TABLE I

POSITIONS AND OSCILLATOR STRENGTHS OF PROMINENT VISIBLE AND NEAR-IR POLARIZED BANDS OF $((C_6H_5)_3P)_2Zn(Co)Cl_2$ at 77°K

$\bar{\nu}$, cm^{-1}	Polarization parallel to	10^4f	Assignment (see Figure 1)
6,400	*a*	3.9	$^4B_1$ or $^4B_2$
8,000	*b*	1.2	$^4B_2$
10,700	*c*	4.2	$^4B_1$ or $^4B_2$
13,550	*c*	4.8	$^4B_1$ or $^4B_2$
15,750	*b*	3.6	$^4A_2$
16,555 16,778 16,863 17,065 17,153 17,405 17,645 18,315	*a*	9.1	$^4B_1$ or $^4B_2$

In tetrahedral symmetry the $^4A_2$ level is the ground state and undoubtedly remains so in $((C_6H_5)_3P)_2CoCl_2$. Transitions are therefore expected from the $^4A_2$ level to the low-symmetry components of the $^4T_2(F)$, $^4T_1(F)$, and $^4T_1(P)$ excited levels. Absorptions involving $^4A_2 \rightarrow {}^4T_2$ are generally not observed however as they occur in the infrared region at ~3000–4000 cm^{-1} and are masked by molecular vibrations. Transitions to the $^4T_1(F)$ and $^4T_1(P)$ levels are commonly observed and in C_{2v} symmetry should be governed by the selection rules shown in Table II.

TABLE II

POLARIZATION BEHAVIOR FOR C_{2v} SYMMETRY

Transition	Polarization
$^4A_2 \rightarrow {}^4B_2$	Allowed *x*
$^4A_2 \rightarrow {}^4B_1$	Allowed *y*
$^4A_2 \rightarrow {}^4A_2$	Allowed *z*

In Figure 1 we see displayed a series of absorption bands spanning ~14,000 cm^{-1}. The lowest three absorptions at 6400, 8000, and 10,700 cm^{-1} are assigned to transitions arising from excitations from the ground $^4A_2$ state to low-symmetry components of the $^4T_1(F)$ level. The upper, more intense grouping of three absorptions is assigned to the $^4T_1(P)$ parent.

Using the selection rules in Table II we may uniquely assign the $\|b$ ($\|z$) bands in Figure 1 as $^4A_2 \rightarrow {}^4A_2$ transitions, while the $\|a$ and $\|c$ absorptions are $^4A_2 \rightarrow {}^4B_1$, $^4B_2$, depending on the choice of *x* and *y* axes.

The only absorption exhibiting any significant degree of fine structure is the band at ~16,700 cm^{-1}. It appears that a vibrational mode of ~250 cm^{-1} is active here. What appears to be an intermingling of spin-orbit components, spin-forbidden transitions, and vibrational fine structure precludes any very accurate determination of the frequency of the vibrational mode in question.

A point of importance is the broad region over which the absorption spectrum of $((C_6H_5)_3P)_2CoCl_2$ is spread. Typically for "tetrahedral" cobalt(II) complexes, one finds the $^4A_2 \rightarrow {}^4T_1(F)$ transition occurring in the 4000–7000-cm^{-1} region with a band breadth of ~3000 cm^{-1}. The $^4A_1 \rightarrow {}^4T_1(P)$ then occurs in the 15,000–20,000-cm^{-1} region with a similar band width.[16] For $((C_6H_5)_3P)_2CoCl_2$, we see that the absorption maxima are distributed over some 13,000 cm^{-1} without the typical gap between the $^4T_1(F)$ and $^4T_1(P)$ levels. This is indicative of a rather large modification of the electronic structure of the Co(II) ion upon the introduction of two sets of dissimilar ligands. This is in contrast to the results found for high-spin five-coordinate cobalt(II) complexes[17] and high-spin six-coordinate complexes.[18]

Turning our attention to Figure 2, we immediately observe two things. (1) The solution and mull spectra are not isomorphic. This indicates that it is likely that the species $((C_6H_5)_3P)_2CoCl_2$ is not present in solution. (2) On the basis of the mull spectrum, were the structure not known in detail, it would be possible to propose a distorted octahedral structure for this compound.[5] This is not to say that polarized absorption spectra will allow one to assign a structure. Certainly optical measurements using polarized radiation are useless without a detailed structural analysis. The strength of the polarized measurement does lie in the fact that we may obtain a reasonable ordering of the energy levels based upon our experiment. This, of course, is impossible with mull or solution spectra.

