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Comparative NMR study of *n*PrBTP and *i*PrBTP

Christian Adam[a,*], Viktoria Rohde[b], Udo Müllich[a], Peter Kaden[c], Andreas Geist[a], Petra J. Panak[a,d], Horst Geckeis[a]

[a]*Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Herrmann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*
[b]*Fraunhofer Institute for Chemical Technology (ICT), Environmental Engineering, Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany*
[c]*Helmholtz-Zentrum Dresden - Rossendorf e. V., Institute of Resource Ecology, Bautzner Landstrasse 400, 01328 Dresden, Germany*
[d]*University of Heidelberg, Department of Physical Chemistry, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany*

Abstract

Bistriazinyl-pyridine type ligands are important extracting agents for separating trivalent actinide ions from trivalent lanthanides. The alkyl substituents on the lateral triazine rings have a significant effect on the stability of the ligand against hydrolysis and radiolysis. Furthermore they influence solubility, extraction behaviour and selectivity. TRLFS and extraction studies suggest differences in complexation and extraction behaviour of BTP ligands bearing *iso*-propyl or *n*-propyl substituents, respectively. As NMR studies allow insight into the metal-ligand bonding, we conducted NMR studies on a range of ^{15}N-labelled *n*PrBTP and *i*PrBTP Ln(III) and Am(III) complexes. Our results show that no strong change in the metal-ligand bonding occurs, thus excluding electronic reasons for differences in complexation behaviour, extraction kinetics and selectivity. This supports mechanistic reasons for the observed differences.

Keywords: NMR Spectroscopy, Bonding, Extraction, BTP, An(III)/Ln(III) separation

* Corresponding author. Tel.: +49 721 608 24900.
  E-mail address: christian.adam@kit.edu

1. Introduction

In order to reduce the long-term radiotoxicity and heat load of spent nuclear fuel as well as for reducing the need for mining large amounts of uranium ores for the production of nuclear fuel, actinide recycling strategies are currently under discussion. [1, 2] These strategies require the separation of actinides from fission products. The greatest challenge in this context is the separation of trivalent actinide ions, An(III), from the trivalent fission lanthanide ions, Ln(III). This separation necessitate highly selective extracting agents, as An(III) and Ln(III) are very similar in chemical properties and ionic radii. Nevertheless, this separation can be performed by liquid-liquid extraction using selective N-donor extracting agents, such as alkylated bis-triazinyl pyridines (BTP). [3-5] They have high separation factors (>100) for trivalent americium over europium. The molecular reason for the selectivity is still not entirely understood.
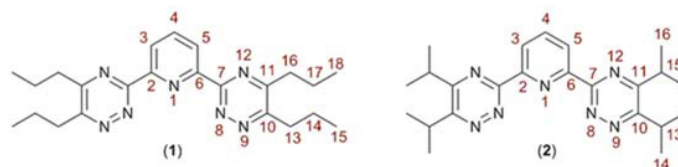

Fig. 1: Structures of nPrBTP (1) and iPrBTP (2) with the used numbering scheme

A wide variety of BTP-type ligands has been synthesized and characterized so far. [6, 7] Among these, *n*PrBTP (**1**) and its Ln(III) and An(III) complexes have been studied extensively by various spectroscopic methods and extraction tests. [7-9] The ligand shows a high selectivity for the complexation of An(III) over Ln(III) ions and forms stable ML_3 complexes, but is labile towards hydrolysis in nitric acidic solutions and radiolysis. The isomer *i*PrBTP (**2**) shows improved stability. [10] This ligand forms stable ML_3 complexes with trivalent actinides and lanthanides as well. However, substantially higher complex stability constants were found for Ln(III) compared to the *n*PrBTP complexes, as well as unexpected complexing and extraction kinetics. [7, 10-13]

Recent studies on *i*PrBTP complexes with Cm(III), which were conducted in our group, propose differences in the mechanism of complex formation for the An(III) *i*PrBTP and *n*PrBTP complexes due to differences in the solvation of both complexes. This concept is supported by TRLFS studies as well as quantum-chemical calculations. [14]

