Polyoxometalate Molecular Magnets

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Electronic Control of Spin Coupling in Keplerate-Type Polyoxomolybdates**

*Bogdan Botar, Arkady Ellern, Raphael Hermann, and Paul Kögerler**

The structural and functional diversity of polyoxometalate (POM) chemistry[1] renders POMs ideal model platforms for a range of applications that require a systematic variation of the molecular electronic properties, such as homogeneous catalysis or molecular magnetism.[2,3] The interaction between itinerant and localized d electrons in such systems is crucial and determines, for example, electron storage properties, optical excitations, or magnetic interactions. However, these processes remain poorly understood, as are the formation mechanisms of the more complex POMs. Nanosized polyoxomolybdates in particular form a wide spectrum of mixed-valent $Mo^{V/VI}$ clusters in which the localization or delocalization (Robin–Day class I to III) of the 4d electrons primarily depend on the linking modes of the MoO_n polyhedra (corner-, edge-, or face-sharing). Furthermore, these structures can incorporate various unusual spin polytopes comprising 3d[4] or 4f[5] ions that interlink or replace POM building blocks, that is, structural fragments with characteristic connectivities that define the structural chemistry of polyoxomolybdates and -tungstates.[6] These spin polytopes exhibit magnetic phenomena that were observed in discrete molecules for the first time, such as metamagnetic spin-phase transitions, which are a consequence of high-symmetry spin frustration.[7]

Of particular importance are the magnetically functionalized derivatives of structural polyoxomolybdate archetypes that were first identified by Müller and co-workers. Keplerate structures, in which 30 mono- or dinuclear linker groups connect 12 pentagonal C_{5v}-symmetric $\{(Mo)Mo_5\}$ building blocks to form a spherical cluster of approximate I_h symmetry,[8] can integrate Fe^{3+},[9] Cr^{3+},[10] or VO^{2+}[11] magnetic linker groups, thus creating a spin icosidodecahedron, that is, a molecular analogue of a Kagomé lattice.[12] Although a stepwise exchange of these spin centers is an advantage of polyoxometalate chemistry compared to classical polynuclear coordination complexes,[13,14] to date, no strategies exist that allow the control and tuning of the intramolecular magnetic exchange energies that are mediated by the (diamagnetic) POM fragments.[15]

We recently identified a synthetic procedure for the isolation of Keplerate structures based on the reaction of multivalent heterometal centers with larger polyoxomolybate(V/VI) units that coexist in a reaction solution at a certain pH. This approach yielded Keplerate clusters of the type $\{Mo_{72}Mo_8V_{22}\}$,[16] $\{Mo_{72}V_{15}Fe_7Mo_8\}$, and $\{Mo_{72}V_{11}Fe_{11}Mo_8\}$,[14] which were obtained as kinetic products within minutes to a few hours following addition of KCl. Herein, we demonstrate for an analogous reaction system, how novel $\{Mo_{72}Fe_{30}\}$ Keplerate species with partially reduced $\{(Mo)Mo_5\}$ building blocks (Robin–Day class III) can be identified, based on Raman spectroscopy time profiles of acidified aqueous molybdate reaction solutions. Crucially, in these systems the 4d electron density on the still diamagnetic POM fragments strongly influences the magnetic exchange. A representative of this class of compounds with 16 4d electrons per cluster anion was isolated as $K_{13}Na_3\{VO(H_2O)_5\}_3$-$[\{Mo_6O_{21}(H_2O)_3(SO_4)\}_{12}(Fe(H_2O)_2)_{30}]\cdot 120\,H_2O\cdot 6\,K_2SO_4$ (**1** = $K_{13}Na_3\{VO(H_2O)_5\}_3$**1a**$\cdot 120\,H_2O\cdot 6\,K_2SO_4$), and its formation was spectroscopically monitored.

