# Trapping the δ Isomer of the Polyoxometalate-Based Keggin Cluster with a Tripodal Ligand

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Abstract: *We report the synthesis, structural, and electronic characterization of the theoretically predicted, but experimentally elusive δ-isomer of the Keggin polyoxometalate polyanion. A family of δ-Keggin polyoxoanions of the general formula, $(TEA)H_pNa_q [H_2M_{12}(XO_4)O_{33}(TEA)]\cdot r H_2O$ where p, q, r = [2,3,8] for* **1** *and [4,1,4] for* **2** *were isolated by the reaction of tungstate(VI) and vanadium(V) with triethanolammonium ions (TEAH), acting as a tripodal ligand grafted to the surface of the cluster thereby stabilizing the polyanionic δ-Keggin archetype. The δ-Keggin species were characterized by single-crystal X-ray diffraction, FT-IR, UV/Vis, NMR, and ESI-MS spectrometry. Electronic structure and structure–stability correlations were evaluated by means of DFT calculations. The compounds exhibited multi-electron transfer and reversible photochromic properties by undergoing single-crystal-to-single-crystal (SC–SC) transformations accompanied with color changes under light.*

Polyoxometalates (POMs) are anionic molecular metal oxides constructed from W, Mo, V, or Nb. They attract much attention owing to their structures, electronic properties,[1] applications in catalysis,[2] magnetism,[3] as well as medicine[4] and molecular electronics.[5] The first polyoxometalate compound was reported by Berzelius[6] in 1826, but it was not until the 1930s that the X-ray structure of this iconic POM compound, the Keggin ion, was first elucidated.[6] This ion has a tetrahedral symmetry with the general formula $[XM_{12}O_{40}]^{n-}$, where X is a heteroatom (P, Si, S, Ge, As, Co, Fe)[7] with four O atoms giving tetrahedral geometry.

Investigations of the POM-based Keggin structure revealed four additional isomers, each resulting from the 60° rotation of the four basic $\{M_3O_{13}\}$ units, giving α, β, γ, δ, and ε isomers, as reported by Baker and Figgis (Figure 1).[8] With the α and β-isomers, the four building blocks are linked together in a corner-shared fashion, whilst in the case of γ, δ, and ε the corner-shared linkages are replaced by one, three, and six edge-shared, respectively.[9] Since the first report of the most common α- and β-Keggin isomers,[10] many researchers have investigated their properties,[11] whilst others reported families of transition metal substituted derivatives of α-, β-, and γ- isomers.[12] The first Keggin species containing an ε-core was reported almost 60 years later as a Rh-
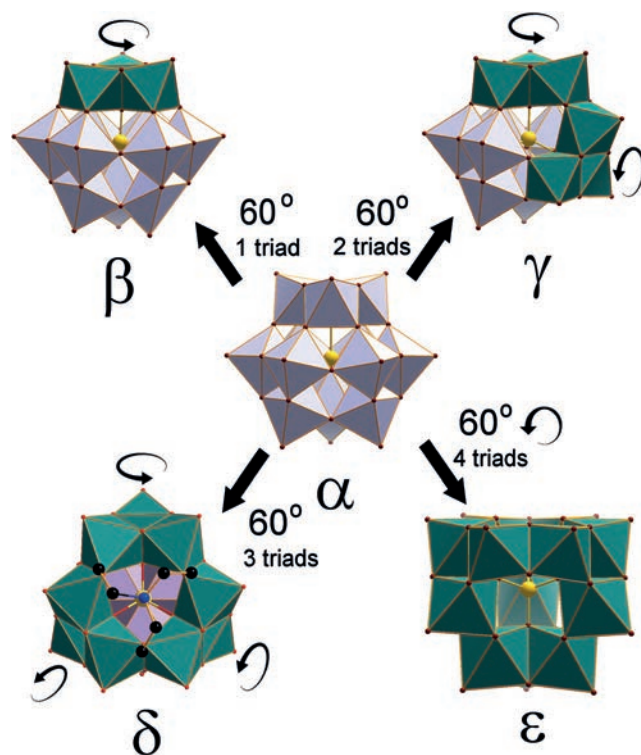
Figure 1. Polyhedral representation of the crystal structures of all the isomers of the Keggin anion: β, γ (top from the left), δ and ε (bottom from the left). The green polyhedra show the $\{M_3O_{13}\}$ units, which have been rotated the 60° with respect to the α-isomer shown in the center. The yellow spheres are the heteroatom templates, the small red spheres are the oxo-ligands. The black and blue ball and stick show the coordinating ligands that allow the δ isomer to form.

