

PARTITIONING-SEPARATION OF METAL IONS USING HETEROCYCLIC LIGANDS

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Abstract

Some guidelines are proposed for the effective design of heterocyclic ligands for partitioning because there is no doubt that the correct design of a molecular extractant is required for the effective separation of metal ions such as actinides(III) from lanthanides(III). Heterocyclic ligands with aromatic ring systems have a rich chemistry, which is only now becoming sufficiently well understood in relation to the partitioning process. The synthesis, characterisation and structures of some chosen molecules will be introduced in order to illustrate some important features. For example, the molecule N-carboxybutyl-2-amino-4,6-di (2-pyridyl)-1,3,5-triazine (BADPTZ), which is an effective solvent extraction reagent for actinides and lanthanides, has been synthesised, characterised and its interaction with lanthanide ions studied. The interesting and important features of this molecule will be compared with those of other heterocyclic molecules such as 2,6-bis(5-butyl-1,2,4-triazol-3-yl) pyridine (DBTZP), which is a candidate molecule for the commercial separation of actinides and lanthanide elements.

Primary co-ordination sphere

One of the most critical features concerning whether a molecule is a suitable extraction reagent is the nature of the binding and co-ordination in the primary coordination sphere of the metal. The resultant effects for partitioning will be considered briefly for selected heterocyclic molecules. It will be shown how the structural types change as the complete lanthanide series is traversed from lanthanum to lutetium. For effective solvent extraction, the ligand(s) should be able completely to occupy the primary co-ordination sphere of the metal ion to be extracted. Interactions in the secondary co-ordination sphere are of less importance.

Inter-complex (Hydrogen Bonding) interactions

Another feature that will be briefly considered is the intermolecular binding between ligands when bound to the metal ion. Thus the intermolecular structures between complex molecules will be considered where these have relevance to the extraction process. For effective separations, the intermolecular interactions should be minimised such that there are only weak van der Waals interactions arising from the hydrophobic exteriors of the complexes.

Implications for partitioning

The effectiveness of the above heterocyclic reagents will be considered in relation to the interactions in the primary co-ordination sphere of the metal and the intermolecular interactions.

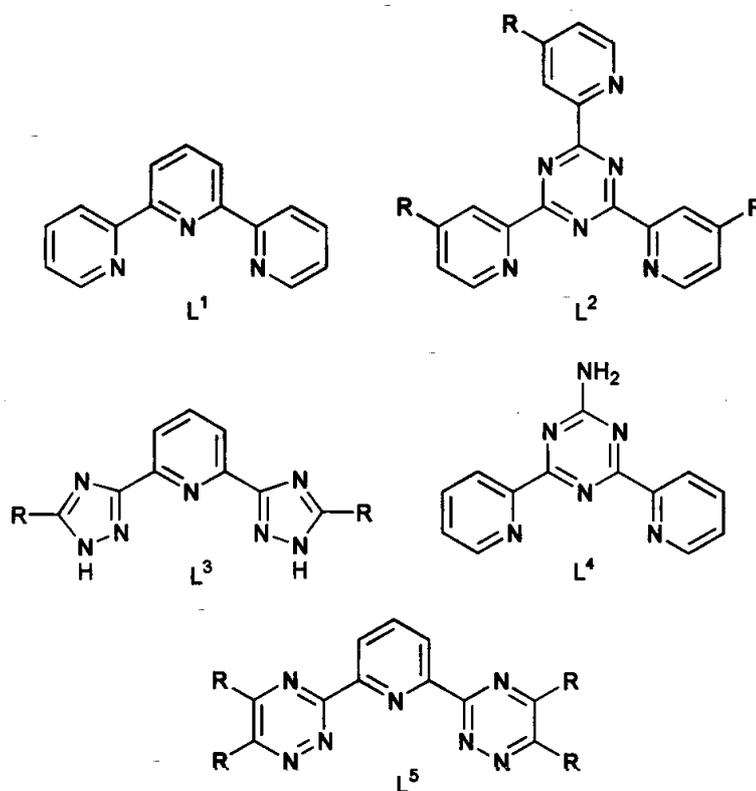
1. Introduction

There is no doubt that the correct design of a molecule is required for the effective separation of metal ions such as actinides(III) from lanthanides using solvent extraction reagents. Recent attention has been directed towards malonamides for coextraction but heterocyclic ligands with aromatic ring systems have a rich chemistry, which is only now becoming sufficiently well understood in relation to the partitioning process for the selective extraction of the actinides [1].

