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SYNTHESIS AND PROPERTIES OF THE DECATUNGSTATE ION

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ABSTRACT

In this paper the synthesis, properties and chemical characterization of 2,4,6-trimethylpyridinium decatungstates have been established. The compounds have been prepared above pH 3 in a solution of water/*N*,*N*-dimethylformamide (2/1). Their composition is: $(BH)_4W_{10}O_{32} \cdot n\,DMF$, where B = organic base and $n = 1$ (pH 3.4); $n = 0$ (pH 4.3); $n = 2$ (pH 5.0 and 5.6).

The colourless organic decatungstates have been characterized in the solid state by elemental analysis, infrared spectroscopy and thermogravimetric decompositions, and by visible–ultraviolet (V–UV) and nuclear magnetic resonance (NMR) spectroscopy in solution.

INTRODUCTION

In the study of isopolytungstates formed in acid solution of tungstate ions, Glemser et al. [1] detected the formation of polytungstate Y which has an absorption maximum in the range 320–325 nm. The same species were found to form immediately on acidification of tungstate solutions to pH 0–3 by Corsini et al. [2]. Above pH 3 the poly Y was not formed in appreciable quantities. Even when solutions in the pH range 0–3 were allowed to stand for some time (5 h), the intensity of the band decreased. However, the intensity of the band remained constant on extraction with *n*-amyl alcohol of aqueous tungstate solutions in the pH range 0–3 immediately after adjustment of the pH [2].

This isopolyanion has been formulated by different research groups as a dodecatungstate $HW_{12}O_{39}^{5-}$ [3], and as a decatungstate $W_{10}O_{32}^{4-}$ [4]. This latter formulation was found in the crystal structure [5,6] of the salt $((C_4H_9)_3NH)_4W_{10}O_{32}$, which can be precipitated from a freshly prepared aqueous solution and a solution of the tributylammonium salt in acetonitrile

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gave an absorption spectrum with a maximum at about 325 nm. Since aqueous solutions of Poly Y species are unstable and are slowly converted into equilibrium mixtures of other isopolytungstates [7–9], an element of uncertainty remained for some time about a positive identification of polytungstate Y as $W_{10}O_{32}^{4-}$. Termes and Pope [10] suggested that the 325 nm band was related to the presence of the near linear (448 K) W–O–W bridges that link both halves of the anion. The only other polytungstates with charge transfer bands (generally falling within the range 240–270 nm) as low as 325 nm are α- and β-$P_2W_{18}O_{62}^{6-}$ which also have dimeric structures linked by almost linear (435 K) W–O–W bridges [11,12].

In the present study, *N,N*-dimethylformamide has been used as solvent. DMF, the simplest disubstituted amide, has been extensively used not only for many laboratory reactions but also in industrial processes as a polymer solvent [13]. 2,4,6-Trimethylpyridinium decatungstates with different amounts of DMF molecules have been prepared by using this organic compound mixed with water as a solvent.

EXPERIMENTAL

Five solutions of 8 g of $Na_2WO_4 \cdot 2H_2O$ and 1.7 g of 2,4,6-trimethylpyridinium chloride in 100 ml of water to which were added 60 ml of *N,N*-dimethylformamide were prepared. The resulting solutions were heated (353 K) and stirred for two hours until they were transparent. By slow dropwise addition of 0.1 M hydrochloric acid solution with intensive stirring, each solution was carried to the corresponding pH: 6.0, 5.6, 5.0, 4.3 and 3.4. The compounds were isolated only after allowing the solutions to stand for several days. From the solution with pH 6.0 no polytungstate was obtained, only some colourless sodium chloride crystals. The crystals from the other four solutions were colourless and prismatic in shape. They were filtered from the mother liquor, washed with water and acetone and left to stand in a desiccator over $CaCl_2$.

The thermal decomposition of the four compounds was carried out in a Perkin-Elmer TGS-1 thermobalance with a programmed rate of heating of 5°C min^{-1} in the temperature range 293–1073 K. The sample weights were about 5 mg. The gas was pure and dry N_2 with a flow rate of 25 ml min^{-1}.

The infrared spectra in KBr pellets in the region 4000–200 cm were taken using a Perkin–Elmer spectrophotometer model 1430.

Electronic (V–UV) spectra of the solutions, in the range 200–700 nm were obtained by using a Beckman model 5260 spectrophotometer.

^{1}HNMR spectra were obtained in dimethylsulfoxide solvent using tetramethylsilane as internal standard by means of a Perkin–Elmer model R-12B spectrometer.

