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SYNTHESIS AND CRYSTAL STRUCTURE OF TWO $[NBu^n_4][V^V_4O_6(OH)(PhPO_3)_4]$ SOLVATES

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ABSTRACT: The compounds $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot Me_2CO$ (**1**) and $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot 0.5MeCN$ (**2**) have been isolated as a minor phase in the reaction of phenylphosphonyl dichloride with the mixed isopolyanion $[NBu^n_4]_4V_2W_4O_{19}$. They crystallize in the triclinic system, space group P–1 with lattice parameters a = 12.6372(17), b = 12.6884(17), c = 19.473(2) Å, α = 104.112(12)°, β = 91.928(11)°, γ = 113.191(9)°, V = 2753.9(7) Å^3, Z = 2 for **1** and a = 12.9020(5), b = 20.1755(19), c = 20.634(2) Å, α = 100.062(8)°, β = 99.696(6)°, γ = 96.159(5)°, V = 5160.9(8) Å^3, Z = 4 for **2**. The hybrid anion structure consists of spherical V/O/P shell of corner-sharing vanadium square pyramids and phenylphosphonate tetrahedra, encapsulating the hydroxo anion (OH^-).

KEYWORDS: *Oxovanadium; Organophosphonate; X-Ray structure.*

RESUME : Les composés $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot Me_2CO$ (**1**) et $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot 0.5MeCN$ (**2**) ont été isolés, comme phases mineures, lors de la réaction du phénylphosphonyl bichlorure sur l'isopolyanion mixte $[NBu^n_4]_4V_2W_4O_{19}$. Ils cristallisent dans le système triclinique groupe d'espace P–1 avec les paramètre de maille a = 12.6372(17), b = 12.6884(17), c = 19.473(2) Å, α = 104.112(12)°, β = 91.928(11)°, γ = 113.191(9)°, V = 2753.9(7) Å^3, Z = 2 pour **1** et a = 12.9020(5), b = 20.1755(19), c = 20.634(2) Å, α = 100.062(8)°, β = 99.696(6)°, γ = 96.159(5)°, V = 5160.9(8) Å^3, Z = 2 pour **2**. La structure de l'anion hybride peut être décrite comme une coquille sphérique (V/O/P) formée par un arrangement de pyramides à base carrée VO_5 et des tétraèdres de phénylphosphonate. Cette coquille renferme au centre un anion hydroxyle.

MOTS-CLES : *Oxovanadium, Organophosphonate, Structure cristallographique.*

INTRODUCTION

Polyoxometalates represent a great class of compounds that show a large variety of structural features. In addition to their remarkable chemical and physical properties they have large and varied fields of applications such as catalysis, medicine and material science [1-4]. IR, Raman spectroscopic studies in solution and in the solid state and X-ray diffraction have shown that the isopolyanion $V_2W_4O_{19}^{4-}$ has the likely Lindqvist structure [5, 6] with two tungsten atoms being replaced by vanadium. Vanadium atoms are usually square pyramidally coordinated by oxygen atoms. The VO_5 square pyramids are then condensed by sharing edges to form dimers as observed in $VOSO_4\cdot 3H_2O$ [7] or larger units, for example the ring of eight edge-shared square pyramids $[V_8O_{24}]$ found in the anions $[V_8O_{24}(OCH_3)_{16}(C_2O_4)]^{2-}$ [8]. There are diverse structural types like $[H_4V_{18}O_{42}(X)]^{9-}$ (X = Cl, Br, I), and $[V_{15}O_{36}(Y)]^{6-}$ (Y = Cl, Br, CO_3). [9-11], $[V_{12}O_{36}(CH_3CN)]^{4-}$ [12]. The inclusion process of the anions in the cavity is reversible, and consequently these compounds can be considered a molecular analogue of the microporous oxides. Generally these compounds can be noted with general formula $[V_xO_yE]^{n-}$ (E = encapsulated anionic unit) as described by Müller and *al* [13]. There are several works in the field of Oxovanadium-organophosphonate system $V/O/RPO_3^{2-}$. Such materials are prepared essentially by hydrothermal reactions [14] and in organic solvents by conventional methods [15-17]. The $(NBu^n_4)[V_4O_6(F)(PhPO_3)_4]$, which encapsulated fluorine anion has been reported by Qin Chen and Zubbieta [18]. This work presents the same molecular cage but encapsulated hydroxo anion (OH^-)

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which presence is confirmed by complementary studies: X-ray diffraction and spectroscopic investigations (IR and ^{1}H NMR).

