Synthesis and Characterization of Fe- or Cu-Substituted Molybdenum-Enriched Tungstodiphosphates

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Stereospecific routes were followed to synthesize five new Fe^{3+} and Cu^{2+}-substituted Mo-enriched Dawson-type heteropolyanions as aqueous soluble potassium salts: α_2-$K_7[Fe(OH_2)P_2W_{12}Mo_5O_{61}]$ and α_2-$K_7[Fe(OH_2)P_2W_{13}Mo_4O_{61}]$, α_1- and α_2-$K_8[Cu(OH_2)P_2W_{12}Mo_5O_{61}]$ and α_2-$K_8[Cu(OH_2)P_2W_{13}Mo_4O_{61}]$. The substituted species as well as their immediate lacunary precursors were characterized by IR, UV/Visible and ^{31}P NMR spectroscopy. In particular ^{31}P NMR spectroscopy indicates that isomerically pure compounds were obtained. The activity of these chemicals in electrocatalysis is illustrated by the reduction of nitrite for Fe^{3+} derivatives and the reduction of nitrate for Cu^{2+} compounds.

Introduction

Dawson-type tungstodiphosphates are interesting in their own right. More particularly, their ability to generate lacunary species and then metal cation substituted derivatives has aroused great attention.[1−10] The impetus was triggered by the pioneering remark of Baker[11] that monosubstituted heteropolyanions can be considered as the analogues of metalated porphyrins and used in catalytic processes with the advantage, relative to their organic counterparts, of thermal stability, robustness and inertness toward oxidizing environments. With regard to their electrochemistry and, correspondingly, their use in electrocatalysis, we are currently studying the parameters which eventually in conjunction with pH effects could induce the overlapping of the first waves of heteropolyanions (HPAs). The basic idea underlying this search is to trigger by reduced HPAs those energetically favourable cathodic processes that require several electrons to become effective.[6,8−10,12] Among several possibilities, the approach making use of substitution effects is considered in detail: in particular the location of the metal in the framework; the nature and number of substituents are expected to more or less influence the interactions between the electroactive centres within the HPA molecule. The two following examples can be cited in support of these anticipated results: i) A remarkably beneficial effect observed for the presence of molybdenum in the framework of Dawson-type HPAs used as electrocatalysts in the reduction of nitrite or nitric oxide aroused our interest.[5] For instance, the presence of a single Mo atom in the framework of $[P_2W_{17}MoO_{62}]^{6-}$ results in an improvement of 0.270 V in the potential at which the catalytic process is observed compared to the same process with $[P_2W_{18}O_{62}]^{6-}$. Such an improvement reaches 0.390 V with $[P_2Mo_{18}O_{62}]^{6-}$ instead of $[P_2W_{18}O_{62}]^{6-}$. At least two questions might result from this observation: they concern the influence of the number of Mo atoms in the molecule and the possible specificity of molybdenum in this particular process; ii) the presence of the Fe^{3+} cation in α_2-$[Fe(OH_2)P_2W_{15}Mo_2O_{61}]^{7-}$, abbreviated as α_2-$FeP_2W_{15}Mo_2$, substantially modifies the electrochemistry of this heteropolyanion compared with the behaviour of α_2-$[P_2Mo_3W_{15}O_{62}]^{6-}$ (α_2-$P_2Mo_3W_{15}$). In a pH 2 medium, the cyclic voltammogram of the latter compound begins with three diffusion-controlled one-electron waves. In contrast, the iron(III)-substituted complex displays a three-electron first wave at pH 2, as a result of the merging of the molybdenum and iron waves.[6,12] A study of this pattern as a function of pH allows the Fe^{3+} wave to be separated from the molybdenum reduction, thus confirming the mechanism leading to overlapping. Provisionally, it is also worth noting the use of Fe-substituted heteropolyanions in electrocatalytic processes.[4,13,14] The copper cation Cu^{2+} is another substituent known to be reducible in the close vicinity of the HPAs framework and therefore likely to result in a first wave in-

