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Trivalent Actinide Ions Showing Tenfold Coordination in Solution

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Trivalent actinides generally exhibit ninefold coordination in solution. nPr-BTP, a tridentate nitrogen donor ligand, is known to form ninefold coordinated 1:3 complexes, $[\text{An}(\text{nPr-BTP})_3]^{3+}$ (An = U, Pu, Am, Cm) in solution.

We report the first Cm(III) complex with tenfold coordination in solution $[\text{Cm}(\text{nPr-BTP})_3(\text{NO}_3)]^{2+}$. This species was identified using time-resolved laser fluorescence spectroscopy (TRLFS), vibronic side band spectroscopy (VSBS), X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT).

Adding nitrate to a solution of the $[\text{Cm}(\text{nPr-BTP})_3]^{3+}$ complex in 2-propanol shifts the Cm(III) emission band from 613.1 nm to 617.3 nm. This bathochromic shift is due to a higher coordination number of the Cm(III) ion in solution, in agreement with the formation of the $[\text{Cm}(\text{nPr-BTP})_3(\text{NO}_3)]^{2+}$ complex. No such shift is observed when adding other anions (NO_2^- , CN^- and OTf^-).

The formation of the $[\text{Cm}(\text{nPr-BTP})_3(\text{NO}_3)]^{2+}$ complex was studied as a function of NO_3^- and nPr-BTP concentrations. Slope analyses confirm the addition of one nitrate anion to the $[\text{Cm}(\text{nPr-BTP})_3]^{3+}$ complex. Experiments with varied nPr-BTP concentration show that $[\text{Cm}(\text{nPr-BTP})_3(\text{NO}_3)]^{2+}$ only forms at nPr-BTP concentrations below 10^{-4} mol/L. For concentrations greater than 10^{-4} mol/L only $[\text{Cm}(\text{nPr-BTP})_3]^{3+}$ is observed.

VSBS allows observing vibrations of coordinated functional groups. The vibronic side band of the $[\text{Cm}(\text{nPr-BTP})_3(\text{NO}_3)]^{2+}$ species exhibits a nitrate stretching mode not observed in the $[\text{Cm}(\text{nPr-BTP})_3]^{3+}$ complex. Moreover, XPS on $[\text{Am}(\text{nPr-BTP})_3(\text{NO}_3)]^{2+}$ yields signals from both non-coordinated and coordinated nitrate. DFT calculations reveal that the energetically most favoured structure is obtained if the nitrate is positioned on the C_2 axis of the D_3 symmetrical $[\text{Cm}(\text{nPr-BTP})_3]^{3+}$ complex with a bond distance of 413 pm.

Combining results from TRLFS, VSBS, XPS and DFT provides sound evidence for a unique tenfold coordinated Cm(III) complex in solution - a novelty in An(III) solution chemistry.

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