



Electrospray ionization mass spectrometry of a cerium(III) phosphomolybdate complex: Condensed and gas-phase cluster chemistry

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ABSTRACT

Electrospray ionization quadrupole ion trap mass spectrometry (ESI-QIT/MS) of the ammonium cerium(III) phosphomolybdate complex $(\text{NH}_4)_{11}[\text{Ce}(\text{III})(\text{PMo}_{11}\text{O}_{39})_2]$ in aqueous media has revealed a concentration-dependent behavior. Under fixed instrumental parameters, the Ce-containing polyoxomolybdate complexes $\text{H}_2\text{Ce}(\text{III})\text{P}_2\text{Mo}_{22}\text{O}_{75}^{3-}$ and $\text{Ce}(\text{III})\text{PMo}_{11}\text{O}_{38}^{2-}$ are the primary species present at 11 mM (pH = 4.3); at 0.7 mM (pH = 3.6), $\text{Ce}(\text{III})\text{PMo}_{10}\text{O}_{35}^{2-}$ is the predominant species, $\text{Ce}(\text{III})\text{PMo}_{11}\text{O}_{38}^{2-}$ is quite diminished, and $\text{H}_2\text{Ce}(\text{III})\text{P}_2\text{Mo}_{22}\text{O}_{75}^{3-}$ is absent. As a result of the complex isotopic fingerprints from multiple molybdenums, compositions of such ions are difficult to assign—successive collision induced dissociation (CID) of large ions produced smaller ions for which calculated and experimental isotopic patterns could be compared. The oxidation state of Ce and the number of counter cations on negative complexes was discerned from spectra of ions containing $^1\text{H}^+$ and $^7\text{Li}^+$. The overall result is an ESI method applicable to phosphomolybdate complexes containing redox sensitive *f*-block metal ions such as Ce(IV) and Pu(III/IV). Dissociation studies also gave insight into favored fragmentation pathways, and generated gas ions with empirical formulae similar to known condensed-phase ions. Deconvolution of concentration- and pH-dependent solution behavior via ESI/MS and ^{31}P NMR spectroscopy showed speciation dependent on solution concentration, not on pH.

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1. Introduction

Polyoxometalates (POMs), metal-oxide clusters built from octahedral MO_6 units (typically $\text{M}=\text{Mo}(\text{VI})$ or $\text{W}(\text{VI})$), have been extensively studied due to their wide array of applications [1]. The complex behavior of iso- and heteropolyoxometalates during transference from solution to gas has been determined from investigations via electrospray ionization mass spectrometry (ESI/MS) [2–11]. ESI, while a “soft” process in principle, has the potential to cause structural and chemical transformations of solution species during ion formation and transport. Concentration and pH changes during desolvation of aqueous droplets can induce structural changes in chemically sensitive molecules [12]. Ion-pairing and addition or loss of neutral species are possible consequences of ESI, and can increase the overall mass/charge ratio (m/z) [12]. An example of this effect is the protonation of surface oxygens and subsequent loss of neutral H_2O molecules from lacunary Keggin ions, e.g., $\text{PMo}_{11}\text{O}_{39}^{7-} + 4\text{H}^+ \rightarrow \text{PMo}_{11}\text{O}_{37}^{3-} + 2\text{H}_2\text{O}$, which has been shown to be an effective method of reducing the charge of these POM ligands during the spray process [9]. Intriguing concentration-dependent behavior has also been reported by Bon-

chio et al., where Keggin ions reform through the formal uptake of $[\text{WO}]^{4+}$ by $\text{PW}_{11}\text{O}_{39}^{7-}$ in dilute solutions of $\text{Li}_7\text{PW}_{11}\text{O}_{39}$ [10]. The inherent electrochemistry of ESI can be used, for example, to employ the different redox properties of nickel and cobalt porphyrins for their independent detection from solution mixtures [13]. An additional ancillary complication of ESI is that fragmentation may occur during ion transport, prior to collection inside the ion trap. As a result of these potential ESI and gas-phase effects, it is common to observe numerous species resulting from a single solution precursor [12]. Until recently, collision induced dissociation (CID) results reported for POMs have focused on the preferred gas-phase degradation pathways of lacunary and plenary Keggin phosphotungstates. The recent seminal work of Ma et al. established a systematic approach to studying the CID fragmentation of these anions, as well as of the mixed metal Keggin derivatives $\text{Co}(\text{II})\text{PW}_{11}\text{O}_{38}^{2-}$ and $\text{Fe}(\text{III})\text{PW}_{11}\text{O}_{39}^{2-}$, the Dawson-Wells derivative $\text{Co}(\text{II})\text{P}_2\text{W}_{17}\text{O}_{59}^{4-}$, and the Tourné sandwich anion derivative $\text{Co}(\text{II})_4\text{P}_2\text{W}_{18}\text{O}_{65}^{4-}$ [11].

