

tert-Butylammonium phosphomolybdates. Synthesis, crystal structure, thermal behaviour and electrochemical properties

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Abstract—Two *tert*-butylammonium phosphopolymolybdates(VI) with the formulae $[(\text{CH}_3)_3\text{CNH}_3]_3[\text{PMo}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O}$ (**1**) and $[(\text{CH}_3)_3\text{CNH}_3]_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \cdot 6\text{H}_2\text{O}$ (**2**) have been synthesized and characterized chemically by means of FT-IR spectroscopy, microanalyses and thermal analyses. The crystal structure of compound **2** has been determined from single-crystal X-ray diffraction data. The structural analysis reveals that the asymmetric unit is composed of one heteropolyanion, $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$, six *tert*-butylammonium cations and six water molecules. The heteropolyanions are disposed in rows parallel to the $[1\bar{1}1]$ direction. The thermal behaviour of both compounds under an atmosphere of air and under an inert atmosphere of argon have been studied. Thermal decomposition of both compounds under oxidant atmosphere starts with the loss of the water molecules, yielding the anhydrous salt of the corresponding phosphopolymolybdate anion which is stable up to 215°C. The decomposition of the anhydrous salt takes place in several exothermic steps finishing at 510°C for compound **1** and at 575°C for compound **2** in a residue that was identified as a mixture of MoO_3 and P_2O_5 . On the other hand, an electrochemical study for both compounds using cyclic voltammetry was carried out, showing reversible cathodic redox processes. © 1997 Elsevier Science Ltd

Keywords: phosphododecamolybdate; diphosphooctadecamolybdate; *tert*-butylammonium cation; crystal structure.

Heteropolyanions with the general formula $[\text{X}_x\text{M}_m\text{O}_y]^{q-}$ ($\text{M} = \text{W}, \text{Mo}, \text{Nb}, \text{V}, \text{etc.}; \text{X} = \text{Si}, \text{P}, \text{S}, \text{B}, \text{Co}, \text{Fe}, \text{Cu}, \text{etc.}$) have been known for well over a century and constitute a large fundamental class of inorganic compounds that in recent years have aroused increasing interest because of their relevance to several disciplines due to their topological and electronic versatilities [1,2]. Important applications are generally attributed to their very high stability at very low concentrations over wide pH ranges, their electron transfer and electron sink properties, the intense colour of reduced forms and their large size.

In medical chemistry, useful properties demonstrated so far include highly selective enzyme inhibition [3–5], antitumoral activity [6] and anti-viral activity against HIV [3,7,8]. In analytical chemistry, polyoxometallates have been used for many years for the detection and/or separation of many elements,

often exploiting their ease of reduction and the formation of the highly colored species formed upon reduction. Heteropolyanions are widely used as oxidative catalysts and, for example, have been used to convert aldehydes to their corresponding carboxylic acids and for the formation of $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds through dehydrogenation of aldehydes, alcohols and carboxylic acids [2].

In spite of the vast number of known polyoxoanions, the number of different structural types is relatively low. Most of them present discrete cluster like structures viewed as molecular fragments of metal oxides formed by closed and highly symmetrical networks of MO_x polyhedra (usually octahedra and tetrahedra) sharing corners, edges or faces.

The $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anion (PMo_{12}) is formed for a $\text{Mo}:\text{P}$ ratio and acid pH[9]. The structure of the phosphododecamolybdic acid with different hydration degrees has been described, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot (29-31)\text{H}_2\text{O}$ [10], $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot 30\text{H}_2\text{O}$ [11] and

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$\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \cdot (13-14)\text{H}_2\text{O}$ [12]. The heteropoly-molybdate $[\text{X}_2\text{Mo}_{18}\text{O}_{62}]^{n-}$ (X_2Mo_{18}) is formed for the systems in which the XMo_{12} type is not very stable ($\text{X} = \text{P}, \text{As}, \text{S}$), while in the systems with very stable XMo_{12} species ($\text{X} = \text{Si}, \text{Ge}$) the X_2Mo_{18} type is not formed [13]. The crystalline structures of the salts $\text{Na}_6\text{P}_2\text{Mo}_{18}\text{O}_{62} \cdot 24\text{H}_2\text{O}$ [14] and $\text{Na}_4\text{H}_2\text{P}_2\text{Mo}_{18}\text{O}_{62} \cdot 20\text{H}_2\text{O}$ [15] have been solved.

As a part of a study on polyoxometallates we have isolated two compounds of formulae $[(\text{CH}_3)_3\text{CNH}_3]_3[\text{PMo}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O}$ (**1**) and $[(\text{CH}_3)_3\text{CNH}_3]_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \cdot 6\text{H}_2\text{O}$ (**2**). This paper describes the synthesis, chemical characterization, thermal behavior and cyclic voltammetry data for both compounds as well as the crystal structure of compound **2**.

EXPERIMENTAL

General and instrumental

All chemicals were procured commercially and used without subsequent purification. Microanalyses of carbon, nitrogen and hydrogen were performed on a Perkin-Elmer 240 C, H, N-analyser and phosphorus and molybdenum were determined thermogravimetrically as $\text{P}_2\text{O}_5 + \text{MoO}_3$ after thermal decomposition of the samples in an argon-oxygen atmosphere.

