

**THEORITICAL AND EXPERIMENTAL STRUCTURAL STUDIES OF THE EXTRACTION
OF ACTINIDES AND LANTHANIDES BY THE TRIDENTATE NITROGEN
LIGAND 4-AMINO, 2,6-DIPYRIDYL TRIAZINE (ADPTZ)**

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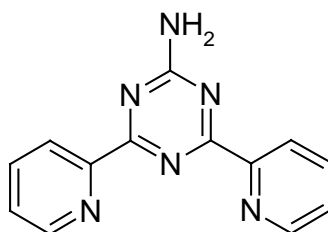
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The separation of lanthanides and actinides by tridentate nitrogen ligands has been studied by a variety of theoretical and experimental techniques. The title ligand ADPTZ has been shown to be particularly useful in synergistic extraction systems with α -bromocapric acid. In the separation process, it has been thought that the species present at low levels of acidity are simple metal coordination compounds. However our own structural studies on a number of terdentate ligands have shown a large variety of structural types which depend on the nature of the ligand and on the lanthanide concerned.



ADPTZ has been found to produce a wide and varied structural chemistry with the lanthanide elements and this has been studied in detail via X-ray crystallography. We have prepared and studied well over 20 samples. In addition, the amino group has been acylated with cyclohexanoyl chloride to form 4-cyclohexanoylamino-2,6-dipyridyl triazine CADPTZ. The results are shown in the Table.

Table. Crystal Structures of Lanthanide Complexes with ADPTZ

Type	Stoichiometry	Charge	CN	Metals
1	L, 3BN, 2W	0	11	La
2	L, 3BN, 1W	0	10	La, Pr, Nd, Sm, Eu
3	L, 2BN, 3W	1	10	Nd, Sm
4	L, 2BN, 2W	1	9	Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
5	L*, 1BN, 4W	2	9	Yb
6	L, 2BN, 1MN, 1W	0	9	Yb, (Y)

L* is CADPTZ, L is ADPTZ

BN is bidentate nitrate, MN is monodentate nitrate, W is water.

The wide range of structural types found for the lanthanides with ADPTZ are evidenced in the Table. As can be seen the co-ordination number is highly dependent upon the size of the ion, but there are also variations in the preferred stoichiometry. The six structure types can be divided into two equal groups. The larger lanthanides, La-Eu, form structure types 1,2 and 3 with co-ordination numbers 11 and 10. La is the only lanthanide to form an 11-co-ordinate complex and indeed forms two different neutral complexes with an additional water molecule being the only difference between the 11 and 10-co-ordinate complexes. Both Nd and Sm form two different 10-co-ordinate complexes, one neutral with three bidentate nitrates and the other a cation with two bidentate nitrates and two water molecules. For the smaller lanthanides there are three structure types, all of which are nine-co-ordinate. The most prevalent type is the cation type 4 with two bidentate nitrates, and two water molecules. However, it is interesting that Eu forms both types 2 and 4. Variations on structure 4 are given by types 5 and 6 but these are only found with Yb and Y. These are most unusual structures as 5 contains a di cation and 6 a monodentate nitrate.

This work shows clearly that the lanthanides (and by implication the actinides) form a variety of complexes in solution and that at least some of these are cationic. It seems unlikely therefore that a single type of complex is responsible for extraction. While these solid state structures indicate that the dominant species can be predicted, there must remain some uncertainty as to the prevalent forms in solution. However, preliminary results from XAS studies provide no evidence for any variations between solid and solution structures. It is noteworthy that these six structural types represent the largest number of different structures ever found across the lanthanide series. In many other cases there are just 1 or 2 changes in co-ordination number across the series. Clearly the terdentate ligands, combined with nitrates and water, offer the potential of a wide range of stoichiometries for metal complexes.

We also report the determination of several other structures relevant to this program. These include the free 4-cyclohexanoylamino-2,6-dipyridyl triazine ligand (CADPTZ). The key feature of interest in this structure is the *cis-cis* conformation of the pyridine rings. This is the first time this conformation has been observed in this type of ligand in the absence of a co-ordinating metal ion or in the absence of a hydrogen bond acceptor when the ligand is in its protonated form. The reason for this is unclear but the *cis-cis* conformation may be stabilised via crystal packing and the formation of an intermolecular hydrogen bond between the amide hydrogen and a pyridine nitrogen atom

The structure of a corresponding Yb(III) complex of CADPTZ together with a Yb(III) complex of 4-*t*-butylacetanoylamino-2,6-dipyridyl triazine (TBADPTZ) - a ligand which was specifically made in an effort to obtain crystalline lanthanide complexes. The CADPTZ complex is interesting because there is only one bidentate nitrate co-ordinated to the Yb(III) and the co-ordination sphere is made up by four water molecules. A nitrate ion is hydrogen bonded to the NH in the amide group. In the complex with TBADPTZ. Yb(III) is co-ordinated to three nitrogen atoms, two bidentate nitrates, one monodentate nitrate and one water molecule. Attempts were also made to prepare Sm(III) and Nd(III) complexes with these ligands but in each case the amide bond was found to hydrolyse and the corresponding Ln/ADPTZ complexes were isolated as crystalline products. The stability of Ln/TBADPTZ complexes in solution is currently being studied by proton NMR.

The structures of a complex formed between Nd(III) and an ADPTZ analogue - 4-amino-2,6-di(4-methylpyridyl)-triazine (ADMPTZ) has also been determined. The methyl groups were added to increase the hydrophobicity of the ligand. This structure is consistent with one of the previously determined Nd/ADPTZ structures - the Nd(III) being co-ordinated to 3 pyridyl nitrogen atoms, three bidentate nitrates and one water molecule.

This work suggests that the extraction process with terdentate planar nitrogen-donor ligands is extremely complicated. The lanthanides can form many different types of complexes and we are as yet uncertain as to the types of complexes formed with the actinides. Further work is clearly needed to elucidate the extraction mechanisms.

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