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Complexation Studies of Bidentate Heterocyclic N-Donor Ligands with Nd(III) and Am(III)

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Abstract A new bidentate nitrogen donor complexing agent that combines pyridine and triazole functional groups, 2-((4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl)pyridine (PTMP), has been synthesized. The strength of its complexes with trivalent americium (Am^{3+}) and neodymium (Nd^{3+}) in anhydrous methanol has been evaluated using spectrophotometric techniques. The purpose of this investigation is to assess this ligand (as representative of a class of similarly structured species) as a possible model compound for the challenging separation of trivalent actinides from lanthanides. This separation, important in the development of advanced nuclear fuel cycles, is best achieved through the agency of multidentate chelating agents containing some number of nitrogen or sulfur donor groups. To evaluate the relative strength of the bidentate complexes, the derived constants are compared to those of the same metal ions with 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), and 2-pyridin-2-yl-1*H*-benzimidazole (PBIm). At issue is the relative affinity of the triazole moiety for trivalent f element ions. For all ligands, the derived stability constants are higher for Am^{3+} than Nd^{3+}. In the case of Am^{3+} complexes with phen and PBIm, the presence of 1:2 (AmL_2) species is indicated. Possible separations are suggested based on the relative stability and stoichiometry of the Am^{3+} and Nd^{3+} complexes. It can be noted that the 1,2,3-triazolyl group imparts a potentially useful selectivity for trivalent actinides (An(III)) over trivalent lanthanides (Ln(III)), though the attainment of higher complex stoichiometries in actinide compared with lanthanide complexes may be an important driver for developing successful separations.

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1 Introduction

A serious challenge to the continued development of nuclear power is the necessity to manage irradiated nuclear fuel in a manner that maximizes efficiency while at the same time increasing safety margins. One strategy for reducing the long-term radiotoxicity of spent nuclear fuel is the transmutation of long-lived α-emitting actinide elements (An) into shorter-lived fission products by bombardment with fast neutrons. This strategy relies on the development of fast-neutron spectrum reactors, but also demands efficient processes for the mutual separation of (primarily) americium from fission product lanthanides, principally all lanthanides from La through Tb. The lanthanide (Ln) fission products, which represent 40% by mass and 1/3 of the atoms created in U/Pu fission, inhibit transmutation because of the high neutron absorption cross sections of some isotopes. The separation of lanthanides from the transplutonium actinides is seen to be critical to developing advanced nuclear fuel management strategies [1].

Owing to the chemical similarities of trivalent Ln and An, the separation of the two groups is one of the most challenging tasks in metal ion separation science [1]. The trivalent ions of the 4f and 5f series are strongly solvated in aqueous solutions with eight or nine water molecules bound in the inner coordination sphere, depending on the size of the trivalent cation [2]. This hydration is further strengthened by second-sphere organization of water, which becomes more pronounced as the charge density of the cations increases. However, successful aqueous separations for process-scale applications are often built around small differences in the solution chemistry of the trivalent Ln and An ions. Both the 4f and 5f series ions are considered to be hard acids in the Pearson classification of acids and bases [3]. As a consequence, these metals prefer interactions with hard donor ligands (oxygen, fluoride) over softer N, S or Cl^- donor ligands. Though in most contexts N-donors are considered to be hard Lewis bases, they do interact more strongly with actinides than lanthanides of similar size, thus they are most appropriately considered "less hard" than donor ligands like H_2O in f-element chemistry. Previous literature has demonstrated that donor atoms softer than oxygen, e.g. N and S, are the most effective means of accomplishing separations of lanthanides from actinides using liquid–liquid extraction systems [4]. However, the overall strength of the interaction between f-element cations and N-donor ligands is substantially lower than would be seen in an isostructural oxygen donor system. For d-series transition metals, the interactions with N-donor ligands are significantly stronger due to greater covalency in the bonding interactions.

Solvent extraction-based separations of metal ions typically require the transfer of ions from polar aqueous media into organic media of substantially lower dielectric constant. In the organic phase, it is of course necessary to maintain electroneutrality. Moreover, the lower dielectric constant inhibits the presence of free cations or anions in this phase. Thus it is necessary to somehow neutralize the cation charge before the metal ion can cross the phase boundary or to do so as the metal ion crosses the interface. As N-donor ligands are neutral species, either the transfer of anions from the aqueous to the organic phase must occur in parallel or cations must be exchanged from lipophilic Brønsted acids already present in the organic phase. The latter case is termed a synergistic system, in which the combined actions of a solvating extractant (the N-donor ligand) and the cation exchanger (most typically

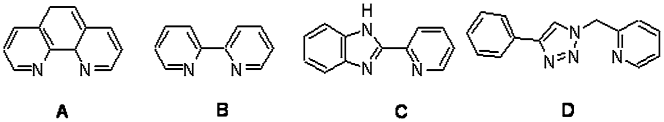


Fig. 1 Nitrogen donor complexants and triazolyl based ligands used in this study with (**A**) 1,10-phenanthroline (phen); (**B**) 2,2′-bipyridine (bipy), (**C**) 2-pyridin-2-yl-1*H*-benzimidazole (PBIm); (**D**) 2-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (PTMP)

oxygen-based) enables the phase transfer reaction. It is clear that in the biphasic systems the solution chemistry quickly becomes quite complex.

