

Project ID: **64965**

Project Title: **Supercritical Carbon Dioxide-Soluble Ligands for Extracting Actinide Metal Ions from Porous Solids**

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DE-FG07-98ER14928

SUPERCritical CARBON DIOXIDE LIGANDS
FOR EXTRACTING ACTINIDE METAL IONS
FROM POROUS SOLIDS
Phase 1

Annual Report for the Period September 16, 1998 to September 15, 1999

Date Published June 10, 1999

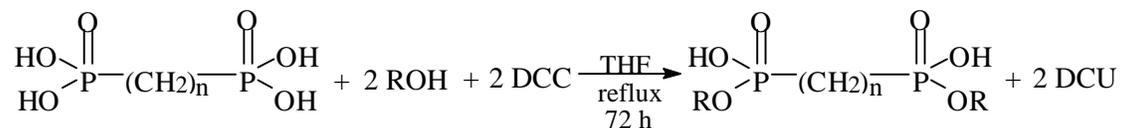
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This is the first annual report for the project entitled: "SUPERCRITICAL CARBON DIOXIDE LIGANDS FOR EXTRACTING ACTINIDE METAL IONS FROM POROUS SOLIDS." The report is being submitted from Loyola University of Chicago, 6525 N. Sheridan Road, Chicago, IL 60626 for Instrument No. DE-FG07-98ER14928. The recipient project director, Dr. Albert W. Herlinger, may be reached at (773) 508-3100. The recipient business officer, Dr. David Crumrine, may be reached at (773) 508-2476. The DOE contract administrator is Ms. Linda A. Hallum.

The focus of the effort during the project period from 9/16/98 to 6/15/99 has been on the synthesis, aggregation, and coordination chemistry of silyl-containing diphosphonic acids that potentially could be useful as solvent extraction reagents in supercritical CO₂. A homologous series of alkylendiphosphonic acids was esterified with 3-(trimethylsilyl)-1-propanol to the symmetrically-substituted diesters. The silicon-containing alcohol 3-(trimethylsilyl)-1-propanol was chosen for esterification of the diphosphonic acids because it contains both a silyl group and a trimethylene linker. Separating the trimethylsilyl from the organo-functional group by three carbon atoms is optimal for achieving chemical stability and synthetic accessibility. The synthesis of these compounds utilizes methodology that relies on dicyclohexylcarbodiimide as the esterification reagent to activate the acid (Figure 1).

Figure 1



n=1-4, R=3-(trimethylsilyl)-1-propylene,
DCC=dicyclohexylcarbodiimide, DCU=dicyclohexylurea

The yields in this esterification reaction are comparable to those we obtained previously with C₈ alkyl alcohols, i.e. ~60%. This is a significant improvement over the yields reported for dialkyl esters of methylenediphosphonic acid prepared by Nylen's method.

The purity of the products was established by ¹H and ³¹P NMR spectroscopy, potentiometric titration, and elemental analysis. The purified P,P'-di-[3-(trimethylsilyl)-1-propylene] alkylendiphosphonic acids each show a single sharp resonance in the ³¹P NMR spectra. As expected, the ³¹P resonance of the diester shifts to lower field as the separation between the phosphonate groups increases. The ¹H NMR spectra of the diesters exhibit resonances of the expected intensities and splitting patterns in the appropriate spectral regions. Elemental analysis shows good agreement between observed and calculated percent composition.

The aggregation properties of the P,P'-di-[3-(trimethylsilyl)-1-propylene] alkylene-diphosphonic acids (H₂TMSP[ADP]) were measured in toluene by vapor phase osmometry. The aggregation of the diesters in 1-decanol was measured by cryoscopy. The vapor phase osmometry studies show that H₂TMSP[MDP] (methylene-) and H₂TMSP[PrDP] (propylene-) are dimeric, H₂TMSP[EDP] (ethylene-) is hexameric, and H₂TMSP[BuDP] (butylene-) is an equilibrium mixture of trimer and hexamer. These findings are similar to those observed for the related di-2-ethylhexyl alkylene-diphosphonic acids. Cryoscopic measurements indicate that the di-[3-(trimethylsilyl)-1-propylene] alkylene-diphosphonic acids are monomeric in 1-decanol. The silyl-substituted diesters are soluble in hexane, but insoluble in perfluorohexane.

A manuscript entitled the "Synthesis and Characterization of Di-[3-(trimethylsilyl)-1-propylene] alkylene-diphosphonic Acids," describing this work has been submitted to *Synthetic Communications*.

Continuous variation infrared studies and molecular mechanics methods have provided useful information about the structure and hydrogen bonding properties of the H₂TMSP[MDP] and H₂TMSP[PrDP] dimers. These studies indicate that the dimers are strongly hydrogen-bonded and presumably adopt rigid symmetrical structures which contain two adjacent, intermolecular hydrogen-bonded eight-member rings. H₂TMSP[EDP] and H₂TMSP[BuDP] adopt structures that are also intermolecularly hydrogen-bonded but more flexible.

Metal complexes of P,P'-di-[3-(trimethylsilyl)-1-propylene] methylenediphosphonic acid were prepared by precipitation of the neutral diphosphonate salts from methanol solution at room temperature. The metal complexation properties of this ligand were found to be similar to those of the previously studied di-(2-ethylhexyl) methylenediphosphonic acid. Qualitative information about phosphonate coordination modes in metal complexes of H₂TMSP[MDP] was obtained using infrared spectroscopy. The shift of $\nu_{\text{asym}}(\text{POO}^-)$ and $\nu_{\text{sym}}(\text{POO}^-)$ to lower frequency in the IR spectra of the metal complexes relative to their values in the sodium salt indicates symmetrical coordination of the phosphonate groups through chelate and/or bridging interactions. The frequency difference $\Delta\nu$ between the symmetric and asymmetric POO⁻ stretching bands in these compounds was investigated as a function of the ionic potential e/r of the metal ion. The frequency difference between the POO⁻ stretching bands becomes smaller as the ionic potential of the metal ion increases. The origin of this effect presumably is a change in the P-O bond order that arises from a change in the strength of the metal-diphosphonate interaction. The change in bond strength could result from P-O bond polarization and/or covalency effects.

A poster presentation entitled "Functionalized Diphosphonic Acid Ligands for Metal Ion Coordination in Supercritical Carbon Dioxide" describing this work will be presented in the symposium "First Accomplishments of the Environmental Management Sciences Program" sponsored by the Division of Nuclear Chemistry and Technology at the 218th National ACS Meeting in New Orleans on August 22, 1999.