These differences in the hydration sphere will only have a weak influence on the electronic structures of the complexes, which are thus expected to closely resemble each other. NMR spectroscopy has been shown recently to give valuable insights into metal ligand bonding and electronic structure in *n*PrBTP and C5-BPP-complexes [15-17]. As the chemical shift is sensitive to the electron density surrounding a nucleus in diamagnetic complexes, changes in the electron distribution in the metal-ligand bond reflect in significant changes of the chemical shifts. This effect is particularly pronounced for the coordinating atoms. To overcome the unfavourable NMR properties of [15]N (low, negative gyromagnetic ratio, low natural abundance of 0.37 %), we synthesized *i*PrBTP with ^{15}N labelling in the vicinal nitrogen atoms of the triazine ring (*cf*. fig. 2). With this ligand in hand, we prepared complexes of the diamagnetic lanthanide ion Lu(III), as well as of Y(III). We also prepared the Sm(III) complex, which is weakly paramagnetic, and the more strongly paramagnetic Eu(III) *i*PrBTP complex. By comparison of the ^{15}N chemical shifts of these complexes to those of the respective *n*PrBTP complexes, the electronic contribution to the differences in ligand behaviour is evaluated.

2. Results and Discussion

2.1. Ln(III) complexes

The chemical shifts of the nitrogen atoms in *n*PrBTP and *i*PrBTP complexes are summarized in table 1. A comparison of the shift values for the free ligand and the diamagnetic Y(III) and Lu(III) complexes shows that the

coordination of a metal ion has a significant influence on the electron distribution in the ligands. The shift differences between the free and the complexed ligand are about 35 ppm for N_1 and 40 ppm for N_8. For the non-coordinating N_9, differences are smaller (13 ppm in *n*PrBTP, 8 ppm in *i*PrBTP), even more for N_{12} (about 4 ppm for both ligands). Effects on the carbon backbone of the ligands and on the proton chemical shifts are less pronounced. These results confirm that the coordination of a metal cation has the strongest effect on the directly coordinating atoms, as it is expected.

Table 1: [15]N chemical shifts in the free ligands and metal complexes of *i*PrBTP (left) and *n*PrBTP (right) at 300 K. Values are given in ppm, *n*PrBTP data are taken from references [16] and [17].

Metal	$\delta(N_1)$	$\delta(N_8)$	$\delta(N_9)$	$\delta(N_{12})$	$\delta(N_1)$	$\delta(N_8)$	$\delta(N_9)$	$\delta(N_{12})$
---	303	353	403	288	303	347	394	289
Y	267	310	390	292	268	307	386	293
Lu	270	312	390	293	269	309	386	293
Sm	227	263	387	293	226	261	383	293
Eu	---	-1389	353	283	---	-1391	353	284
[243]Am	-31	-16	421	289	-26	-18	418	289

The profound influence of paramagnetism on chemical shifts is evident on the nitrogen shifts in the Sm(III) complex. Although Sm(III) is only weakly paramagnetic with a measured effective magnetic moment of 1.64 μ_B at room temperature [18], additional paramagnetic chemical shifts of about 40 ppm for N_1 and 50 ppm for N_8 arise compared to the diamagnetic compounds. With a measured effective magnetic moment of 3.36 μ_B, Eu(III) is more paramagnetic than Sm(III). [18] This reflects in the stronger paramagnetic relaxation enhancement (PRE), which accounts for the invisibility of the N_1 resonance signal, as well as the stronger paramagnetic shift of the N_8 atoms, in both complexes approximately 1700 ppm. This paramagnetic chemical shift, often referred to as Knight shift, consists of two contributions: Fermi contact shift (FCS) is due to electron spin transfer through covalent bonds. Pseudo contact shift (PCS) originates in the coupling of the unpaired electron magnetic moments and the nuclear spins, and depends on the molecular geometry and the distance between the cation and the observed nucleus. [19-22] While the Knight shift is appreciable for the coordinating nuclei, the non-coordinating nitrogen atoms in the ligands are hardly affected, with N_9 in the Sm(III) complex showing a Knight shift of 3-4 ppm, and N_{12} less than 1 ppm.

As FCS is transferred through covalent bonds, it rapidly decreases along a chain of connected nuclei. In the Eu(III) complexes, the coordinating nuclei N_8 show a very strong chemical shift, whereas N_9 are only shifted about 35 ppm relative to the diamagnetic complexes. This indicates that an appreciable amount of FCS is present on the directly coordinating nuclei. This interpretation is further substantiated by results of temperature-independent model free methods which allow the separation of FCS and PCS. [23] Our results clearly indicate that even for Ln(III) complexes covalent contributions in the bonding between trivalent metal ions and organic ligands are not negligible.

