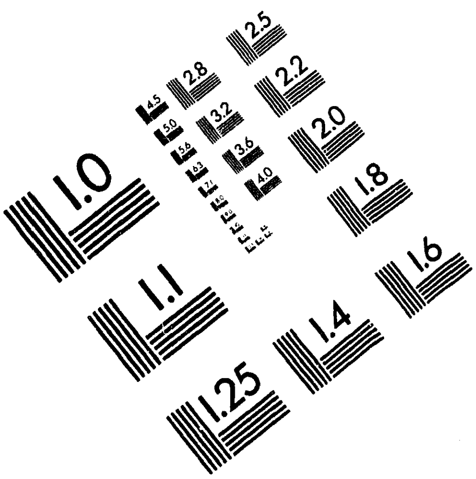

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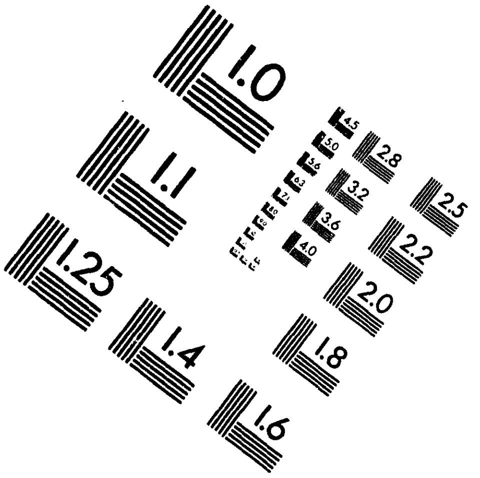

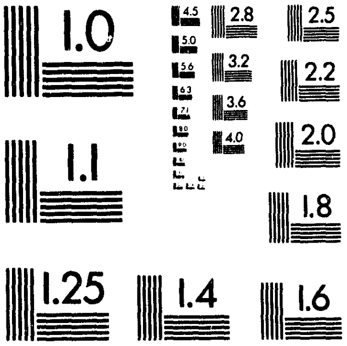

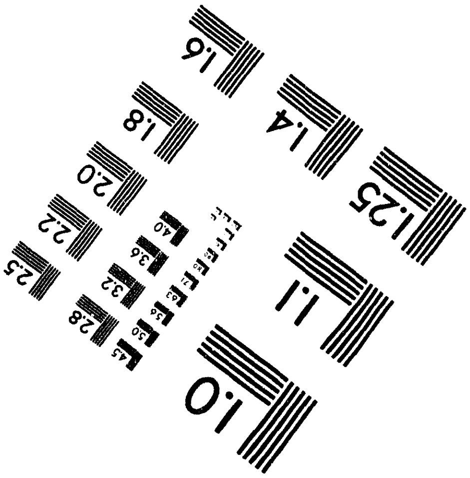

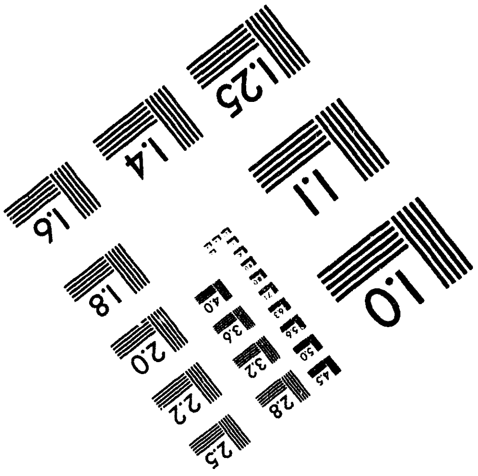

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Submitted for publication in Symposium Volume on Separations of f-Elements,
K.L. Nash, G.R. Choppin, Eds.) based on San Diego ACS Mtg., Spring 1994.

ANL/CHM/CP--83879
Conf-940301--40

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New Water Soluble Phosphonate and Polycarboxylate Complexants for Enhanced f Element Separations

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Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38 and the Westinghouse Hanford Company.

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ABSTRACT

While lipophilic extractant molecules and ion exchange polymeric materials are clearly essential to efficient separation of metal ions by solvent extraction or ion exchange, the most difficult separations often could not be accomplished without the use of water soluble complexants. This report focuses on recent developments in the design, synthesis and characterization of phosphonic acid and polycarboxylic acid ligands for enhanced f element separations. Emphasis is on the basic solution chemistry and crystal structures of complexes of the f elements with selected amino-derivatives of methanediphosphonic acid and with tetrahydrofuran-2,3,4,5-tetracarboxylic acid. The former series of compounds exhibit high affinity for lanthanides and actinides in acidic solutions. The latter ligand exhibits an unusual (and very useful) "anti-selectivity" for uranyl ion in a solvent extraction process, which permits efficient separation of uranyl from more radioactive components of nuclear wastes. Most of the observed effects can be explained through examination of the structure of the ligand, and comparison of the spectroscopic and thermodynamic parameters for complexation of various metal ions.

INTRODUCTION

It is appropriate to begin the discussion of aqueous complexation of f elements in separations with a brief summation of the relevant chemical parameters which lead to differences in the chemical behavior of these important metal ions in separations processes. Both series are characterized by valence electrons which occupy f orbitals: lanthanides the 4f, actinides the 5f. The 4f orbitals in the lanthanides are relatively deeply submerged and do not participate directly in bonding under normal conditions. The 5f orbitals of the actinides exhibit a slightly greater spatial extension, and some "hybridization" involving these orbitals is indicated for the light members of the series. This is particularly evidenced by the existence of the upper oxidation states of uranium, neptunium, plutonium, and americium as linear dioxocations in solution (1). The three principal chemical characteristics critical to their separations chemistry are the multiplicity of oxidation states of the light actinides, the steadily decreasing radii of the trivalent cations, and the slightly stronger interaction of actinides with soft-donor ligands.

The light actinides (U to Am) exist in aqueous solutions in the III, IV, V, and VI oxidation states. The upper two oxidation states are linear dioxocations AnO_2^+ or AnO_2^{2+}. The multiplicity of oxidation states of the light actinides can be utilized to accomplish very efficient separation of these elements, both from the lanthanides and from each other. Except for actinium (only trivalent), the actinide ions through plutonium either exist predominantly in higher oxidation states (Th(IV), Pa(IV,V)) or can be interconverted with relative ease among any of four oxidation states (III, IV, V, VI). The relative strength of complexes formed by the actinide cations in these oxidation states is

An(IV) > An(VI) > An(III) > An(V), which order also applies to most separations reactions involving these cations. The tri-, tetra-, and hexavalent oxidation states are most important in separations.

The separation of individual members of the trivalent lanthanide and transplutonium actinide series is based on the decrease in ionic radius which occurs with increasing atomic number (2). Trivalent lanthanide/actinide cation radii decrease with increasing atomic number because the valence f electrons compensate relatively poorly for the steadily increasing nuclear charge. Decreasing radii result in increased strength of cation-anion interactions and ion-dipole, ion- induced dipole type interactions. The expected increase in ion-dipole interactions across the series implies that the heavy members of both series should bind solute (and suitable solvent) molecules more tightly than the light members. Decreasing cationic radii of the trivalent ions is only useful for intragroup separations as the cation radii for the trivalent actinides overlap those of the lanthanide cations.

