

Triangular Geometrical and Magnetic Motifs Uniquely Linked on a Spherical Capsule Surface**

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Dedicated to Professor Francis Sécheresse on the occasion of his 60th birthday

Polygons can be placed on spherical surfaces such that periodical structures of a cyclic nature result, while these can be considered as discrete models for two-dimensional (extended) structures. If we wish to construct a chemical structure on a spherical capsule surface in the same way, we have to remember that 1) pentagons are the basic units for sphere constructions, as is well known, for example, from virus structures, 2) they exist, for example, in the form of $\{(Mo^{VI})Mo^{VI}_5\}$ type units, and that 3) they occur in Keplerates of the type $\{(Mo^{VI})Mo^{VI}_5\}_{12}[Linker]_{30}$ ^[1–5] (linker can be of the mononuclear M (M = metal center) or dinuclear type M_2 ; for the definition of Keplerates, see ref. [5b]). However, until now it was not possible to synthesize a spherical capsule surface directly by the addition of linkers to the pentagonal units that are available in a dynamic library.^[1–5] It is significant that in the Keplerates the linkers describe generic Archimedean solids: in the case of dinuclear linkers M_2 a distorted truncated icosahedron, $\{M_2\}_{30}$, and in the case of mononuclear linkers the unique icosidodecahedron (Figure 1)^[6] $\{M_{30}\}$, which has—geometrically speaking—linked M_3 triangles. Surprisingly the related consequences for chemistry have not been discussed until now. In the $\{M_{30}\}$ situation, there is a

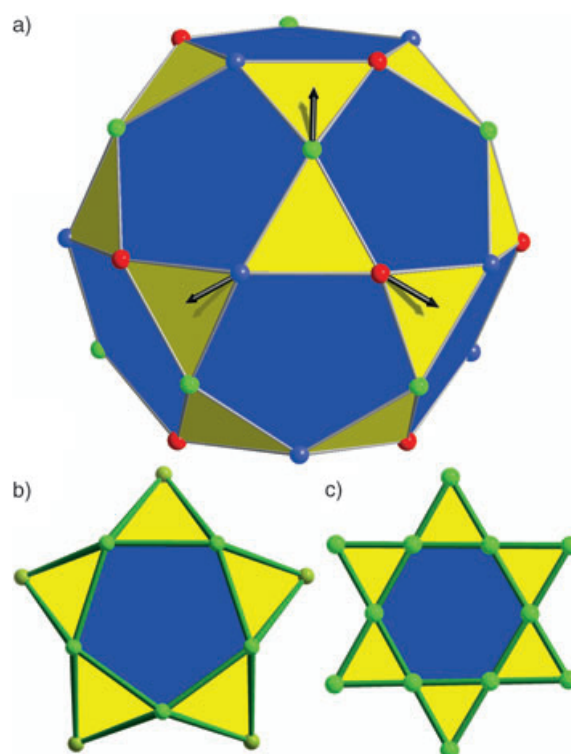


Figure 1. a) The M centers (small colored spheres) of the $\{(Mo^{VI})Mo^{VI}_5\}_{12}M_{30}$ type Keplerates (e.g., $M = V^{IV}$, Fe^{III}) describe the icosidodecahedron shown, which is unique among the icosahedral Archimedean solids as all edges are equivalent and all dihedral angles equal. Referring to the special situation of $M = Fe^{III}$, there are three groups (“sublattices”) of 10 spins (colors: red, blue, green), with all spins of a sublattice pointing in the same direction, while nearest-neighbor spin vectors (three are highlighted) differ in angular orientation by 120° . Also shown: b) A fragment highlighting five linked triangles around a pentagon. c) A fragment of a planar Kagomé lattice with six linked triangles around a hexagon.

network of corner-shared triangles on the sphere surface, this can result unique magnetic properties as in the case of the “classical” Keplerate $\{(Mo^{VI})Mo^{VI}_5\}_{12}Fe^{III}_{30}$ ^[7,8]. This is the first laboratory example of a “zero-dimensional” system that at low temperatures embodies characteristics of geometrical frustration/magnetic ordering^[8b] which otherwise have only been observed in selected one-, two-, and three-dimensional lattice spin systems.^[9] Herein we report on the spherical cluster **1a** where the twelve $\{(Mo^{VI})Mo^{VI}_5\}$ type units fix 30 $d^1 V^{IV}$ linkers/centers with spin $S = 1/2$ in the form of an icosidodecahedron, and thus 1) demonstrating for the first time that the spherical capsule/Keplerate can be directly constructed from the mononuclear linkers and the appropriate molybdate library,^[5c] 2) providing the chance to obtain new information regarding the unique molecular magnetism of the $\{M_{30}\}$ type network of linkers/triangles, and 3) clarifying the quantum effects of the spin $S = 1/2$ vanadyl linkers especially in connection with the two-dimensional $S = 1/2$ Kagomé lattice which contains linked triangles and exhibits unique magnetic properties.^[9a]

After adding vanadyl sulfate to an acidified molybdate solution, in the presence of K^+ ions, compound **1** precipitates after some time in high yield. (A simpler expression for the

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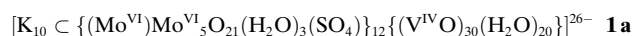
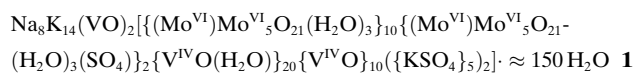
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cluster anion **1a** without referring to structural differences is given as well.)



Compound **1**, which crystallizes in the monoclinic space group $C2/c$, was characterized by elemental analysis, thermogravimetry (to determine the crystal water content), redox titrations (to determine the number of V^{IV} centers), spectroscopic methods (IR, Raman, UV/Vis), single-crystal X-ray structure analysis (including bond valence sum (BVS) calculations),^[10] and susceptibility measurements (including related quantum Monte Carlo calculations).

The cluster anion **1a** of **1** is of the expected $(\text{Pentagon})_{12}(\text{Linker})_{30}$ type and is a slightly compressed sphere, while the heptacoordinate Mo^{VI} centers of the 12 pentagonal units correspondingly describe a slightly distorted icosahedron and the 30 V^{IV} centers—acting as linkers for the pentagonal $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}$ type units—describe a (slightly distorted) icosidodecahedron (Figure 2; the $\text{V}^{\text{IV}}\text{--V}^{\text{IV}}$ distances in the distorted Archimedean solid vary from 6.3 to 6.6 Å). The distortion is in agreement with the fact that 20 V^{IV} centers in the equatorial region have octahedral coordination and the two sets of five V^{IV} centers in the polar area have square-pyramidal coordination; the distances from the 10 equatorial V^{IV} units to the center of the cluster are a little shorter (10.3 Å) than the related distances of the other 20 V^{IV} units

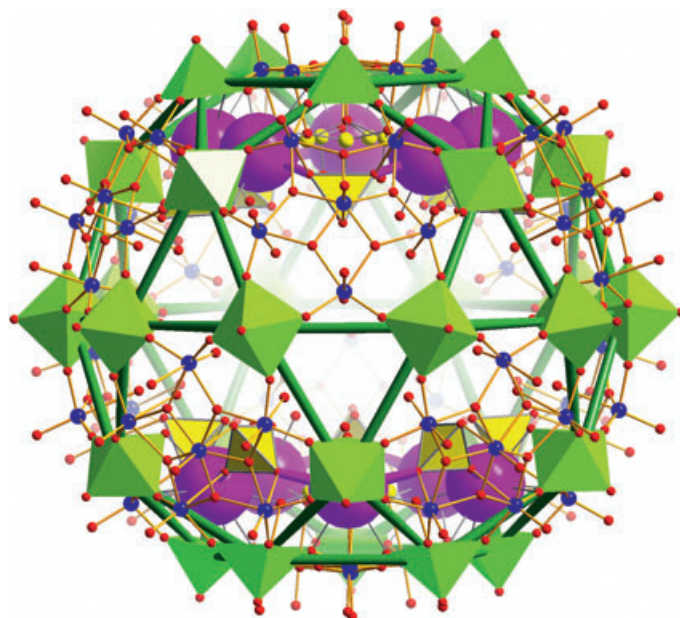


Figure 2. Combined polyhedral and ball-and-stick representation of the structure of **1a** showing the triangles and pentagons of the icosidodecahedron (green sticks), and additionally the basic $\{\text{VO}_3\}$ and $\{\text{VO}_6\}$ units as green polyhedra; as the interaction between the “lattice K^+ ” ions and the 20 pores is not homogeneous, this interaction was not considered here (blue Mo, red O, purple K, yellow tetrahedra: $\{\text{SO}_4\}$ groups; yellow spheres: disordered S atoms).

