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Synthesis and properties of new materials with cobalt(II), iron(III) and manganese(III)-substituted Keggin polyoxotungstates and 1-alkyl-3-methylimidazolium cations

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ABSTRACT

Several novel compounds with 1-alkyl-3-methylimidazolium cations (alkyl = butyl and octyl) and first row transition metal-substituted Keggin polyoxoanions were synthesised, having the general formula $(cation)_m[PW_{11}O_{39}M(H_2O)]\cdot xH_2O$ or $(cation)_{m-1}H[PW_{11}O_{39}M(H_2O)]\cdot xH_2O$, M = Co, Fe, Mn and m = anion charge. All compounds were characterized by spectroscopic and analytical techniques. These studies indicated that both the polyoxometalates and the cations are present in the solids without major alterations. Cyclic voltammetry studies were performed for compounds with 1-butyl-3-methylimidazolium. Disregarding the loss of crystallization or coordinated water, the compounds were found to be stable up to near 300 °C. The onset of the decomposition of the organic cations, as determined by thermogravimetry, occurred in the 300–350 °C range. The metal-substituted polyoxoanions are stable up to around 300 °C, but after this temperature the anions transform into the parent $[PW_{12}O_{40}]^{3-}$ anion, with loss of the substituting metal. Final decomposition to a mixture of oxides occurred only above 600 °C. It was also possible to obtain the crystalline compounds $Na_2K(Bmim)_2[PW_{11}O_{39}Co(H_2O)]\cdot 7.5H_2O$ and $Na(Bmim)_4[PW_{11}O_{39}Co(H_2O)]\cdot 2H_2O$ and determine their structures by single crystal X-ray diffraction.

Compounds with substituted imidazolium cations and metal-substituted polyoxometalates are expected to present a set of properties that make them interesting in many fields, like catalysis. This study aimed at contributing to the understanding the effect of altering the substituting metal and the counter-cation in the properties of this type of compounds.

1. Introduction

Transition metal-substituted polyoxometalates (TMSP) have been studied for several years due to an assortment of properties and possible applications in fields as diverse as catalysis, materials science, and medicine [1–9]. Many TMSP may be viewed as complexes of transition metal ions with lacunary Keggin or Dawson anions as ligands. They include mono-, di- and trisubstituted polyoxotungstates, such as α-$[XW_{11}O_{39}M(H_2O)]^{n-}$, γ-$[SiW_{10}O_{38}M_2(H_2O)_2]^{n-}$ and α-$[XW_9O_{37}M_3(H_2O)_3]^{n-}$ (X = P, Si, As, etc., M = transition or *p*-block metal) and many other anionic species with a large variety of composition and structural arrangements [1,3,10,11]. The use of TMSP units in the building up of complex architectures, frequently in combination with organic and coordination entities, led to the development of new materials with particular properties and applications [2,6,8,12].

In the last three decades or so, *N*,*N*′-dialkylimidazolium cations, in conjunction with a variety of anions, have been used in the preparation of ionic liquids (ILs), substances that are entirely composed by ions and melt at temperatures below 100 °C [13]. The association of *N*,*N*'-dialkylimidazolium cations with polyoxometalates (POMs) usually does not lead to the formation of ionic liquids. Yet, several compounds with these cations and Keggin-type anions have been synthetized. The majority contains parent Keggin anions, like $[PW_{12}O_{40}]^{3-}$ [14–18], $[SiW_{12}O_{40}]^{4-}$ [19–21] or $[PMo_{12}O_{40}]^{3-}$ [18,21–27]. Studies with lacunary or transition metal substituted Keggin polyoxometalates are much less abundant [28–32]. Two of these studies describe iron-monosubstituted polyoxotungstates, with either 1,3-dimethylimidazolium [28] or 1-*n*-butyl-3-methylimidazolium (Bmim) cations [32]. Another paper reports the use in catalysis of several compounds formulated as

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$(Bmim)_x[PW_{11}O_{39}M]\cdot 3H_2O$ (M^{II} = Mn, Co, Ni, Cu, Zn, M^{III} = Cr, Fe), but, except for the compound with M = Zn, the characterization data are not presented [31].

Following our interest in the catalytic activity of metal-monosubstituted Keggin polyoxotungstates, $[XW_{11}O_{39}M(H_2O)]^{n-}$, X = P, Si, B, M = 1st row transition metal [33–36], we have previously studied the reaction of the iron-monosubstituted polyoxotungstates with Bmim [32]. Here, we report the formation of new organic-inorganic hybrid salts with metal-substituted phosphotungstates and Bmim or 1-*n*-octyl-3-methylimidazolium (Omim) cations. Compounds with the formula $(cat)_{5-x}H_x[PW_{11}O_{39}Co^{II}(H_2O)]\cdot nH_2O$, cat = Bmim ($x = 0$, $n = 0.5$), Omim ($x = 1$, $n = 1$), and $(cat)_4[PW_{11}O_{39}M^{III}(H_2O)]\cdot nH_2O$, cat = Bmim (M = Mn, $n = 1$), Omim (M = Fe, $n = 1$ or Mn, $n = 0$) were obtained and fully characterized by spectroscopic techniques (FTIR, UV–Vis, DRS, ^{1}H NMR, ^{31}P NMR and ^{31}P MAS NMR), thermal analysis, cyclic voltammetry and magnetic moment determination. Crystal structures of $Na_2K(Bmim)_2[PW_{11}O_{39}Co(H_2O)]\cdot 7.5H_2O$ and $Na(Bmim)_4[PW_{11}O_{39}Co(H_2O)]\cdot 2H_2O$ were determined by X-ray diffraction.

