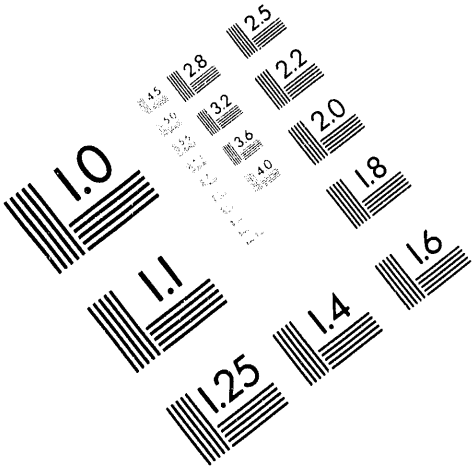

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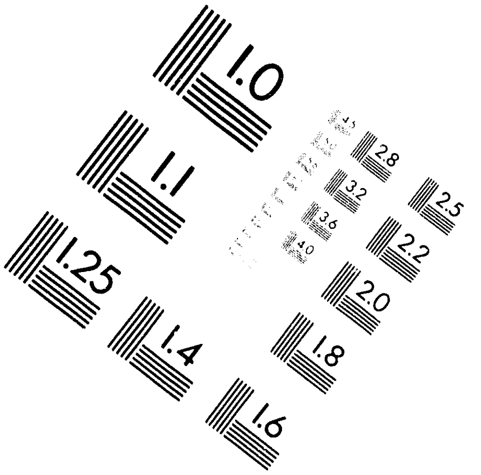

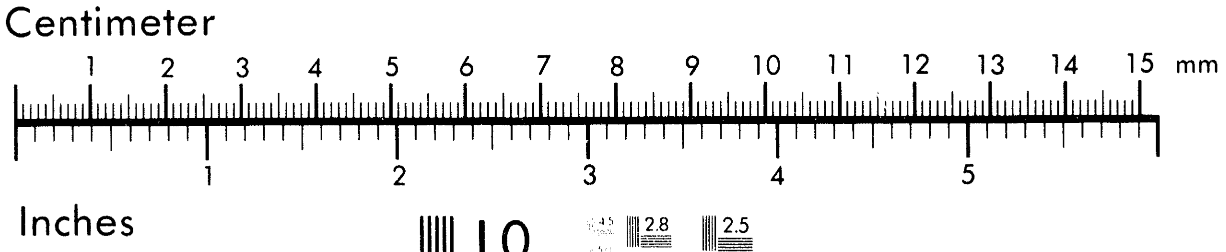

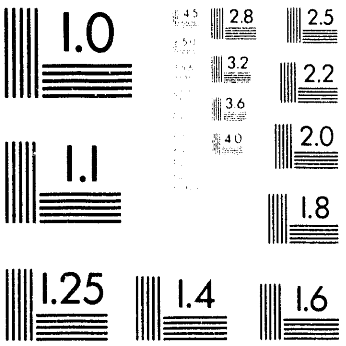

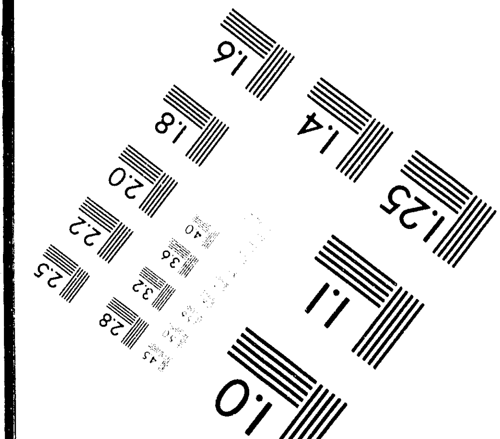

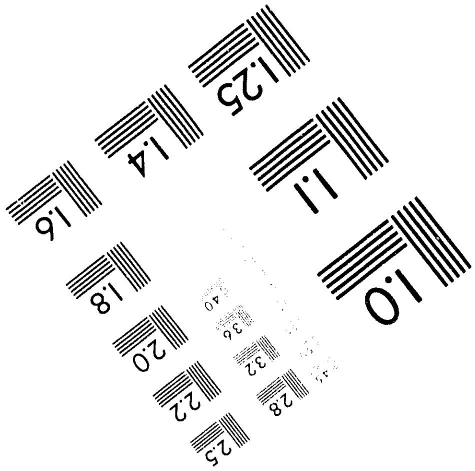

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DOE/ER/13915--T4

Final Report

Program Title: Development of Immobilized Ligands for Actinide Separations

Principal Investigator: R.T. Paine
Department of Chemistry
University of New Mexico

Agency: Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences

Grant No.: DE-FG04-91ER13915

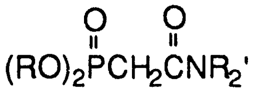
Dates: 6/91 to 5/94

MASTER

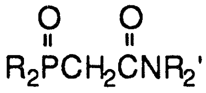
A. Background

The coordination chemistry of transition metal or d-block ions has been thoroughly studied for more than a century.[1] Nonetheless, the subject continues to provide exciting new advances and regularly reveals its importance to new technological areas in the chemical, biological, and materials sciences. In contrast, the coordination chemistry of the f-block elements has been much less thoroughly developed. Many of the advances that have occurred in f-element coordination chemistry have been driven by practical needs to devise separation schemes for the individual lanthanide (Ln) and actinide (An) ions. However, few of the schemes that have evolved are completely satisfactory, and the basic chemical data base needed for achieving improvements in separations is sparsely developed. As a result, studies of the fundamental aspects of f-element coordination chemistry pertinent not only to the evolution of new generation separations, but also waste remediation schemes, biological and medical applications, and new materials development are in demand. These areas have, in fact, been highlighted in seveal reports detailing critical technology needs for the twenty-first century.[2]

Responding to this need, our group has contributed to a more detailed understanding of factors that influence Ln and An coordination chemistry in general as well as in solvent extraction processes. Our initial efforts were devoted to the elucidation of the coordination properties of the popular carbamoylmethylphosphonates (CMP) and carbamoylmethylphosphine oxides (CMPO) ligands. A brief overview of selected highlights in this area is provided below since that work provides a rational foundation for the directions of our group during the last grant period.


$(\mathrm{RO})_2\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{CH}_2\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NR}_2'$

CMP


$\mathrm{R}_2\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{CH}_2\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NR}_2'$

CMPO

In 1963, in a search for improved separation schemes, Siddall[3-8] reported on the outcome of liquid-liquid distribution (D) measurements between aqueous solutions of Ce(III), Pm(III), and Am(III) and organic solutions containing CMPs. These studies indicated that bifunctional CMP ligands were superior extractants compared to monofunctional organophosphoryl and organoamide fragments. Subsequent studies by Schulz and coworkers[9-12] and Horwitz and coworkers[13-17] showed that one ligand, $(HxO)_2P(O)CH_2C(O)NEt_2$(DHDECMP), was particularly effective for extraction of trivalent Ln and An ions present in nitric acid solutions (>2M). However, several troublesome problems associated with DHDECMP, including its cost, preparation, purification, and solution behavior, limited its practical utility. These shortcomings led to attempts to systematically design related bifunctional extractants and to understand basic electronic and steric influences on CMP extractant efficacy. In particular, McDowell[18] noted in some cases that CMP alkyl group branching led to decreased extractant solubility in water, increased extractant solubility in alkane diluents, but reduced extraction ability toward Am(III). Myasoedov and coworkers[19] examined additional ligand modifications and extractions of Am(III), Pu(IV) and U(VI). They concluded that increasing the basicity of the phosphoryl group by substituent group variations, e.g., replacement of RO groups by alkyl or phenyl groups, seemed to increase the extraction capacity of the CMP ligand, but decreased the organic phase solubility and selectivity of the extractant. Further, they noted that variation of the amide R' group only seemed to affect organic phase solubility and not the extraction capacity.

Horwitz, and coworkers[20] in a very comprehensive study of substituted CMP ligands, found that carbamoylmethylphosphine oxides (CMPOs) of the type $R(Ph)P(O)CH_2C(O)NR_2'$ were the most effective extractants for Am(III). The ligands showed high distribution ratios (Ds) at high acid, low Ds at low acid, good selectivity over fission products, and favorable loading solubility. These findings resulted in the design and implementation of a new generic actinide ion extraction process, TRUEX. The Argonne National Laboratory group also continues to design and test variations on the CMPO theme as well as other new ligand types[21-34].

