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Building blocks as disposition in solution: $[\{Mo^{VI}O_3(H_2O)\}_{10}\{V^{IV}O(H_2O)\}_{20}\{(Mo^{VI}/Mo^{VI}{}_5O_{21})(H_2O)_3\}_{10}(\{Mo^{VI}O_2(H_2O)_2\}_{5/2})_2(\{NaSO_4\}_5)_2]^{20-}$, a giant spherical cluster with unusual structural features of interest for supramolecular and magneto chemistry†

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The unique polyoxometalate compound $Na_{20}[\{Mo^{VI}O_3(H_2O)\}_{10}\{V^{IV}O(H_2O)\}_{20}\{(Mo^{VI}/Mo^{VI}{}_5O_{21})(H_2O)_3\}_{10}(\{Mo^{VI}O_2(H_2O)_2\}_{5/2})_2(\{NaSO_4\}_5)_2]\cdot xH_2O$ 1 ($x \approx 170$) shows remarkable structural features: *e.g.* (i) $\{Mo^{VI}/Mo^{VI}{}_5\}$-type pentagons as building blocks (being present in the relevant reaction medium as disposition), (ii) a 'magnetic ring-shaped band' built up by ten linked $\{V^{IV}{}_3\}$ triangles having common corners and (iii) two $\{NaSO_4\}_5$ rings encapsulated inside the cavity of an icosidodecahedron formed by twenty triangular and twelve pentagonal faces built up by ten Mo^{VI} and twenty V^{IV} centres, respectively.

The generation of a variety of extremely large complex molecular systems under one-pot reaction conditions requires variably linkable units as disposition in the related solution.[1,2] Knowledge of polyoxometalate systems allows for instance the generation and linking of pentagons of the type $\{Mo^{VI}/Mo^{VI}{}_5\}$, which contain a central pentagonal bipyramid sharing edges with five MoO_6 octahedra. Here we report on the isolation of a related aggregate which displays interesting structural features. The basic structure can be optimally described by referring to the faces of an icosidodecahedron (one of the thirteen Archimedean solids) spanned by ten Mo^{VI} and twenty V^{IV} centres.

If vanadyl sulfate is added to an acidified molybdate solution,‡ the compound $Na_{20}[\{Mo^{VI}O_3(H_2O)\}_{10}\{V^{IV}O(H_2O)\}_{20}\{(Mo^{VI}/Mo^{VI}{}_5O_{21})(H_2O)_3\}_{10}(\{Mo^{VI}O_2(H_2O)_2\}_{5/2})_2(\{NaSO_4\}_5)_2]\cdot xH_2O$ **1** ($x \approx 170$) precipitates in high yield in the presence of a high electrolyte concentration.§ Compound **1** was characterized by elemental analysis, thermogravimetric analysis for determination of the crystal water content, single crystal X-ray structure analysis¶ (including bond valence sum calculations mainly for a determination of the positions of the H atoms and the number of V^{IV} centres), electronic absorbtion as well as vibrational spectra, magnetic susceptibility and redox titrations [for the (additional) determination of the number of V^{IV} centres].

The anionic cluster **1a** has a nearly spherical shape with longest and shortest outer dimensions of 25 and 23 Å, respectively, and possesses a C_5-symmetry axis [Fig. 1(*b*)]. The structure of the anion **1a** can be best described with reference to a distorted icosidodecahedron formed by twenty triangular and twelve pentagonal faces built up by ten Mo^{VI} and twenty V^{IV} centres [see Fig. 1(*a*)]. Ten triangles spanned by the twenty V^{IV} centres form an unusual equatorial 'magnetic ring-shaped band'. The remaining ten triangles above and below this equatorial band, each formed by one V^{IV} (common to the above mentioned triangular faces) and two Mo^{VI} centres, complete the (distorted) icosidodecahedron. Whereas ten of the twelve pentagonal faces—each formed by one Mo^{VI} and four V^{IV} centres—are 'capped' by a $\{Mo/Mo_5\}$-type pentagonal unit [see Fig. 1(*a*) and consider that the earlier reported more symmetrical structure with I_h symmetry[6] contains twelve pentagonal units], the remaining two (top and bottom) faces, each spanned by five Mo^{VI} centres, are 'capped' in a similar way but show two significant differences: (i) the central pentagonal bipyramidally coordinated Mo^{VI} centre is missing and (ii) the (five) MoO_6 octahedra do not share common oxygen atoms (see Fig. 2). In addition, these five Mo^{VI} positions are under-occupied such that the occupancy factors add up to 2.5 per face [therefore referred to as the $\{Mo\}_{5/2}$ unit in the formula and in Fig. 1(*a*)].

