circulating water. All solvents were dried using molecular sieves and were carefully deoxygenated prior to use. Particular care was taken in drying and deoxygenating pyrrolidine, using the method for drying of amines described in ref 2. Maleic anhydride was sublimed *in vacuo* immediately prior to use.

The olefin–iron tetracarbonyls were recrystallized from acetone and then either resuspended in benzene or treated directly with pyrrolidine. The results were the same.

All reactions were carried out with rigorous exclusion of oxygen and moisture. Reaction mixtures were kept in tubes sealed with rubber serum stopples, from which samples could be withdrawn periodically for examination.

Infrared spectra were obtained using the Perkin-Elmer Model 521 dual grating spectrometer, run at *ca.* 1-cm^{-1} spectral slit width in the 2000-cm^{-1} region. Barnes Engineering Co. 0.025 mm KBr demountable liquid cells were used for all spectra.

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The Polarized Spectrum of Dichlorobis(triphenylphosphine)cobalt(II)

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Prominent features of the electronic spectrum of Co^{2+} in tetrahedral coordination have been interpreted, with reasonable success, using crystal field theory.[2-4] Investigations involving the spectroscopic properties of the "tetrahedrally" coordinated Co^{2+} ion have been mainly of two types, however: those which are designed to provide a rigorous test for crystal field theory[2,3] and those which are intended only for identification of a species as "tetrahedral" cobalt.[5,6]

The first type of experiment requires that the species to be investigated be as close to a regular tetrahedron as possible in order to minimize the difficulty involved in sorting out effects due to lowered site symmetry, spin–orbit coupling, and vibrational fine structure.

The second type of experiment requires little more than a knowledge of the molecular formula of the compound to be studied and provides, on most occasions, information as to whether the complex in question possesses a pseudo-tetrahedral structure.

There is, however, lack of detailed experimental information about the electronic structure of tetrahedral Co^{2+} complexes which are fairly strongly distorted from regular. The need for information pertaining to magnitude of splitting of energy levels to be expected upon deforming a regular tetrahedral configuration or by reducing symmetry through introduction of nonequivalent ligands has recently been pointed out in the case of $\mathrm{Co(etu)_2(OAc)_2}$.[5]

An early attempt to investigate low-symmetry "tetrahedral" systems was made by Ferguson.[7] Ferguson observed incomplete polarization in the room-temperature crystal spectra of $\mathrm{CoPy_2Br_2}$ and $\mathrm{CoPyI_2}$ and concluded that the spectra were interpretable only in terms of the next nearest neighbor interaction. In order to help remedy the lack of information in this area, we have undertaken the investigation of the low-temperature polarized spectrum of $\mathrm{((C_6H_5)_3P)_2CoCl_2}$.

Crystal Structure

Based on zero- and first-layer Weissenberg photographs, $\mathrm{((C_6H_5)_3P)_2CoCl_2}$ and $\mathrm{((C_6H_5)_3P)_2ZnCl_2}$ are isomorphous and isostructural with $\mathrm{((C_6H_5)_3P)_2NiCl_2}$. $\mathrm{((C_6H_5)_3P)_2NiCl_2}$ crystallizes in the space group P2/c with two molecules per unit cell.[8] The site symmetry of the complex is C_2; however, if one ignores the phenyl groups, the effective symmetry is C_{2v}. The C_2 molecular axis is parallel to the *b* crystallographic axis. Both the nickel and the cobalt compounds form a complete range of solid solutions with the isomorphous zinc compound.

Experimental Section

$\mathrm{((C_6H_5)_3P)_2MCl_2}$ (M = Zn or Co) were prepared as described by Venanzi.[9] Mixed crystals of $\mathrm{((C_6H_5)_3P)_2(Co,Zn)Cl_2}$ were grown by slow evaporation of their nitromethane solution.