The composition of such reaction solutions is complex, particularly within pH ranges in which structural types such as spherical Keplerate clusters and molybdenum blue-type ring clusters coexist.[17] However, resonance Raman spectroscopy (the excitation line at 1064 nm coincides with $Mo^{VI}\leftarrow Mo^{V}$ IVCT transitions) allows us to follow the dominant reduced molybdate species and their specific reactions (Figure 1). Addition of vanadyl sulfate and a large excess of ferrous sulfate to an acidified molybdate solution (pH 1.8) affords a dark blue solution within 5–10 min, the corresponding Raman spectrum of which has a line pattern in the 200–500 cm^{-1} region that is characteristic for molybdenum blue ring clusters.[18] This pattern is retained with little change over the following 24 h. Interestingly, at this stage, the addition of a large excess of KCl results in the precipitation of Keplerate species that are thus present in equilibrium with the molybdenum blue-type ring clusters. The crystalline product was identified spectroscopically and crystallographically as Keplerate clusters $\{Mo_{72}Mo^{V}{}_{x}Fe^{III}{}_{y}V^{IV}{}_{z}\}$ in which $[VO(H_2O)]^{2+}$, $[Fe(H_2O)_2]^{3+}$, and $[MoO(H_2O)]^{3+}$ groups are statistically distributed over the 30 linker positions of the Keplerate spheres.

The exclusive precipitation of Keplerate cluster anions (and not of ring clusters) is caused by the the specific affinity

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[*] Dr. B. Botar, Prof. Dr. P. Kögerler
Institut für Festkörperforschung, Forschungszentrum Jülich
52425 Jülich (Germany)
Fax: (+49) 2461-61-2620
E-mail: p.koegerler@fz-juelich.de
Dr. A. Ellern
Dept. of Chemistry, Iowa State University, Ames, IA 50011 (USA)
Dr. R. Hermann
Dept. of Physics, Université de Liège, 4000 Sart-Tilman (Belgium)
Prof. Dr. P. Kögerler
Institut für Anorganische Chemie, RWTH Aachen University
52074 Aachen (Germany)
Fax: (+49) 241-80-92642
E-mail: paul.koegerler@ac.rwth-aachen.de

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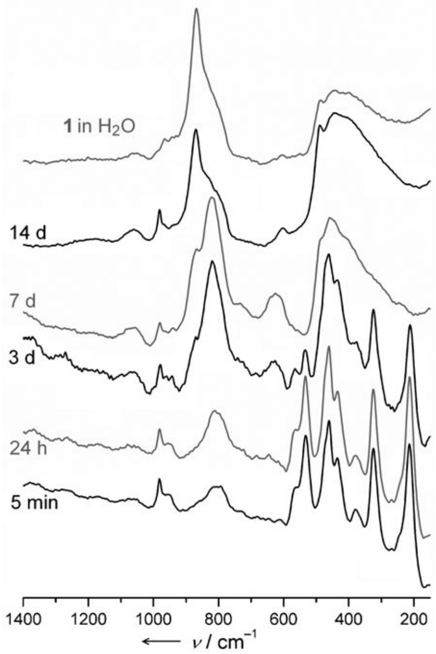

Figure 1. Time profile of the formation of **1a** showing the (resonance) Raman spectra ($\lambda_e = 1064$ nm) of the reaction solution after 5 minutes and 1, 3, 7, and 14 days. The Raman spectrum of an aqueous solution of **1** is shown for comparison.

