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## Hydrophilic 2,9-bis-triazolyl-1,10-phenanthroline ligands enable selective Am(III) separation: a step further towards sustainable nuclear energy†

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**The first hydrophilic, 1,10-phenanthroline derived ligands consisting of only C,H,O and N atoms for the selective extraction of Am(III) from spent nuclear fuel are reported herein. One of these 2,9-bis-triazolyl-1,10-phenanthroline (BTrzPhen) ligands combined with a non-selective extracting agent, was found to exhibit process-suitable selectivity for Am(III) over Eu(III) and Cm(III), providing a clear step forward.**

The ever-increasing demand for cost-effective, secure and environmentally benign energy, has led to a recently renewed global interest in nuclear power.<sup>1</sup> In addition to the existing nuclear nations, there are now in excess of twenty emerging countries considering the prospects of nuclear energy programmes.<sup>2</sup> This projected growth means that the environmental impact and thus public perception of nuclear energy is becoming an increasing priority for the international nuclear community.<sup>3,4</sup> Many nations are now developing innovative nuclear fuel cycles to separate the transuranic elements (Pu, Np, Am and Cm) from spent nuclear fuel in order to either use them in recycled fuel or transmute these relatively long-lived transuranic isotopes. These spent fuel management strategies aim to reduce the long-term radiotoxicity and heat generation of the spent fuel, to improve resource utilisation and facilitate the long term safety of a geological disposal facility (GDF).<sup>5,6</sup> Within this approach, multiple advanced hydrometallurgical actinide(III)/lanthanide(III) partitioning processes have been proposed for the treatment of advanced PUREX (Plutonium URanium EXtraction) raffinate, which consists of the transuranic

elements and fission products including the lanthanides (Ln).<sup>1,7</sup> This partitioning is a pre-target fabrication necessity due to the high neutron capture cross section of the Ln.<sup>8</sup> Within Europe, the recently developed SANEX (Selective Actinide EXtraction) process has allowed this challenging An(III)/Ln(III) separation to be readily accomplished using lipophilic, soft *N*-type donor BTP (bis-triazinyl-pyridine)<sup>9</sup>, BTBP (bis-triazinyl-bipyridine)<sup>10</sup> or BTPPhen (bis-triazinyl-1,10-phenanthroline)<sup>11–13</sup> ligand systems to selectively remove the trivalent actinides (An) from DIAMEX (DIAMide EXtraction) extract. The DIAMEX process removes both An(III) and Ln(III) from the non-Ln fission products using a non-selective diglycolamide in advanced PUREX raffinate and is an essential prerequisite to a SANEX type process.<sup>14</sup>

More recently, the *i*-SANEX (*innovative*-SANEX)<sup>15</sup> process has emerged as a promising alternative for An(III)/Ln(III) separations. This advanced multi-step, partitioning process uses the diglycolamide *N,N,N',N'*-tetraoctyl-diglycolamide TODGA, Fig. S1 to co-extract both An(III) and Ln(III) into an organic phase followed by selective An(III) back-extraction using a hydrophilic complexant, removing the need to implement individual DIAMEX and SANEX type processes. The most promising hydrophilic complexants for implementation in *i*-SANEX, studied thus far, are sulfonated versions of the BTP, BTBP and BTPPhen ligands explored for use in SANEX (e.g. SO<sub>3</sub>-Ph-BTBP/BTPPhen; Fig. S1). An additional spent fuel management strategy being considered post An(III) separation from Ln(III) is the partitioning of Am(III) from Cm(III). One such process being explored is AmSel (Americium Selective EXtraction).<sup>16</sup> Accomplishing this extremely challenging separation is most advantageous as curium isotopes are short-lived (e.g. <sup>244</sup>Cm, *t*<sub>1/2</sub> = 18 years), intensely radioactive and strong neutron emitters, making Cm(III) based fuel fabrication unfeasible.<sup>17</sup> In contrast, Am based fuels can be feasibly produced for fast reactor systems. The AmSel process separates Am(III) from Cm(III) and Ln(III) by stripping only Am(III) from a TODGA solvent containing Am(III), Cm(III) and Ln(III). A subtle selectivity of TODGA for Cm(III) over Am(III) (*SF*<sub>Cm(III)/Am(III)</sub> ≈ 1.6) in conjunction with the similar subtle selectivity for Am(III) over Cm(III) by hydrophilic SO<sub>3</sub>-Ph-BTBP/BTPPhen (*SF*<sub>Am(III)/Cm(III)</sub> ≈ 1.6) is exploited<sup>16,18,19</sup>