During the course of these studies, a few attempts were made to establish the nature of the coordination complexes formed in two-phase extraction processes. A mechanism proposed by Siddall[3-5] and by Schulz and coworkers[9-12] suggested that trivalent Ln and An ions formed complexes of the general type $M(NO_3)_3(L)_3$ from nitric acid solutions, and they proposed that the neutral ligands bonded to the metal ions in a bidentate mode. Horwitz and coworkers[13-17,20] reevaluated the extraction mechanisms for both CMP and CMPO ligands, and they deduced compositions $Ln(NO_3)_3(L)_3 \cdot (H_2O)_x$, $UO_2(NO_3)_2(L)_2$, $Th(NO_3)_4(L)_{2 \text{ or } 3}$, and $Pu(NO_3)_4(L)_2$. They also proposed that, under process conditions (low metal concentration, high extractant concentration), the bifunctional extractants were neutral and bound to the metals in a monodentate mode through the phosphoryl oxygen atom. Spectroscopic data were interpreted to support this conclusion.[16,17,21,22]

Prior to 1982, relatively little attention was given to elucidating the detailed molecular features of extractant complex formation. Indeed, this deficiency stimulated our initial studies[35-47] in which methods for improving the syntheses of bifunctional CMP and CMPO derivatives were examined, and solid state structures of selected extraction complexes were determined. In our approach, the extraction complexes were necessarily obtained under "metal-loaded" conditions where the metal ion concentration is significantly higher than encountered in practical extraction processes. The compositions and structures, as determined by solution infrared and NMR techniques and by single crystal X-ray diffraction analyses, showed interesting differences from those deduced from distribution ratio/ligand dependency measurements. In particular, the compositions in the solid state, in several instances, showed fewer CMP or CMPO ligands bonded to the metal, e.g., $Ln(NO_3)_3(L)_2$ with Ln=La-Eu,[37] $Ln(NO_3)_3(L)_2 \cdot (H_2O)$ with Ln=Gd-Lu,[37] $UO_2(NO_3)_2(L)$,[38] and $Th(NO_3)_4(L)_2$.[35] In addition, except for small, late lanthanides, the ligands were bonded to the metal ions with a bidentate coordination mode. With late Ln(III) ions, the CMP ligands were found bonded in a monodentate mode through the phosphoryl oxygen atom, as deduced from the extraction analyses. The C=O donor groups in the amide units were uniquely hydrogen bonded to a metal bound water molecule.

The differences between the compositions and structures determined by solvent extraction and solid state structure analyses are important, and they reveal that CMP and CMPO extraction complexes are likely very sensitive to solution conditions including dynamic organophosphoryl ligand and water exchange processes, competitive ligand protonation reactions and aqueous phase/organic phase interfacial chemistry. These features in turn are dependent on steric and electronic features in the organic ligands, metal ion coordination numbers and charge/radius ratios, counter ions (e.g., NO_3^- and Cl^-), aqueous solution acidity and extraction solvent. In short, "real-life" solvent extraction systems are very complicated at the molecular level, and this makes the rational design of improved extractants very difficult. In fact, the most significant "take-home message" from attempts to prepare improve extractants is that a better understanding of the fundamental coordination chemistry of Ln and An ions is still required, and one of the goals of our past studies has been to shed more light on coordination principles for f-element ions.[35-58]

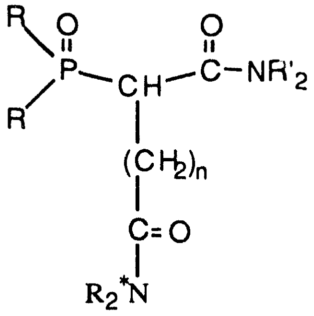
The primary goals during the present grant period were to 1) synthesize new bifunctional chelating ligands, 2) characterize the structural features of the Ln and An coordination complexes formed by these ligands, 3) use structural data to iteratively design new classes of multifunctional ligands, and 4) explore additional routes for attachment of key ligands to solid supports that could be useful for chromatographic separations. Some highlights of recently published work[59-63] as well as a summary of submitted,[64-68] unpublished and/or still in progress research are outlined below.

B. Results: 1991-Present

1. Ligand Design, Synthesis and Coordination Chemistry

a. CMP/CMPO-like Ligands

During the previous and present grant periods, we posed the questions: Can CMP/CMPO-like ligands be prepared that contain more than one P=O and one C=O group, and will these ligands show enhanced chelate binding properties? As noted above, both solid state structural studies and solution distribution measurements had shown that Ln(III) and An(III) ion-CMP/CMPO complexes contain two or three bifunctional ligands and three nitrate ions in the inner coordination sphere. Together, these groups provide the desired charge neutralization and high coordination number (8-10) typical of f-element ions. "Chelate effect" coordination principles[1,69,70] derived from numerous studies of transition metal ion binding with multifunctional ligands suggest that the collection of several donor groups into a single ligand gives rise to enhanced complex stability. Such an effect should also appear for Ln(III) and An(III) ions and early studies of polyketonate complexes confirmed this proposal.[69,70] We, therefore, set out to prepare new families of multifunctional phosphonates of the general types represented by **1-7** (R-aryl, alkyl, or alkoxy). It was reasoned that each of the ligands **1-6**



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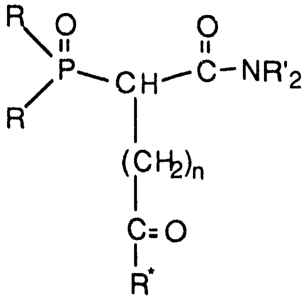

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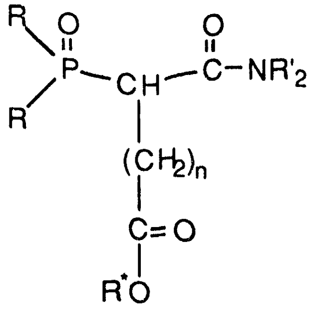

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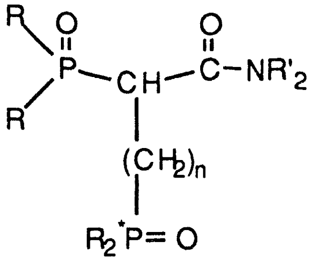

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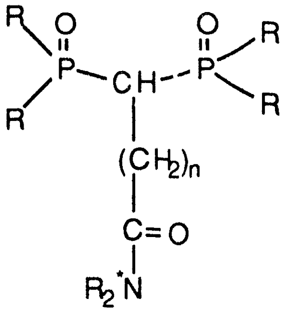

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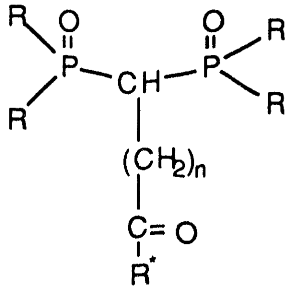

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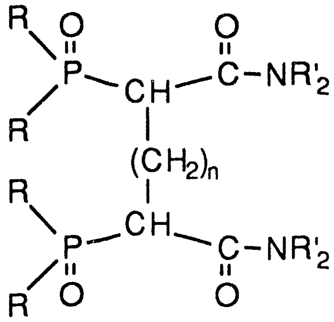
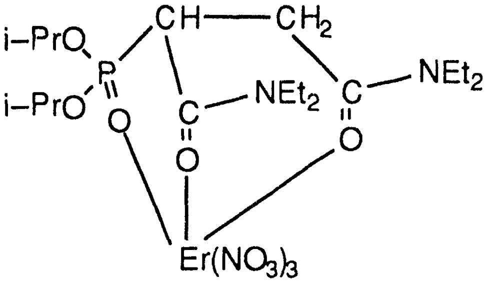


7

would provide at least one bidentate CMP/CMPO or diphosphonate six-membered chelate interaction with the central metal ion. If a third interaction could be accomplished with the donor group terminating the "dangling arm" then additional chelate rings of larger size would result. These ligands would then be tripodal in ligation character. Ligands of type **7** represented an initial attempt to preorganize two CMP fragments on a carbon backbone. Overall, the synthesis program was quite successful. Numerous representatives of each class of ligands were prepared with various dangling arm lengths (n=1-3) and each ligand was fully characterized. Much of this chemistry has been published.[44,45,48,49,56,59-61,63]

As expected, the coordination chemistry of **1-6** is rich and varied. Space filling models suggest that ligands with n=1 and 2 have the best opportunities for formation of tripodal (tridentate) chelate structures. However, in only a few instances (e.g., **8**) has this preferred coordination mode been achieved. Instead, the predominant coordination mode for **1-6** involves bidentate coordination of the CMP/CMPO or diphosphonate fragment to one metal and bridge bonding of the "dangling arm" functional group to another metal center. This coordination mode is even found for ligands of type **4** that contain a strongly binding phosphine oxide on the "dangling arm." Few quantitative distribution measurements were undertaken with these ligands, but some limited data indicate that the



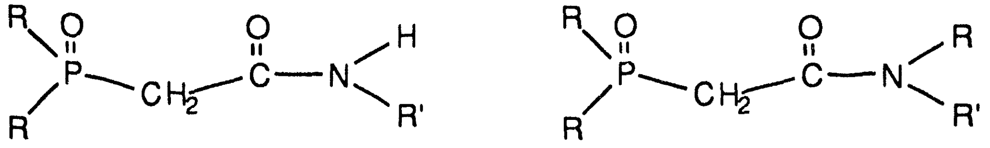
8

introduction of the third donor center provides for little enhanced ligation or separation capability.

