

Characterization of Keggin's Type Polyoxometalates with Multiple Metal-Nitrogen Bonds by Ion-Trap Mass Spectrometry

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Polyoxometalates, also called polyanions, are clusters made of high oxidation state metals as tungsten (VI), molybdenum (VI) or vanadium (V), linked together by oxo ligands. Lindqvist's and Keggin's are two well-known families of polyanions. The Lindqvist's (respectively Keggin's) type structure has the general formula $[M_6O_{19}]^{n-}$ (resp. $[XM_{12}O_{40}]^{n-}$) where M is the metal and X is an heteroatom. We are interested in the functionalization of polyoxometalates, which formally consists of replacing an oxo ligand by an organic one. In the Lindqvist serie, both the imido ($[Mo_5O_{18}\{Mo^V NAr\}]^{2-}$) [1] and the hydrazido ($[Mo_5O_{18}\{Mo^V N_2(Ph)(Me)\}]^{2-}$) [2] derivatives are known. In order to functionalize Keggin's type polyanions, two methods have been considered: (i) incorporation of a {metal-ligand} function into a lacunary Keggin's compound of the general formula $[XM_{11}O_{39}]^{n-}$; (ii) direct reaction of a complete polyoxometalate with an appropriate organic reagent. The resulting products were studied under negative and positive modes electrospray ion-trap mass spectrometry [3] and sequential MSⁿ experiments (Bruker Esquire 3000).

The first method was tested in the reaction of $[Re^V(NPh)Cl_3(PPh_3)_2]$ with the well-known lacunary Keggin's species $[(n-Bu)_4N][H_3PW_{11}O_{39}]$. By this synthetic procedure, we were able to prepare the imido derivative $[(n-Bu)_4N][PW_{11}O_{39}\{Re^V(NPh)\}]$, which is obtained as a mixture with $[(n-Bu)_4N][PW_{11}O_{39}\{Re^VO\}]$. Under soft declustering conditions, the mass spectrum showed two main signals at m/z 985 and m/z 960 attributed respectively to $[HPW_{11}O_{39}\{Re^V(NPh)\}]^{3-}$ and $[HPW_{11}O_{39}\{Re^VO\}]^{3-}$. In a lower extent, two peaks are observed corresponding to $[H_2PW_{11}O_{39}\{Re^V(NPh)\}]^{2-}$ m/z 1477 and $[(n-Bu)_4N][HPW_{11}O_{39}\{Re^V(NPh)\}]^{2-}$ m/z 1596. Under these conditions, the structure of the polyanion and its functionalization are maintained in the gas phase. Interestingly, the isolation of m/z 985 induces the formation of m/z 1477 involving that the triply charged species were able to trap a proton. Such behavior can be explained by considering that water molecules are present in the bath gas of the ion trap cell. Using a higher declustering potential, low mass-to-charge ratio ions are displayed at m/z 326 and m/z 251 which were attributed to $[Re^VII(NPh)O_3]^-$ and $[Re^VII(O)_3]^-$. The former confirms the presence of the metal-nitrogen multiple bond.

The direct reaction of a complete polyoxometalate with an appropriate organic reagent has been applied to the reaction of $[(n-Bu)_4N][PW_{11}O_{39}\{Mo^VO\}]$ with 2,6-dimethyl- or 2,6-diisopropylaniline or N,N-dimethyl- or N-methyl-N-phenylhydrazine in the presence of DCC (dicyclohexylcarbodiimide), and pyridine (in the case of anilines) in distilled acetonitrile. This second procedure results in the reduction of the polyanion. Under soft declustering conditions, it was possible to observe signals at m/z 930, 1396, 1517, 1639, 3032, 3274 and 3514 respectively assigned to $[HPW_{11}O_{39}\{Mo^VO\}]^{3-}$, $[H_2PW_{11}O_{39}\{Mo^VO\}]^{2-}$, $[(n-Bu)_4N][HPW_{11}O_{39}\{Mo^VO\}]^{2-}$, $[(n-Bu)_4N]_2[PW_{11}O_{39}\{Mo^VO\}]^{2-}$, $[(n-Bu)_4N][H_2PW_{11}O_{39}\{Mo^VO\}]$, $[(n-Bu)_4N]_2[HPW_{11}O_{39}\{Mo^VO\}]^-$ and $[(n-Bu)_4N]_3[PW_{11}O_{39}\{Mo^VO\}]$. The CID spectrum of m/z 1517 revealed signals at m/z 1396 and at m/z 1424. The latter can be attributed to the fragmentation of the $[(n-Bu)_4N]^+$ counter-ion linked with the polyoxometalate onto $H^+ + [But-H] + NBut_3$, which demonstrates its reactivity and interactions. The MS/MS of m/z 1639 gave analogous results displaying signals corresponding to fragmentation of $[(n-Bu)_4N]^+$ cation. The MS spectra in negative mode indicates clearly that the direct reaction of the complete polyanion $[(n-Bu)_4N][PW_{11}O_{39}\{Mo^VO\}]$ with either an aniline or an hydrazine does not lead to the functionalized expected products. Nevertheless ¹H NMR experiments displayed unattributed signals. In order to rationalize this observation, positive mode mass spectrometry was undertaken. In the corresponding spectrum, in addition to the expected signal at m/z 242 for the $[(n-Bu)_4N]^+$ cation, a new signal attributed to an other organic cation derived from the anilin or hydrazin oxidised and condensed with DCC appears.

ESI-MS and low energy CID are efficient methods to discriminate between functionalized polyanions and organic counter-cations.