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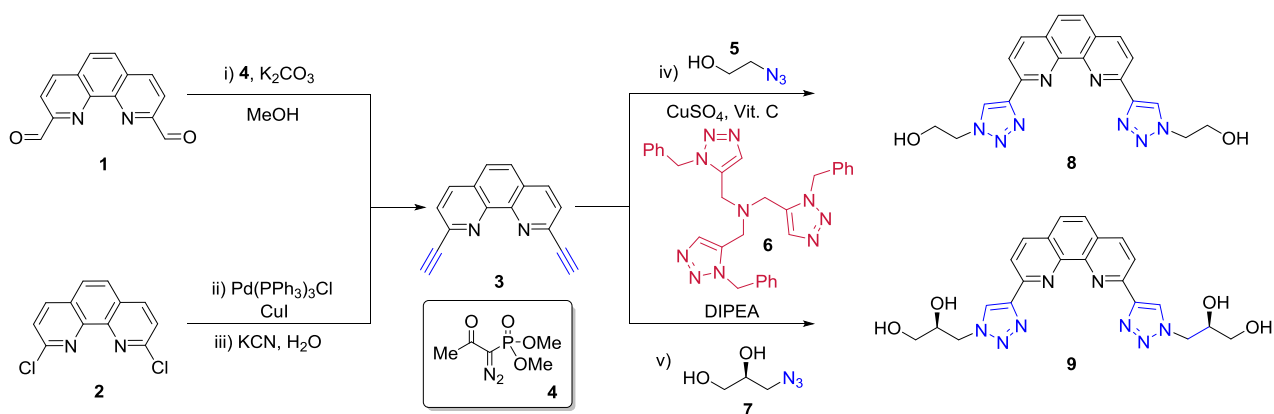
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† Electronic Supplementary Information (ESI) available: Full synthetic details, key NMR spectra, solvent extraction procedures and additional data, TRLFS setup and procedures and X-ray crystallographic data. See DOI: 10.1039/x0xx00000x