We have recently prepared two ligands, **3** with R=i-PrO, R'=Et, R^*=H and **4** with R=i-PrO, R'=Et, R^*=OH that are unique in this class. In these molecules, each dangling arm contains a Bronsted acid group and these ionize at modest pH's. The resulting anionic ligands are very strong chelators. Attempts are in progress to isolate and crystallize representative complexes in order to determine the precise coordination mode adopted by the ligands.

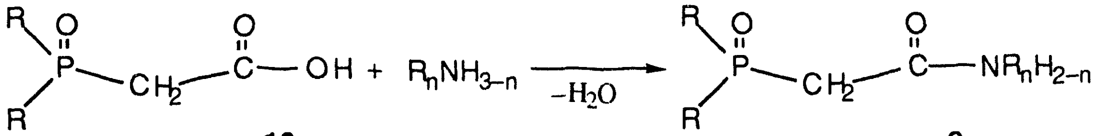
The coordination chemistry of **7** also is tantalizing. With ligands having n=1 and 2, spectroscopic data suggest that tetrapodal(tetradentate) binding is achieved with at least early Ln(III) ions. Unfortunately, none of these complexes has yet provided adequate single crystals for X-ray analysis that would confirm this proposal. Extraction measurements with these ligands have not been undertaken since advances with other ligand systems have occupied the majority of our attention. The synthesis results have, however, stimulated other related approaches for "tethering" or preorganizing CMP fragments around a central core or platform. Some aspects of that chemistry are outlined below.

During the previous grant period, we had briefly sought to prepare CMP ligands **9** with secondary amide or asymmetric tertiary amide functional groups. The standard synthesis for CMPs involves an



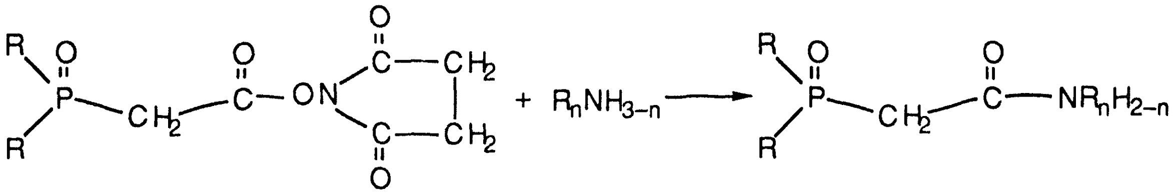
9

Arbusov reaction of the appropriate organophosphite $R_2P(OR)$ with a halomethylamide, $XCH_2C(O)NR'_2$. Few of the latter reagents are commercially available, and many literature approaches for the synthesis of $XCH_2C(O)N(H)R$ and $XCH_2C(O)NRR'$ analogues are cumbersome or unreliable. Alternatively, we chose to develop a simple route to the formation of phosphonoacetic acids **10**, and found that these can be converted to amides by reaction with the desired amine (equation 1). The direct amidation reaction is often sluggish, and it can be promoted through use of DCC(dicyclohexylcarbodiimide). These reactions are smooth, but they are complicated by the fact that it is often difficult to completely



10 **9** (1)

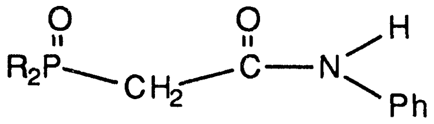
R = Ph, OR



11 **9** (2)

remove amide coupling byproducts such as dicyclohexyl urea. We have now developed another alternative approach that involves the synthesis of the succinamide derivatives **11**. Subsequent reactions with primary and secondary amines (equation 2) lead to high yields of the desired N-derivatized CMP ligands **9**.

The utility of equation 2 goes well beyond the simplified preparation of new CMP ligands. Indeed, it is immediately obvious that this chemistry should be useful for tethering CMP fragments on polyamine backbones. For example, derivatives of **11** (R=EtO, i-PrO, n-BuO, Ph) react smoothly with aniline, 1,2-diaminobenzene, and 2,3,5,6-tetraaminobenzene giving the amido derivatives **12**-**14**. A crystal structure determination for **14** reveals that the molecule has an inversion center, and the C=O and P=O vectors in each CMP fragment are rotated out of coplanarity by ~90°. Preliminary



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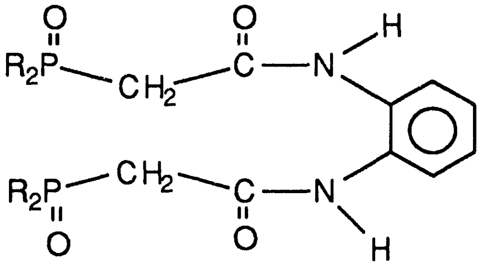

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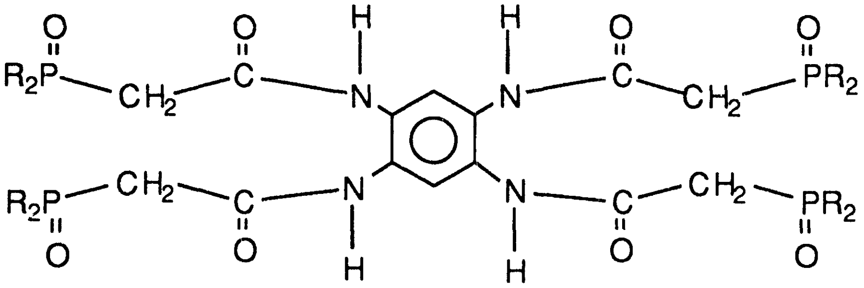

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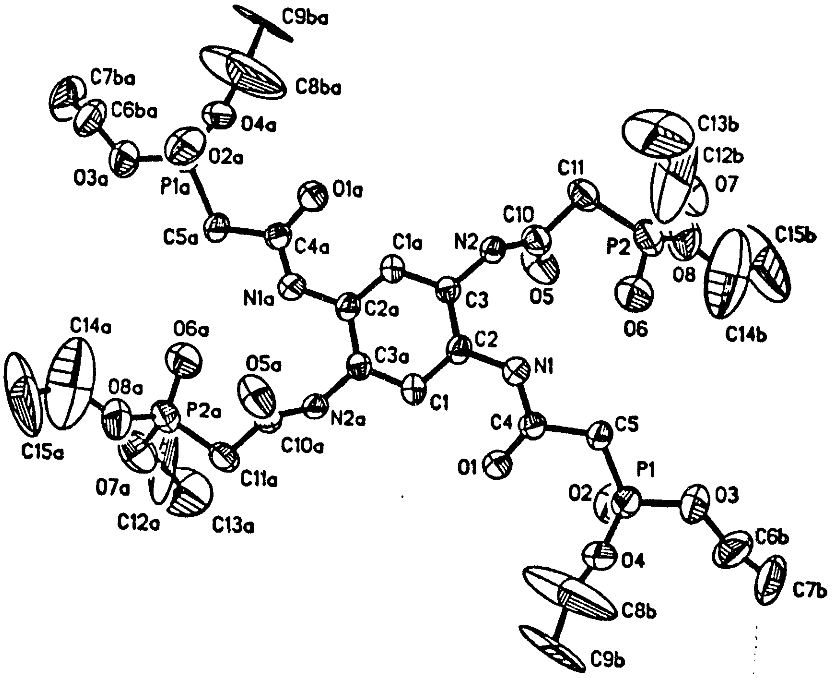

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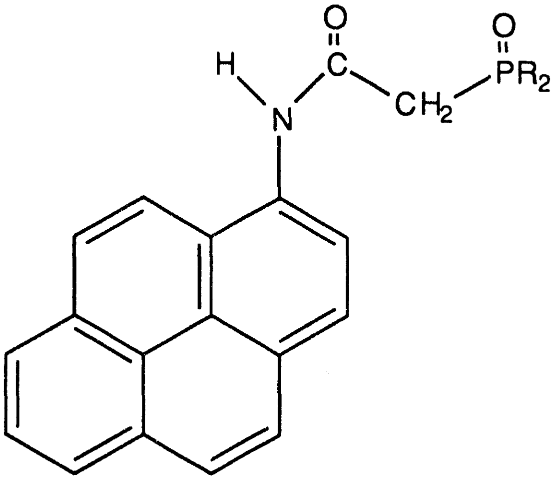
molecular modeling (CAChe) suggests that adjacent CMP fragments can rotate relatively freely about their respective aryl C-N(H) bonds. This allows, for example, CMP fragments in the 2,3 positions to orient in a fashion that should permit bis-bidentate ligand coordination with a metal ion. Presumably, the fragments in the 5,6 positions would simultaneously form a bis-bidentate chelate with a second metal ion. It is clear from the modeling that the four ligands can not simultaneously bind to a single metal center. In order to verify these coordination proposals, we have attempted to prepare crystalline complexes of derivatives of **14** bonded to Ln(III) and Th(IV). Indeed, 1:1 and 2:1 metal-ligand complexes have been isolated; however, suitable single crystals have not yet been obtained. Efforts will be made in the next year to obtain distribution ratio data for the ligands with R=EtO and Ph. Similar studies will be considered for ligand **13** as well.

