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Characterization of tetra, dodeca and tetradeca Mo^V polyoxometalate wheels structured by etidronate ligands

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ARTICLE INFO

Article history:

Received 23 June 2009

Accepted after revision 11 September 2009

Available online 28 November 2009

Keywords:

Polyoxometalate

Molybdenum (V)

Wheel shaped anions

Crystal structure

Diphosphonate

ABSTRACT

The reactivity of the $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ dinuclear unit with the $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3]^{4-}$ etidronate ligand has been investigated. Three complexes have been isolated and characterized by IR spectroscopy, elemental analysis and single crystal X-Ray diffraction studies. Structural determination of the tetranuclear compound $(\text{CN}_3\text{H}_6)_6[(\text{Mo}^{\text{V}}_2\text{O}_4)_2(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_2]\cdot 12\text{H}_2\text{O}$ (**1**) revealed that the hydroxo group of the etidronate ligand can be deprotonated in presence of Mo^{V} even in acidic media. It follows that its coordination mode thus differs from that of the methylenediphosphonate ligand $[\text{O}_3\text{P}(\text{CH}_2)\text{PO}_3]^{4-}$, which reactivity with Mo^{V} has been previously widely studied. In contrast, no such deprotonation of the hydroxo group is observed in the $(\text{NH}_4)_{18}[(\text{Mo}^{\text{V}}_2\text{O}_4)_6(\text{OH})_6(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)_6]\cdot 35\text{H}_2\text{O}$ complex **2**. This species contains a dodecanuclear core analogous to the one previously found in the $[(\text{Mo}^{\text{V}}_2\text{O}_4)_6(\text{OH})_6(\text{O}_3\text{P}(\text{CH}_2)\text{PO}_3)_6]^{18-}$ methylenediphosphonate polyanion. In **2**, six interconnected $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)\}$ units form a cyclohexane-like ring in a chair conformation. In the $(\text{CN}_3\text{H}_6)_{18}\text{Na}_3[(\text{Mo}^{\text{V}}_2\text{O}_4)_7(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)_7(\text{CH}_3\text{COO})_7]\cdot 5\text{CH}_3\text{COONa}\cdot 52\text{H}_2\text{O}$ compound **3**, seven $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)(\text{CH}_3\text{COO})\}$ units are connected, forming an almost planar tetradecanuclear wheel. This compound represents the largest homometallic Mo^{V} polyoxometalate cyclic system reported to date. Finally, ^{31}P NMR studies revealed that only complex **1** is stable in aqueous solution.

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R É S U M É

La réactivité de l'unité dinucléaire $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ avec le ligand étidronate $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3]^{4-}$ a été étudiée. Trois complexes ont été isolés et caractérisés par spectroscopie IR, analyse élémentaire et analyse par diffraction des rayons X sur monocristal. La détermination structurale du composé tétranucléaire $(\text{CN}_3\text{H}_6)_6[(\text{Mo}^{\text{V}}_2\text{O}_4)_2(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_2]\cdot 12\text{H}_2\text{O}$ (**1**) a révélé que le groupement hydroxo du ligand étidronate peut être déprotonné en présence de Mo^{V} même en milieu acide. Il s'ensuit que celui-ci possède alors un mode de coordination qui diffère de celui du ligand méthylendiphosphonate $[\text{O}_3\text{P}(\text{CH}_2)\text{PO}_3]^{4-}$ dont la réactivité avec le Mo^{V} a été largement étudiée précédemment. À l'inverse, une telle déprotonation du groupement hydroxo n'est pas observée dans le cas du composé $(\text{NH}_4)_{18}[(\text{Mo}^{\text{V}}_2\text{O}_4)_6(\text{OH})_6(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)_6]\cdot 35\text{H}_2\text{O}$ (**2**). Cette espèce contient un cœur dodecanucléaire analogue à celui précédemment observé dans le cas du polyanion $[(\text{Mo}^{\text{V}}_2\text{O}_4)_6(\text{OH})_6(\text{O}_3\text{P}(\text{CH}_2)\text{PO}_3)_6]^{18-}$ qui comporte le ligand méthylendiphosphonate. Le composé **2** consiste en six unités $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)\}$ interconnectées qui forment un édifice adoptant une topologie de type cyclohexane dans sa conformation chaise.

