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Removing Compositional Boundaries in Mixed-Linker Keplerate Clusters

Bogdan Botar,*[a] Arkady Ellern,[b] Moulay T. Sougrati,[c] and Paul Kögerler*[a,d]

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The formation of a self-assembled multi-heterometal Keplerate polyoxomolybdate demonstrates compositional control of linker groups in spherical clusters. The resulting partially reduced $\{Mo^{V/VI}{}_{72}Fe^{III}{}_{20}V^{IV}{}_{8}Mo^{V}{}_{2}\}$-type cluster exhibits intramolecular ferrimagnetic ordering characteristic of such mixed-spin Keplerate systems.

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Introduction

The self-organized formation of nanoscaled polyoxomolybdate cluster anions – wheel-shaped molybdenum blue-type anions and spherical Keplerate structures in particular – allows access to functional metal oxide cluster systems of importance in numerous fields including molecular magnetism and molecular electronics.[1–4] Compositional control of the building groups defining these structures (i.e. both polyoxomolybdate and heterometal fragments) is central to the functional development of this class of molecular compounds. We recently have identified an approach that allows varying the identity and ratio of linker groups in spherical Keplerate polyoxomolybdates.[5] These clusters comprise twelve pentagonal $\{(Mo)Mo_5\}$ = $[Mo^{VI}{}_6O_{21}(H_2O)_6]^{6-}$ building blocks that are connected by 30 linker groups L to form structures of approximate I_h symmetry with the general formula $\{Mo_{72}L_{30}\}$ (L = $\{Mo^{V}{}_2\}$[6] or a 3d transition-metal cation such as Fe^{III},[7] Cr^{III},[8] and V^{IV}[9]). Using this approach, we reported the first Keplerate derivatives containing mixed-spin $\{s = 1/2\ [O{=}V(OH_2)]^{2+}$ and $s = 5/2\ [Fe(OH_2)_2]^{3+}\}$ linkers, formulated as $K_{23}Na_4[\{Mo^{V/VI}{}_6O_{21}(H_2O)_3(SO_4)\}_{12}\{V^{IV}O(H_2O)\}_{15}\{Mo^{V}O(H_2O)\}_8\{Fe^{III}(H_2O)_2\}_7]\cdot150H_2O$ = $K_{23}Na_4\{Mo^{V/VI}{}_{72}V_{15}Fe_7Mo^{V}{}_8\}\cdot150H_2O$ (**1**) and $K_{21}Na_2[\{Mo^{V/VI}{}_6O_{21}(H_2O)_3(SO_4)\}_{12}\{V^{IV}O(H_2O)\}_{11}\{Mo^{V}O(H_2O)\}_8\{Fe^{III}(H_2O)_2\}_{11}]\cdot150H_2O$ = $K_{21}Na_2\{Mo^{V/VI}{}_{72}V_{11}Fe_{11}Mo^{V}{}_8\}\cdot150H_2O$ (**2**).[5] These compounds self-assemble in acidified aqueous solutions containing molybdate, vanadyl sulfate and ferrous sulfate. The incorporation of two different magnetic heterometal centers in **1** and **2**, which are coupled by O–Mo–O pathways mediating antiferromagnetic exchange, resulted in ferrimagnetic ordering and in high-spin ground-state properties previously not observed in any other Keplerate structures. Significantly, the realization of two isostructural derivatives with two different sets of Fe/V ratios in the 30 linker positions suggests that a whole family of magnetic derivatives may be synthetically accessible. An important challenge in this context is to garner a measurable degree of control over the formation and the heterometal ratio of these intriguing magnetic clusters with implications for their electronic and magnetic properties. Herein we report a new mixed-spin Keplerate derivative featuring a significantly higher Fe^{III}/V^{IV} ratio than **1** and **2**, isolated as $K_{19}Na_3[\{Mo_6O_{21}(H_2O)_3(SO_4)\}_{12}\{Fe(H_2O)_2\}_{20}\{VO(H_2O)\}_8\{MoO(H_2O)\}_2]\cdot150H_2O\cdot2K_2SO_4$ = $K_{19}Na_3\{Mo^{V/VI}{}_{72}V^{IV}{}_8Fe^{III}{}_{20}Mo^{V}{}_2\}\cdot150H_2O\cdot2K_2SO_4$ (**3**).