substituted oxomolybdenum(V) complex,[13] followed by the report of a mixed-valence Mo^V/Mo^{VI} iso-polyanion,[14] the La- and Ni-substituted oxomolybdenum ε-Keggin isomers,[15] and recently the Bi-substituted vanadium-based ε isomer.[16] However, the only related δ-Keggin structures observed so far are not POM anions but cationic species, for example, the $\{Al_{13}\}$ cation[17] and the "reverse-Keggin" ions incorporating either p-block elements (Sb^{5+}) or first row transition metal ions (Co^{2+}, Mn^{2+}, or Zn^{2+}).[18]

Herein, we report the synthesis and characterization of the first members of the δ-Keggin polyanionic polyoxometalate-based isomers to be isolated, compounds **1** and **2**, with the general formula: $TEAH_pNa_q[H_2M_{12}(XO_4)O_{33}(TEA)]\cdot r H_2O$ where p, q, r = [2,3,8] for **1** and [4,1,4] for **2** [TEAH: $C_6H_{16}NO_3$ (N, O atoms fully protonated); M: $W^{VI}_4V^V_8$; X: V^V; TEA: $C_6H_{13}NO_3$: hydroxy groups fully deprotonated),

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respectively. The clusters were characterized in the solid state by X-ray diffraction and FT-IR analysis as well as in solution by electrospray ionization mass spectrometry (ESI-MS), UV/Vis, and cyclic voltammetry.

Crystallographic studies revealed that **1** crystallizes in the monoclinic system in $P2_1/c$ space group, and the anion can be formulated as $[H_2W_4V_8(VO_4)O_{33}(C_6H_{13}NO_3)]^{5-}$ (**1a**). The anions exhibit a δ-Keggin structural motif, which is derived from the α-Keggin isomer by 60° rotation of the three $\{M_3O_{13}\}$ subunits that are directly bonded to the top TEA (triethanolamine) tripodal ligand and edge-shared to each other (Figures 1 and 2). The fourth $\{M_3O_{13}\}$ subunit remains at its
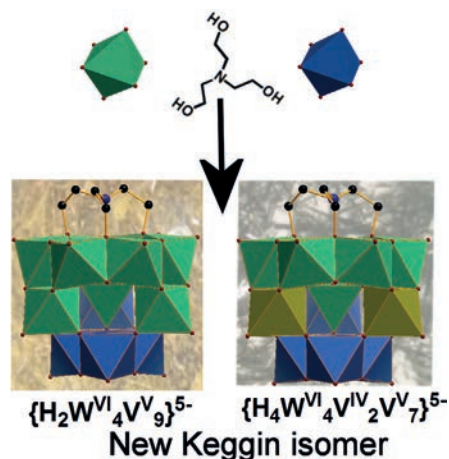
Figure 2. Polyhedral representations of the structure of the δ-Keggin found in compounds **1** and **2**. The left and right images show the positions of the V^V (green) and W^{VI} (blue) centers, and the V^{IV} (yellow: right) centers produced upon reduction resulting from irradiation. The coordinated tripodal ligand TEA is shown. Color scheme: W^{VI}: blue, V^V: green, V^{IV}: dark yellow, C: black, N: blue. Counterions have been omitted for clarity.

original position and is located at the bottom cap opposite to the coordinated TEA ligand along a C_3 axis and is corner-shared with the three neighboring $\{M_3O_{13}\}$ subunits. Structure refinements revealed that the central XO_4 template and six metal centers that are directly bonded to the TEA tripodal ligand are fully occupied by vanadium atoms, whilst the remaining bottom $\{M_3O_{13}\}$ and the three belt sites are occupied by four tungsten and two vanadium atoms disordered over the six positions. Crystallographic studies and bond valence sum (BVS)[19] calculations have been carried out to establish the oxidation states of the metal centers. The tungsten atoms were found to be in the oxidation state VI ($BVS_{av} = 6.02$), while all the vanadium atoms were found to be in the oxidation state V ($BVS_{av} = 5.04$).

