RAMAN AND INFRARED SPECTROSCOPIC INVESTIGATION OF In(OH)$_2$$_6^{3+}$(aq).

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**Abstract:** Raman and infrared spectra of aqueous In(III)- perchlorate, nitrate and sulfate solutions have been measured and the different aqua In$^{3+}$ complexes with nitrate and sulfate have been characterised. The modes of the [In(OH)$_2$$_6^{3+}$] ion (in acidified perchlorate solution only) have been assigned. Ab initio geometry optimizations and frequency calculations are reported for In(III) – water clusters including a second hydration sphere.

The behaviour of metal ions in aqueous solution is of quintessential interest in many fields, including biochemistry, mineralogy and geochemistry, industrial chemistry, and environmental chemistry. The measurement of Raman spectra of aqueous solutions, supplemented by ab initio computational chemistry [1-9], has helped to resolve many uncertainties regarding the nature of the metal ion in aqueous solution, such as the coordination number of lithium [1] and scandium [6], and supported traditional physicochemical and structural measurements of other metals. For ion pairing [6b], it is also important to understand the nature of the anion [10-11]. We report here our studies of the aqueous indium(III) cation.

Raman and infrared spectra of aqueous In(III)- perchlorate, - nitrate and -sulfate solutions were measured. The Raman spectrum on In(III)- perchlorate solutions reveals a strongly polarized mode of medium intensity at 487 cm$^{-1}$ and two depolarized modes at 410 cm$^{-1}$ and 306 cm$^{-1}$. These modes have been assigned to $\nu_1(a_{1g})$, $\nu_2(e_g)$ and $\nu_5(f_{2g})$ of the hexaaquaindium(III) ion, [In(OH)$_2$$_6^{3+}$] (O$_h$ symmetry), respectively. The infrared active mode at 472 cm$^{-1}$ has been assigned to $\nu_3(f_{1u})$. The Raman spectroscopic data suggest that the hexaaquaindium(III) ion is thermodynamically stable in acidified perchlorate solution only have been assigned. Ab initio geometry optimizations and frequency calculations are reported for In(III) – water clusters including a second hydration sphere.

In a concentrated In(NO$_3$)$_3$ solution, indium(III) can exist in the form of both an inner-sphere complex, [In(OH)$_2$$_5$ONO$_2$]$^{2+}$ and an outer-sphere complex [In(OH)$_2$$_6^{3+}$ NO$_3$$^-$. Upon dilution the inner-sphere complex dissociates and the amount of the outer-sphere complex increases. In a dilute solution most indium occurs as [In(OH)$_2$$_6^{3+}$] and unbound nitrate. The nitrato complex is thermodynamically weak and completely disappears upon dilution.

Indium sulfate solutions show a different picture and a thermodynamically stable indium(III) sulfato complex could be detected using Raman spectroscopy and 115-In NMR. The formation of the sulfato complex is favoured with increase in temperature and thus entropically driven. At higher temperatures a basic indium(III) sulfate of the alunite type is precipitated and was characterised by wet chemical analysis and X - ray diffraction (XRD). Ab initio geometry optimizations and frequency calculations of [In(OH)$_2$$_n^{3+}$] clusters with $n$ equal to 1 to 6 were carried out at the Hartree-Fock and second order Møller- Plesset levels of theory, using various basis sets up to 6-31+G*. The global minimum structure of the aqua In(III) species was reported. The unscaled
vibrational frequencies of the $\text{[In(OH}_2\text{)]}_6^{3+}$ cluster were reported and do not correspond well with experimental values because of the missing second hydration sphere. The theoretical binding enthalpy for $\text{[In(OH}_2\text{)]}_6^{3+}$ was calculated and accounts for ca. 60% of the experimental single ion hydration enthalpy for In(III).

*Ab initio* geometry optimizations and frequency calculations are also reported for the $\text{[In(OH}_2\text{)]}_{18}^{3+}$ cluster (In[6+12]) with 6 water molecules in the first sphere and 12 water molecules in the second sphere (T symmetry). The calculated $\nu_1(\text{InO}_6)$ mode of the Indium [6+12] cluster occurs at 483 cm$^{-1}$ (HF/6-31G*), and is in good agreement with the experimental value at 488 cm$^{-1}$, as are the other frequencies. The theoretical binding enthalpy for $\text{[In(OH}_2\text{)]}_{18}^{3+}$ was calculated and slightly underestimates the experimental single ion hydration enthalpy of In(III).

References: