$[\{(Mo)Mo_5O_{21}(H_2O)_3(SO_4)\}_{12}(VO)_{30}(H_2O)_{20}]^{36-}$: A molecular quantum spin icosidodecahedron†

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Self-assembly of aqueous solutions of molybdate and vanadate under reducing, mildly acidic conditions results in a polyoxomolybdate-based $\{Mo_{72}V_{30}\}$ cluster compound $Na_8K_{16}(VO)(H_2O)_5[K_{10}\subset\{(Mo)Mo_5O_{21}(H_2O)_3(SO_4)\}_{12}(VO)_{30}(H_2O)_{20}]\cdot150H_2O$, 1, a quantum spin-based Keplerate structure.‡

The vast structural variety that is inherent to molecular molybdenum oxide clusters offers a versatile entry to large and complex molecular spin arrays.[1] With their magnetic interactions confined to the individual molecules, such magnetic molecules are a source of new physical properties and are of interest with respect to *e.g.* quantum computing, information storage, or magnetic imaging.[1b] Generally, polyoxomolybdates act as structurally rigid and diamagnetic nanometer-sized frameworks in which a large number of magnetic centers can be integrated. Recently, highly symmetric spherical clusters (Keplerates) have been magnetically functionalized, resulting in new and fascinating magnetic phenomena.[2,3] The prototype of a magnetic Keplerate, $\{Mo_{72}Fe_{30}\}$, features an I_h-symmetric spin array of thirty $s = 5/2$ Fe^{III} centers that connect twelve pentagonal $\{(Mo)Mo_5\} = [Mo^{VI}{}_6O_{21}(H_2O)_6]^{6-}$ building blocks and that define the vertices of corner-sharing triangles spanning an icosidodecahedron, thus equidistantly distributing the spins over the surface of the spherical cluster surface.[4] Within each $\{Mo_{72}Fe_{30}\}$ cluster, the thirty spin centers interact antiferromagnetically with their nearest neighbors *via* a single exchange interaction through –O–Mo–O– exchange pathways. Due to the quasi-classical nature of its $s = 5/2$ centers and the system's particular symmetry one of the striking features of $\{Mo_{72}Fe_{30}\}$ is the absence of quantum effects even at very low temperatures: the classical ground state is characterized by symmetrical spin frustration, whereby the 30 classical spin vectors are organized into three sublattices of 10 collinear vectors each.[2] Furthermore, these purely classical arguments have been the basis for a successful approximate quantum model for $\{Mo_{72}Fe_{30}\}$.[5] This prompted the search for analogous Keplerate structures that include magnetic centers of lower spin quantum numbers for which quantum effects become more prevalent, in order to probe the limits of the classical models derived for $\{Mo_{72}Fe_{30}\}$. Vanadium(IV) centers represent ideal quantum spins with $s = 1/2$ and are of particular interest as they are known to couple strongly within polyoxomolybdate frameworks. However, previous attempts to prepare a quantum spin analogue of $\{Mo_{72}Fe_{30}\}$ only led to partially complete spin arrays such as $\{Mo^{VI}{}_{72}Mo^{V}{}_8V^{IV}{}_{22}\}$.[6] Here we present a new synthetic route to a $\{Mo_{72}V_{30}\}$ Keplerate cluster anion that comprises a complete icosidodecahedral array of thirty V^{IV} centers, $[K_{10}\subset\{(Mo)Mo_5O_{21}(H_2O)_3(SO_4)\}_{12}(VO)_{30}(H_2O)_{20}]^{26-}$ (**1a**), isolated as $Na_8K_{16}(VO)(H_2O)_5$**1a**$\cdot150H_2O$ (**1**).

Reaction of molybdate with excess of vanadate in acidic aqueous solutions (pH 2.8) in the presence of hydrazine sulfate (as the reducing agent) and addition of KCl produces crystals of **1** (35% isolated yield) that were characterized by elemental analysis, thermogravimetry, differential scanning calorimetry, spectroscopic methods (IR, UV/VIS-NIR), potentiometric titrations, magnetic measurements, and single-crystal X-ray structure analysis (including bond valence sum (BVS) calculations).§¶||

The reaction was carried out at pH 2.8 in the presence of a large excess of vanadate in order to avoid the reduction of molybdenum and subsequent formation of molybdenum blue-type clusters (*i.e.*, of the $\{Mo_{154}\}$, $\{Mo_{176}\}$ or $\{Mo_{368}\}$ type)[7,8] or of spherical clusters comprising both V^{IV} and Mo^{V} linkers such as $\{Mo_{80}V_{22}\}$,[6] species typically obtained at a pH below 2.0. Several lines of evidence are consistent with the absence of Mo^{V} centers in **1**. All thirty V^{IV} positions in **1** are disorder-free and display normal thermal parameters. BVS values for all Mo atoms range between 5.7 and 6.2. The electronic absorption spectrum of **1** does not show the intense band at around 840 nm observed in $\{Mo_{80}V_{22}\}$, attributed to $Mo^{V} \rightarrow Mo^{VI}$ intervalence charge transfer bands (Figure S1 in the ESI†).[6] Potentiometric titrations show a single end point corresponding to the oxidation of 30.8 ± 1 V^{IV} centers.