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Thermodynamics of the Mercaptopropionate Complexes of the Lanthanides

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A large number of complexing systems of lanthanide ions with several ligands have been studied previously. The earlier studies emphasized large complex systems such as the aminopolycarboxylate complexes.[1–3] In the past few years, a number of simple ligands have been investigated.[4–7] This study presents the results obtained for the α- and β-mercaptopropionate complexes of the lanthanide ions.

Experimental Section

Reagents and Apparatus.—Stock solutions of the lanthanide perchlorates were prepared by dissolving a given amount of the

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oxide (Lindsay Chemical Co., 99.99%) in concentrated perchloric acid. The excess acid was evaporated under a heat lamp. The stock solutions were then adjusted to pH 3. The concentrations of the stock solutions were determined by passing a given amount of the stock solutions through a hydrogen-form cation-exchange resin (Dowex 50) and titrating the liberated acid with carbonate-free sodium hydroxide. Working solutions of 2.00 M ionic strength were prepared using $NaClO_4$.[8]

α- and β-mercaptopropionate buffer solutions were prepared from reagent grade solutions (K & K Laboratories, Inc.). These were made and standardized following the method used earlier.[8]

The calorimeter used was designed in our laboratories and is similar to that used by Schlyter.[9] The modifications are presented elsewhere.[6,7] This calorimeter makes possible the simultaneous determination of the stability constants and the heats of formation of a given complex. The pH-measuring system consisted of a Beckman Research pH meter, Model 1019, and a combination electrode (A. J. Thomas and Co.). The remainder of the apparatus was used for the determination of the heats of complexation as described earlier.[7]

Results and Discussion

All studies were carried out in a medium of 2.00 M ionic strength, dilute with respect to the reacting species. The thermodynamic values are, therefore, related to a standard state where the solvent medium is 2.00 M ($NaClO_4$).

The pH and enthalpy data[10] were treated as described earlier[7] using the CDC 6400 computer of The Florida State University Computer Center. Table I lists the stability constants, enthalpies, and entropies for the reaction

$$Ln^{3+}(aq) + X^{-}(aq) = LnX^{2+}(aq)$$

Only the parameters for the monoligand complex are reported owing to the magnitude of the error limits for subsequent complexes. The estimated values for K_2, ΔH_2, and ΔS_2 are of the order of 10, 1.6 kcal mol^{-1}, and 10 eu, respectively, for the β-mercaptopropionate complexes and 2, 1.0 kcal mol^{-1}, and 9 eu, respectively, for the α-mercaptopropionate complexes. The error limits in Table I represent the standard deviation from the mean of three to five titrations of each metal–ligand combination.

The values reported here for the stability constants are not in good agreement with those reported earlier from this laboratory,[11] particularly for the β-mercaptopropionate system. Attempts to understand the origin of this disagreement have been fruitless. However, since the later data were thoroughly rechecked many times in light of the discrepancy, we conclude they are the correct values. The values of ΔH_1 and ΔS_1 of both mercaptopropionate systems are quite similar to those of the monodentate propionate complexes measured under the same experimental conditions.[6] Moreover, they differ significantly from those of the lactate chelates.[7] This is taken as evidence that these ligands function as monodentates with the lanthanide cations. The strong preference of the lanthanide ions for oxygen rather than nitrogen or sulfur is again obvious in these results. It has been suggested previously[8] that the β-mercaptopropionate complexes might be weak chelates but this is no longer tenable.