Numerous reports in both the separations literature and the classical inorganic chemistry of actinides indicates that actinides ions interact more strongly with soft donor ligands, particularly for the lighter members of the series (3). There is no clear agreement on whether this difference is attributable to a covalent contribution to bonding or a more subtle polarizability effect, particularly in solution. What is clear is that extractants and water-soluble complexants containing "soft" donor atoms are central to most ion exchange and solvent extraction separations of lanthanides from trivalent actinides.

Actinide separations processes based on exploiting differences in cation oxidation states typically achieve the separation based on a difference in interaction strength of the cation with a lipophilic complexant or resin. For the separation of trivalent ions, however, aqueous complexants are often critical, both for group (lanthanide-actinide) and intragroup (lanthanide-lanthanide or actinide-actinide) separations. Two examples of efficient group separations based on aqueous complexants are chloride based anion exchange (4) and the TALSPEAK process (5). Each process depends on the stronger interaction of trivalent actinides with soft donor ligands (Cl^- in anion exchange, DTPA in TALSPEAK). The feature example of aqueous complexants for intragroup separations is the α–hydroxyisobutyric acid cation exchange separation of lanthanides or trivalent actinides (6).

Aside from these very specific examples of the use of aqueous complexants in f element separations, efficient complexing agents are often used in processing by solvent extraction or ion exchange to improve the efficiency of (for example) stripping of used process solvent (or resin) to allow its recycle. In this case, cation selectivity is often secondary in importance to complex strength. Occasionally, a stripping agent may be employed to partition actinides based on differences in complexation strength of actinide ions in different oxidation states (7).

A variety of different types of ligands are available when a complexant is required for improved process efficiency. The five general classes typically considered for f elements are: inorganic acids, polycarboxylic acids, aminopolycarboxylic acids, macrocycles, and phosphonic acids. The use are generally diffusion controlled. Stability differences are manifested in relative complex dissociation rates (17).

Our earlier investigation of the stability of europium complexes with THFTCA suggested the importance of ligand backbone rigidity in the determination of relative complex stability (12). THFTCA was reported to form complexes five times stronger than the analog complexant diglycolic acid in dilute acid solution. More stable complexes are observed at lower pH partly because of the lower pK's of THFTCA and partly as a result of rigidity imparted to the oxydiacetate coordination zone by the tetrahydrofuran backbone. This ligand exhibits excellent solubility of both the ligand and its lanthanide complexes from pH 2 to 6.

The multiple purposes of the present report is to update our investigation of simple methanediphosphonic acid derivatives with additional insights, to report results on some ongoing investigations of amino-derivatives of methanediphosphonic acid, and to explore in greater detail the chemistry of THFTCA, its unique properties in actinide separations, and its f element complexes. The results of these investigations are reported within the context of potential applications of these chelating agents for enhanced f element separations.

EXPERIMENTAL

The results described in this paper are derived from a variety of different experiments, some of which either have been or will soon be published independently elsewhere. The experimental methods will be described to the appropriate degree of detail in this section.

Synthesis of amino methane/ethane diphosphonic acids

The aminomethane diphosphonate ligands in Table 1 were synthesized from the appropriate amides or nitriles using the approach of Rusinia (18) as adapted from Ploger et al (19). Aminomethanediphosphonic acid (AMDPA), dimethylaminomethanediphosphonic acid (DMAMDPA), morpholinomethanediphosphonic acid (MMDPA), and piperidinylmethanediphosphonic acid (PMDPA) were prepared by dropwise addition of the parent amide to a solution of $PCl_3 + H_3PO_3$. The basic reaction is described in equation 1:

$$PCl_3 + H_2PO_3 + R^1R^2NCH(O) \rightarrow R^1R^2CH(PO_3H_2)_2 \qquad (1).$$

Chloride was hydrolyzed with ice water, and the liberated HCl removed by vacuum distillation. The respective acids were precipitated with methanol.

The 1-aminoethane-1,1-diphosphonic acid (AEDPA) was prepared by dropwise addition of acetonitrile to PCl_3. The mixture was stirred overnight. Glacial acetic acid was added to this solution and again stirred overnight. The top layer containing acetic acid was removed leaving a thick oil. Water was slowly added to the oil to hydrolyze chloride. Water and HCl were removed by vacuum distillation and the AEDPA was precipitated from 6 M HCl by adding ethanol.

The product aminophosphonic acids were characterized by melting point, ^{31}P and ^{1}H NMR spectroscopy, and potentiometric titration. The parent amides were selected to provide a variety of different geometries for the amine and simultaneously a range of basicities (Table 1). Previous reports have appeared in the literature for each of these ligands, most detailing the protonation equilibria or stability of transition metal complexes (20).

Purification of THFTCA

THFTCA was further purified from the previous report by dissolution of the solid (purchased from Aldrich), filtration to remove insoluble residues, an acetone wash, and recrystallization from water. In contrast to earlier attempts, large, well-defined single crystals were precipitated from concentrated aqueous solutions. The crystals were characterized by potentiometric titration. The isomer was established as the trans,cis,trans isomer (see below) by single crystal x-ray diffraction courtesy of Professor Robin Rogers at Northern Illinois University.

Potentiometric titration of ligands and complexes

Potentiometric titrations of both free ligand solutions and metal-ligand mixtures were done using a Mettler DL21 titrator interfaced to a 386SX computer with titrator control provided by Mettler's TS^2 software package. All titrations were run under nitrogen atmosphere at 25.0 (±0.1) °C and constant ionic strength (0.1 or 0.2 M), maintained with $NaClO_4$. Fresh titrant either purchased from Aldrich or prepared in our laboratory from 99.999% pure solid NaOH were used for titrations. Titrant solutions were standardized by titration of primary standard (NIST certified) potassium hydrogenphthalate. An Orion-Ross micro combination electrode was used as the pH probe. The electrode/measurement system was calibrated daily by titration of $HClO_4/NaClO_4$ solutions to generate a pH-p[H] calibration curve which was used to convert measured pH to p[H]. The accuracy of volume addition of the automatic burette was determined gravimetrically, and a quadratic correction applied to the indicated volume of titrant delivered. Metal ion complexation reactions were investigated for La^{3+}, Eu^{3+}, and Tm^{3+} in the aminodiphosphonic acid systems, and for La^{3+}, Nd^{3+}, Eu^{3+}, Dy^{3+}, and Tm^{3+} in the THFTCA system. Potentiometric titration data for 1:1 and 1:2 metal:ligand solutions with the same standardized base used for the free ligand titrations was analyzed using the program BEST (21). Because of persistent problems with solubility for the lanthanide complexes with the other aminodiphosphonate ligands, we were able to determine metal complex stability constants only the MMDPA and PMDPA systems.