To evaluate in a more straight forward manner the relative stability of trivalent actinide and lanthanide complexes with N-donor polydentate ligands, it has been determined that preliminary screening of these new ligands and related systems should be completed in polar organic media. The resultant lower dielectric constant and reduced solvation energies of cations can significantly facilitate charaterization of metal–ligand interactions. This strategy follows that used by European researchers who are most responsible for the development of N-donor ligand systems for this application [5–11]. In the following the relative strength and complex stoichiometry of Am^{3+} and Nd^{3+} complexes with the N-donor ligands 1,10-phenanthroline (phen), 2,2′-bipyridyl (bipy), 2-pyridin-2-yl-1*H*-benzimidazole (PBIm) and 2-[(4-phenyl-1*H*-1,2,3-triazol-1-yl)methyl]pyridine (PTMP) (Fig. 1) were studied. Nd^{3+} was chosen as a representative lanthanide because its ionic radius, chemical, and hydration properties are similar to those of Am^{3+}. In addition, the hypersensitivity exhibited by some spectral bands in the Nd^{3+} visible-NIR spectrum makes them (uncharacteristically for a lanthanide) responsive to changes in composition of the primary coordination sphere of the cation. The 503 nm band of Am^{3+} is also known to respond to changes in the cation coordination environment. These ions are useful probes of the coordination chemistry of the system. Methanol was selected as the medium of choice for a more rapid evaluation and because in such media it is possible to minimize the influence of ligand protonation reactions and cation hydrolysis.

2 Experimental

All reagents were ACS reagent grade or higher purity. The 1,10-phenanthroline, 2,2′-bipyridyl, anhydrous methanol, anhydrous sodium nitrate, 2-(chloromethyl)pyridine hydrochloride, sodium azide, and phenylacetylene were used as received without further purification. The intermediate 2-pyridin-2-yl-1*H*-benzimidazole (PBIm) was produced as a side product in the reported synthesis of N,N′-bis-[pyridin-2-ylmethylene]benzene-1,2-diamine (BPMDIB) [12] and matched the previously reported characterization of this compound [13].

2.1 Synthesis of the PTMP Ligand

The ligand was synthesized by adjusting procedures established in the previous literature [14, 15]. In general, 2-azidomethyl pyridine was synthesized by reacting 2-chloromethyl pyridine with sodium azide in water. The Sharpless “Click” and Sonogashira coupling products were synthesized by reacting the azide with the alkyne in a 1:1 molar ratio in a mixture of 1:1 tert-butanol/H_2O, with ascorbic acid and cupric sulfate (Cu(I) catalyzing the coupling reaction). The reaction mixture was purified by pouring into ice cold deionized (D.I.) water and extracting with methylene chloride. The organic phase was dried (sodium sulfate), filtered, and the solvent removed by rotary evaporation.

2.2 Synthesis of 2-Azidomethyl Pyridine

To prepare the PTMP, the starting material 2-azidomethyl pyridine was first synthesized as follows. Sodium azide (11.805 g, 181.59 mmol) and 2-chloromethylpyridine hydrochloride (5.749 g, 45.07 mmol) were added to 200 mL of DI water in a 500 mL round bottom flask with a stirring bar. The reaction was heated to 50 °C and allowed to stir for 24 h. The reaction was neutralized with sodium bicarbonate (11.800 g, 140.46 mmol). The organic material was extracted with CH_2Cl_2 (3 × 30 mL), dried with $MgSO_4$, filtered and the solvent was evaporated. The product, 2-azidomethyl pyridine, was obtained as a yellow oil (75.6% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.42 (s, 2H), 7.28 (t, 1H), 7.36 (d, 1H), 7.77 (t, 1H), 8.64 (d, 1H). ^{13}C NMR (80 MHz, $CDCl_3$): δ 55.95, 122.13, 123.09, 137.14, 149.80, 155.81.

2.3 Synthesis of 2-((4-Phenyl-1*H*-1,2,3-triazol-1-yl)methyl)pyridine (PTMP)

In a 100 mL round bottom flask, 2-azidomethyl pyridine (2.320 g, 17.29 mmol) and phenylacetylene (1.753 g, 17.16 mmol) were added to a 1:1 tert-butanol/water (40 mL) solution. Sodium ascorbate (1.17 mL of a 1 mol·L^{-1} solution) and cupric sulfate (46 mg, 0.184 mmol) were added. This solution was stirred at room temperature for 12 h. The reaction was poured into 100 mL of ice cold DI water and a precipitate formed. The mixture was extracted with CH_2Cl_2 (3 × 30 mL), dried with Na_2SO_4, filtered and evaporated. The product was obtained as a crystalline solid (64% yield). ^{1}H NMR (300 Hz, $CDCl_3$): δ 5.71 (s, 2H), 7.24 (m, 1H), 7.33 (m, 1H), 7.44 (m, 2H), 7.72 (m, 2H), 7.84 (m, 1H), 7.86 (m, 1H), 7.96 (s, 1H), 8.67 (d, 1H). ^{13}C NMR (80 Hz, $CDCl_3$): δ 56.36, 120.81, 122.43, 125.74, 128.22, 128.87, 130.45, 130.92, 137.64, 148.28, 149.73, 154.32.

2.4 Stock Solutions of Metal Ions

The $Nd(NO_3)_3$ stock was made up from a NIST standard (25 mL) $Nd(NO_3)_3$ (0.06933 mol·L^{-1}) solution in 5% HNO_3; the solution was fumed to near dryness several times to remove excess HNO_3. The stock was then reduced in volume to produce $Nd(NO_3)_3$ crystals. The crystals were collected and then dissolved in anhydrous MeOH (99.8%). The methanol was evaporated 5 times to remove excess water from the stock solution. An aliquot of this solution was taken and a working solution prepared. The concentration of Nd^{3+} [4.62(2) × 10^{-3} mol·L^{-1}] in MeOH was verified by spectroscopic methods at $\lambda_{max} = 579.95$ nm and the molar absorptivity determined, $\varepsilon_{max} = 11.3$ mol^{-1}·cm^{-1}.

