Preliminary communication / Communication

Synthesis and structure determination of a new ball-shaped polyoxovanadate with a hexadecanuclear core

Synthèse et détermination structurale d'un nouveau polyoxovanadate sphérique formé de 16 polyèdres

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

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Abstract

A new polyoxovanadate species formulated $[V_{16}O_{42}]^{4-}$ was isolated in DMF solvent. Its structure was solved at 100 K by single-crystal X-ray diffraction in the centrosymmetric monoclinic $C2/c$ (no. 15) space group with lattice parameters $a = 25.554(6)$ Å, $b = 14.227(3)$ Å, $c = 28.485(6)$ Å, $\beta = 113.21(1)°$, $V = 9518(4)$ Å^3. The refinement of the structure of $[(SO_4) \subset V_{16}O_{42}]\cdot(SO_4)_2((CH_3)_2NH_2)_{10}((CH_3)_2NCHO)_4$ using 11 389 independent $I > 2\sigma(I)$ reflections led to reliability factors $R_1(F_o)$ and $wR_2(F_o{}^2)$, respectively, equal to 0.0434 and 0.1269. The structure of the V_{16} polyanion, templated by a tetrahedral sulphate group, is built up from one ring of 12 edge-shared V^VO_5 square pyramids capped on each side by a dimeric unit. Each entity carries out a six-negative charge, the neutrality of the structure is ensured by the appropriate amount of dimethyl ammonium ions. **To cite this article: J. Marrot et al., C.R. Chimie 8 (2005).**

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Résumé

Un nouveau polyoxovanadate de formule $[V_{16}O_{42}]^{4-}$ a été isolé dans le DMF. La structure de $[(SO_4) \subset V_{16}O_{42}]\cdot(SO_4)_2((CH_3)_2NH_2)_{10}((CH_3)_2NCHO)_4$ a été résolue par diffraction des rayons X sur monocristal à 100 K dans le groupe d'espace monoclinique centrosymétrique $C2/c$ (no. 15) avec les paramètres de maille suivants: $a = 25.554(6)$ Å, $b = 14.227(3)$ Å, $c = 28.485(6)$ Å, $\beta = 113.21(1)°$, $V = 9518(4)$ Å^3. L'affinement a été mené avec 11 389 réflexions indépendantes satisfaisant au critère $I > 2\sigma(I)$ jusqu'aux facteurs de reliability $R_1(F_o) = 0.0434$ et $wR_2(F_o{}^2) = 0.1269$. Chaque polyanion, organisé autour d'un groupe tétraédrique sulfate, présente une structure composée d'une couronne de 12 pyramides à base carrée

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$V^V O_5$ à arêtes communes coiffée de part et d'autre par un dimère de vanadium. L'ensemble porte une charge négative 6– neutralisée par la quantité nécessaire de cations diméthylammonium. **Pour citer cet article : J. Marrot et al., C.R. Chimie 8 (2005).**

Keywords: Polyoxovanadate; X-Ray Diffraction; IR spectroscopy

Mots clés : Polyoxovanadate ; Diffraction X ; Spectroscopie IR

1. Introduction

It is well known that the structural chemistry of vanadium is characterised by an exceptional diversity. Indeed, the vanadium in the solid state gives currently rise to the oxidation states +3 up to +5, each one dealing with different coordinations. In the large domain of the mixed organic/inorganic compounds, the hydrothermal way favours the synthesis of solids with infinite layers [1] or even three-dimensional frameworks [2], whereas condensation processes at room temperature rather lead to molecular species [3]. In alkaline medium, the V^{5+} ions provide tetra, penta and decavanadate species, but the works of M. Pope and A. Müller especially have allowed to extend this chemistry to an important number of molecular species with V^{IV}/V^V mixed valence which exhibit very different features. Their structures are (i) compact as $[V_{13}O_{34}]^{3-}$ [4], (ii) hollow and templated by anionic (halide, chlorate, phosphate, e.g.) or neutral entities in $[V_{15}O_{36}]^{5-}$, $[V_{18}O_{42}]^{12-}$ [5] or $[V_{22}O_{54}]^{8-}$ [6], or (iii) open as exemplified by $[V_{12}O_{32}]^{4-}$ [7]. Among this large class of materials, the V_{16} stoichiometry is scarcely encountered. To our knowledge, it is just reported V_{16} species whose structures are build up from the assembling of smaller units (two octanuclear units in [8] or two hexa and one tetranuclear oligomers in [9] fused by oxo anions).