The "capping" TEA ligand adopts a $\eta_2{:}\eta_2{:}\mu_3$ coordination mode, completing the octahedral coordination sphere of the upper "cap" vanadium centers (Supporting Information, Figure S12), and appears to stabilize the δ-Keggin structure according to experimental evidence obtained from our control experiments. The vanadium atom in the VO_4 tetrahedron is coordinated to four μ_3-O^{2-} bridges, with the V−O bonds within the range of 1.679(9)–1.752(1) Å. Each V atom

in the VO_6 octahedra exhibits one terminal oxo group, with a V=O bond length of 1.585(6)–1.690(6) Å, four μ-O^{2-} and one μ_4-O^{2-} bridges with V−O bonds spanning the range 1.785(5)–2.050(5) Å and 2.269(5)–2.372(5) Å, respectively.

The remaining W atoms in the WO_6 octahedra support one terminal oxo group, with the W=O bond length in the range of 1.630(5)–1.679(6) Å, four μ-O^{2-} and one μ_4-O^{2-} bridges with W−O bond lengths in the range of 1.861(5)–1.938(5) Å and 2.305(5)–2.382(5) Å, respectively. Compound **1** was prepared under one-pot conditions from a warm aqueous solution of $NaVO_3$, $Na_2WO_4{\cdot}2H_2O$, TEA·HCl, and NaCl, where $Na_2S_2O_4$ was subsequently added, followed by the adjustment of the pH of the reaction mixture with HCl. Yellow needles of suitable quality for X-ray diffraction analysis were isolated 2–3 weeks later, but both the purity and crystallization time improved to under 5 days when excess TEA·HCl was used (see the Experimental Section). However, structural analysis revealed an isostructural species to compound **1** with the formula $(C_6H_{16}NO_3)_4Na[H_2W^{VI}_4V^V_8\text{-}(V^VO_4)O_{33}(C_6H_{13}NO_3)]{\cdot}4H_2O$ **2**. The structure crystallizes in space group ($P2_1/m$) with a crystallographic mirror plane passing through the center of the cluster with the main difference being the $TEAH^+{:}Na^+$ ratio.

To determine the role and the impact of the reducing agent, $Na_2S_2O_4$, on the formation of the final product, the same experimental procedure was carried out in the absence of $Na_2S_2O_4$. Orange needles of **1** were isolated from an orange solution along with unidentified green precipitate after one week, indicating that the presence of the $Na_2S_2O_4$ is important for the purity and increased yield of the isolated product. It is worth noting that the crystallization time was also reduced from 2–3 weeks to 1 week. Further attempts to synthesize the δ-Keggin isomer in the absence of the TEAH ions have been unsuccessful, suggesting the crucial role of the tripodal ligand in the formation and stabilization of the final product. Further control experiments showed that the absence of an appropriate number of M_3O_{13} building blocks (mainly responsible for the isomerism in POM chemistry), where the TEA can coordinate to and "lock" the δ-Keggin, led to the formation of an α-Keggin instead (Supporting Information, Figure S13). Reversing the $VO_3^-{:}WO_4^{2-}$ ratio to 3:7 generated more tungsten-based M_3O_{13} building blocks with lower coordination affinity to the TEA ligand, which inhibited the "locking" and isolation of the δ-isomer. When **1** and **2** were illuminated under a 150 W Xe lamp,[20] the crystals underwent a color change from yellow to green, observed at room temperature after 2 and 12 hours, respectively. Under these conditions a single-crystal-to-single-crystal (SC–SC) transformation occurs, whereby compounds **1** and **2** become dark green to give compounds **1′** and **2′** (Figure 2; Supporting Information, Figures S8–S10). X-ray studies showed that the structure of compound **1′** and **2′** are identical to **1** and **2**, but a BVS analysis indicates the δ-Keggin shell is two electrons reduced and two more oxygen atoms are now protonated (the source of the electrons appears to be the TEA in combination with the water content in the crystal lattice of **1** and **2**),[21] while the M−O (M = W, V) lengths of compounds **1′** and **2′** have changed, as expected for the reduced species (Supporting Information, Table S1). If the compounds are left in air, then they slowly

return back to their fully oxidized state (yellow colored crystals) if kept under dark. In the presence of atmospheric oxygen, **1′** converted back to **1** (8–9 months) and **2′** to **2** (4 months), respectively. Furthermore, X-ray diffraction data of the single-crystal samples were collected before and after the irradiation, confirming the structural integrity and composition of the cluster.[21]