This amide derivatization process is not limited to the few examples presented above. We have accomplished related chemistry, for example, with 1-aminopyrene, which gives intensely colored compounds of the general type represented by **15**. It is likely that these ligands could be employed as lanthanide fluorescent tags, and this point will be explored further. The reactions of **11** with ethylene diamine, diethylenetriamine, and tris-(2-aminoethyl)amine have been examined. In each case, a CMP fragment is added at each primary amine group, giving the compounds **16-18**. Compounds **17** and



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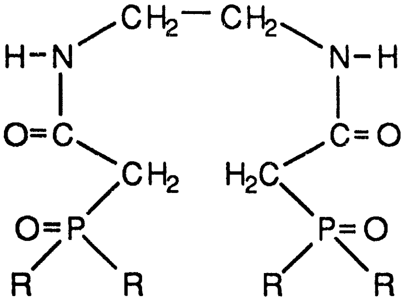

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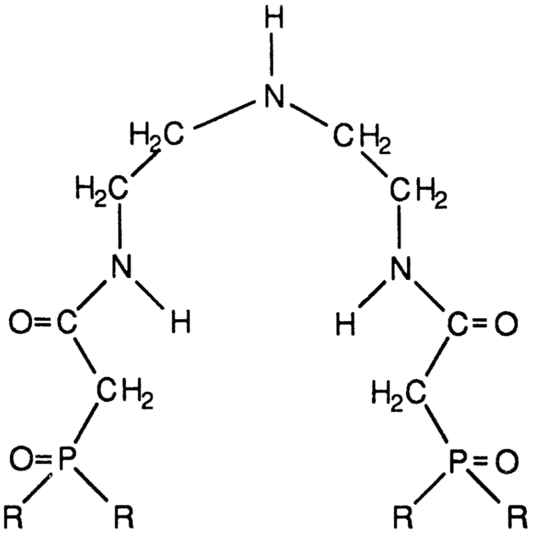

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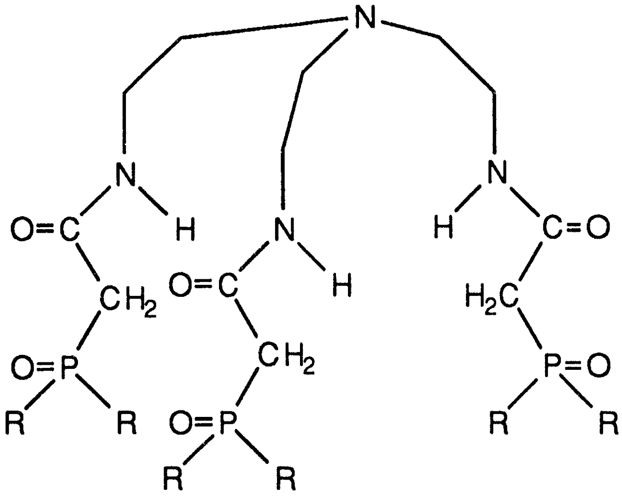

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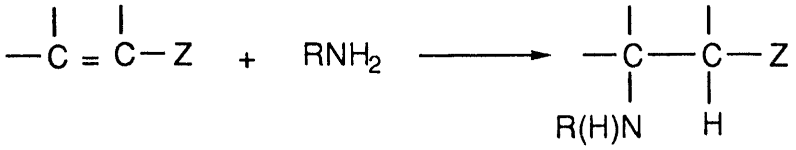
18 clearly bring CMP fragments into close enough proximity to encourage <u>bis</u>- and perhaps <u>tris</u> ligand binding to a single metal. Some coordination chemistry of **16** has been briefly examined, but crystalline complexes have not yet been isolated. Compounds **17** and **18** have only recently been obtained in reasonable yields, and the final stage purifications are still in progress. We will to continue our efforts with this chemistry during the remaining grant period as well as in the future. In fact, the successes realized in this chemistry will guide extensions that are outlined in the proposal for new studies.

b) Organophosphonate and Organophosphine Oxides

The coordination chemistry of monofunctional organophosphonates, $(RO)_2P(O)R'$, and organophosphine oxides, $R_2P(O)R'$, with Ln(III) and An(III) ions has been extensively studied, and of course some of these ligands have been employed in practical separations schemes. It is also known that some diphosphonates, $(RO)_2P(O)CH_2P(O)(OR)_2$ and $(RO)_2P(O)CH_2CH_2P(O)(OR)_2$, and diphosphine oxides, $R_2P(O)CH_2P(O)R_2$, display interesting coordination behavior, and Myasoedov[19] and Rozen[71] have indicated that such ligands are used in some actinide separations done in Russia. In a related vein, a German group headed by Herrmann[72] has described novel coordination and extraction properties displayed by imidodiphosphonates $[(RO)_2P(O)]_2NH$. These intriguing observations, along with general interests in the preparation of multiply phosphonated organic monomers and polymers led us to explore the following chemistry.

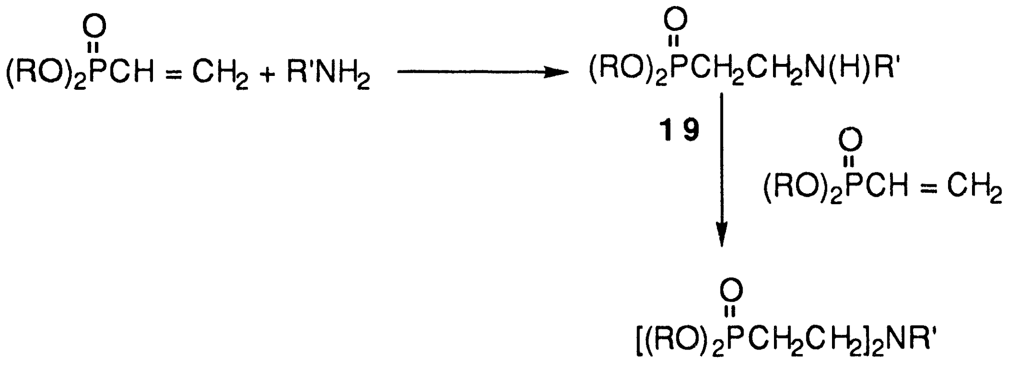
It is well known that alkenes normally undergo direct amination by nucleophilic (Michael type) addition only when activated by an electron withdrawing group Z, (e.g., CHO, COR, COOR, SOR, SO_2R (equation 3). The phosphoryl group also might be considered to be an



$$-\overset{|}{C}=\overset{|}{C}-Z \quad + \quad RNH_2 \longrightarrow -\underset{R(H)N}{\underset{|}{\overset{|}{C}}}-\underset{H}{\underset{|}{\overset{|}{C}}}-Z \qquad (3)$$

activating group Z; however, examination of the usual organic reaction reviews and summaries make no reference to the use of phosphoryl groups for the activation of alkenes toward amination. We, therefore, set out to explore this chemistry for the purpose of obtaining new organophosphine oxide ligands as well as another route for functionalizing polymers. Subsequently, we have found mention of phosphoryl activation in Russian literature from 1978.[73] Although this reduces some of the "first-report" character of our observations, it remains that the chemistry we have developed will be quite useful for the preparation of novel, new phosphonated ligands.

We have explored the aminations of several vinyl phosphonates, $(EtO)_2P(O)CH=CH_2$, $(i\text{-}PrO)_2P(O)CH=CH_2$ and $(PhO)_2P(O)CH=CH_2$, with a series of primary and secondary amines as well as NH_3[66], as shown in general in equation 4. The mono- and diphosphono amines **19** and **20** are obtained in good yields with high pruity. The molecular structure of one of these compounds $[Ph_2P(O)CH_2CH_2]_2NCH_3$ **21** is shown here.