This paper deals with the synthesis and the structure characterisation of a new polyoxovanadate molecular entity whose spherical ball-shaped architecture is build up from $16V^{5+}$ polyhedra. We apologize to Francis Sécheresse for failing in our attempt to give a rugby ball shape to this new polyoxovanadate moiety.

2. Experimental

2.1. Synthesis

The synthesis of the title compound was achieved in a closed flask at room temperature from a mixture of VOSO$_4$·5H$_2$O (Prolabo), 1,4-benzenedicarboxylic acid (Aldrich, 99.8%) and *N,N*-dimethylformamide (Aldrich, 99.8%) in the molar ratio 1:2:117. After several weeks, thin green hexagonal platelets grew which then agglomerated into large blocks. It is worth noting that (i) these crystals are quickly destroyed after some minutes outside of the medium synthesis, (ii) the same mixture hydrothermally treated at 473 K leads to the three-dimensional microporous vanado(III)carboxylate MIL-68 already described [10]. This last point justifies the presence of the terephthalic acid in the medium. Maybe, this acid acts as a catalyst for the hydrolysis of DMF into dimethylammonium ions. The very poor stability of the crystal outside of the mother liquor prohibits a lot of characterisation methods (elemental analysis, thermal analysis...).

2.2. Structure determination

One monocrystalline fragment was glued on a glass fibre with paratone then quickly aligned on a Brüker X8 APEX2 CCD diffractometer operating at 100 K. The intensities were recorded using graphite monochromatic Mo(Kα) = 0.71073 Å wavelength. The data were reduced and corrected from Lorentz-Polarization and absorption effects with the SADABS program (G. Sheldrick, version 2.10 unpublished). The structure was solved by applying the direct methods of SHELXTL-V6.12 (TREF option), the vanadium, sulphur and oxygen atoms were first located then the remaining atoms were deduced from Fourier difference maps. All atoms except hydrogen (found using geometrical constraints) were anisotropically refined. The contribution to the intensities of one fully disordered DMF molecule was corrected using the PLATON/SQUEEZE program [11] in view to improve the quality of the structural model of the polyoxovanadate species.

The details for the data collection as well as the principal bond lengths are summarised in Tables 1 and 2, respectively.

Table 1

Details of data collection and principal crystallochemical data for $[(SO_4) \subset V_{16}O_{42}] \cdot (SO_4)_2 (CH_3)_2 NH_2)_{10} ((CH_3)_2 NCHO)_4$

Empirical formula	$C_{32}H_{108}N_{14}O_{58}S_3V_{16}$
Formula weight	2528 g.mol^{-1}
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*C*2/*c* (No. 15)
Lattice parameters	*a* = 25.554(6) Å
	b = 14.227(3) Å
	c = 28.485(6) Å
	β = 113.21(1)°
Volume, *Z*	9518(4) Å^3, 4
Density (Calc.)	1.765 g.cm^{-3}
Absorption coefficient	16.55 cm^{-1}
F(000)	5112
Crystal size	$0.120 \times 0.100 \times 0.060$ mm
θ range for data collection	1.56–30.00°
Limiting indices	$-35 \le h \le 35$
	$-20 \le k \le 12$
	$-40 \le l \le 32$
Reflections collected	55 683
Independent reflections	13,877 [*R*(int) = 0.0366]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13 877/0/560
Goodness-of-fit on F^2	1.082
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0434, wR_2 = 0.1269
Extinction coefficient	none
Largest difference peak and hole	2.337 and −1.008 e Å^{-3}

2.3. IR spectroscopy

IR spectrum (cm^{-1}) of $[(SO_4) \subset V_{16}O_{42}] \cdot (SO_4)_2 ((CH_3)_2NH_2)_{10}((CH_3)_2NCHO)_4$ in KBr pellets was recorded on a FTIR Nicolet Magna-550 spectrophotometer.