2.2. Am(III) complex

Recent experiments employing the Evans NMR method for the determination of the magnetic susceptibilities for trivalent actinide ions show that Am(III) is not diamagnetic, as expected from a $J = 0$ ground state, but has an effective magnetic moment of 1.42 μB [24, 25]. A paramagnetic chemical shift approximately in the magnitude of Sm(III) is thus expected. However, the resonance signals for the coordinating nitrogen atoms in the Am(III) complexes show a chemical shift of -16 to -31 ppm, *i.e.* about 300 ppm relative to the diamagnetic Lu(III) complex.

This represents a paramagnetic chemical shift of remarkable extent, much stronger than expected from the magnetic moment of the ion. Compared to the strong paramagnetic shifts of the N_1 and N_8 atoms, only a small paramagnetic chemical shift is registered for N_9. As for the lanthanide complexes, this indicates that a significant part of the shift on the coordinating nuclei originates from FCS and thus covalence is a significant contribution to the chemical bond between Am(III) and the N-donor ligands. The extent of the paramagnetic shifts proves a stronger covalent interaction between Am(III) and the ligands in comparison to the Ln(III) complexes. For the quantitative determination of the degree of covalence in actinide-ligand bonding, a broader set of data for complexes with ligands of different complexation strengths and with systematic variations of the ligand motive, as well as a deeper understanding of the theoretical foundations on the effects of covalence in NMR spectra is needed.

Regarding the different complexation properties of the two ligands, the two complex series show little difference in the chemical shifts of *n*PrBTP and *i*PrBTP complexes. For both ligands, the paramagnetic chemical shift for a given metal ion has the same sign and is of comparable magnitude. With only a few exceptions, the shift difference compared to the free ligand or the Lu(III) complex is slightly larger for the *i*PrBTP complexes than for the *n*PrBTP complexes, yet the shifts differ in most cases by less than 5 ppm. As the trend follows the observed complexation strength, it can be concluded that the variation in electronic structure has some influence on the bonding, yet the differences are small in comparison to the overall paramagnetic or complexation shifts and cannot explain the differences in the complexation behaviour. Our results indicate that the bonding in *i*PrBTP and *n*PrBTP complexes is fairly similar, and thus substantiate the notion that differences in complexation behaviour originate in the different solvation of the complexes, which is affecting the complexation mechanisms strongly.

3. Conclusion and Outlook

We used NMR spectroscopy to study a series of ^{15}N-labelled *i*PrBTP complexes with different Ln(III) ions and [243]Am(III) to elucidate the origin of differences in extraction and complexation behaviour to the closely related ligand isomer *n*PrBTP. Our results clearly show that the electronic structures of the complexes of the two ligands are highly similar. Observed differences are too small to explain the distinct differences in complex formation and extraction. Indeed, this is supported by recent quantum chemical analysis of the complexation reaction in our group: As the bulkier *i*PrBTP effectively block escape pathways for water molecules from the hydration sphere of the M(III) ions, the structural differences in the aliphatic side chains influence the hydration of the ML_3 complex, thus explaining the differences in complex stability and extraction kinetics. [14]

Furthermore, we show that NMR spectroscopy offers a wealth of valuable data regarding metal ligand bonding. For example, the results prove that even in Ln(III) complexes covalence has an important contribution to the overall bonding, as covalently transferred spin density (FCS) is detected on the coordinating nitrogen atoms. As this effect is significantly stronger in the Am(III) complexes, this is in excellent agreement with predictions on the higher covalence of actinide compounds being the reason for the observed ligand selectivity for the complexation of An(III) over Ln(III).

4. Experimental Section

4.1. General

All NMR spectra were recorded at T = 300 K on a Bruker Avance III 400 spectrometer operating at 400.18 MHz for ^{1}H, 100.63 MHz for ^{13}C and 40.56 MHz for [15]N. The spectrometer was equipped with a *z*-gradient broadband observe probe optimized for *x*-magnetization detection. Chemical shifts are referenced internally to TMS (δ(TMS) = 0 ppm). [15]N chemical shifts are referenced to [15]NH_4Cl with $\delta(NH_4Cl) = 0$ ppm by the lock signal. For all direct excitation and correlation spectra, standard Bruker pulse sequences were used. All 1D spectra except for the Eu(III) complex were recorded with 32k data points and are zero-filled to 64k points. The reported chemical shifts are taken from 1D spectra unless stated otherwise. [15]N data from ^{1}H,[15]N-gHMQC spectra are labelled with an asterisk (*).

