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Final Report
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Task # 67

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During this two year period we have studied various aspects of the chemistry of new pyridine phosphonates that are of specific interest to separations chemistry issues at LANL. This work has been done in partnership with a DOE-BES program currently underway at UNM. In particular we have used newly derived synthetic approaches to form several pyridine N-oxide phosphonates, we have fully characterized these new species, we have studied their coordination chemistry toward several lanthanide and actinide ions and we have initiated solvent extraction studies of two ligands. The results for most of this work are described in three manuscripts that have been submitted or soon will be submitted for publication. Preprints of those papers are enclosed with this report. The information in those preprints is not repeated here.

In addition to that work we have also embarked on a major effort to survey the utility of computer assisted molecular modelling for the design of new chelating ligands for actinide ions. This effort has been both interesting and frustrating. The following general conclusions have been made. The existing commercially available force field packages are not adequate for handling all of the important details of our ligands binding with An ions. In particular, the force fields do not correctly represent the valence condition in a pyridine N-oxide ring. Nonetheless, some useful preliminary findings were obtained. The computational packages, however, seem to give logical results on steric influences on metal binding geometries. Further, the placement of a methylene spacer between the ring and PO group is handled well and we were able to assess the effect of this group on chelate ring geometries. The steric effects of substituent groups on the PO groups were also assessed and logical results were obtained. Indeed, the results have suggested potentially useful ligand synthesis goals and we expect to undertake these efforts in the near future under the DOE-BES program. It is anticipated that much improved force fields will be required in order to gain reliable energetics useful for predicting thermodynamic binding constant data.

Finally, during this period we began to prepare large samples of selected ligands that will be used in future LANL/UNM collaborative studies of extraction properties. It is expected that several of the new ligands will have superior extraction properties compared to existing chelate systems.

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