Mots clés :

Polyoxométallates

Molybdène (V)

Roues anioniques

Structure cristalline

Diphosphonate

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Dans le cas du composé $(\text{CN}_3\text{H}_6)_{18}\text{Na}_3[(\text{Mo}^{\text{V}}_2\text{O}_4)_7(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)_7(\text{CH}_3\text{COO})_7] \cdot 5\text{CH}_3 \cdot 5\text{CH}_3\text{COONa} \cdot 52\text{H}_2\text{O}$ (**3**), sept unités $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)(\text{CH}_3\text{COO})\}$ sont connectées, formant une roue tétradécanucléaire quasiment plane. Ce composé représente le polyoxométallate cyclique ne comportant que des ions métalliques Mo^{V} de plus haute nucléarité reporté à ce jour. Finalement, des études par RMN du ^{31}P ont révélé que seul le complexe **1** est stable en solution.

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1. Introduction

Polyoxometalate (POM) clusters can be formed in acidic solution by condensation reactions of monomeric oxoanions of transition metals belonging mainly to groups V and VI [1]. In particular, a huge number of species featuring tungsten, molybdenum, vanadium and/or niobium atoms have been isolated. In this family of compounds, it has to be distinguished between the compounds comprising only one type of heavy atom, called isopolyoxometalates, and the compounds obtained in presence of a $\{\text{XO}_4\}$ additional group ($\text{X} = \text{P}^{\text{V}}, \text{As}^{\text{V}}, \text{Si}^{\text{IV}}, \text{Ge}^{\text{IV}}, \dots$), called heteropolyoxometalates. To date, four families of compounds and their derivatives dominate the chemistry of POMs, namely Lindquist $\{\text{M}_6\text{O}_{19}\}$, Keggin $\{\text{XM}_{12}\text{O}_{40}\}$, Dawson $\{\text{X}_2\text{M}_{18}\text{O}_{62}\}$ and Anderson $\{\text{M}'\text{M}_6\text{O}_{24}\}$ (where M' is an octahedrally coordinated cation) type systems. For these species, the heavy atoms are generally in their highest oxidation state ($\text{W}^{\text{VI}}, \text{Mo}^{\text{VI}}, \text{V}^{\text{V}}, \text{Nb}^{\text{V}}, \dots$), but, in some cases, related reduced POMs can be chemically or electrochemically obtained, as shown, for example, by the characterization of the mixed-valence four electron reduced $\beta\text{-}[\text{H}_4\text{PMo}_{12}\text{O}_{40}]^{3-}$ polyanion [2]. It has to be noticed that, beside these archetypal families of POMs, the chemistry of molybdenum mixed-valence POM clusters developed by Achim Müller and his collaborators has afforded spectacular, very high nuclearities compounds, such as a species which contains as many as 368 metal atoms [3]. Focusing on polyoxomolybdate systems where all the molybdenum centers are reduced in their V oxidation state, a large number of species have been isolated both in organic or aqueous media. In all cases, these polyanions contain the dinuclear dicationic $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ unit, where a metallic bond connects the two d^1 centers, leading to a diamagnetic behavior of this fragment even at room temperature. The connection of $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ units by various organic ligands (oxalate, squarate, polycarboxylate, carbonate, ethanolate, methanolate, etc.) has afforded systems containing from one to six dinuclear fragments [4]. On the other hand, the ability of the related $[\text{Mo}^{\text{V}}_2\text{O}_2\text{S}_2]^{2+}$ oxothiofragment to form polyoxothiometalates has also been studied, affording cyclic systems with nuclearities ranging from 8 to 16 [5].

In our group, we have focused our investigations involving the $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ building unit on the polycondensation of this dinuclear fragment via pyrophosphate $[\text{O}_3\text{POPO}_3]^{4-}$ and methylenediphosphonate $[\text{O}_3\text{P}(\text{CH}_2)\text{PO}_3]^{4-}$ ligands in the eventual presence of other coordinating groups (carboxylate, carbonate, sulfite...) in aqueous media. Our investigations have allowed us to isolate a wide variety of pure Mo^{V} cyclic POM clusters of various nuclearities. For example, the triangular cluster