Distribution of THFTCA into Combined Process solvent

The distribution of THFTCA between various aqueous solutions and the Combined Process solvent (0.2 M di(t-butylcyclohexano)18-crown-6, 0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, 1.2 M diamyl(amyl)phosphonate, in Isopar L) was investigated by potentiometric titration and NMR spectroscopy. Solutions of THFTCA at several different concentrations were prepared and standardized by potentiometric titration using the DL21 titrator. The consecutive protonation constants of THFTCA are well enough separated to permit (via Gran analysis of the titration curves) the observation of individual endpoints for the second, third, and fourth ionizations under most conditions. It is also possible in this analysis to determine from a single titration $[THFTCA]_t$ and total acidity. Titrimetric analysis was performed before and after equilibration of the THFTCA solution with the Combined Process solvent. To asssess the contributions of the crown ether and DA(A)P to THFTCA extraction, parallel experiments were run with 0.2 M CMPO, 1.2 M DA(A)P in Isopar L, and with 1.2 M DA(A)P in Isopar L. Phases were equilibrated overnight with rotator mixing, separated by centrifugation, and the aqueous analyzed titrimetrically. In all cases, phase separation was clean and mass balance was assumed to calculate distribution ratios. In one experiment, mass balance was checked by extensive water washing of the organic phase and found to be greater than 95%. The relative importance of interaction of THFTCA with CMPO and DA(A)P was determined by ^{31}P NMR spectroscopy of the loaded organic phases.

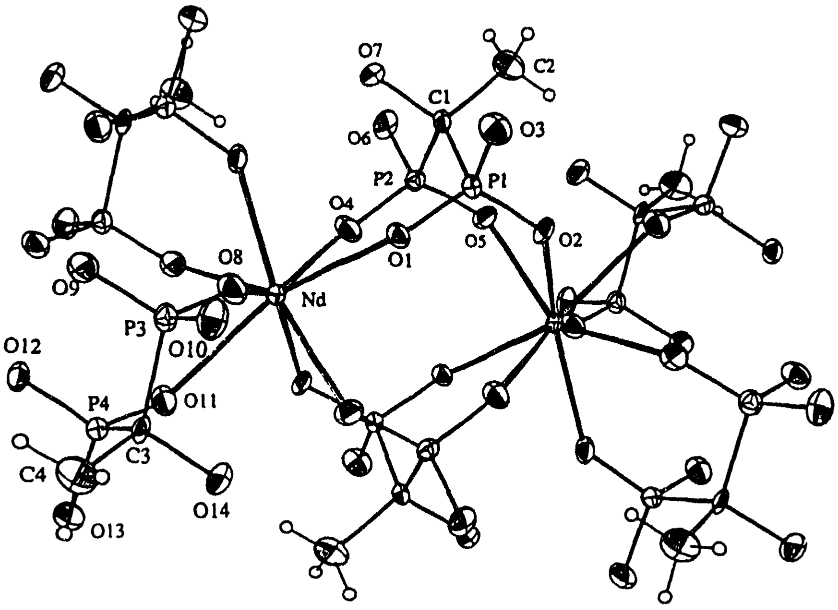
RESULTS AND DISCUSSION

Lanthanide Diphosphonate Complexes

Earlier results from this laboratory indicated that europium complexes (MH_2L^+) with 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) are 3 times stronger than the equivalent complex with ethane-1,1-diphosphonic acid (9). HEDPA complexes are formed with more exothermic heats and smaller positive entropies than those with methanediphosphonic acid or vinylidene-1,1-diphosphonic acid (which have no α-hydroxy group) (16). This difference has not been specifically attributed to an interaction between the metal ion and the α-hydroxy group, but it is tempting to do so. We have examined the inner coordination sphere of lanthanide complexes in the solid state and in aqueous solution to provide new insight into this question

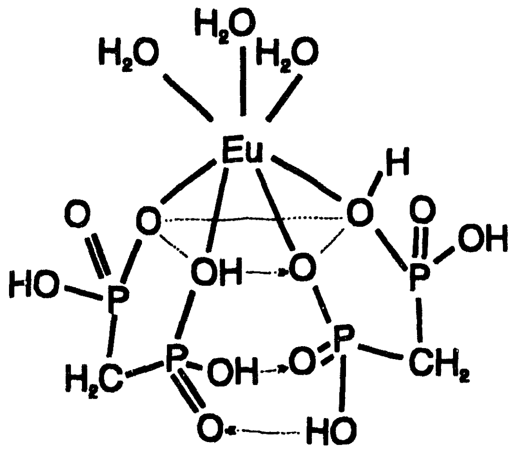
A crystal structure of the $Nd(H)(H_2HEDP)_2 \cdot 6H_2O$ was recently determined for us by Professor Robin Rogers at Northern Illinois University. The complex crystallizes in the P1 point group with cell constants 9.318, 10.272, 11.766, 91.09, 111.24, 98.40. The crystal contains two formula units per unit cell. The resolved structure (Figure 1) indicates the existence of two bridging and two terminal (chelated) HEDP ligands per unit cell. The inner coordination sphere of Nd is populated exclusively by phosphonate oxygens in an 8-coordinate geometry. The six water molecules and the free hydronium ions are in inter layer spaces remote from the metal ion. This structure is consistent with one reported earlier for the analogous erbium complex (22) indicating no significant relationship between metal complex geometry and the radius of the lanthanide cation. The positioning of the α–hydroxy group suggests that it is not directly coordinated with the metal ion.

FIGURE 1. Crystal structureof $Nd(H)(H_2HEDP)_2 \cdot 6H_2O$.



In contrast, laser induced fluorescence studies of the 1:2 europium complexes ($Eu(H_3L)_2^+$) with diphosphonic acids indicate that in acidic aqueous solutions 3 water molecules are present in the inner coordination sphere of the metal ion (16). Based on a combination of metal complexation enthalpies, the fluorescence results, and molecular modeling calculations, the probable structure for this complex is as shown in Figure 2. Extensive intracomplex hydrogen bonding is suggested to explain the very low complexation entropies observed for the formation of a 1:2 complex despite the high degree of dehydration of the metal ion. The difference between the inner coordination sphere in the solid and solution states illustrates the danger of extrapolating structural data obtained from solid

FIGURE 2. Proposed structure of $Eu(H_3MDP)_2^+$ in aqueous solution.



state crystal structure determination with solution structure. No consistent difference in cation hydration is indicated between the HEDPA and MDPA complexes, again suggesting that the α–hydroxy group is not coordinated directly with the metal ion.

Protonation and Complexation Equilibria for Aminomethanediphosphonic Acids

For the parent methanediphosphonic acid, the protonation constants (Table 1) are $pK_1 = 1.51$, $pK_2 = 2.60$, $pK_3 = 6.85$, and $pK_4 = 10.05$. Addition of an amino functionality to methanediphosphonic acid fundamentally alters the pattern of protonation constants. In solution, the strongly basic amino group binds a hydrogen ion leaving the formally neutral ligand as a zwitterion. The presence of a formal positive charge on the nitrogen in H_4L reduces the affinity of the phosphonate oxygens for hydrogen ion and produces the pattern of constants $pK_1 = 1.5$, $pK_2 = 4.7$-5.4, $pK_3 = 8.0$-8.6, and $pK_4 = 11.5$-12.5 (or more). Accurate determination of both pK_1 and pK_4 is difficult by direct potentiometry because the fourth proton associates with the neutral molecule very weakly and the first associates with the amino nitrogen extremely strongly. Except for the morpholino derivative, the relative order of the protonation constants for the amino nitrogens correlates with the basicity of the corresponding free amines. The amines in the diphosphonates bind H^+ about 100 times stronger than the free amine reflecting the relative basicity of primary, secondary and tertiary amines.

