The Affinity of Indium(III) for Nitrogen-donor Ligands in Aqueous Solution. A Study of the Complexing of Indium(III) with Polyamines by Differential Pulse Voltammetry, Density Functional Theory, and Crystallography

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Dedicated to Prof. Helgard G. Raubenheimer on the occasion of his 65th birthday

The affinity of In(III) for N-donor ligands was investigated by differential pulse voltammetry, DFT calculations, and crystallography. The structure of $[In(tpen)(CH_3COO)](ClO_4)_2 \cdot 0.5\,H_2O$ (**1**) is reported (tpen = N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine): Monoclinic, $P2_1/n$, $a = 8.687(4)$, $b = 7.767(8)$, $c = 20.432(10)$ Å, $\beta = 93.372(8)°$, $Z = 4$, $R = 0.0518$. The In(III) center is 7-coordinate, with six In–N bonds to the tpen ligand in the range $2.306 - 2.410$ Å, and a unidentate acetate group with In–O = 2.247 Å. The formation constants of In^{3+} in 0.1 M $NaNO_3$ at 25 °C are (M = In(III), L = ligand, H = proton): L = triethylenetetramine, $\log\beta(MLH_2) = 25.3 \pm 0.3$, $\log K_1 = 14.43 \pm 0.09$, and $\log\beta(ML(OH)_2) = 27.7 \pm 0.1$; tetraethylenepentamine, $\log\beta(MLH) = 20.8 \pm 0.2$, and ML ($\log\beta(ML) = 20.1 \pm 0.3$); diglycolic acid, ($\log\beta(MLH) = 8.06 \pm 0.06$), $\log K_1 = 6.02 \pm 0.06$, $\log\beta_2 = 9.40 \pm 0.08$; tpen, $\log K_1 = 17.71 \pm 0.07$; N,N'-bis(2-pyridylmethyl)ethylenediamine, $\log K_1 = 14.69 \pm 0.05$; 1,10-phenanthroline, $\log K_1 = 6.81 \pm 0.07$, $\log K_2 = 6.44 \pm 0.07$, $\log K_3 = 6.20 \pm 0.08$. Correlations are shown between the determined formation constants for the polyamines and $\log K_1(NH_3)$ values for a wide variety of metal ions. For M(II) ions, the $\log K_1(NH_3)$ values are experimental data, but for M(III) ions the data are predicted by an empirical dual-basicity equation, including $\log K_1(NH_3) = 4.0$ for In(III). DFT calculations are used to obtain ΔE for the reaction $[M(H_2O)_6]^{n+} + NH_3 \leftrightarrows [M(H_2O)_5NH_3]^{n+} + H_2O$ for M(II) through M(IV) ions in water, represented as a structureless medium with the dielectric constant of water. Correlations are found that support the predicted value of $\log K_1(NH_3)$ for In(III) of 4.0. The nature of the intercepts on such correlations are discussed.

Key words: Indium, Formation Constants, Polarography, Nitrogen Donor Ligands