$[(\text{Mo}^{\text{V}}_2\text{O}_4)_3(\text{O}_3\text{P}(\text{CH}_2)\text{PO}_3)_3(\text{CH}_3\text{AsO}_3)]^{8-}$ has been obtained in presence of methyl arsenate, [6] while ellipsoidal octanuclear clusters have been isolated when the synthetic process is performed in presence of sulfite or carbonate [7]. A larger complex, a dodecanuclear wheel which adopts a cyclohexane-like ring in a chair conformation has been obtained in absence of any additional coordinating groups. Nevertheless, the presence of ammonium cations in the reacting medium is crucial for the obtaining of this species, highlighting the importance of the nature of the counterions on the resulting POM [6]. In addition to these cyclic systems, bicyclic compounds have also been obtained. The isolated isostructural complexes $[\text{Na}_2\{(\text{Mo}^{\text{V}}_2\text{O}_4)_{10}(\text{O}_3\text{P}(\text{X})\text{PO}_3)_{10}(\text{CH}_3\text{COO})_8\}]^{24-}$ ($\text{X} = \text{O}, \text{CH}_2$) are made of two interconnected and nearly perpendicular octanuclear and dodecanuclear wheels, respectively [8]. Recently, we have shown that such diphosphonate Mo^{V} species are able to form and stabilize metal nanoparticles (NPs), which, from an electrocatalytic point of view, can combine the properties of metal NPs and POM complexes. Moreover, such nanosystems are obtained in a one-pot procedure, in water, at room temperature and without any additional surfactant. For example, by simply mixing the cyclohexane-like dodecanuclear compound mentioned above and Pd^{II} cations in aqueous solution, NPs with diameter of 9–14 nm containing a Pd^0 core and capped by POMs are obtained [6]. Additionally, it has also been shown that Ag^0 [9] and Pt^0 [10] POM capped NPs can be obtained using this procedure. Beside the observation that this family of POMs allows the formation of NPs, it has also been stated that the sizes and shapes of the obtained nanosystems depend on the nature of the polynuclear Mo^{V} complex used. In order to synthesize NPs with the desired morphology, it is thus essential to elaborate a library of reduced POMs with different structural and redox characteristics.

In this article, we present our results concerning the synthesis and the characterization of polynuclear Mo^{V} POMs obtained by condensation of the dinuclear $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ fragment with the 1-hydroxyethane 1,1-diphosphonate (or etidronate) ligand $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3]^{4-}$ (Fig. 1a). Our goal was to answer two questions: (a) do the potentially available Mo^{V} /etidronic POMs display the same topologies as those obtained by condensation of dinuclear $[\text{Mo}_2\text{O}_4]^{2+}$ fragments with methylenediphosphonic ligands; and (b) can the hydroxo group grafted on the carbon center linking the two phosphorous atoms in $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3]^{4-}$ act as a ligand for the Mo^{V} cations? We thus report here the structural characterization of the tetranuclear compound $(\text{CN}_3\text{H}_6)_6[(\text{Mo}^{\text{V}}_2\text{O}_4)_2(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_2] \cdot 12\text{H}_2\text{O}$ (**1**), the dodecanuclear complex $(\text{NH}_4)_{18}[(\text{Mo}^{\text{V}}_2\text{O}_4)_6(\text{OH})_6(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)_6] \cdot 35\text{H}_2\text{O}$ (**2**) and the tetradecanuclear

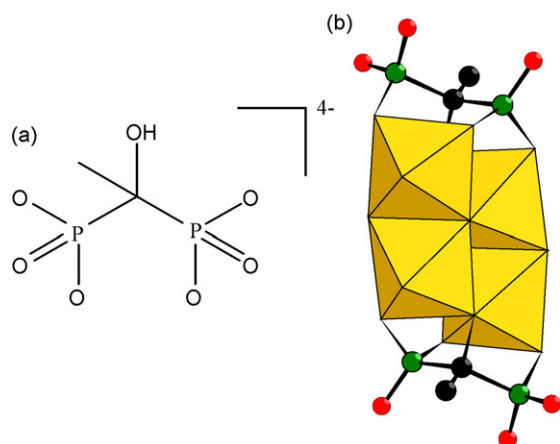


Fig. 1. (a) Representation of the $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3]^{4-}$ etidronate ligand; (b) Mixed ball-and-stick and polyhedral representation of the tetranuclear $[(\text{Mo}^{\text{V}}_2\text{O}_4)_2(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_2]^{4-}$ polyanion in **1**. The hydrogen atoms are omitted for clarity. Yellow octahedra, MoO_6 ; green spheres, P; black spheres, C; red spheres, O.

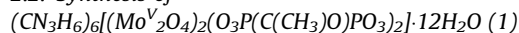
species $(\text{CN}_3\text{H}_6)_{18}\text{Na}_3[(\text{Mo}^{\text{V}}_2\text{O}_4)_7(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_7(\text{CH}_3\text{COO})_7]\cdot 5\text{CH}_3\text{COONa}\cdot 52\text{H}_2\text{O}$ (**3**). Their stability in aqueous media has also been studied by ^{31}P NMR.