Within the cluster cavity, ten sulfate groups (each attached *via* three oxygen atoms to three adjacent Mo^{VI} centres of each $\{Mo^{VI}/Mo^{VI}{}_5\}$ group) and ten Na^+ ions are encapsulated in a manner not previously observed. The Na^+ cations are located between adjacent sulfate groups thereby forming two novel

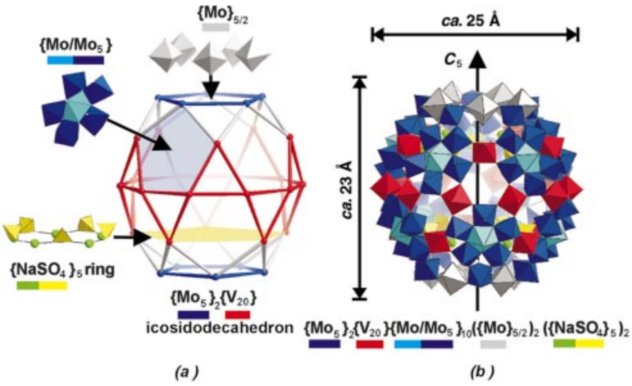

Fig. 1 (*a*) Basic framework structure of **1a** spanned by ten Mo^{VI} (blue) and twenty V^{IV} centres (red) thus forming a distorted icosidodecahedron with twenty triangles and twelve pentagons. Additional structural details shown (see text): (i) one of the $\{Mo^{VI}/Mo^{VI}{}_5\}$ units which cap ten of the twelve pentagonal faces (MoO_7 pentagonal bipyramid: light blue, MoO_6 octahedra: dark blue); (ii) array built up by five $MoO_4(H_2O)_2$ octahedra (see text) capping the two remaining pentagonal faces (grey); (iii) the 'magnetic ring-shaped band' formed by ten $\{V^{IV}{}_3\}$ triangles (red); (iv) one of the two encapsulated $\{NaSO_4\}_5$-type rings (Na atoms: green, SO_4 tetrahedra: yellow). (*b*) Polyhedral representation of the complete, nearly spherical structure of **1a** [colour code as in (*a*)].

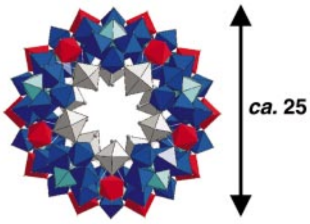

Fig. 2 Polyhedral representation of **1a** with view perpendicular to that shown in Fig. 1(*b*) (parallel to the C_5 axis).

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† Disposition can be interpreted as the tendency of an object or system (here polyoxometalate solutions) to act or react in characteristic ways under certain situations (conditions); in this sense the units, such as the pentagons, which finally appear can in principle be called virtual ones.

$\{NaSO_4\}_5$ rings [Na–O(SO_3) 2.48–2.60 Å] lying above and below the equatorial ring of ten V^{IV} centres [see Fig. 1(*a*)]. Interestingly, these Na atoms possess a unique pentagonal bipyramidal coordination environment in which five of the corresponding oxygen centres belong to the cluster shell.

Although the individual metal centres all have an octahedral (or pentagonal bipyramidal) coordination geometry, the environment of some metal centres is complicated for example by disorder phenomena and can—referring to the formula—be described as follows: (i) all six Mo^{VI} centres constituting each of the ten equivalent $\{Mo^{VI}/Mo^{VI}_5\}$ groups, are surrounded by four (or five) bridging oxygen atoms; three possess a terminal oxygen atom projecting outward and a *trans*-μ_2-O atom of the tridentate sulfate ligand (see formula); two Mo centres exhibit outward projecting terminal oxygen and *trans*-OH_2 ligands; the remaining Mo centre (the type closest to the equator), possesses mainly outward projecting OH_2 ligands as well as *trans*-terminal oxygen atoms with the related disorder; (ii) all twenty V^{IV} centres have four bridging oxygen atoms but whereas the ten equatorial V^{IV} centres possess (predominantly) outward projecting OH_2 ligands and *trans*-terminal oxygen, the remaining V^{IV} centres exhibit (without the related disorder), outward projecting terminal oxygen and *trans*-OH_2 ligands; (iii) each of the five Mo^{VI} centres of the $\{Mo\}_{5/2}$ unit ($\{Mo^{VI}O_2(H_2O)_2\}_{5/2}$ part of the formula) has only two bridging (μ_2-type), and consequently four terminal ligands (two oxygen as well as two OH_2 ligands); (iv) the remaining ten Mo^{VI} centres ($\{Mo^{VI}O_3(H_2O)\}_{10}$ part of the formula) also possess disordered terminal oxygen and *trans*-OH_2 ligands; owing to the under-occupancy of the neighbouring molybdenum atoms of the $\{Mo\}_{5/2}$-type centres (occupancy factors 0.25–0.75), one or two μ_2-O atoms become terminal oxygen atoms depending on the related occupancy of the next neighbour position.

Magnetic susceptibility measurements show that χT decreases drastically from 200 to 100 K (3.4–2.3 cm^3 K mol^{-1}) indicating relatively strong antiferromagnetic exchange interactions in spite of the rather large V^{IV}–V^{IV} distances within the magnetic band (6.27–6.46 Å).

