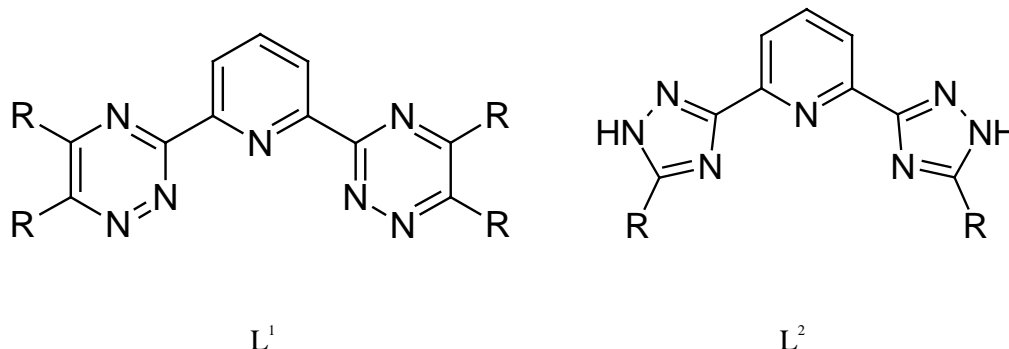


**THEORETICAL AND EXPERIMENTAL STRUCTURAL STUDIES OF THE EXTRACTION
OF ACTINIDES AND LANTHANIDES BY TRIDENTATE NITROGEN LIGANDS
CONTAINING 1,2,4-TRIAZINES OR 1,2,4-TRIAZOLES**

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The separation of lanthanides and actinides by tridentate nitrogen ligands has been studied by a variety of theoretical and experimental techniques. Various oligoamines have been shown to separate actinides from lanthanides in nitric acid solutions. In this work we concentrate on two ligands L^1 and L^2 that have recently been shown to have remarkable separation properties [1].



In the separation process, it has been thought that the species present at low levels of acidity are simple metal co-ordination compounds. However, our own structural studies on a number of tridentate ligands have shown a large variety of structural types which depend on the nature of the ligand and on the lanthanide concerned. In order to gain insights into the coordinative mechanism of extraction and separation, we have carried out X-ray structural studies on these two ligands with remarkable properties.

We have studied 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine L^1 with $R = t$ butyl and obtained structures of the metal complexes with $M = La$, and Nd . The lanthanum structure contains two equivalent cations and two equivalent anions in the asymmetric unit, of formula $[La(L^1)_2(NO_3)_2]^+$ and $[La(L^1)(NO_3)_4]^-$ respectively. The two ions are 10 and 11 co-ordinate. By contrast, the neodymium structure contains two such identical cations $[Nd(L^1)_2(NO_3)_2]^+$ with $[Nd(NO_3)_4(HOEt)_2]^-$ and $(NO_3)^-$ anions. Further structural studies are in progress and show that this cation is predominant throughout the lanthanide series. While these structures have been determined with $R = t$ butyl, it seems likely that

equivalent structures are to be found with similar ligands containing different alkyl groups. The predominance of the $[M(L^1)_2(NO_3)_2]^+$ cation in the lanthanide series is consistent with our structural studies of terpyridine which show cations with this formulation are also often to be found.

We have studied 2,6-bis(5-alkyl-1,2,4-triazol-3-yl)pyridine, L^2 with R = methyl and R = butyl. The ligand with good extraction properties has R=butyl but we were unable to obtain suitable crystals of metal complexes with this ligand and so used R=methyl. However, with R=butyl we were able to obtain a crystal structure of the free ligand. There are two molecules in the asymmetric unit each with C_2 symmetry and these are interleaved surrounding a water molecule. The four triazole nitrogen atoms from two ligands are hydrogen bonded to one water molecule in a tetrahedral arrangement. The location of the hydrogen atoms on the nitrogen atoms could not be determined unequivocally in the crystal structure but it appears likely that two of the nitrogen atoms are protonated and act as hydrogen bond donors while the other two are unprotonated and act as hydrogen bond acceptors. This is supported by *ab initio* Gaussian94 calculations on the ligand which show that the hydrogen atom in the ligand is found preferentially in the 4 position but there is only a 1 kcal mol⁻¹ difference when placed in the 1 position. By contrast placement in the 2 position is shown to be unlikely as the energy increases by 4.5 kcal mol⁻¹.