of potassium ions to the 20 crown ether like $\{Mo_3M_3O_6\}$ pores in the Keplerate structure.[16] Upon the addition of only a small amount of KCl to the reaction solution after 24 h (which caused no precipitation), the color of the air-exposed solution gradually changed within two weeks from dark blue to black, and the Raman spectrum of the reaction solution transforms into a line pattern characteristic of reduced Keplerate polyanions.[17] Addition of a further amount of KCl solution then results in the precipitation of Keplerate cluster compound **1**, in which all 30 linker positions are occupied by $[Fe(H_2O)_2]^{3+}$ groups. The exclusive occupation by $[Fe(H_2O)_2]^{3+}$ linker groups (and the corresponding absence of $[O{=}Mo(H_2O)]^{3+}$ or $[O{=}V(H_2O)]^{2+}$ linker groups) follows from several observations: 1) the thermal parameters of the crystallographically independent heterometal positions in the single-crystal X-ray diffraction analysis (space group $P\bar{1}$); 2) the structurally unambiguously defined coordination environments with two aqua ligands (Fe−O: 1.95(5)–2.10(4) Å) and the absence of shorter M=O bonds; 3) the elemental analysis results for Fe in **1**; 4) the absence of ferromagnetic characteristics in the magnetic susceptibility, which are pronounced for $\{Mo_{72}Mo^{V}_{x}Fe^{III}_{y}V^{IV}_{z}\}$ clusters with mixed spin centers;[14] 5) the uniform Fe^{III} coordination environment as observed by Mössbauer spectroscopy; and 6) the limited number of lines in the resonance Raman spectrum of an aqueous solution of **1** (compared to corresponding spectra of $\{Mo_{72}Mo^{V}_{x}Fe^{III}_{y}V^{IV}_{z}\}$-type compounds) owing to the near-I_h symmetry of the Keplerate sphere **1a**.

The solid-state structure of **1** comprises discrete cluster anions **1a**, and the framework of these anions corresponds to that of the oxidized, that is, Fe^{III}/Mo^{VI}-based, Keplerate cluster $[Mo^{VI}_{72}Fe^{III}_{30}O_{252}(CH_3COO)_{12}\{Mo^{VI}_2O_7(H_2O)_2\}\{H_2Mo^{VI}_2O_8(H_2O)\}(H_2O)_{91}]$ (**2a**; **2** = **2a**·ca. 150 H_2O).[9] The twelve slightly domed[19] $[Mo^{VI}_{6-n}Mo^{V}_{n}O_{21}(H_2O)_3(SO_4)]^{(8+n)-}$ building blocks consist of a central pentagonal bipyramidal MoO_7 group and five MoO_6 octahedra that share edges with the central MoO_7 group. Each of these blocks coordinate to *trans*-$[Fe(OH_2)_2]^{3+}$ groups by two equatorial oxo groups (Figure 2). The resulting triangles of neighboring iron sites are part of the hexagonal $(\text{-}Mo^{VI}\text{-}O\text{-}M\text{-}O\text{-})_3 = M_3Mo_3O_6$ pores (M: heterometal, here M = Fe) that are virtually isostructural to the pores found in $\{Mo_{57}M_6\}$-type POMs.[13] The average Fe···Fe distance in **1a** (6.38 Å) is nearly identical (< 1 %) to that found in **2a** (6.44 Å). However, although disordered acetate and $\{Mo_2\}$ ligands bind to the inner cluster surface in **2a**, in **1a**, 12 disordered sulfate ligands inside the sphere bind to the $\{(Mo)Mo_5\}$ building blocks in tripodal μ_3 bridging modes. Potassium ions coordinate to the $Fe_3Mo_3O_6$ pores in **1**, as observed for other highly charged Keplerate cluster anions, but not for the neutral species **2**. The 30 iron(III) centers in **1a** adopt slightly distorted octahedral coordination environments with Fe−O distances of 1.92(3) to 2.10(4) Å. The formal oxidation state +III for all 30 iron centers is derived from bond valence sums (averaged to 3.29) and Mössbauer spectra (Supporting Information, Figure S5) that show a single Fe^{III} doublet at 298 K, and from which any possible Fe^{II} content above 3 % can be excluded. In the solid-state structure of **1**, the cluster anions **1a** are stacked along [111] to form linear chains by ion–dipole interactions between a potassium ion coordinated to a $Fe_3Mo_3O_6$ pore and to a terminal oxo site of an adjacent $\{(Mo)Mo_5\}$ group (Figure 2b).

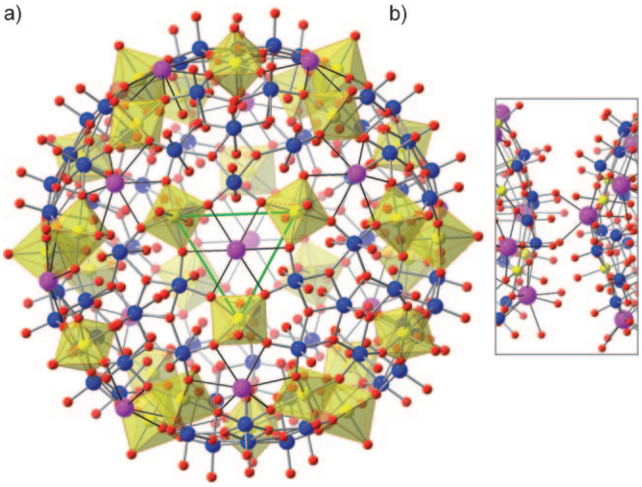

Figure 2. a) Structure of **1a** (Mo blue, Fe yellow, O red) with potassium ions (purple) coordinated to the $\{Mo_3Fe_3O_6\}$ pores. The 12 disordered sulfate groups (coordinated to the inner cluster surface) and aqua ligands bound to potassium ions are not shown for clarity. One Fe_3 triangle is highlighted by green lines. b) Potassium ion mediated contacts between two neighboring **1a** cluster units in the solid-state structure of **1**. Shortest intercluster Fe···Fe distance: 6.63 Å.

The polyanion **1a** is the first partially reduced Keplerate cluster with 30 Fe^{III} spin centers; previously reported partially reduced systems always incorporate mixed spin centers in their 30 linker positions.[14] The field- and temperature-dependent magnetic susceptibility of compound **1** indicates weak antiferromagnetic interactions between 2–290 K and accurately follows the Curie–Weiss expression $\chi = C/(T-\Theta)$ above 15 K, which is also the case for **2**.[7a] The antiferromagnetic coupling between each iron site and its four nearest neighbors in the Fe_{30} icosidodecahedron (consisting of twenty corner-sharing equilateral Fe_3 triangles), mediated by O–Mo–O exchange pathways, results in highly symmetrical geometric frustration, with a uniform 120° orientation of each quasi-classical spin vector with respect to its neighbors.[7]

Assuming pure spin magnetism of the $s = 5/2$ Fe^{III} centers ($^6A_{1g}$), the uniform exchange energy J can be deduced directly from the Weiss temperature Θ derived from low-field susceptibility data (Figure 3).[7a] For **1**, a least-squares fit results in $C = 128.3$ emu K mol^{-1}, which corresponds to 30 uncoupled $s = 5/2$ centers with $g = 1.986$ and is nearly identical to the value found for **2**. Whereas $\Theta = -21.6$ K and $J/k_B = 1.57$ K for **2**, for **1** we find $\Theta = -10.4$ K and $J/k_B = -0.76$ K. The relative change in the exchange energy J of about 50% is of a magnitude that has not previously been observed for isostructural classical coordination complexes. The decrease in J is explained with a change in the frontier orbital energies of the molybdate building blocks caused by the partial reduction, which in turn reduces the overlap with the magnetic Fe(3d)-centered orbitals.