Anion **1a** is structurally similar to the inorganic superfullerene of the type $\{Mo/Mo_5\}_{12}\{Mo^V_2\}_{30}$[6] where the thirty centres (mid-points) of the $\{Mo^V\}_2$ dumb-bells span an icosidodecahedron. In this case, twelve $\{Mo^{VI}/Mo^{VI}_5\}$ pentagons cap all of the twelve faces of a distorted truncated icosahedron which is formed by the sixty atoms of the $\{Mo^V\}_2$ units. An important challenge for the future will be the apparently feasible planned synthesis of a variety of spherical clusters using the described pentagonal units.[7] In this context the encapsulation of a variety of multifunctional groups/guests as well as the integration of magnetic centres is of special interest.

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Notes and references

‡ $VOSO_4 \cdot 5H_2O$ (2.53 g, 10 mmol) was added under stirring to a solution of Na_2MoO_4 (2.42 g, 10 mmol) in 16.4 ml of 1.0 M hydrochloric acid. Subsequently, NaCl (1.16 g, 19.8 mmol) (which accelerates precipitation) was added to the resulting red–brown solution which was stirred under argon for 10 min before storage under exclusion of air. The red–black rhombic crystals of **1** which precipitated after 7 days were filtered off, washed with 50 ml H_2O and dried in a nitrogen stream. Yield: 0.65 g (28.6%), based on Mo (Found: Na, 3.59; S, 1.85; V, 5.29. Calc.: Na, 3.7; S, 1.72; V 5.5%). The compound is soluble in water and the resulting red solution oxidises slowly on exposure to air.

Characteristic spectroscopic data for **1**: IR ν/cm^{-1} (KBr pellet prepared under argon, 1700–400 cm^{-1}): 1197w, 1125w, 1052w [ν(S–O)]; 968m [ν(V=O)/ν(Mo=O)]; 768s, 690(sh), 631m, 571s; Raman ν/cm^{-1} (solid, KBr dilution, λ_e = 1064 nm): 944w, 880m [ν(V=O)/ν(Mo=O)]; UV–VIS λ_{max}/nm (degassed water): 498, 677 (VO^{2+} chromophore).

§ In an earlier investigation of the Mo^{VI}/V^{VI} system[3,4] it was erroneously proposed that solutions with a relative concentration Mo^{VI}/V^{IV} = 1 yield $K_2H_6[V_3Mo_3O_{19}] \cdot 7H_2O$ at pH 4.75 and the highly soluble product $H_8[V_3Mo_3O_{19}]$ at pH < 3.1. The authors assumed that both compounds would contain Lindquist-type anions.[3,5]

¶ *Crystal data* for **1**: $H_{480}Mo_{75}Na_{30}O_{550}S_{10}V_{20}$, *M* = 18 508.44, monoclinic, space group *C*2/*c*, *a* = 47.065(2), *b* = 43.157(2), *c* = 26.946(1) Å, β = 104.26°, *U* = 53045(4) $Å^3$, *Z* = 4, D_c = 2.318 g cm^{-3}, μ = 2.23 mm^{-1}, *F*(000) = 35 920, crystal size = 0.4 × 0.2 × 0.1 mm. Crystals of **1** were removed from the mother-liquor and immediately cooled to 183(2) K on a Bruker axs SMART diffractometer (Mo-Kα, graphite monochromator). A total of 155 219 reflections (1.56 < θ < 26.99°) were collected of which 57 074 unique reflections (R_{int} = 0.069) were used. An empirical absorption correction using equivalent reflections was performed with the program SADABS. The structure was solved using the program SHELXS-97 and refined using the program SHELXL-97 to *R* = 0.062 for 33 490 reflections with $I > 2\sigma(I)$. SHELXS/L , SADABS from G. M. Sheldrick, University of Göttingen, 1997; structure graphics with Diamond 2.1 from K. Brandenburg, Crystal Impact GbR, 1999. Because of the disorder, not all of the Na positions could be detected as is usual in the case of the said type of compounds. An initial view of the packing of the cluster anions suggested that they are linked through the $\{Mo\}_{5/2}$ units, parallel to the approximate fivefold symmetry axis. However a closer inspection of the corresponding under-occupied Mo centres, (which would correspondingly be responsible for the linking through Mo–O–Mo bridges, reveals that the anions are (probably) not connected at all. The fact that the occupancy factors of the Mo centres of adjacent anions add up to 1.0, indicating that these positions are *alternately* occupied, suggests that a connection of the clusters is improbable. The under-occupied Mo centres (occupancy factor between 0.25 and 0.75) cannot be treated as fully occupied V atoms due to the unrealistic number of terminal ligands (three including two terminal O atoms for octahedral V) and the V analysis. Additionally, as the terminal ligands are also under-occupied, fully occupied V atoms would have an incomplete coordination sphere. Furthermore the resulting necessary linkage of the clusters—owing to the full occupancy—would significantly increase the cluster charge which is impossible considering the Na analysis.

The remainder of the anion shows nearly no disorder. Only very few atoms show a $O=Mo–OH_2 \leftrightarrow O=Mo–OH_2$ disorder. The bond valence sums for the ordered Mo and the V positions lie in the ranges 5.8–6.1 and 4.1–4.2, respectively. Further details of the crystal structure determination 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 No. CSD391073.

CCDC 182/1382. See http://www.rsc.org/suppdata/cc/1999/1885/ for crystallographic files in .cif format.

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