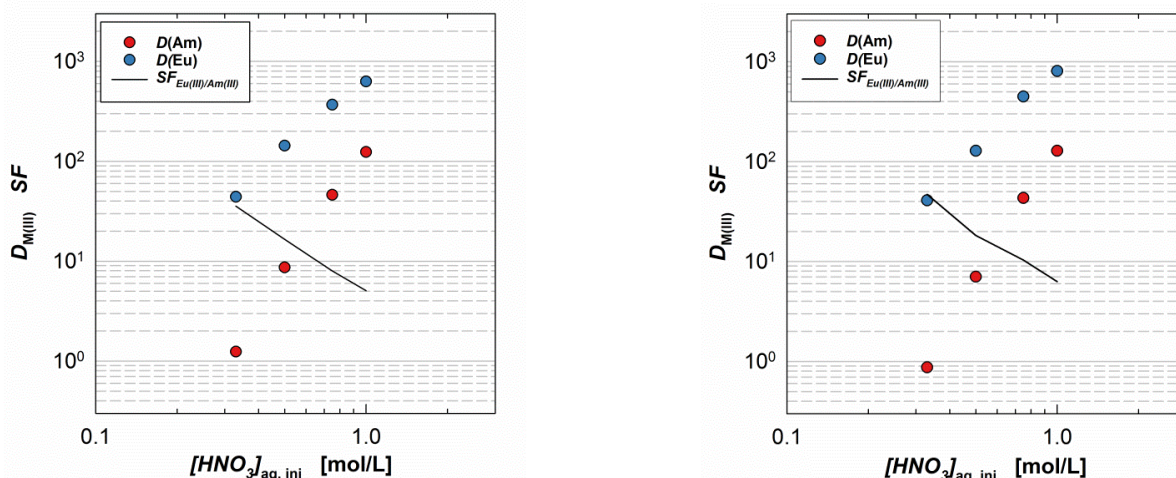


**Scheme 1** Synthesis of hydrophilic, 2,9-bis-(1,2,3)-triazolyl-1,10-phenanthroline (BTrzPhen) ligands **8** and **9**.

Despite their many advantages, the *i*-SANEX and AmSel processes currently propose the use of sulfur containing extractants, which are unsuitable for incineration and as a result generate additional radioactive waste-streams. Consequently, a series of hydrophilic, pyridine-2,6-bis(1*H*-1,2,3-triazol-4-yl) (PyTri) ligands (Fig. S1) was evaluated by Casnati *et al.* In synergy with TODGA, these PyTri ligands were reported to be highly An(III) selective ( $SF_{Eu(III)/Am(III)} \approx 100$ ) however, no useful Am(III)/Cm(III) selectivity was observed.<sup>20</sup>

With this in mind, we have developed a C,H,O,N compliant extractant, suitable for use in the *i*-SANEX and/or AmSel processes thus allowing for the efficient partitioning and reuse of Am(III) in spent nuclear fuel. During this process, we sought to combine the superior chelating properties of the 1,10-phenanthroline scaffold with the hydrophilicity of hydroxylated-1,2,3-triazolyl moieties. The resulting 2,9-bis-(1*H*-1,2,3-triazol-4-yl)-1,10-phenanthroline (BTrzPhen) ligands (**8-9**) are shown in Scheme 1. During the synthesis of ligands **8** and **9**, two alternative synthetic routes to the 2,9-diethynyl-1,10-phenanthroline intermediate (**3**) were explored (Scheme 1). The first of these routes employed a Seyferth–Gilbert homologation of commercially available 1,10-phenanthroline-2,9-dicarb-aldehyde (**1**) using the Bestmann–Ohira reagent (**4**). Following column chromatography, this protocol provided

intermediate **3** in a modest, 49 % yield. The second protocol entailed a Sonogashira coupling of commercial 2,9-dichloro-1,10-phenanthroline (**2**) and (*t*-butyldimethyl-silyl)acetylene, followed by subsequent deprotection. Over the two steps, **3** was obtained in 50 % yield. Azides **5** and **7** were synthesised as previously described.<sup>20</sup> Finally, the click reaction of bis-alkyne **3** with azides **5** and **7** was carried out in the presence of a pre-prepared, copper(II) tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl] amine (TBTA, **6**) complex, to inhibit competing copper(II) complexation with 1,10-phenanthroline.<sup>21</sup> The target BTrzPhen ligands **8** and **9** were obtained in yields of 89 % and 64 % respectively. Both ligands **8** and **9** were found to be sufficiently soluble in aqueous 0.3–3.0 M HNO<sub>3</sub> ( $\approx 10 \text{ mmol L}^{-1}$ ). The tetraol (**9**) was also found to be readily soluble at HNO<sub>3</sub> concentrations <0.3 M (down to 0.01 M). The solubility of **8** and **9** in aqueous HNO<sub>3</sub> solutions is a required property, as it is anticipated that advanced liquid-liquid extraction processes will be directly implemented on advanced PUREX raffinate ([HNO<sub>3</sub>] ( $\leq 4 \text{ M}$ )). The ability of ligands **8** and **9** to back-extract the trivalent actinides selectively from a TODGA containing organic phase (5 vol% 1-octanol in kerosene) was assessed using a series of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) spiked extraction experiments. To ensure that equilibrium was attained, the biphasic mixtures were shaken for 12 h on a benchtop shaker



**Fig. 1** Distribution ratios ( $D_{M(III)}$ ) and separation factors ( $SF_{Eu/Am}$ ) obtained in the extraction of <sup>241</sup>Am(III) and <sup>152</sup>Eu(III) by **8** (left) and **9** (right). Organic phase: TODGA (0.2 mol L<sup>-1</sup>) and 5 vol% 1-octanol in kerosene. Aqueous phase: HNO<sub>3</sub> (0.33–1.0 mol L<sup>-1</sup>)<sup>†</sup> and BTrzPhen ligands **8** and **9** (10 mmol L<sup>-1</sup>). Vortex Shaker (40Hz) for 12 hours at 20 °C ± 0.5 °C.

and the subsequent distribution ratios ( $D_{M(III)}$ ) recorded using  $\gamma$ -spectroscopy. The resulting equilibrium extraction data as a function of  $\text{HNO}_3$  concentration are presented in Fig. 1.