The densities were measured by flotation in $\text{CHBr}_3/\text{CCl}_4$. IR spectra were recorded in the 4000–400 cm^{-1} range on a Nicolet 740 FT-IR and the solid compounds were mixed with potassium bromide (Fluka, FT-IR spectroscopy grade) into transparent disks. A Setaram TAG 24S 16 thermobalance was used to obtain simultaneously the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) curves in a synthetic air atmosphere and in an inert atmosphere of argon with a heating rate of 5°C min^{-1} .

The electrochemical study was carried on by means of cyclic voltammetry in a polarograph PAR 174A coupled to a register X-Y Houston 2000. The cell of measurement consists of three electrodes: $\text{Ag}/\text{AgCl}(\text{s})/\text{KCl}$ as reference electrode, a Pt wire as auxiliary electrode and an electrode of glassy C METROHM (diameter = 3 mm) as working electrode. KCl (1 M) was used as electrolyte and the concentration of the electroactive species was of the order 10^{-3} M. All the solutions were deoxygenated by passing through a current of nitrogen before the measurement. The potential scan was carried out at a speed of 20 mV s^{-1} in the range from 1.0 to -2.0 V.

Synthesis of compounds

Tris(tert-butylammonium)phosphododecamolybdate(VI) dihydrate, $[(\text{CH}_3)_3\text{CNH}_3]_3[\text{PMo}_{12}\text{O}_{40}] \cdot 2\text{H}_2\text{O}$ (**1**). An aqueous suspension (90 cm^3) of anhydrous MoO_3 (5.81 g, 40 mmol) and *tert*-butylamine (2.0 cm^3 ,

19 mmol) was heated under reflux for 90 min, yielding a colorless solution of pH = 3. Na_2HPO_4 (0.49 g, 3.4 mmol) dissolved in 5 cm^3 of distilled water was then added and the color of the solution changed from colorless to light yellow. Then, *tert*-butylammonium chloride (2.08 g, 19 mmol) was added and the solution acidified with hydrochloric acid (1 mol dm^{-3}) up to pH = 1, causing the precipitation of a yellow powder of tris(*tert*-butylammonium)phosphododecamolybdate dihydrate. This compound is insoluble in water, but dissolves in DMF and mixtures of $\text{H}_2\text{O}/\text{DMF}$. Found: C, 6.9; H, 1.9; N, 2.0; Mo/P ($\text{MoO}_3 + \text{P}_2\text{O}_5$) 84.8. Calc. for $\text{C}_{12}\text{H}_{40}\text{Mo}_{12}\text{N}_3\text{O}_{42}\text{P}$: C, 6.9; H, 1.9; N, 2.0; Mo/P ($\text{MoO}_3 + \text{P}_2\text{O}_5$) 86.4%.

Hexakis(tert-butylammonium)diphosphooctadecamolybdate(VI) hexahydrate, $[(\text{CH}_3)_3\text{CNH}_3]_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \cdot 6\text{H}_2\text{O}$ (**2**). This compound can be prepared by two methods:

(a) A solution (50 cm^3) of sodium molybdate dihydrate (0.91 g, 4.5 mmol) and sodium hydrogen phosphate (0.07 g, 4.8 mmol) was prepared and acidified with hydrochloric acid (1 mol dm^{-3}) up to pH = 1. On the other hand, an aqueous solution (50 cm^3) of *tert*-butylamine (0.5 cm^3 , 4.7 mmol) was also acidified with hydrochloric acid up to the same pH value. Both solutions are mixed and a layer of diethylene ether is added. Four months later prismatic yellow crystals of compound **2** were collected, mixed with a yellow powder that was characterized by means of IR, microanalyses and thermogravimetric techniques as the tris(*tert*-butylammonium)phosphododecamolybdate dihydrate, compound **1**.

(b) Na_2HPO_4 (0.36 g, 2.77 mmol) was dissolved in HClO_4 (3.65 cm^3 of acid in 1 cm^3 of distilled water). On the other hand, an aqueous solution (10 cm^3) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (5.43 g, 22.5 mmol) was prepared. The molybdate solution was added dropwise over the hydrogen phosphate solution. A yellow precipitate appeared that was dissolved after addition of more water. Then a solution of *tert*-butylammonium chloride (0.43 g, 4.0 mmol) in 3 cm^3 of distilled water was added dropwise. The solution was filtered to eliminate any residues yielding a lemon yellow solution of pH = 3. Two weeks later yellow crystals of the compound hexakis(*tert*-butylammonium)diphosphooctadecamolybdate hexahydrate were collected. The crystals were found to be stable to air and light, but the colour changed to green after X-ray exposure. Found: C, 8.6; H, 2.5; N, 2.5; Mo/P ($\text{MoO}_3 + \text{P}_2\text{O}_5$), 82.3. Calc. for $\text{C}_{24}\text{H}_{84}\text{Mo}_{18}\text{N}_6\text{O}_{68}\text{P}_2$: C, 8.6; H, 2.5; N, 2.5; Mo/P ($\text{MoO}_3 + \text{P}_2\text{O}_5$), 82.0%.