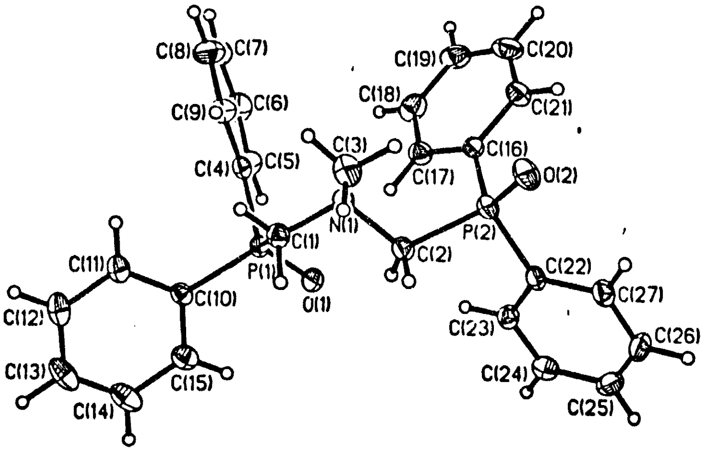
$$(RO)_2\overset{O}{\overset{\|}{P}}CH=CH_2 + R'NH_2 \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2N(H)R'$$

19

$$\downarrow (RO)_2\overset{O}{\overset{\|}{P}}CH=CH_2$$

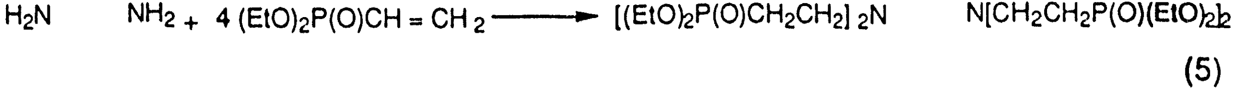
$$[(RO)_2\overset{O}{\overset{\|}{P}}CH_2CH_2]_2NR' \qquad (4)$$

20



21

Clearly, this chemistry should also be useful for making multiphosphonate ligands. For example, we have found that ethylene diamine and the tetraza macrocycle **22** (12-ane N_4) undergo tetra-phosphonation^{66}, as shown in equations 5 and 6. The coordination chemistry of these interesting ligands is under study. Initial indications are that the ligands form very stable complexes toward Ln(III) ions, but the structural features are unconfirmed. We have also found that the aza pyridine macrocycle **23** can be tetra-phosphonated, and attempts are underway to oxidize the pyridine nitrogen atoms without destruction of the macrocycle. The coordination chemistry of this ligand is also under examination. Finally, the bis phosphanation of piperazine occurs (eg.8) and the molecular structure of the product **24** is shown.



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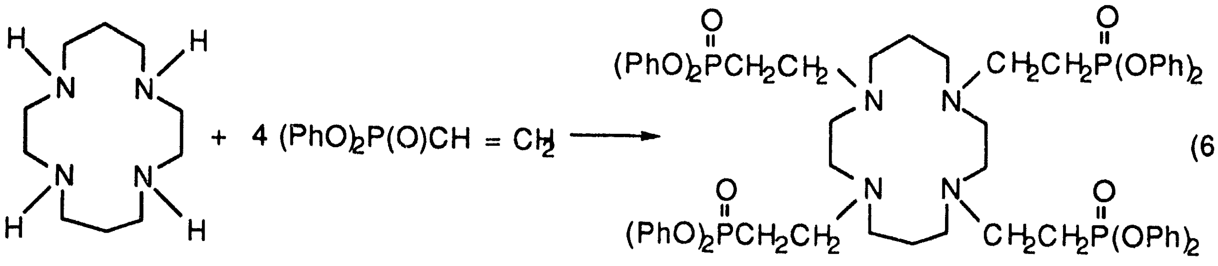

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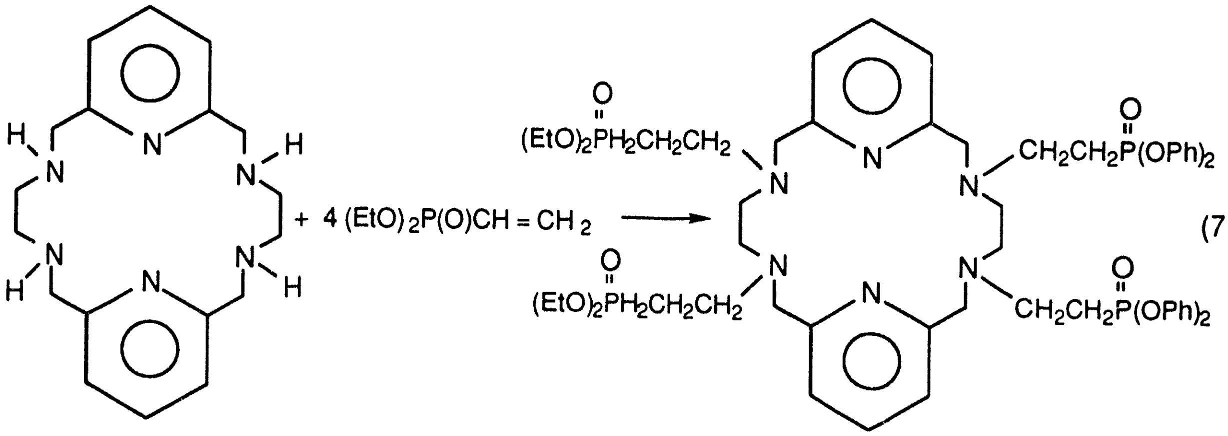

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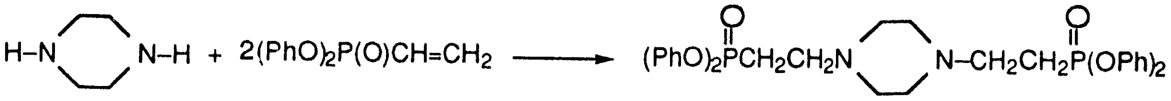

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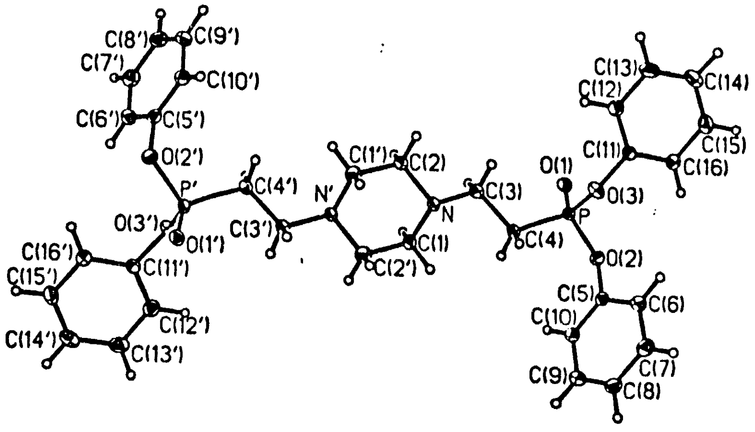

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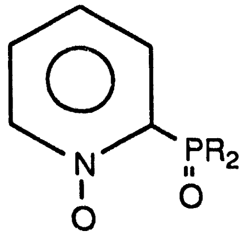
We expect to make extensive use of this chemistry in the next grant period to prepare a number of preorganized phosphonate ligands that should have novel coordination chemistry.

c) Phosphinopyridine N,P-Oxides

The original ligand design concept proposed by Siddall[3-8] for the development of CMP ligands was straightforward. He reasoned that, since monofunctional carbonyls and phosphoryls are good ligands toward Ln(III) and An(III) ions, then a ligand containing both functional groups, in a geometric arrangement that permits favorable chelate ring formation, should be an even more strongly binding ligand. This of course proved to be the case, but it is also true that the efficacy of CMPs as extractants stems from the favorable action of several chemical factors in addition to the possible operation of the chelate effect. Hoping to expand on this design concept, we asked what other combinations of donor groups might be assembled on a hydrocarbon backbone. We initially attempted to prepare ligands with P=O and S=O groups and P=O and SO_2 groups, but these compounds were not found to be especially attractive.[54] Subsequent examination of the solvent extraction literature revealed that pyridine N-oxide derivatives have found some use as extractants, and the N-oxide group is stable and an excellent oxide donor toward hard Ln(III) and An(III) ions. We, therefore, chose to explore methods for the synthesis of potentially chelating ligands containing both phosphoryl and N-oxide donor centers. This effect has been very successful, and we have spent the majority of our effort in this grant period developing these ligands.

Prior to our work there appears to have been no reports of the formation of chelating ligands containing both N-O and P=O donors. Some examples of pyridine compounds substituted with phosphide $-PR_2$ or phosphonate $-P(O)(OR)_2$ groups were known and that chemistry has recently been reviewed.[74] Initially, we selected as our target bifunctional 2-(dialkoxyphosphono)pyridine N,P-dioxides **25** (R=OR). The first examples of these ligands were prepared in the preceding grant period;[47] however, many of the synthetic extensions and charaterizations were accomplished in the last two years.[75] This includes a molecular structure determination for (2-diphenylphosphino)isoquinoline-N, P-dioxide **28**.[75] It is interestion that the N-O and P=O donor groups have a more or less anti orientation in the free ligand state.