As anticipated, **8** and **9** exhibit similar extraction behaviour to one another, with both signifying a clear selectivity for Am(III) over Eu(III) from a TODGA containing organic phase. Gratifyingly, ligand **9** was found to exhibit process suitable  $D_c$  values at 0.33 M  $\text{HNO}_3$  with  $D_{Am} < 1$  and  $D_{Eu} > 10$ . Separation factors ( $SF_{Eu/Am}$ ) of 36 and 47 were obtained for **8** and **9** in 0.33 M  $\text{HNO}_3$  respectively, and decrease as a function of increasing  $[\text{HNO}_3]$ . This observed loss in separation performance with increasing  $[\text{HNO}_3]$  is also observed for hydrophilic BTP<sup>15</sup>, BTBP<sup>16</sup>, BTPPhen<sup>18</sup> and PyTri<sup>20</sup> ligands and is attributed to the increased degree of ligand protonation and thus decreased free ligand concentration.

Despite the  $SF_{Eu/Am}$  for ligands **8** and **9** being approximately half of those reported for the PyTri series ( $SF_{Eu/Am} \approx 100$ ), it is worth noting that extraction with these latter complexants requires exceptionally high ligand concentrations (80 mmol L<sup>-1</sup> *c.f.* 10 mmol L<sup>-1</sup> (BTrzPhen) due to their limited affinity ( $\text{EuCl}_3 \log\beta_{1:1} = 2.4\text{--}3.0$ ). The selectivity of **9** for Am(III) over Cm(III) from a TODGA containing organic phase was then assessed using a second series of extraction experiments spiked with <sup>244</sup>Cm. The equilibrium distribution ratios at 0.3 M  $\text{HNO}_3$  were determined as  $D_{Cm(III)} \approx 5$  and  $D_{Am(III)} \approx 2$  by  $\alpha$ -spectroscopy, leading to a  $SF_{Cm/Am}$  of 2.5. This separation factor is identical to that reported for the  $\text{SO}_3$ -BTBP/BTPPhen and TODGA containing systems.<sup>16</sup> Despite providing no improvement in Am vs Cm selectivity, this is the first C,H,O,N compliant, 1,10-phenanthroline derived donor ligand to achieve this Am/Cm separation. In order to probe the complexation behaviour of the BTrzPhen ligands further, a Eu(III) complex of ligand **8** was synthesised using Eu(III) triflate. Growth of single crystals suitable for XRD analysis was accomplished by the slow evaporation of a saturated  $\text{CH}_3\text{CN}$  solution. The inner-coordination sphere of the resulting (1:2, [M:L]) 9-coordinate Eu(III) complex comprises two BTrzPhen molecules (**8**) and a molecule of water (Fig. 2). Three non-coordinating triflate anions for charge neutrality are located in the asymmetric unit, with structure refinement revealing one anion to be highly disordered. Since our focus surrounds the structure of the  $[\text{Eu}(\mathbf{8})_2\text{H}_2\text{O}]^{3+}$  complex cation and not the intermolecular bonding within the crystal structure, it was deemed appropriate to make use of the SQUEEZE procedure embedded

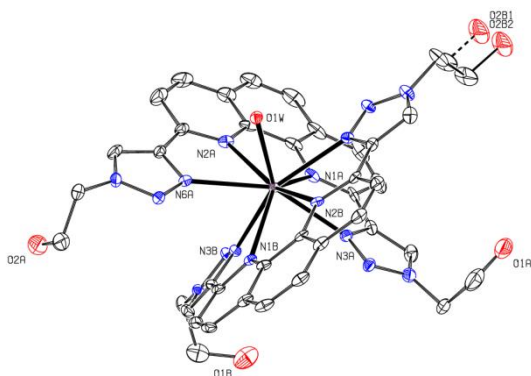


Fig. 2. Single crystal X-ray diffraction structure of the  $[\text{Eu}(\mathbf{8})_2\text{OTf}_3]$  complex.