The potential presence of Keggin-based phosphomolybdate anions in nuclear waste spurred systematic solution and solid state investigations into their complexation of trivalent lanthanides [14,15]. These compounds form metal:ligand complexes, with the stoichiometries largely dependent on the metal-to-ligand ratios used during synthesis [16]. In the case of the **1:2** complex, $(\text{NH}_4)_{11}[\text{Ce}(\text{PMo}_{11}\text{O}_{39})_2]$, the structure has been determined and

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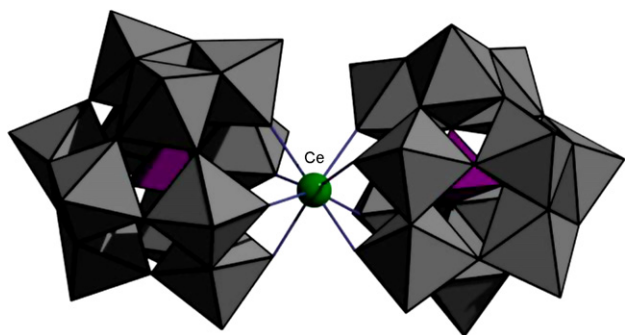


Fig. 1. Polyhedral representation of the solid state 1:2 Ce-phosphomolybdate complex $[\text{Ce}(\text{PMo}_{11}\text{O}_{39})_2]^{11-}$ [14].

reveals the Ce(III) metal ion resides in the vacancy of two lacunary phosphomolybdates (Fig. 1). This structure-type is found across the trivalent lanthanide series, as well as for the tetravalent metals Ce(IV) and Th(IV). Comparison of solution and solid-state IR and ^{31}P NMR provide evidence that these complexes are stable in solution and as solids. Although this system has been studied extensively in the condensed-phase [17,18], little has been reported regarding the gas-phase chemistry of POM-coordinated *f*-block metal complexes. However, ESI has been used as a characterization tool for lanthanide-phosphotungstate complexes [19]; the results reveal that these complexes can indeed be transferred to the gas phase, concurrent with evaporation of water to deplete surface POM oxygens [19]. We report the ESI behavior of the trivalent lanthanide lacunary phosphomolybdate complex $(\text{NH}_4)_{11}[\text{Ce}(\text{III})(\text{PMo}_{11}\text{O}_{39})_2]$. Methods for identifying prominent cerium-phosphomolybdate species and determining the number of counter cations are described, which enables verification of the cerium oxidation state, Ce(III) or Ce(IV). A notable result is that these ligands stabilize cerium with respect to redox activity throughout the ionization and ion transport processes. An overarching goal of this work is to promote ESI/MS as a complementary investigative tool, along with solution and solid state spectroscopic and structural characterizations, for large inorganic complexes.

2. Experimental

2.1. Synthesis and preparation of complexes

Polyoxometalate salts were prepared as previously described: $(\text{NH}_4)_{11}[\text{Ln}(\text{PMo}_{11}\text{O}_{39})_2]$, Ln(III)POM where Ln = Ce, Pr, Eu or Tm [14,15,17]. In summary [15], $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ was dissolved in H_2O with stirring and the pH adjusted by the addition of Li_2CO_3 to 4.3 to yield $[\text{PMo}_{11}\text{O}_{39}]^{7-}$ as the dominant phosphomolybdate species. Ln(III)(NO_3) $_3 \cdot 6\text{H}_2\text{O}$ was then added in a stoichiometric 2:1 $\text{PMo}_{11}:\text{Ln}(\text{III})$ ratio, resulting in a drop of ~ 1 pH unit. The pH was adjusted back to 4.3 by the addition of Li_2CO_3 and NH_4Cl . As in the previous work [15], ^{31}P NMR was used to confirm that the complex anion was present in solution. No free ligand was observed in solutions produced from precipitated Ln(III)POM salts. H_2O used in preparation of all solutions was microfiltered to 0.22 μm and purified to 18.5 M Ω using a Gradient A-10 Milli-Q distiller. All solutions were filtered with 0.2 μm nylon microfilters prior to ESI/MS or ^{31}P NMR measurements.