The ^{243}Am stock was prepared by reconstituting a dry sample using 2000 μL of D.I. water and 100 μL of 15.8 mol·L^{-1} HNO_3. A working stock was made by taking 250 μL of the mother solution in 14.0 mL of D.I. water. The aqueous concentration of Am^{3+} (2.379 × 10^{-3} mol·L^{-1}) was verified by spectroscopic methods at $\lambda_{max} = 815.9$ nm using $\varepsilon_{max} = 64.4$ mol^{-1}·cm^{-1} [9]. The ^{243}Am working solution was then made up in MeOH following the same approach described above for Nd^{3+}. The phen and bipy titrations were run with a fresh stock of Am^{3+} that was the same concentration as in the earlier experiments (2.379 × 10^{-3} mol·L^{-1}) but the solution was evaporated 8 times rather than 5. To conserve Am^{3+} stock, the bipy and phen spectrophotometric titrations were conducted using a less concentrated working solution made up to the correct ionic strength (0.03 mol·L^{-1} ionic strength by addition of $NaNO_3$).

2.5 Spectrophotometric Titrations of Nd(III) and Am(III)

All titrations were carried out at 0.03 mol·L^{-1} ionic strength (by addition of $NaNO_3$). To an aliquot of the metal working solution, in a stoppered quartz cuvette capable of magnetic stirring (1 cm path length), incremental additions of a ligand solution in MeOH were made. Spectra were recorded using an Ocean Optics S2000 spectrophotometer calibrated for operation in the wavelength range of 348–1000 nm. The spectral region used to fit the stability constant were 720–770 nm for Nd(III) and 495–525 nm for Am(III). It was assumed that hydrogen ion concentration [H^+] and ionic strength remained constant. Stability constants were calculated using the SQUAD program [16] taking into account metal ion dilution. SQUAD is designed to calculate the best values for stability constants from absorbance data by employing a nonlinear least-squares approach. A satisfactory model of the complexation occurring in solution is determined by an iterative process reducing the standard deviation in calculated SQUAD parameters, the absorption data (σ_{DATA}), the refined stability constant (σ_{CONST}), and the standard deviation of each spectrum (σ_{SPECT}). The validity of the species model can also be indicated by the overall quality and shape of the calculated molar absorptivities. The non-negative least-squares algorithm (NNLS) was used to remove negative molar absorptivity values after all plausible models had been tested.

3 Results

3.1 Determination of Stability Constants

The spectra of Nd^{3+} and Am^{3+} in anhydrous methanol are markedly different from those in aqueous solution, as can be seen in the starting spectra of all the spectrophotometric titrations (Figs. 2 and 3). The effect of changing from aqueous to methanolic media for these ions has been discussed previously [12]. The hypersensitive behavior of Nd^{3+} changes in methanol and the peak between 720–770 nm displays the most significant changes with changing M:L ratios rather than the peak at 570–600 nm in aqueous solution. The change in media (from water to methanol) does not cause the hypersensitive behavior of the Am^{3+} spectrum as with Nd^{3+}. The spectral patterns for Am^{3+} are noticeably different, in aqueous solution a single intense sharp peak at 503 nm is observed whereas a more complex envelope observable in the 503 nm region certainly indicates a mixture of species are present in methanol.

All of the complex formation constants determined in this work must be considered "conditional" for two reasons. First, it was necessary to assume that the ligands are not protonated and that the metal ions are not hydrolyzed in methanol solutions. With these assumptions, the analysis was completed. Hydrolysis of the cation would represent the most rational source of free H^+ and, if there were excess H^+ in the system, it could impact the speciation of the free complexant molecule. It is also assumed that only M:L species are formed and that there are no mixed hydroxyl (or methoxy)/metal/ligand complexes formed in solution. As there was no observable increase in baseline (that might have resulted from precipitation of either metal ion, free complexant or metal complex), it is likely that the system does not suffer this complication. There have been no previous reports of hydrolysis for either of the metal species investigated in non-aqueous media. Secondly, all of the experiments were performed at low ionic strength (0.03 mol·L^{-1} total nitrate) in non-aqueous media (MeOH). Nitrate is known to be a weak complexing agent for An(III). Under methanolic conditions it has been determined that nitrate along with MeOH will enter the inner coordination sphere of Nd(III) and Am(III) [12]. The effect of nitrate complexation was not included in the refinement that led to the reported stability constants.