Distances / Å	Eu-N	Eu-N	Eu-O
	(phen/bypy)	(triazine/ole)	( $\text{H}_2\text{O}/\text{NO}_3/\text{OTf}$ )
$[\text{Eu}(\text{BTrzPhen}(\mathbf{8}))_2\text{H}_2\text{O}]$	2.540	2.547	2.4183
$[\text{Eu}(\text{CyMe}_4\text{-BTPhen})_2\text{H}_2\text{O}]^{22}$	2.515	2.540	2.414
$[\text{Eu}(\text{CyMe}_4\text{-BTBP})_2\text{NO}_3]^{22}$	2.566	2.572	2.564
$[\text{Eu}(\text{CyMe}_4\text{-BTBP})_2\text{NO}_3]^{23}$	2.578	2.572	2.560
$[\text{Eu}(\text{CyMe}_4\text{-BTBP})_2\text{NO}_3]^{24}$	2.563	2.588	2.563
$[\text{Eu}(\text{CyMe}_4\text{-BTPhen})_2\text{NO}_3]^{11}$	2.582	2.587	2.567
$[\text{Eu}(\text{bispyridinyl-Phen})_2\text{H}_2\text{O}]$ , Z' = 2 <sup>25</sup>	2.541	2.615	2.431
$[\text{Eu}(\text{ethylene-BisPhen})_2\text{OTf}]^{25}$	2.576	2.576	2.392
$[\text{Eu}(\text{bis-tetrazolyl-bipyridine})_2\text{H}_2\text{O}]^{26}$	2.565	2.528	2.442

Table 1: Average bond distances in the first coordination sphere between the Eu(III) ion and heterocyclic N-donor ligands and O atoms (coordinated water, nitrate or triflate) in the complex compounds indicated. Complex charge omitted.

in PLATON<sup>27</sup> to eliminate this disordered counter-ion and thus allow refinement to converge to  $R=5.75\%$ . Metrical coordination parameters obtained, Eu—N, Eu—O bond lengths, N—Eu—N angles, inter-ligand angle and the Eu(III) 'shift', defined as the distance of Eu(III) from the intersection of the two ligand mean planes, are provided in the ESI, Table S2. Nearest neighbour bond lengths are presented in Table 1. For comparative purposes, coordination parameters for similar [1:2] complexes of Eu(III) with tetradentate, N-donor ligands based on phenanthroline or bipyridine (containing flanking triazine, pyridine or tetrazolyl moieties) and water, nitrate or triflate molecule are also included.

This comparison reveals that the  $[\text{Eu}(\mathbf{8})_2\text{H}_2\text{O}]^{III}$  complex has the similar bond distances as analogous, N-donor ligand complexes. There are some subtle differences in the average Eu—N<sub>triazine/triazole</sub> and Eu—N<sub>phen/bipy</sub> bond lengths, with the  $[\text{Eu}(\mathbf{8})_2\text{H}_2\text{O}]^{III}$  complex found to have marginally longer M-L bonds than the analogous  $[\text{Eu}(\text{CyMe}_4\text{-BTPhen})_2\text{H}_2\text{O}]$  complex, suggesting slightly weaker bonding.<sup>22</sup> Further analysis of the data in Table 1 highlights that complexes containing an inner-coordination sphere  $\text{NO}_3^-$  anion, typically have longer average M-L bond lengths than those containing water. This is in excellent agreement with the recent report of EXAFS data by Dai *et al.* on  $\text{Me}_2\text{-BTPhen}$ .<sup>28</sup>

The stability constants for the formation of the Eu(III) complexes of **8** and **9** were determined using a series of UV-vis titrations in organic ( $\text{CH}_3\text{CN}:\text{CH}_2\text{Cl} 1:1$ ) and aqueous ( $\text{HNO}_3$ ) media. The resulting spectroscopic data were processed and analysed by HyperQuad<sup>29</sup>, providing the apparent  $\log\beta_{1:1}$  and  $\log\beta_{1:2}$  values (Table 1). Titration of ligand **8** with Eu(III) in organic media, provided both  $\log\beta_{1:1}$  and  $\log\beta_{1:2}$  values; conversely, titration of **8** in 0.1 M  $\text{HNO}_3$  (see ESI<sup>†</sup> section 2.3) revealed exclusive formation of a 1:1 complex. Unfortunately, the insolubility of BTrzPhen **8** prevented titrations in 0.01 M  $\text{HNO}_3$ . The titration of ligand **9** in 0.01 M  $\text{HNO}_3$  provided both  $\log\beta_{1:1}$  and  $\log\beta_{1:2}$  values. The 1:2 stepwise stability constant is larger than that of the 1:1 complex so that the 1:2 complex of