Results and Discussion

The synthesis of **3** is based on the same self-assembly strategy used in the preparation of **1** and **2**.[5] The most critical factor for the unambiguous and reproducible preparation of **3** is the Fe^{II}/V^{IV} molar ratio employed in the reaction mixture. In the course of our work that led to the preparation of **1** and **2** it became apparent that VO^{2+} groups can be preferentially incorporated into the Keplerate framework, whereas incorporation of Fe^{III} cations requires excess of $FeSO_4$. Thus, **3** is prepared by using a large excess of ferrous sulfate (22:1 ratio of $FeSO_4\cdot7H_2O/VOSO_4\cdot5H_2O$, compared to a 5.5:1 ratio used for **2**). The use of excess ferrous sulfate, which in the synthesis of **3** is not only a reactant but also the reducing agent, facilitates the formation of highly negatively charged mixed-valent pentagonal units having high affinity for electrophiles such as Fe^{III}.

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[a] Institut für Festkörperforschung, Forschungszentrum Jülich GmbH,
52425 Jülich, Germany
E-mail: b.botar@fz-juelich.de
p.koegerler@fz-juelich.de
[b] Department of Chemistry, Iowa State University,
Ames, IA 50011, USA
[c] Department of Physics, Université de Liège,
4000 Sart-Tilman, Belgium
[d] Institut für Anorganische Chemie, RWTH Aachen University,
52074 Aachen, Germany
E-mail: paul.koegerler@ac.rwth-aachen.de

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The spherical shell (virtual I_h symmetry) in **3** follows the general Aufbau principle of Keplerate structures and is composed of 12 slightly domed (virtual C_{5v} symmetry), mixed-valent $\{(Mo)Mo_5\}$ pentagonal units connected by 30 paramagnetic linker groups: a mixture of 20 $[Fe^{III}(H_2O)_2]^{3+}$, 8 $[V^{IV}O(H_2O)]^{2+}$ and 2 $[Mo^{V}O(H_2O)]^{3+}$ groups statistically distributed over the 30 corners of an icosidodecahedron (Figure 1). The close association of the K^+ cations to the twenty $\{Mo_3M_3O_6\}$ hexagonal pores reminiscent of K^+-specific crown ethers, previously observed in other highly charged Keplerates, is also evident in **3**.[5,10] The spherical shell encapsulates 12 heavily disordered (five possible binding modes to each of the pentagonal units) tridentate sulfate groups.