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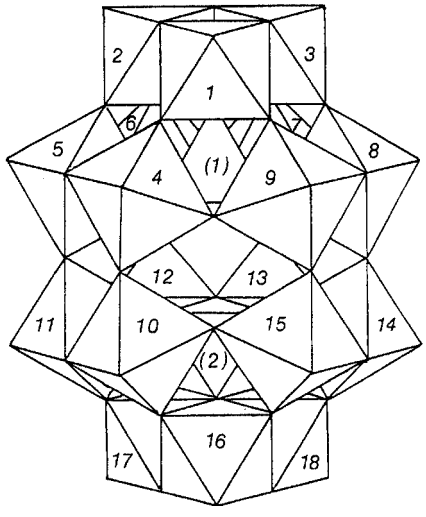
volving several electrons.[9,10,15] Furthermore, copper and iron complexes exhibit useful behaviours in several catalytic processes.[16,17]

The purpose of the present paper is to give a detailed account of the synthesis and characterization of pure samples of several Mo-rich Dawson-type tungstodiphosphates monosubstituted by Fe^{3+} or Cu^{2+}. The electrocatalytic behaviours of these chemicals are also illustrated briefly.

Results and Discussion

Numbering of Atoms and Main Abbreviations

The new heteropolyanions (HPAs) are: α_2-K_7-$[Fe(OH_2)P_2W_{12}Mo_5O_{61}]$ (α_2-$P_2W_{12}Mo_5Fe$) and α_2-K_7-$[Fe(OH_2)P_2W_{13}Mo_4O_{61}]$ (α_2-$P_2W_{13}Mo_4Fe$); α_1 and α_2-$K_8[Cu(OH_2)P_2W_{12}Mo_5O_{61}]$ (α_1- and α_2-$P_2W_{12}Mo_5Cu$) and α_2-$K_8[Cu(OH_2)P_2W_{13}Mo_4O_{61}]$ (α_2-$P_2W_{13}Mo_4Cu$). Scheme 1 gives the numbering of atoms in the framework of $[P_2W_{18}O_{62}]^{6-}$ from which all the present compounds are derived. In conjunction with Table 1, it permits a precise localization of all the substituent atoms in the W skeleton.



Scheme 1. Numbering scheme for $[P_2W_{18}O_{62}]^{6-}$ (Dawson structure)

Syntheses

Table 1 summarises the formulas of the main intermediate compounds and those of the final substituted products described in the following. Stereospecific routes to obtain the precursor lacunary species were established by one of the present authors.[18] The substituted compounds of interest here were then synthesized along the same lines as those followed for α_2-$P_2W_{15}Mo_2Cu$ and α_2-$P_2W_{15}Mo_2Fe$.[6,8] Specific details are given in the Exp. Sect. Table 1 also emphasizes the remarkably high yields obtained for all the syntheses in the present work. ^{31}P NMR spectra indicated that isomerically pure compounds were obtained. This observation is remarkable because several isomeric species could have been expected owing to possible migration of molybdenum atoms in all the compounds. The lack of heating might be one of the reasons for obtaining such pure samples.

UV/Vis and IR Characterization

As expected, no characteristic absorption band was observed in the UV/Vis spectra of the new HPAs except for some shift in the yellow direction due to the presence of Mo atoms in the molecules. However, in anticipation of subsequent work, the stability of these complexes in pH 3 and 5 media was checked by monitoring their UV/Vis spectra over a period of at least 24 hours. The species were found to be stable in these media. Figure 1 allows a comparison of the IR characteristics of the main new HPAs synthesized in this work. In tungstophosphates, the most characteristic IR band shifts correspond to P−O vibrations between 1200 and 1000 cm^{-1}, and these shifts characterize lacunary species. With an iron or a copper atom added in the vacancy, despite the presence of Mo atoms a greater symmetry is restored in the substituted molecule, at least as far as IR spectra are concerned. It is worth noting an important broadening of the bands, which become somewhat featureless roughly in the 850−700 cm^{-1} region. On the whole, in a first approximation, the IR spectra are close to those of the corresponding saturated compounds, even though a few new bands or slight differences could be detected on comparative scrutiny of the spectra. This situation prevents any sharp identification by IR spectra of a given anion.

