providing a complete analysis of this case. In contrast, if the ratio of signals varies with crystallization conditions or indicates unusual ratios of methyltin(IV) compounds present in the sample, then the presence of more than one crystalline modification (type B polymorphism) is strongly indicated; isolation of the individual crystalline forms for characterization (by NMR, X-ray, etc.) would provide absolute confirmation of this analysis.

Experimental Section

$[Me_2SnS]_3$ and $MeSnPh_3$ were obtained from commercial sources. $Me_2Sn(S_2CNEt_2)_2$ was prepared according to the published procedure.[6] The purity of different recrystallization crops of these compounds was established by melting point and/or solution ^{13}C NMR. Small, colorless hexagonal plates (orthorhombic modification[8]) of $Me_2Sn(S_2CNEt_2)_2$ were obtained from slow evaporation of a $CHCl_3/EtOH$ solution at room temperature. Mixed crops containing the orthorhombic and the known monoclinic and triclinic modifications were obtained from recrystallizing at reduced temperature or by adding water to the recrystallization solution. Their presence in the mixtures was demonstrated by single-crystal X-ray unit cell determinations. Under no conditions were we able to obtain pure the other crystalline modifications.

Slow crystallization of $[Me_2SnS]_3$ from cyclohexane solution at room temperature gave well-formed octagons which match the description[9a] of the tetragonal form. Recrystallization of *n*-hexane solutions at low temperatures (+5 to −70 °C) gave variable, mixed crops containing small amounts of octagonal crystals (as little as ca. 10%) and larger amounts of small needles and plates. Mixed crops of very small crystals were also obtained by sublimation.[9b] The small size of these crystals prevented separation by hand of amounts (0.1–0.4 g) sufficient for NMR analysis of the individual modifications.

$MeSnPh_3$ as obtained commercially gave a slightly broadened NMR spectrum in which two distinct Me resonances were present. Recrystallization from hydrocarbon solvents gave microcrystalline powders; clear, colorless crystals were obtained upon very slow crystallization from methanol or isopropyl alcohol. Twinning of the crystals prevented successful X-ray analysis.

NMR spectroscopic equipment and methods have been described elsewhere.[10c]

Note Added in Proof. The X-ray structure of allyltriphenyltin has just appeared (Ganis, P.; Furlani, D.; Marton, D.; Tagliavini, G.; Valle, G. *J. Organomet. Chem.* **1985**, *293*, 207). This compound also crystallizes with two independent, though structurally nearly identical molecules in the unit cell.

Registry No. $[Me_2SnS]_3$, 16892-64-1; $Me_2Sn(S_2CNEt_2)_2$, 19413-37-7; $MeSnPh_3$, 1089-59-4.

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Complexes of Rare-Earth Elements with 1,3-Diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetic Acid

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There has appeared a literature summary dealing with 1,3-diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetic acid (DHPTA) and its complex formation with various metal ions.[1] Thompson et al.,[2] in particular, determined the stabilities of some divalent metal complexes formed with the DHPTA anion at 25 °C and $I = 0.1$ (KNO_3). Their results showed that both normal and protonated complex species existed and that neglect of the latter had contributed to the widely discordant results previously published for alkaline-earth metals. The values obtained were compared with results for trimethylenediamine-*N*,*N*,*N*′-*N*′-tetraacetic acid (TMDTA), and it was concluded that in such complexes, with the possible exception of those of strontium and barium, there is no participation of the OH group in the coordination sphere.

Table I. Anion Protonation Constants of DHPTA and TMDTA at 25 °C and $I = 0.1$ (KNO_3)

	log K_n				
K_n	definition	DHPTA	1	2	TMDTA[9]
K_1	$[HL]/[H][L]$	9.49	9.49	9.49	10.46 − 0.2
K_2	$[H_2L]/[H_2][H]$	7.04	6.36	6.96	8.02 − 0.1
K_3	$[H_3L]/[H_2L][H]$	2.62	2.52	2.60	2.57 + 0.1
K_4	$[H_4L]/[H_3L][H]$	1.47	1.6	~1.6	1.88 + 0.1

On examining the available literature, we found that someone had been interested in the stabilities of Ln(DHPTA) complexes[2] and that others[3] professed to have studied the complex behavior of DHPTA with rare-earth metals, but we were unable to find any published data.