Bands attributed to the $[(SO_4) \subset V_{16}O_{42}]^{6-}$ species: (*v* S–O): 1116 (s), 1020 (m), (*v* V=O) [12,13]: 980 (sh) and 956 (s), (*v* V–O–V): 796 (m), 620 (m), 584 (m) , 516 (w), 490 (w), and 447 (w).

Bands attributed to the dimethylammonium and DMF organic species: 3434 (br), 3055 (br), (*v* C–H): 2964 (w), 2921 (w), and 2857 (w), 2777 (br), 1629 (m), 1464 (m), 1431 (w), 1403 (vw), 1383 (vw), 1251 (w).

The bands due to the NH$_2$ groups of the dimethylammonium ions are not unambiguously showed. Indeed, the presence of residual water in KBr gives rise to a broad band at 3434 cm^{-1}, in the range expected for the N–H vibrators.

3. Discussion

$[(SO_4) \subset V_{16}O_{42}] \cdot (SO_4)_2((CH_3)_2NH_2)_{10}((CH_3)_2NCHO)_4$ exhibits a molecular structure built up from discrete $[(SO_4) \subset V_{16}O_{42}]^{6-}$ species between them are interleaved free sulphate groups, disordered DMF molecules and dimethylammonium ions which neutralise

Table 2

Principal bond lengths (Å) in each $[(SO_4) \subset V_{16}O_{42}]^{6-}$ polyoxovanadate moiety. In italic, the valence bond (u.v.) for the vanadium and the sulphur atoms

V(1)–O(1)	1.615(2)	V(4)–O(12)	1.618(2)	V(7)–O(19)	1.616(2)
V(1)–O(2)	1.732(2)	V(4)–O(13)	1.730(2)	V(7)–O(20)	1.7910(7)
V(1)–O(3)	1.881(2)	V(4)–O(8)	1.878(2)	V(7)–O(16)	1.916(2)
V(1)–O(4)	1.903(2)	V(4)–O(14)	1.911(2)	V(7)–O(2)	1.935(2)
V(1)–O(5)	2.066(2)	V(4)–O(11)	2.065(2)	V(7)–O(10)	1.964(2)
4.938		*4.924*		*4.775*	
V(2)–O(6)	1.607(2)	V(5)–O(15)	1.606(2)	V(8)–O(21)	1.616(2)
V(2)–O(7)	1.763(2)	V(5)–O(16)	1.749(2)	V(8)–O(22)	1.7872(7)
V(2)–O(8)	1.938(2)	V(5)–O(3)	1.933(2)	V(8)–O(13)	1.919(2)
V(2)–O(5)	1.983(2)	V(5)–O(11)	1.987(2)	V(8)–O(7)	1.943(2)
V(2)–O(4)	1.989(2)	V(5)–O(14)	2.007(2)	V(8)–O(18)	1.964(2)
4.726		*4.748*		*4.765*	
V(3)–O(9)	1.612(2)	V(6)–O(17)	1.617(2)		
V(3)–O(10)	1.727(2)	V(6)–O(18)	1.728(2)	*sulphate group*	
V(3)–O(4)	1.902(2)	V(6)–O(14)	1.893(2)	S(1)–O(23)	1.483(2) (2×)
V(3)–O(11)	1.902(2)	V(6)–O(5)	1.907(2)	S(1)–O(24)	1.486(2) (2×)
V(3)–O(8)	2.041(2)	V(6)–O(3)	2.039(2)	*5.768*	
4.960		*4.945*			