TABLE 1. Protonation Constants for aminodiphosphonic acids at 0.2 M ionic strength , 25.0 °C.

Compound	pK_1	pK_2	pK_3	pK_4	Parent Amine
MDPA[a]	1.51	2.60	6.85	10.05	NA
AMDPA[b]	(1.4)	5.30	8.07	11.47	9.25 (NH_3)
DMAMDPA[c]	(0.4)	4.84	8.59	(12.6)	10.73 $(CH_3)_2NH$
AEDPA[d]	1.46	5.35	8.57	11.72	9.25 (NH_3)
MMDPA[e]	(0.8)	4.68	8.35	12.21	8.33 (morpholine)
PMDPA[f]	1.35	4.72	8.57	(12.6)	11.12 (piperidine)

a. Methanediphosphonic acid, FW = 176.02 g (I=0.1 M).
b. Aminomethanediphosphonic acid, FW = 190.01 g.
c. Dimethylaminomethanediphosphonic acid, FW = 219.07 g.
d. 1-Aminoethane-1,1-diphosphonic acid, FW = 204.04 g.
e. Morpholinomethanediphosphonic acid, FW = 261.11 g.
f. Piperidinylmethanediphosphonic acid, FW = 259.14 g.

Figure 3 is a sample titration curve for the potentiometric analysis of the protonation of

PMDPA and a 1:1 solution of PMDPA with Eu^{3+}. The free ligand titration curve shows the three distinct breaks expected for the well-separated protonation constants presented in Table 1. Resolved metal complexation equilibrium constants (I=0.1 M, T=25.0 °C) for La^{3+}, Eu^{3+}, and Tm^{3+} are shown in Table 2. Stability constants are resolved for the 1:1 complexes in each system, but only a few parameters corresponding to the 1:2 complexes are determined. The apparent exclusion of the 1:2 complexes may be a result of the relative bulk of the ligand as compared with the parent MDPA, where several protonated complexes having both 1:1 and 1:2 metal:ligand stoichiometry are known (9). It is somewhat surprising that only the lanthanide complexes with the largest aminosubstituents are sufficiently soluble to permit analysis by potentiometry. Perhaps it is the bulk of the amine which interferes with formation of stable solid species. Solubility problems for DMAMDPA complexes with Nd^{3+} and Gd^{3+} were suggested in a previous report (23).

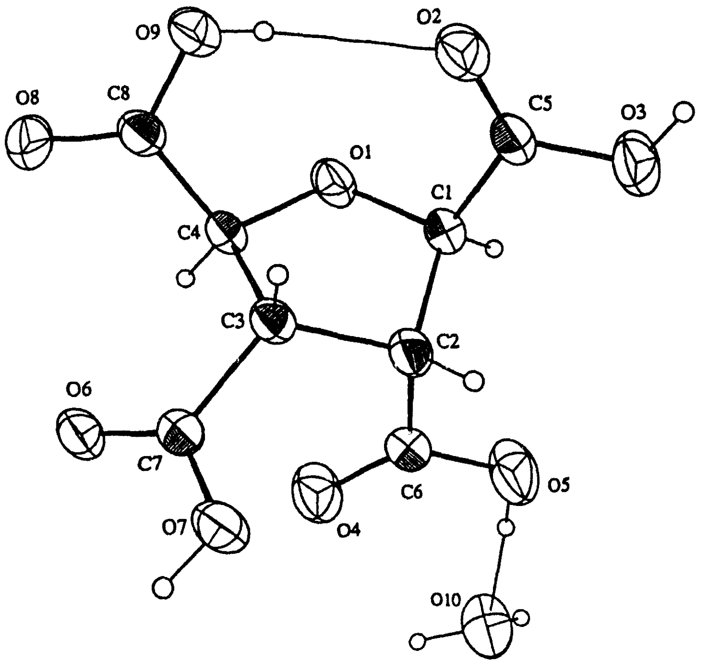
TABLE 2. Lanthanide complex stoichiometries and stability constants for complexes with morpholinomethanediphosphonic acid (MMDPA) and piperidinylmethanediphosphonic acid (PMDPA) at 0.2 M ionic strength and 25.0°C.

Stoichiometry	La^{3+} MMDP	Eu^{3+} MMDP	Tm^{3+} MMDP	La^{3+} PMDP	Eu^{3+} PMDP	Tm^{3+} PMDP
MH$_2$L$^+$	26.0	28.4	27.6	27.5	27.5	26.7
MHL	23.6	25.5	24.9	24.4	24.4	24.3
ML$^-$	15.0	16.7	16.0	14.0	14.4	14.7
M(OH)L^{2-}	4.2	5.3	5.8	-	-	3.3
MH$_3$L$_2^{2-}$	-	-	-	48.4	-	-
MH$_2$L$_2^{3-}$	-	41.6	41.2	41.4	42.2	24.0
MHL^2	-	-	31.8	-	-	-
ML$_2^{5-}$	-	21.2	-	-	19.6	21.3

Tetrahydrofuran-2,3,4,5-tetracarboxylic acid Crystal Structure

Crystallographic analysis of duplicate samples of replicate preparations of single crystal samples of THFTCA were identified as the trans,cis,trans isomer, as shown in Figure 4. This crystallographic analysis also was conducted by Professor Rogers. THFTCA crystallizes in the P1 space group with indices 7.594, 8.137, 9.404, 107.08, 102.48, 101.30. There was no evidence in either sample for the presence of any other geometric isomer of THFTCA. This structure is consistent with previous reports of crystal structures of THFTCA complexes with Cs$^+$, Ca^{2+},(24) and Co(en)$_3^{3+}$ (25). This isomer was previously indicated as one of the most probable species based on molecular mechanics calculations (13).

FIGURE 4, Crystal Structure of THFTCA.



THFTCA as a Stripping Agent in the Combined Process

The Combined Process is a solvent extraction based process designed to simultaneously remove actinides, lanthanides, and strontium from radioactive wastes (26). Solvent extraction processes for transuranic elements (TRUEX, 27) and strontium (SREX, 28), combined in a single process solvent, permits the simultaneous removal of these radioactive metals from the bulk of the less-radioactive or nonradioactive components. The radioactive elements can then be selectively stripped from the loaded extractant phase through a combination of pH adjustments and selective chelating agents. Ongoing experiments indicate that THFTCA selectively strips trivalent and tetravalent actinides from the loaded solvent leaving uranyl and strontium in the extractant phase (29). Selective separation of uranyl from the trivalent and tetravalent actinides is important as the volume of wastes requiring disposal in a geologic repository could be significantly reduced if uranium is removed from other TRU's.

However, polycarboxylic acids are known to distribute significantly into extractant solutions containing octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) (30). Design of a process to use THFTCA for selective separation of uranium from the transuranium components of the waste must take into account the tendency of THFTCA to distribute to the CMPO phase. Successful design of THFTCA into the Combined process requires that the distribution of THFTCA between the phases be known accurately under a variety of conditions and preferably reduced.