Experimental Section

Reagents and Apparatus. 1,3-Diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetic acid was obtained from Aldrich Chemical Co. Approximately 0.1 M $Ln(NO_3)_3$ solutions were prepared by dilution of previously prepared[4] stock solutions and carefully analyzed prior to use.[5] All other chemicals used were of AR grade and all solutions were prepared from deionized water.

A Corning pH meter 130 was used for the pH_c measurements and was calibrated as described elsewhere.[6]

Anion Protonation Constants. The anion's four protonation constants were obtained from pH_c measurements on a series of independently prepared solutions of the ligand acid and carbonate-free KOH. In the final determinations, exactly enough KNO_3 was added to adjust the ionic strength to 0.100 M.

Stability Constants of the Chelate Species. The individual formation constants of the Ln- and Y(DHPTA) species were determined by the usual potentiometric method employed in this laboratory[6] at 25.0 °C and $I = 0.100$ (KNO_3).

Results and Discussion

Anion Protonation Constants. The anion protonation constants obtained are listed in Table I along with data sets reported by two other groups.[1,2] The values coincide well with each other. Comparison of the DHPTA protonation constants with corresponding values for the analogous ligand, trimethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate (TMDTA), which differs only by having a hydrogen atom in place of the OH, reveals that DHPTA is definitely the more readily dissociated acid.

Stability Constants. A summary of the data obtained in this work is given (along with data for TMDTA and EDTA) in Table II and plots of log K_{ML} vs. crystal ionic radius[7] are compared for DHPTA, TMDTA, EDTA, EEDTA, and BPETA in Figure 1.

As known, the neutralization of DHPTA in the presence of an equivalent amount of rare-earth metal cation indicates release of four protons at a relatively low pH, but a much higher pH is required to release the hydroxyl proton. We are concerned only with complex formation at low pH values, which are ambient in the application of polyamino polycarboxylates to cation-exchange elution separations. Thus DHPTA can be considered to be a tetraprotic acid. Only one species, LnL^-, is prevalent at pH 3–5. For lanthanum, the rare earth having the least affinity for the DHPTA anion, the value of the calculated complex formation constant was observed to vary somewhat with pH, and subsequent

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Table II. Stability Constants of Ln(DHPTA) and Other Chelate Species at 25 °C and $I = 0.1$ (KNO_3)[a]

rare-earth metal	ionic radius,[7] Å	log K_{ML}				α_Z^{Z+1}	
		DHPTA	TMDTA[9]	EDTA[10]	DHPTA	TMDTA	EDTA
La	1.061	11.61	11.28	15.50	3.0	3.0	3.0
Ce	1.034	12.08	11.75	15.98	3.1	1.9	2.6
Pr	1.013	12.57	12.04	16.40	2.0	2.2	1.6
Nd	0.995	12.88	12.39	16.61			
Pm	(0.979)				6.0	6.6	3.4
Sm	0.964	13.66	13.21	17.14	2.0	2.6	1.6
Eu	0.950	13.96	13.62	17.35	1.0	1.4	1.0
Gd	0.938	13.94	13.76	17.37	4.1	3.0	3.6
Tb	0.923	14.55	(14.24)	17.93	1.9	3.0	2.3
Dy	0.908	14.83	14.71	18.30	1.1	1.2	2.0
Ho	0.894	14.88	(14.78)	(18.60)	1.1	1.2	2.0
Er	0.881	15.09	14.85	18.85	1.7	2.0	3.0
Tm	0.869	15.31	(15.16)	19.32	2.6	2.0	1.5
Yb	0.858	15.72	15.47	19.51	1.4	1.3	2.0
Lu	0.848	15.87	15.59	19.81			
Y	0.88	14.15	...	18.08			

[a] Data in parentheses are interpolated values.

