8.4 Structural investigations on radioactive materials in solution by NMR-Spectroscopy

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Introduction

Originally derived from the bis-triazinyl pyridine (BTP) motif, bis-pyrazolyl pyridine (BPP) type ligands have the ability to achieve the separation of trivalent actinides (An) from lanthanides (Ln) in liquid-liquid extraction processes [1-2]. The preferred complexation of An(III) ions in the presence of chemically highly similar Ln(III) ions also poses an intriguing research topic, as it includes the understanding of structure and bonding in *f*-element complexes. In-depth knowledge of the underlying mechanisms is not only desirable from a scientific point of view, but could also enable the rational design of improved tailored extractants.

The substituents on the triazine rings in BTPs and the pyrazolyle rings in BPP ligands are of crucial importance for the solubility in organic or aqueous media. They also influence the extraction behavior, stability against hydrolysis and radiolysis, and the selectivity of the ligands. However, this influence has so far not been studied in a systematic manner. Previous efforts in our group contain a comparative study of *n*-propyl- and *iso*-propyl substituted BTP ligands [3-4] and studies of C5-BPP (1) complexes with Ln(III) and Am(III) ions [5-6]. Recently, the aliphatic *neo*-pentyl side chains of C5-BPP were exchanged to *tert*-butyl substituents in C4-BPP (2) at FAU Erlangen-Nürnberg.

As both molecules are very similar in structure, resembling properties in terms of complex stability and formation were expected. However, initial extraction studies performed at FZJ-IEK-6 showed inexplicable extraction kinetics, which prompted us to perform a thorough investigation of the lanthanide and actinide C4-BPP complexes. For this, we employed a combination of further extraction studies, Nuclear Magnetic Resonance (NMR) and Time-Resolved Laser Fluorescence Spectroscopy (TRLFS).

TRLFS studies

The complexation of Cm(III) and Eu(III) with C4-BPP was studied with TRLFS. Cm(III) and Eu(III) are used as representatives of the trivalent actinides and lanthanides because of their excellent fluorescence properties which allow spectroscopic investigations at very low metal concentrations. Conditions of the experiments were chosen as for previous studies on C5-BPP [2] to allow for maximum comparability of the results. With TRLFS the speciation of the Cm(III) and Eu(III) C4-BPP complexes as well as the thermodynamic parameters of the complexation reaction are determined.

The complexation of Eu(III) with C4-BPP was studied in dependence of the ligand concentration $(c(Eu^{3+})_{ini} = 1 \cdot 10^{-5} \text{ mol} \cdot L^{-1}$, $c(C4\text{-BPP}) = 0\text{-}1.01 \cdot 10^{-2}$ mol·L^{-1}). The fluorescence spectra of the pure components (Eu(III) aquo, 1:1, 1:2 and 1:3 Eu(III) C4-BPP complexes) were used to determine the fractions of these species by peak deconvolution of the emission spectra. In the ligand concentration range of up to 10^{-2} mol·L^{-1} only the 1:1 (log K'$_1$ = 6.2) and 1:2 (log K'$_2$ = 4.1) Eu(III) C4-BPP complexes are formed. No evidence for 1:3 complexes have been found in the TRLFS experiments. Considering the complex stability constants, which are comparable to the Cm(III) complexation of C5-BPP (*cf.* Table 1; complex stability constants for Eu(III) complexes are not available in literature), where 1:3 complexes were found, this result seems surprising. First temperature-dependent TRLFS measurements to determine the thermodynamic parameters of the complexation show that the first complexation step is exothermic, while the formation of the 1:2 complex is endothermic. If the third complexation step is even more endothermic, this might explain the observed complexation behavior.

The complexation of Cm(III) with C4-BPP in dependence of the ligand concentration was also studied using TRLFS. While 1:1 and 1:2 complexes are formed during the titration, evidence for a 1:3 com-

Fig. 1: Structures of the C5-BPP (1) and C4-BPP (2) ligands.

Tab. 1: Conditional complex stability constants for the Cm(III) complex species of C4-BPP and C5-BPP [2].

Species	log K' C4-BPP	log K' C5-BPP
1:1	7.0	6.9
1:2	2.6	4.3
1:3	---	3.6

plex was only found in a batch experiment at decidedly higher ligand-to-metal ratios.

The comparison of the conditional complex formation constants with those of the Cm(III) C5-BPP complexes (Table 1) shows that the 1:1 complexes have almost the same stability constants, while the C4-BPP 1:2 complex is 1.3 orders of magnitude less stable. We assume that this is an effect of the greater steric hindrance in the C4-BPP complexes: the bulky *tert*-butyl groups are closer to the aromatic ligand core, and with the absence of the methylene group in the side chain the molecule loses its flexibility. This leads to an increased ligand-ligand repulsion in the first coordination sphere of the metal ion.