^{31}P NMR Spectroscopy

The NMR study of paramagnetic element-containing HPAs was performed by Jorris et al.[19] on $[P_2W_{17}O_{61}]^{10-}$ derivatives. In agreement with their observations, work of this group[6,8] has confirmed that the chemical shift of the P atom furthest from the paramagnetic centre and noted P(2) is practically unaffected by the presence of this centre, while P(1) resonances are shifted radically and broadened. This shift and broadening might be important enough to make the corresponding signal hardly or not at all observable. Table 2 gives the chemical shifts measured for all the Fe^{3+} and Cu^{2+}-substituted compounds synthesized in this work. Values for the same metal complexes derived from $[(1),2,3\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ are included for comparison. The expected features were obtained throughout and do not call for further comments. Figure 2 illustrates specifically the ^{31}P NMR spectrum of α_1-$CuP_2Mo_5W_{12}$. For this compound, a single resonance peak was observed, corresponding to P(2). As shown in Table 2 and Figure 2, the two spectra for the α_1 and α_2 isomers are sufficiently different to

Table 1. Main characteristics of the HPAs synthesised in this work; the new HPAs are those substituted by Fe^{3+} and Cu^{2+}; abbreviated formulas are used, with the numbers of effectively determined water molecules; for further details, see text

Heteropolyanion	Position of Fe or Cu atom	Positions of Mo atoms	Molecular weight	Yield (%)	Colour
α_2-$K_{10}[P_2W_{12}Mo_5]\cdot 20H_2O$	–	4, 9, 10, 15, 16	4475	82	white
$K_6[P_2W_{12}Mo_6]\cdot 14H_2O$	–	1, 4, 9, 10, 15, 16	4322	98	yellow
$K_6[P_2W_{13}Mo_5]\cdot 14H_2O$	–	4, 9, 10, 15, 16	4411	89	orange
$K_6[P_2W_{14}Mo_4]\cdot 14H_2O$	–	4, 9, 10, 15	4499	96	orange
α_2-$K_{10}[P_2W_{13}Mo_4]\cdot 19H_2O$	–	4, 9, 10, 15	4545	88	white
α_1-$K_9Li[P_2W_{12}Mo_5]\cdot 20H_2O$	–	1, 9, 10, 15, 16	4443	95	white
α_2-$K_7[FeP_2W_{12}Mo_5]\cdot 14H_2O$	1	4, 9, 10, 15, 16	4306	73	dark yellow
α_2-$K_8[CuP_2W_{12}Mo_5]\cdot 16.5H_2O$	1	4, 9, 10, 15, 16	4398	74	yellow
α_1-$K_8[CuP_2W_{12}Mo_5]\cdot 15.5H_2O$	4	1, 9, 10, 15, 16	4380	66	yellow
α_2-$K_7[FeP_2W_{13}Mo_4]\cdot 15H_2O$	1	4, 9, 10, 15	4412	94	yellow
α_2-$K_8[CuP_2W_{13}Mo_4]\cdot 16.5H_2O$	1	4, 9, 10, 15	4485	89	yellow