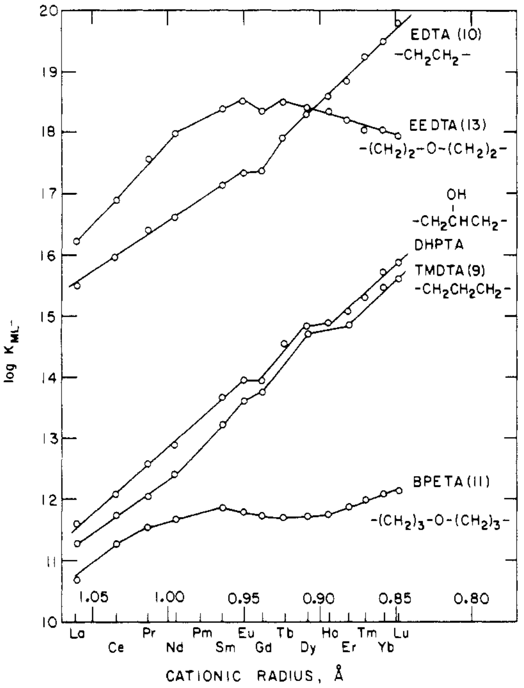

Figure 1. Comparison of log K_{ML} sequences of various 1:1 polyamino polycarboxylate chelates of the rare-earth metals.

calculations with a program that evaluates both K_{HML} and K_{ML} gave log values of 6.33 and 11.27, respectively.

Comparison of the stability constants of DHPTA (Table II) with those of TMDTA[8,9] and EDTA[10] reveals that the stability constants of the Ln chelates of both DHPTA and TMDTA are on the order of 10 000-fold less than those of EDTA. As has been reported in a previous paper,[11] a great difference in chelate stability constants exhibited by homologous ligands may be caused by two factors: an inductive effect and the effect of chelate-ring size. In going from EDTA to TMDTA, one chelate ring out of five changes from penta- to hexadentate. Simultaneously, the added methylene group produces an inductive effect that enhances the donor capability of the nearby N atoms,[12] but the net effect is a nearly 10 000-fold attenuation in lanthanon affinity.

An analogous effect can be seen by comparing the corresponding log K_{ML} values for (bis(2-aminoethyl) ether)-*N*,*N*,*N*′,*N*′-tetraacetate (EEDTA)[13] to those for (bis(3-aminopropyl) ether)-*N*,*N*,*N*′,*N*′-tetraacetate (BPETA).[11] In this case, adding a methylene group to each of two (out of six) five-membered rings in the case of lighter lanthanon (La–Eu) chelates attenuates affinity by almost a million-fold.

DHPTA differs from TMDTA only by having an OH instead of an H attached to the central C atom of the backbone. It would seem, however, that the O atom of the hydroxyl group could become a donor atom to cause the DHPTA to act heptadentately, as EEDTA apparently does, in bonding to the lighter lanthanons. Obviously, the DHPTA backbone is not sufficiently flexible for this to happen, since the affinities of the lighter lanthanons (La–Eu) for DHPTA are nearly 100 000-fold less than for EEDTA. Actually DHPTA resembles TMDTA, which has no potential donor atom on its backbone, very closely.

Unlike EEDTA,[14] DHPTA exhibits a stability sequence that offers no likelihood that it would prove useful in partitioning Am and other tervalent actinons from lanthanide–actinide mixtures, since there is no rise to a maximum and subsequent decline in stability.

The separation factors for adjacent lanthanons, calculated from Ln(DHPTA) stability constant ratios, are displayed in Table II. From these values, we conclude that DHPTA might prove useful for separations of most lanthanons from each other, but not the Eu–Gd pair (and probably not the Dy–Ho pair). With DHPTA the Nd–Sm separation factor appears to be 2-fold greater than in the cases of EDTA, DTPA, and HEDTA, which are often used for recovering promethium from nuclear wastes (Pm occurs between Nd and Sm in the Ln series). Faster exchange kinetics should result from the overall lower chelate stabilities in the case of DHPTA and produce smaller theoretical plate heights than are observed with EDTA and DTPA under comparable conditions. Thus DHPTA might prove to be a very effective reagent for isolating promethium from nuclear wastes.

Of further great interest is the behavior of Y(DHPTA). In contrast to other systems, its stability falls between those of Gd(DHPTA) and Tb(DHPTA). The resultant Dy–Y separation factor thus is about 4.8, significantly higher than that observed for EDTA (ca. 1.5). This behavior conceivably could be exploited in recovering yttrium by various two-step recovery schemes.

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