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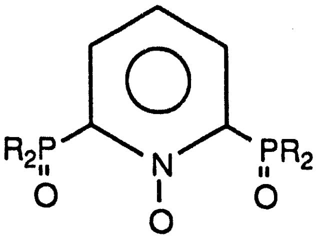

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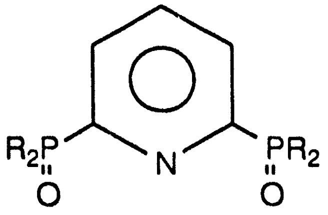

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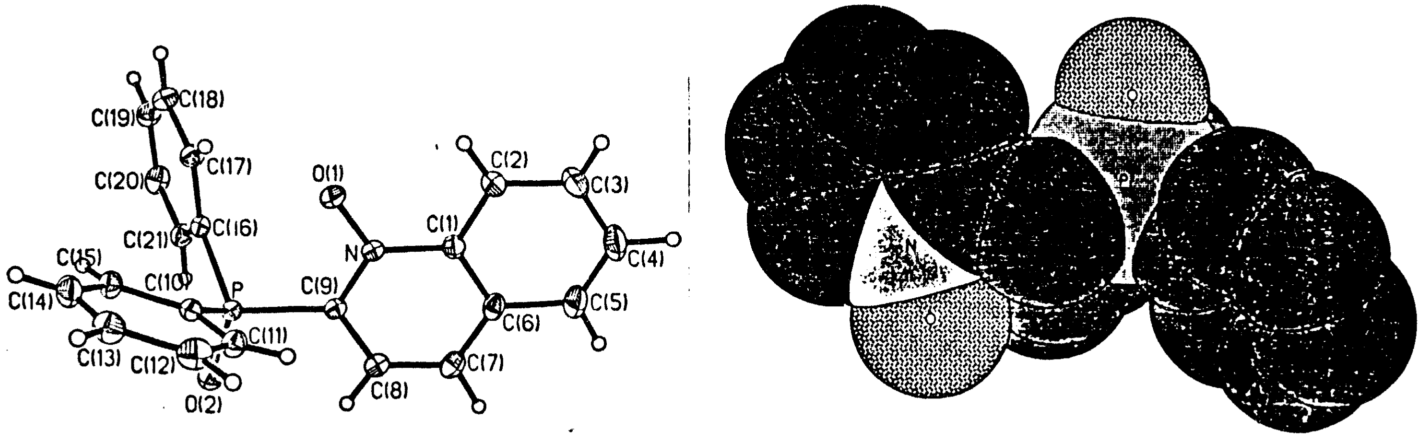

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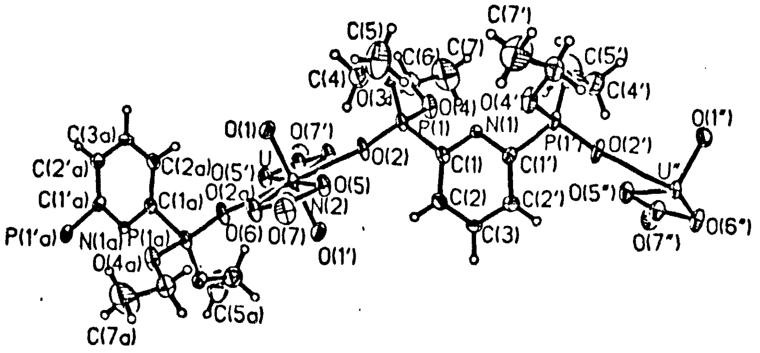
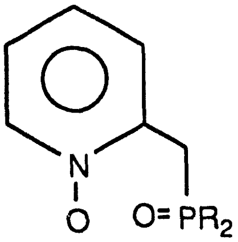
The coordination chemistry of ligands of type **25** has been explored. It was found, for example, that stable complexes of the general types $UO_2(NO_3 \cdot L$ and $Ln(NO_3)_3 \cdot 2L$ are produced.[52,56] Spectroscopic and X-ray crystallographic data indicated that the isolate complexes contain bidentate bonded ligands so clearly the ligand undergoes reorganization of the <u>anti</u> conformation. Liquid-liquid extraction data for these systems were also collected, and they show some favorable behavior partitioning Ln(III) ions from the aqueous phase into the organic phase at low acid concentrations.

The initial success with ligands of type **25** (R=EtO, i-PrO, n-BuO, HexO, Ph) encouraged us to attempt to prepare examples of **26**. It was reasoned that such compounds might function as tripodal (tridentate) ligands and display even stronger ligation behavior. Unfortunately, it has so far proven impossible to obtain these compounds.[76] The intermediates **27** are obtained in good yield, but all attempts to N-oxidize **27** gave rise to pyridine ring decomposition. A limited amount of coordination chemistry was accomplished for **27**, and this in fact indicates that **26** might not serve as a tripodal ligand. The molecular structure of $UO_2(NO_3)_2 \cdot$**27** (R=OEt), for example, is shown below.[76] The structure is an infinite chain in which $UO_2(NO_3)_2$ groups are bridged by the ligand **27**. In this structure the two P=O bond vectors are turned out and away from the pyridine N atom. Without the N-O donor group this ligand can not function in a chelating fashion.



Attention was then directed toward modifying these ligand systems. Although ligand **25** formed complexes containing the usually favored six-membered chelate ring, the N-O and P=O bond vectors are not coplanar and the chelate rings exist in a "twisted" chair conformation. Subsequent molecular modeling in fact suggested that these chelate rings are somewhat strained. This strain might be releaved by introduction of a methylene group between the pyridine ring and the phosphoryl group; therefore,the next synthesis targets became ligands **29** and **30**. We have succeeded in preparing these new ligands,[62,64] and the molecular structures of **29** and **30** (R=Ph) have been determined.[76]. Views are shown below.



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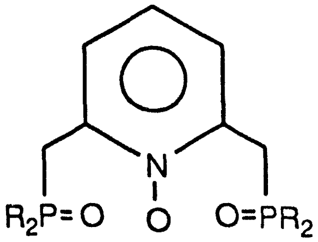

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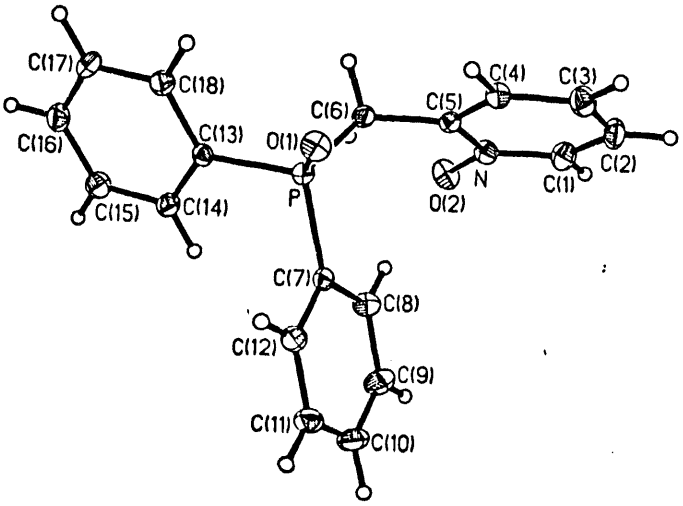
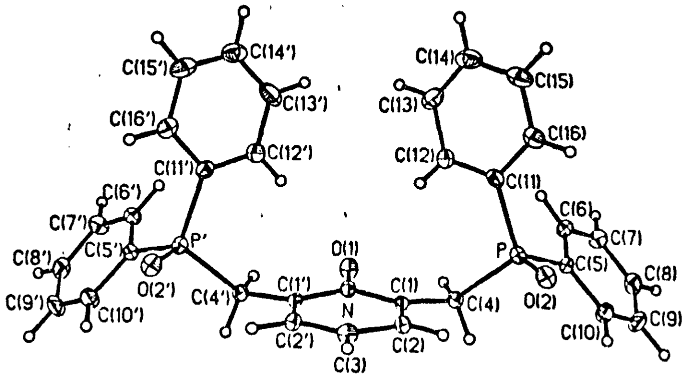
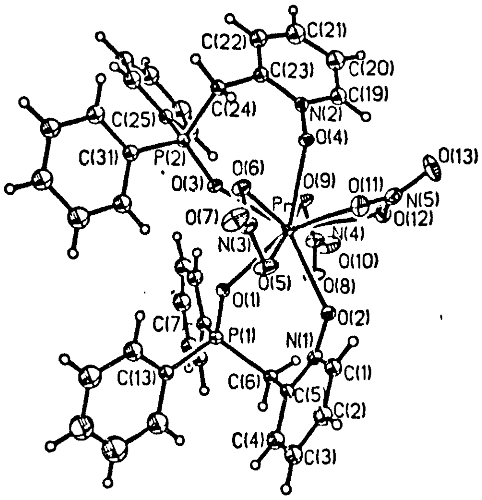
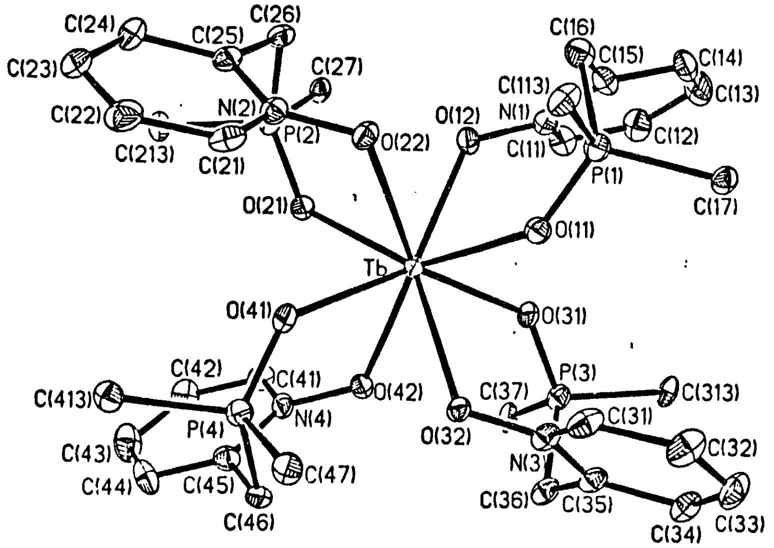