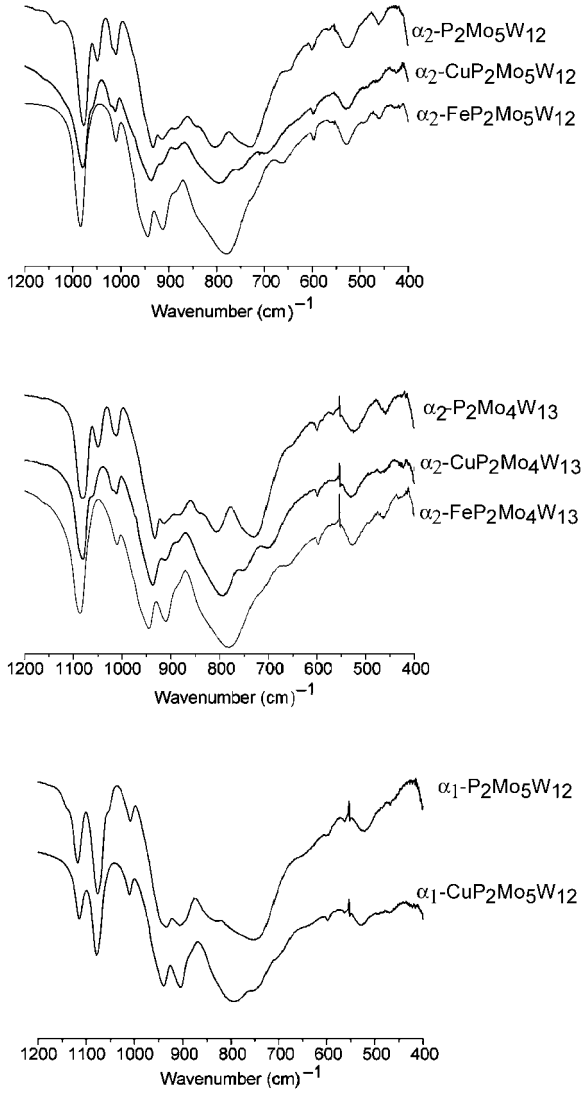


Figure 1. Selected IR spectra (KBr) for the hydrated heteropolyanions studied in this work

allow for the characterization of each isomer and the determination of their respective proportion in a mixture.

Electrocatalytic Behaviours of the (Fe or Cu)-Substituted Mo-Containing HPAs

The assessment of the behaviours of HPAs towards the reduction of NO_x constitutes one of our favourite electrocatalytic tests. Table 3 and 4 summarize several results selected to illustrate the combined influences of Mo and Fe or Cu in the HPA molecules. Our work establishes the beneficial effect of the presence of Mo atoms within the framework of HPAs on the electrocatalytic reduction of nitrites[5,17] and nitrates.[16] Cyclic voltammetry at a scan rate of 2 $mV\cdot s^{-1}$ was used throughout for these tables. Quantitatively, the activities of the HPAs were expressed through the catalytic efficiency, defined as $CAT = 100 \times [I_{(HPA + NO_x)} - I^d_{(HPA)}]/I^d_{(HPA)}$, where $I_{(HPA + NO_x)}$ is the peak current for the reduction of the heteropolyanion (HPA) in the presence of NO_x and $I^d_{(HPA)}$ is the corresponding diffusion peak current for the HPA alone. The quantity of NO_x is defined in terms of the excess parameter γ ($\gamma = C^\circ_{NO_x}/C^\circ_{HPA}$).

For the electrocatalytic reduction of nitrites, Table 3 illustrates the example of Fe-HPA derivatives: a pH 5 medium was selected to avoid competition between several NO_x species for the catalytic process; the increase of the catalytic efficiency with the number of Mo atoms is obvious. Typically, the catalytic efficiency showed a threefold increase when the number of Mo atoms increased from 2 to 5.

The catalytic efficiencies for the catalytic reduction of nitrate by reduced Cu-monosubstituted Mo-containing HPAs are given in Table 4. It is gratifying that the electrocatalytic reduction of nitrate by substituted HPAs could be observed for the first time. The process is efficient with all the compounds in Table 4 and also with compounds of the $P_2W_{17}Cu$ series (not shown). The comparison clearly indicates[16] the beneficial effect of the presence of Mo atoms for enhancing the catalytic current. In Table 4, the correlation between the number of Mo atoms and the catalytic efficiency is not straightforward, probably because the electrocatalysis is triggered at least partly by the electrodeposited

Table 2. ^{31}P NMR chemical shifts for $[M^x(H_2O)(P_2Mo_yW_{17-y}O_{61})]^{(10-x)-}$ with $M^x = Fe^{3+}$, Cu^{2+} or □, (□ designates a vacancy), y = 3, 4 or 5