(10.6 Å). Ten of the twelve $[\text{SO}_4]^{2-}$ ligands are coordinated by three oxygen atoms to three adjacent Mo^{VI} centers of the $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}$ groups such that two $\{\text{KSO}_4\}_5$ rings parallel to the equator result, with the K^+ ions (formally) bridging the $[\text{SO}_4]^{2-}$ ions (Figure 3). The other two sulfate groups are

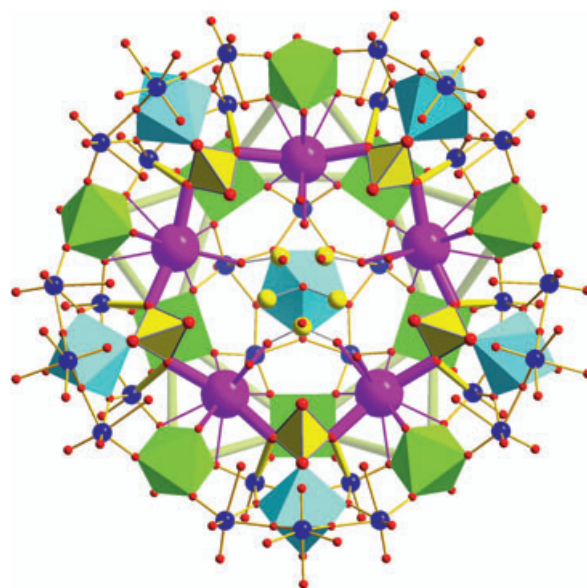
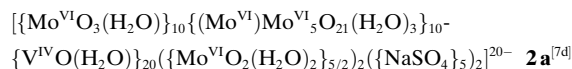


Figure 3. Combined polyhedral and ball-and-stick representation of a fragment of **1a** (view in direction of the C_2 axis) showing one of the two $\{\text{KSO}_4\}_5$ rings and the coordination of $\{\text{SO}_4\}$ groups to Mo centers as well as the disorder of one of the two sulfate groups (color code as in Figure 2, additional light blue pentagonal bipyramids: $\{\text{MoO}_7\}$).

disordered and act as ligands to the two polar $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}$ groups. The structure of **1a** comprising the twenty triangular and twelve pentagonal faces of the icosidodecahedron built up by 30 V^{IV} centers shows an interesting relation to the much less symmetrical cluster anion **2a** which has a non-complete spherical $\{\text{V}_3\}$ type net. In **2a**, a strongly distorted icosidodecahedron is described by 10 Mo^{VI} and 20 V^{IV} centers, while the equatorial $\{\text{V}_{20}\}$ belt—formed by 10 linked $\{\text{V}_3\}$ triangles—is identical to the related equatorial segment of **1a**.



The presence of K^+ and $[\text{SO}_4]^{2-}$ ions in the reaction medium seems to be of fundamental importance for the structure formation, as the potassium cations of the two $\{\text{KSO}_4\}_5$ rings of **1a** attract the two negatively charged polar $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}$ units thus causing the slight compression of the sphere. This distortion leads to an inclination of the adjacent $\{\text{VO}_5\}$ polyhedra and thus prevents an octahedral coordination of the 10 polar V^{IV} centers. The sixth (H_2O) ligand required for octahedral coordination would be too close to the $[\text{SO}_4]^{2-}$ ligands of the $\{\text{KSO}_4\}_5$ rings.

The investigations nicely show that $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}$ type units are potentially available in a dynamic polymolybdate library; remarkably, they can be “used” in the present case as

virtual units in the presence of potential linkers. In aqueous solution at low pH values, the pentagonal structural unit occurs in the $[\text{Mo}^{\text{VI}}_{36}\text{O}_{112}(\text{H}_2\text{O})_{16}]^{8-}$ ion,^[11] which is the only(!) abundant species under those conditions. Correspondingly, **1a** is formed from that solution in the presence of VO^{2+} linkers by a “split-and-link” process with the $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}$ unit being formed from the $\{\text{Mo}_{36}\}$ species after the addition of the linkers. The option to extend this to mixed-metal species such as $\{\text{Mo}^{\text{V}}_8\text{V}^{\text{IV}}_{22}\}$,^[12] $\{\text{Mo}^{\text{V}}_4\text{V}^{\text{IV}}_{26}\}$, or $\{\text{Fe}^{\text{III}}_{22}\text{V}^{\text{IV}}_8\}$ ^[13] will be reported elsewhere.