Deuterated solvents were purchased from Euriso-Top GmbH. Chemicals for synthesis were purchased from VWR International and used as-is. ^{15}N-labelled hydrazine hydrate (98% [15]N) was purchased from Sigma-Aldrich

and used as-is. Melting points were measured using a Stuart SMP30 melting point apparatus. All mass spectra were recorded at the mass spec facility of the Institute of Organic Chemistry at the University of Heidelberg. Mass spectra using EI ionization mode were recorded using a JEOL AccuTOF GCx instrument coupled to an AGILENT 7890B GC system. GC conditions were: Injector temperature 250°C, column: 30 m HP-5, 0.320 mm diameter, 0.25 μm film. Temperature was 30°C initially for 3 minutes, which was raised by 20°C/min up to 280°C. Mass spectra using ESI ionization methods were recorded using a Bruker ApexQe FT-ICR instrument.

4.2. Synthesis of ^{15}N-labelled ligands

The strategy for the synthesis of ^{15}N-labelled iPrBTP is given in fig. 2. The synthesis is an adapted version of the original synthesis [26] and the synthesis of ^{15}N-labelled *n*PrBTP. [16]
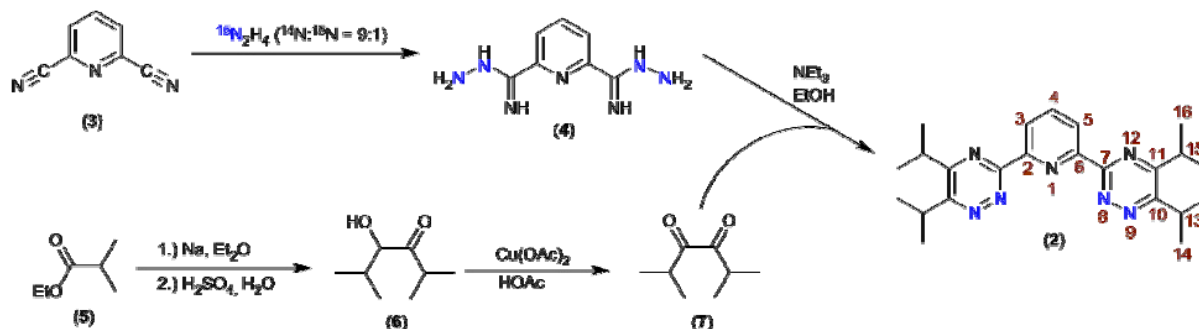
Fig. 2: Synthesis and ^{15}N labelling scheme for *i*PrBTP.

4.2.1. ^{15}N-2,6-Bis(carboxyimidhydrazide)pyridine

A solution of 248 mg (1.92 mmol) 2,6-dicyanopyridine and 1.0 g hydrazine hydrate (20.0 mmol, 90 mol% [14]$N_2H_4 \cdot H_2O$, 10 mol% [15]$N_2H_4 \cdot H_2O$) in 10 mL ethanol was stirred for 24 h at room temperature. The resulting white precipitate was filtrated off the yellowish solution and washed three times with 10 mL portions of ice-cold water. The white, crystalline product (**4**) (220 mg, 1.14 mmol, 59 %) was dried in high vacuum.

^{1}H-NMR (400.18 MHz, DMSO-d6): δ [ppm] = 7.87 (d, 2H, H_3, H_5, $^3J_{H3/5-H4}$ = 7.7 Hz), 7.71 (t, 1H, H_4, $^3J_{H4-H3/5}$ = 7.7 Hz), 6.10 (broad signal, 3H), 5.33 (broad signal, 3H).
^{13}C-NMR (100.63 MHz, DMSO-d6): δ [ppm] = 150.7 (C_q), 143.9 (C_q), 136.1 (C_t, C_4), 118.2 (C_t, $C_{3/5}$).
^{15}N-NMR (40.56 MHz, DMSO-d6): δ [ppm] = 285 (N_1)*, 253 (N-H)*, 95 (d, N-H_2).