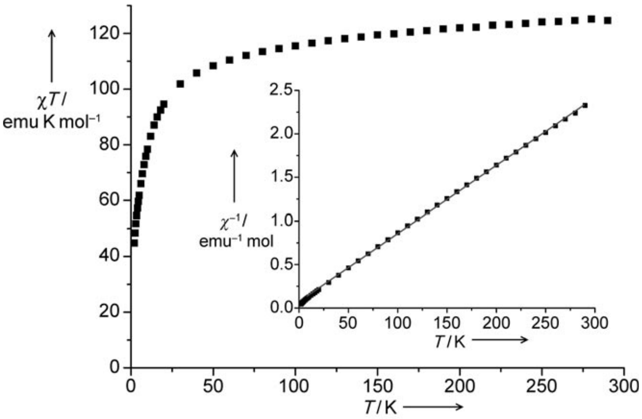

Figure 3. Temperature dependence of χT and the inverse susceptibility χ^{-1} (inset) of **1** at 0.1 Tesla. The gray line represents the best fit to a Curie–Weiss expression (>15 K).

In summary, the high affinity of the Keplerate-type polyoxomolybdates for vanadyl linker groups, which is also evident from the consistently high V:M′ ratio in Keplerates with mixed linker groups, can be circumvented by a Raman-monitored synthesis approach. This method allows a complete exchange by other linker groups, such as iron(III), and we postulate that the exchange reaction, observed over a timeframe of two weeks, is connected to the slow partial air oxidation of the reaction intermediates. The partial reduction of the molybdate-based building blocks induces a pronounced change in the superexchange between the adjoined iron(III) centers, whilst the structure of these $\{(Mo)Mo_5\}$ electron reservoirs[20] is fully retained. These findings underscore the unique and broad range of chemical reactions these Keplerate architectures can undergo whilst remaining intact.

Experimental Section

Crystal data for **1**: $H_{462}O_{558}K_{25}Na_3S_{18}V_3Fe_{30}Mo_{72}$, $M = 19753.25$ g mol^{-1}; triclinic, space group $P\bar{1}$ (No. 2); $a = 26.45(2)$, $b = 29.96(5)$, $c = 33.93(6)$ Å, $\alpha = 91.58(4)$, $\beta = 93.62(4)$, $\gamma = 94.35(4)°$, $V = 26789(81)$ Å^3, $Z = 2$, $\rho = 2.453$ g cm^{-3}, $\mu = 2.86$ mm^{-1}, $F(000) = 19190$, crystal dimensions $0.30 \times 0.25 \times 0.22$ mm^3. Crystals of **1** were taken directly from the mother liquor, mounted on a cryoloop, and immediately cooled to 163(2) K on a Bruker CCD-1000 diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. 138749 reflections ($0.77 < \Theta < 20.82°$) collected, 55977 unique ($R_{int} = 0.0748$). $R = 0.0858$ for 34748 reflections with $I > 2\sigma(I)$, $R = 0.1458$ for all reflections; ρ(min./max.): 3.12/−2.33 e Å^{-3}. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-420735.

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[15] The recently published synthesis of $\{(W^{VI})W^{VI}_5\}$-based Keplerate clusters, for example, the $\{Mo_{72}(Mo_2)_{30}\}$ analogue $[(W^{VI}_6O_{21}(H_2O)_5(CH_3COO)_{0.5})_{12}(Mo^V_2O_4(CH_3COO))_{30}]^{48-} = \{W_{72}(Mo_2)_{30}\}$ (C. Schäffer, A. Merca, H. Bögge, A. M. Todea, M. L. Kistler, T. Liu, R. Thouvenot, P. Gouzerh, A. Müller, *Angew. Chem.* **2009**, *121*, 155 – 159; *Angew. Chem. Int. Ed.* **2009**, *48*, 149 – 153) indicates that magnetic derivatives of the type $\{W^{VI}_{72}M_{30}\}$ also exist. The $\{W^{VI}_{72}V^{IV}_{30}\}$ analogue of $\{Mo_{72}V_{30}\}$[11] with shorter V···V distances was indeed isolated shortly thereafter; see: A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, *Chem. Commun.* **2009**, 3351 – 3353; the average exchange, in this case mediated by O–W–O bridges, is reduced as well.

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