A future goal in nuclear fuel reprocessing may be the conversion or transmutation of the long-lived radioisotopes of minor actinides, such as americium, into short-lived isotopes by irradiation with neutrons [1]. In order to achieve this transmutation, it is necessary to separate the trivalent minor actinides from the trivalent lanthanides by solvent extraction, otherwise the lanthanides absorb neutrons too effectively and hence limit neutron capture by the transmutable actinides. Solvent extraction using ligands containing only carbon, hydrogen, nitrogen and oxygen atoms is desirable because they are completely incinerable and thus the final volume of waste is minimised [2]. Nitric acid is used in the extraction experiments because it is envisaged that the An(III)/Ln(III) separation process could take place after the existing PUREX process. For the ensuing discussion the heterocyclic ligands are considered as free bases but in practice one or more of the nitrogen atoms will be protonated – this should not influence the overall discussion since co-ordination to metal ion dominates over protonation particularly in the chelating molecules under consideration.

There is clearly a need to study future processes such as SANEX in which the minor actinides are selectively separated from the lanthanides. For the reasons outlined below, the solvent extraction reagents depicted in Figure 1 have been evaluated.

Figure 1. The ligands L^1 , L^2 , L^3 , L^4 and L^5



The terpyridyl reagent (ligand L^1) has been extensively studied previously [3]. With common ligands such as L^1 and 2,4,6-tri(2-pyridyl)-1,3,5-triazine (L^2), Am(III)/Eu(III) separation factors between 7 and 12 have been obtained when 2-bromohexanoic acid is used as a synergistic reagent [4]. The alkyl derivatives of tripyridyl-*s*-triazines (L^2) may well be good candidates for future studies but difficulties of synthesis has limited the availability of these reagents. The design of molecules such as the 2,6-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-pyridines (BTPs) (L^5) has lead to improved separation factors [5] without the requirement for reagents such as 2-bromohexanoic acid, which is required with most other heterocyclic reagents. The evaluation of the structures of complexes formed by L^4 with some trivalent metal ions has enabled the co-ordination of these ligands with the entire range of lanthanides to be evaluated. This has meant that the limitations on co-ordination caused by the lanthanide contraction are now better understood.

We have studied the molecule N-carboxybutyl-2-amino-4,6-di(2-pyridyl)-1,3,5-triazine (BADPTZ), which is an effective solvent extraction reagent for actinides and lanthanides. This molecule co-ordinates to the metal ions to L^4 but has improved Am(III)/Eu(III) separation factors of over 10. Thus it will shortly be possible to correlated precise solvent extraction data with known metal-ligand interactions.

2. Guidelines

One of the most important features concerning whether or not a molecule is a suitable extraction reagent is the nature of the binding and co-ordination in the primary and secondary co-ordination spheres of the metal ion. Thus it is possible to formulate some general guiding suggestions (not rules) for the purposeful design of ligands:

- The extractant molecules (ligands) should be designed so as to exploit the differences in the co-ordination chemistries (including ion-pair formation) of the ions to be separated.
- For effective solvent extraction, the ligand molecule(s) should be able completely to occupy the primary co-ordination sphere of the metal ion to be extracted.
- Interactions in the secondary co-ordination sphere are of less importance even though the counter-ions are in the secondary co-ordination sphere.
- There should be limited intermolecular interactions between the extracted species – preferably only van der Waals interactions such that even hydrogen bonding is minimised.
- There should only be a single species that is extracted.
- The chemical bonds within the primary co-ordination sphere should be strong but not so strong as to prevent subsequent bond breaking for the subsequent stripping process.
- There should be acceptable resistance to radiolysis.
- The likely decomposition products should have minimal interference with the solvent extraction process.