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 [3] M.J. Deery, O.W. Howarth, K.R. Jennings, *J. Chem. Soc., Dalton Trans.*, **1997**, 4783.

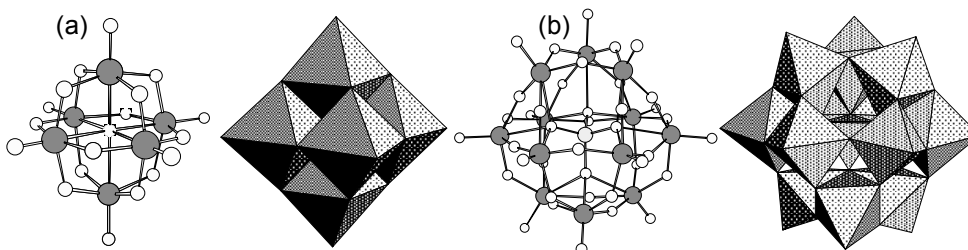


Figure 1: Ball and stick and polyhedral view of (a) Lindqvist's and (b) Keggin's type polyoxometalates.

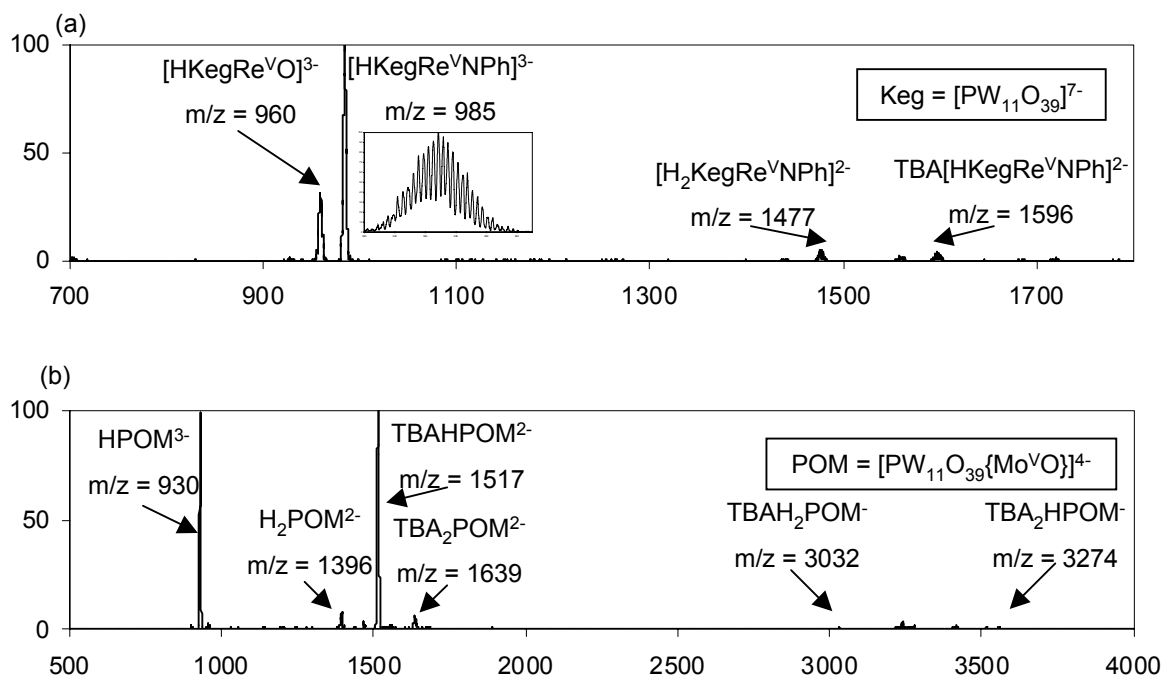


Figure 2: Negative mode electrospray mass spectrum of a 10 pmol/μL MeCN solution of (a) $[\text{PW}_{11}\text{O}_{39}\{\text{Re}^{\text{V}}(\text{NPh})\}]^{4-}$ and (b) $[\text{PW}_{11}\text{O}_{39}\{\text{Mo}^{\text{VO}}\}]^{4-}$ recorded under low declustering conditions.

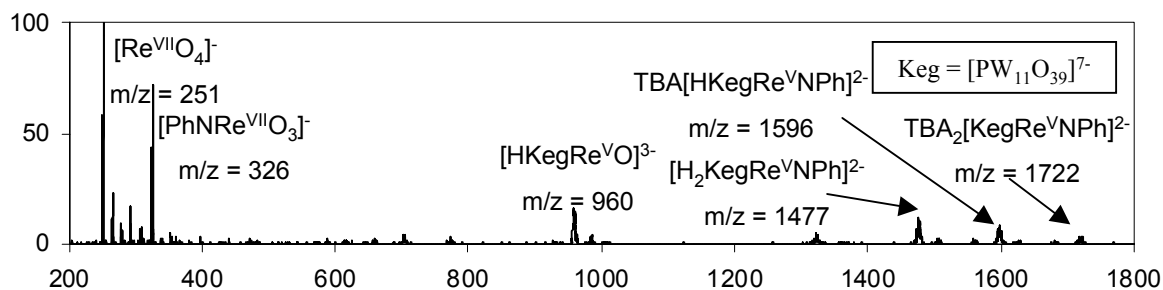


Figure 3: Negative mode electrospray mass spectrum of a 10pmol/μL MeCN solution of $[\text{PW}_{11}\text{O}_{39}\{\text{Re}^{\text{V}}(\text{NPh})\}]^{4-}$ recorded under higher declustering conditions.