X-ray diffraction

Single crystals of compound **2** were obtained as described above. Table 1 summarizes crystal data and data collection procedures for this compound. The structure was solved from a model by means of the program DIRDIF [16] and was completed from suc-

Table 1. Crystallographic data for compound 2

Formula	(C ₄ H ₁₂ N) ₆ [P ₂ Mo ₁₈ O ₆₂] · 6H ₂ O
M _r	3333.8
System	Triclinic
Space group	P $\bar{1}$ (no. 2)
a (Å)	12.836(4)
b (Å)	13.875(3)
c (Å)	27.144(3)
α (°)	87.41(3)
β (°)	83.42(3)
γ (°)	65.09(3)
V (Å ³)	4355(2)
Z	2
F(000)	3200
D ₀ (Mg m ⁻³)	2.53(1)
D _x	2.541
μ [Mo-K α] (cm ⁻¹)	25.79
Form	Prism
Dimensions (mm)	0.26 × 0.36 × 0.68
Colour	Yellow-orange
Diffractometer	Enraf-Nonius CAD4
Temperature (K)	295(1)
Radiation (Å)	0.71069
Monochromator	Oriented graphite
Scan mode	$\omega/2\theta$
θ range	1–25
h k l	0 → 15; -16 → 16; -32 → 32
Controls	Intensity and orientation
—Reflexions	34 $\bar{1}$ 3; 56 $\bar{8}$
—Periodicity	7200 s; 100 reflexions
Independent reflexions	15,311
Observed reflexions	11,684 [$I \geq 3\sigma(I)$]
No. of variables	1048
$\Delta\rho$ (e Å ⁻³)	1.85 (1.3 Å del Mo(11))
Absorption correction	DIFABS; T _{min} = 0.723, T _{max} = 1.628
R	0.073
R _w	0.086

cessive Fourier maps. An empirical absorption correction (DIFABS) [17] was applied when all the non-hydrogen atoms had been located.

The crystal structure was then refined with anisotropic thermal parameters for all the non-hydrogen atoms, except for the anionic oxygen atoms O(9), O(14) and O(29), by full-matrix least-squares analysis. A weighting scheme of the type $1/\sigma$ was used. The hydrogen atoms were generated at geometrically fixed positions. Most calculations were carried out using the XRAY 76 [18] system running on a Micro VAXII computer.

RESULTS AND DISCUSSION

Thermal analyses

Compound 1 was dihydrated and compound 2 hexahydrated. Table 2 lists steps, initial and final temperature (°C), partial and total weight loss, enthalpy (endothermic or exothermic) and the maximum peak

Table 2. Steps, initial and final temperature (°C), partial and total weight loss, enthalpy (endothermic or exothermic) and maximum peak for each step in the thermal decomposition of compounds 1 and 2 under a synthetic air atmosphere

Step	T _i –T _f	T _m	ΔH	% Δm
Compound 1				
1	35–100	60	Endo	1.70
2	215–285	260	Exo	3.85
3 ^a	285–510	285	Exo	9.60
			$\Sigma\% \Delta m$	15.15
			Calc.	13.58
Compound 2				
1	50–105	100	Endo	1.44
2	105–140	120	Endo	1.18
3	140–180	140	Endo	0.45
4	215–295	250	Exo	5.15
5 ^b	295–345			1.39
6	345–410	395	Exo	3.17
7	410–460	425	Exo	2.39
8	460–575	530	Exo	1.97
			$\Sigma\% \Delta m$	17.14
			Calc.	18.00

^a Overlapping steps.

^b Progressive weight loss without clear peaks in the DTG or DTA curves.

for each step in the thermal decomposition of both compounds in a synthetic air atmosphere.

Thermal decomposition of both compounds starts with the loss of the water molecules. The dehydration of compound 1 takes place in only one step, yielding the anhydrous salt of the phosphododecamolybdate anion which is stable up to 215°C. This high thermal stability of the anhydrous compound is also observed in the study of the thermal decomposition of the compounds tris(hexylammonium)phosphododecamolybdate dihydrate, diethylenetriammoniumphosphododecamolybdate tetrahydrate and tris(4-aminopyridinium)phosphododecamolybdate dihydrate [19], with the anhydrous salt from compound 1 being the least stable of all of them. The decomposition of the anhydrous salt takes place in several exothermic steps finishing at 510°C. The final residue has been identified by powder X-ray diffraction as a mixture of MoO₃ (ASTM 5-0508) and P₂O₅ (ASTM 5-0488).

Compound 2 loses its water molecules in three overlapping endothermic steps (45–105, 105–140 and 140–180°C) that correspond to the loss of three, two and one molecule. The anhydrous compound is then stable up to 215°C. Then, several exothermic steps without intermediate compounds take place and the decomposition process finishes at 575°C, yielding a stable residue which was identified as a mixture of MoO₃ (ASTM 5-0508) and P₂O₅ (ASTM 5-0488).

Figure 1 shows the TG, DTG and DTA curves corresponding to the thermal decomposition in synthetic air atmosphere of compounds 1 and 2.