4.2.2. Synthesis of 2,5-Dimethyl-3,4-hexandione

Synthesis of (**6**) followed an established procedure [27]. For the oxidation to (**7**) the isobutyroin (**6**) (3.53 g, 24.5 mmol) were dissolved in 80 mL acetic acid (70 %) and 11.0 g Cu(II) acetate monohydrate (55.0 mmol) were added. The solution was refluxed for 10 minutes and allowed to cool to room temperature. Water (80 mL) was added and the solution was extracted with three 40 mL portions of diethyl ether. The combined organic phases were washed with saturated Na_2CO_3 solution (25 mL) and saturated $NaHCO_3$ solution (40 mL) until a colour change from green to yellow indicated neutral reaction. The ether solution was dried with $MgSO_4$. Distillation (20 mbar, 70°C) yielded the desired product as a yellow oil (2.02 g, 14.2 mmol, 58 %).

^{1}H-NMR (400.18 MHz, CDCl₃): δ [ppm] = 3.35 (sept, 2H, CH, $^3J_{H-H}$ = 7.0 Hz), 1.09 (d, 12H, CH_3, $^3J_{H-H}$ = 7.0 Hz).
^{13}C-NMR (100.63 MHz, CDCl₃): δ [ppm] = 204.2 (C_q, CO), 34.1 (C_t, CH), 17.3 (C_p, CH_3).

MS (EI$^+$): m/z calculated for $C_8H_{14}O_2$ [M]$^+$ 142.09883, found 142.09926; calculated for C_4H_7O [M - (CH$_3$)$_2$CHCO]$^+$ 71.04914, found 71.04931; calculated for C_3H_7 [M - (CH$_3$)$_2$CHCO – CO]$^+$ 43.05423, found 43.05496.

4.2.3. Synthesis of ^{15}N-labelled i*PrBTP*

Under an argon atmosphere 240 mg (1.24 mmol) ^{15}N-bis(carboximidhydrazide)pyridine (**4**) was dissolved in 10 mL dry ethanol. 2,5-Dimethyl-3,4-hexanedione (600 mg, 4.16 mmol) diluted with 5 mL dry ethanol were added and the solution was stirred for 30 minutes at room temperature. 0.1 mL Triethylamine were added and the solution was refluxed overnight. The solvent was removed by distillation (1 mbar, 90°C). The waxy yellow residue was purified by two recrystallization steps from diisopropyl ether to yield the desired product (**2**) (0.69 mmol, 56%) as a brightly yellow crystalline solid.

^{1}H-NMR (400.18 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 8.66 (d, 2H, H$_3$, H$_5$, $^3J_{H3/5-H4}$ = 7.8 Hz), 8.29 (t, 1H, H$_4$, $^3J_{H4-H3/5}$ = 7.9 Hz), 3.65 (sept, 2H, H$_{13}$, $^3J_{H13-H14}$ = 6.8 Hz), 3.54 (sept, 2H, H$_{15}$, $^3J_{H15-H16}$ = 6.7 Hz), 1.51 (d,12H, H$_{14}$, $^3J_{H14-H13}$ = 6.8 Hz), 1,47 (d, 12H, H$_{16}$, $^3J_{H16-H15}$ = 6.7 Hz).

^{13}C-NMR (100.63 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 168.4 (C$_q$, C$_{11}$), 165.3 (C$_q$, C$_{10}$), 161.8 (C$_q$, C$_7$), 154.5 (C$_q$, C$_6$), 140.0 (C$_t$, C$_4$), 126.8 (C$_t$, C$_{3/5}$), 32.0 (C$_t$, C$_{15}$), 31.1 (C$_t$, C$_{13}$), 22.3 (C$_p$, C$_{14}$), 21.7 (C$_p$, C$_{16}$).

^{15}N-NMR (40.56 MHz, MeOD-d4/D$_2$O 3:1) δ [ppm] = 402 (N$_9$)*, 353 (N$_8$), 303 (N$_1$)*, 288 (N$_{12}$)*.

MS (ESI$^+$, CH$_3$OH): m/z calculated for $C_{23}H_{32}N_7$ [M+H]$^+$ 406.27137, found 406.27230; calculated for $C_{23}H_{31}N_7Na$ [M+Na]$^+$ 428.25332, found 428.25426; calculated for $C_{46}H_{62}N_{14}Na$ [2M+Na]$^+$ 833.51741, found 833.51943.