Further studies have been carried out to unambiguously identify the reduction state of the cluster. By conducting ^{1}H NMR studies exploiting the Evans method,[22] it was possible to deduce that the compounds have been reduced by 2 electrons ($\mu_{eff} = 2.4$ and $S = 1.6$; $S =$ number of unpaired electrons). Also, in compounds **1′** and **2′**, V4 and V5 are likely to be in oxidation state V^{4+}, $BVS_{av} = 4.3$ and 4.2, respectively (Figure 2). Also, a similar study for compounds **1** and **2** confirms the oxidized nature of the cluster shell of the δ-Keggin clusters (Supporting Information, Figures S18 and S19).

The composition of **1** was verified further using high resolution electrospray ionization mass spectrometry (ESI-MS).[23] The studies were performed in a mixture of H_2O/CH_3CN solvents. At the m/z range of 1364–2110, the observed distribution envelopes could be assigned to the anionic fragment of compound **1**, with the formula $[W_4V^V_5V^{IV}_4O_{37}H_9\text{-}(C_6H_{13}NO_3)(C_6H_{16}NO_3)(H_2O)]^{1-}$, or even the anionic dimer and trimer of **1** species, formulated as $\{[W_4V_5V_4^{IV}O_{37}H_9\text{-}(C_6H_{13}NO_3)]_2 (C_6H_{16}NO_3)(H_2O)_2\}^{3-}$ and $\{[W_4V^V_6V^{IV}_3O_{37}H_7\text{-}(C_6H_{13}NO_3)]_3 Na_4(C_6H_{16}NO_3)(H_2O)_9\}^{4-}$, respectively. Moreover, the peak located at $m/z = 969.2$ corresponds to the fragment $\{[V^V_5V_2^{IV}O_{25}H_7Na_5(C_6H_{13}NO_3)](C_6H_{16}NO_3)_5(H_2O)_9\}^{2-}$, whilst the peak centered at $m/z = 835.7$ could be assigned to the cluster fragment $\{[V^V_4V^{IV}_3O_{25}H_7Na_8(C_6H_{13}NO_3)](C_6H_{16}NO_3)_3(H_2O)_7\}^{2-}$. Finally, peaks in the region m/z 1054–1209, correspond to the $\{[WV^VV^{IV}_6O_{25}H_8Na(C_6H_{13}NO_3)](C_6H_{16}NO_3)_6(H_2O)_5\}^{2-}$ and $\{[WV^VV^{IV}_7O_{25}H_{11}(C_6H_{13}NO_3)Na](H_2O)_2\}^{1-}$ species (Figure 3). The observed fragmentation is due to the experimental conditions used during the ionization process of the species in the gas phase. The stability of the species in solution has been verified by UV/Vis spectroscopy prior to the ESI-MS studies.

To investigate the electronic structure of the clusters, we performed density functional theory (DFT) analysis to elucidate the most favorable positions of the two crystallographically disordered over 6 positions vanadium (V^{IV}) centers, and consequently the location of the two unpaired electrons injected in the cluster shell. Figure 4 shows the relative energies with respect to the most stable positional isomer for the parent compound, $[W^{VI}_4V^V_8(V^VO_4)O_{33}\text{-}(C_6H_{13}NO_3)]^{7-}$, and the two electron reduced species, $[W^{VI}_4V^{IV}_2V^V_6(V^VO_4)O_{33}(C_6H_{13}NO_3)]^{9-}$. Note that we have omitted the protons in the {M_{12}} cage, therefore the negative charge of the cluster increased accordingly. For the parent compound the relatively most stable geometries are δK-1, with one vanadium in the bottom cap and the second one in the belt, and δK-2 with two vanadium atoms in the bottom cap. Nevertheless, the relatively small energy difference (3.5 kcal mol^{-1}) with respect to geometries δK-3 and -4 makes these results rather inconclusive, since the average
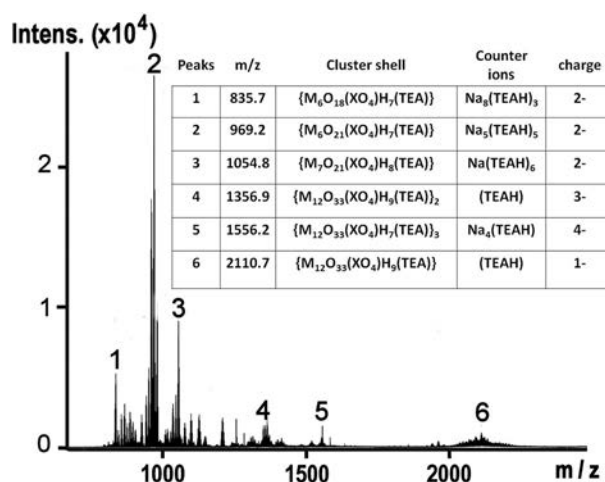