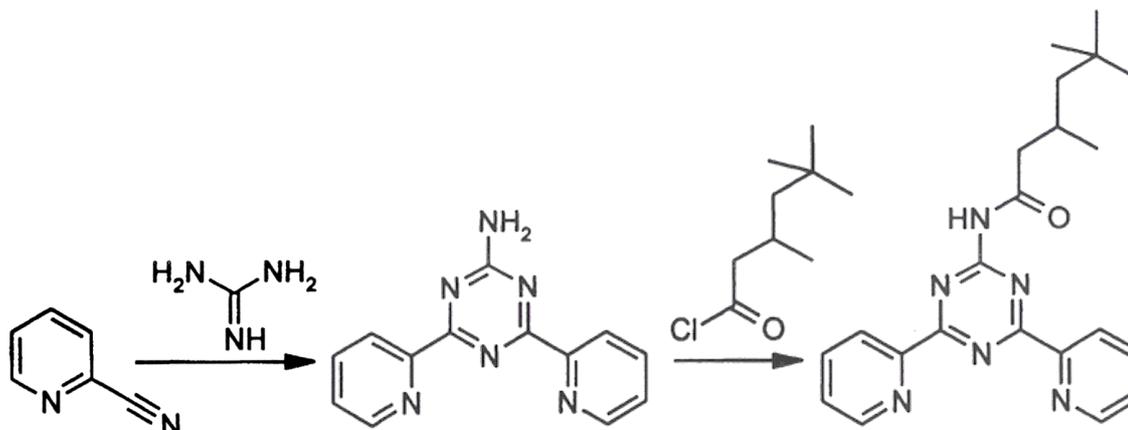
2.1 Primary co-ordination sphere

The primary co-ordination sphere of the metal ion is defined by the covalent binding between the metal atom and the immediate ligand atoms and the stereochemical arrangement of the ligands (or solvent extraction reagents). For lanthanides and minor actinides, metal-ligand binding is considered

to be much more ionic than is the case with the trivalent transition metals for which Crystal Field Effects play an important thermodynamic part. Thus the ligands are much more loosely bound in many cases – such that the metal-ligand bonds are broken and reformed much more readily than is the case with the transition metals or with the major actinides prior to Am. The design of polydentate nitrogen ligands, which complex minor actinides such as Am(III) preferentially to lanthanides, has proved to be challenging because the chemistries are so similar. Such differences that can be identified include the marginally enhanced selectivity of “soft” nitrogens in a heteraromatic ring for Am(III) than for Eu(III). Moreover, there is a body of evidence to suggest that the polydentate ligands are more firmly bound to the metal than is the case with monodentate ligands. Accordingly, we have been varying the nature of the donor nitrogen ligands in order to enhance these small differences so that they are manifested in increased separation factors (Am(III)/Ln(III) [2,3].

In order to do this, however, it is essential to understand the fundamental chemistries involved and to evaluate the structural types that are formed with different stereochemistries and bound ligand atoms. For example, the molecule N-carboxybutyl-2-amino-4,6-di-(2-pyridyl)-1,3,5-triazine (BADPTZ), which is an effective solvent extraction reagent for actinides and lanthanides, has been synthesised, characterised and its interaction with metal ions studied – see Figure 2. A low pressure cyclisation route has proved to be particularly useful in the synthesis of these reagents and has enabled a wide range to be prepared. In particular, the ligand ADPTZ (L^4) in which there are no alkyl groups on the amide group, has enabled the study of the range of structures that are manifest across the whole lanthanide series [6]. There are five structure types, which can be broadly divided into two equal groups. The larger lanthanides from La to Sm form structure types in which the co-ordination numbers are 11 and 10. La is the only lanthanide to form an 11-coordinate complex $La(ADPTZ)(NO_3)(H_2O)_2$ in which the ligand is tridentate and the nitrates are all bidentate. The La cation is too large to fit into the tridentate cavity of the ligand and sits outside. One general feature of the lanthanide complexes and the minor actinides is that there is rather rich co-ordination chemistry and several complexes have been identified for the same metal and ligands. For example, Nd and Sm both form two different 10-coordinate complexes. The first, $M(ADPTZ)(NO_3)_3(H_2O)$ is neutral with three bidentate nitrates and one water molecule. The second, $[M(ADPTZ)(NO_3)_2(H_2O)_3]^+$ is a cation with two bidentate nitrates and three water molecules. For the smaller lanthanides, there are two structure types, each of which is nine co-ordinate. One of these structures, $[LnL^4(NO_3)_2(H_2O)_2](NO_3)$, is rather unusual in that a dication is formed together with two nitrate anions. The complex $[Yb(ADPTZ)(NO_3)_3(H_2O)]$ is unusual in that it contains a monodentate nitrate anion. Without exception, the structures show intermolecular hydrogen bonding between the amine group of the metal complexes or solvent molecules. Such an observation is contrary to Guideline 4 but the inclusion of an alkyl or other hydrophobic group on the amine group greatly restricts the intermolecular hydrogen bonding so that BADTPTZ remains a candidate molecule for partitioning [7].