the negative charges of the polyoxovanadate moieties. From the observation of the residual electronic density calculated by Fourier difference syntheses, It was assumed that the DMF solvent was partially degraded to give rise to dimethylammonium ions. Indeed, this is the only possibility being the absence of alkaline or alkaline-earth ions in the medium synthesis, to obtain the positive ions necessary to neutralise the electrical charges of the polyanions. Moreover, the geometric characteristics of the ions deduced from the structure determination are in perfect agreement with those of dimethylammonium units. Six independent DMA ions were localised then refined with a fixed 5/6 multiplicity for electroneutrality requirements.
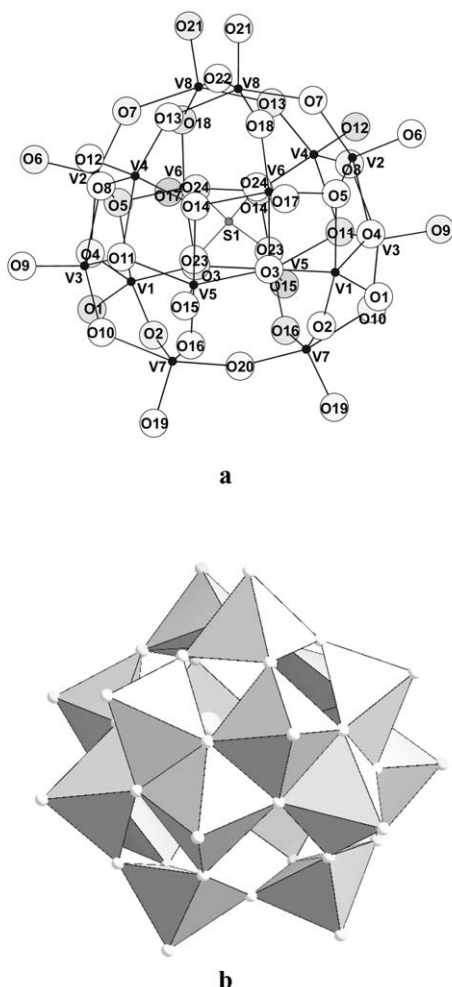

a

b

Fig. 1. (**a**) 'Balls and Sticks' and (**b**) polyhedral representations of one $[(SO_4) \subset V_{16}O_{42}]^{6-}$ entity.

The polyanions correspond to $[(SO_4) \subset V_{16}O_{42}]^{6-}$ polyoxovanadates built up from the connection by edges and vertices of $16V^VO_5$ square pyramids (Fig. 1). Both the geometry of the polyhedra (three V–O distances slightly smaller than 2 Å and one around 1.7 Å in the basal plane with one short ~1.6 Å vanadyl linkage perpendicularly disposed) and the valence bonds calculations [14] demonstrate that all the vanadium ions are in the +5 oxidation state (Table 2). The polyanion is itself built up from two sub-units (Fig. 2): one 12-membered ring of edge-shared square pyramids with all the terminal vanadyl bonds pointing outside the ring and two dimers of square pyramids sharing one oxo anion. Each ring whose diameter is close to 7 Å (V–V distances), is vertices-capped on both sides by one dimer, each dimer sharing all the vertices of the basal planes of the two square pyramids. The resulting polyoxovanadate moiety exhibits a spherical shape with 16 terminal vanadyl linkages pointing on the outer surface of the ball. Inside the sphere is encapsulated one tetrahedral sulphate group whose oxygen atoms are slightly bonded to some of the vanadium atoms (V–O > 2.45 Å). Consequently, the coordination of these vanadium atoms could be described as very elongated octahedra, the long distance being trans-located to the short vanadyl linkage.

It is worth noting that the 12-membered rings show some structural relation-ships with the parental vana-
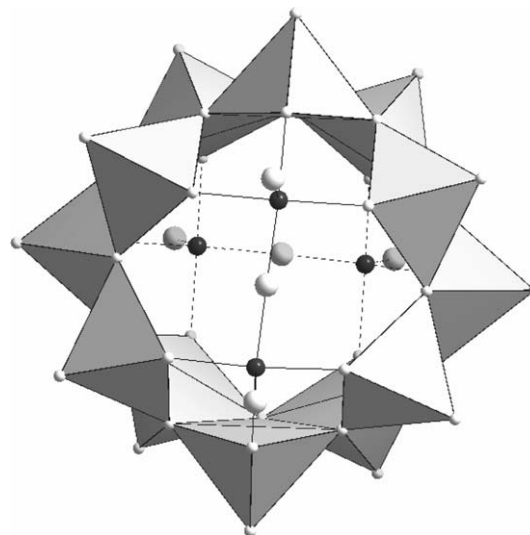