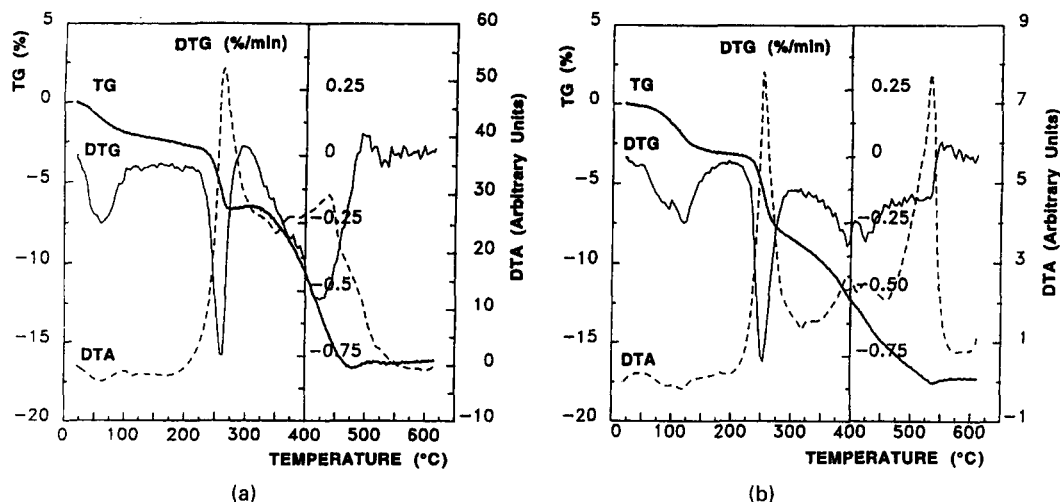


Fig. 1. Thermal decomposition in an oxidant atmosphere of (a) compound **1** and (b) compound **2**.

On the other hand, the study of the thermal decomposition in an inert atmosphere of argon for both compounds has also been done. Table 3 summarizes the thermogravimetric data in argon atmosphere for compounds **1** and **2**, respectively.

Compound **1** is slightly more stable in argon atmosphere than in an oxidant atmosphere. The dehydration process takes place at higher temperatures (50–90°C) and passes through the monohydrate compound which is stable up to 125°C. The process finishes at 600°C after three more endothermic steps and a progressive mass loss without stable intermediate products. The presence of Mo^V in the black final residue has been confirmed by means of EPR.

Table 3. Steps, initial and final temperature (°C), partial and total weight loss, enthalpy (endothermic or exothermic) and maximum peak for each step in the thermal decomposition of compounds **1** and **2** under an argon atmosphere

Step	T_i-T_f	T_m	ΔH	% Δm
Compound 1				
1	50–90	80	Endo	0.83
2	125–200	165	Endo	0.80
3	200–230	225	Endo	0.50
4	230–270	260	Endo	5.30
5 ^a	270–600			12.90
			$\Sigma\% \Delta m$	20.33
Compound 2				
1	35–100	95	Endo	1.57
2	100–140	115	Endo	1.19
3	140–180	145	Endo	0.60
4	215–255	250	Endo	4.40
5	255–305	265	Endo	5.39
6 ^a	305–600			9.35
			$\Sigma\% \Delta m$	22.50

^a Progressive weight loss without clear peaks in the DTG or DTA curves.

The thermal decomposition of compound **2** in an argon atmosphere begins with the loss of the six water molecules in the same way as in an oxidant atmosphere, yielding the anhydrous salt that is stable up to 40°C. Then two overlapping endothermic steps (215–255 and 255–305°C) take place followed by a progressive weight loss finishing the process at 600°C. The presence of Mo^V in the residue was confirmed by means of EPR spectroscopy. Figure 2 shows the TG, DTG and DTA curves for compounds **1** and **2** in an argon atmosphere.

IR spectroscopy

The IR spectra, with the corresponding assignation, for the phosphododecamolybdate(VI) and diphosphooctadecamolybdate(VI) anions are shown in Fig. 3.

Crystal structure of $[(\text{CH}_3)_3\text{CNH}_3]_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \cdot 6\text{H}_2\text{O}$ (**2**)

The structural analysis reveals that the asymmetric unit of compound **2** is composed of one heteropolyanion, $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$, six *tert*-butylammonium cations and six water molecules. The diphosphooctadecamolybdate anion also called the Dawson anion can be described as the result of the joining of two trivacant units, $[\text{PMo}_9\text{O}_{34}]^{9-}$, which result from the elimination of three octahedra from the Keggin structure, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. Figure 4 shows an ORTEP of this anion with the molybdenum atom numbering scheme used.

