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Aminobenzylphosphonate functionalized polyoxometalates

C.R. Mayer*, J. Marrot, F. Sécheresse

Institut Lavoisier, UMR CNRS 8637, Université de Versailles Saint Quentin, 45 Avenue des Etats-Unis, 78035 Versailles, France

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Abstract

The phosphonic acid $H_2O_3PCH_2C_6H_4(NH_3)_2$ has been obtained by acidic hydrolysis of the corresponding ester, and the functionalized $(NH_4)_2[Mo_5O_{21}(PCH_2C_6H_4NH_3)_2]$ (1) POM was prepared by reaction of the phosphonic acid with a solution of molybdate. (1) was characterized by IR, ³¹P NMR and single-crystal X-ray diffraction analysis. Five MoO₆ octahedra are linked by edges and corners to form the $\{Mo_5O_{21}\}$ ring from which two monoaminobenzylphosphonates are dangling. The phenyl groups of the organic branches orientate in the solid state to form $\pi - \pi$ stacking. The molecular structure is stable in dmso solution on the basis of ³¹P NMR. Similarly, $(NH_4)_2$ [Mo₅O₂₁(PCH₂C₆H₃(NH₃)₂)₂] **2** was obtained by reaction of diaminobenzylphosphonate with the $\{Mo_5O_{21}\}$ inorganic core. IR, ³¹P NMR spectra confirm the structure of **2** is identical to that of **1**.

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1. Introduction

Polyoxometalates (POMs) form an important family of metal-oxygen clusters studied for their structural variety and for their implication in catalysis, medicine, and materials science [1,2]. If the first POMs were reported from a long time, the development of single-crystal X-ray diffraction techniques together with the need of new architectures active in oxidation have boosted the research for novel POMs with different shapes and sizes.

The derivatization of polyoxoanions by grafting organic groups to the surface of metal-oxo frameworks is an old field that recently developed over different directions. One is related to pharmaceutical applications [3], the functionalized POM need to be water-soluble and stable at physiological pH, another is the synthesis of POM based materials. Many organic modified POMs have been reported and this field has been recently reviewed [4]. Aminoacids [5], phosphonates [6], phosphites [7] are the groups most frequently grafted on the surface of POMs. Very recently, $[Mo_5O_{21}]$ derivatives have been structurally characterized with covalently bound phosphonocarboxylates [8]. Here we report on the functionalization of the $[Mo_5O_{21}]$ core by aminophosphonates. The presence of a single terminal amino-group in **1** makes this compound a good candidate for the condensation with aromatic monoketones, e.g. diazafluoren-9-on while the presence of two terminal amino groups in **2** will permit the condensation with metal chelating diketones. Thus, these compounds are good precursors for the synthesis of extended structures with specific properties, luminescence (Ru-derivatives), magnetism (Fe-derivatives) and others.

2. Experimental

2.1. Materials and methods

All the chemicals used were purchased from commercial sources and used, unless otherwise specified, without further purification. Infrared spectra ($4000-200 \text{ cm}^{-1}$) were recorded on a Nicolet Magna-550 FTIR spectrometer using the technique of pressed KBr pellets. ³¹P NMR spectra were obtained at room temperature in 5 mm o.d. tubes on a Bruker AC 300 spectrometer equipped with a QNP probehead at the frequency of 121.5 MHz. Chemical shifts are given according to the IUPAC convention with respect to 85% H₃PO₄.

^{*} Corresponding author. Tel.: +33-1-39-25-43-97; fax: +33-1-39-25-43-81.

E-mail address: cmayer@chimie.uvsq.fr (C.R. Mayer).

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Fig. 1. Molecular structure of $(NH_4)_2[Mo_5O_{21}(PCH_2C_6H_4NH_3)_2]$ (1). The Mo_5O_{21} central core is represented by co-ordination polyhedra, the organic branches as ball-and-stick models.

2.2. Syntheses of $(NH_2)_2C_6H_3CH_2PO_3H_2$, and $NH_2C_6H_4CH_2PO_3H_2$

The synthesis of the precursor *ortho*-4,5-(NH₂)₂C₆H₃-CH₂PO₃Et₂ will be described elsewhere [9]. *Ortho*-4,5-(NH₂)₂C₆H₃CH₂PO₃Et₂ (1 g, 3.9 mmol) was dissolved in 12 M HCl (30 ml) and the resulting acidic solution was stirred at reflux for 3 h. Then, the expected 2HCl-(NH₂)₂-C₆H₃CH₂PO₃H₂ phosphonic acid was recovered after evaporation of the solution under vacuum (EtOH is formed and eliminated) and triturating the solid with acetonitrile and ether. Yield: 0.85 g (79%). ³¹P NMR (121.5 MHz, DMSO-d6, H₃PO₄): δ =26.3 ppm. For HCl-NH₂C₆H₄-CH₂PO₃H₂, the experimental procedure was similar except that the starting material was NH₂C₆H₄CH₂PO₃Et₂ (1 g, 4.1 mmol) instead of *ortho*-4,5-(NH₂)₂C₆H₃CH₂PO₃Et₂. Yield: 0.90 g (98%). ³¹P NMR (121.5 MHz, DMSO-d6, H₃PO₄): δ =21.2 ppm.