Fig. 2. View of one $[V_{16}O_{42}]^{4-}$ polyoxovanadate moiety showing the two types of building sub-units: the 12-membered ring (polyhedra) capped by the two dimers ('Balls and Sticks' representation, dashed and full lines for the dimers below and above the ring, respectively). Dark grey circles for the vanadium atoms.
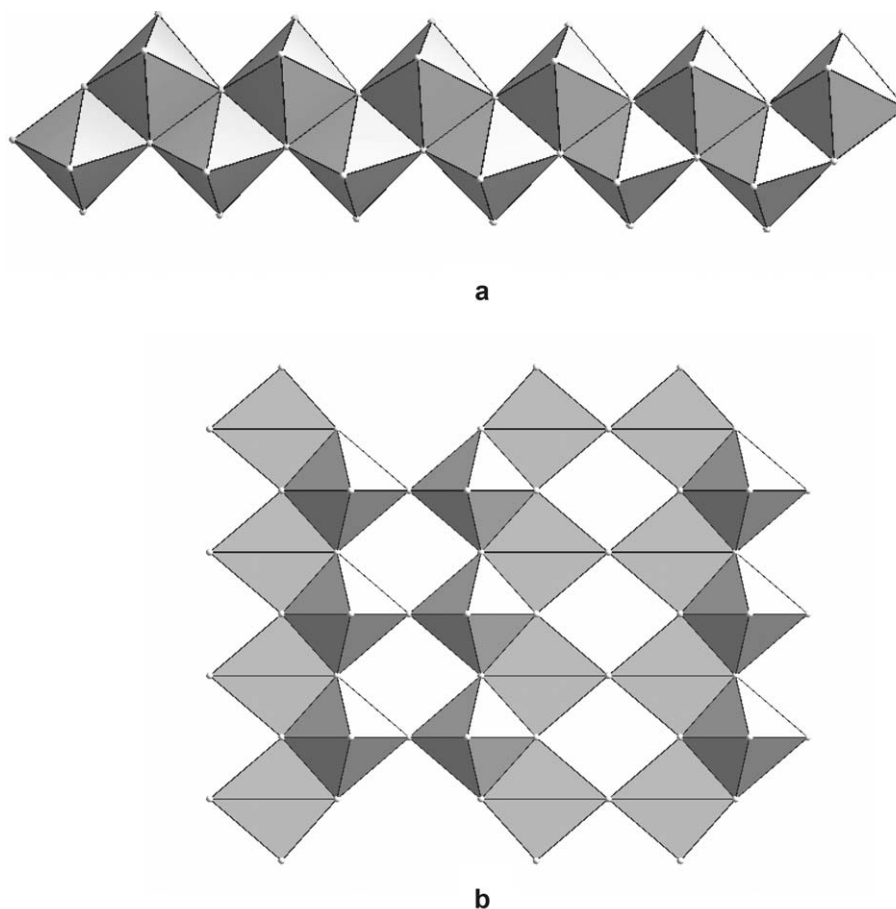
a

b

Fig. 3. (**a**) {UU} chain of VO$_5$ square pyramids as encountered in V$_3$O$_7$, and (**b**) one layer of V$_2$O$_5$ build up from the vertices-connections of {UD} chains of VO$_5$ square pyramids.

dium oxides V$_2$O$_5$ and V$_3$O$_7$. Indeed, this ring can be thought as the result of the cyclisation of one linear ribbon of 12 edge-shared square pyramids. This ribbon (Fig. 3a) is well-known in the chemistry of the vanadium oxides, it was labelled {UU} chains by Zavalij and Whittingham [1] relatively to the up-position of all the vanadyl linkages; it is a constitutive building block of the three-dimensional structure of V$_3$O$_7$ [15]. In an another hand, V$_2$O$_5$ [16] presents a two-dimensional structure whose layers are built up from the connection of closely related ribbons of edge-shared square pyramids. In this case, they are labelled {UD} chains since the vanadyl linkages alternatively point up and down the middle plane of the chains.

Finally, this new [V$_{16}$O$_{42}$]$^{4-}$ discrete entity shows the curious feature to give rise to structural overlaps

between the two very different families of polyoxovanadates and extended vanadium oxides structures.

An ORTEP drawing of the polyanion, the IR spectrum and the complete cif file are given as supplementary material. Furthermore, the cif file corresponding to the structure determination of [(SO$_4$) $\subset$ V$_{16}$O$_{42}$]·(SO$_4$)$_2$((CH$_3$)$_2$NH$_2$)$_{10}$((CH$_3$)$_2$NCHO)$_4$ has been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK and can be obtained under No. 242770 by contacting the CCDC.

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