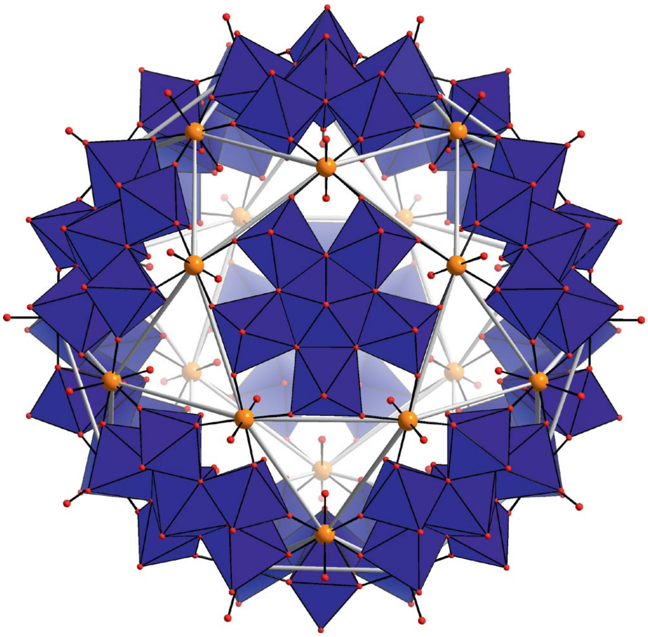

Figure 1. Simplified representation of the Keplerate-type cluster sphere in **3** emphasizing the 12 pentagonal $\{(Mo)Mo_5\}$ building groups (blue polyhedra) and the 30 mixed $Fe^{III}/V^{IV}/Mo^{V}$ (M) linker groups (orange spheres) with their two axial terminal ligands (red), viewed along a C_5 axis. Grey lines indicate the nearest-neighbor M···M contacts. The K^+ ions coordinating to the 20 $\{Mo_3M_3O_6\}$ pores and the 12 disordered sulfate groups coordinating to the inner sides of $\{(Mo)Mo_5\}$ groups are not shown for clarity.

Establishing the exact composition and formula of **3** proved to be challenging due to the disorder of the V^{IV}, Fe^{III} and Mo^{V} cations over the 30 linker sites as well as the additional presence of Mo(4d) electrons. For this purpose, several independent analysis techniques had to be employed: elemental analysis results (reproduced on separately synthesized batches), magnetic measurements (see below), and thermogravimetric studies are consistent with the above-given formula of **3**. Furthermore, the crystallographic refinement provides useful information on the coordination environments of the 3d-metal centers and the occupancy factors of these sites. The 30 linkers in **3** (15 crystallographic independent sites) adopt weakly distorted coordination environments and show only a weak axial distortion indicative of metal–oxo bonding. This means that only a small fraction of V^{IV} compared to Fe^{III} occupies these sites. The fractional occupancies of the linker sites were fixed at values consistent with the Fe/V ratio determined analytically. The two Mo^{V} linker sites in **3** could no be inferred from the crystallographic data (only 6% of the linker sites are occupied by Mo^{V}), but their presence was confirmed by elemental analysis. As observed for all other Keplerate structures containing oxometal groups in the linker positions ($[V^{IV}{=}O]^{2+}$,[5] $[Mo^{V}{=}O]^{3+}$),[11] the terminal metal–oxo vector points toward the interior of the sphere. A careful analysis of the structures of complexes **1**–**3** clearly indicates the presence of a higher electron density in the linker sites of **1** and **2**, fully consistent with a higher Mo^{V} fractional occupancy of these positions (both **1** and **2** contain 8 Mo^{V} linker sites).[5] Potentiometric titrations indicate the presence of 18 (±2) reduced electrons, associated with the reduced linker sites (V^{IV} and Mo^{V}) and 8 Mo(4d) electrons fully delocalized over the pentagonal units. These combined results support the above-given formula for **3** and unequivocably demonstrate that the metal composition in the linker sites is quite distinct from that in compounds **1** and **2**. The Mößbauer spectra of **3** at 298 K and 60 K (Figure 2, inset) are fully consistent with all iron centers in the oxidation state of +3 and residing in a slightly distorted octahedral coordination environment [the spectrum at 60 K rules out an Fe^{II} content of more than 3.5(5)% of total Fe in **3**]. Note that upon taking into account the accuracy limits of the afore-mentioned analytical methods, we have to postulate a possible stoichiometric uncertainty of the exact composition of the 30 linker sites of ±2 for each of the involved linker types.

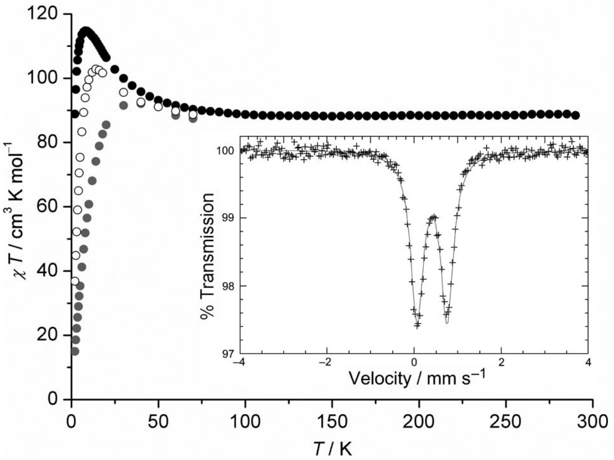

Figure 2. Temperature-dependence of χT at 0.1 T (black circles), 1.0 T (open circles), and 5.0 T (grey circles) for **3**. Inset: ^{57}Fe Mößbauer spectrum of **3** at 298 K (right).