Figure 3. ESI-Mass spectrum in negative-mode of **1** in the m/z range of 800–2500 showing the major peaks of charged fragments.
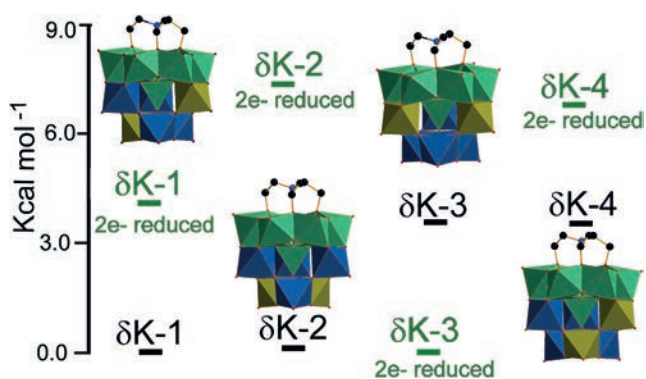

Figure 4. Theoretical relative energies with respect to the most stable positional isomer (δK-1 to δK-4), with the formula $[W^{VI}_4V^V_8(V^VO_4)O_{33}\text{-}(C_6H_{13}NO_3)]^{7-}$ (black lines) and its two electron reduced analogues, $[W^{VI}_4V_2^{IV}V^V_6(V^VO_4)O_{33}(C_6H_{13}NO_3)]^{9-}$ (green lines). These results helped us to determine the more favorable positions of the two V^{IV} atoms. W: Indigo, V^V: green, V^{IV}: dark yellow, C: black, N: blue.

method error is around 1–2 kcal mol^{-1} ($< 5\%$).[24] The investigation of the two electron reduced species shows the most stable isomer is δK-3, where both V^{IV} atoms are in the belt region, and three of the four tungsten atoms form a triad $[M_3O_{13}]$. Previous studies of the formation mechanism of POM clusters have shown that triads can be considered as structural building blocks, which is in agreement with our energy calculations.[25] This is interesting since it shows how the ligand grafting allows this organization.

In conclusion, we described the isolation and complete characterization in solid state and solution of the polyoxometalate-based polyanionic δ-Keggin isomer, with the formula $[H_2W^{VI}_4V^V_8(V^VO_4)O_{33}(C_6H_{13}NO_3)]^{5-}$. This elusive isomer was synthesized under one-pot conditions utilizing a tripodal ligand. DFT studies suggest that the TEA ligand is able to effectively "lock" or stabilize the δ- isomer through coordination, and this was confirmed experimentally with comparative synthesis and spectroscopic studies, with and without the use of the TEA ligand. The compound type was shown to undergo a cation-modulated photochemical two-

electron process upon illumination, observed as SC-to-SC transformation studied by X-ray diffraction. Future work will explore the effects this isomerism has on the electronic properties, looking at control of electron transfer both in solution and the solid state.

