Polyoxotungstates now also with pentagonal units: supramolecular chemistry and tuning of magnetic exchange in $\{(M)M_5\}_{12}V_{30}$ Keplerates (M = Mo, W)†‡

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The deliberate synthesis of the Keplerate $[K_{20}\subset\{(W)W_5O_{21}(SO_4)\}_{12}(VO)_{30}(SO_4)(H_2O)_{63}]^{18-}$ 1a with 20 pores all closed by K^+ in a supramolecular fashion proves that it is possible to follow new routes in polyoxotungstate chemistry based on pentagonal $\{(W)W_5\}$-type units and to tune magnetic exchange couplings in $\{(M)M_5\}_{12}M'_{30}$ type Keplerates.

The unique spherical Keplerates of the type $\{(Mo)Mo_5\}_{12}M'_{30}$ ($M' = Fe^{III}, Cr^{III}, V^{IV}$) have received a lot of attention and not only because of their magnetic properties[1–3] (Keplerate definition in ref. 2*b*). They exhibit spherical networks based on corner-shared M'_3 triangles causing geometrical frustration analogous to that of the planar Kagomé lattices[4] (see also title of ref. 1*b*) being of importance in materials science. In this context the question arose whether the degree of exchange interactions between the 30 magnetic centers positioned on spheres' surfaces can be deliberately changed/tuned. According to our knowledge of the geometrical and electronic structures of polyoxomolybdates and -tungstates[5,6] this should be possible if one could succeed in replacing the molybdenum-oxide based $\{(Mo)Mo_5\}$ units in the Keplerates[2b] by those containing tungsten atoms. In this context it has to be mentioned that in spite of the thousands of known polyoxotungstates none of those contained the pentagonal units before a related synthesis was published only recently.[7] In the present paper we will show that the $\{(W)W_5\}$ units/ligands can be deliberately generated; this allowed the preparation of the spherical Keplerate with its desired magnetic properties which is furthermore a remarkable host/attractor for cations.

After adding vanadyl sulfate to an acidified aqueous tungstate solution, in presence of K^+ ions, compound **1** precipitates after some time in high yield.§ Compound **1**, which crystallizes in the orthorhombic space group *Cmca*, was characterized by elemental analysis (including redox titration of V^{IV}), thermogravimetry (to determine the crystal water content), spectroscopic methods (IR, Raman, UV-Vis), single-crystal X-ray structure analysis (including bond valence sum calculations)¶ and susceptibility measurements (including related quantum Monte Carlo calculations).

$$K_{14}(VO)_2[K_{20}\subset\{(W)W_5O_{21}(SO_4)\}_{12}(VO)_{30}(SO_4)(H_2O)_{63}]\cdot ca.150H_2O \equiv K_{14}(VO)_2\cdot\mathbf{1a}\ ca.150H_2O \qquad \mathbf{1}$$

The anion **1a** belongs to the family of polyoxometalate based Keplerates having the general formula $(pentagon)_{12}(linker)_{30}$.[2,3,6,7] The 12 $\{(W)W_5\}$-type pentagonal units are positioned at the vertices of an icosahedron while connected by 30 V^{IV} centers with the V^{IV}–V^{IV} distances varying from 6.37 to 6.60 Å, *i.e.* less than in the $\{(Mo)Mo_5\}$ based cluster **2a**.[3a] The V^{IV} ions—all adopting an octahedral coordination—span an icosidodecahedron.‖

$$Na_8K_{14}(VO)_2[\{(Mo)Mo_5O_{21}(H_2O)_3\}_{10}\{(Mo)Mo_5O_{21}(H_2O)_3(SO_4)\}_2\{VO(H_2O)\}_{20}\{VO\}_{10}(\{KSO_4\}_5)_2]\cdot ca.150H_2O \equiv Na_8K_{14}(VO)_2\cdot\mathbf{2a}\ ca.150H_2O \qquad \mathbf{2}^{3a}$$

There are altogether 13 SO_4^{2-} ligands located inside the cavity of **1a**, 12 of which are coordinated in a tridentate manner to the $\{(W)W_5\}$-type pentagonal units, *i.e.* one per unit (see Fig. 1). The 13th sulfate ligand is coordinated (with bridging function) to a V as well as to two W atoms.