RESULTS

Chemical analyses are given in Table 1. Tungsten was analyzed as WO after calcination of the compounds at 1073 K. These values correspond to the stoichiometric formula $(BH)_4W_{10}O_{32} \cdot n$DMF, where B is 2,4,6-trimethylpyridine and n is the number of molecules of *N*,*N*-dimethylformamide of crystallization. The values obtained are in good agreement with those calculated for n values of 1, 0, 2 and 2, respectively. These results suggest that compounds from solutions at pH 5.0 and 5.6 are the same.

The compounds, prismatic in shape, were insoluble in the usual organic solvents and soluble in dimethylsulfoxide and *N*,*N*-dimethylformamide.

The three decatungstates with DMF molecules turned bright blue when they were exposed to sunlight. This is a common phenomenon in heteropoly and isopoly compounds, i.e., their photosensitivity in the presence of organic compounds [14–17]. A quantitative study will be the subject of future works.

Figure 1(a)–(d) shows the thermogravimetric decomposition of the compounds. The decomposition of the compound obtained from a solution with pH 4.3 occurred in three steps with WO_3 as the final product. The curves a, c and d confirm the presence of one DMF molecule in the decatungstate (pH 3.4) and two in the compounds obtained at pH 5.0 and 5.6 per formula unit. The three compounds leave DMF molecules in discrete, distinguishable steps. The crystals begin to lose DMF at temperatures of 410, 412 and 414 K, respectively, all of them higher than those for water molecules in similar compounds, about 353 K [18].

After having lost DMF molecules, the shape of the curves is similar and the temperatures for the decomposition are 528, 533 and 524 K, all of them higher than those for octamolybdate and decavanadate of the same organic base, 438 and 432 K, respectively, that were studied in our laboratory in previous works [19,20].

TABLE 1

Analytical data for the compounds

Compound $(C_8H_{11}NH)_4W_{10}O_{32} \cdot n$DMF		%C	%H	%N	$\%WO_3$
pH = 3.4; $n = 1$	Found	14.49	1.89	2.40	78.80
	Calcd.	14.41	1.89	2.40	79.59
pH = 4.3; $n = 0$	Found	13.40	1.85	1.90	81.64
	Calcd.	13.54	1.70	1.97	81.65
pH = 5.0; $n = 2$	Found	15.50	2.08	2.80	77.68
	Calcd.	15.28	2.09	2.81	77.66
pH = 5.6; $n = 2$	Found	15.37	2.10	2.80	78.30
	Calcd.	15.28	2.09	2.81	77.66

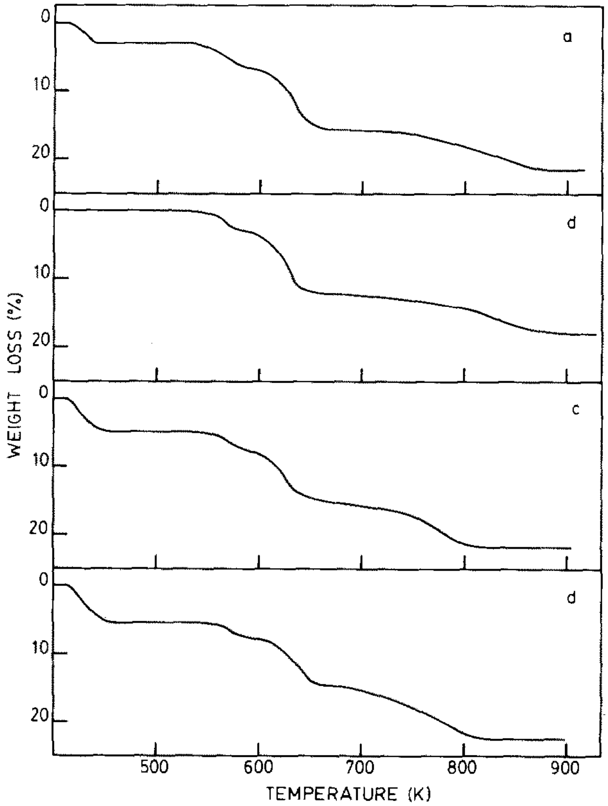

Fig. 1. Weight loss percentages in the thermogravimetric decomposition in the non-isothermal regime of compound at pH 3.4 (a); compound at pH 4.3 (b); compound at pH 5.0 (c); and compound at pH 5.6 (d).