Ligand	Eu(III) Salt	Solvent	Log $\beta_{1:1}$	SD <sup>a</sup>	Log $\beta_{1:2}$	SD <sup>a</sup>
<b>8</b>	Eu(OTf) <sub>3</sub>	MeCN/CHCl <sub>3</sub>	<b>8.1</b>	0.150	<b>14.7</b>	0.270
<b>8</b>	Eu(NO <sub>3</sub> ) <sub>3</sub>	0.1 HNO <sub>3</sub>	6.1	0.008	n/a <sup>b</sup>	n/a <sup>b</sup>
<b>9</b>	Eu(NO <sub>3</sub> ) <sub>3</sub>	0.01 HNO <sub>3</sub>	<b>6.6</b>	0.050	<b>13.5</b>	0.060

**Table 2:** Metal–Ligand Stability Constants Determined Least Square Fits to UV–Visible Spectroscopic Titration Data Using HypSpec<sup>29</sup> (T = 25 °C) <sup>a</sup>Standard deviations determined by the fitting process, <sup>b</sup>Unobtainable.

Eu(III) and ligand **9** dominates speciation in 0.01 M HNO<sub>3</sub> (*c.f.* speciation diagram, ESI<sup>†</sup> section 2.4); only a large excess of Eu(III) drives dissociation of the 1:2 species to the 1:1 complex. Generally, ligands **8** and **9** show good ability to coordinate Eu(III) although stability constants for **8** in organic media are smaller than those of CyMe<sub>4</sub>-BTPhen<sup>30</sup>. Future studies will encompass the determination of stability constants of **8** and **9** with Am(III) or Cm(III).

The luminescence properties of the Eu(III) triflate complex of ligand **8** were also investigated by fluorescence spectroscopy (see ESI<sup>†</sup> section 2.5). The most intense peak in the emission spectrum at 617 nm is the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> “hypersensitive transition”. Rather than direct excitation to the 4f states, the organic ligands are chromophores, absorbing light which is efficiently transferred via intramolecular energy transfer to 4f resonance levels of the Eu(III) ion; from there to the emitting excited <sup>5</sup>D<sub>0</sub>, leading to enhanced luminescence. The very efficient ligand-to-metal energy transfer is reflected in the absorption spectra being a near superposition of the excitation spectra measured at the 616 nm metal centred emission (ESI, Fig. S15).<sup>31</sup> The lifetime of this Eu(III) complex ( $\lambda_{\text{max}} = 617$  nm) was found to be 1.8 ms ( $\sigma = 1.56$   $\mu\text{s}$ ,  $\chi^2 = 1.209$ ), which is similar to the lifetimes reported for Eu-BTPhen/BTBP complexes.<sup>22</sup>

In summary, we have two new, hydrophilic, 2,9-bis-triazolyl-1,10-phenanthroline (BTrzPhen) ligands which show considerable promise for the recycling and management of minor actinides from spent nuclear fuel. We disclose the synthesis, Eu(III) speciation and liquid-liquid extraction properties of this exciting new ligand family. The BTrzPhen ligand **9** was found to exhibit process-suitable Am(III):Eu(III) and Cm(III):Am(III) separation factors from TODGA (at only 10 mmol L<sup>-1</sup>) containing organic phases. These promising, preliminary extraction results make ligand **9**, the first C,H,O,N, compliant, 1,10-phenanthroline derived ligand to display suitable properties for the selective removal of Am(III) from Ln(III) and Cm(III). Further process development will be implemented in order to examine the impact of; additional Ln(III) ions, fission products (FP) and radiolysis on this promising extraction behaviour.

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‡ D<sub>M(III)</sub> values at 3M [HNO<sub>3</sub>] were too large to be accurately determined (>>1000).

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