EXPERIMENTAL

Compounds synthesis

Finely grounded (3 g; 1.42 mmol) of $[NBu^n_4]_4V_2W_4O_{19}$ [19] was added in 100 mL degassed dichloromethane. Then $PhPOCl_2$ (0.2 mL; 1.46 mmol) were added drop to drop, under argon, to the suspension which was stirred vigorously at room temperature overnight. Let us note that the resulting mixture becomes homogeneous after *ca* 15 mn. The dark orange solution was filtered to remove residual insoluble product, then the filtrate was evaporated using a rotary evaporator until obtaining dark viscous oil. Addition of ethanol (50 mL) to this oil followed by scraping with a glass spatula leads to an orange powder. This powder was filtered by suction filtration (glass frit porosity 4), washed with 50 mL of ethanol, 50 mL of ether. The compound was dissolved in a minimum amount of acetonitrile (ca 10 mL), then 50 mL of ethanol was added and the precipitated product was collected by suction filtration (glass frit porosity 4), washed with 50 mL of ethanol, 50 mL of ether and dried under vacuum (yield 2.7 g of crud product). The yellow-orange solid was dissolved in a minimum amount of acetone (ca 30 mL) and heated to increase solubility then filtered by glass frit N°4 to eliminate insoluble products named “A” (ca 2.3 g). After cooling the filtrate ultracentrifugation is required to remove insoluble impurities. The dark orange solution was left to spontaneous evaporation and the crystals of $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot Me_2CO$ (**1**) slowly grow from the solution at room temperature (yield 0.5 g of crystals; 11.5 % based on V). The insoluble product “A” was identified by IR and X-ray analysis as hexatungstate $[NBu^n_4]_2W_6O_{19}$.

Crystals of $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot 0.5MeCN$ (**2**) were obtained after a week, in 5mm o.d. NMR tube, from acetonitrile solution of (**1**). **IR (1480−300 and 3700−300 cm^{-1})** ν tilde: 304 (s), 387 (m), 441 (s), 459 (s), 503 (s), 526 (m), 569 (s), 625 (m), 673 (m), 696 (s), 721 (m), 756 (s), 966 (vs), 989 (vs), 1005 (vs), 1030 (s), 1068 (s), 1082 (s), 1136 (vs), 1379 (w), 1439 (m), 1460 (w), 1479 (m), 3689 (vw), 3080 (w), 3059 (w). **^{1}H NMR** (CD_3CN): δ = 3.16 (t, 8H, $N{-}\mathbf{CH_2}{-}CH_2{-}CH_2{-}CH_3$), 1.62 (q, 8H, $N{-}CH_2{-}\mathbf{CH_2}{-}CH_2{-}CH_3$), 1.35 (m, 8H, $N{-}CH_2{-}CH_2{-}\mathbf{CH_2}{-}CH_3$), 0.94 (t, 12H, $N{-}CH_2{-}CH_2{-}CH_2{-}\mathbf{CH_3}$), 7.64 (m, 8H, meta), 7.56 (m, 4H, para), 7.94 (m, 8H, ortho).**^{31}P NMR** (CD_3CN): δ = 19.95,

Single crystal analysis

Crystals of title compounds were mounted on a Kappa-CCD Brüker AXS diffractometer using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Data were collected at 293 K. Lattice parameters for both compounds were performed by Dirax/lsq (Duisenberg & Schreurs, 1989–2000) and data reduction by EvalCCD (Duisenberg & Schreurs, 1990–2000) programs. The positional parameters of metal and most oxygen atoms of the clusters were obtained by direct methods and refined with full-matrix least-squares technique on F using the SHELXS86 [20]. The crystallographic software CRYSTALS [21] served for the refinement of the structure and the preparation of data for the publication. The structure representations were drawn with DIAMOND program v 2.1 [22]. The crystal data and details of data collection and refinement for crystals of $[NBu^n_4][V^V_4O_6(OH)(PhPO_3)_4]\cdot Me_2CO$ and $[NBu^n_4][V^V_4O_6(OH)(PhPO_3)_4]\cdot 0.5MeCN$ are summarized in Table 1.

Table 1: Crystallographic data and refinement parameters for compounds 1 and 2.