The structure of **1a** (Fig. 1) shows a slightly distorted icosahedron of twelve $\{(Mo)Mo_5\}$ pentagonal units linked by thirty VO^{2+} groups. Out of the thirty V^{IV} linkers, ten (V1 to V5 and their symmetry-related counterparts) are five-coordinate (square pyramidal coordination) and are arranged in two groups of five located at opposite ends of the cluster. This results in a flattening of the icosahedron at these two ends. The other twenty V^{IV} centers adopt octahedral coordination which is more common for Keplerate-type species. The non-crystallographic symmetry of the polyanion is approximately D_{5h} with the C_5 axis passing through the center of the pentagon defined by the V1–V5 atoms. The polyanion **1a** is stabilized by two groups of five K^+ cations located inside the cavity just below the ten distorted hexagonal $\{Mo_3V_3O_6\}$ pores each containing two five-coordinate vanadium centers. They occupy alternate positions between the tridentade sulfate ligands to form $\{KSO_4\}_5$ rings (see Figs. 1 and 2). The more regular $\{Mo_3V_3O_6\}$ pores involving exclusively 6-coordinate V positions are capped by K^+ cations in a manner previously observed.[6] As a result of the distortion of the icosahedron and the

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† Electronic Supplementary Information (ESI) available: TGA/DSC data, VIS-NIR spectrum of **1**. See http://www.rsc.org/suppdata/cc/b5/b504491j/

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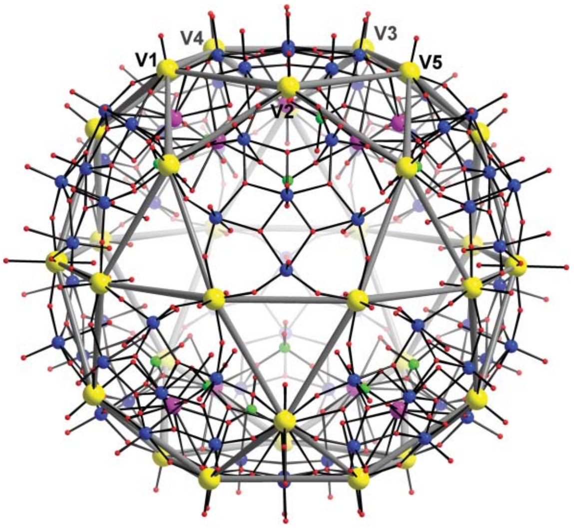

Fig. 1 Ball-and-stick representation of **1a** emphasizing the V_{30} structural motif (view approximately perpendicular to the anion's C_5 axis; Mo-blue, V-yellow, K-purple, S-green, O-red).

anion's low crystallographic symmetry (C_i), the V–V distances within the twenty $\{V_3\}$ triangles range between 6.280(2) and 6.619(6) Å.

The magnetic properties exhibited by **1** (Fig. 3) indicate strong antiferromagnetic intramolecular coupling between the $s = 1/2$ vanadyl groups as it has been observed for $\{Mo_{57}V_6\}$ or Keplerate-type structures that also feature trigonal, molybdate-bridged $V^{IV}{}_3$ motifs and exchange constants of *ca.* -150 to $-200\ cm^{-1}$ for nearest-neighbor V–V interactions.[6,9,10] Emerging from a singlet ground state, the measured χT constantly increases and at room temperature reaches a value of 6.12 emu K mol^{-1}, around 55% of the value for thirty non-coupled vanadyl groups. Only above 280 K the susceptibility data starts to follow a Curie–Weiss-type expression $\chi = C/(T - \Theta)$ with $\Theta \approx -250$ K. For the special case of an icosidodecahedral spin array,[2] this relates to an estimated, effective nearest-neighbor exchange in excess of $-160\ cm^{-1}$. However, the wide range of V–V contact distances results in a range of nearest-neighbor exchange constants, and next-nearest neighbor coupling involving longer –O–Mo–O–Mo–O– bridges is assumed to be significant as well. Thus, contrary to the $\{Mo_{72}Fe_{30}\}$ analogue a model based on a single exchange constant will not suffice for **1**. The susceptibility displays a relatively broad maximum at 11 K, which indicates a large number of closely spaced low-lying excited magnetic states. Preliminary pulsed-field magnetization measurements at 0.5 K up to 28 Tesla[11] show a slow increase in the magnetization with a net rise of nearly one Bohr magneton but do not show apparent steps due to