The infrared spectra obtained are shown in Fig. 2(a)–(d). The intense absorption bands observed for all the compounds at: 960, 890, 800, 580, 435, 400 and 330 cm^{-1} can be ascribed to vibrations of W–O$_t$, W–O$_b$–W and W–O$_c$–W groups [21,22]. The colidinium cation bands have been identified by comparison with the colidine and colidinium chloride spectra. The compounds studied show an intensive and broad absorption between 2300 and 3460 cm^{-1} the same as that present in the colidinium chloride spectrum, which does not appear in the organic base spectrum. This band can be ascribed to N–H$^+$ stretching vibration. The CO stretching vibration of the free DMF at 1678 cm^{-1} [23], that could appear at lower frequencies by bonding, can not be observed because the strong absorption at 1635 cm^{-1} that presents all the compounds and the colidinium chloride owing to the C=C and C=N stretching modes. The same happens with the CN stretching frequency (1490 cm^{-1}) for the DMF.

Figure 3 shows the electronic spectra of the decatungstates (a–d) and the colidinium chloride (e). In Fig. 3a–d the compounds dissolved in dimethyl-

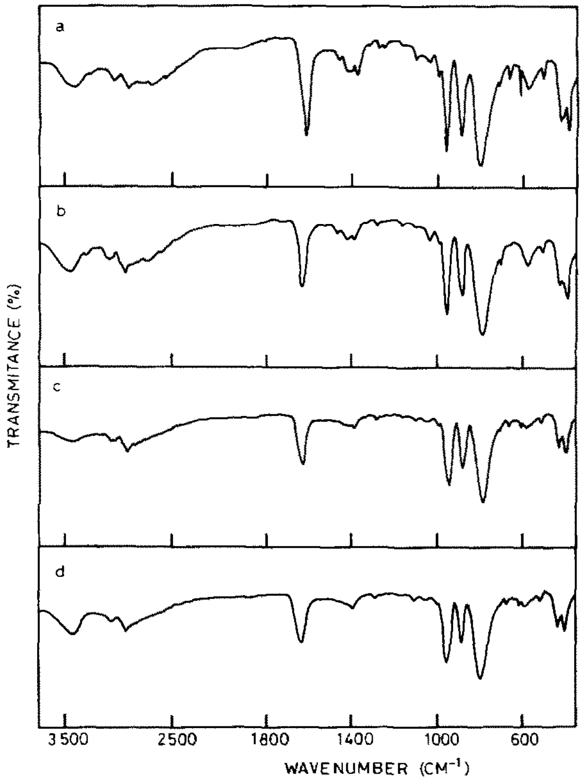

Fig. 2. Infrared spectra of compounds at pH 3.4 (a), 4.3 (b), 5.0 (c) and 5.6 (d).

sulfoxide with the solvent as reference (———), and in aqueous solution, with 2,4,6-trimethylpyridinium chloride aqueous solution of the same concentration in organic base as reference (- - - - - -) are shown for the compounds obtained at pH 3.4, 4.3, 5.0 and 5.6, respectively. The four compounds present an absorption peak at 325 nm ($\epsilon = 14300$) in dimethylsulfoxide, that appears in water solution although with less intensity, and a shoulder at 230 nm, besides the characteristic organic cation absorption at 269 nm.

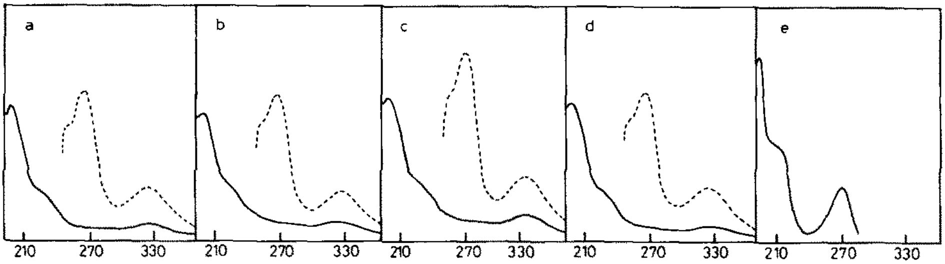

Fig. 3. Electronic spectra of compounds at pH 3.4 (a), 4.3 (b), 5.0 (c) and 5.6 (d) in DMSO (———), and in water (- - - - - -). 2,4,6-Trimethylpyridinium chloride in water (e).