The combination of *N,N'*-dialkylimidazolium cations and 1st row transition metal-substituted polyoxotungstates is predicted to lead to new materials with interest to catalysis, electrocatalysis and sensors, among other possible applications.

2. Experimental

2.1. Reagents and synthetic procedures

All chemicals were used as received from the suppliers. The polyoxotungstates were prepared in aqueous solution by procedures adapted from the literature [37–39]. Addition of (Bmim)Br or (Omim)Br to those solutions lead to the immediate precipitation of powders with low crystallinity or amorphous, as shown by powder X-ray diffraction. The prepared compounds are sparingly soluble in water, but soluble in organic solvents like acetonitrile and dimethylsulfoxide.

*$(Bmim)_5[PW_{11}O_{39}Co^{II}(H_2O)]\cdot 0.5H_2O$ (**1**).* A solution of $CoCl_2\cdot 6H_2O$ (0.90 g; 3.78 mmol; 5 cm^3 H_2O) was added dropwise to a heated solution containing $Na_3[PW_{12}O_{40}]\cdot 21H_2O$ (10.52 g; 3.16 mmol; 50 cm^3 H_2O). KOH or NaOH was added to the filtrate until pH 5–5.5. After the adjustment of pH, (Bmim)Br was added (3.4 g; 15.5 mmol; 5 cm^3 H_2O) and a carmine precipitate immediately appeared. The precipitate was separated, washed with cold water and dried in a desiccator over silica gel. Yield: 7.78 g, 68%. Melting point: 210 °C. IR (cm^{-1}): ν_{as}(P–O), 1073 (s), 1055 (s), ν_{as}(W–O_d), 951 (vs), ν_{as}(W–O_b–W), 885 (vs), ν_{as}(W–O_c–W), 816 (s), 796 (s), ν_{as}(W–O_c–Co), 749 (vs), 704 (m), ν(P–O), 509 (m). *Anal.* (%): Found (calc.) for $C_{40}H_{78}CoN_{10}O_{40.5}PW_{11}$: C, 13.33 (13.89); H, 2.39 (2.27); N, 4.05 (4.05); hydration H_2O, 0.3 (0.3); total weight loss (%TG), 21.5 (22.01). μ_{eff} = 5.5 μ_B.

*$Na_2K(Bmim)_2[PW_{11}O_{39}Co(H_2O)]\cdot 7.5H_2O$ (**1b**).* Small pink single crystals suitable for X-ray diffraction were obtained from the mother liquid on standing, when KOH was used for the pH adjustment.

*$Na(Bmim)_4[PW_{11}O_{39}Co(H_2O)]\cdot 2H_2O$ (**1c**).* Crystals suitable for monocrystal X-ray diffraction were obtained from the mother liquid on standing when the synthesis was performed as for **1** but using NaOH for the pH adjustment and 4.8 g (21.9 mmol; 10 cm^3 H_2O) of (Bmim)Br. In these conditions the precipitated material was the same as **1**.

*$(Bmim)_4[PW_{11}O_{39}Mn^{III}(H_2O)]\cdot H_2O$ (**2**).* A solution of $MnSO_4\cdot H_2O$ (0.70 g; 4.14 mmol; 10 cm^3 H_2O) was added to a heated solution containing $Na_3[PW_{12}O_{40}]\cdot 21H_2O$ (10.52 g; 3.08 mmol; 50 cm^3 H_2O). After the adjustment of pH to 5–5.5 as for compound **1**, a solution of $K_2S_2O_8$ (1.27 g; 4.70 mmol; 5 cm^3 H_2O) was added in order to oxidize Mn^{II} to Mn^{III}. The resulting solution was stirred for 30 min at 85–90 °C, to insure the complete oxidation of the Mn^{II} cation, and then cooled down to room temperature. The subsequent addition of (Bmim)Br (3.4 g; 15.5 mmol; 5 cm^3 H_2O) resulted in the precipitation of a dark raspberry powder. This precipitate was separated, washed with cold water and dried in a desiccator over silica gel. Yield: 7.30 g, 71%. Melting point: 220 °C. IR (cm^{-1}): ν_{as}(P–O), 1089 (s), 1072 (s), ν_{as}(W–O_d), 962 (vs), ν_{as}(W–O_b–W), 883 (vs), ν_{as}(W–O_c–W), 798 (vs), δ(P–O), 507 (m). *Anal.* (%): Found (calc.) for $C_{32}H_{64}MnN_8O_{41}PW_{11}$: C, 10.34 (11.56); H, 1.80 (1.94); N, 3.38 (3.37); hydration H_2O, 0.6 (0.5); total weight loss (%TG), 17.8 (18.1). μ_{eff} = 4.8 μ_B.