2. Experimental section

2.1. Preparation of a $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ solution

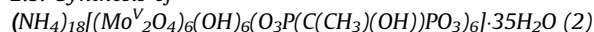
Two hundred and ten microliters (4.29 mmol) of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ are added to a suspension of 2.30 g (16.0 mmol) of MoO_3 in 80 mL of 4 M HCl. The mixture is then stirred at 80°C for ca. 3 h. The resulting deep red solution is allowed to cool down to room temperature before further use.

2.2. Synthesis of



One hundred and forty-one milligrams (0.63 mmol) of etidronic acid $\text{H}_2\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3\text{H}_2\cdot\text{H}_2\text{O}$ are dissolved in 6.25 mL of a solution of $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ prepared as described above. A 8 M NaOH solution is added dropwise until reaching pH = 6.4, followed by the addition of 1 g (10.4 mmol) of guanidinium chloride. The resulting deep red solution is filtrated and left to evaporate slowly at room temperature. Red parallelepipedic crystals are collected by filtration after one day. Yield: 309 mg (67% based on Mo). Anal. calc. for $\text{C}_{10}\text{H}_{66}\text{O}_{34}\text{N}_{18}\text{P}_4\text{Mo}_4$ (found): C 8.06 (7.73), H 4.46 (3.83), N 16.92 (15.94), P 8.31 (8.38), Mo 25.75 (25.68). IR (KBr pellets): $\nu = 1449$ (w), 1443 (w), 1369 (w), 1191 (m), 1140 (sh), 1127 (s), 1046 (s), 1000 (s), 965 (s), 951 (sh), 930 (m), 903 (m) cm^{-1} .

2.3. Synthesis of



One hundred and forty-one milligrams (0.63 mmol) of etidronic acid $\text{H}_2\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3\text{H}_2\cdot\text{H}_2\text{O}$ are dissolved in 6.25 mL of a solution of $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ prepared as

described above. A 33% NH_3 solution is added dropwise until reaching pH = 7.4. The resulting deep red solution is filtrated and left to evaporate slowly at room temperature. Red parallelepipedic crystals are collected by filtration after three days. Yield: 110 mg (28% based on Mo). Anal. calc. for $\text{C}_{12}\text{H}_{172}\text{O}_{107}\text{N}_{18}\text{P}_{12}\text{Mo}_{12}$ (found): C 3.79 (3.78), H 4.56 (4.25), N 6.63 (6.88), P 9.77 (9.65), Mo 30.26 (29.61). IR (KBr pellets): $\nu = 1398$ (s), 1144 (s), 1131 (sh), 1082 (m), 1052 (s), 1007 (s), 961 (w), 920 (m), 903 (m) cm^{-1} .

2.4. Synthesis of $(\text{CN}_3\text{H}_6)_{18}\text{Na}_3[(\text{Mo}^{\text{V}}_2\text{O}_4)_7(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)_7(\text{CH}_3\text{COO})_7]\cdot 5\text{CH}_3\text{COONa}\cdot 52\text{H}_2\text{O}$ (**3**)

In 10 mL of 4 M $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer (pH = 4.9) are dissolved 242 mg (1.0 mmol) of $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$, 112 mg (0.5 mmol) of etidronic acid $\text{H}_2\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3\text{H}_2\cdot\text{H}_2\text{O}$, 500 mg (5.2 mmol) of guanidinium chloride and 50 μL (1.0 mmol) of hydrazine hydrate. The resulting suspension is stirred for 15 min at room temperature before filtration. The red filtrate is left to evaporate slowly at room temperature. Small red cubic crystals are collected by filtration after one day. Yield: 240 mg (55% based on Mo). Anal. calc. for $\text{C}_{56}\text{H}_{294}\text{N}_{54}\text{O}_{153}\text{P}_{14}\text{Mo}_{14}\text{Na}_8$ (found): C 10.96 (11.01), H 4.83 (4.07), N 12.33 (12.37), P 7.07 (7.05), Mo 21.90 (22.45) Na 3.00 (2.91). IR (KBr pellets): $\nu = 1558$ (m), 1539 (m), 1434 (m), 1162 (m), 1136 (m), 1109 (w), 1081 (w), 1037 (s), 1002 (s), 966 (sh), 923 (w) cm^{-1} .