2.2. In situ dilution

Gaunt et al. reported crystalline structures corresponding to $(\text{NH}_4)_{11}[\text{Ln}(\text{PMo}_{11}\text{O}_{39})_2] \cdot 16\text{H}_2\text{O}$ [14]; Copping et al. subsequently reported that bulk Ln(III)POM samples contain somewhat more water [15], as in $(\text{NH}_4)_{11}[\text{Ce}(\text{PMo}_{11}\text{O}_{39})_2] \cdot 21\text{H}_2\text{O}$. In computing the

solution concentrations, we employ the extent of hydration determined by Copping et al. [15] for materials prepared and handled under similar conditions as ours; although the reported absolute concentrations are considered uncertain by up to $\sim 10\%$, the relative concentrations of the diluted solutions are accurate to within $< 5\%$. 11.2 mM Ce(III)POM solutions (pH = 4.4) were prepared by dissolving 60 mg Ce(III)POM in 1.3 mL H_2O . A syringe of the 11.2 mM solution was injected into the MS and spectra were acquired. The solution in the syringe was diluted by a factor of four, i.e. 20 μL 11.2 mM Ce(III)POM was diluted to 80 μL 2.8 mM by drawing 60 μL H_2O into the syringe; mixing was ensured by ejecting the solution into a small vial and redrawing it into the syringe. A 0.70 mM Ce(III)POM solution was similarly prepared by dilution of the 2.8 mM solution. In view of the concentration uncertainties, the concentrations of the three primary Ce(POM) solutions are referred to as 11 mM, 3 mM and 0.7 mM. Solutions of Ce(III)POM were also prepared at 3 mM (pH = 3.9) and 0.7 mM (pH = 3.6) by diluting an 11 mM stock solution. Additionally, 1.2–1.3 mM solutions of Ln(III)POM (Ln = Pr, Eu, and Tm) were prepared by dissolving 5.2 mg, 5.4 mg, and 5.0 mg of each salt, respectively in 1 mL H_2O .

2.3. pH dependence

The pH of an 11.2 mM solution of Ce(III)POM was adjusted with 0.1% HCl to values of 4.43, 3.96, 3.60, 3.20, and 2.84. Subsequent to each pH adjustment, an aliquot was removed for ESI/MS and a ^{31}P NMR spectrum was acquired from the remaining solution. Each pH adjustment equated to an addition of 1–2 drops of acid, thereby minimizing variations in the concentration of Ce(III)POM.

2.4. Concentration dependence

An 11.2 mM solution was diluted with water to concentrations of 5.6 mM, 1.1 mM, 0.56 mM, and 0.11 mM. After each dilution, the solution pH was adjusted back to 4.3 with 0.1% HCl or 1% NH_4OH . ESI/MS and ^{31}P NMR spectra were taken in a similar manner as with the pH dependence experiments.

2.5. Effect of metal:ligand ratio

ESI/MS and ^{31}P NMR spectra were taken before and after addition of one equivalent of Ce as $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to an 11.3 mM solution of Ce(III)POM. The solution pH was adjusted back to 4.3 with 0.1% HCl and 1% NH_4OH .

2.6. ESI/MS

Experiments were performed with an Agilent 6340 Quadrupole Ion Trap (QIT) mass spectrometer with MS n CID capabilities. In high resolution mode, the instrument has a detection range of 50–2200 m/z and resolution of $\sim 0.25 m/z$. Mass spectra were recorded in the negative ion detection mode. Spectra were taken with the following instrumental parameters: solution flow rate, 60 $\mu\text{L}/\text{min}$; nebulizer gas pressure, 15 psi; capillary voltage and current, 3500 V, 4.883 nA; end plate voltage offset and current, -500 V, 10 nA; dry gas flow rate, 5 l/min; dry gas temperature, 325 $^\circ\text{C}$; capillary exit, -100 V; skimmer, -40 V; octopoles 1 and 2 DC, -12.00 V and -1.70 V; octopole RF amplitude, 108.9 Vpp; lenses 1 and 2, 5.0 V and 60.0 V; trap drive range, 99–149. Solutions were directly injected into the electrospray capillary using a syringe pump. Nitrogen gas was supplied from a vapor–liquid nitrogen dewar. CID experiments were performed using the He trapping gas; tickling voltages ranged between 0.30 V and 1.50 V, applied for 40 ms. The instrumental parameters were chosen to optimize the mass spectral intensity and resolution. No systematic study of the effects of drying gas temperature (or other instrumental parameters) was performed;

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