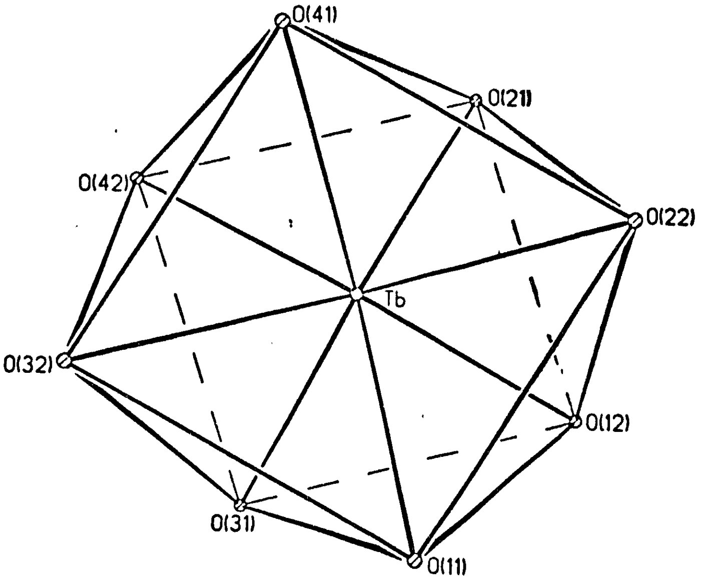


Several features are worth summarizing. The P=O and N-O bond vectors in the free ligands again are oriented in an *anti* conformation, and the $Ph_2P(O)$ groups are in a low strain condition. Molecular modeling infact indicates that the $P-CH_2$ and CH_2-C(ring) bonds are relatively free to rotate. Of course the *anti* configuration in the free ligands is preferred probably as a result of dipole-dipole repulsion, but coordination of these dipoles should allow them to align in a *syn*-like conformation. Indeed, ligand **29** forms a series of lanthanide complexes with L/M ratios 1:1, 2:1, and 4:1.[62] In the 1:1 and 2:1 complexes, the counter anions (typically NO_3^-) remain in the inner coordination sphere. The molecular structure of one complex $Pr(NO_3)_3\cdot(\mathbf{29})_2$(R=Ph) is shown here and it reveals that **29** forms a bidentate chelate ring on Pr(III).[62] In 4:1

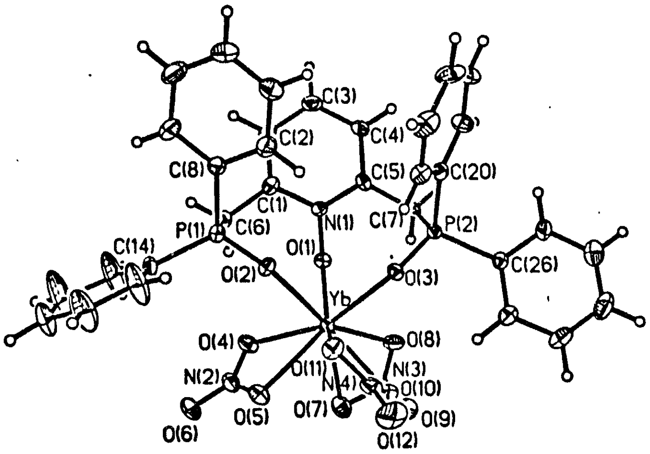


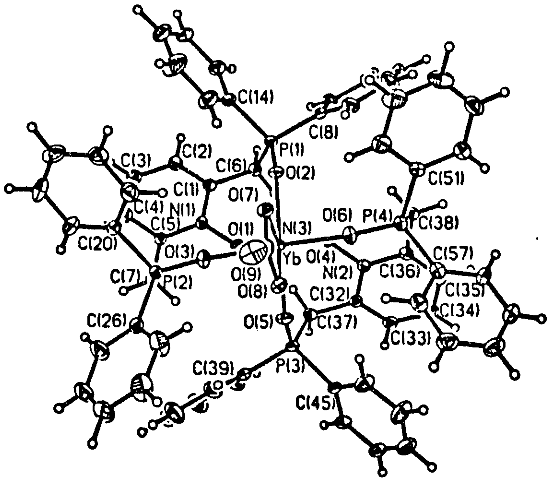
complexes, on the other hand, the four molecules of **29** completely displace the anions to the outer coordination sphere, as shown below (Ph groups on P atoms removed for clarity). The ligands also adopt a bidentate chelate coordination that, by molecular modeling, appears unstrained, and the coordination polybedron is a square anti-prism. Indeed, the CH_2 group provides geometric flexibility without apparent sacrifice of strain energy. Preliminary measurement of distribution ratios for aqueous Nd(III) solutions indicate that **29** (R=Ph) extracts well at moderate acid strengths (1-3 M HNO_3), and further studies of the extraction abilities are planned.





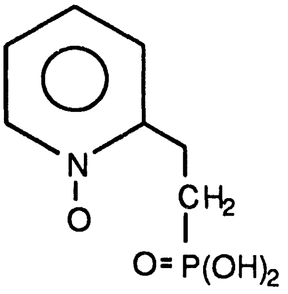
Ligand **30** (R=Ph) forms a series of 1:1 and 2:1 lanthanide complexes in which the ligands are bonded in a tripodal (tridentate) fashion. The 1:1 complexes retain the three counter anions (e.g. NO_3^-) in the inner coordination sphere. However, in the 2:1 complexes, two of the NO_3^- ions, for example, are displaced to the outer sphere. The molecular structures of the 1:1 and 2:1 complexes of Yb, shown below, illustrate this point. With thorium(IV), two





nitrates are also displaced. Initial distribution studies confirm that the complexes formed under extraction conditions, namely in the presence of a large excess of ligand, are quite stable. Many of the details of the structures and chemistry of the complexes formed by **29** and **30** have recently appeared.[62] Finally, we have recently observed that combination of $Bi(NO_3)_3$ with **30** (even in excess) results only in a 1:1 complex.[64] This is interesting since Bi(III) is larger for example than Yb(III) which forms the bis-tripod coordination complex.[64] Comparison of the triangular coordination "foot print" for **30** in these complexes shows that as expected the triangle is significantly larger in the Bi(III) complex. We are attempting to use molecular modeling to determine if this larger coordination foot print induces unfavorable chelate ring strain which might "block" addition of the second ligand molecule on Bi(III).

In general, the various derivatives of **29** and **30** are stable toward acid decomposition in 1 M HNO_3. However, we have also found that, if **29** (R=OEt) and **30** (R=OEt) are N-oxidized under too vigorous conditions, or they are allowed to react with Me_3SiBr and then hydrolyzed in water, the respective phosphonic acids **31** and **32** are obtained.