4.3. Synthesis of the Ln(i*PrBTP*)$_3$(NO$_3$)$_3$ complexes

4.3.1. General procedure

6 μmol of the lanthanide salt Ln(NO$_3$)$_3$·xH$_2$O were dissolved in 150 μL D$_2$O and heated until dry. This process was repeated three times to minimize the H$_2$O content of the salts. *i*PrBTP (**2**) (7.29 mg, 18 μmol) was dissolved in 450 μL MeOD-d4 and added to the dry lanthanide salt. The complex solution was transferred to an NMR tube and 150 μL D$_2$O were added. The sample was degassed by three freeze-pump-thaw-cycles and the NMR tube was subsequently flame sealed.

4.3.2. Y(i*PrBTP*)$_3$(NO$_3$)$_3$

^{1}H-NMR (400.18 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 9.11 (d, 2H, H$_3$, H$_5$, $^3J_{H3/5-H4}$ = 8.0 Hz), 8.64 (t, 1H, H$_4$, $^3J_{H4-H3/5}$ = 8.0 Hz), 3.41 (sept, 2H, H$_{15}$, $^3J_{H15-H16}$ = 6.7 Hz), 3.31 (sept, 2H, H$_{13}$, $^3J_{H13-H14}$ = 6.8 Hz), 1.39 (d, 6H, H$_{16a}$, $^3J_{H16a-H15}$ = 6.7 Hz), 1.33 (d, 6H, H$_{16b}$, $^3J_{H16b-H15}$ = 6.6 Hz), 0.77 (d, 6H, H$_{14a}$, $^3J_{H14a-H13}$ = 6.7 Hz), 0.48 (d, 6H, H$_{14b}$, $^3J_{H14b-H13}$ = 6.7 Hz).

^{13}C-NMR (100.63 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 172.0 (C$_q$, C$_{11}$), 166.1 (C$_q$, C$_{10}$), 163.7 (C$_q$, C$_7$), 152.7 (C$_q$, C$_6$), 144.2 (C$_t$, C$_4$), 129.1 (C$_t$, C$_{3/5}$), 32.5 (C$_t$, C$_{15}$), 30.4 (C$_t$, C$_{13}$), 22.8 (C$_p$, C$_{14a}$), 22.0 (C$_p$, C$_{14b}$) 21.9 (C$_p$, C$_{16a}$), 21.0(C$_p$, C$_{16b}$).

^{15}N-NMR (40.56 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 390 (N$_9$)*, 310 (N$_8$), 292 (N$_{12}$)*, 267 (N$_1$)*.

MS (ESI$^+$, CH$_3$OH): m/z calculated for $C_{69}H_{93}N_{21}Y$ [Y(*i*PrBTP)$_3$]$^{3+}$ 434.89883, found 434.90012; calculated for $C_{69}H_{93}N_{22}O_3Y$ [Y(*i*PrBTP)$_3$(NO$_3$)]$^{2+}$ 683.34243, found 683.34420; calculated for $C_{46}H_{62}N_{16}O_6Y$ [Y(*i*PrBTP)$_2$(NO$_3$)$_2$]$^+$ 1023.40912, found 1023.41214.

4.3.3. Lu(i*PrBTP*)$_3$(NO$_3$)$_3$

^{1}H-NMR (400.18 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 9.10 (d, 2H, H$_3$, H$_5$, $^3J_{H3/5-H4}$ = 7.8 Hz), 8.63 (t, 1H, H$_4$, $^3J_{H4-H3/5}$ = 7.9 Hz), 3.41 (sept, 2H, H$_{15}$, $^3J_{H15-H16}$ = 6.7 Hz), 3.30 (sept, 2H, H$_{13}$, $^3J_{H13-H14}$ = 6.8 Hz), 1.38 (d, 6H, H$_{16a}$, $^3J_{H16a-H15}$ = 6.7 Hz), 1.32 (d, 6H, H$_{16b}$, $^3J_{H16b-H15}$ = 6.6 Hz), 0.77 (d, 6H, H$_{14a}$, $^3J_{H14a-H13}$ = 6.8 Hz), 0.45 (d, 6H, H$_{14b}$, $^3J_{H14b-H13}$ = 6.7 Hz).

^{13}C-NMR (100.63 MHz, MeOD-d4/D$_2$O 3:1):δ [ppm] = 172.3 (C$_q$, C$_{11}$), 166.5 (C$_q$, C$_{10}$), 163.7 (C$_q$, C$_7$), 152.7 (C$_q$, C$_6$), 144.7 (C$_t$, C$_4$), 129.4 (C$_t$, C$_{3/5}$), 32.8 (C$_t$, C$_{15}$), 30.6 (C$_t$, C$_{13}$), 23.1(C$_p$, C$_{14a}$), 22.2 (C$_p$, C$_{14b}$) 22.2 (C$_p$, C$_{16a}$), 21.2 (C$_p$, C$_{16b}$).