Crystal data and refinement details	1	2
Empirical formula	$X\cdot Me_2CO$	$X\cdot 0.5MeCN$
CCDC N°	665144	665143
Formula weight	1242.63	1203.7
Crystal system	Triclinic	Triclinic
Space group	P–1	P–1
a (A˚)	12.6372(17)	12.9020(5)
b (A˚)	12.6884(17)	20.1755(19)
c (A˚)	19.473(2)	20.634(2)

α (°)	104.112(12)	100.062(8)
β (°)	91.928(11)	99.696(6)
γ (°)	113.191(9)	96.159(5)
V (A° ^{3})	2753.9(7)	5160.9(8)
Z	2	4
Dc (g cm^{-3})	1.497	1.548
μ(Mo*Kα*) (mm^{-1})	0.846	0.899
θ Range (deg)	2.101-29.999	1.591-30.076
Limiting indices	-17≤h≤17, 0≤k≤26, -	-18≤h≤17, -27≤k≤27, -
Reflection collected	15330	97193
Data completeness	97.2%	99.4%
Data used/restraints/parameters	5713/0/649	12895/0/1252
Goodness-of-fit on F	0.9688	0.7017
Final R1, wR2 [I>3σ(I)]	0.0625, 0.0643	0.0402, 0.0539
Largest differential peak and hole (eA°	—0.67, 0.85	—0.46, 0.85

X = $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]$

Spectroscopic analysis

The IR spectra have been recorded from KBr pellets on a spectrometer FT-IR Bio-rad Win-IR FTS 165 with a resolution of 4 cm^{-1}.

^{1}H NMR spectra were obtained at 300 K from CD_3CN solutions in 5 mm o.d. tubes at 300 and 75.5 MHz respectively on a Brüker AC300 or Brüker AvanceII spectrometer. Chemical shifts values for ^{1}H is internally referenced to tetramethylsilane (TMS) using the solvent peak as secondary standard.

^{31}P spectra were recorded in 5 mm o.d. tubes at 121.49 MHz on a Bruker AC300 spectrometer equipped with a QNP probehead. The chemical shifts are given according to the IUPAC convention, with respect to 85% H_3PO_4.

RESULTS AND DISCUSSION

Synthesis

The obtaining of such structure, in our case, results from reaction of $PhPOCl_2$ and $V_2W_4O_{19}^{4-}$. All our attempts to obtain grafted isopolyanion are failed and the hexatungstate is obtained in major quantities; this suggests that the $V_2W_4O_{19}^{4-}$ framework is sufficiently labile to lose vanadium under $PhPOCl_2$ attack. It is not easy to propose a mechanism, but when we observe the P–O–V linkage mode it is evidently that $PhPO^{2+}$ attack bridging oxygen atoms (V–O–W) in the $V_2W_4O_{19}^{4-}$.

Crystal structure description

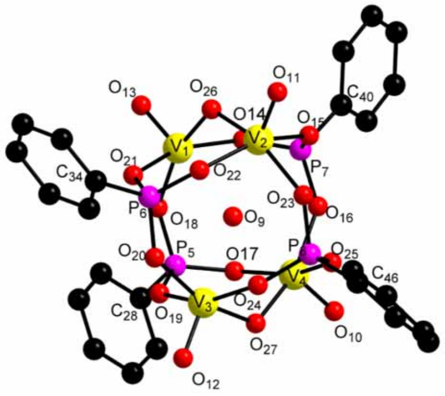

Figure 1: A view of the structure of the molecular anion $[V_4O_6(OH)(PhPO_3)_4]^-$, showing the atom labelling scheme.

The molecular structures of title compounds are similar except the crystallization solvent molecule. In the discussion below we focus on the structure of compound **(2)** for entire discussion. The X-ray crystallographic study of $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot$ 0.5MeCN reveals that the structure consists of one tetrabutylammonium cation, crystallization solvent molecule MeCN and tetra-metallic anion cluster $[V_4O_6(OH)(PhPO_3)_4]^-$ as shown in Figure 1.

