$, $M_r = 24\,025.51$ g mol^{-1} ; purple, tetrahedral crystal; $0.18 \times 0.16 \times 0.16$ mm^3 ; $T = 150(2)$ K.; cubic, space group $I-43d$, $a = 38.3390(2)$ Å, $V = 56\,353.7(5)$ Å³, $Z = 4$, $\rho = 2.832$ g cm^{-3} , $\mu(\text{Cu}_{\text{K}\alpha}) = 30.300$ mm^{-1} , $F(000) = 43\,840$, 19 728 reflections measured, 1524 unique ($R_{\text{int}} = 0.0662$), 345 refined parameters, $R1 = 0.0524$, $wR2 = 0.1339$ (all data). Crystal data

were measured on a Gemini Oxford diffractometer using $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 150(2) K. Crystallographic data for $\text{Co}^{\text{III}}\text{Si}$ (**3b**): $\text{C}_{160}\text{H}_{536}\text{Co}_{12}\text{N}_{40}\text{O}_{376}\text{Si}_7\text{W}_{72}$, $M_r = 23\,178.28 \text{ g mol}^{-1}$; brown, tetrahedral crystal; $0.18 \times 0.16 \times 0.16 \text{ mm}^3$; $T = 150(2) \text{ K}$; cubic, space group $I-43d$, $a = 38.1239(5) \text{ \AA}$, $V = 55\,410.5(13) \text{ \AA}^3$, $Z = 4$, $\rho = 2.843 \text{ g cm}^{-3}$, $\mu(\text{Cu}_{\text{K}\alpha}) = 30.552 \text{ mm}^{-1}$, $F(000) = 43\,336$, 12804 reflections measured, 3280 unique ($R_{\text{int}} = 0.0729$), 268 refined parameters, $R1 = 0.0883$, $wR2 = 0.2439$ (all data). Crystal data were measured on a Gemini Oxford diffractometer using $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 150(2) K. Crystallographic data for $\text{Co}^{\text{III}}\text{Ge}$ (**4b**): $\text{C}_{160}\text{H}_{700}\text{Co}_{12}\text{Ge}_7\text{N}_{40}\text{O}_{458}\text{W}_{72}$, $M_r = 24\,967.21 \text{ g mol}^{-1}$; brown, tetrahedral crystal; $0.18 \times 0.16 \times 0.16 \text{ mm}^3$; $T = 150(2) \text{ K}$; cubic, space group $I-43d$, $a = 38.0191(3) \text{ \AA}$, $V = 54\,954.8(8) \text{ \AA}^3$, $Z = 4$, $\rho = 2.904 \text{ g cm}^{-3}$, $\mu(\text{Cu}_{\text{K}\alpha}) = 31.071 \text{ mm}^{-1}$, $F(000) = 43\,840$, 15941 reflections mea-

sured, 3577 unique ($R_{\text{int}} = 0.0776$), 340 refined parameters, $R1 = 0.0617$, $wR2 = 0.1494$ (all data). Crystal data were measured on a Gemini Oxford diffractometer using $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 150(2) K. Owing to the instability of the Co^{III} oxidation state in the oxidized frameworks $\text{Co}^{\text{III}}\text{Si}$ and $\text{Co}^{\text{III}}\text{Ge}$, without the persistent presence of oxidizing agent, it was not possible to collect full and accurate elemental analysis on these materials. Consequently, the reported crystallographic formulae have been estimated based on the original formulae, **3a** and **4a**, combined with the charge balance required for these oxidized frameworks. CCDC 666405 (**3a**), 666406 (**4a**), 783645 (**3b**), and 783646 (**4b**) 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.