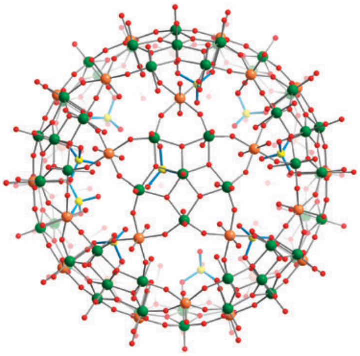

Fig. 1 Ball and stick representation of the anion **1a** (for clarity not all atoms at the back are shown); 12 SO_4^{2-} ligands are coordinated in tridentate fashion to the 12 $\{(W)W_5\}$-type pentagons while each ligand is disordered over the five relevant positions (disorder not shown here). The 13th ligand (not shown here) is coordinated to a V as well as to two W atoms and disordered over eight positions (color code: W green, V orange, O red, S yellow spheres).

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† Dedicated to Prof. Reinhard Nesper on the occasion of his 60th birthday.

‡ CCDC 728890. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b907188a

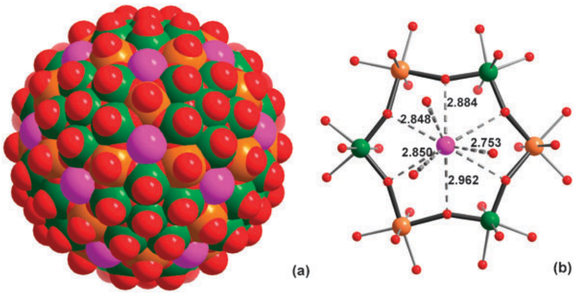

Fig. 2 (a) Space filling representation of **1a** highlighting the affinity of the $\{V_3W_3O_6\}$ pores to the K^+ cations (violet) located on the C_3-axes. (b) Shown is one of the 20 pores with an integrated K^+ cation; K···O distances including those to the related H_2O ligands are also presented (color code as in Fig. 1).

In each of the 20 $\{V_3W_3O_6\}$ rings/pores of **1a** there is a K^+ cation incorporated. Correspondingly, we can refer here to an interesting type of molecular recognition on a sphere surface in contrast to that *via* the natural macrocyclic polyethers (displaying antibiotic properties) and synthetic macropolycyclic ligands.[8] The present $\{\text{metal}_6O_6\}$ pore (Fig. 2b) is comparable to the 18-crown-6 which has a high K^+/Na^+ selectivity.

Measurements of the weak-field molar susceptibility, $\chi = M/H$, were done using a superconducting quantum interference device magnetometer (Quantum Design) in the temperature range 5–300 K in a fixed applied magnetic field of $H = 0.5$ T. These data, as corrected for two uncorrelated VO^{2+} ions (spin $s = 1/2$) per molecular unit that are magnetically and structurally independent from the cluster skeleton, are shown in Fig. 3. The limiting behavior of $T\chi$ at low T justifies the assignment $S = 0$ for the angular quantum number of the ground state. (The alternative scenario of $S = 1$, or larger, and the absence of uncorrelated VO^{2+} ions, is incompatible with our measured raw data.) We compared the measured susceptibility with that of a Heisenberg model where each of the 30 magnetic ions in the individual molecular unit interacts *via* isotropic antiferromagnetic exchange with its four nearest-neighbors. The interaction term for magnetic ions i and j is $J\vec{S}_i\cdot\vec{S}_j$, a ($s = 1/2$) spin operator $\vec{S}_i$ is in units of $\hbar$, and the exchange energy J is an adjustable constant, determined as follows. Accurate values of the Heisenberg model susceptibility were obtained using the quantum Monte Carlo method (QMC) for $T > 0.5\ J/k_B$. (Reliable results cannot be obtained for lower temperatures by the QMC method for spins on the sites of an icosidodecahedron that interact with antiferromagnetic exchange.) We added to the intrinsic (Heisenberg model) susceptibility a second variable constant, c, that equals the sum of the separately unknown contributions of diamagnetism and temperature independent paramagnetism (TIP). The solid curve shown in Fig. 3, extending over the range 70–300 K, provides the optimal fit to the experimental susceptibility upon adopting the value $g = 1.95$ appropriate for VO^{2+} ions. The optimal values are $J/k_B = 115$ K and $c = -0.0045$ emu mol^{-1}, each with an uncertainty of approximately 5%. We also remark that the slow descent of $T\chi$ on cooling below 30 K suggests that additional weak spin interactions supplement the strong nearest-neighbor exchange interactions.