2.3. Synthesis of $(NH_4)_2[Mo_5O_{21}(PCH_2C_6H_4NH_3)_2]$ ($(NH_4)_2$ -1)

After Na₂MoO₄·2H₂O (1.21 g, 5 mmol) and HCl–NH₂-C₆H₄CH₂PO₃H₂ (0.38 g, 2 mmol) were dissolved in 70 ml H₂O, HCl (2 ml, 3 M) was added drop wise while the mixture was stirred for 30 min at reflux. Then, NH₄Cl (0.22 g in 2 ml) was added and the solution was stirred for 15 min. A colorless crystalline solid was obtained after the mother solution was kept at room temperature overnight. Yield: 1.05 g (86%). {¹H}-³¹P NMR (121.5 MHz, DMSO-d6, H₃PO₄): $\delta = 23.0$ ppm, (²J_{PH} = 18 Hz, t). IR (KBr): $\tilde{\nu} = 1149$ (w), 1100 (s), 1046 (s), 976 (s), 911 (vs), 687 (vs) cm⁻¹.

2.4. Synthesis of $[Mo_5O_{21}(PCH_2C_6H_3(NH_3)_2)_2]$ (2)

After dissolution of a mixture of $Na_2MoO_4 \cdot 2H_2O$ (1.21 g, 5 mmol) and $2HCl-(NH_2)_2C_6H_3CH_2PO_3H_2$ (0.41 g, 2 mmol) in 70 ml H₂O, HCl (2 ml, 3 M) was added dropwise and the mixture was stirred over 30 min at reflux. A brown crystalline powder was obtained after the mother solution was maintained at room temperature for several hours. Yield: 0.8 g (66%). ${}^{1}H{}^{-31}P$ NMR (121.5 MHz, DMSO-d6, H₃PO₄): $\delta = 28.0$ ppm, (${}^{2}J_{PH} = 19$ Hz, t). IR (KBr): $\tilde{\nu} = 1145$, 1095 (s), 1041 (s), 981 (s), 927 (vs), 905 (vs), 683 (vs) cm⁻¹.

2.5. Single crystal X-ray diffraction

Single crystal X-ray data for **1** (NH₄)₂[Mo₅O₁₅{(O₃-PCH₂C₆H₄NH₃)₂] were collected at 293 K on a SMART CCD diffractometer using Mo K α radiation (0.71073 Å). The structure was solved by direct methods SHELX-TL [10]. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program [11] based on the method of Blessing [12]. Crystal data: orthorhombic, space group *Pbcn* (no 60), a = 19.4598(5) Å, b = 9.8265(2) Å, c = 16.8835(2) Å, V = 3228.49(11) Å³, Z = 4, $\rho_{calc} = 2.395$ g cm⁻³. The structure, refined on F^2 , converged for 4399 unique reflections and 228 parameters to give R1 = 0.0534

 Table 1

 Selected bond lengths [Å] for 1

Mo(1)-O(1)	1.705(5)
Mo(1)-O(2)	1.714(5)
Mo(1)-O(3)	1.9033(18)
Mo(1)-O(4)	1.973(4)
Mo(1)-O(5)	2.286(5)
Mo(1)-O(6)	2.346(4)
Mo(2)-O(7)	1.679(6)
Mo(2)-O(8)	1.713(5)
Mo(2)-O(9)	1.919(5)
Mo(2)-O(4)	1.964(4)
Mo(2)-O(6)	2.195(4)
Mo(2)-O(10)	2.389(5)
Mo(3)-O(11)	1.712(6)
Mo(3)-O(9)	1.924(5)
Mo(3)-O(10)	2.311(5)
P(1)-O(5)	1.503(5)
P(1)-O(10)	1.536(5)
P(1)-O(6)	1.556(4)

Symmetry transformations used to generate equivalent atoms: #1 - x, y, -z + 3/2 #2 - x + 1, -y, -z.