2.5. X-ray structure determination of **1**, **2** and **3**

Intensity data collections were carried out with a Siemens SMART three-circle diffractometer for **1** and **2** and with a Bruker Nonius X8 APEX 2 diffractometer for **3**, each equipped with a CCD bidimensional detector using the monochromatized wavelength $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$. The absorption corrections were based on multiple and symmetry-equivalent reflections in the data set using the SADABS program [11] based on the method of Blessing [12]. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package [13]. In the structures of **2**, NH_4^+ and H_2O could not be distinguished according to the observed electron densities; therefore all the positions were labelled O and assigned the oxygen atomic diffusion factor. As **3** rapidly loses water at room temperature, a single crystal of this compound was glued in Paraton-N oil and the data set collected at 100 K. However, despite many efforts, it was not possible to obtain an entirely satisfying data set for **3** probably because of its great instability. It was thus not possible to locate the guanidinium counter-ions. The number of guanidinium cations indicated in the formula of compound **3** has then been determined considering the elemental analysis results. As generally observed for POM compounds, in all three structures there is a discrepancy between the formulae determined by elemental analysis and the formulae deduced from the crystallographic atom list because of the difficulty in locating all the disordered water molecules and counter-ions [8]. The data sets for **2** and **3**, which contain large voids occupied by solvent molecules were corrected with the program SQUEEZE, a part of the PLATON package of crystallographic software

Table 1
Crystallographic data and details of diffraction experiments for **1–3**.

	1	2	3
Empirical formula	C ₁₀ H ₆₆ O ₃₄ N ₁₈ P ₄ Mo ₄	C ₁₂ H ₁₇₂ O ₁₀₇ N ₁₈ P ₁₂ Mo ₁₂	C ₅₆ H ₂₉₄ N ₅₄ O ₁₅₃ P ₁₄ Mo ₁₄ Na ₈
Formula weight (g)	1490.39	3804.53	6133.94
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>m</i>
<i>a</i> /Å	12.362(1)	31.040(5)	24.868(4)
<i>b</i> /Å	13.085(1)	17.130(2)	33.141(6)
<i>c</i> /Å	15.595(1)	23.651(3)	28.910(5)
α /deg	89.170(2)	90	90
β /deg	89.418(2)	101.017(4)	101.15(1)
γ /deg	89.430(2)	90	90
<i>V</i> /Å ³	2522.0(3)	12344(3)	23376(7)
<i>Z</i>	2	4	4
<i>T</i> /K	293	293	100
ρ_{calc} /g cm ⁻³	1.943	1.986	1.483
μ /mm ⁻¹	1.212	1.451	0.917
Data/parameters	14282/622	17856/606	15455/681
<i>R</i> _{int}	0.0328	0.0711	0.1070
GOF	1.075	1.043	0.940
<i>R</i> (>2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0566 <i>wR</i> ₂ = 0.1435	<i>R</i> ₁ = 0.0789 <i>wR</i> ₂ = 0.1990	<i>R</i> ₁ = 0.0696 <i>wR</i> ₂ = 0.1884

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_c|} \quad ^b wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$$

used to calculate the solvent disorder area and remove its contribution to the overall intensity data [14]. Crystallographic data are given in Table 1. Selected bond lengths are given in Table 2.

2.6. NMR spectroscopy

The ³¹P NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 121.5 MHz in 5-mm tubes with ¹H decoupling.

2.7. Elemental analysis

The elemental analysis of complexes **1**, **2** and **3** were performed by the Service central d'analyse élémentaire, CNRS, 69390 Vernaison, France.

2.8. FTIR spectroscopic analysis

The IR spectra of complexes **1**, **2** and **3** were recorded on an IRFT Magna 550 Nicolet spectrophotometer using the technique of pressed KBr pellets.

3. Results and discussion

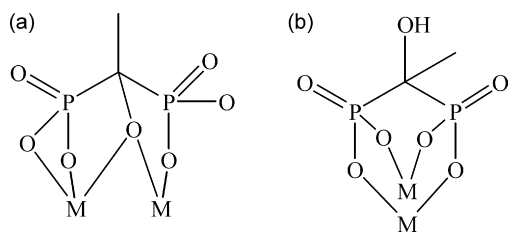
Compound **1** has been obtained by adding solid etidronic acid to a solution of [Mo^V₂O₄(H₂O)₆]²⁺. The pH of the mixture was raised to 6.4 with sodium hydroxyde, followed by an addition of guanidinium chloride. After slow evaporation of the filtrate, red crystals of **1** were obtained. A single crystal X-ray diffraction study revealed that **1** is made of a [(Mo^V₂O₄)₂(O₃P(C(CH₃)O)PO₃)₂]⁶⁻ tetranuclear polyanion (Fig. 1b) with six guanidinium

Table 2
Selected bond lengths (Å) for **1–3**.

