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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

^aKarlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), Herrmann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

^bFraunhofer Institute for Chemical Technology (ICT), Environmental Engineering, Joseph-von-Fraunhofer-Str. 7, 76327 Pfinztal, Germany

^cHelmholtz-Zentrum Dresden - Rossendorf e. V., Institute of Resource Ecology, Bautzner Landstrasse 400, 01328 Dresden, Germany

^dUniversity 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 ¹⁵N-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.

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* 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.

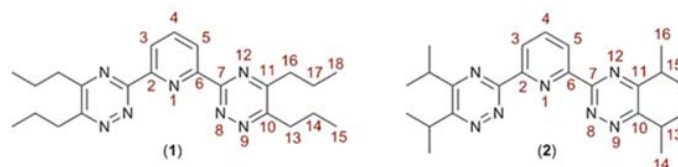


Fig. 1: Structures of *n*PrBTP (1) and *i*PrBTP (2) with the used numbering scheme

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 ML₃ 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 ML₃ 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 ¹⁵N (low, negative gyromagnetic ratio, low natural abundance of 0.37 %), we synthesized *i*PrBTP with ¹⁵N 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 ¹⁵N 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

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