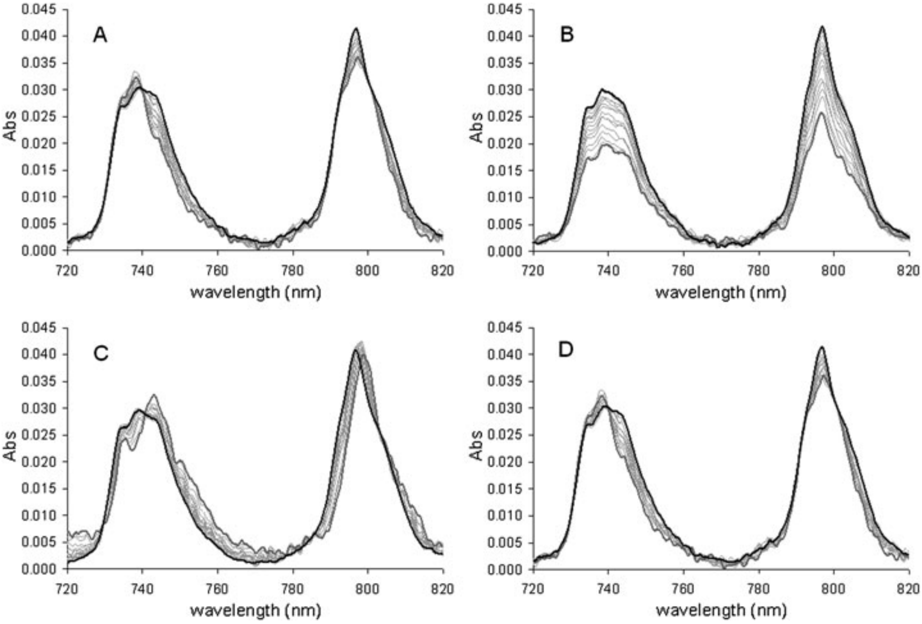


Fig. 2 Spectrophotometric titrations of incremental additions of bidentate N-donor ligands with 0.005 mol·L^{-1} Nd(NO$_3$)$_3$ in MeOH solution (*black line*). Incremental ligand additions are shown in *grey*; (**A**) phen resulting in a final M:L ratio of 1:2; (**B**) bipy resulting in a final M:L ratio of 1:8; (**C**) BPIm resulting in a final M:L ratio of 1:6; (**D**) PTMP resulting in a final M:L ratio of 1:11

The types of species present in solution were fitted by an iterative process by minimization of the error data in the SQUAD output files fitting the absorbance data. ML and ML$_2$ as an example can be distinguished quite readily from the error in the data. If in the model only ML is fitted but ML and ML$_2$ are present, in absorbance data as the ratio of metal to ligand is increased, both σ_{DATA} and σ_{CONST} values will be high and the standard deviation of each spectrum (σ_{SPECT}) would progressively increase in value. The reverse situation would present itself if only ML were present yet the spectra was fitted using ML and ML$_2$ values, in that case σ_{DATA} would be high but no trend in σ_{SPECT} would be observable. The stability constant value for ML$_2$ can be successively reduced leading to the eventual elimination of ML$_2$ contributions to the refinement process. For Nd^{3+} 1:2 M:L complexes with all ligands, no σ_{SPECT} was observable and the ML$_2$ value was eventually eliminated from the refinement process [16].

The spectrophotometric titrations of Nd^{3+} with each ligand are shown in Fig. 2. For all complexants, spectral changes can be seen to occur in the 720–770 nm envelope. The changes in the bipy spectra (2B) are more subtle than is seen for the other three ligands. In general, the features of these spectra suggest the presence of two absorbing species, free metal ion and a metal complex. In Fig. 3 the spectrophotometric titrations of Am^{3+} with the same bidentate ligands in MeOH are shown. As with Nd^{3+}, the changes in the spectra of Am^{3+} binding with increasing [bipy] and [PTMP] are much more subtle than the spectra for Am^{3+} complexes with PBIm and phen. It is seen that spectral features in the vicinity of the isosbestic point (between 503 and 510 nm) suggest the possible existence of multiple complex species in the PBIm and phen systems. Another noteworthy feature in the spectral

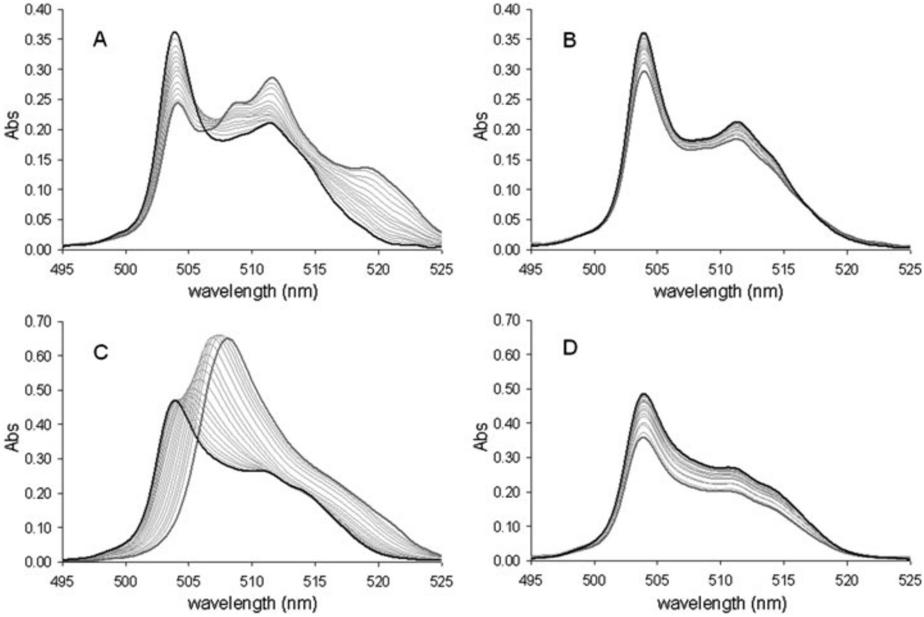


Fig. 3 Spectrophotometric titrations of incremental additions of bidentate N-donor ligands with either 0.0012 mol·L^{-1} (**A**) and (**B**) or 0.0022 mol·L^{-1} (**C**) and (**D**) $Am(NO_3)_3$ in MeOH solution (*black line*). Incremental ligand additions are shown in *grey*; (**A**) phen resulting in a final M:L ratio of 1:4; (**B**) bipy resulting in a final M:L ratio of 1:9; (**C**) BPIm resulting in a final M:L ratio of 1:10; (**D**) PTMP resulting in a final M:L ratio of 1:10

Table 1 Overall stability ($\pm 3\sigma$) constants for the binding of bidentate soft N ligands with Am^{3+} and Nd^{3+} in MeOH (structures are given in Fig. 1)

Ligand	$\log_{10}\beta_{101}$ Nd^{3+}	$\log_{10}\beta_{101}$ Am^{3+}	$\log_{10}\beta_{102}$ Am^{3+}
phen	1.61 ± 0.03	3.03 ± 0.09	5.7 ± 0.1
bipy	1.8 ± 0.2	2.4 ± 0.2	E/F[a]
PBIm	1.50 ± 0.06	1.89 ± 0.04	4.24 ± 0.02
PTMP	1.40 ± 0.06	2.30 ± 0.06	E/F[a]

[a] E/F = eliminated from fitting

patterns of phen and PBIm is the development of the spectral peak in the 520 nm region (in the Am^{3+} system), which is usually indicative of a 1:2 M:L species forming in solution [17]. The spectra for PTMP and bipy were fitted assuming that the ligands only form 1:1 M:L complexes in solution. The least-squares values (at 21 °C) for the overall stability constants are given in Table 1. As suggested above, all Nd^{3+} spectral data were adequately adjusted considering only 1:1 complexes, while in the Am-phen and Am-PBIm data the results were best described considering both 1:1 and 1:2 complexes being present simultaneously.