	1	2	3
Mo ^V =O	1.677(4)–1.687(4) [1.684]	1.679(6)–1.706(6) [1.691]	1.630(4)–1.704(5) [1.667]
Mo ^V –O _b ^a	1.941(3)–2.076(3) [2.014]	1.918(6)–2.107(6) [2.011]	1.838(5)–2.151(4) [2.016]
Mo ^V –O _t ^b	2.329(3)–2.477(3) [2.394]	2.209(5)–2.240(5) [2.222]	2.221(5)–2.332(4) [2.282]
Mo ^V –Mo ^V	2.5755(6)–2.5801(6) [2.578]	2.5752(11)–2.5852(9) [2.580]	2.5482(9)–2.5708(10) [2.561]
P=O	1.489(4)–1.577(4) [1.504]	1.498(6)–1.519(6) [1.508]	1.434(6)–1.522(7) [1.449]
P–O _{Mo}	1.547(4)–1.577(4) [1.562]	1.513(6)–1.550(6) [1.531]	1.475(4)–1.564(4) [1.521]
P–C	1.828(5)–1.852(5) [1.838]	1.813(9)–1.848(10) [1.825]	1.736(10)–1.941(7) [1.809]
POM size	7 × 12	16 × 18	23 × 23

^a Mo–O bond with bridging oxygen atoms.

^b Mo–O bond trans to the Mo=O bond.



Scheme 1. Representation of the coordination modes of the etidronate ligand in (a) complex **1** and (b) complexes **2** and **3**.

counter-ions. Two crystallographically non-equivalent $[(\text{Mo}^{\text{V}}_2\text{O}_4)_2(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_2]^{6-}$ subunits have been found in the unit cell. Nevertheless, these two subunits are highly similar and will be considered as identical for the forthcoming discussion. Each $[(\text{Mo}^{\text{V}}_2\text{O}_4)_2(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_2]^{6-}$ unit contains a centrosymmetric, rhomboid $\{\text{Mo}_4\text{O}_{16}\}$ core with localized metal–metal bonds. Such topology is recurrent in the Mo^{V} chemistry [15]. The two crystallographically equivalent etidronate groups constituting each $[(\text{Mo}^{\text{V}}_2\text{O}_4)_2(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_2]^{6-}$ fragment in **1** act as tetradentate ligands, respectively (see Scheme 1a). For each $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3]^{5-}$ ligand, one $\{\text{PO}_3\}$ group is monocoordinated to a Mo^{V} center, while the other phosphonato group is coordinated via two oxygen atoms to an adjacent metallic center. Additionally, the hydroxo group bound to the carbon atom connecting the P^{V} centers is found to be deprotonated, and acts as a $\mu_2\text{-O}$ ligand. The characterization of **1** then allows one to answer the questions asked in the introduction section: the hydroxo group of an etidronate ligand can be deprotonated and connect Mo^{V} centers even in slightly acidic medium, and then the reactivity of this ligand can be different from the reactivity of the methylenediphosphonate ligand. Moreover, it should be mentioned that, despite the large number of Mo^{V} / methylenediphosphonate ligands characterized to date, no complex possessing a $\{\text{Mo}_4\text{O}_{16}\}$ core had been observed using this ligand, confirming that the Mo^{V} chemistry involving the methylenediphosphonate ligand cannot be transposed to that involving the etidronate ligand. The stability of **1** in aqueous medium has been studied. The ^{31}P NMR spectrum in water is represented in Fig. 2. It exhibits a doublet of doublets at 32.28, 32.10, 22.12 and 21.93 ppm ($J = 22.1$ Hz). Such a spectrum is in agreement with the presence of two independent and coupled phosphorous atoms, indicating that the structure observed in the solid state for the anion constituting **1** is maintained in solution.

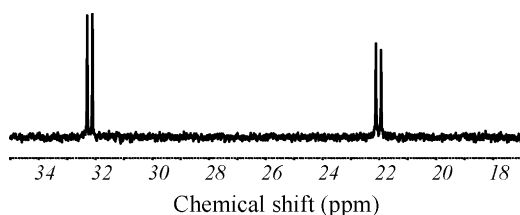


Fig. 2. ^{31}P NMR spectrum of a ca. 0.02 mol.L^{-1} solution of $(\text{CN}_3\text{H}_6)_6[(\text{Mo}^{\text{V}}_2\text{O}_4)_2(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_2] \cdot 12\text{H}_2\text{O}$ (**1**) in unbuffered $\text{H}_2\text{O}/\text{D}_2\text{O}$ (9:1).