Turning to the magnetic properties, two circumstances are of pivotal importance for the possible occurrence of geometrical frustration in the type of system considered herein: First, the 30 mononuclear magnetic Keplerate linkers occupy the vertices of an icosidodecahedron, which may be pictured as 20 linked (corner sharing) triangles arranged around 12 pentagons and corresponds to an equidistant distribution of the spins on the surface of a spherical cluster; second, each magnetic center (“spin vector”) interacts with its four nearest-neighbors by isotropic antiferromagnetic exchange as a consequence of the special geometry of the unique $\{\text{M}_{30}\}$ type quasi-regular solid (Figure 1). Analogous to what occurs for the Kagomé spin system (planar lattice of triangles framed around hexagons; Figure 1c),^[9] the geometric frustration of the individual Keplerate can be achieved by the cooperative interactions among the full set of spin vectors. In the special case of the above mentioned $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}_{12}\text{Fe}^{\text{III}}_{30}$, we may refer to it as a “classical” Keplerate (because of the relatively high spin, $S=5/2$, of individual Fe^{III} centers) and the spin frustration/magnetic ordering may therefore be visualized in geometrical terms^[8c] (Figure 1). The 30 spin vectors are composed of three groups (“sublattices”) of 10 spins each; all spins of a given sublattice point in the same direction, and any pair of nearest-neighbor spin vectors differ in angular orientation by 120° (Figure 1).^[8c] In **1a** we have replaced the Fe^{III} centers by VO^{2+} ions which have the much smaller spin of $S=1/2$, that is, “quantum spins”. In addition, in **1a** the 3d electrons are not “localized” at the vertices of the icosidodecahedron as is approximately the case in the $\{\text{Fe}^{\text{III}}_{30}\}$ Keplerate.^[14] However, the spin frustration of these quantum spins can not be visualized in geometric terms. More generally the magnetism of the “quantum” Keplerate **1a** is expected to be significantly different from that of its classical counterpart $\{\text{Fe}_{30}\}$, and more properties are expected to emerge.

Our experimental susceptibility data versus T , recorded for an applied field of $H=0.1$ T, and corrected for the d^1 centers of two VO^{2+} ions which are magnetically/structurally independent from the cluster skeleton **1a**, are shown in Figure 4.^[15] These results show the strong antiferromagnetic coupling in **1a**, in contrast to the $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}_{12}\text{Fe}^{\text{III}}_{30}$ case.^[16] The behavior of $T\chi$ at low T is qualitatively what could be expected for a spin system having a ground state with $S=0$ and with very strong exchange coupling. This situation can be explained by a strong delocalization of the 3d electrons which arises because the 3d V levels are comparable in energy with the LUMOs of the molybdate fragment system.^[16] This is a completely different situation than the classical $\{\text{Fe}_{30}\}$ type Keplerate where the exchange interaction is very weak, and

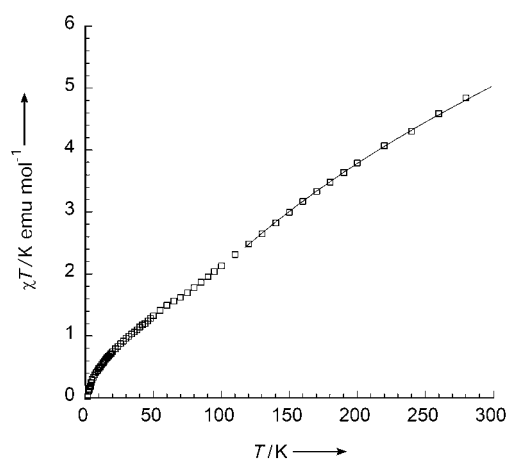


Figure 4. Magnetic susceptibility of $\{\text{V}_{30}\}$ versus temperature: Experimental data corrected for the two d^1/VO^{2+} centers (\square);^[15] quantum Monte Carlo results (solid curve).