Fig. 2. View of the packing of $(NH_4)_2[Mo_5O_{21}(PCH_2C_6H_4NH_3)_2]$ showing the $\pi-\pi$ stacking of the phenyl groups.

and wR2 = 0.1082. Hydrogen atoms have been stereochemically placed using constraints (C–H, 0.93 Å, N–H, 0.89 Å). Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, on quoting the deposit number CCDC 223192. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Molecular structure

The complete structure of $(NH_4)_2$ -1 is formed of isolated $[Mo_5O_{15}\{(O_3PCH_2C_6H_4NH_3)_2\}]^{2-}$ anions and two NH_4^+ cations. The molecular structure of $(NH_4)_2[Mo_5O_{15}\{(O_3PCH_2C_6H_4NH_3)_2\}]$ is represented in Fig. 1. The inorganic core of $[Mo_5O_{15}\{(O_3PCH_2C_6H_4NH_3)_2\}]^{2-}$ consists of a ring of five distorted MoO₆ octahedra linked through four edge-sharing and one corner-sharing junctions. Three types of Mo–O distances are observed within the inorganic ring, short terminal Mo=O bonds (1.679–1.714 Å), long terminal bonds trans to the Mo=O groups (2.195–2.389 Å) and Mo–O–Mo bridges (1.919–1.973 Å), see Table 1. The $\{Mo_5O_{21}\}$ core was first observed in molybdophosphates [7] and more recently in molybdophosphonotes [6,7], in peptides [5] and very recently in molybdophosphono-carboxylates [8].

In 1, two pending aminobenzylphosphonate ligands are attached on opposite sides of the ring by the two PO_3 groups. The terminal amino group of each branch is unambiguously protonated. The two organic branches are oriented in almost perpendicular directions relative to

the Mo₅-ring. These orientations are probably imposed by the strong $\pi - \pi$ interactions that exist between the phenyl rings of adjacent polyoxoanions as revealed by the stacking in the solid state, see Fig. 2. This orientation is possible by the free rotation of the organic chains around the two PO₃ tripods anchored to the Mo₅ inorganic ring. Each polyanion is balanced in the lattice by two ammonium cations.

3.2. Lattice arrangement

Within an isolated anion, the two organic branches decorating the inorganic rings are antiparallel. In a branch, the terminal NH_3 group interacts via hydrogen bonds with three oxygen atoms of the closest inorganic ring of a neighbouring anion as represented in Fig. 3. The related



Fig. 3. View of the packing of $(NH_4)_2[Mo_5O_{21}(PCH_2C_6H_4NH_3)_2]$ illustrating the hydrogen bonding scheme.

Table 2 Hydrogen bonds **1** [Å and deg.]

D–H···A	d(D-H)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	$d(\mathbf{D} \cdot \cdot \cdot \mathbf{A})$	<(DHA)
$N(1) - H(1C) \cdots O(11) #3$	0.89	1.96	2.847(10)	174.7
N(1)−H(1D)···O(7)#4	0.89	2.28	2.797(9)	116.9
$N(1)-H(1E)\cdots O(5)#6$	0.89	2.18	3.014(10)	156.3

Symmetry transformations used to generate equivalent atoms: #1 -x,y, -z + 3/2 #2 - x + 1, -y, -z #3 x + 1/2,y + 1/2, -z + 3/2 #4 -x + 1/2, -y + 3/2,z - 1/2 #5 - x + 1,y + 1, -z + 1/2 #6 x + 1/2,y - 1/2,z.



Fig. 4. ${}^{1}H{}^{-31}P$ NMR of $[Mo_5O_{21}(PCH_2C_6H_3(NH_3)_2)_2]$ (2).



Fig. 5. IR spectra of $(NH_4)_2[Mo_5O_{21}(PCH_2C_6H_4NH_3)_2]$ (1) (upper) and of $[Mo_5O_{21}(PCH_2C_6H_3(NH_3)_2)_2]$ (2) (lower).

N-H···O distances are given in Table 2. This hydrogenbonding scheme probably reinforces the orientation of the phenyl rings engaged in $\pi - \pi$ stacking.

3.3. Spectroscopies

The solid state structures of **1** and **2** are maintained in dmso solution as confirmed by ³¹P-NMR spectra carried out on solutions of re-dissolved solids. Triplets with a chemical shift of 23 ppm (${}^{2}J_{\text{PH}} = 18$) for **1** and 28 ppm for **2** are

observed as only features, illustrating the stability of 1 and 2 in DMSO, see Fig. 4. These chemical shifts are quite comparable to the value $\delta = 22$ ppm observed for the related molybdophosphonocarboxylates [8].

IR spectra of **1** and **2** are similar and clearly reflect the coordination of the organic chains to the central $\{Mo_5O_{21}\}$ group, see Fig. 5. The bands located about 1000 cm⁻¹ are characteristic of the PO₃ group and are very sensitive to symmetry. Thus, they represent a very good probe for the mode of bonding of this group with the polyoxometalate core, the three bands observed in this region for **1** and **2** are in agreement with a local *C*3*v* symmetry. The bands at 980, 920 and 905 cm⁻¹ are unambiguously attributed to Mo=O groups while the band at 680 cm⁻¹ corresponds to Mo-O bridges [6].

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