The bond distances Mo—O and P—O for compound **2** are listed in Table 4. The MoO₆ octahedra can be classified in two groups, type I [Mo(1)–(3) and Mo(16)–(18)] and type II [Mo(4)–(15)], each of these types shows a particular distribution of the distances Mo—O: (a) Octahedra type I that present two short

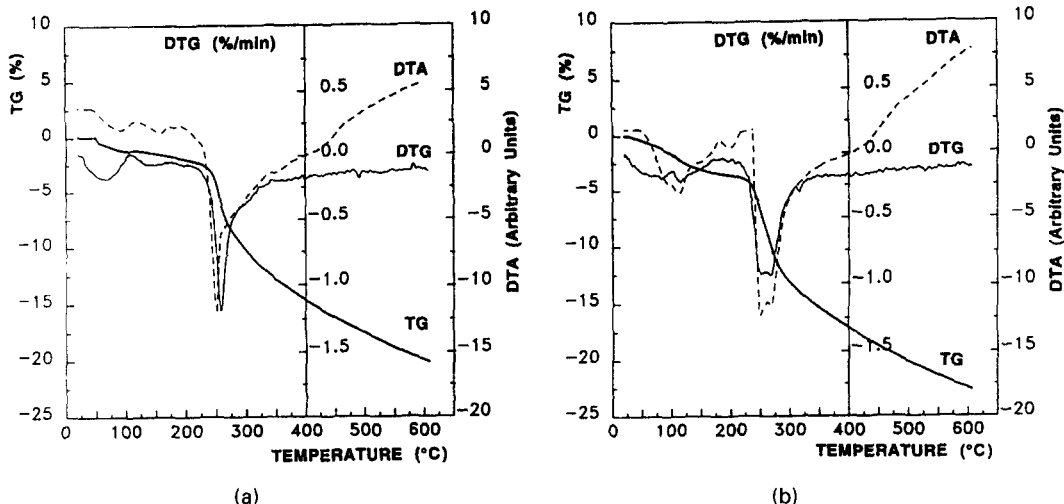


Fig. 2. Thermal decomposition in an inert atmosphere of (a) compound 1 and (b) compound 2.

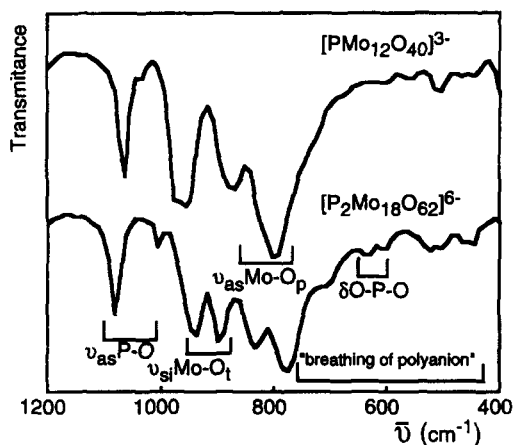


Fig. 3. IR spectra for both anions.

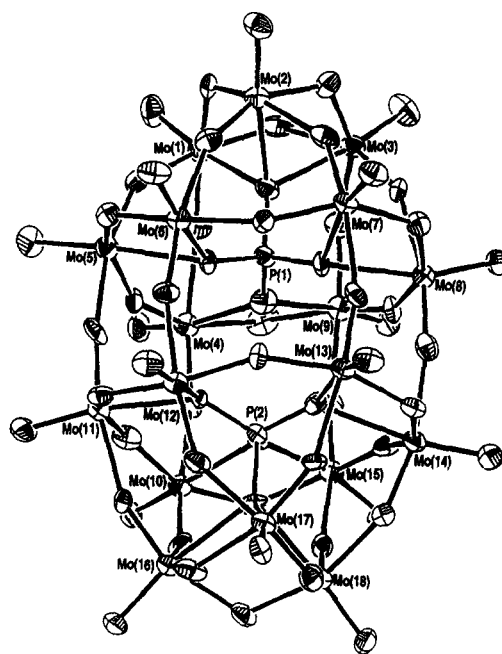


Fig. 4. ORTEP view of the Dawson anion in compound 2.

distances (1.70–1.80 Å); a medium one (~1.85–1.90 Å); two long ones (~2.05–2.10 Å) and a very long one (~2.40–2.45 Å). (b) Octahedra type II that have two short distances (~1.70–1.80 Å); two medium ones (~1.90–2.00 Å); a long one (~2.10–2.20 Å) and a very long one (~2.35–2.40 Å).

The anion α -[P₂Mo₁₈O₆₂]⁶⁻ does not have crystallographic symmetry, but it is close to the D_{3h} ideal point symmetry. The equation of the line that joins the two phosphorous atoms, corresponding to the ideal three-fold axis, as well as the equation of the horizontal plane delimited by the oxygen atoms from the equatorial level, O(34), O(35), O(36), O(37), O(38) and O(349), which belong to both PMo₆ units, have been calculated. It is observed that the atoms P(1) and P(2) are located at 2.082(4) and 2.095(4) Å from the plane, respectively.

The polyanions are disposed in rows, with P—P axis almost parallel to the [111] direction, being joined

by means of hydrogen contacts through cation 4 and the water molecule O(64)w (Fig. 5). The remaining cations and water molecules, located between the rows of polyanions, connect polyanions belonging to different rows by hydrogen contacts of the types N—H···O (2.86–3.12 Å), N—H···Ow (2.83–3.11 Å), Ow—H···O (2.96–3.59 Å), Ow—H···Ow (2.75–2.96 Å) and C—H···O (3.18–3.46 Å) [20] (Table 5).

The water molecules O(65)w, O(66)w and O(67)w are joined by hydrogen contacts among them, then being possible that these three molecules were lost in the same step of the thermal decomposition.