^{15}N-NMR (40.56 MHz, MeOD-d4/D$_2$O 3:1):δ [ppm] = 390 (N$_9$)*, 312 (N$_8$), 293 (N$_{12}$)*, 270 (N$_1$)*.

MS (ESI$^+$, CH$_3$OH): m/z calculated for C$_{69}$H$_{93}$N$_{21}$Lu [Lu(*i*PrBTP)$_3$]$^{3+}$ 463.57713, found 463.57857; calculated for C$_{69}$H$_{93}$N$_{22}$O$_3$Lu [Lu(*i*PrBTP)$_3$(NO$_3$)]$^{2+}$ 726.35989, found 726.36183; calculated for C$_{46}$H$_{62}$N$_{16}$O$_6$Lu [Lu(*i*PrBTP)$_2$(NO$_3$)$_2$]$^+$ 1109.44404, found 1109.44825.

4.3.4. Sm(iPrBTP)$_3$(NO$_3$)$_3$

^{1}H-NMR (400.18 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 9.61 (d, 2H, H$_3$, H$_5$, $^3J_{H3/5-H4}$ = 8.0 Hz), 9.10 (t, 1H, H$_4$, $^3J_{H4-H3/5}$ = 8.1 Hz), 3.27 (sept, 2H, H$_{15}$, $^3J_{H15-H16}$ = 6.7 Hz), 2.97 (sept, 2H, H$_{13}$, $^3J_{H13-H14}$ = 6.7 Hz), 1.42 (d, 6H, H$_{16a}$, $^3J_{H16a-H15}$ = 6.7 Hz), 1.21 (d, 6H, H$_{16b}$, $^3J_{H16b-H15}$ = 6.7 Hz), 0.70 (d, 6H, H$_{14a}$, $^3J_{H14a-H13}$ = 6.7 Hz), 0.31 (d, 6H, H$_{14b}$, $^3J_{H14b-H13}$ = 6.7 Hz).

^{13}C-NMR (100.63 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 172.2 (C$_q$, C$_{11}$), 165.3 (C$_q$, C$_{10}$), 164.9 (C$_q$, C$_7$), 157.7 (C$_q$, C$_6$), 145.6 (C$_t$, C$_4$), 129.9 (C$_t$, C$_{3/5}$), 32.5 (C$_t$, C$_{15}$), 30.2 (C$_t$, C$_{13}$), 22.3 (C$_p$, C$_{14a}$), 22.10 (C$_p$, C$_{14b}$), 22.07 (C$_p$, C$_{16a}$), 21.5 (C$_p$, C$_{16b}$).

^{15}N-NMR (40.56 MHz, MeOD-d4/D$_2$O 3:1):δ [ppm] = 387 (N$_9$)*, 292 (N$_{12}$)*, 263 (N$_8$), 226 (N$_1$)*.

MS (ESI$^+$, CH$_3$OH): m/z calculated for C$_{69}$H$_{93}$N$_{21}$Sm [Sm(*i*PrBTP)$_3$]$^{3+}$ 455.90363, found 455.90458; calculated for C$_{69}$H$_{93}$N$_{22}$O$_3$Sm [Sm(*i*PrBTP)$_3$(NO$_3$)]$^{2+}$ 714.84963, found 714.85129; calculated for C$_{46}$H$_{62}$N$_{16}$O$_6$Sm [Sm(*i*PrBTP)$_2$(NO$_3$)$_2$]$^+$ 1086.42300, found 1086.42584.

4.3.5. Eu(iPrBTP)$_3$(NO$_3$)$_3$

^{1}H-NMR (400.18 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 5.03 (t, 1H, H$_4$, $^3J_{H4-H3/5}$ = 7.9 Hz), 4.87 (sept, 2H, H$_{15}$, $^3J_{H15-H16}$ = 6.7 Hz), 4.39 (d, 6H, H$_{14a}$, $^3J_{H14a-H13}$ = 6.7 Hz), 4.17 (sept, 2H, H$_{13}$, $^3J_{H13-H14}$ = 6.7 Hz), 3.23 (d, 2H, H$_3$, H$_5$, $^3J_{H3/5-H4}$ = 8.0 Hz), 2.35 (d, 6H, H$_{16a}$, $^3J_{H16a-H15}$ = 6.7 Hz), 1.01 (d, 6H, H$_{14b}$, $^3J_{H14b-H13}$ = 6.6 Hz,), 0.95 (d, 6H, H$_{16b}$, $^3J_{H16b-H15}$ = 6.6 Hz).