Experimental Section

Synthesis of $(C_6H_{16}NO_3)_2Na_3[H_2W_4V_8(VO_4)O_{33}(C_6H_{13}NO_3)]\cdot 8H_2O$ **1** : Method A: $NaVO_3$ (0.854 g, 7 mmol), $Na_2WO_4\cdot 2H_2O$ (0.990 g, 3 mmol), TEA·HCl (0.464 g, 2.5 mmol) and NaCl (0.117 g, 2 mmol) were dissolved in deionized water (10 mL) giving a cloudy yellow solution. The reaction mixture was heated at 80–90 °C for 1 hour, during which time the cloudy yellow solution changed to clear orange. After cooling the reaction mixture down to room temperature, $Na_2S_2O_4$ (0.087 g, 0.5 mmol) was added to the reaction mixture resulting to dark brown solution and the pH was adjusted to 2.0–2.5 by addition of 37% HCl followed by a color change to dark green. The reaction mixture was filtered and the filtrate was left undisturbed to crystallize at 18 °C. Orange needles suitable for X-ray diffraction analysis were obtained after 2–3 weeks. Yield: 80 mg (8.1% based on W). MW: 2448.48 g mol^{-1}. IR (cm^{-1}): 3410.2 (b), 1627.9 (m), 1384.9 (m), 1211.3 (m), 1064.7 (m), 975.9 (s), 891.1 (s), 833.25 (m), 775.4 (s), 636.5 (w), 551.6 (w). Elemental analysis calcd for $C_{18}H_{63}N_3Na_3O_{54}V_9W_4$: C 8.83, H 2.59, N: 1.72, Na 2.82, V 18.73, W 30.04%. Found: C 9.04, H 2.19, N 1.69, Na 3.00, V 19.66, W 28.24%.

Method B: The above synthetic procedure was repeated in the absence of $Na_2S_2O_4$. The reaction mixture was filtered and the filtrate was left undisturbed to crystallize at 18 °C. Orange needles suitable for X-ray diffraction analysis were obtained after 1 week. Yield: 150 mg (15.2% based on W). The obtained spectroscopic and crystallographic data of the isolated compound are identical to **1**.

Synthesis of $(C_6H_{16}NO_3)_4Na[H_2W_4V_8(VO_4)O_{33}(C_6H_{13}NO_3)]\cdot 4H_2O$ **2**: Compound **2** was synthesized as compound **1** (method A) using an increased amount of TEA·HCl (1.857 g, 10 mmol) instead. Orange needles suitable for X-ray diffraction analysis obtained after 5 days. Yield: 120 mg (12.1% based on W). MW: 2630.83 g mol^{-1}. IR (cm^{-1}): 3354.2 (b), 1627.9 (m), 1384.9 (m), 1213.2 (w), 1066.6 (m), 970.2 (s), 891.1 (s), 831.3 (m), 777.3 (m), 624.9 (w), 547.8 (w). Elemental analysis calcd for $C_{30}H_{87}N_5NaO_{56}V_9W_4$: C 13.70, H 3.33, N: 2.66, Na 0.87, V 17.43, W 27.96%. Found: C 13.40, H 3.09, N 2.63, Na 0.67, V 17.06, W 25.45%.

Computational method: Geometry optimizations performed using B3LYP method as implemented in TURBOMOLE V6.3.1 package.[26] TZVP basis set was used on all atoms. To allow for solvation effects, the conductor-like screening model (COSMO) method was used with ionic radii of the atoms, which define the dimensions of the cavity surrounding the molecule, are chosen to be (in Å) 2.23 for W and V, 2.0 for C, 1.8 for N, 1.72 for O, and 1.3 for H.

Acknowledgements

[1] a) M. T. Pope, A. Müller, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34–48; *Angew. Chem.* **1991**, *103*, 56–70; b) H. N. Miras, J. Yan, D.-L. Long, L. Cronin, *Chem. Soc. Rev.* **2012**, *41*, 7403–7430.

[2] a) I. M. Mbomekalle, B. Keita, L. Nadjo, P. Berthet, K. I. Hardcastle, C. L. Hill, T. M. Anderson, *Inorg. Chem.* **2003**, *42*, 1163–1169; b) R. Neumann, A. M. Khenkin, I. Vigdergauz, *Chem. Eur. J.* **2000**, *6*, 875–882.

