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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,  $[An(nPr-BTP)_3]^{3+}$  (An = U, Pu, Am, Cm) in solution.

We report the first Cm(III) complex with tenfold coordination in solution  $[Cm(nPr-BTP)_3(NO_3)]^{2+}$ . 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  $[Cm(nPr-BTP)_3]^{3+}$  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  $[Cm(nPr-BTP)_3(NO_3)]^{2+}$  complex. No such shift is observed when adding other anions (NO<sub>2</sub><sup>-</sup>, CN<sup>-</sup> and OTf<sup>-</sup>).

The formation of the  $[Cm(nPr-BTP)_3(NO_3)]^{2+}$  complex was studied as a function of  $NO_3^-$  and nPr-BTP concentrations. Slope analyses confirm the addition of one nitrate anion to the  $[Cm(nPr-BTP)_3]^{3+}$  complex. Experiments with varied nPr-BTP concentration show that  $[Cm(nPr-BTP)_3(NO_3)]^{2+}$  only forms at nPr-BTP concentrations below  $10^{-4}$  mol/L. For concentrations greater than  $10^{-4}$  mol/L only  $[Cm(nPr-BTP)_3]^{3+}$  is observed.

VSBS allows observing vibrations of coordinated functional groups. The vibronic side band of the  $[Cm(nPr-BTP)_3(NO_3)]^{2+}$  species exhibits a nitrate stretching mode not observed in the  $[Cm(nPr-BTP)_3]^{3+}$  complex. Moreover, XPS on  $[Am(nPr-BTP)_3(NO_3)]^{2+}$  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  $[Cm(nPr-BTP)_3]^{3+}$  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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