therefore the room temperature value of $T\chi$ corresponds to 30 uncoupled $S=5/2$ ions. The quantum Monte Carlo (QMC) method provides accurate values of susceptibility for the Heisenberg model of the $\{\text{V}_{30}\}$ system for $T>0.5J/k_B$, and as seen in Figure 4, a very good fit to $T\chi$ is achieved for $T>120$ K for the choices $J/k_B=245$ K and $g=1.95$. Unfortunately, reliable results cannot be obtained for lower temperatures using the QMC method owing to the “sign problem” that occurs for spin systems with antiferromagnetic exchange based on lattice geometries where the classical counterpart exhibits spin frustration.

To summarize: We have demonstrated that it is possible to “use” pentagonal units as “building units” which play, geometrically speaking, the same role as the pentagonal units in other sphere-based constructions, such as spherical viruses, fullerenes, and geodesic domes; in our context they are used as a glue for trapping magnetic centers, such that triangles are linked to form an icosidodecahedron, that is, a part of a Keplerate. As the “quantum” Keplerate **1a** obtained is a new example of a frustrated magnetic system which shares a topological feature with the classical Keplerate $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}_{12}\text{Fe}^{\text{III}}_{30}$ and the Kagomé-lattice antiferromagnet, its exploration is expected to provide a deeper understanding of basic aspects of magnetic frustration and the role played by the size of the intrinsic spin of the interacting magnetic ions. This study should also shed light on the parallel problem, and the focus of an intense effort, to characterize and understand the $S=1/2$ Kagomé lattice, which is considered to have unique magnetic/electronic properties originating in the small value of S .^[9] The behavior of the magnetization of the quantum Keplerate **1a** in high magnetic fields will be of key importance in studies aimed at elucidating the characteristics of its magnetic frustration.^[17]

Experimental Section

A solution of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (2.53 g, 10 mmol) in H_2O (35 mL) was added to a stirred solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (2.42 g, 10 mmol) in H_2SO_4 (0.5 M; 8 mL) in a conical flask. The resulting dark purple

mixture was stirred at room temperature for 30 min (flask closed with a rubber stopper) and then treated with KCl (0.65 g, 8.72 mmol). After additional stirring for 30 min the solution was stored in the flask which was closed with a rubber stopper. After 5 days, the purple-black rhombic crystals of **1** were collected by filtration, washed with cold water, and finally dried in air. Yield: 1 g; elemental analysis: calcd (%) for $\text{Na}_8\text{K}_{24}\text{Mo}_{72}\text{V}_{32}\text{S}_{12}\text{O}_{538}\text{H}_{412}$: Na 0.96, K 4.92, V 8.55, S 2.02; found: Na 1.0, K 5.1, V 8.5, S 2.1. IR (KBr pellet): $\tilde{\nu}$ = 1622 (m), ($\delta(\text{H}_2\text{O})$) 1198 (w), 1130 (w), 1055 (w) ($\nu_{\text{as}}(\text{SO}_4)$ triplet), 964 (s) ($\nu(\text{V}=\text{O})/\nu(\text{Mo}=\text{O})$), 791 (vs), 631 (w), 575 (s), 449 (w) cm^{-1} ; FT-Raman (solid; λ_c = 1064 nm): $\tilde{\nu}$ = 941 (w, $\nu(\text{V}=\text{O})/\nu(\text{Mo}=\text{O})$), 872 (s, $\text{A}_{1g}\text{O}_{\text{br}}$ breathing) cm^{-1} ; UV/Vis (in H_2O): λ = 510 (vs), 689 (w), 845 (w) nm.