Figure 2. The synthesis of ADTPTZ and then BADTPTZ

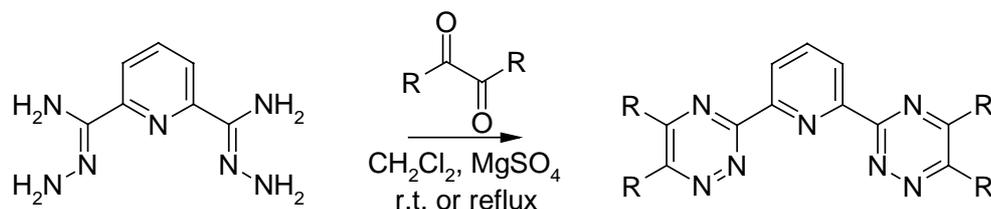


Thus, it can be seen even from this limited account of structures formed in the solid state that there is a wide range of structural types to be found with the lanthanides (and minor actinides). Probably the same also holds true for the actinides in that there is a wide range of structures for a given ligand plus nitrate and water. EXAFS studies have shown that structures to be found in the solid state are also present in the liquid phase. The principal implication for solvent extraction, however, is that there are several possible candidate species that may move across the aqueous and organic solvent interface during extraction or stripping [8]. In each of the above structures the metal is bound to ligand molecules (solvent extraction reagent) but in addition there are nitrate anions and/or water molecules. However, since these species have high rates of self exchange compared with polydentate groups, there is the possibility that a wide range of structural types are formed during solvent extraction. Therefore, the above Guideline 4 is pertinent throughout partitioning studies – particularly so if the species may have very different rates of transfer across the aqueous/organic interface.

2.2 Partitioning – enclosing the primary co-ordination sphere with only the ligand molecules

When the metal cation is completely surrounded by the ligand molecule(s) the rates of self-exchange of the ligands are minimised because the more mobile ligands such as water and nitrate are excluded from the co-ordination sphere of the metal. Thus it might be expected that there are enhanced solvent extraction properties when this is the case. BTPs are reagents in which the co-ordination sites of the metals may be satisfied by only the ligand. These reagents include 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine and one general method of synthesis of these reagents is shown in Figure 3. For R = propyl, the ligand gave D_{Am} values of between 22 and 45 and $SF_{Am/Eu}$ of 131-143 when 0.034 M of the ligand in modified TPH was used to extract from 0.9 -0.3 M HNO_3 and different amounts of NH_4NO_3 [5]. Other BTPs give separation factors between 50 and 150, which values are also far in excess of those obtained with many other ligands containing just carbon, hydrogen, nitrogen and oxygen atoms [5,6]. In addition, these BTP ligands do not require the use of a synergist such as 2-bromodecanoic acid, which is frequently necessary when extractions are carried out with other nitrogen heterocycles.