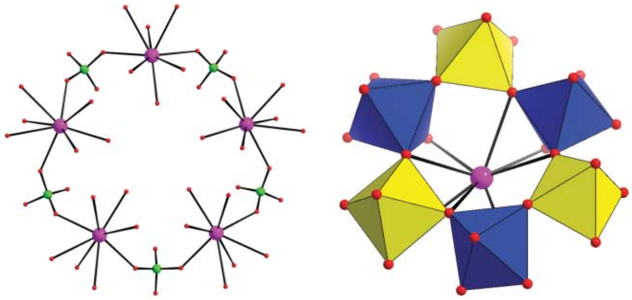

Fig. 2 Left: one of the $\{KSO_4\}_5$ rings inside **1a**; right: distorted $\{Mo_3V_3O_6\}$ pore stabilized by a K^+ cation. K-purple, S-green; O-red; VO_5/VO_6 polyhedra-yellow, MoO_6 octahedra-blue.

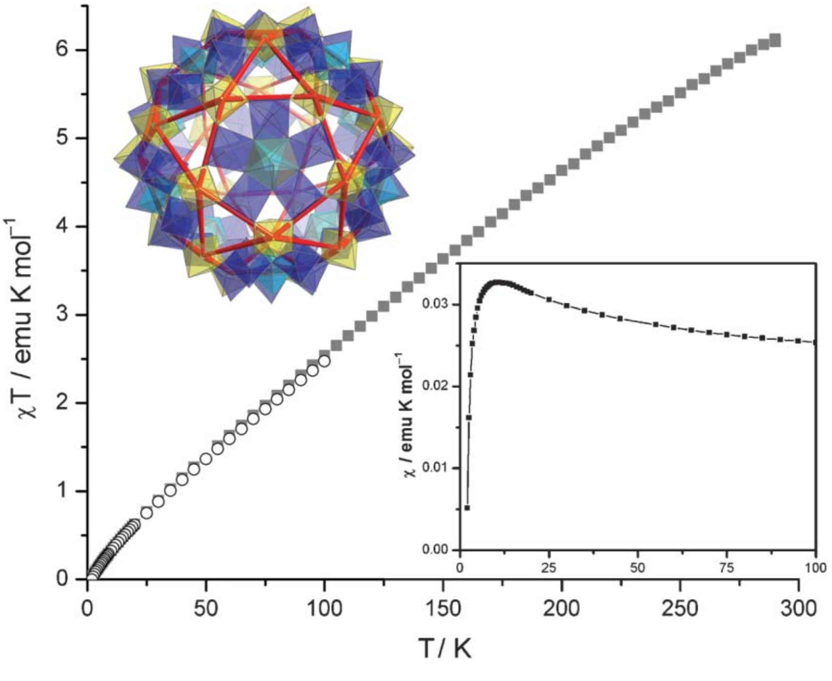

Fig. 3 Temperature dependence of χT of **1** for 0.1 Tesla (grey squares, 2–290 K) and 1.0 Tesla (black circles, 2–100 K). Upper inset: The magnetic framework of **1a**, *i.e.*, the icosidodecahedron (red) defined by the thirty V^{IV} centers imposed on a schematic semi-transparent polyhedral representation of the cluster anion (Mo: blue, V: yellow). Lower inset: temperature dependence of the low-field molar susceptibility in the low-temperature region, featuring a maximum at 11.0 K.

spin-level crossing expected for a fully antiferromagnetically coupled system. To place these observations in the context of the existing and new models, however, will require further investigations of the magnetic level spectrum (*e.g.*, high-field magnetization, EPR, neutron scattering) that we will pursue and address in upcoming work.[11]

Given that the thermal stability of magnetic materials is important in context with their ultimate development and use, we evaluated the thermogravimetric and differential scanning calorimetric profiles of **1** (Figures S2 and S3 in the ESI†). Noteably, the only prominent process below 500 °C is the loss of all H_2O molecules (crystallization and coordination).

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Notes and references

‡ We recently learned that the group of Achim Müller independently prepared a similar polyoxoanion *via* a different synthetic route (*Angew. Chem. Int. Ed.*, in press). We appreciate this personal communication from A. Müller.