4 Discussion

4.1 Non-aqueous Spectroscopy of Stock Solutions

The spectral differences between aqueous and the methanolic solutions of Nd^{3+} and Am^{3+} most probably indicate the presence of anions (i.e., nitrate) in the inner coordination sphere of the metal in anhydrous methanol. In aqueous solution for Am^{3+} in the 450–850 nm region, 2 distinct peaks are present. A single very intense sharp peak at typically 503 nm (ε approx. 311 $L \cdot mol^{-1} \cdot cm^{-1}$) is the hypersensitive ${}^7F_0 \rightarrow {}^5L_6$ absorption and a broader absorption of much lower intensity is observable at λ_{max} 816 nm ($\varepsilon = 64.4\ L \cdot mol^{-1} \cdot cm^{-1}$). For Nd^{3+} in aqueous solution in the 550–950 nm region, 4 distinct sharp peaks can be seen at 580, 738, 797 and 867 nm respectively. The moderately sharp peak at 580 nm is the hypersensitive peak (${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$) in aqueous solution. With its markedly higher dielectric constant, the corresponding species in water are generally accepted to be outer-sphere ion pairs. It is unclear why the hypersensitive behavior of Nd^{3+} changes in methanolic solution. The Nd^{3+} peak between 720–770 nm displays greater sensitivity to changes in the inner coordination sphere (${}^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$) which is distinctive from the hypersensitive peak at 570–600 nm in aqueous systems.

The change in medium does not significantly alter the hypersensitivity behavior of the ${}^7F_0 \rightarrow {}^5L_6$ absorption (503 nm in aqueous solution) for Am^{3+}. As is true of several other actinide ions, this peak is quite responsive to changes in the composition of the inner coordination sphere. It is reasonable to suggest that this observation may reflect the greater involvement of 5f electrons/orbitals in metal–ligand bonding interactions, which can result from the greater radial extension of these orbitals (as compared with the corresponding lanthanide 4f electrons). The actual origin of enhanced covalency in actinide bonding remains a topic of discussion in both experimental and computational actinide chemistry; 5f, 6d, even 7s orbitals have variously been suggested as possible contributors. In aqueous media, the 503 nm band is accepted as representing $Am(H_2O)_9{}^{3+}$. The more complex envelope seen in methanol certainly indicates a mix of inner-sphere interactions of Am^{3+} with H_2O, CH_3OH and NO_3^-. These species are present at concentrations decreasing in the order $CH_3OH > NO_3^- > H_2O$ (or maybe $CH_3OH > NO_3^- = H_2O$). The fundamental interaction strength (electrostatic ion–ion or ion–dipole interactions) should be in the order $Am^{3+}\text{–}NO_3^- > Am^{3+}\text{–}OH_2 > Am^{3+}\text{–}CH_3OH$. It is tempting to attribute the features at 505 nm, 511 nm and 514 nm to these specific interactions, but the present data offer no guidance in correlating spectral bands with specific metal–ligand interactions or higher order Am–nitrate complexes. Explicit interpretation of these spectral features does not impact the interpretation of the metal complexation equilibria with the nitrogen donor ligands.

4.2 Determination of Stability Constants

The stability constants for complexing of the bidentate nitrogen based heterocyclic ligands to Nd^{3+} are seen to be not dramatically different (Table 3). The PTMP value is lower, possibly due to the fact that the complex is characterized by a six-membered chelate ring while the bidentate complexes of the other three ligands form five-membered rings. The differences in stability are slight, but aside from phen–bipy, they are statistically significant. Considering the uncertainties, the relative complexation strength is PMBP < PBIm < Phen ≤ Bipy. The respective stability constants for Nd^{3+} complexes with acetate ($HO_2C\text{–}CH_3$), glycolate ($HO_2C\text{–}CH_2(OH)$), and glycine ($HO_2C\text{–}CH_2(NH_2)$) are $\log_{10} K_{acetate} = 2.10$, $\log_{10} K_{glycolate} = 2.89$ and $\log_{10} K_{glycine} = 3.26$ at $I = 0.1\ mol \cdot L^{-1}$, $t = 25\ {}^\circ C$ in aqueous media [18]. In the carboxylate systems, the electrostatic driving force from combining cations and anions contributes to this greater stability. Entropic stabilization, resulting from cation dehydration, also contributes to the carboxylate systems but is less important in the methanolic medium.

Fitting of a 1:2 M:L species to the Nd^{3+} data for phen and PBIm in Fig. 2 was attempted but such adjustment provided little to no improvement in the fit and generated either undefined or poorly defined equilibrium constants. The binding constant of phen with Nd^{3+} at 0.03 $mol{\cdot}L^{-1}$ ionic strength ($\log_{10} K_{101} = 1.61 \pm 0.03$) is lower than that reported by Choppin and coworkers [19] in 5.0 $mol{\cdot}L^{-1}$ ionic strength NaCl aqueous solution ($\log_{10} K_{101} = 2.83 \pm 0.06$). The smaller equilibrium constant in the present study may reflect the impact of the reduced entropic stabilization that is gained from cation desolvation, which is certainly less in the methanolic system. The high ionic strength of the previous study is also certainly a factor. In contrast, the binding constant of bipy at 0.03 $mol{\cdot}L^{-1}$ ionic strength in methanol is higher ($\log_{10} K_{101} = 1.8 \pm 0.2$) than the value reported by Hancock and coworkers in 0.5 $mol{\cdot}L^{-1}$ aqueous $NaNO_3$ ($\log_{10} K_{101} = 0.9$) [20]. It can be assumed that in MeOH media there are fewer waters molecules and more MeOH in the inner coordination sphere of the Nd^{3+} so that the soft-donor bipy must displace to form complexes.