Figure 3. One method of the synthesis of BTP-type reagents



The initial solvent extraction studies indicated that the formula of the extracting species for Eu was possibly $ML_3(NO_3)_3 \cdot HNO_3$. The co-ordination of three tridentate heterocyclic aza-aromatic ligands to an actinide (III) or a lanthanide (III) ion in the presence of a co-ordinating anion such as nitrate was unprecedented and we initiated structural studies in order to verify the composition of the complexes formed with the 2,6-bis(5,6-dialkyl-1,2,4-triazol-3-yl)pyridines. Whereas for the larger lanthanides (La-Sm), centrosymmetric dimers of the form $[M_2L_6(NO_3)_6]$ were confirmed for the smaller lanthanides (Sm-Lu) $[ML_3]^{3+}$ cations were found with a variety of complex anions. These results contrast markedly with the types of complexes formed by lanthanum nitrates with other terdentate nitrogen ligands. For example, we have recently studied complexes formed between the lanthanide nitrates and the ligand 2,6-bis(5-methyl-1,2,4-triazol-3-yl)pyridine [8] and those formed with the terpyridyl ligand. The terpyridyl ligand also forms 1:1 complexes of several formulations but with excess ligand it is possible to form complexes with two ligands e.g. $[M(NO_3)_2(terpy)_2]$ $[M(NO_3)_4(terpy)]$, where M = La, Nd, Sm, Tb and Dy. Our work with other terdentate ligands has established similar structural features where the majority of complexes showed M:L ratios of 1:1 but for the larger lanthanides M:L ratios of 1:2 were occasionally observed.

The structure of $[Yb(L)_3]^{3+}$ where L is the BTP molecule with propyl groups is shown in Figure 4. Thus, we can conclude that our structural studies provide the first solid state evidence for the unique type of complex, which is involved in the extraction process using these new solvent extraction reagents. This structure is also to be found in the with the elements from Sm-Lu and include the complex cation $[Eu(L)_3]^{3+}$ cation. The structure shows that the nitrogen atoms in the tridentate cavity are bound to the central metal cation. Thus the co-ordination sphere, which results in a co-ordination number nine is completely satisfied by the ligand molecules with no nitrate or water in the primary co-ordination sphere (Guidelines 2 and 4). The rates of exchange of the ligand(s) are minimised so that as far as possible there is one extracted species.

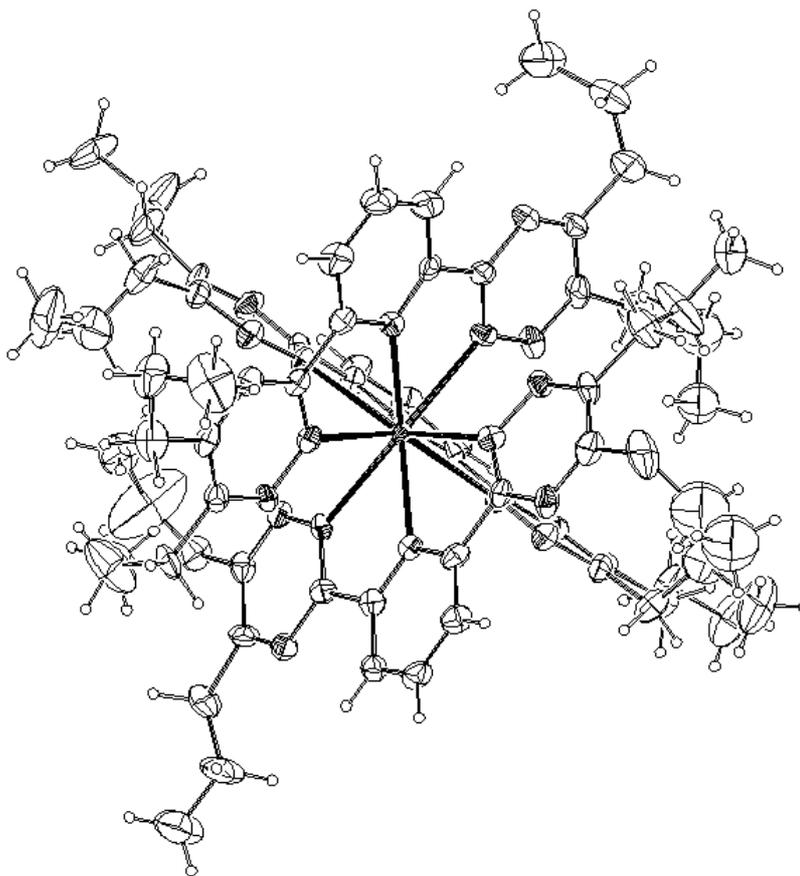
2.3 Intermolecular interactions

When the ligand or solvent extraction reagent is bound to the metal ion, there is the possibility to have a hydrophilic or hydrophobic “external” surface presented to the solvent. In the case where there is extensive hydrogen bonding, the interaction between the neighbouring extracted species may be too high. For the $[Yb(L)_3]^{3+}$ cation, the counter anion may be nitrate or a complex anionic species. In spite of this, the intermolecular interactions are minimised owing to the hydrophobic nature of the outer regions of the ligand. These would be further minimised if a neutral species could be extracted. Perhaps anionic groups could be built into the ligand.