Table 4. Bond Lengths Mo—O and P—O (Å) for compound **2**

	Mo(1)		Mo(2)		Mo(3)		Mo(4)
O(1)	1.70(1)	O(2)	1.72(2)	O(3)	1.73(1)	O(4)	1.70(2)
O(19)	2.06(2)	O(19)	1.84(1)	O(20)	1.87(2)	O(22)	2.16(1)
O(21)	1.89(1)	O(20)	2.06(1)	O(21)	2.06(1)	O(28)	1.91(1)
O(22)	1.77(2)	O(24)	1.80(1)	O(26)	1.76(1)	O(33)	1.98(1)
O(23)	2.10(1)	O(25)	2.08(1)	O(27)	2.05(2)	O(35)	1.77(1)
O(55)	2.43(1)	O(55)	2.39(1)	O(55)	2.44(1)	O(56)	2.39(1)
	Mo(5)		Mo(6)		Mo(7)		Mo(8)
O(5)	1.73(1)	O(6)	1.70(2)	O(7)	1.70(2)	O(8)	1.74(1)
O(23)	1.82(1)	O(24)	2.18(1)	O(25)	1.80(1)	O(26)	2.20(1)
O(28)	1.92(1)	O(29)	1.95(1)	O(30)	1.93(1)	O(31)	1.95(2)
O(29)	1.90(2)	O(30)	1.94(1)	O(31)	1.91(1)	O(32)	1.91(1)
O(34)	2.13(1)	O(36)	1.75(1)	O(37)	2.16(1)	O(38)	1.76(1)
O(57)	2.42(1)	O(57)	2.35(1)	O(58)	2.35(2)	O(58)	2.39(1)
	Mo(9)		Mo(10)		Mo(11)		Mo(12)
O(9)	1.73(1)	O(10)	1.70(1)	O(11)	1.71(1)	O(12)	1.73(2)
O(27)	1.81(1)	O(35)	2.12(1)	O(34)	1.77(1)	O(36)	2.15(1)
O(32)	1.89(1)	O(40)	1.94(1)	O(40)	1.89(2)	O(41)	1.93(1)
O(33)	1.96(1)	O(45)	1.89(1)	O(41)	1.96(2)	O(42)	1.94(1)
O(39)	2.12(1)	O(46)	1.82(1)	O(47)	2.18(1)	O(48)	1.81(1)
O(56)	2.39(1)	O(60)	2.38(1)	O(61)	2.35(1)	O(61)	2.37(1)
	Mo(13)		Mo(14)		Mo(15)		Mo(16)
O(13)	1.72(2)	O(14)	1.75(1)	O(15)	1.71(1)	O(16)	1.74(1)
O(37)	1.77(1)	O(38)	2.14(1)	O(39)	1.76(1)	O(46)	2.05(1)
O(42)	1.95(1)	O(43)	1.91(2)	O(44)	1.90(1)	O(47)	1.76(1)
O(43)	1.96(1)	O(44)	1.90(2)	O(45)	2.01(1)	O(52)	1.85(2)
O(49)	2.16(1)	O(50)	1.81(1)	O(51)	2.19(1)	O(54)	2.09(1)
O(62)	2.34(1)	O(62)	2.41(1)	O(60)	2.36(1)	O(59)	2.41(1)
	Mo(17)		Mo(18)		P(1)		P(2)
O(17)	1.68(1)	O(18)	1.70(1)	O(55)	1.59(1)	O(59)	1.59(1)
O(48)	2.05(1)	O(50)	2.06(1)	O(56)	1.52(2)	O(60)	1.55(2)
O(49)	1.78(1)	O(51)	1.78(1)	O(57)	1.54(1)	O(61)	1.59(1)
O(52)	2.08(1)	O(53)	2.06(2)	O(58)	1.54(1)	O(62)	1.55(1)
O(53)	1.85(1)	O(54)	1.88(1)				
O(59)	2.41(1)	O(59)	2.40(1)				

Electrochemical studies

Table 6 summarizes the cathodic and anionic peak potentials (mV) as well as the difference potential for both compounds. Figure 6(a) shows the CV for compound **1** carried out at a sensitivity of 20 μA . If the measurement is carried out at a sensitivity of 100 μA it is seen that besides the former processes, that now are observed like shoulders, there are two more cathodic processes, a shoulder at -1100 mV and a peak at -1300 mV. The corresponding anionic processes appear at -780 (shoulder) and at -1120 mV (shoulder), Fig. 6(b).

On the other hand, the electrochemical reduction of compound **2** takes place in two reversible processes. The values of $\Delta E_p = -110$ and -70 mV indicate that these are two reversible cathodic processes that

involve one electron. The reversibility criteria used was $\Delta E_p = E_p - E_a = 59/n$ mV (n = number of electrons). The voltammogram is presented in Fig. 6(c).