From the spectrophotometric titrations of phen and PBIm it was possible to fit an ML_2 species in solution. The values for the $\log_{10} \beta_{102}$ of phen and PBIm with Am^{3+} are 5.7 ± 0.1 and 4.24 ± 0.02, respectively, and lead to $\log_{10} K_{102}$ (step-wise equilibrium) values of 2.7 ± 0.1 and 2.35 ± 0.02. It is very unusual that $\log_{10} K_{102}$ (2.35) is larger than $\log_{10} K_{101}$ (1.89) when binding PBIm to Am^{3+}. This pattern may be due to the effect of the bulk of the ligand on the solvation of the inner coordination sphere making it preferential to bind another PBIm ligand. This effect has been shown in the binding constants of 2,6-bis(5,6-dimethyl-1,2,4-triazine-3-yl)pyridine (Me-BTP) with Eu^{3+} at low ionic strength (0.0022 $mol{\cdot}L^{-1}NO_3^-$ in 50% MeOH) using electrospray mass spectrometry (ES-MS) [7]. The binding of phen follows the expected trend when comparing the $\log_{10} K_{101}$ value (2.7) with $\log_{10} K_{102}$ (3.03), although the energetic cost of complexing a second phen to Am^{3+} is seen to be close to that of adding a single ligand.

In a solid state study of Nd^{3+} with thiocyanate (SCN^-) as the counter ion in complexes of PBIm, Thakur et al. observed that the isolated solid was an $ML_2(NCS)_3$ species. The electronic spectra of this compound were recorded by dissolving the compound in MeOH [21]. No spectra were presented in [21] but the cited λ_{max} of the complex in solution is in good agreement with the spectra for Nd(PBIM) (Fig. 2). The comparisons between these spectra are given in Table 2. The authors of the previous study attribute this spectrum directly to a $ML_2(NCS)_3$ species, but considering the lability of the metal complex, the possibility that there is a 1:1 complex in solution must be considered. For coordination compounds in which the metal ion engages in predominantly covalent interactions with ligand donor atoms, it can

Table 2 Comparison of literature values for λ_{max} $Nd(PBIm)_2(NCS)_3$ in MeOH [21] with Nd spectra in Fig. 2

Lit. λ_{max} (cm^{-1})	Lit. λ_{max} (nm)	Nd^{3+} spectra PBIm λ_{max} (nm)
17,182	582.00	581.40
13,495	741.02	743.03
13,333	750.02	749.87
12,468	802.05	798.57

be safely assumed that the structural features identified in the solid state (via crystal structures) are representative of the corresponding structures in solution. However, for metal ions that engage in predominantly ionic interactions with ligand donor atoms (e.g., lanthanides and actinides), the labile nature of the complexes makes this correlation less certain. This is especially true when soft-donor ligands compete with hard donor species like MeOH, residual water, or NO_3^- ions present in solution.

In the spectrophotometric titrations of the bidentate ligands with Am^{3+} in MeOH, more complex behavior is indicated. A noteworthy feature in the spectral patterns of phen and PBIm is the development of the spectral peak in the 520 nm region, which is usually indicative of a 1:2 M:L species forming in solution [17]. Addition of a second complex to the model did not improve the quality of the fit for bipy or PTMP. The $\log_{10} K_{101}$ values calculated for bidentate ligands with Am^{3+} and Nd^{3+} in MeOH are shown in Table 1. The stability constants are higher for Am^{3+} than Nd^{3+} in solution in every ligand system. This is representative of the selectivity of N-containing soft donor ligands for actinides in the trivalent oxidation state over trivalent lanthanides. This selectivity is attributed to a greater covalent nature for the interaction between the N-donor ligand and Am^{3+} due to the greater spatial extension of the 5f orbitals and hence better overlap with the nitrogen donor orbitals [22]. The only report indicating thermodynamic evidence for greater covalency in actinide bonding with N-donors is by Miguirditchian and coworkers who reported a more exothermic enthalpy of binding of Am(III) with 2-amino-4,6-di(2-pyridyl)-1,3,5-triazine (ADPTZ) [23]. Other attempts to demonstrate that this greater covalency results from a greater degree of orbital overlap via thermodynamics has proven elusive for polyaminocarboxylates [24] as well as those ligands belonging to the 2,6-bis(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine (BTP) class of compounds [25, 26].