§ *Synthesis of* **1**: A solution of $NaVO_3$ (2.6 g, 21.3 mmol) dissolved in 55 mL H_2O at 70 °C and then cooled to room temperature was added to a solution of $Na_2MoO_4{\cdot}2H_2O$ (6 g, 24.8 mmol) dissolved in 75 mL H_2O at room temperature. The mixture was acidified to pH 2.0 with H_2SO_4 (2 M; 14 mL) and then treated with $N_2H_6SO_4$ (0.9 g, 6.9 mmol). The solution turned dark violet and the pH increased to 2.8. After stirring for 3 h a solution of KCl (3 g, 40.2 mmol) in 20 mL H_2O was added to the mixture. Finally, the solution was filtered and the filtrate was left standing at room temperature. Black-purple hexagonal plates formed overnight. Yield 2.2 g (35% based on Mo). Anal. Calcd for $H_{422}O_{542}K_{26}Na_8S_{12}V_{31}Mo_{72}$: K, 5.30, Na, 0.96, V, 8.24. Found: K, 5.19, Na, 0.83, V, 8.06. IR (2% KBr pellet; 2000–400 cm^{-1}): 1621 (m, $\delta(H_2O)$), 1198 (w), 1128 (w), 1054 (w) (all $\nu_{as}(SO_4)$), 966 (m–s, $\nu(Mo–O_t)/\nu(V–O_t)$), 791 (vs), 631 (m), 575(s), 449 (m). VIS-NIR (in H_2O, pH 2.5) [λ_{max}/nm (ε/L mol^{-1} cm^{-1})]: *ca.* 690 (sh), 510 ($V^{IV} \rightarrow Mo^{VI}$ IVCT, 7.1×10^4).

¶ *Crystal data* for **1**: $H_{422}O_{542}K_{26}Na_8S_{12}V_{31}Mo_{72}$, $M = 19169.44$ g mol^{-1}, monoclinic, space group *C*2/*c*, $a = 47.177(3)$, $b = 42.460(3)$, $c = 26.497(2)$ Å, $\beta = 90.134(2)$, $V = 53078(6)$ Å^3, $Z = 4$, $\rho = 2.40$ g cm^{-3}, $\mu = 2.54$ mm^{-1}, $F(000) = 37076$, crystal size = $0.23 \times 0.16 \times 0.04$ mm. Crystals of **1** were taken directly from the mother liquor, mounted on a cryoloop and immediately cooled to 173(2) K on a Bruker D8 SMART APEX CCD sealed tube diffractometer with graphite monochromated Mo-Kα (0.71073 Å) radiation. A total of 279499 reflections ($1.38 < \Theta < 24.71°$) were collected of which 45269 reflections were unique (R(int) = 0.0824). An empirical absorption correction using equivalent reflections was performed with the program SADABS V2.10.[12] The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to $R = 0.0687$ for 34017 reflections with $I > 2\sigma(I)$, $R = 0.0946$ for all reflections; max./min. residual electron density: 3.82 (0.85 Å from Mo27) and -2.31 e Å^{-3}. K, Mo (except for Mo41–Mo53), V, S (except for the disordered S6–S8 atoms) and anionic O atoms were refined anisotropically. No hydrogen atoms were included in the refinement. Further refinement details can be found in the ESI†. Structure solution, refinement and generation of publication materials were performed by using SHELXTL, V 6.12 software.[13] CCDC 268073. See http://www.rsc.org/suppdata/cc/b5/b504491j/ for crystallographic data in CIF format.

|| Susceptibility measurements were performed using a Quantum Design MPMS-5 SQUID magnetometer at fields from 0.1 to 5.0 Tesla. All susceptibility values were corrected for inherent diamagnetism and temperature-independent paramagnetism, a crucial procedure for magnetically functionalized polyoxomolybdates. The correction term $\chi_{dia/TIP}(\mathbf{1}) = -3350 \times 10^{-6}$ emu mol^{-1} had to be derived from both tabulated increments and diamagnetic polyoxomolybdates containing the $\{(Mo)Mo_5\}$-type fragments. Inter-cluster dipole–dipole interactions are negligible due to the large separation of the clusters in the crystal lattice (minimum inter-cluster V–V distance of 5.708(2) Å). In accordance with the analysis results, field-dependent magnetization measurements at 2.0 K confirmed the presence of 1.1 additional, isolated vanadyl cations per cluster unit, the corresponding Brillouin function (with $g = 1.97$) was subtracted from the susceptibility data. Attempts to eliminate this additional vanadyl cation by reducing the amount of vanadate used in the synthesis have thus far been unsuccessful.

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