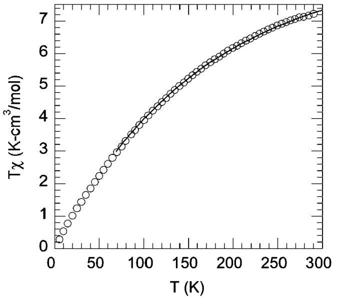

Fig. 3 Magnetic susceptibility of **1** *versus* temperature: experimental data corrected for two VO^{2+} centers (○); theory (solid curve).

It is noteworthy that the present exchange energy of **1a** is a factor of two smaller than that for $\{Mo_{72}V_{30}\}$ **2a** as predicted in the Introduction. The reason for this decrease is the fact that the gap between the HOMO (mainly with contributions of the 3dV centers) and the LUMO (mainly with contributions of the Mo or W centers, respectively) is much smaller in the case of **2a** exhibiting stronger electron delocalization and correspondingly a stronger exchange coupling. The differences in the HOMO–LUMO gaps can be nicely proven by the different energies of the V(IV)–M(VI) intervalence charge transfer transitions, which are observed in the case of **2a** at 540 nm and in **1a** at 389 nm.

Some basic remarks about synthetic aspects of the present study: Keplerates of the type $\{(Mo)Mo_5\}_{12}M'_{30}$ can be obtained directly by the addition of mononuclear linkers M′ such as Fe^{3+}, Cr^{3+} and VO^{2+} to a dynamic library containing the pentagonal $\{(Mo)Mo_5\}$-type units[3] or by reaction of, *e.g.* Fe^{3+} with a solution of the $\{(Mo)Mo_5\}_{12}\{Mo_2\}_{30}$ Keplerate thereby exchanging binuclear by mononuclear linkers.[2a] As the pentagonal $\{(Mo)Mo_5\}$ type units appear in this context as (transferable) ligands the mentioned clusters can be called coordination polymers with spherical periodicity.[3c] (As linking pentagonal units cannot lead to translational invariance the related species have been called (quasi)crystal balls.[9]) Whereas the $\{(Mo)Mo_5\}$ type building block occurs as a structural unit in polyoxomolybdates especially in the well-known $[Mo_{36}O_{112}(H_2O)_8]^{8-10}$ present at low pH in H_2O[10a] (the base for the predictable syntheses of corresponding Keplerates) no related pentagonal units have been observed until recently among the thousands of known polyoxotungstates.[5]** Due to the present work, there is not only the option for the extension of the molybdate-based Keplerate chemistry to that of the tungstate type including magnetic features but also to follow new routes in polyoxotungstate chemistry based on the use of pentagonal units which can now be considered really as transferable.

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Notes and references

§ *Synthesis of* **1**: A mixture of WO_3 (1.16 g, 5.00 mmol), KOH (0.90 g, 16.04 mmol) and 50 mL H_2O was heated with stirring to 90 °C until a clear solution was obtained. After cooling to room temperature H_2SO_4 (0.5 M; 9.5 mL) was added (pH ~4), followed by the addition of $VOSO_4 \cdot 5H_2O$ (1.27 g, 5.00 mmol). The final pH of the reaction medium was ~2. The resulting dark green solution was stirred at 65 °C for 2 h in an Erlenmeyer flask covered with a watch glass and then left to cool to room temperature. The precipitate formed during this time was filtered off and the filtrate was kept in an Erlenmeyer flask covered with a rubber stopper. After 5–7 d the dark crystals were filtered off, washed with cold water and finally dried in air. Yield: 0.55 g, 31% based on W.

