Electronic Supporting Information

Evidence of covalence in N-donor complex of Americium(III)

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1.) LIFDI-MS spectra of $^{15}$N-labelled compounds

a. 2,6-Bis(carboximidhydrazide)pyridine.

![Graph showing LIFDI-MS spectra of 2,6-Bis(carboximidhydrazide)pyridine.](Image)

Fig. S1 MS (LIFDI) of 2,6-Bis(carboximidhydrazide)pyridine in CH$_3$OH, 10% $^{15}$N-enrichment at secondary and primary amine position; ion mode: FD+; detail m/z range 155 to 235; m/z (M)$^+$ 193.18, (M+H)$^+$ 194.18, m/z ($^{15}$N)$_2$M)$^+$ 195.19.

![Graph showing comparison of MS (LIFDI) spectra of 2,6-Bis(carboximidhydrazide)pyridine.](Image)

Fig. S2 Comparison of the MS (LIFDI) spectra of 2,6-Bis(carboximidhydrazide)pyridine in CH$_3$OH. Left: no isotopic labeling, right: 10% $^{15}$N-enrichment at secondary and primary amine position; ion mode: FD+ detail m/z range 186 to 199; m/z (M)$^+$ 193.19, m/z ($^{15}$N)$_2$M)$^+$ 195.20.
b. 2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine.

Fig. S3 MS (LIFDI) of 2,6-Bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine in CH₃OH, 10% $^{15}$N-enrichment at position 8 and 9; ion mode: FD+ detail m/z range 365 to 457; m/z (M)$^+$ 405.36, m/z (M+H)$^+$ 406.36, m/z ($^{15}$N)₂M)$^+$ 407.36, m/z ($^{15}$N)₄M)$^+$ 409.33.
2.) 1D $^{15}$N direct excitation spectrum of $[\text{Eu}^{15}\text{N}_2-\text{nPrBTP}]_3(\text{NO}_3)_3$

Fig. S4: Direct excitation 1D $^{15}$N spectrum of $^{15}$N-labelled $[\text{Eu}(\text{nPrBTP})_3]\text{([NO}_3)_3$ in 450 µL MeOD-d4 and 150 µL D$_2$O. Due to fast relaxation (PRE) of coordinated N$_8$, no signal for that nucleus was obtained. N$_1$ and N$_{12}$ are not $^{15}$N labelled and thus cannot be observed; the observed resonance signal corresponds to N$_9$. Acquisition details: TD 8k data points, relaxation delay D1 0.01 s, sweep width 4000 ppm, spectral offset 650 ppm, pre-scan delay 12.5 µs to avoid probehead ringing. Processing: window function em, 10 Hz line broadening, zero filling to 16k data points, linear back prediction of the first 128 data points out of all 8k datapoints to correct baseline distortions due to the wide sweep.
3.) 1D- and 2D-NMR spectra of \([^{243}\text{Am}(n\text{PrBTP})_3](\text{NO}_3)_3\)

Fig. S5 $^1\text{H}$ spectrum of \([^{243}\text{Am}(n\text{PrBTP})_3](\text{NO}_3)_3\) in MeOD-d4 and D$_2$O (3:1). The spectra have excellent resolution. Although the complex was found to be paramagnetic, the chemical shift is in the diamagnetic range with a linewidth (FWHM) of 1.9 Hz.

Fig. S6 Proton decoupled direct excitation $^{13}\text{C}$ spectrum of \([^{243}\text{Am}(n\text{PrBTP})_3](\text{NO}_3)_3\) in MeOD-d4 and D$_2$O (3:1).
Fig. S7 $^{15}$N spectrum of $^{15}$N-labelled $[^{243}\text{Am}(n\text{PrBTP})_3](\text{NO}_3)$ in MeOD-d$_4$ and D$_2$O (3:1). To emphasize the differences between complexed (red) and uncomplexed (blue) ligand and to preclude any possible effects of free $^{243}$Am, a slight excess of ligand in the sample was used. From the narrow linewidth in all spectra, we conclude that no exchange between bound and free ligand occurs, since this would lead to significant line broadening. Insets are expanded view of the $N_8$ and $N_9$ signals.

Fig S8 $^1$H, $^{13}$C-gHMBC of $[^{243}\text{Am}(n\text{PrBTP})_3](\text{NO}_3)_3$ in MeOD-d$_4$ and D$_2$O (3:1). The good resolution and high S/N at $J = 10$Hz allows complete assignment of all $^{13}$C resonances, including all quaternary carbon atoms.
Fig. S9 $^1$H,$^{15}$N-gHMQC spectrum of the doubly $^{15}$N-labelled nPrBTP in $^{243}$Am(nPrBTP)$_3$(NO$_3$)$_2$] in MeOD-d$_4$ and D$_2$O (3:1). Resonance signals from the complex are labelled in red, residual signals from uncomplexed ligand are in blue and labelled with an *.

Fig. S10 $^1$H,$^{15}$N-gHMQC spectrum of $^{243}$Am(nPrBTP)$_3$(NO$_3$)$_3$ in MeOD-d$_4$ and D$_2$O (3:1) at natural abundance of $^{15}$N. No resonances from free ligand are observed.