HPA	δP(1) (ppm)	Δν P(1) (Hz)	δP(2) (ppm)	Δν P(2) (Hz)
α_2-$P_2Mo_2W_{15}$□ [a]	−4.93	5	−13.75	5
α_2-$P_2Mo_4W_{13}$□	−5.45	8	−11.31	7
α_2-$P_2Mo_5W_{12}$□	−5.53	5	−10.62	5
α_1-$P_2Mo_5W_{12}$□	−7.4	8	−9.94	110
α_2-$FeP_2Mo_2W_{15}$ [a]	≈ 900	> 30 000	−13.6	100
α_2-$CuP_2Mo_2W_{15}$ [a]	−27.2	1100	−13.0	60
α_2-$FeP_2Mo_4W_{13}$	not observed	not observed	−11.7	257
α_2-$CuP_2Mo_4W_{13}$	−39.5	2420	−10.2	80
α_2-$FeP_2Mo_5W_{12}$	not observed	not observed	−11.0	247
α_2-$CuP_2Mo_5W_{12}$	−38.4	2500	−9.64	22
α_1-$CuP_2Mo_5W_{12}$	not observed	not observed	−8.68	100

[a] See ref.[8]

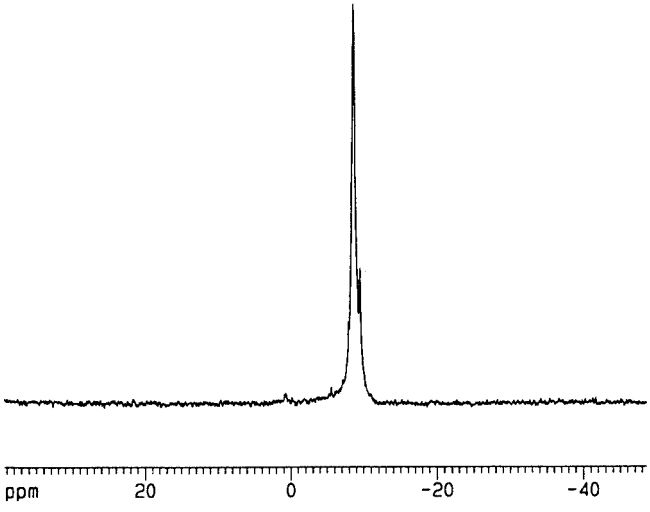


Figure 2. ^{31}P NMR spectrum of a mixture of α_1- (92%) and α_2-$Cu(OH_2)P_2Mo_5W_{12}$ (8%)

Table 3. Selected values of catalytic efficiencies in cyclic voltammetry for the electrocatalytic reduction of nitrite by Fe-substituted Mo-containing heteropolyanions; pH = 5; potential vs. SCE chosen for the evaluation: −0.700V; concentration of HPA: 2×10^{-4} M; γ = 100; scan rate: 2 mV·s^{-1}

Heteropolyanion	CAT%
α_2-$P_2W_{15}Mo_2Fe$	757
α_2-$P_2W_{13}Mo_4Fe$	1309
α_2-$P_2W_{12}Mo_5Fe$	2276

copper. Finally, a small isomeric effect between α_1- and α_2-$P_2W_{12}Mo_5Cu$ must be noted.

Conclusions

One of the basic ideas underlying this work originates in the observation that the presence of Mo atoms within the skeleton of tungsten-containing heteropolyanions results in a substantial improvement in the electrocatalytic behaviours of these compounds toward the reduction of nitrite or nitric oxide. Therefore, it was desirable to study the possibility of a correlation between the number and/or the location of these atoms in the framework with the catalytic efficiency. However, it soon appeared that an additional monosubstitution of the already Mo-substituted skeleton by Fe^{3+} or Cu^{2+} is also necessary in these catalysts. It was found that stereospecific synthesis routes available for obtaining several Mo-rich tungstodiphosphates allow direct access to the useful lacunary precursor species. It is gratifying that our procedures for the synthesis of the subsequent Fe^{3+} and Cu^{2+}-substituted derivatives result in pure compounds, as proved by several analytical techniques including IR spectroscopy and ^{31}P NMR spectroscopy. The usefulness of these new species in the electrocatalysis of nitrite and nitric oxide reduction was assessed. It is worth emphasizing particularly the activity of the present Cu-substituted derivatives toward the electrocatalytic reduction of nitrates. To the best of our knowledge, this process was observed for the first time with substituted heteropolyanions.