NMR studies

In continuation of the TRLFS experiments, NMR titration experiments with the C4-BPP ligand were performed. As NMR is an inherently less sensitive method, higher metal and ligand concentrations are required. A solution of Lu(OTf)$_3$ in deuterated methanol ($c(Lu^{3+})_{ini} = 10$ mmol·L^{-1}) was titrated with a concentrated ligand solution in deuterated methanol. Lu(III) was chosen as it is diamagnetic and does not perturb the chemical shifts by paramagnetic chemical shifts [7]. The results of the titration are shown in Figure 2 for the resonance signals of the *tert*-butyl groups of the ligand molecules. The resonance signals show a clear shift dependence on the coordination number, as the number of molecules in the complex influences the local symmetry and electronic structure. The composition of the individual complex species was identified by diffusion-ordered NMR spectroscopy [8-9] which links the observed NMR signals to the diffusion coefficient and thus molecular weight of the molecule. In the concentration range used for NMR experiments it was clearly shown that the 1:3 complex is preferably formed for a range of lanthanide ions (Ln(III) = La, Sm, Eu, Yb, Lu and Y) and that it is the dominating complex species for stoichiometric 1:3 compositions of ligand and metal ion. Furthermore, the existence of the 1:3 complexes has been proven by HR-ESI mass spectrometry.

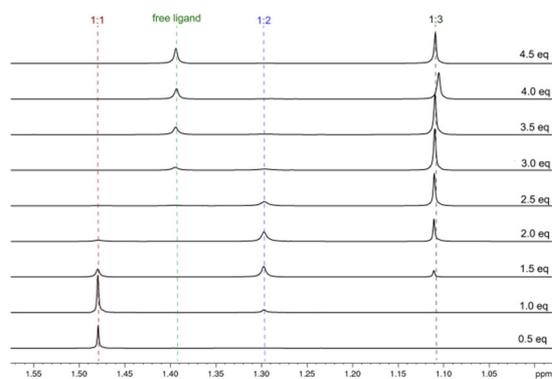Temperature-dependent NMR measurements in a temperature range from 185 K to 335 K were per-
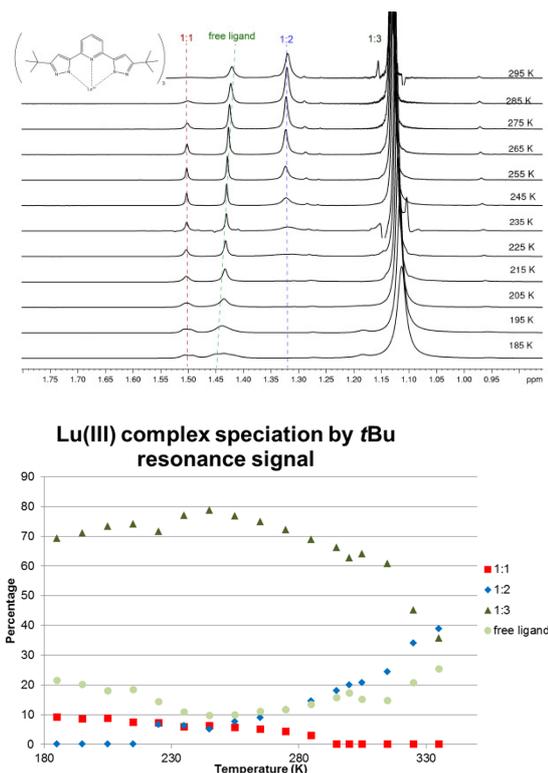

Fig. 3: *Top: Temperature-dependent ^1H direct excitation spectra of the tBu signals in different Lu(III) complex species of C4-BPP. The spectra exhibit a clear dependence of the speciation on the temperature. Bottom: Resulting speciation diagram.*

formed to gain insight into the magnetic behavior of complexes of the paramagnetic ions Eu(III), Sm(III) and Yb(III). In the diamagnetic reference compounds Lu(III) and La(III) a dependence of the complex speciation on the temperature was observed (Figure 3). While at low temperatures the 1:3 complex is the dominating species, the fraction of this complex decreases with rising temperature in favor of the free ligand and the 1:2 complex. This result is in line with observations from TRLFS spectroscopy. High temperatures favor the endothermic formation of the 1:2 complex. While the formation of a probably even more endothermic 1:3 complex should in principle be favored as well, an increased molecular motion of the bulky ligand molecules within the sterically crowded first coordination sphere effectively hinders the formation of this complex species.