TABLE I

THERMODYNAMIC PARAMETERS

Ion	K_1	ΔH_1, kcal mol^{-1}	ΔS_1, cal deg^{-1} mol^{-1}
	α-Mercaptopropionate Complexes		
La	17 ± 5	2.64 ± 0.37	13.6 ± 1.9
Ce	23 ± 3	2.31 ± 0.22	14.1 ± 0.8
Pr	78 ± 5	1.42 ± 0.24	13.4 ± 0.9
Nd	85 ± 5	1.34 ± 0.09	13.1 ± 0.1
Sm	116 ± 5	0.98 ± 0.23	12.3 ± 1.4
Eu	100 ± 8	1.21 ± 0.13	13.2 ± 0.1
Gd	56 ± 4	1.77 ± 0.15	13.3 ± 0.1
Tb	45 ± 4	1.57 ± 0.20	11.6 ± 0.8
Dy	38 ± 2	1.73 ± 0.23	12.7 ± 0.9
Ho	34 ± 8	1.87 ± 0.07	13.3 ± 0.2
Er	34 ± 8	2.45 ± 0.33	15.1 ± 1.4
Tm	30 ± 9	2.56 ± 0.67	14.8 ± 3.5
Tb	27 ± 6	3.19 ± 0.22	17.2 ± 1.1
Lu	32 ± 1	1.66 ± 0.14	12.4 ± 0.3
Y	50 ± 6	1.34 ± 0.09	12.0 ± 0.9
	β-Mercaptopropionate Complexes		
La	35 ± 6	2.64 ± 0.31	15.8 ± 1.3
Ce	37 ± 4	2.39 ± 0.17	15.3 ± 0.5
Pr	37 ± 6	2.59 ± 0.19	15.6 ± 0.5
Nd	55 ± 2	2.45 ± 0.60	16.2 ± 1.7
Sm	55 ± 2	1.73 ± 0.33	13.7 ± 0.1
Eu	44 ± 3	2.20 ± 0.04	15.2 ± 0.3
Gd	51 ± 5	2.59 ± 0.17	16.5 ± 0.7
Tb	42 ± 3	2.93 ± 0.15	17.2 ± 0.4
Dy	40 ± 2	3.54 ± 0.35	19.2 ± 1.1
Ho	29 ± 2	3.23 ± 0.07	17.5 ± 0.5
Er	26 ± 1	4.77 ± 0.20	22.9 ± 1.0
Tm	25 ± 3	4.71 ± 0.73	22.1 ± 2.2
Yb	27 ± 4	3.98 ± 0.22	20.1 ± 0.7
Lu	31 ± 5	4.87 ± 0.61	22.8 ± 2.2
Y	32 ± 1	5.04 ± 0.71	23.7 ± 2.3

The variation of ΔH and ΔS with lanthanide atomic number for these latter complexes,[6,7] as well as for many others,[4] has been related to the difference in hydration sphere between the lighter (La and Nd) and heavier (Dy to Lu) lanthanides. The similarity in the variation of the enthalpy and entropy curves with atomic number for the mercaptopropionate complexes to those for the propionate and lactate complexes indicate a similar explanation.

Models of the monomercaptopropionate complexes were built using Leybold atom models (LaPine Scientific Co.). In the case of the α-mercaptopropionate, the movement of the hydrocarbon chain portion of the complex was hindered by the position of the mercapto group in the middle of this chain. For the β-mercaptopropionates less steric hindrance was found since the mercapto group is at the end of the hydrocarbon chain. The result of this group in the β position could, then, be a larger disruption of the water structure around the β-mercaptopropionate complex. Such

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a disruption of the water around the complex would account for the higher entropies and more endothermic enthalpies of the β-mercaptopropionate complexes compared to their α analogs.