[3] a) C. Ritchie, A. Ferguson, H. Nojiri, H. N. Miras, Y. F. Song, D.-L. Long, E. Burkholder, M. Murrie, P. Kögerler, E. B. Brechin, L. Cronin, *Angew. Chem. Int. Ed.* **2008**, *47*, 5609–5612; *Angew. Chem.* **2008**, *120*, 5691–5694; b) S. Bertaina, S. Gambarelli, T. Mirta, B. Tsukerblat, A. Müller, B. Barbara, *Nature* **2008**, *453*, 203–206.

[4] a) K. Nomiya, H. Torii, T. Hasegawa, Y. Nemoto, K. Nomura, K. Hashino, M. Uchida, Y. Kato, K. Shimizu, M. Oda, *J. Inorg. Biochem.* **2001**, *86*, 657–667; b) T. Yamase, *J. Mater. Chem.* **2005**, *15*, 4773–4782.

[5] a) E. Coronado, C. Giménez-Saiz, C. J. Gómez-García, *Coord. Chem. Rev.* **2005**, *249*, 1776–1796; b) M. Carraro, N. H. Nsouli, H. Oelrich, A. Sartorel, A. Sorarù, S. S. Mal, G. Scorrano, L. Walder, U. Kortz, M. Bonchio, *Chem. Eur. J.* **2011**, *17*, 8371–8378; c) C. Busche, L. Vilà-Nadal, J. Yan, H. N. Miras, D.-L. Long, V. P. Georgiev, A. Asenov, R. H. Pedersen, N. Gadegaard, M. M. Mirza, D. J. Paul, J. M. Poblet, L. Cronin, *Nature* **2014**, *515*, 545–549.

[6] a) J. J. Berzelius, *Ann. Phys. Chem.* **1826**, *82*, 369–392; b) J. F. Keggin, *Nature* **1933**, *131*, 908–909.

[7] a) J. Server-Carrió, J. Bas-Serra, M. E. González-Núñez, A. García-Gastaldi, G. B. Jameson, L. C. W. Baker, R. Acerete, *J. Am. Chem. Soc.* **1999**, *121*, 977–984.

[8] L. C. W. Baker, J. S. Figgis, *J. Am. Chem. Soc.* **1970**, *92*, 3794–3797.

[9] M. T. Pope, *Inorg. Chem.* **1976**, *15*, 2008–2010.

[10] a) A. Kobayashi, Y. Sasaki, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 885–888; b) J. Fuchs, A. Thiele, R. Z. Palm, *Z. Naturforsch. B* **1981**, *36*, 161–171; c) F. Robert, A. Tézé, G. Hervé, Y. Jeannin, *Acta Crystallogr. Sect. B* **1980**, *36*, 11–15; d) J. N. Barrows, G. B. Jameson, M. T. Pope, *J. Am. Chem. Soc.* **1985**, *107*, 1771–1773.

[11] a) N. Shimizu, T. Ozeki, H. Shikama, T. Sano, M. Sadakane, *J. Cluster Sci.* **2014**, *25*, 755–770; b) A. Ishii, T. Ozeki, *Polyhedron* **2005**, *24*, 1949–1952.

[12] a) B. Botar, A. Ellern, P. Kögerler, *Dalton Trans.* **2009**, 5606–5608; b) A. S. Assran, S. Sankar Mal, N. V. Izarova, A. Banerjee, A. Suchopar, M. Sadakane, U. Kortz, *Dalton Trans.* **2011**, *40*, 2920–2925; c) E. Cadot, V. Béreau, B. Marg, S. Halut, F. Sécheresse, *Inorg. Chem.* **1996**, *35*, 3099–3106; d) K. Uehara, T. Taketsugu, K. Yonehara, N. Mizuno, *Inorg. Chem.* **2013**, *52*, 1133–1140; e) A. Tézé, E. Cadot, V. Béreau, G. Hervé, *Inorg. Chem.* **2001**, *40*, 2000–2004.

[13] a) V. K. Day, W. G. Klemperer, D. E. Páez Loyo, *Inorg. Chem.* **1992**, *31*, 3187–3189.

[14] See for example: a) M. I. Khan, A. Müller, S. Dillinger, H. Bögge, Q. Chen, J. Zubieta, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1780–1782; *Angew. Chem.* **1993**, *105*, 1811–1814; b) B. Nohra, H. El Moll, L. M. R. Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keeffe, R. N. Biboum, J. Lemaire, B. Keita, L. Nadjo, A. Dolbecq, *J. Am. Chem. Soc.* **2011**, *133*, 13363–13374.