The results in Figure 5 indicate first order dependence of the distribution ratio of THFTCA into PS12 solvent. Saturation of the extractant is apparently reached at about 0.5 M $[\mathrm{THFTCA}]_t$. The distribution at low concentrations of THFTCA clearly favors the organic phase. The ^{31}P chemical shifts for CMPO in these solutions are shown in Figure 6. A significant downfield shift of nearly 7 ppm is indicated with saturation indicated at 1:1 stoichiometry (0.2 M). Excess THFTCA above 0.2 M is probably weakly associated with the phase mod'fier DA(A)P (small shift in ^{31}P resonance), but association of THFTCA with the crown ether cannot be ruled out. Complementary experiments run with 0.2 M CMPO, 1.2 M DA(A)P in Isopar L, and with 1.2 M DA(A)P in Isopar L suggest come contribution of each extractant to THFTCA extraction into the Combined Process Solvent. Addition of nitric acid to the aqueous solution effects the observed D's unpredictably. More recent work (in progress) indicates that the mono- and disodium salts of THFTCA are less extracted. In the pH 2.5 regime ($\mathrm{Na}_{1.5}\mathrm{H}_{2.5}$THFTC), THFTCA remains primarily in the aqueous phase while trivalent and tetravalentt actinides are selectively stripped (leaving uranyl in the organic phase for subsequent isolation) (29).

THFTCA Complexes with Lanthanides:

If consistent trends are observed for a series of lanthanides, separations procedures analogous to α-hydroxyisobutyric acid are feasible. The relationship between metal ion separation factors and the stability of water soluble metal complexes is illustrated in equation 1.

$$S_B^A = \frac{D^A}{D^B} = \frac{D_o^A(1+\Sigma\, \beta_i^B\, (L)^i)}{D_o^B(1+\Sigma\, \beta_i^A\, (L)^i)} \qquad (2)$$

Note that while the separation factor ($S_B{}^A$) is directly proportional to the relative distribution coefficients of the metal in the absence of aqueous complexants, it is inversely dependent on the relative strength of their aqueous complexes. In the α-hydroxyisobutyric acid system, $D_A = D_B$ (Dowex 50 exhibits little inherent selectivity for individual lanthanides). Lanthanide separations in this system are based primarily on the relative strength of the lanthanide (or trivalent actinides) complexes with α-hydroxyisobutyric acid.

To assess whether THFTCA might improve on the performance of the α-hydroxyisobutyric acid system, we determined the stoichiometry and stability of La, Nd, Eu, Dy, and Tm complexes. These metals were selected to represent a spread of light and heavy lanthanides. The resolved constants are given in Table 3. Most of the possible protonated complexes from MH_2L to ML_2 are indicated for each metal ion. Hydrolysis is also indicated for the complexes at pH > 8. Solubility of the complexes was generally good from pH2 to 10 (in the 0.001 to 0.01 M concentration range). Calcu-

TABLE 3. Selected lanthanide stability constants (log β_{mhl}) with THFTCA at 0.1 M ionic strength, 25.0°C.

Stoichiometry	La^{3+}	Nd^{3+}	Eu^{3+}	Dy^{3+}	Tm^{3+}
MH_2L^+, log β_{121}	15.33	16.16	16.74	17.59	17.38
MHL, log β_{111}	12.05	13.38	14.15	14.79	14.78
ML^-, log β_{101}	8.45	9.47	10.22	10.46	10.37
$M(OH)L^{-2}$, log β_{1-11}	-1.97	1.00	2.10	2.19	2.62
$M(OH)_2L^{-3}$, log β_{1-21}	-	-9.76	-8.34	-8.07	-7.12
$MH_4L_2^-$, log β_{142}	30.02	32.04	31.80	32.20	-
$MH_3L_2^{-2}$, log β_{132}	26.73	28.70	28.56	29.11	-
$MH_2L_2^{-3}$, log β_{122}	-	25.36	25.44	25.70	24.91
MHL_2^{-4}, log β_{112}	-	20.10	20.47	20.66	20.00
ML_2^{-5}, log β_{102}	11.65	15.61	15.98	15.17	14.93

lated speciation for DyTHFTCA at 0.001 M Dy^{3+}, 0.002 M THFTCA is shown in Figure 7.

For a viable separation scheme, equation 2 indicates the desirability of consistent trends in the stability constants of the complexes with members of the series. In Figure 8, the β_{101} values for the lanthanide THFTCA complexes are compared with literature data for structurally similar ligands. Note that lanthanide complexes with α-hydroxyisobutyric acid exhibit a consistent trend with decreasing cation radii, but the slope is relatively low. The slope is higher at higher concentrations due to the presence of 1:2 and 1:3 complexes. Separation factors for adjacent lanthanides using α-hydroxyisobutyric acid as the eluant average 1.6 (±0.3). It is somewhat surprising that, despite the steady decrease of lanthanide cation radii across the series, the linear trend exhibited by the α-hydroxyisobutyrate complexes is not more generally observed. This apparent inconsistency is a manifestation of the complexity of overlapping effects which contribute to metal complex stability.

In the first half of the lanthanide series, a much steeper slope is observed for lanthanide-THFTCA complexes than for the 1:1 α-hydroxyisobutyric acid system. Similar relationships are noted for the various protonated complexes. The difference between oxydiacetic acid and THFTCA is particularly striking, as it indicates the impact of ligand preorganization on thermodynamic stability. The structural rigidity effect (largely entropy derived) is further supported by a comparison of DCPA with NTA (DCPA is NTA with a piperidine ring constraining the ligand binding groups). The slope for lanthanide stability constants with DCPA is measurably steeper than that for NTA, particularly for the lighter members of the series. We are presently examining the separation potential of this system for both lanthanides and trivalent actinides.

Conclusion:

Two classes of ligands which form strong complexes with f elements have been examined for their potential use in f element separations. Aminodiphosphonic acids form strong complexes with trivalent lanthanide cations, but it appears unlikely that the α-amino group can be directly coordinated with the metal ion. Two derivatives, morpholinomethanediphosphonic acid (MMDPA) and piperidinylmethanediphosphonic acid (PMDPA), form complexes with La^{3+}, Eu^{3+}, and Tm^{3+} which are soluble (at millimolar concentrations) from pH 2 to 10. However, thermodynamic data indicate little difference in complex stability across the lanthanide series. These ligands may have potential as general stripping agents as a result of the enhanced solubility of the complexes, but do not appear to have any significant potential for separation of individual members of either the lanthanide or actinide series.

The second category of f element complexants examined is a polycarboxylic acid, tetrahydrofuran-2,3,4,5-tetracarboxylic acid. Like the aminodiphosphonic acids, this complexant also promotes lanthanide solubility over a substantial range of pH. Investigations of the basic thermodynamics of lanthanide complexation suggests the potential for THFTCA as a viable reagent for enhanced separation of individual lanthanides. Investigations of its performance in a Combined TRUEX-SREX solvent extraction process for treatment of radioactive wastes suggest that THFTCA may be a key reagent for selective partitioning of uranyl from transuranium actinides. This is an important and desirable objective as the low specific activity of natural uranium allows its disposal in relatively inexpensive near-surface disposal sites rather than a deep geological repository. Work continues on both classes of reagents to assess their usefulness in specific separations applications and the science underlying their behavior.

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Figure Captions:

Figure 3. Titration results for 0.01 M piperidinylmethanediphosphonic acid (PMDPA) and 0.001 M Eu^{3+}, 0.001 M PMDPA at 25.0°C, I= 0.2 M.

