



5<sup>th</sup> International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles

## Gamma radiolysis of the highly selective ligands CyMe<sub>4</sub>BTBP and CyMe<sub>4</sub>BTPhen: Qualitative and quantitative investigation of radiolysis products

Holger Schmidt<sup>a</sup>, Andreas Wilden<sup>a</sup>, Giuseppe Modolo<sup>a\*</sup>, Dirk Bosbach<sup>a</sup>, Beatrix Santiago-Schübel<sup>b</sup>, Michelle Hupert<sup>b</sup>, Jaroslav Švehla<sup>c</sup>, Bohumir Grüner<sup>c</sup>, Christian Ekberg<sup>d</sup>

<sup>a</sup>Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research IEK-6: Nuclear Waste Management, 52425 Jülich, D

<sup>b</sup>Forschungszentrum Jülich GmbH, Central Institute for Engineering, Analytics (ZEA-3), 52425 Jülich, D

<sup>c</sup>Institute of Inorganic Chemistry, Academy of Sciences, Hlavni 1001, 25068 Husinec-Rež, CZ

<sup>d</sup>Department of Chemical and Biochemical Engineering, Chalmers University of Technology, 41296 Gothenburg, SE

### Abstract

The highly selective nitrogen donor ligands CyMe<sub>4</sub>BTBP and CyMe<sub>4</sub>BTPhen were  $\gamma$ -irradiated under identical experimental conditions in 1-octanol with and without contact to nitric acid solution. Subsequently, solvent extraction experiments were carried out to evaluate the stability of the extractants against  $\gamma$ -radiation monitoring Am(III) and Eu(III) distribution ratios. Generally, decreasing distribution ratios with increasing absorbed dose were detected for both molecules. Furthermore, qualitative mass spectrometric analyses were performed and ligand concentrations were determined by HPLC-DAD after irradiation to investigate the radiolysis mechanism. An exponential decrease with increasing absorbed dose was observed for both ligands with a faster rate for CyMe<sub>4</sub>BTPhen. Main radiolysis products indicated the addition of one or more diluent molecules (1-octanol) to the ligand via prior production of  $\alpha$ -hydroxyoctyl radicals from diluent radiolysis. The addition of nitric acid during the irradiation led to a remarkable stabilization of the system, as the extraction of Am(III) and Eu(III) did not change significantly over the whole examined dose range. Quantification of the remaining ligand concentration on the other hand showed decreasing concentrations with increasing absorbed dose. The stabilization of D values is therefore explained by the formation of 1-octanol addition products which are also able to extract the studied metal ions.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of ATALANTE 2016

\* Corresponding author. Tel.: +49 2461 61-4896; fax: +49 2461 61-2450.  
E-mail address: [g.modolo@fz-juelich.de](mailto:g.modolo@fz-juelich.de)

**Keywords:** N-donor ligands; gamma radiolysis; solvent extraction; mass spectrometry, CyMe<sub>4</sub>BTBP, CyMe<sub>4</sub>BTPhen

## 1. Introduction

Within the past and current European research on the development of new separation processes for the partitioning of minor actinides (MA: Np, Am and Cm) from highly active nuclear waste solutions, the group of BTBPs was developed and found to be very efficient. Especially the separation of the trivalent actinides Am(III) and Cm(III) from trivalent lanthanides (Ln(III)) is crucial. Therefore, the group of soft nitrogen donor ligands such as BTBPs is very promising, since it also fulfills the CHON principle.<sup>[1]</sup> Radiolytic as well as chemical stability are important aspects for a potential ligand application in industrial partitioning processes. The annulated 6,6'-bis(1,2,4-triazin-3-yl)-2,2'-bipyridine ligands appeared to be more stable against radiolytic degradation than the tetra-*n*-alkyl substituted derivatives such as C5-BTBP.<sup>[2-4]</sup> The CyMe<sub>4</sub>BTBP (6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]-triazin-3-yl)-[2,2']-bipyridine) ligand (Fig. 1a) was successfully studied and finally chosen as European reference molecule for MA partitioning.<sup>[3, 5-8]</sup> Due to rather slow extraction rates of CyMe<sub>4</sub>BTBP, a derivative, CyMe<sub>4</sub>BTPhen (2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-1,10-phenanthroline) (Fig. 1b), was invented. This new ligand showed faster extraction kinetics, which is caused by its rigidity and the juxtaposition of the N-donor atoms in *cis* conformation that leads to a faster as well as thermodynamically favored complex formation.<sup>[9-11]</sup>

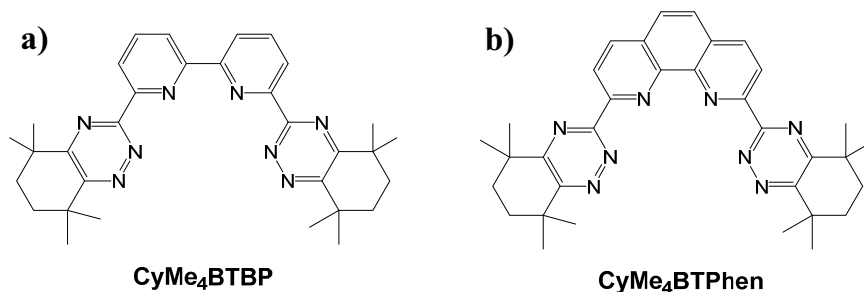


Fig. 1: Investigated ligand molecules CyMe<sub>4</sub>BTBP (a) and CyMe<sub>4</sub>BTPhen (b), which were irradiated as 10 mmol/L solutions in 1-octanol.

In this paper, we will study and compare the radiolytic stability of the before mentioned ligands CyMe<sub>4</sub>BTBP and CyMe<sub>4</sub>BTPhen and its influence on the actinide/lanthanide extraction. Therefore, radiolysis experiments were conducted at the Department of Chemical and Biochemical Engineering at the Chalmers University of Technology in Gothenburg, Sweden. A description of the gamma radiolysis experiments as well as liquid-liquid extraction can be found in our previous work.<sup>[12]</sup> Furthermore, quantitative and qualitative analyses were performed and the influence of nitric acid contact during irradiation was investigated. These measurements were done at the Institute of Inorganic Chemistry, Academy of Sciences, Husinec-Rež, Czech Republic.<sup>[12-13]</sup>

## 2. Results and Discussion

CyMe<sub>4</sub>BTBP and CyMe<sub>4</sub>BTPhen were irradiated in parallel (<sup>60</sup>Co, dose rate ~9.5 kGy/h) in 1-octanol solution (10 mmol/L) with and without contact to 1.0 mol/L nitric acid. Liquid-liquid extraction studies were performed and distribution ratios of <sup>241</sup>Am and <sup>152</sup>Eu were measured. For both ligands, decreasing Am(III)/Eu(III) D-values were observed with increasing absorbed dose, while CyMe<sub>4</sub>BTPhen started at higher initial distribution ratios (Fig. 2, filled symbols). This effect did not occur when the organic phase was irradiated in contact with a 1.0 mol/L nitric acid solution (Fig. 2, open symbols). Under these conditions, distribution ratios for both nuclides remained high. For CyMe<sub>4</sub>BTPhen in contact with nitric acid, an increasing/ decreasing behavior in the low-dose area for D<sub>Am</sub> was observed. This phenomenon could be attributed to a radiolytic buildup of extracting species (increasing D-values), which are prone to radiolysis themselves with increasing absorbed dose (decreasing D-values).

Download English Version:

<https://daneshyari.com/en/article/4910906>

Download Persian Version:

<https://daneshyari.com/article/4910906>

[Daneshyari.com](https://daneshyari.com)