[15] a) A. Müller, C. Beugholt, P. Kögerler, H. Bögge, S. Bud'ko, M. Luban, *Inorg. Chem.* **2000**, *39*, 5176–5177; b) P. Mialane, A. Dolbercq, L. Lisnard, A. Mallard, J. Marrot, F. Sécheresse, *Angew. Chem. Int. Ed.* **2002**, *41*, 2398–2401; *Angew. Chem.* **2002**, *114*, 2504–2507.

[16] J. Tucher, L. C. Nye, I. Ivanovic-Burmazovic, A. Notarnicola, C. Streb, _Chem. Eur. J._ **2012**, _18_, 10949–10953.

[17] W. H. Casey, _Chem. Rev._ **2006**, _106_, 1–16.

[18] a) V. Baskar, M. Shanmugam, M. Helliwell, S. J. Teat, R. E. P. Winpenny, _J. Am. Chem. Soc._ **2007**, _129_, 3042–3043; b) B. K. Nicholson, C. J. Clark, S. G. Telfer, T. Groutso, _Dalton Trans._ **2012**, _41_, 9964–9970.

[19] N. E. Brese, M. O'Keeffee, _Acta Crystallogr. Sect. B_ **1991**, _47_, 192–197.

[20] a) J. Forster, B. Rosner, M. M. Khusniyarov, C. Streb, _Chem. Commun._ **2011**, _47_, 3114–3116; b) C. Lydon, C. Busche, H. N. Miras, A. Delf, D.-L. Long, L. Yellowlees, L. Cronin, _Angew. Chem. Int. Ed._ **2012**, _51_, 2115–2118; _Angew. Chem._ **2012**, _124_, 2157–2160.

[21] a) A. Harriman, K. J. Elliott, M. A. H. Alamiry, L. Le Pleux, M. Séverac, Y. Pellegrin, E. Blart, C. Fosse, C. Cannizzo, C. R. Mayer, F. Odobel, _J. Phys. Chem. C_ **2009**, _113_, 5834–5842; b) K. V. Mikkelsen, M. A. Ratner, _Chem. Rev._ **1987**, _87_, 113–153; c) K. Kishore, G. R. Dey, T. Mukherjee, _Res. Chem. Intermed._ **2004**, _30_, 837–845.

[22] a) D. F. Evans, _J. Chem. Soc._ **1959**, 2003–2005; b) J. Loliger, R. Scheffold, _J. Chem. Educ._ **1972**, _49_, 646–647.

[23] a) H. N. Miras, E. F. Wilson, L. Cronin, _Chem. Commun._ **2009**, 1297–1311; b) H. N. Miras, D.-L. Long, P. Kögerler, L. Cronin, _Dalton Trans._ **2008**, 214–221; c) E. F. Wilson, H. N. Miras, M. H. Rosnes, L. Cronin, _Angew. Chem. Int. Ed._ **2011**, _50_, 3720; _Angew. Chem._ **2011**, _123_, 3804; d) H. N. Miras, H. Y. Zang, D.-L. Long, L. Cronin, _Eur. J. Inorg. Chem._ **2011**, 5105–5111; e) H. N. Miras, D. Stone, D.-L. Long, E. J. L. McInnes, P. Kögerler, L. Cronin, _Inorg. Chem._ **2011**, _50_, 8384–8391.

[24] a) L. Goerigk, S. Grimme, _WIREs Comput. Mol. Sci._ **2014**, _4_, 576–600; b) A. Hansen, C. Bannwarth, S. Grimme, P. Petrovic, C. Werl, J.-P. Djukic, _ChemistryOpen_ **2014**, _3_, 177–189.

[25] L. Vilà-Nadal, A. Rodríguez-Fortea, L. Yan, E. Wilson, L. Cronin, J. M. Poblet, _Angew. Chem. Int. Ed._ **2009**, _48_, 5452–5456; _Angew. Chem._ **2009**, _121_, 5560–5564.

[26] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, _Chem. Phys. Lett._ **1989**, _162_, 165–169; b) F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, _WIREs Comput. Mol. Sci._ **2014**, _4_, 91–100.