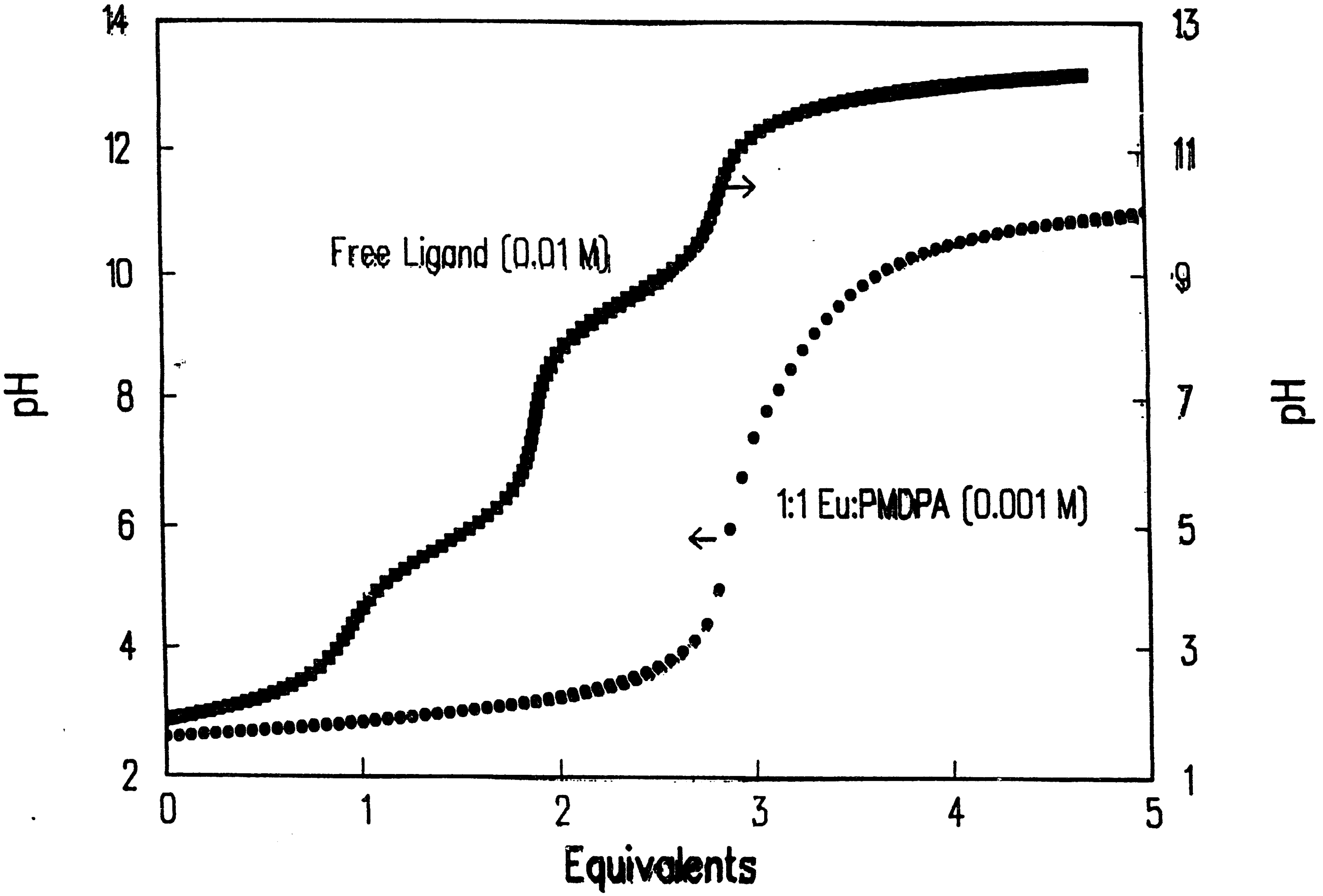
Figure 5. Distribution of tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) into PS12 Combined Process Solvent (0.2 M di(t-butylcyclohexano)18-crown-6, 0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, 1.2 M diamyl(amyl)phosphonate, in Isopar L).

Figure 6. ^{31}P Chemical shift for CMPO in PS12 Combined Process Solvent as a function of the [THFTCA] extracted into the organic phase.

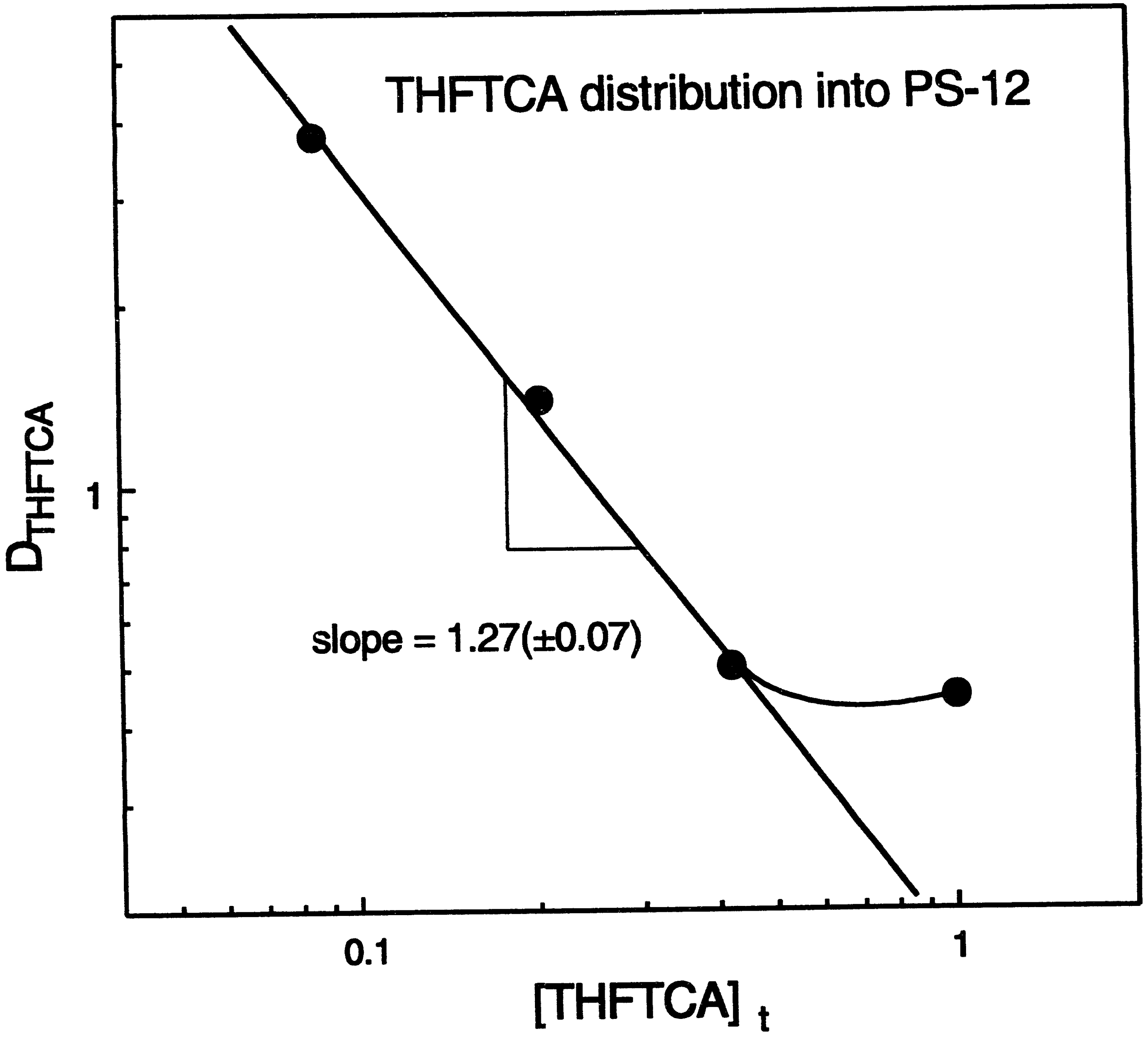
Figure 7. Calculated species distribution of Dy^{3+}-THFTCA at 0.001 M $[Dy^{3+}]_t$, 0.002 M $[THFTCA]_t$ from pH 2 to 10, T = 25.0°C, I = 0.1 M.