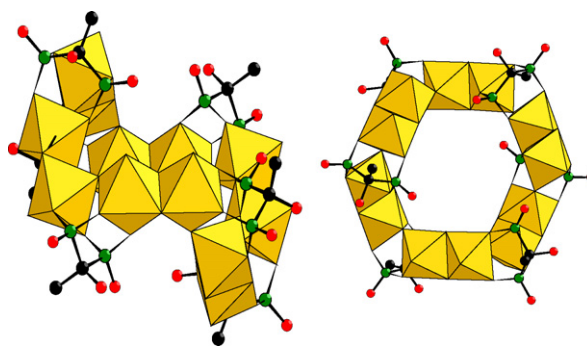


Fig. 3. Mixed ball-and-stick and polyhedral representations of the dodecanuclear $[(\text{Mo}^{\text{V}}_2\text{O}_4)_6(\text{OH})_6(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_6]^{18-}$ polyanion in **2**. The hydrogen atoms are omitted for clarity. Yellow octaedra, MoO_6 ; green spheres, P; black spheres, C; red spheres, O.

Compound **2** has been synthesized using a similar procedure to that described for compound **1**, but in this case the pH of the solution was adjusted to 7.3 with ammonia and no additional cationic species was added. Its structure (Fig. 3) is similar to that previously described for the $[(\text{Mo}^{\text{V}}_2\text{O}_4)_6(\text{OH})_6(\text{O}_3\text{P}(\text{CH}_2)\text{PO}_3)_6]^{18-}$ methylenediphosphonate complex that we recently reported [6]. It consists in six connected $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)\}$ units which form a cyclohexane-like ring in a chair conformation and where the tetracoordinated etidronate ligands (see Scheme 1b) are at the vertices and the edge-sharing metallic octahedra are at the edges, leading to a wheel with a pseudo S_6 symmetry. Bond valence summations indicate that six Mo^{V} bridging oxygen atoms are protonated [16]. Additionally, contrary to compound **1**, in **2** the hydroxo groups of the etidronate ligands are not deprotonated, explaining why the analogous methylenediphosphonate complex can be obtained. As previously found for this last compound, ^{31}P NMR studies indicate that **2** degrades rapidly in pure water into unknown products. Moreover, we have not been able to find an aqueous medium (1 M LiCl, 1 M NaCl...) where compound **2** can be stabilized.

Compound **3** was prepared by mixing sodium molybdate, etidronic acid, guanidinium chloride and hydrazine in 4 M $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer (pH = 4.9). After slow evaporation of the filtrate for one day, crystals of **3** were obtained. In **3**, seven $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)(\text{CH}_3\text{COO})\}$ units (Fig. 4a) are interconnected, forming a tetradecanuclear wheel (Fig. 4b) with an internal diameter of ca. 12 Å. In each dinuclear building unit, the oxygen atoms of the $\mu_{1,1}$ acetato ligand are located in axial position of the distorted $\{\text{Mo}^{\text{V}}\text{O}_6\}$ octahedra, in trans position of the terminal $\text{Mo}=\text{O}$ oxo groups. As in complex **2**, the hydroxo groups of the etidronate ligands are not deprotonated. It follows that in each $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)(\text{CH}_3\text{COO})\}$ building unit, the $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3]^{4-}$ groups are doubly coordinated to the $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ fragment (see Scheme 1b), the oxygen atoms of the etidronate ligand connected to the Mo^{V} center occupying two equatorial positions. The connection of seven building units affords an almost planar cyclic system. From a crystallographic point of view, a mirror plane passing through the phosphorous atoms of an