^{13}C-NMR (100.63 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 184.8 (C$_q$, C$_{11}$), 156.1 (C$_q$, C$_6$), 150.3 (C$_t$, C$_4$), 145.9(C$_q$, C$_{10}$), 133.9 (C$_q$, C$_7$), 95.6 (C$_t$, C$_{3/5}$), 34.9 (C$_t$, C$_{13}$), 29.0 (C$_t$, C$_{15}$), 26.1 (C$_p$, C$_{14a}$), 25.7 (C$_p$, C$_{16a}$) 23.6 (C$_p$, C$_{16b}$), 22.0 (C$_p$, C$_{14b}$).

^{15}N-NMR (40.56 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 353 (N$_9$)*, 283 (N$_{12}$)*, -1389 (N$_8$).

MS (ESI$^+$, CH$_3$OH): m/z calculated for C$_{69}$H$_{93}$N$_{21}$^{151}Eu [Eu(*i*PrBTP)$_3$]$^{3+}$ 455.57016, found 455.57174; calculated for C$_{69}$H$_{93}$N$_{22}$O$_3$^{151}Eu [Eu(*i*PrBTP)$_3$(NO$_3$)]$^{2+}$ 715.35063, found 715.35245; calculated for C$_{46}$H$_{62}$N$_{16}$O$_6$^{151}Eu [Eu(*i*PrBTP)$_2$(NO$_3$)$_2$]$^+$ 1085.42312, found 1085.42772.

4.4. Synthesis of ^{243}Am(iPrBTP)$_3$(NO$_3$)$_3$

In a 2 mL screw-cap vial, 250 µL of an ^{243}Am(NO$_3$)$_3$ stock solution (c(Am^{3+}) = 4 mg·mL^{-1}, 16.8 mmol·L^{-1}) were heated to dryness. The pale-pink residue was dissolved in 150 µL portions of D$_2$O and heated until dry three times to reduce the H$_2$O content. To this salt, 5.1 mg (12.5 mmol) of *i*PrBTP (**2**), dissolved in 450 µL MeOD-d4 and 150 µL D$_2$O were added. After careful shaking of the vial, the orange colored solution was transferred into a J. Young-type NMR tube.

^{1}H-NMR (400.18 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 8.61 (d, 2H, H$_3$, H$_5$, $^3J_{H3/5H4}$ = 8.1 Hz), 7.76 (t, 1H, H$_4$, $^3J_{H4-H3/5}$ = 8.0 Hz), 3.90 (sept, 2H, H$_{15}$, $^3J_{H15-H16}$ = 6.7 Hz), 3.39 (sept, 2H, H$_{13}$, $^3J_{H13-H14}$ = 6.7 Hz), 1.52 (d, 6H, H$_{16a}$, $^3J_{H16a-H15}$ = 6.6 Hz), 1.33 (d, 6H, H$_{16b}$, $^3J_{H16b-H15}$ = 6.6 Hz), 0.87 (d, 6H, H$_{14a}$, $^3J_{H14a-H13}$ = 6.6 Hz), 0.79(d, 6H, H$_{14b}$, $^3J_{H14b-H13}$ = 6.6 Hz).

^{13}C-NMR (100.63 MHz, MeOD-d4/D$_2$O 3:1): δ [ppm] = 178.4 (C$_q$, C$_{11}$), 169.6 (C$_q$, C$_7$), 166.1 (C$_q$, C$_6$), 164.6 (C$_q$, C$_{10}$), 149.5 (C$_t$, C$_4$), 122.8 (C$_t$, C$_{3/5}$), 31.3 (C$_t$, C$_{13}$), 30.9 (C$_t$, C$_{15}$), 24.1(C$_p$, C$_{16a}$), 22.9 (C$_p$, C$_{16b}$) 22.7 (C$_p$, C$_{14a}$), 21.6 (C$_p$, C$_{14b}$).

^{15}N-NMR (40.56 MHz, MeOD-d4/D2O 3:1): δ [ppm] = 421 (N$_9$)*, 289 (N$_{12}$)*, -16 (N$_8$), -31 (N$_1$)*.

Acknowledgements

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