From the First Sulfurated Keggin Anion to a New Class of Compounds Based on the $\left[\text{M}_2\text{O}_2\text{S}_2\right]^{2+}$ Building Block $\text{M=Mo, W}$

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Abstract. Different strategies of synthesis were developed to introduce sulfur atoms in a polyoxometalate framework. Every synthetic route provides new and specific sulfur-containing compounds, characterized by single crystal X-ray diffraction and multinuclear NMR spectroscopy in solution. The first investigations based on conventional routes of synthesis give predictable oxo-thio Keggin-like clusters while an original strategy, based on the acid-base self-condensation of an oxo-thio building block is the origin of a new generation of polymetalates. Finally, under hydrothermal conditions, successive replacements of sulfur atoms by oxygen atoms take place and unexpected molecular associations between fully oxygenated saturated Keggin anions were obtained.

Keyword: Polyoxothiometalates, cyclic cluster, molybdenum, $^{31}\text{P}$ NMR, $^{183}\text{W}$ NMR

1 Introduction

The synthesis of large and discrete species resulting from transition metal and chalcogenide combinations is still an exciting challenge for the inorganic chemist since this prominent class of compounds is involved in many areas of science and these compounds are often studied for their model character, especially in the field of magnetochemistry, bio-inorganic chemistry, and theoretical problems in materials [1,2]. Such systems display also potential applications in heterogeneous catalysis and in oxidation as in acidic processes [3-5]. Many studies involve the model character of polyoxometalates (POMs) to mimic the reactivity of metal oxide surface as their catalytic properties and their ability to bind covalently functional groups. Conversely, alumina-supported molybdenum and tungsten are industrially used in the hydrotreating of crude oils and the activation of dihydrogen [6,7]. An approach of the catalytic mechanisms consists to regard the molecular Mo-S associations as functional analogues of the active surface of $\text{MoS}_2$ [8,9]. Although a large number of thio- and oxothio-molybdates were reported in the literature [10], most of these compounds are structurally based on archetypal architectures with low nuclearity ranging from the simplest mononuclear anion, $\left[\text{MoO}_{4}\text{S}_n\right]^2$ (with $n=1$ to $4$) to some tetrnuclear oxothiomolybdates such as in the dimeric $\left[\text{Mo}_2\text{O}_4\text{S}_4\right]^2$ anions [11] or in the cubane-like cluster $\left[\text{Mo}_4\text{S}_4\text{CN}\right]^5$ [12]. The first step for the preparation of these compounds is generally the direct sulfurization which provides thioanions, precursors for more sophisticated species via reactions with electrophiles ($\text{H}^+$ or $\text{Cu}^+$) [13,14], and nucleophiles (cyanide or trialkyl phosphine) [15,16]. Conversely, the functionalization of POMs through the replacement of oxo ligands by functional groups (i.e nitrosyl, organometallic fragment and organic substituant) are still of current interest [17]. On this basis the introduction of sulfur atoms in a polyanionic framework is expected to
this basis the introduction of sulfur atoms in a polyanionic framework is expected to modify both the electronic and chemical properties. To complete this stimulating challenge, we have combined polyoxometalate and thiometalate chemistries and developed successively three types of syntheses. The first method we used to introduce sulfur in a polyoxoanionic framework was inspired from the previous work of Klemperer and co-worker [18] and is illustrated here by the synthesis of \( \alpha-\{\text{PW}_{11}\text{NbSO}_4\}^{4+} \). The thio-functionalized anion was obtained by direct reaction of the saturated oxo-parent with an adequate sulfurating agent. Another elegant way consists in the stereo-specific addition of an adapted-preformed thiofragment to polyvacant heteropolyanions. The dinuclear thio-fragment \([\text{M}_2\text{S}_2\text{O}_3]^{3+}\) (M=W, Mo) exhibits interesting properties, especially a good hydrolytic stability, coordination requirements, size and cationic character. Thus, the expected heteropolyoxothiometalates are built on well-defined structural types and exhibit molecular structures imposed by the nature of the polyvacant anion. Depending on the complementarities (geometry, symmetry and coordination requirements) between the POM and the thio-fragment, saturated or sandwich-like compounds have been obtained and characterized. Nevertheless, the compounds designed through this method have a very low sulfur content, always limited by the low nuclearity of the thio-fragment with respect to those of the lacunary oxo-precursors. So, we have now engaged a new Strategy, based on the one-step self-condensation of the \([\text{M}_2\text{S}_2\text{O}_3]^{3+}\) sulfur containing building-block. The self-condensation reaction is relevant of acido-basic process and is performed by controlled addition of hydroxide ions to an aqueous solution of the building block. The polycondensation reaction can be monitored in the presence of structurating agent giving the first members of a new class of compounds directly derived from the \([\text{Mo}_3\text{S}_2\text{O}_2]\) building block [19].

2 Sulfur in Keggin heteropolyanions

2.1 SULFURIZATION OF PREFORMED KEGGIN UNIT

Introduction of sulfur in polyoxothioanions by direct oxygen-sulfur exchange appeared difficult because the substitution was often accompanied by reduction of the metal centers. The change of both the charge and the coordination of the metal center during the O/S exchange process appeared unfavourable to retain the polyanionic framework and led to the breaking of the POM architecture. The sensible use of the mixed \( \alpha-\{\text{PW}_{11}\text{NbO}_4\}^{4+} \) anion avoids these difficulties because the increase of the negative

Fig. 1. Schematic representation of the O/S substitution in the oxo \( \alpha-\{\text{PW}_{11}\text{NbO}_4\}^{4+} \) parent