Table 4. Selected values of catalytic efficiencies in cyclic voltammetry for the electrocatalytic reduction of nitrate by Cu-substituted Mo-containing heteropolyanions; pH = 5; potential vs. SCE chosen for the evaluation: −0.800V; concentration of HPA: 2×10^{-4} M; γ = 500; scan rate: 2 mV·s^{-1}

Heteropolyanion	CAT%
α_2-$P_2W_{15}Mo_2Cu$	753
α_2-$P_2W_{13}Mo_4Cu$	882
α_2-$P_2W_{12}Mo_5Cu$	629
α_1-$P_2W_{12}Mo_5Cu$	780

Experimental Section

NMR, IR and UV/Visible Spectroscopy and Elemental Analysis: ^{31}P NMR spectra were recorded in 5 mm outer diameter tubes on a Bruker Avance 400 apparatus operating at 161.97 MHz, in the Fourier transform mode. The ^{31}P chemical shifts were measured

for 0.01 M solutions of the polyanions in 1 M LiCl/D_2O solutions and were referenced to H_3PO_4. IR spectra were recorded in 1% weight of HPA in a KBr pellet on a Bruker IFS 66 FT-IR spectrophotometer. UV/Visible spectra were recorded on a Perkin−Elmer Lambda 19 spectrophotometer. Elemental analyses were performed by CNRS Service Central d′Analyse at Vernaison (France). The crystal water content was determined by the following procedure: Two silica crucibles were thoroughly cleaned, dried at 250° C in an oven and finally left to cool to room temperature in a drying vessel containing P_2O_5 as a desiccant. Each crucible was loaded with 150 to 300 mg of the complex of interest and then heated at 250° C in the oven for one hour. After cooling in the drying vessel, the mass loss was measured and converted into mol of water per mol of complex.

Electrochemical Experiments: Pure water was used throughout. It was obtained by passing through a Milli-RO_4 unit and subsequently through a Millipore Q water purification set. All chemicals were of high-purity grade and were used as received. CH_3COONa and CH_3COOH were commercial products (Prolabo). The pH 5 solution was made up with 0.5 M CH_3COONa + CH_3COOH. The solutions were de-aerated thoroughly for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments. The source, mounting and polishing of the glassy carbon (GC, Tokai, Japan) electrodes has been described previously.[17] The glassy carbon samples had a diameter of 3 mm. The electrochemical setup was an EG & G 273 A driven by a PC with 270 software. Potentials are quoted relative to a saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area. All experiments were performed at room temperature.

Preparations: The potassium salts of α_2-$[P_2W_{12}Mo_5]^{10-}\cdot 20H_2O$, $[P_2W_{12}Mo_6]^{6-}\cdot 14H_2O$, $[P_2W_{13}Mo_5]^{6-}\cdot 14H_2O$, $[P_2W_{14}Mo_4]^{6-}\cdot 14H_2O$, α_2-$[P_2W_{13}Mo_4]^{10-}\cdot 19H_2O$ and the mixed potassium/lithium salt of α_1-$[P_2W_{12}Mo_5]^{10-}\cdot 20H_2O$ were prepared by the published stereospecific routes.[18]

α_2-$K_7[Fe(OH_2)P_2W_{12}Mo_5O_{61}]\cdot 14H_2O$: A sample of α_2-$K_{10}[P_2W_{12}Mo_5O_{61}]\cdot 20H_2O$ (9.40 g, 2.10 mmol) was dissolved in 20 mL of 0.12 M $Fe(NO_3)_3$ (2.4 mmol) and 60 mL of Millipore water and the mixture stirred for 30 min. After treatment with solid KCl (15 g) followed by a saturated KCl solution (60 mL), a dark yellow solid (6.57 g) was filtered off and dried in air. $K_7[Fe(OH_2)P_2W_{12}Mo_5O_{61}]\cdot 14H_2O$: calcd. H_2O 6.27, Fe 1.30, K 6.36, Mo 11.14, P 1.44, W 51.24; found H_2O, 5.85, Fe 1.27, K 7.50, Mo 10.70, P 1.67, W 48.90.