As the ultimate purpose of this investigation is to assess the viability of these bidentate nitrogen complexants for the development of advanced Am/Ln separations systems, it is appropriate to consider the applicability of these data to a hypothetical separations problem. Though N-donor systems of the type described here are ultimately not well-suited to this application as aqueous complexants in solvent extraction (or probably ion exchange) separations, the thermodynamic data generated do permit an assessment of the relative affinity of the reagents for the metal ions of interest. If these reagents were introduced into the aqueous phase, it would be appropriate to consider metal complex stability and stoichiometry and their competing affinity for free hydrogen ions (H^+). In methanol solution, we have assumed that the latter is not an important facet. If we treat the hypothetical separation system generically and assume that the complexes described here would be representative of Nd^{3+}/Am^{3+} complexes in the counter-phase of our hypothetical separation, it is possible to predict a selectivity factor using the data in Table 1. Starting from the hypothetical metal ion mass balance expression and assuming for simplicity that $[L] \gg [M^{3+}]$, the mass balance expression is;

$$[M]_t = [M]_{\text{phase 1}} + [M^{3+}]_{\text{phase 2}} + [ML]_{\text{phase 2}} + [ML]_{\text{phase 2}}$$

which can be written in terms of the metal complexation equilibrium constants (β_i) as,

$$[M]_t = [M]_{\text{phase 1}} + [M^{3+}]_{\text{phase 2}} + \beta_1 \cdot [M^{3+}]_{\text{phase 2}} \cdot [L]_{\text{phase 2}} + \beta_2 \cdot [M^{3+}]_{\text{phase 2}} \cdot [L]^2_{\text{phase 2}}$$

This expression defines the total mass balance for the metal ion. As we are trying to define a separation efficiency, it is appropriate to introduce a phase ratio (distribution ratio, D_M) as,

$$D = \frac{[M]_{\text{phase 1}}}{[M^{3+}]_{\text{phase 2}} + \beta_1 \cdot [M^{3+}]_{\text{phase 2}} \cdot [L]_{\text{phase 2}} + \beta_2 \cdot [M^{3+}]_{\text{phase 2}} \cdot [L]^2_{\text{phase 2}}}$$

which can be rearranged to:

$$D = \frac{[\mathrm{M}]_{\mathrm{phase\,1}}}{[\mathrm{M}^{3+}]_{\mathrm{phase\,2}} \cdot (1 + \beta_1 \cdot [\mathrm{L}]_{\mathrm{phase\,2}} + \beta_2 \cdot [\mathrm{L}]^2_{\mathrm{phase\,2}})}$$

The ratio $[\mathrm{M}]_{\mathrm{phase\,1}}/[\mathrm{M}^{3+}]_{\mathrm{phase\,2}}$ can be considered to be the distribution ratio in the absence of L, D_o and the alteration of the partitioning that results from introduction of L into phase 2 as:

$$D_o/D = 1 + \beta_1 \cdot [\mathrm{L}]_{\mathrm{phase\,2}} + \beta_2 \cdot [\mathrm{L}]^2_{\mathrm{phase\,2}}$$

Thus it is seen that the efficiency of the phase transfer reaction (as altered by the ligand L) is proportional to (1) the thermodynamic stability of the complex (β_i), (2) the concentration of the ligand [L] and (3) the stoichiometry of the metal complexes formed. However this is only valid under the assumption that D_o is identical for lanthanides and actinides and that the metal portioning reaction makes no contribution to the overall separation.

If we are also interested in the mutual separation of two metal ions (M and M′), we can further define a separation factor as:

$$S^{\mathrm{M}}_{\mathrm{M}'} = (D^{\mathrm{M}}_o/D^{\mathrm{M}})/(D^{\mathrm{M}'}_o/D^{\mathrm{M}'}) = \frac{1 + \beta^{\mathrm{M}}_1 \cdot [\mathrm{L}]_{\mathrm{phase\,2}} + \beta^{\mathrm{M}}_2 \cdot [\mathrm{L}]^2_{\mathrm{phase\,2}}}{1 + \beta^{\mathrm{M}'}_1 \cdot [\mathrm{L}]_{\mathrm{phase\,2}} + \beta^{\mathrm{M}'}_2 \cdot [\mathrm{L}]^2_{\mathrm{phase\,2}}}$$

Using the equilibrium constants in Table 1 and assuming that a ligand solubility range of 0–0.2 $\mathrm{mol{\cdot}L^{-1}}$ is attainable, the following potential separation efficiency for Am^{3+} from Nd^{3+} can be calculated. It is seen that PTMP slightly outperforms bipy, but the PBIm and phen systems show markedly higher potential due to the presence of the 1:2 complexes. Though achieving a solubility limit of phen in any medium as high as 0.2 $\mathrm{mol{\cdot}L^{-1}}$ is challenging, these data indicate a considerable separation potential for this ligand system. The PBIm is about 10 times lower throughout the range of concentrations. In principal, this assessment should apply to the functional groups (to a first approximation) in any system that allows higher order complexes. The reality of developing a separation system around this concept is of course more challenging than this analysis indicates, but these data describe the potential of the separation system. It is clear that more nitrogen donors increase stability, but more importantly if suitable structures can be found that allow the greater affinity of An^{3+} for N (or S) donor ligands to create higher order complexes, the separation potential of comparatively simple chelating agents can be amplified.

This trend and the attributed separation factor was developed under the assumption that the 1:1 M:L complex would be extracted into the organic phase under the theoretical extraction conditions and that solvation effects would not substantially alter the relative stability of Am and Nd complexes in a biphasic system. Interestingly, the 1,2,3-triazolyl imparts a surprisingly high degree of selectivity for An(III) over Ln(III) based on the $\log_{10} K_{101}$ values. The overall binding affinity of the PTMP ligand could perhaps be increased by removal of the methyl bridging group between the 1,2,3-triazolyl and 2-pyridyl groups (which would result in the formation of a five-membered ring in the complex). Decreased bulk of the complexant may also increase the possibility of an ML_2 species forming much like phen and PBIm.