The magnetic properties of **3** are analogous to those of **1** and **2** in that they are characterized by intramolecular ferrimagnetic ordering caused by antiferromagnetic exchange interactions between neighboring $s = 1/2$ vanadyl and $s = 5/2$ iron(III) groups,[5] as evidenced by a field-dependent maximum in χT vs. T that is suppressed by an increasing external field (Figure 2). At 5.0 T, the maximum has shifted to ca. 40 K. The 10 Mo(4d) electrons are strongly coupled (as they are in **1** and **2** and other partially reduced Keplerate-type polyoxomolybdates[11]) and thus do not significantly contribute to the susceptibility within the experimentally probed temperature range (2.0–290 K). At 290 K the measured χT value of 88.5 $cm^3\,K\,mol^{-1}$ approaches the spin-only value of 89.57 $emu\,K\,mol^{-1}$ calculated for 20 uncoupled $s = 5/2$ Fe^{III} centers ($g = 1.99$) plus 8 uncoupled $s = 1/2$ VO^{2+} groups ($g = 1.98$). With lower temperatures, χT slowly increases to reach a maximum at 8.0 K ($\chi T = 114.7\ cm^3\,K\,mol^{-1}$, approx. corresponding to a purely hypothetical $S = 29/2$ state), i.e. at a higher temperature than the maxima observed for **1** (4.5 K) and **2** (5.5 K). Note that as encountered with all previous mixed-linker Keplerate structures, the non-magnetic Mo^V centers and the Fe^{III} and V^{IV} spin centers are distributed statistically over their 30 sites, resulting in a plethora of possible linker distributions. Therefore, the fully reproducible magnetic measurements on crystalline bulk material represent an average of all possible site permutations and consequently an average of various magnetic order scenarios. Correspondingly, the measured magnetization data cannot be ascribed to a single spin ground state, and the observed susceptibility data cannot be modeled by a single Heisenberg-type Hamiltonian.

Compound **3** was also characterized in solution by Raman and Vis/NIR spectroscopy. The Vis/NIR electronic spectrum of **3** shows two very intense absorption bands both attributed to IVCT (intervalence charge transfer) transitions. The broad band with a maximum at 825 nm is the result of homonuclear $Mo^{VI} \leftarrow Mo^V$ IVCT transitions since it is the dominant feature in the spectra of any mixed-valent ring type cluster such as $\{Mo_{154}\}$.[12] The second band at higher energy arises from heteronuclear $Mo^{VI} \leftarrow V^{IV}$ IVCT transitions.

Conclusion

The realization of **3** confirms our early predictions that a wide range of mixed-spin Keplerate derivatives exist. This also exemplifies how the manipulation of reaction conditions allows us to tune the electronic and magnetic properties of Keplerates, a finding that we will seek to extend to other related nanostructures. In addition to further expanding this type of cluster chemistry, including networking of these magnetic Keplerates to 1D[13] and 2D[14] structures, we will focus on possible applications of these large magnetic clusters (compounds **1**–**3**) as contrast agents for magnetic resonance imaging of biological tissues. This is motivated by the exposed $H_2O\text{-}VO^{2+}$ and $H_2O\text{-}Fe^{3+}$ groups that are sufficiently labile for rapid water exchange.

Experimental Section

Synthesis of $K_{19}Na_3[\{Mo_6O_{21}(H_2O)_3(SO_4)\}_{12}\{Fe(H_2O)_2\}_{20}\{VO(H_2O)\}_8\{MoO(H_2O)\}_2]\cdot150H_2O\cdot2K_2SO_4$ (3): A solution of $Na_2MoO_4\cdot2H_2O$ (12 g, 49.6 mmol), dissolved in H_2O (120 mL) at room temperature, was acidified to pH = 1.8–1.9 with H_2SO_4 (2 M; 24 mL) and then treated with solid $VOSO_4\cdot5H_2O$ (1.5 g, 5.9 mmol). As soon as the solution had become clear, solid $FeSO_4\cdot7H_2O$ (36 g, 129.5 mmol) was quickly added, and the resulting dark-blue mixture was stirred at room temperature for 24 h. The mixture was then treated with a solution of KCl (4.5 g, 60.4 mmol), dissolved in H_2O (35 mL), added in small portions. The dark blue solution was filtered and the filtrate left standing at room temperature. Blue-black pyramidal crystals started to form after 24 h. Yield ca. 4 g (35% based on Mo). $H_{472}O_{544}K_{23}Na_2S_{14}V_8Fe_{20}Mo_{74}$ (19380.56): calcd. K 4.64, Na 0.36, S 2.32, V 2.10, Fe 5.76; found K 4.81, Na 0.21, S 2.45, V 2.17, Fe 5.42; duplicate K 4.63, Na 0.3, S 2.7, V 2.13, Fe 5.60 (ICP-OES, Zentrale Chemische Analytik, Forschungszentrum Jülich). The number of crystal water molecules was determined by thermogravimetric analysis (TGA/DTA; Figure S1). IR (KBr pellet; 2000–400 cm^{-1}): $\tilde{\nu}$ = 1622 (w) [$\delta(H_2O)$]; 1210 (w), 1122 (w), 1048 (w) [all $\nu_{as}(SO_4)$]; 961 (m-s) [$\nu(Mo–O_t)$/$\nu(V–O_t)$]; 780 (vs), 627 (m-s), 568 (s), 439 (m) cm^{-1} (Figure S2). Raman (in H_2O; λ_e = 1064 nm): $\tilde{\nu}$ = 819 (s), 628 (m), 464 (m) cm^{-1} (Figure S3). Electronic absorption spectra (in H_2O; c = 0.1 mM, d = 2 mm, 400–1000 nm): λ_{max} ($\varepsilon/M^{-1}\,cm^{-1}$) = 825 (IVCT $Mo^{VI} \leftarrow Mo^V$; 2.5×10^4), 535 (IVCT $Mo^{VI} \leftarrow V^{IV}$; 2.3×10^4) nm (Figure S4). ^{57}Fe Mössbauer (298 K): $\delta^{\alpha\text{-}Fe}$ = 0.41(1) $mm\,s^{-1}$, ΔE_Q = 0.69(1) $mm\,s^{-1}$, Γ = 0.35(1) $mm\,s^{-1}$. Cerimetric redox titrations: 18.6 ± 2.0 electrons (V^{IV} and Mo^V centers).

X-ray Crystal Structure Determination: Crystal data for **3**: orthorhombic, space group *Pccn*, a = 38.853(15), b = 38.917(15), c = 32.984(13) Å, V = 49874(34) $Å^3$, Z = 4, ρ = 2.57 $g\,cm^{-3}$, μ = 2.882 mm^{-1}, $F(000)$ = 37508; crystal size: 0.28 × 0.21 × 0.08 mm. Crystals of **3** were taken directly from the mother liquor, mounted on a cryoloop sample holder and immediately cooled to 173(2) K on a Bruker CCD-1000 diffractometer [Mo-K_α (0.71073 Å) radiation]. A total of 230911 reflections ($1.32° < \Theta < 20.83°$) were collected of which 26123 reflections were unique [R(int) = 0.2106]. R = 0.0865 for 14544 reflections with $I > 2\sigma(I)$; ρ(max./min.) = 3.60 and –1.82 $e\,Å^{-3}$. Structure solution, refinement and generation of publication materials were performed by using SHELXTL software. Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-420735.

Supporting Information (see footnote on the first page of this article): Magnetochemical analysis details and field dependence of the magnetization, IR/Raman/UV/Vis spectra, and TGA/DTA curves.

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