2.4 Implications for partitioning

The above guidelines are able to provide general ideas for the design and implementation of new solvent extraction reagents with enhanced properties. Of course, in one way the guidelines may be called a “wish-list” of desirable properties. Consideration of the guidelines does, however, indicate that there is still a lack of fundamental knowledge particularly with respect to the comparison between the chemistries of the lanthanides and the actinides.

Figure 4. **The structure of $[\text{Yb}(\text{L})_3]^{3+}$ where L is the BTP molecule with propyl groups [9]**
(Note how the ligands completely occupy the co-ordination sphere of the metal ion with Yb-N distances ranging from 2.450(11) to 2.499(11)Å)



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REFERENCES

- [1] Gabriel Y.S. Chan, Michael G.B. Drew, Michael J. Hudson, Peter B. Iveson, Jan-Olov Liljenzin, Mats Skålberg, Lena Spjuth and Charles Madic, *Solvent Extraction of Metal Ions From Nitric Acid Solution Using N,N – Substituted Malonamides. Experimental and Crystallographic Evidence for Two Mechanisms of Extraction, Metal Complexation and Ion-pair Formation*, J. Chem. Soc., Dalton Trans, 1997 6 649-660.
- [2] Michael J. Hudson, Michael G.B. Drew, Mark L. Russell, Peter B. Iveson and Charles Madic, *Experimental and Theoretical Studies of a Triazole Ligand and Complexes Formed With the Lanthanides*, J. Chem. Soc. Dalton, 1999, 2433-2440.
- [3] Michael G.B. Drew, Michael J. Hudson, Peter B. Iveson, Jan-Olov Liljenzin, Lena Spjuth and Charles Madic, *Crystal Structures of Two Different Ionic Complexes Formed Between Protonated Terpyridine Cation and Lanthanide Nitrates*, *Polyhedron*, 1998 18(17) 2845-2849.
- [4] Michael J. Hudson, I. Hagström, L. Spjuth, Å. Enarsson, J.O. Liljenzin, M. Skålberg, Peter B. Iveson, Charles Madic, Pierre-Yves Cordier, Clement Hill and N. Francois, *Synergistic Solvent Extraction of Trivalent Americium and Europium by 2-bromodecanoic Acid and Neutral Nitrogen-containing Reagents*, *Solvent Extraction and Ion-Exchange*, 178, 221-242 (1999).
- [5] Zdenek Kolarik, U. Müllich and F. Gassner, *Ion. Exch. Solvent Extr.*, 1999 17 23; Z. Kolarik, U. Müllich and F. Gassner, *Ion. Exch. Solvent Extr.*, 1999, 17, 1155.
- [6] Michael J. Hudson, Michael G.B. Drew, Peter B. Iveson, Charles Madic and Mark L. Russell, *A Study of Lanthanide Complexes Formed With the Terdentate Nitrogen Ligand 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine*, J. Chem. Soc., Dalton Trans., 2000, 2711-2720.
- [7] Patent (Application) PCT/GB96/01700: Separation of Lanthanides and Actinides with Heterocyclic Ligands.
- [8] Michael J. Hudson, Michael G.B. Drew, Peter B. Iveson and Charles M. Madic, *Comparison of the Extraction Behaviour and Basicity of Some Substituted Malondiamides*, *Solvent Extraction and Ion Exchange*, 18, 2000 1-23.
- [9] Michael J. Hudson, Michael G.B. Drew, Denis Guillaneux, Mark L. Russell, Peter B. Iveson and Charles Madic, *Lanthanide(III) Complexes of a Highly Efficient Actinide(III) Extracting Agent – 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)-pyridine*, *Inorg. Chem. Commun.* 2000, in press.