We also synthesized the Am(III) complex as a representative of An(III) complexes. It turned out that in contrast to expectations from C5-BPP, C4-BPP does not readily form complexes with Am(III). The NMR spectra of a titration of one equivalent of Am(OTf)$_3$ with up to 8 equivalents of ligand are shown in Figure 4. The free ligand increases during the titration and always remains the dominating species while the share of the different complexes is always below 10% for each complex species. Furthermore, after waiting for 48 hours after the last titration step we found that the relative shares of the complexes had changed. This
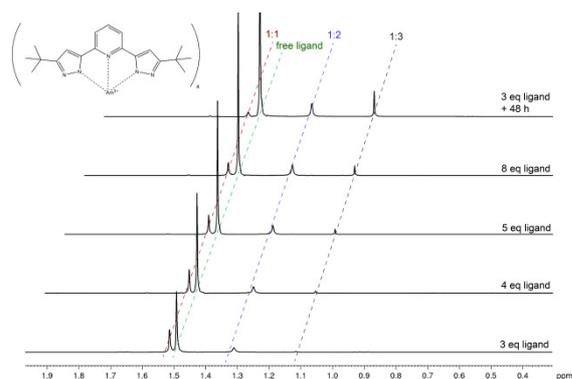

Fig. 2: *Resonance signals of the tBu groups of C4-BPP in Lu(C4-BPP)$_x$(OTf)$_3$ complexes in a NMR titration.*

Fig. 4: *Spectra of the tBu region of a titration of an Am(OTf)₃ solution with C4-BPP. The free ligand is the dominating species. The slow kinetics of the complexation reaction are shown by comparison to the topmost spectrum, acquired after a waiting period of 48 h.*

indicates that the C4-BPP complexation with Am(III) has slow kinetics.

We were also able to acquire $^1H,^{15}N$-gHMQC correlation spectra from the mixture of complex species, even without ^{15}N enrichment. This had previously been needed for the C5-BPP ligand. These spectra show that upon coordination to the Am(III) the resonance signal of the coordinating nitrogen atom N_8 is shifted upfield to 13 ppm in the 1:1 complex and -4 ppm in the 1:3 complex. In the paramagnetic Lu(III) complex, this signal is found at 265 ppm. A paramagnetic chemical shift of this magnitude has been observed previously in the *n*PrBTP [3,5], *i*PrBTP [4] and C5-BPP [5-6] complexes. This shift is interpreted as being mainly a Fermi contact shift (FCS), *i.e.* a paramagnetic chemical shift that originates from the actual transfer of unpaired electron spin density from the metal ion onto the ligand nuclei [7]. This argument is furthermore supported by the comparably small change of the chemical shift upon the structural rearrangement by the complexation of two additional ligand molecules to form the 1:3 complex. The second contributor to the paramagnetic chemical shift (pseudo contact shift, PCS) depends very strongly on the geometrical relation between metal ion and ligand nuclei. If the paramagnetic chemical shift was mainly PCS, a stronger chemical shift dependence on the coordination number would be found.

The comparability of the chemical shifts originating from the complexation of the Am(III) for C4-BPP and C5-BPP show that the bonding situation in complexes of both ligands is fairly similar. This in turn is a clear indication that the better complexation of Am(III) by C5-BPP is not due to electronic or bonding differences, but is a direct consequence of the greater steric hindrance in the first coordination sphere.

The slow complexation kinetics found in NMR experiments also helped to explain the extraction behavior of the C4-BPP. In the first extraction tests, the contact time of the aqueous and organic phase containing the extractant was too short and the samples were not in equilibrium. The NMR results prompted new extraction tests at FZJ with longer contact times.

In these experiments, the contact time was prolonged and an extraction curve complying to expectations was obtained.

Conclusion and Outlook

The case of C4-BPP exemplifies how a minor modification on the ligand periphery of an established extraction ligand (C5-BPP) produces a major influence on the speciation of the formed complexes, the coordination kinetics and ligand selectivity. While C5-BPP forms stable complexes with Ln(III) and Am(III) ions, An(III) coordination is disfavored for C4-BPP. This is obvious by a low ratio of 1:3 complexes observed by NMR spectroscopy, as well as lower complex stability constants in TRLFS experiments. By NMR spectroscopy important insights into the bonding situation of the C4-BPP complexes were obtained. Our results highlight once more that the combination of TRLFS and NMR for Ln(III) and An(III) complexation studies is highly valuable.

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