When taking into consideration the formation of higher order complexes and the possibility that the higher order complexes are more hydrophobic in nature, and hence more readily extracted into an organic phase in a solvent extraction process, then the ability of the individual ligand to separate Am^{3+} from Nd^{3+} follow the separation trend, considering the formation of 1:2 complexes with Am^{3+} over just 1:1 with Nd^{3+}:

$$\mathrm{Phen} > \mathrm{PBIm} > \mathrm{PTMP} > \mathrm{Bipy}$$

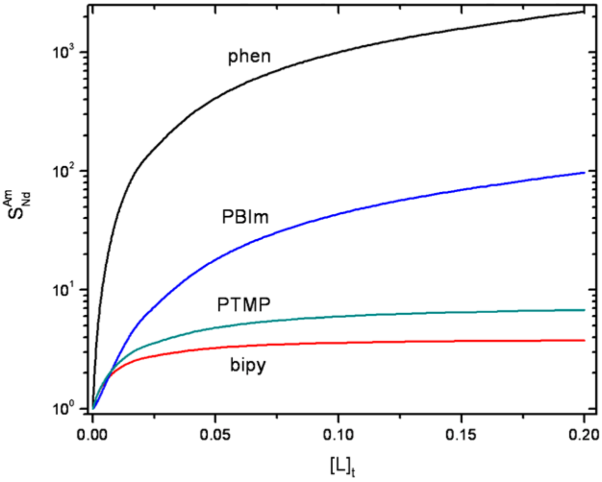


Fig. 4 Hypothetical separation potential curve for Am/Nd partitioning based on bidentate nitrogen donor ligand systems

This is a potentially important distinction that could be manipulated to enhance the separation potential of polyaza ligands for An^{3+}/Ln^{3+} separations; specifically, adjusting the steric bulk of complexants to simultaneously enhance both fundamental metal–ligand interaction strength and elevate the stoichiometry of the preferred An(III) relative to the lanthanide.

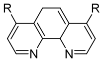
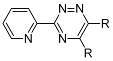
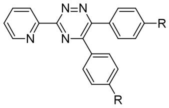
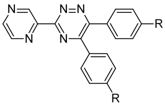
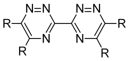
5 Conclusion

UV–vis spectrophotometry has been applied to a study of the binding of Am^{3+} and Nd^{3+} to a series of nitrogen donor ligands. Application of this method can give profound insight into the selectivity of ligands over one another for lanthanides and actinides. This allows the identification and screening of particular ligands for their selectivity without having to determine the best extraction conditions for the most efficient separation. From the data presented it is clear that the 1,2,3-triazoly group achieves reasonable selectivity for Am^{3+} over Nd^{3+} although it is plainly lower than phen or PBIm. When comparing the results in Fig. 4 with the data from the literature shown in Table 3, the separation factors attainable by the bidentate ligands are similar.

It is interesting to note that bidentate ligands containing just the triazine moiety have reduced extraction and separation coefficients when compared with the bidentate extractants containing mixed pyridyl and triazine moieties [16] (compare 2 and 5 in Table 3). This result does suggest that in the complexation of trivalent actinides and lanthanides, the pyridyl group is essential to the binding. It is unclear whether this observation represents a direct complexation effect or more an effect of reducing the number of available protonation sites. The incorporation of the harder pyridyl donor atom gives a stronger electrostatic interaction that allows the ligand to successfully compete with water in the inner coordination sphere. The presence of the pyridyl group reduces the number of protonation sites available and hence creates a lower number of positive charges upon protonation, thus decreasing aqueous phase solubility. This last factor does depend on the pK_as of the ligand.

To achieve a higher separation factor, a higher net denticity, achieved either through more donor atoms in the chelating agent or higher ligand–metal stoichiometry, is required. The 1,2,3-triazolyl ligand offers a high degree of selectivity worthy of future exploration

Table 3 Separation factors for selected N-donor extractants, the effect of substitution and the synergist used

Number	Ligand	Substitution	Synergist	$SF_{\mathrm{Am/Eu}}$	Ref.
1		R = H	α-BDA[a]	17.4	[5]
		R = Phenyl	dhmpp[b]	190	[6]
2		R = Methyl	α-BDA[a]	5.5	[7, 10, 11]
		R = Ethyl		5.9	
		R = Phenyl		7.0	
3		R = Br	α-BDA[a]	5.7	[7, 10, 11]
		R = OMe		1.8	
		R = t-Butyl		10.0	
4		R = Br	α-BDA[a]	3.1	[7, 10, 11]
		R = H		2.9	
		R = OMe		4.0	
5		R = Methyl	α-BDA[a]	5.3	[11]
		R = Phenyl		1.3	

[a] α-BDA = 2-bromodecanoic acid, [b] dhmpp = 4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione

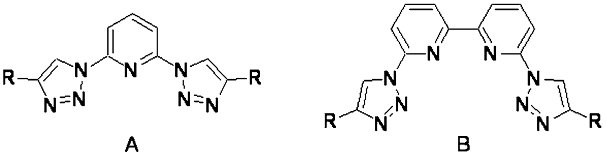


Fig. 5 Higher denticity 1,2,3-triazolyl containing N-donor heterocycles: (**A**) 2,6-bis(4-alkyl-1*H*-1,2,3-triazol-1-yl)pyridine, (**B**) 6,6′-bis(4-alkyl-1*H*-1,2,3-triazol-1-yl)-2,2′-bipyridine

as it allows further substitution and adaption of the donor groups to increase aliphatic diluent compatibility along with the addition of further functionality by inclusion of different donor groups. Using Sharpless "Click" chemistry [27] it should be possible to produce tridentate and tetradentate ligands comparable (Fig. 5) to the BTP and 6,6′-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2′-bipyridine (BTBP) type ligands proposed in Europe for the SANEX process [1]. These ligands would also have the added benefit of adhering to the CHON principle. With the functionalization of the acetylene used to make the 1,2,3-triazolyl, these ligands can be readily made compatible with the organic diluents used for solvent extraction processes. Also 1,2,3-triazolyl may display better strong acid stability than the BTP and BTBP counterparts [7], but this has yet to be explored. This work is part of an on-going study to design and synthesize ligands for the selective extraction of An(III) over Ln(III).

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