Elemental Analysis: Calc. S 1.61, W 51.25, V 6.31, K 5.15%; found: S 1.9, W 50.1, V 6.2, K 5.9% (Mikroanalytisches Labor Egmont Pascher, An der Pulvermühle 3, 53 424 Remagen, Germany).

Characteristic IR bands (ν/cm^{-1}; KBr pellet): 1622 (m, $\delta(H_2O)$), [1230 (m), 1111 (m), 1060 (m)] $\nu_{as}(SO_4)$ triplet, 974 (s) and 950 (sh) ($\nu(V{=}O)/\nu(W{=}O)$), 812 (vs), 655 (m), 577 (s), 430 (w).

Characteristic (*resonance*) *Raman bands* (ν/cm^{-1}; H_2O; λ_e = 765 nm): 970, 900 (s, $\nu(V{=}O)/\nu(W{=}O)$), 860 (m), *ca.* 400 ($\nu_{br.}$).

Characteristic UV-Vis bands (λ/nm; H_2O): 389 (IVCT), 645, 844 (d–d).

¶ *Crystal data for* **1**: $H_{426}K_{34}O_{549}S_{13}V_{32}W_{72}$, M = 25826.87 g mol^{-1}, space group *Cmca*, a = 35.3141(16), b = 38.7680(18), c = 38.5949(17) Å, V = 52 839(4) $Å^3$, Z = 4, ρ = 3.247 g cm^{-3}, μ = 16.581 mm^{-1}, F (000) = 46 944, crystal size = 0.28 × 0.24 × 0.20 mm^3. A total of 152 606 reflections ($1.18 < \Theta < 26.98°$) were collected of which 29 183 reflections were unique (R(int) = 0.0734). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.10. The structure was solved with the program SHELXS-97 and refined using SHELXL-97 to R = 0.0533 for 20 684 reflections with $I > 2\sigma(I)$, R = 0.0903 for all reflections; max./min. residual electron density 2.685 and −2.594 e $Å^{-3}$. 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, Mo-Kα 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). (SHELXS/L, SADABS from G. M. Sheldrick, University of Göttingen 1997/2003; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 2001). Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany http://www.fiz-karlsruhe.de/request for deposited data.html. CSD 420482.

‖ In the case of **2a**[3a] the incorporation of two $\{KSO_4\}_5$ rings causes a slight compression of the approximately spherical structure; the distortion is in agreement with the fact that only the 20 V^{IV} in the equatorial and intermediate region have octahedral and the two sets of five V^{IV} in the polar area square pyramidal coordination. (A sixth H_2O ligand required for octahedral coordination is not possible as this would be too close to the SO_4^{2-} ligands of the internal $\{KSO_4\}_5$ rings.) Whereas in **1a** the V atoms have almost only terminal/external O^{2-} ligands—in part disordered with H_2O ligands based on the *trans* $OV(H_2O)$ units—the cluster surface in **2a** is different: (1) the 5 + 5 polar metal sites correspond, according to their square pyramidal coordination, to VO groups; (2) the 10 equatorial V atoms have H_2O ligands pointing outside and O^{2-} pointing inside while the reverse holds for the 5 + 5 metal atoms in between the two mentioned areas.

** Whereas the reason for the high formation tendency and stability of the spherical type species $\{\text{pentagon}\}_{12}M'_{30}$ (see Introduction) has been discussed earlier and especially in the context of "Chemical Darwinism"[11] (see corresponding highlight ref. 12), it only recently became evident[7] that the formation of the related pentagonal units can be considered in the framework of "constitutional dynamic chemistry" formulated by Lehn,[12] while considering systems responding to the appropriate action of stimuli. These are in the present case the $M' = VO^{2+}$ ions in the sense that they direct the formation of the pentagonal units from $[H_2W_{12}O_{40}]^{6-}$ present in the reaction medium.[7]

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