Figure 8. Stability constants for lanthanide complexes with thiodiacetic acid (TDA), α-hydroxyisobutyric acid (α–HIB), oxydiacetic acid (ODA), iminodiacetic acid (IMDA), tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA)n 2,6-dicarboxypiperidine-N-acetic acid (DCPA), and nitrilotriacetic acid (NTA). All data except the THFTCA taken from reference 31.

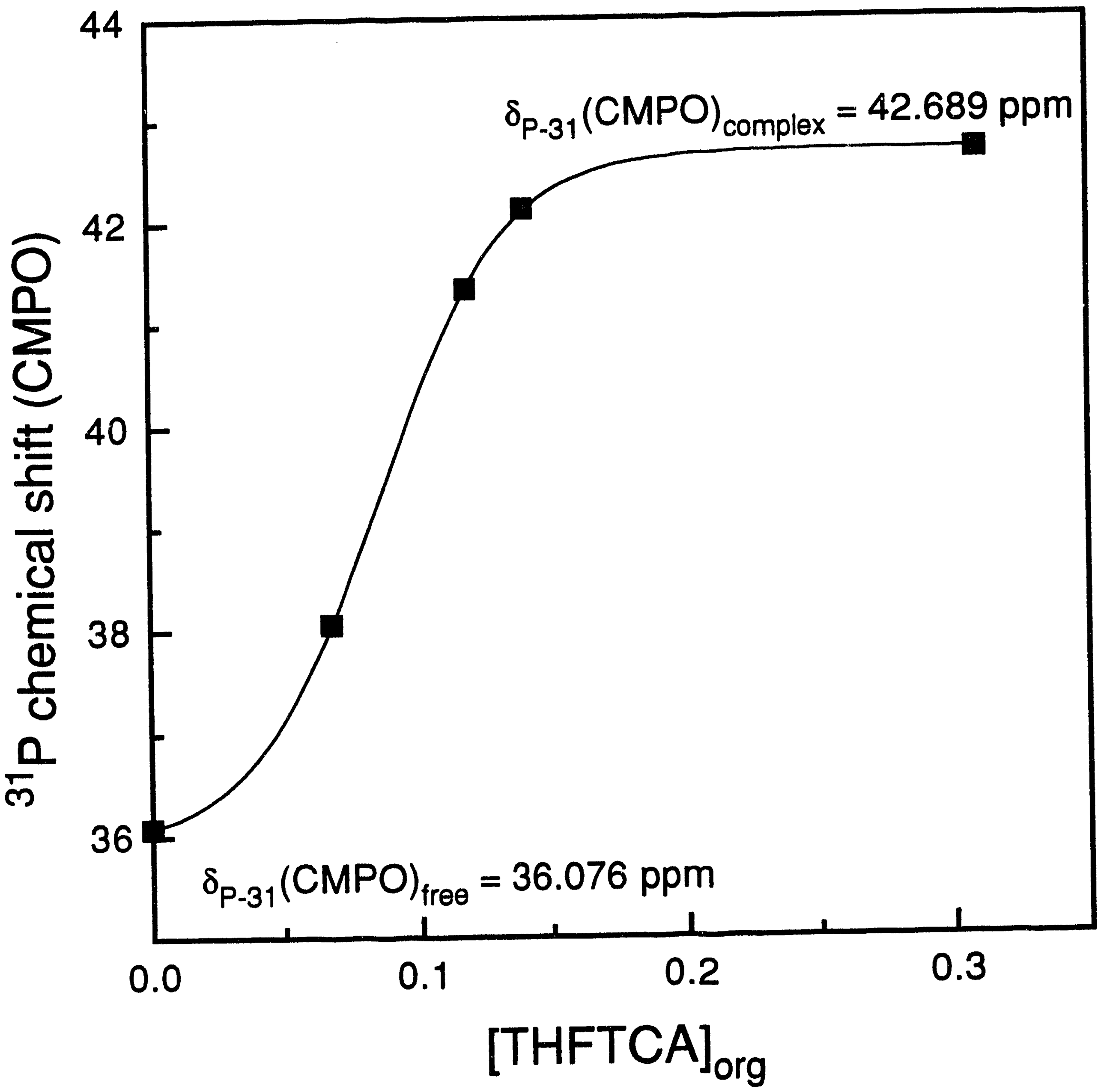
Fig 3



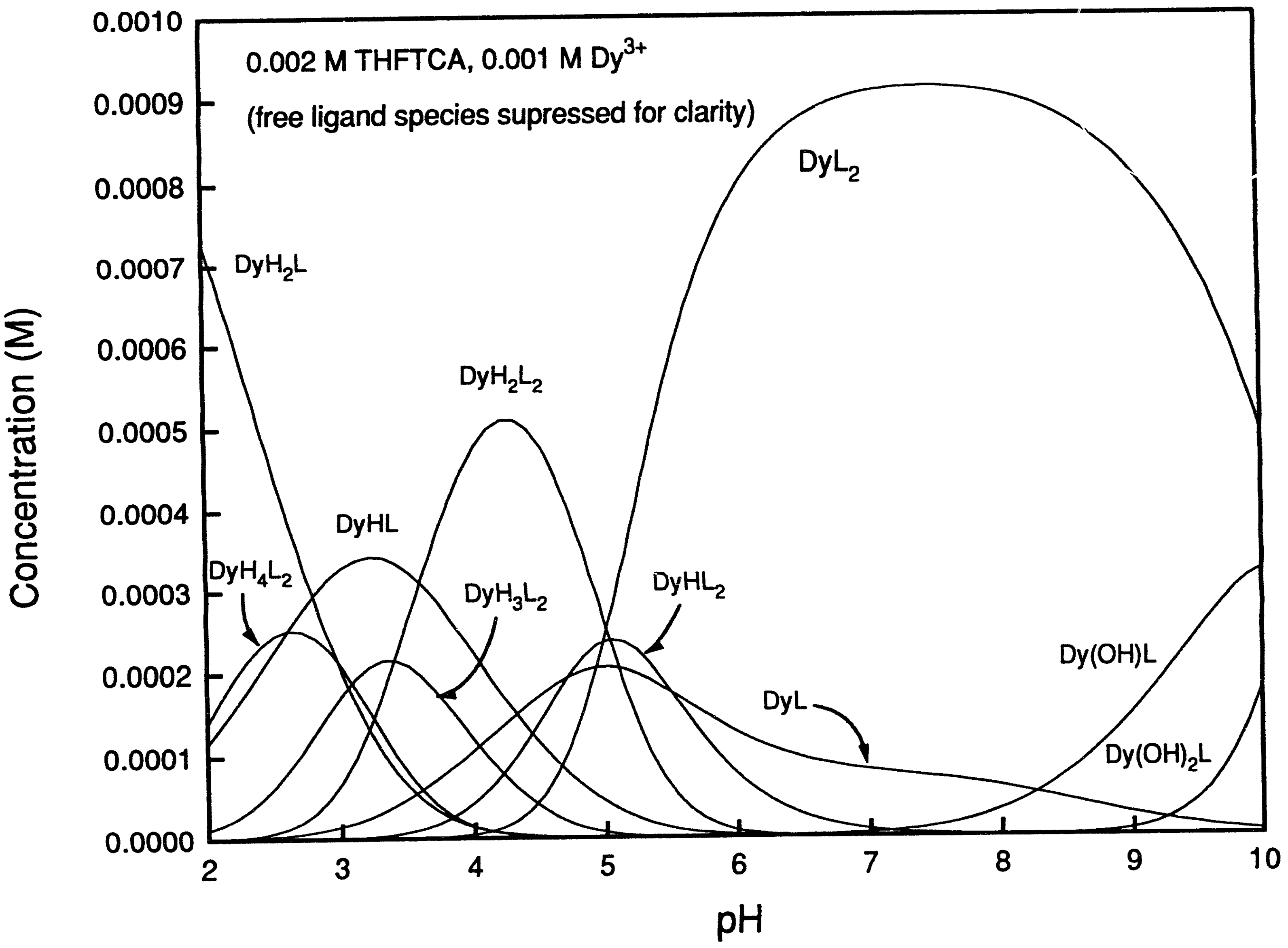
14
12
10
8
6
4
2
pH
13
11
9
7
5
3
1
pH
0
1
2
3
4
5
Equivalents
Free Ligand (0.01 M)
1:1 Eu:PMDPA (0.001 M)



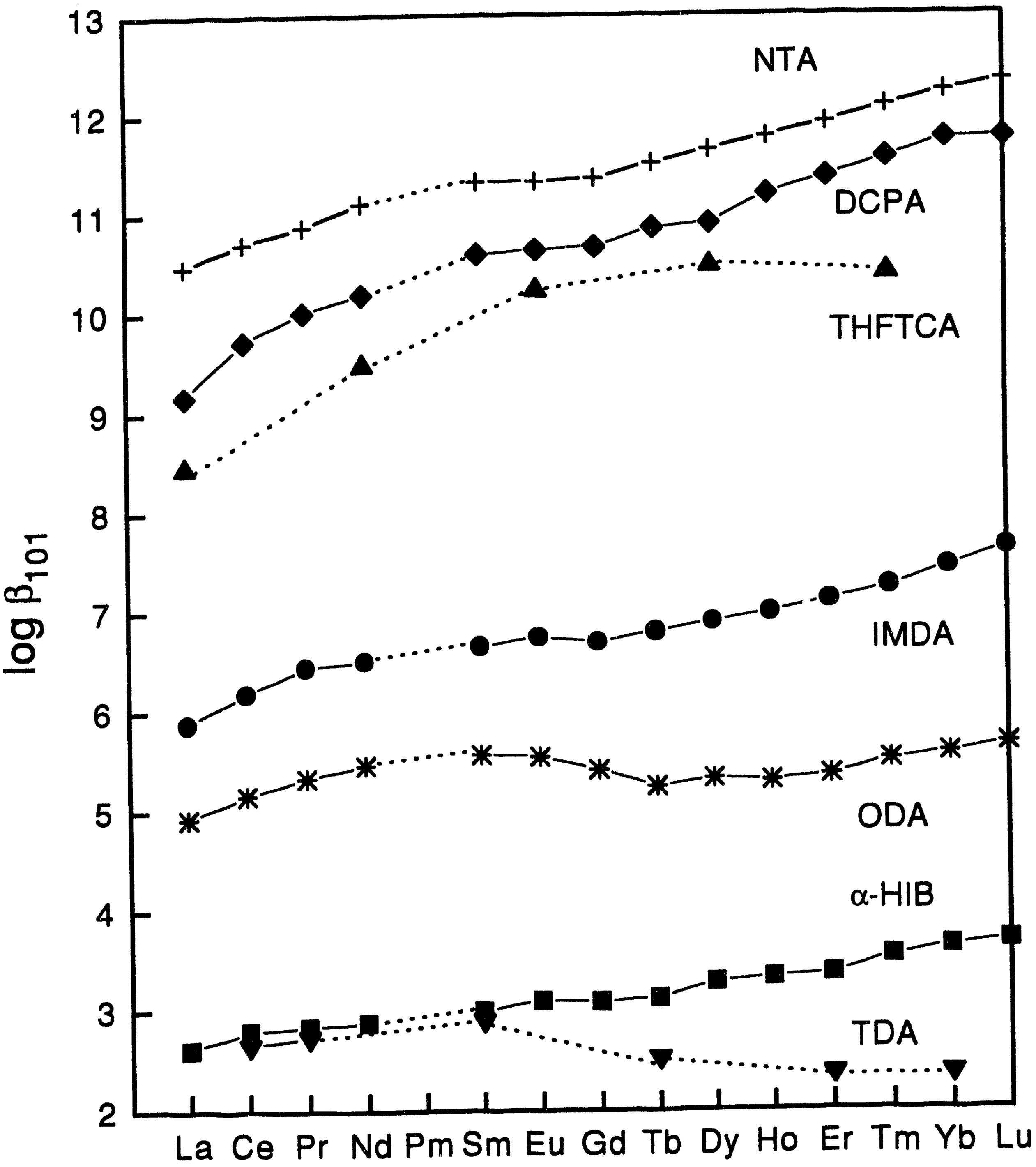
THFTCA distribution into PS-12
slope = 1.27(±0.07)
1
D_THFTCA
0.1
1
[THFTCA] t



44
42
40
38
36
^{31}P chemical shift (CMPO)
$\delta_{P\text{-}31}(\text{CMPO})_{\text{complex}} = 42.689$ ppm
$\delta_{P\text{-}31}(\text{CMPO})_{\text{free}} = 36.076$ ppm
0.0
0.1
0.2
0.3
$[\text{THFTCA}]_{\text{org}}$



0.002 M THFTCA, 0.001 M Dy^{3+}
(free ligand species supressed for clarity)
DyL_2
DyH_2L
DyH_2L_2
$DyHL$
DyH_4L_2
DyH_3L_2
$DyHL_2$
DyL
$Dy(OH)L$
$Dy(OH)_2L$
Concentration (M)
0.0010
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
2
3
4
5
6
7
8
9
10
pH



NTA
DCPA
THFTCA
IMDA
ODA
α-HIB
TDA
log β_{101}
13
12
11
10
9
8
7
6
5
4
3
2
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

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10/11/94

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