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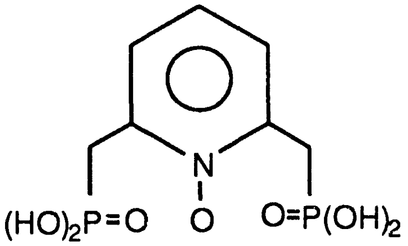
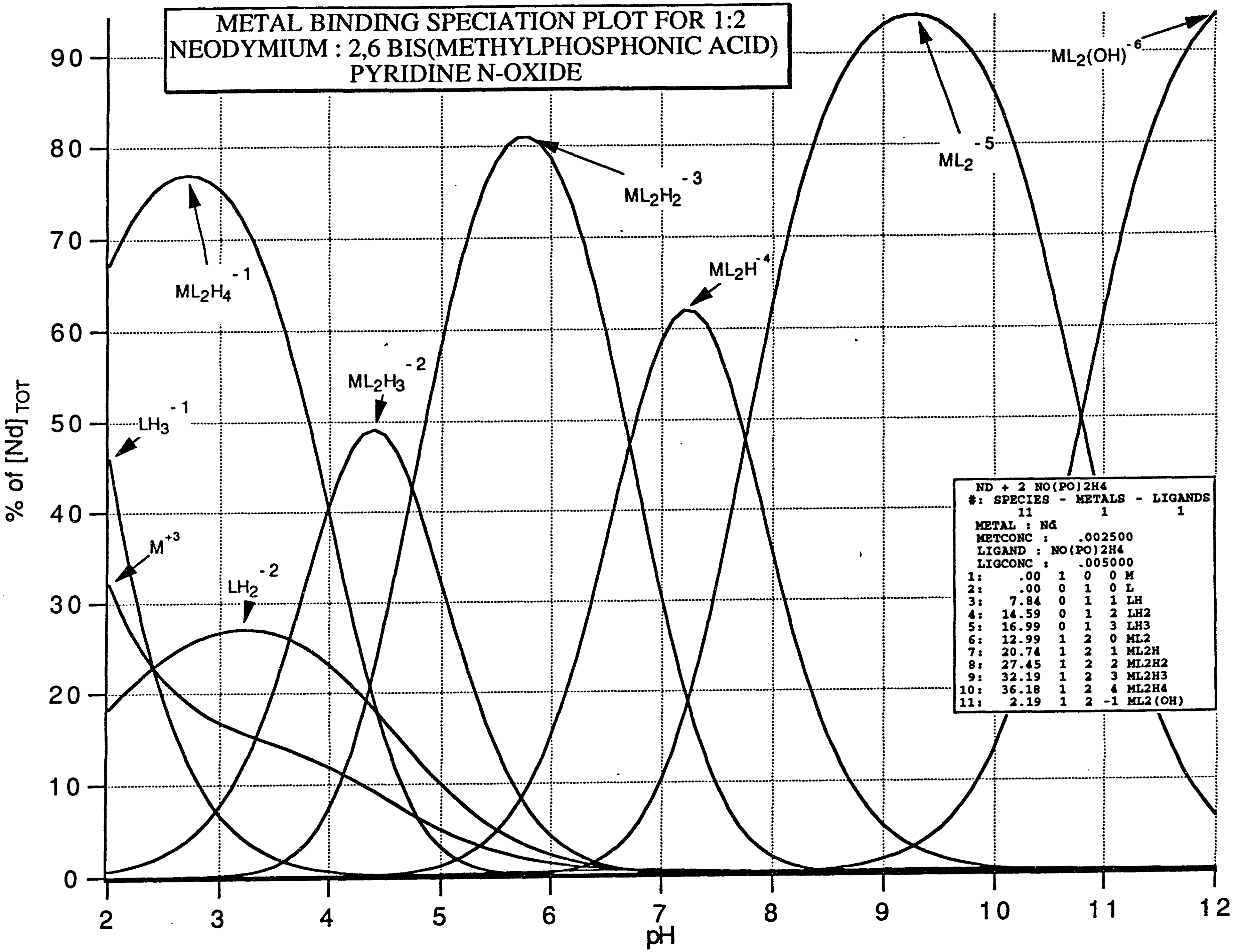


32

These ligands have been fully characterized, and their coordination chemistry is under investigation. Due to the fact that these ligands easily ionize (**31**: pK_a = 1.8 and 6.9; **32**: pK_a = 2.4, 6.8, 7.8), they form a complicated array of coordination complexes depending on the pH of the solution. Figure 1 represents a speciation plot for the system Nd(III)/**32** in a 1:2 ratio as a function of pH. Efforts are in progress to isolate one or more of the complexes for single crystal structure analysis. The relatively large formation constant for the ML_2^{5-} species indicates that the anionic ligands are very strongly bound, and they may have some practical solution scrubing utility if they can be attached to a chromatographic support.

We have also considered the possibility of making derivatives like **31** and **32** based on polypyridine fragments. To this end, we have recently prepared **33** that is based on the bipyridyl fragment.[65]



METAL BINDING SPECIATION PLOT FOR 1:2
NEODYMIUM : 2,6 BIS(METHYLPHOSPHONIC ACID)
PYRIDINE N-OXIDE

```
  ND + 2 NO(PO)2H4
 #: SPECIES - METALS - LIGANDS
       11         1         1
  METAL : Nd
  METCONC :     .002500
  LIGAND : NO(PO)2H4
  LIGCONC :     .005000
 1:     .00  1   0   0 M
 2:     .00  0   1   0 L
 3:    7.84  0   1   1 LH
 4:   14.59  0   1   2 LH2
 5:   16.99  0   1   3 LH3
 6:   12.99  1   2   0 ML2
 7:   20.74  1   2   1 ML2H
 8:   27.45  1   2   2 ML2H2
 9:   32.19  1   2   3 ML2H3
10:   36.18  1   2   4 ML2H4
11:    2.19  1   2  -1 ML2(OH)
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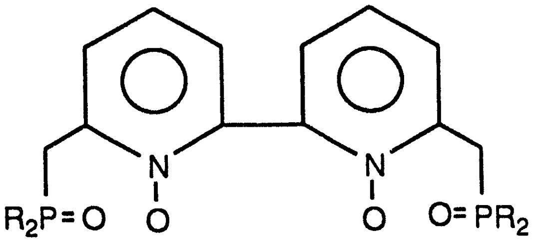
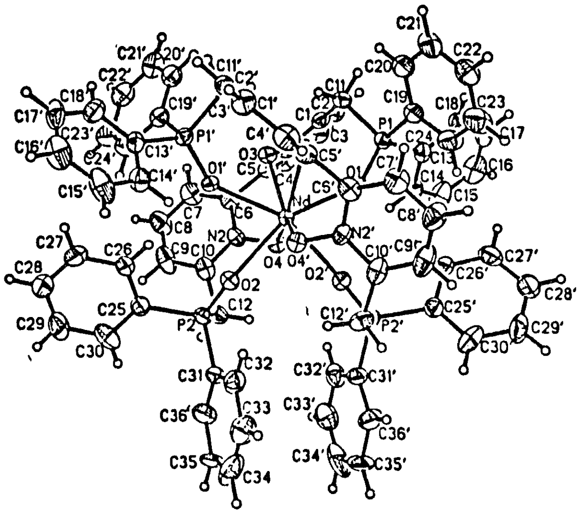
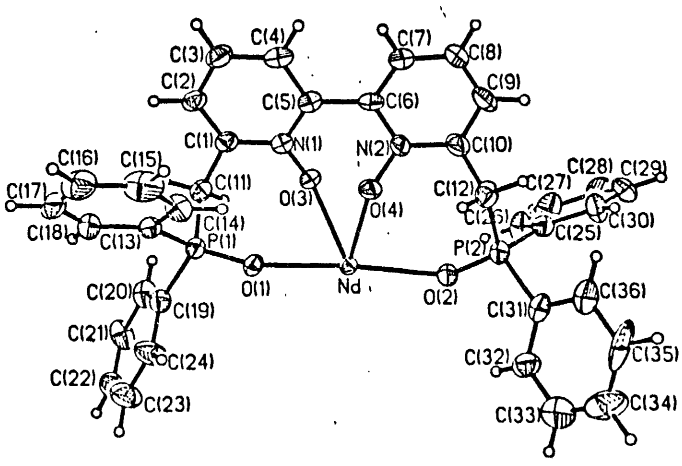


33

This molecule is potentially a tetrapodal (tetradentate) ligand. A limited amount of coordination chemistry has been completed.[65] Initial results indicate that only a 2:1 L/M stoichiometry is achieved on Ln(III) ions. The molecular structure determination of the Nd(III) complex shows that **33** completely displaces NO_3^- ions from the inner coordination sphere, and the two ligands do a good job of encapsulating the metal. A full view of the structure is shown below along with a simplified view of half of the molecule. The strong binding properties of this ligand are encouraging, and we will continue this theme into the proposal for new work.





d) Ligand Immobilization Chemistry

During each year of the present and past grant periods, a portion of our efforts has been given to the development of chemistry that would immobilize ligand fragments on organic (e.g., polystyrene-DVB)[55,57] and inorganic (e.g., silica and zirconium phosphate),[57] supports. Over the years, we have been relatively successful in this venture; however, in all cases except those involving zirconium phosphate functionalization, the ligand loadings that have been achieved are relatively low. In fact, in most cases, it is unlikely that the density of support bound ligands is great enough for formation of bis-ligand/metal complexes. If each ligand fragment contains only two effective donor centers, the stability of the resulting immobilized metal complex is probably significantly reduced compared to the bis- or tris- ligand complexes formed under liquid-liquid extraction conditions. This feature was noted in our last proposal. Several approaches were presented in the proposal that should result in higher densities of functional groups, and we have seriously explored one of these.

It was pointed out three years ago that we might succeed in bringing multiple ligand donor sites to a metal ion by functionalizing the relatively new family of polymers referred to as "starburst dendrimers."[78] The dendrimers of choice were terminated with amino groups, and a schematic representation of a generation 1 (**G1**) polymer with six terminal NH_2 is shown here. Our goals were to use either amide coupling chemistry (equation 2) to bind one CMP fragment to each NH_2 unit or Michael-type amination of vinyl phosphonates (equation 4) that could potentially place two phosphoryl groups on each terminal amine.

Our first attempts at completing this chemistry on a commercially available generation 3 (**G3**) polymer (24 terminal NH_2 groups) were successful in that we gained clear evidence that both reaction types worked on the dendrimer. However, we encountered considerable difficulties in purifying the polymeric products. It was eventually determined that the commercially available materials contained impurities that complicated purifications. We therefore set out to prepare our own dendrimer samples with the hope of obtaining more reliable samples of small dendrimers. This had an added benefit that we could have access to the 1.0 and 2.0 generation polymers whose coupling products would be more easily characterized. At the present time, we have succeeded in preparing and characterizing our own dendrimers, and the coupling and vinylic addition chemistry is in progress.[79] This will be an active area of study for the remainder of the contract period and for the future.

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