With R = methyl (DMTZP), we have prepared a series of metal complexes. So far, seven structures have been determined and four different structural types (A-D) have been observed (see Table 1). In each type the lanthanide is bound to only one terdentate ligand. In type A (La) the metal is bonded to one ligand, one nitrate anion and five water molecules to give a ten-co-ordinate 2+ cation. The triazole nitrogen atoms co-ordinated to the lanthanides are those in the four position. There are two further nitrates which are uncoordinated. Structures with Nd, Sm, Tb and Dy are isomorphous (type B) and show the metal ion bound to one pyridine, two triazole nitrogen atoms and also interestingly to four bidentate nitrate ions – giving a co-ordination number of eleven. There are no accompanying cations in the cell and, therefore, the charge balance must be provided by an extra proton in the triazole ligand. This is consistent with the intermolecular contacts in the unit cell which show a hydrogen bonding network with water molecules which “connect” adjacent ligands. We conclude that the exact disposition of the hydrogen atoms is disordered with any three of the four triazole nitrogen atoms being protonated in any particular ligand. It is interesting that the co-ordination number of (Nd-Dy) is 11, while that of La is only 10 despite its larger size, but this is consistent with the fact that the two monodentate water molecules take up relatively more space than the bidentate nitrate anions.

The third structural type C (Ho + Er) involves the co-ordination of three nitrogen atoms, two bidentate nitrates, one monodentate nitrate and one water molecule. It appears that the triazole rings in the nine co-ordinate complexes are doubly protonated and one of these protons is hydrogen bonded to an acetonitrile molecule. The final structural type D (Yb) shows a nine co-ordinate metal ion is bound to three nitrogen atoms and three bidentate nitrates. One of the nitrogen atoms in the protonated triazole ring is again hydrogen bonded to an acetonitrile solvent

In all these complexes, the ligands are planar and the lanthanides co-ordinate in the plane of the ligand. We have used computer modelling techniques to investigate the effect of changing the chain lengths from methyl to butyl. Starting from the crystal structures, we have increased the chain lengths from one to four carbon atoms and have established that these alkyl chains have no significant steric effect on the metal co-ordination sphere.

Table 1 : **Structure Types of DMTZP complexes established by X-ray Crystallography**

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
A			B		B			B	B	C		C	D	

It will be very interesting to see whether the different structural types found for the lanthanide structures can be correlated with the extraction properties of specific lanthanides. It can be argued that there would be a wide range of structures for each lanthanide in solution and that conclusions cannot be drawn from isolated crystal structures. But in our view it seems likely that for example the large difference in structure between type B (11-co-ordination, four nitrates, protonated ligand) and C (9-co-ordination, three nitrates – one monodentate, ligand) are related to differences in structure and physical properties in solution which would significantly effect extraction properties. Work is in progress to study these complexes with EXAFS to see whether the structure types persist in solution.

Our structural studies indicate that the extraction mechanism for L^1 and L^2 is likely to be very different. The predominance of the $[M(L^1)_2(NO_3)_2]^+$ cation in the chemistry of metal complexes of L^1 is clearly significant. By contrast there is no evidence for the formation of such an ion with L^2 , indeed there are no structures where the metal to ligand ratio is 1:2. It seems likely that in this case, the important factor is the formation of the $M(LH)(NO_3)_4$ neutral complex with concomitant protonation of the ligand. However for both ligands knowledge of the stoichiometry of the actinide(III) complexes is required before conclusions can be drawn again. These studies are in progress.

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REFERENCES

- [1] Z. Kolarik, U. Mullich, private communication and poster, this conference (1998)