Table 2: Selected distances for $[V_4O_6(OH)(PhPO_3)_4]^-$ and bond valence sums calculation [25]

Metal–oxygen bonds within the anion (Å) and valence bond sums							
V1— O13	1.582(13)	V2—O11	1.593(8)	V3—O12	1.59(1)	V4—O10	1.587(15)
—O26	1.834(7)	—O26	1.784(11)	—O27	1.802(14)	—O27	1.817(11)
—O14	1.940(11)	—O22	1.943(11)	—O24	1.938(10)	—O25	1.929(10)
—O18	1.951(8)	—O15	1.954(13)	—O19	1.945(11)	—O17	1.935(11)
—O21	1.947(13)	—O23	1.968(16)	—O20	1.959(17)	—O16	1.948(11)
—O9	2.422(20)	—O9	2.480(9)	—O9	2.444(13)	—O9	2.456(22)
$\sum s_{ij}$= 4.957		$\sum s_{ij}$= 4.962		$\sum s_{ij}$= 4.991		$\sum s_{ij}$= 5.014	

The structure can be described as a one corner sharing assembly of four VO_6 octahedra. Two orthogonal edge sharing bioctahedra $\{V_2O_{10}\}$ share the vertex on which hydroxo anion is located. The set of tetra nuclear oxo-vanadium $\{V_4O_{19}\}$ adopts a local tetrahedral symmetry (Figure 2a). This tetrahedral disposition allows the capping of each face by the tetrahedral {PhP} group. Alternatively, the structure can be viewed as a spherical V/P/O shell of corner-sharing vanadium square pyramids and organophosphonate tetrahedra, encapsulating the hydroxo anion (Fig. 2b). In the VO_6 octahedron we can distinguish four types of oxygen atoms: the first type consists of one terminal oxygen linked to the vanadium atom (V=O) and the average bond length is c.a. 1.59 Å. The second one is one oxygen atom which bridge two vanadium atoms (V–O–V) of the same pair $\{V_2O_{10}\}$ with an average distance V–O c.a. 1.81 Å. The third type of oxygen atoms is three P–O–V oxo bridges; the V–O distance is significantly longer than that of the second group (1.94 Å *vs* 1.81 Å). Finally the fourth type form the central oxygen atom shared by four vanadium atoms with an average distance c.a. 2.45 Å. This distance is slightly longer than those reported in the polyoxometalates of Lindqvist structure type (2.38, 2.33 Å respectively for $Nb_6O_{19}^{8-}$ and $W_6O_{19}^{2-}$ [26, 27]).

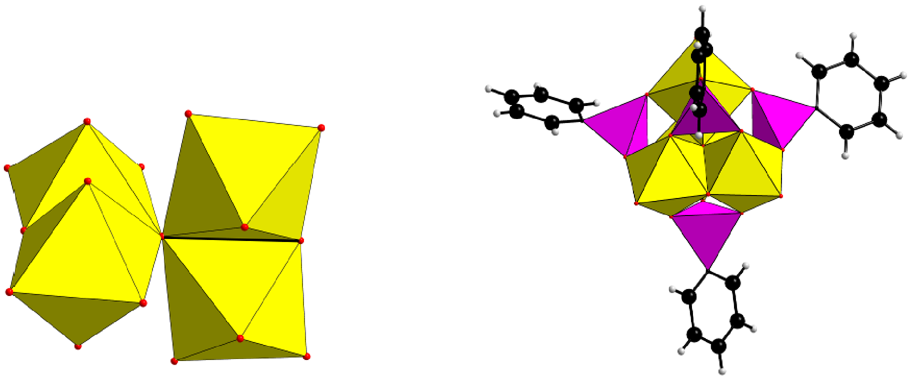

Figure 2: **(a)** right, orthogonal edge sharing bioctahedra $\{V_2O_{10}\}$. **(b)** left, polyhedral representation of $[V_4O_6(OH)(PhPO_3)_4]^-$ anion, yellow VO_6; purple Ph─PO_3 tetrahedra; black carbon, grey hydrogen.

X-ray study shows the presence of one oxygen atom inside the anionic cavity. The electroneutrality of the whole molecule, taking in account the BVS calculations for all vanadium atoms, is consistent with hydroxo anion.

As previously reported [18] the tetranuclear cavity cannot encapsulates Cl^- because of its ionic radius which is considerably larger than that of F^- (1.81 *vs.* 1.31Å). However the effective ionic radii for OH^- ion was estimated by Shannon [28] and is comparable to that of F^- (1.35 *vs.* 1.31Å).