*$(Omim)_4[PW_{11}O_{39}Fe^{III}(H_2O)]\cdot H_2O$ (**3**).* A solution of $Fe(NO_3)_3\cdot 9H_2O$ (0.758 g; 1.876 mmol; 5 cm^3) was added dropwise to a heated solution containing $Na_3[PW_{12}O_{40}]\cdot 21H_2O$ (5.26 g; 1.54 mmol; 25 cm^3 H_2O). After cooling to ambient temperature and filtration of the formed yellow precipitate, the pH of the solution was adjusted to 5–5.5 with KOH or NaOH. During the base addition, a fine brick-colored powder appeared which was separated by centrifugation. A re-adjustment of pH was made followed by the addition of (Omim)Br (1.92 g; 6.98 mmol; 5 cm^3 H_2O). A yellow precipitate immediately appeared, which was separated and washed with cold water and dried in a desiccator over silica gel. Yield: 4.03 g, 74%. Melting point: 220 °C. IR (cm^{-1}): ν_{as}(P–O), 1063 (s), ν_{as}(W–O_d), 959 (s), ν_{as}(W–O_b–W), 886 (s), ν_{as}(W–O_c–W), 808 (vs). *Anal.* (%): Found (calc.) for $C_{48}H_{96}FeN_8O_{41}PW_{11}$: C, 16.76 (16.24); H, 2.71 (2.73); N, 3.32 (3.16); hydration H_2O, 0.4 (0.5); total weight loss (%TG), 24.2 (23.9). μ_{eff} = 5.5 μ_B.

*$(Omim)_4H[PW_{11}O_{39}Co^{II}(H_2O)]\cdot H_2O$ (**4**).* The procedure was similar to the described for compound **1**. A solution of $CoCl_2\cdot 6H_2O$ (0.41 g; 1.72 mmol; 5 cm^3 H_2O) was added dropwise to a heated solution containing $Na_3[PW_{12}O_{40}]\cdot 21H_2O$ (5.26 g; 1.54 mmol; 25 cm^3 H_2O). (Omim)Br (2.34 g; 8.50 mmol; 5 cm^3 H_2O) was used instead of (Bmim)Br. A carmine precipitate was obtained. Yield: 3.92 g, 72%. Melting point: 215 °C. IR (cm^{-1}): ν_{as}(P–O), 1074 (sh), 1058 (s), ν_{as}(W–O_d), 953 (s), ν_{as}(W–O_b–W), 886 (s), ν_{as}(W–O_c–W), 817 (vs), 794 (vs), ν_{as}(W–O_c–Co), 747 (s), 707 (s). *Anal.* (%): Found (calc.) for $C_{48}H_{97}CoN_8O_{41}PW_{11}$: C, 16.36 (16.22); H, 2.69 (2.75); N, 3.24 (3.15); hydration H_2O, 0.5 (0.5); total weight loss (%TG), 21.5 (24.1). μ_{eff} = 5.2 μ_B.

*$(Omim)_4[PW_{11}O_{39}Mn^{III}(H_2O)]$ (**5**).* The procedure was similar to the described for compound **2**, using (Omim)Br instead if (Bmim)Br. The following solutions were used: $MnSO_4\cdot H_2O$ (0.28 g; 1.65 mmol; 5 cm^3 H_2O); $Na_3[PW_{12}O_{40}]\cdot 21H_2O$ (5.25 g; 1.54 mmol; 25 cm^3 H_2O); $K_2S_2O_8$ (0.653 g; 2.35 mmol; 5 cm^3 H_2O); (Omim)Br (1.92 g; 6.98 mmol; 5 cm^3 H_2O). A dark magenta precipitate was obtained. Yield: 3.99 g, 73%. Melting point: 220 °C. IR (cm^{-1}): ν_{as}(P–O), 1087 (s), 1073 (vs), ν_{as}(W–O_d), 964 (s), ν_{as}(W–O_b–W), 885 (s), ν_{as}(W–O_c–W), 801 (s), 781 (sh). Anal. (%): Found (calcd.) for $C_{48}H_{94}MnN_8O_{40}PW_{11}$: C, 16.09 (16.32); H, 2.62 (2.68); N, 3.20 (3.17); total weight loss (%TG), 24.4 (23.5). μ_{eff} = 5.0 μ_B.

2.2. Instrumentation and methods

C, H, N elemental analyses, thermogravimetric analysis and differential scanning calorimetry were carried out as described in [32]. The values of the total weight loss (%TG) were calculated assuming decomposition to a mixture of oxides at the end of the experiment (700 °C). Melting points were determined on a Barnstead Electrothermal A9100 apparatus, with a temperature ramp rate of 5 °C min^{-1}. For combined thermal decomposition/FTIR studies, spectra were obtained after heating each sample in an oven at a heating rate of 5 °C min^{-1} to a predetermined temperature and a stabilization period of 45 min. A small portion was then taken out and allowed to cool down to room