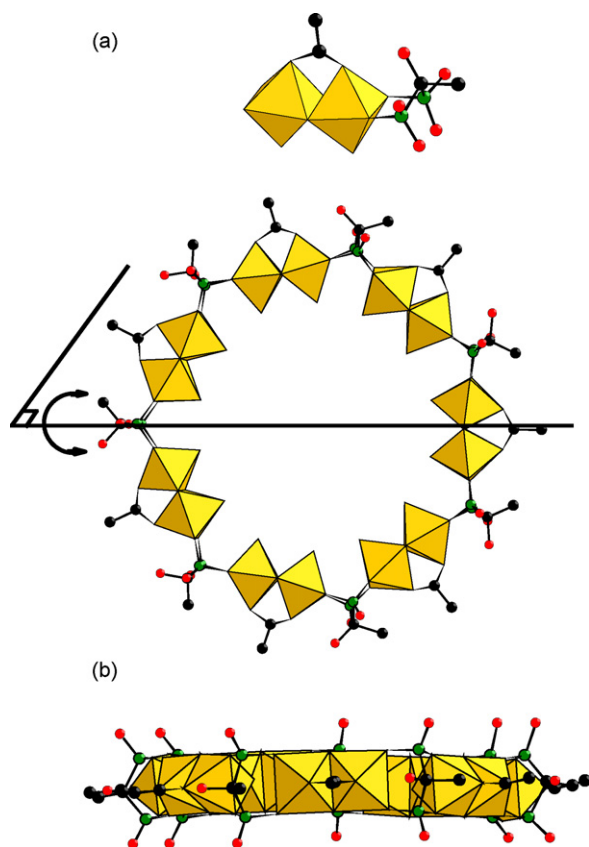


Fig. 4. (a) Mixed ball-and-stick and polyhedral representation of the $\{(\text{Mo}^{\text{V}}_2\text{O}_4)(\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3)(\text{CH}_3\text{COO})\}$ building units in **3**; (b) the tetradecanuclear $[(\text{Mo}^{\text{V}}_2\text{O}_4)_7(\text{O}_3\text{P}(\text{C}(\text{CH}_3)\text{O})\text{PO}_3)_7(\text{CH}_3\text{COO})_7]^{21-}$ polyanion in **3**, with the representation of the σ_v mirror plane. The double arrow indicates the two methyl and hydroxo groups disordered in **3**. The hydrogen atoms are omitted for clarity. Yellow octahedra, MoO₆; green spheres, P; black spheres, C; red spheres, O.

etidronate ligand and the carbon atoms of an acetate ligand (see Fig. 4b) is observed. The presence of this symmetry element induces a crystallographic disorder of the methyl and the hydroxo group of the etidronate ligand located on the mirror plane, these groups occupying two crystallographic sites with an occupancy factor of 0.5, respectively. It then follows that **3** exhibits only a C_s symmetry. The solution behaviour of this compound has also been studied. As for compound **2**, ³¹P NMR studies revealed that **3** degrades into unknown products in aqueous media.

4. Conclusion

We have shown here that it is possible to isolate Mo^V/etidronate cyclic systems of various shapes and nuclearities. Moreover, depending on the synthetic conditions, it appears that the hydroxo group of the $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3]^{4-}$ can either be deprotonated and then connect Mo^V centers (compound **1**) or remain protonated (compound **2** and **3**). The experimental factors governing the possible deprotonation of this ligand in presence of Mo^V cations have not been clearly elucidated, but it can be remarked that the deprotonation processes

cannot be attributed exclusively to the pH of the reacting medium. Indeed, **1** has been isolated at pH = 6.4 while **2** was obtained at pH = 7.4. The role of the counter-ions on the formation of the final product then seems crucial, as previously observed for the family of methylenediphosphonate POMs [8]. Obviously, when deprotonation occurs, systems that cannot be obtained using the methylenediphosphonate ligands are isolated, but it can be noticed that to date, surprisingly, no methylenediphosphonate Mo^V complex analogous to complex **3** has been isolated. Finally, to the best of our knowledge, complex **3** represents the homometallic Mo^V polyoxometalate cyclic system with the highest nuclearity reported to date. The next step is now to study the ability of these systems to form and stabilize metal nanoparticles. Additionally, the synthesis of analogous POM compounds containing functionalized diphosphonate ligand $[\text{O}_3\text{P}(\text{C}(\text{OH})\text{R})\text{PO}_3]^{4-}$ where R is an alkyl group bearing amino, phenolato, thiophene, etc. functional groups will be published soon. Finally, the reactivity of these diphosphonate ligands with Mo^{VI} cations must be studied [17].

5. Supplementary materials

The supplementary material has been sent to the Cambridge Crystallographic Structural Database, 12 Union Road, Cambridge, CB2 1EZ, UK, as supplementary material CCDC Nos. 734898, 734899 and 734900, for **1**, **2** and **3**, respectively, and can be obtained by contacting the CCDC, (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

6. Table of content

The reactivity of the $[\text{Mo}^{\text{V}}_2\text{O}_4]^{2+}$ dinuclear unit with the $[\text{O}_3\text{P}(\text{C}(\text{CH}_3)(\text{OH}))\text{PO}_3]^{4-}$ etidronate ligand has been investigated for the first time. Three complexes of nuclearities ranging from four to 14 have been isolated and characterized by IR spectroscopy, elemental analysis and single crystal X-Ray diffraction studies. Their stability in aqueous solution has been studied by ³¹P NMR.

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