CONCLUSIONS

In the course of our studies on the crystal structure of different *tert*-butylammonium polyoxometallates we have observed that these compounds can be classified into two large groups: on one hand, the *tert*-butylammonium cation which has three hydrophobic methyl groups tends to pack with its methyl groups forming hydrophobic regions, for example, for those structures that consist of tetrahedral units [21], in the case of polyanions which have planar faces [22–23] and also when the polyanions are joined by means of

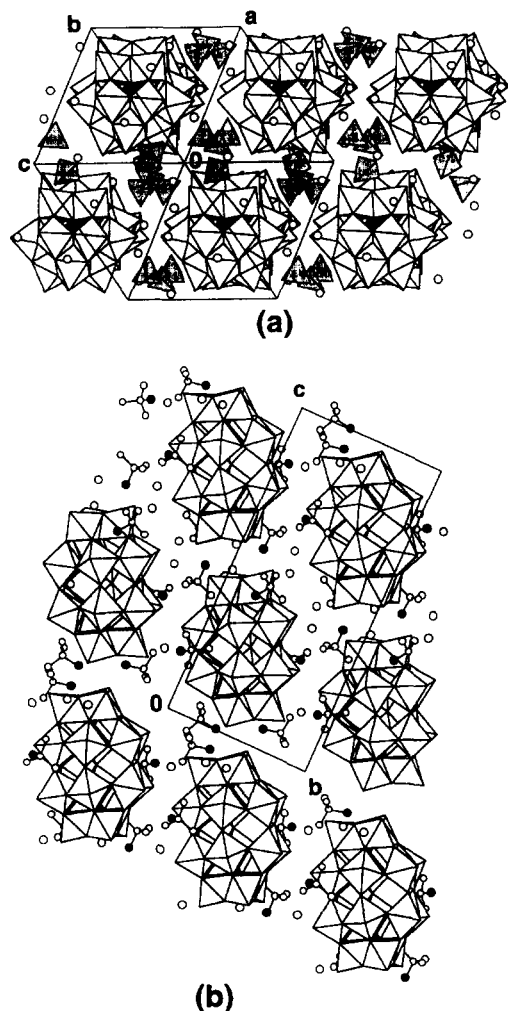


Fig. 5. Compound 2: (a) view along the $[1\bar{1}1]$ direction. Water molecules are represented by open circles and *tert*-butylammonium cations are presented by tetrahedra for clarity. (b) Arrangement of polyanions in rows parallel to the $[1\bar{1}1]$ direction. N atoms are represented by filled circles.

Table 6. Cathodic peak potential (E_{cp}) and anodic (E_{ap}) (mV) and potential difference for compounds 1 and 2

E_{cp}	E_{ap}	ΔE_p
Compound 1 (sensitivity 20 μ A)		
0 (sh)	450	450
-100 (sh)	270	370
-250	100	350
-480	-10 (sh)	470
-640 (sh)	-330	310
Compound 1 (sensitivity 100 μ A)		
0 (sh)	450	450
-100 (sh)	270	370
-250 (sh)	100	350
-480 (sh)	-10 (sh)	470
-640 (sh)	-330	310
-1000 (sh)	-780 (sh)	220
-1300	-1120 (sh)	180
Compound 2 (sensitivity 10 μ A)		
260	370	110
90	160	70

hydrogen contacts forming chains [24]. On the other hand, salts of anions type I [1], which possesses only one Mo—O_t bond, as in the case of the compound 2 described in this paper, do not present clear hydrophobic regions in the crystal structure [25]. It is important to notice that the thermal decomposition is different from both types of compounds [23,25–26]. In the case of the salts whose structures do not present clear hydrophobic regions, the thermal decomposition takes place in a similar way in oxidant and inert atmospheres. The dehydration of compound 2 takes place, in both atmospheres, in three overlapping steps that corresponds to the loss of three, two and one water molecules. Probably the water molecules O(65)w, O(66)w and O(67)w that are bonded between them by means of hydrogen contacts are lost in the same

Table 5. Hydrogen contacts (\AA) for the compound $[(\text{CH}_3)_3\text{CNH}_3]_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \cdot 6\text{H}_2\text{O}$ (2)

Bond type	X...O	Bond type	X...O	Bond type	X...O
N(11)—H(111)...	O(6) ¹ 2.99(2)	N(51)—H(513)...	O(18) ⁵ 3.12(2)	O(66)w—H(661)w...	O(65)w ⁴ 2.75(2)
N(11)—H(112)...	O(33) 2.91(2)	N(61)—H(611)...	O(8) ³ 3.05(2)	O(66)w—H(662)w...	O(12) ¹ 3.13(2)
N(11)—H(113)...	O(64)w 2.93(3)	N(61)—H(612)...	O(63)w 2.83(3)	O(66)w—H(662)w...	O(15) 3.18(2)
N(21)—H(211)...	O(2) ² 2.93(3)	N(61)—H(613)...	O(11) ⁶ 3.09(3)	O(67)w—H(671)w...	O(10) ⁴ 3.38(3)
N(21)—H(212)...	O(19) 2.86(2)	N(61)—H(613)...	O(41) 3.06(2)	O(67)w—H(672)w...	O(37) ³ 3.22(2)
N(21)—H(213)...	O(68)w ¹ 2.97(2)	O(63)w—H(631)w...	O(3) ³ 3.04(2)	O(68)w—H(681)w...	O(23) ¹ 3.17(2)
N(31)—H(311)...	O(7) ³ 3.01(2)	O(63)w—H(632)w...	O(5) ⁶ 2.96(2)	O(68)w—H(682)w...	O(28) ⁴ 3.59(2)
N(31)—H(312)...	O(16) ⁴ 2.92(2)	O(64)w—H(641)w...	O(3) 3.12(3)	C(25)—H(253)...	O(11) ⁶ 3.23(3)
N(31)—H(313)...	O(13) ³ 2.93(2)	O(64)w—H(642)w...	O(19) 3.11(2)	C(34)—H(343)...	O(9) ⁷ 3.18(2)
N(41)—H(411)...	O(53) 2.83(2)	O(64)w—H(642)w...	O(20) ³ 3.27(2)	C(54)—H(542)...	O(15) ⁵ 3.42(3)
N(41)—H(412)...	O(52) ⁶ 3.03(2)	O(64)w—H(642)w...	O(21) ³ 3.06(2)	C(55)—H(551)...	O(16) ⁴ 3.46(4)
N(41)—H(413)...	O(66)w ⁴ 3.04(3)	O(65)w—H(651)w...	O(67)w 2.96(2)	C(64)—H(643)...	O(10) ⁴ 3.36(3)
N(51)—H(511)...	O(54) ⁴ 2.89(2)	O(65)w—H(652)w...	O(51) ⁴ 3.20(2)	C(64)—H(643)...	O(45) ⁴ 3.41(3)
N(51)—H(512)...	O(66)w ⁵ 3.11(2)	O(65)w—H(652)w...	O(54) ⁴ 3.17(2)		