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- [10] Crystal data for **1**: $\text{H}_{412}\text{K}_{24}\text{Mo}_{72}\text{Na}_8\text{O}_{538}\text{S}_{12}\text{V}_{32}$, M_r = 19068.10 g mol^{-1} , monoclinic, space group $C2/c$, a = 47.155(2), b = 42.5364(18), c = 26.5344(12) Å, β = 90.2510(10)°, V = 53222(4) Å³, Z = 4, ρ = 2.380 g cm^{-3} , μ = 2.530 mm^{-1} , $F(000)$ = 36848, crystal size = $0.30 \times 0.20 \times 0.02$ mm³. Crystals of **1** were removed from the mother liquor and immediately cooled to 183(2) K on a Bruker AXS SMART diffractometer (three circle goniometer with 1 K CCD detector, MoK_α radiation, graphite monochromator; hemisphere data collection in ω at 0.3° scan width in three runs with 606, 435, and 230 frames (ϕ = 0, 88, and 180°) at a detector distance of 5 cm). A total of 158364 reflections ($1.50 < \theta < 26.99^\circ$) were collected of which 57718 reflections were unique ($R(\text{int})$ = 0.0612). An empirical absorption correction using equivalent reflections was performed with the program SADABS. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to R = 0.0567 for 40563 reflections with $I > 2\sigma(I)$, R = 0.0916 for all reflections; max/min residual electron density 3.456 and -2.026 e Å⁻³. (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen **1997**; structure graphics with DIAMOND2.1 from K. Brandenburg, *Crystal Impact GbR*, **2001**.) As usual the cations not bound to the capsule as well as the crystal water molecules could not be found completely due to disorder. As this is also the case for the $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ centers, the H_2O ligand sphere was not considered in the formula. 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-415055.
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- [13] A. Müller, S. K. Das, H. Bögge, M. Schmidtman, M. Dressel, J. van Slageren, unpublished results.
- [14] In spite of these expected differences, there are some important features common to the two Keplerates, such as similar characteristics of the ground state and the low-lying excitation states, which arise because of their otherwise common geometrical structure and the existence of antiferromagnetic exchange between nearest-neighbor spins. As one example, the total spin quantum number of the ground state eigenvector for the “quantum” Keplerate **1** is expected to be $S=0$, as it is for the “classical” Keplerate $\{\text{Fe}_{30}\}$, and its direct manifestation would be in the vanishing of T_χ (proportional to $\langle S^2 \rangle$), in the low-temperature regime; χ is the zero-field susceptibility.
- [15] The raw M/H ($\equiv \chi$) data display a rapid rise on decreasing the temperature below 50 K that is very accurately simulated by a term proportional to $1/T$ (Curie behavior). This observation suggests the presence of additional non-interacting paramagnetic centers in the sample. In fact, fitting the low temperature data leads to a value of approximately $2 S = 1/2$ centers. These centers are considered to be the non-interacting VO^{2+} (d^1) ions. In large cluster systems like **1**, they can take the same place as the other diamagnetic cations, which are usually disordered in the large voids between the clusters and can therefore not be discovered by single-crystal structure analysis (see ref. [10]). On subtracting the contribution of these discrete paramagnetic centers, we obtain a corrected magnetization M' as well as the corrected susceptibility data, $T_\chi \equiv T'/H$, shown in Figure 4. The Curie behavior of the paramagnetic centers shows that they do not interact with each other and with the $\{\text{V}_{30}\}$ cluster. The possibility that the finite T_χ value at low temperatures is due to a non-zero spin ground state can be precluded. Regarding the presented T_χ curve: As always there is uncertainty as to the appropriate choices for diamagnetic and temperature-independent paramagnetism (TIP) corrections. Additionally, because of the large voids between the clusters the VO^{2+} groups need not be present stoichiometrically in the compound; correspondingly, there is a very small error limit in the given/used number of two VO^{2+} groups which influences the correction of the raw magnetic data ($(\text{VO})_{1.8}$ could, for example, correspond to $\text{K}_{14.4}$).
- [16] The exchange coupling difference between the classical and quantum Keplerates discussed herein is analogous to that of the cluster pair with 6 V^{IV} and 6 Fe^{III} centers embedded in the $\{\text{Mo}_{57}\}$ type skeleton; see D. Gatteschi, R. Sessoli, W. Plass, A. Müller, E. Krickemeyer, J. Meyer, D. Sölter, P. Adler, *Inorg. Chem.* **1996**, 35, 1926–1934.
- [17] Note added in proof, April 27, 2005: Very recent measurements by H. Nojiri (Tohoku University) of M versus H at 0.5 K up to 27 Tesla, as well as ESR measurements at 190 GHz for several temperatures, show features which are fully consistent with our physical interpretation of a strong intracluster exchange constant and approximately two VO^{2+} ions per formula unit that are magnetically independent of the $\{\text{V}_{30}\}$ cluster. Full details will be published elsewhere.