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Ion Pairing and Interionic Distances in Solution. Proton Magnetic Resonance Shifts of the Butyltriphenylphosphonium Ion in the Presence of Paramagnetic Anions[1]

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The observation[2-5] of large proton chemical shifts for diamagnetic cations in the presence of certain paramagnetic anions is perhaps the most sensitive technique for detecting ion pairing or aggregation in solution. These shifts (resonance frequency displacements from their diamagnetic positions) result from a dipolar interaction between the unpaired electron spin and the nuclear spin and generally occur when one of the ions in the ion pair exhibits significant magnetic anisotropy and there is a preferred orientation of the partners.[3] Dipolar shifts $\Delta\nu_D$ for axially symmetric octahedral cobalt(II) systems are given by[6-8]

$$\Delta\nu_D = -[\beta^2\nu S'(S'+1)/3kT][f(g)]\langle(3\cos^2\chi - 1)/R^3\rangle_{av} \tag{1}$$

where S' is the effective spin quantum number and $f(g)$ is a function of the g values and g-tensor anisotropy. Its value depends on the relative magnitudes[8] of the Zeeman anisotropy energy, the correlation time for tumbling in solution, and the electron spin-lattice relaxation time. The final factor in eq 1 is known as the geometric factor. χ is the angle made by a vector from the paramagnetic ion to the nucleus in question with the principal ligand field axis; R is the length of this vector. Very likely equations of similar form hold[8] for the present tetrahedral d^7 and d^8 systems. Thus far, dipolar shifts related to ion pairing have been observed for only symmetric cations: tetraalkylammonium ions[2-4] and the tetraphenylarsonium ion.[5] No studies wherein the *anion* size has been varied for related species have been reported. The present investigation deals with complexes of the type $[C_4H_9(C_6H_5)_3P][M(C_6H_5)_3PX_3]$ (M = Co, Ni; X = Br, I), involving an unsymmetrical cation and related anions of differing size.

Preparation of Complexes.—The complexes were prepared by the following general procedure. Equimolar quantities of butyltriphenylphosphonium halide and triphenylphosphine were dissolved in hot butanol and added to a hot, filtered solution of anhydrous metal halide in the same solvent. The resulting crystals were washed with butanol and ether and recrystallized. Analytical and other pertinent data are listed in Table I.

TABLE I
ANALYTICAL[a] AND SYNTHETIC DATA

	Analyses, %						
	Calcd		Found				
Compound	C	H	C	H	Recrystallized from	Mp, °C	Color
$[(C_4H_9)(C_6H_5)_3P][Co(C_6H_5)_3PBr_3]$	54.57	4.47	54.27	4.65	Nitromethane–ether	188–188.5	Blue
$[(C_4H_9)(C_6H_5)_3P][Ni(C_6H_5)_3PBr_3]$	54.59	4.47	54.03	4.44	Butanol	182.5–183.5	Green
$[(C_4H_9)(C_6H_5)_3P][Co(C_6H_5)_3PI_3]$	47.04	3.85	47.17	3.97	Chloroform–ethyl acetate	168–169	Dark green
$[(C_4H_9)(C_6H_5)_3P][Ni(C_6H_5)_3PI_3]$[b]	47.05	3.85	46.88	4.03	Nitromethane–ether	160	Green

[a] Galbraith Laboratories, Knoxville, Tenn. [b] The reaction solvent has 3:1 butanol–ethyl acetate.

Pmr Results and Discussion.—The cation pmr spectra for the $Co(C_6H_5)_3PBr_3^-$ and $Ni(C_6H_5)_3PBr_3^-$ salts along with that of diamagnetic $[C_4H_9(C_6H_5)_3P][Br]$ are shown in Figure 1. The cation phenyl proton dipolar shifts, together with their widths at half-height, are given in Table II. The cation phenyl proton resonances are shifted upfield for the cobalt and downfield for the nickel complexes owing to the opposite senses of the magnetic anisotropies in the two cases. The cation phenyl resonances of $[C_4H_9(C_6H_5)_3P][Ni(C_6H_5)_3PI_3]$ were not resolved and will not be considered further. The butyl proton resonances (Figure 1) are shifted in the same sense as the phenyl resonances, but the individual methyl and methylene peaks are not as well resolved as they were for the $(C_4H_9)_4N^+$ salts.[2] The resonances observed for the anion triphenylphosphine protons correspond very well with those reported for the $M(C_6H_5)_3PI_3^-$ ions in salts of other cations.[2,5]

Estimates of interionic distances can, in principle at least, be made from observed dipolar shifts or shift ratios (eq 1). Such estimates have been made[5,9] for interionic distances between $Co(C_6H_5)_3PI_3^-$ and the

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