Infrared spectroscopy

The infrared spectrum (Figure 3) exhibited a set of strong bands at (1004 – 966 cm^{-1}) corresponding to ν(V=O), the 756 cm^{-1} can be assigned to ν_{as}(V–O–V) and 569 cm^{-1} ν_s(V–O–V) [21]. The bands at 1136 cm^{-1} is relative to ν(P–C) and those at 1031, 1068 and 1081 cm^{-1} are relative to ν(P–O–V) [13]. The presence of band 389 cm^{-1} reminds us the ν(M–O_c, O_c central oxygen) in the Lindqvist structure $V_2W_4O_{19}^{4-}$.

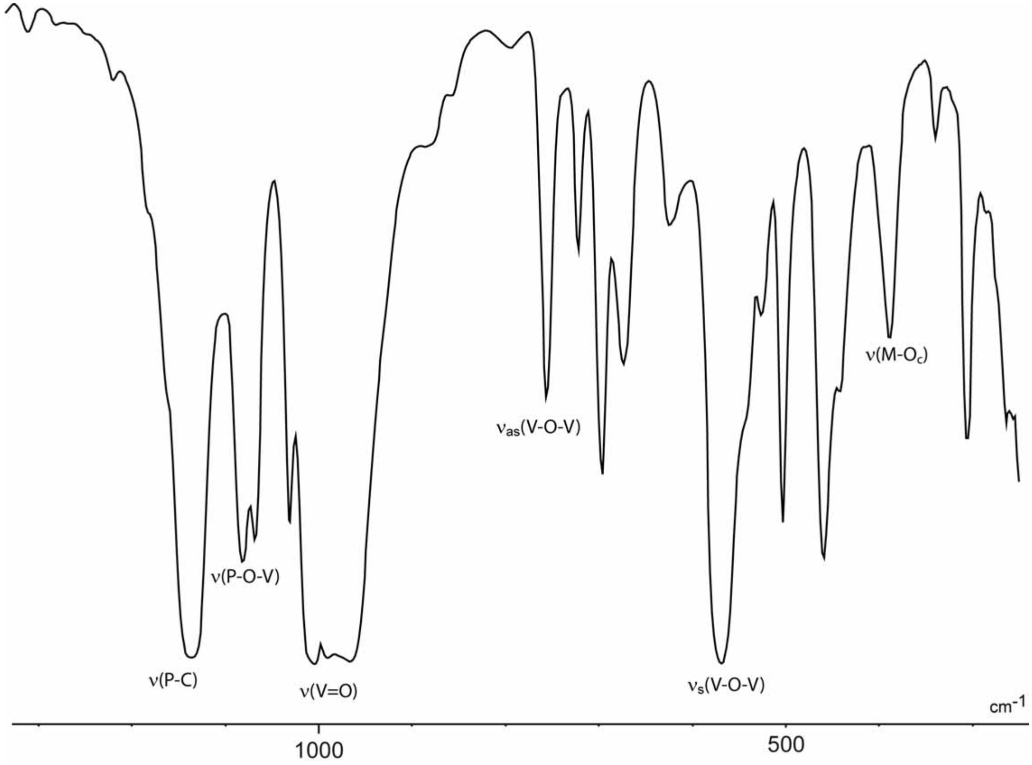

Figure 3: Infrared spectrum region 1700 – 300 cm^{-1} of $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot0.5MeCN$

NMR spectroscopy

The ^1H spectrum of the $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]\cdot0.5MeCN$ presents the characteristic signals of the organophosphonyl part along with those of the tetrabutyammonium cation (See experimental part). The relative integration of the signals agrees with one tetrabutyammonium for four phenyl group according to the formula $[NBu^n_4][V_4O_6(OH)(PhPO_3)_4]$. ^{31}P NMR spectrum exhibits only one signal (T_d symmetry) at 19.95 ppm which is relatively broad ($\Delta\nu_{½}$ ~ 86Hz); this is due to the vicinity of the quadrupolar nucleus ^{51}V.

CONCLUSION

This work illustrates complementarities between different analysis techniques (X-ray, IR, NMR) to determine without ambiguity the real structure of the compounds. In our case the X-ray diffraction reveals the entire structure except the central oxo-anion. Infrared spectroscopy proves that this oxo-anion is in reality a hydroxyl anion. The NMR investigations confirm both precedent spectroscopic methods and support the formula stoechiometry of title compounds.

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Crystallographic Data CCDC 665143 and CCDC 665144 contain supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request/ or e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Tel/fax: +441223336408 / +441223336033.

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