TABLE 2

^{1}HMNR spectra data (δ ppm)

Compound	H–C=O DMF	H-3	H-1	$-CH_3$	DMF	CH_3-2	CH_3-4
pH 3.4	7.93 s (1H)	7.52 s (8H)	3.0–4.2 s (4H)	2.91 s (3H)	2.74 s (3H)	2.66 s (18H)	2.53 s (12H)
pH 4.3	–	7.58 s (8H)	3.1–4.2 s (4H)	–	–	2.68 s (18H)	2.54 s (12H)
pH 5.0	7.91 s (2H)	7.56 s (8H)	3.1–4.0 s (4H)	2.89 s (6H)	2.72 s (6H)	2.64 s (18H)	2.52 s (12H)
pH 5.6	7.92 s (2H)	7.56 s (8H)	3.2–4.1 s (4H)	2.90 s (6H)	2.74 s (6H)	2.66 s (18H)	2.53 s (12H)

The ^{1}HNMR results are reported in Table 2. All the peaks have been assigned to the organic base, and DMF molecules in compounds obtained at pH 3.4, 5.0 and 5.6. The *cis* and *trans* methyl groups of DMF shifted to low field after hydrogen bonding [24].

DISCUSSION

The elemental analysis is not a good criterion for checking the purity of polyoxometalate compounds, since the mass percentages of some of their constituent elements can be very low (1.2%). Therefore, thermogravimetric analysis (TG) coupled with careful spectroscopic measurements throughout the sample preparation allowed us to define unambiguously the compounds as $(BH)_4W_{10}O_{32} \cdot n\text{DMF}$. The DMF content seems to be not dependent on the pH values of solution but on the history of the compounds (storage conditions, etc.). However, the use of mixtures water/DMF as solvents has permitted us to obtain decatungstate salts at pH values higher than those appearing in literature [2,6].

The thermal stabilities of these compounds are higher than those of colidinium octamolybdate and decavanadate, which seems to be related to the size of the anion. The DMF molecules made the compounds slightly less stable (278 K one molecule per unit formula and about 283 K two molecules).

The IR spectra of the compounds are quite similar to those obtained for the decatungstate anion in tri- and tetrabutylammonium salts [6,25]. The structure of this anion was described by Fuchs et al. [6] in the $((C_4H_9)_3NH)_4W_{10}O_{32}$ compound as two W_5O_{18} units bonded mirror-symmetrically through four corner-sharing oxygen atoms with formation of empty octahedral space. In the W_5O_{18} unit five distorted WO_6 octahedra are bonded via common edges with one O_c atom common to each of them. The symmetry of the anion $W_{10}O_{32}^{4-}$ is nearly D_{4h}. The decatungstate ions are connected to four tributylammonium cations via hydrogen bonds.

The symmetric and asymmetric stretchings of the $W-O_t$ bonds can be considered as pure vibrations. They are observed at 956 cm^{-1}. The stretching involving O_b (μ-oxo junctions, through edges or corners of octahedra) and O_c (μ_5-oxo junctions) atoms present some bend character and are observed at 890, 800 and 580 cm^{-1}. This can be assumed from geometrical considerations and has been confirmed by a normal-coordinate treatment on another parent polyoxometalate, the hexametalate anion [26].

Only the $\nu_{as}W-O_c$ mode which had to be assigned to the 330 cm^{-1} band is a rather pure one. It can be tentatively described as a vibration of the central oxygen atoms within the framework.

There are no pure bending modes. The O_b-W-O_t bend contributes significantly to many modes at relatively high frequency. The other bend modes appear as mixed modes in the medium and low frequency regions.

The anion–anion interactions have been correlated with the cation size [22] since the smaller the cation is the higher the W–O_t stretching frequencies are. Colidinium cation seems to be similar to tri- and tetrabutylammonium, all of them large enough to keep the polyanions far apart.

The four IR spectra are quite similar, thus DMF molecules of crystallization do not shift the vibration frequencies.

The UV spectra show the characteristic absorption band for the decatungstate ion at 325 nm of charge transfer, stable in organic solvents (dimethylsulfoxide) and unstable in water.

The ^{1}HNMR spectra of the compounds with one or two DMF molecules show a single peak for each methyl group, indicating hydrogen bond on the colidinium cation to the oxygen of the DMF. If the nitrogen of the DMF were involved in the interaction, the methyl groups would become equivalent and, consequently, only one peak would be observed because of the loss of carbon–nitrogen double-bond character [20].

In no case did a narrow resonance line appear downfield from water as could be expected for metatungstate ion and other polytungstates with non-exchangeable protons [9].

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