Symmetry codes: (1) 1+x, y, z; (2) -x, -y, 1-z; (3) 1-x, -y, 1-z; (4) 1-x, 1-y, 1-z; (5) x, y, 1+z; (6) -x, 1-y, 1-z; (7) 2-x, -y, 1-z.

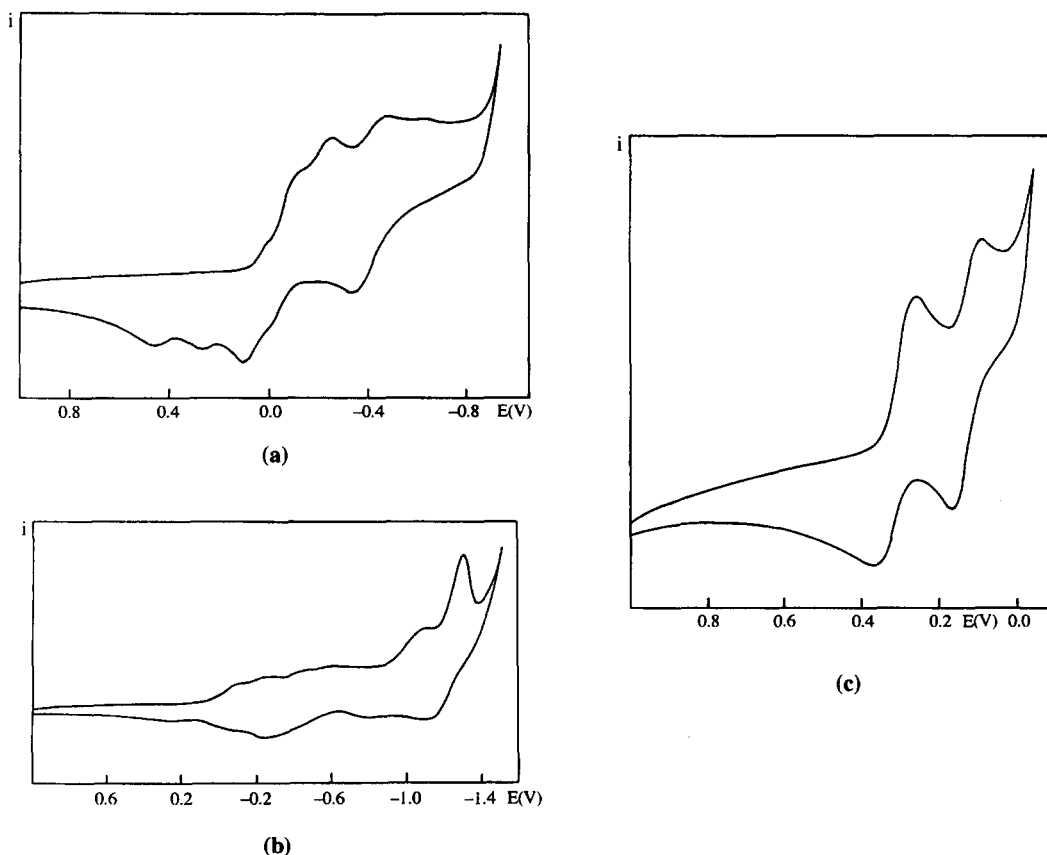


Fig. 6. (a) CV of compound **1** in KCl (1 M), sensitivity $20 \mu\text{A}$, $V = 20 \text{ mV s}^{-1}$. (b) CV of compound **1** in KCl (1 M), sensitivity $100 \mu\text{A}$, $V = 20 \text{ mV s}^{-1}$. (c) CV of compound **2** in KCl (1 M), sensitivity $10 \mu\text{A}$, $V = 20 \text{ mV s}^{-1}$.

step and the water molecule O(63)w, that joins different rows of polyanions by quite strong hydrogen contacts, could be the last one that is lost.

The cyclic voltammetry indicates that both compounds undergo reversible cathodic processes, as was expected for salts of anion type I.

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