α_2-$K_8[Cu(OH_2)P_2W_{12}Mo_5O_{61}]\cdot 16.5H_2O$: A sample of α_2-$K_{10}[P_2W_{12}Mo_5O_{61}]\cdot 20H_2O$ (9.40 g, 2.10 mmol) was dissolved in 20 mL of 0.12 M $Cu(NO_3)_2$ (2.4 mmol) and 60 mL of Millipore water and the mixture stirred for 20 min. After treatment with a saturated KCl solution (60 mL), a yellow-green solid (6.84 g) was filtered off and dried in air. $K_8[Cu(OH_2)P_2W_{12}Mo_5O_{61}]\cdot 16.5H_2O$: calcd. H_2O 7.16, Cu 1.44, K 7.11, Mo 10.91, P 1.41, W 50.17; found H_2O 6.75, Cu 1.31, K 7.69, Mo 10.32, P 1.65, W 47.18.

α_1-$K_8[Cu(OH_2)P_2W_{12}Mo_5O_{61}]\cdot 15.5H_2O$: A sample of α_1-$K_{10}[P_2W_{12}Mo_5O_{61}]\cdot 20H_2O$ (9.40 g, 2.10 mmol) was dissolved in 20 mL of 0.14 M $Cu(NO_3)_2$ (2.8 mmol) and 60 mL of Millipore water and the mixture stirred for 20 min. After treatment with a saturated KCl solution (60 mL), a yellow solid (6.07 g) was filtered off and dried in air. $K_8[Cu(OH_2)P_2W_{12}Mo_5O_{61}]\cdot 15.5H_2O$: calcd. H_2O, 6.78, Cu 1.45, K 7.14, Mo 10.95, P 1.42, W 50.38; found H_2O, 6.37, Cu 1.45, K 7.23, Mo 9.89, P 1.53, W 48.89.

α_2-$K_7[Fe(OH_2)P_2W_{13}Mo_4O_{61}]\cdot 15H_2O$: A sample of α_2-$K_{10}[P_2W_{12}Mo_5O_{61}]\cdot 20H_2O$ (9.40 g, 2.10 mmol) was dissolved in 20 mL of 0.14 M $Fe(NO_3)_3$ (2.8 mmol) and 60 mL of Millipore water and the mixture stirred for 10 minutes. After treatment with solid KCl (15 g) followed by a saturated KCl solution (30 mL), a yellow orange solid (8.4 g) was filtered off and dried in air. $K_7[Fe(OH_2)P_2W_{12}Mo_5O_{61}]\cdot 15H_2O$: calcd. H_2O, 6.53, Fe 1.26, Mo 8.70, K 6.20, P 1.41, W 54.18; found H_2O 6.12, Fe 1.24, K 6.30, Mo 7.70, P 1.43, W 52.86.

α_2-$K_8[Cu(OH_2)P_2W_{13}Mo_4O_{61}]\cdot 16.5H_2O$: A sample of α_2-$K_{10}[P_2W_{12}Mo_5O_{61}]\cdot 20H_2O$ (9.40 g, 2.10 mmol) was dissolved in 20 mL of 0.14 M $Cu(NO_3)_2$ (2.8 mmol) and 60 mL of Millipore water and the mixture stirred for 15 min. After treatment with a saturated KCl solution (30 mL), a yellow solid (8.06 g) was filtered off and dried in air. $K_8[Cu(OH_2)P_2W_{13}Mo_4O_{61}]\cdot 16.5H_2O$: calcd. H_2O 7.02, Cu 1.42, K 7.2,, Mo 8.61 P 1.39, W 53.61; found H_2O 6.62, Cu 1.33, K 7.57, Mo 8.10, P 1.60, W 52.14.

Acknowledgments

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