Thin crystals of optical quality, for spectra parallel to *a* and *c*, were easily obtained by sectioning along the cleavage plane parallel to the (010) face. Typical crystal dimensions were 3 × 4 × 1 mm. Cobalt concentration was estimated by absorbance of its thiocyanate complex at 625 mμ.[10] The extinction coefficient of the $\mathrm{((C_6H_5)_3P)_2CoCl_2}$ in single crystals was estimated according to $c = al^{-1}d^{-1}c^{-1} \times 10^{-3}$, where *a* is absorbance, *l* is crystal thickness (cm), *d* is crystal density ($\mathrm{g/cm^3}$), and *c* is cobalt concentration (mol/g). Polarized absorption spectra were measured at 298 and 77°K using a Cary Model 14 spectrophotometer. Polarized incident radiation was obtained using a matched pair of Glan–Thomson prisms.

Crystals were mounted on cylindrical brass plugs, which were in turn fixed in a holder and placed in contact with liquid nitrogen. Extinction axes were determined using a polarizing microscope. Correspondence between the extinction and crystallographic axes was obtained by Weissenberg and precession techniques.

Results and Discussion

The 80°K polarized spectrum of $\mathrm{((C_6H_5)_3P)_2CoCl_2}$ is shown in Figure 1. Figure 2 contains the spectra of the pure compound taken both in nitromethane solution and in a Nujol mull.

Approximate oscillator strengths of the prominent bands are collected in Table I. These were estimated using the relationship $f = 4.6 \times 10^{-9}\epsilon\Delta\nu$, where ϵ is $\epsilon_{\max}$ and $\Delta\nu$ is the band width at $\epsilon = {}^1/_2\epsilon_{\max}$.[11] As expected for symmetry-allowed transitions, the

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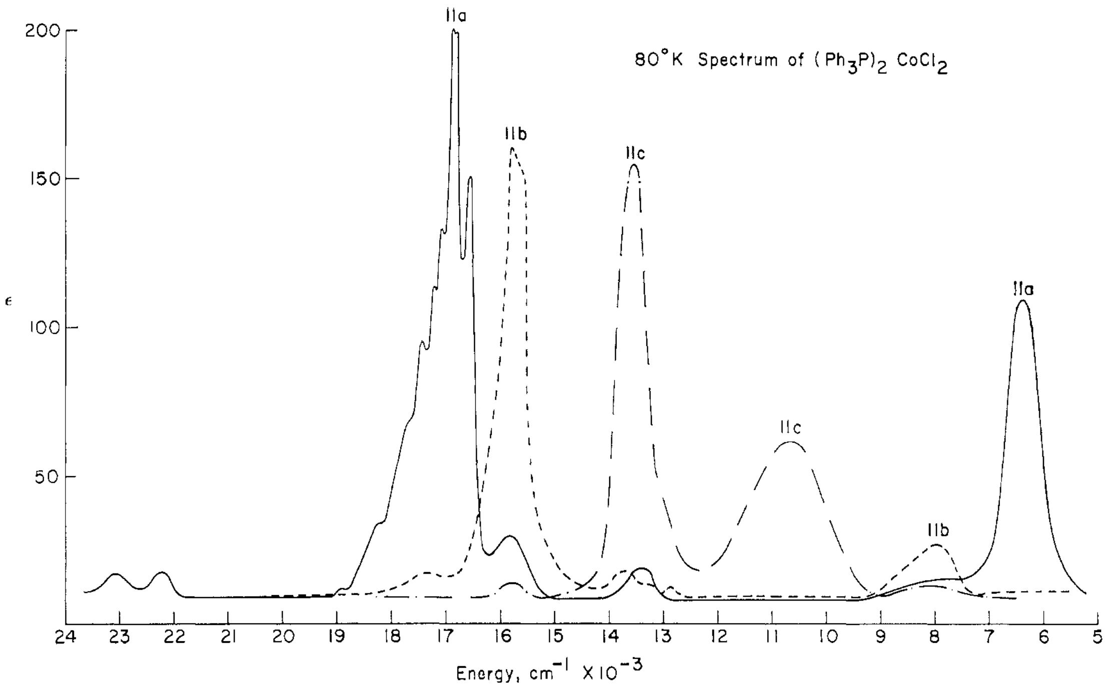

Figure 1.—The 80°K spectrum of $((C_6H_5)_3P)_2CoCl_2$.

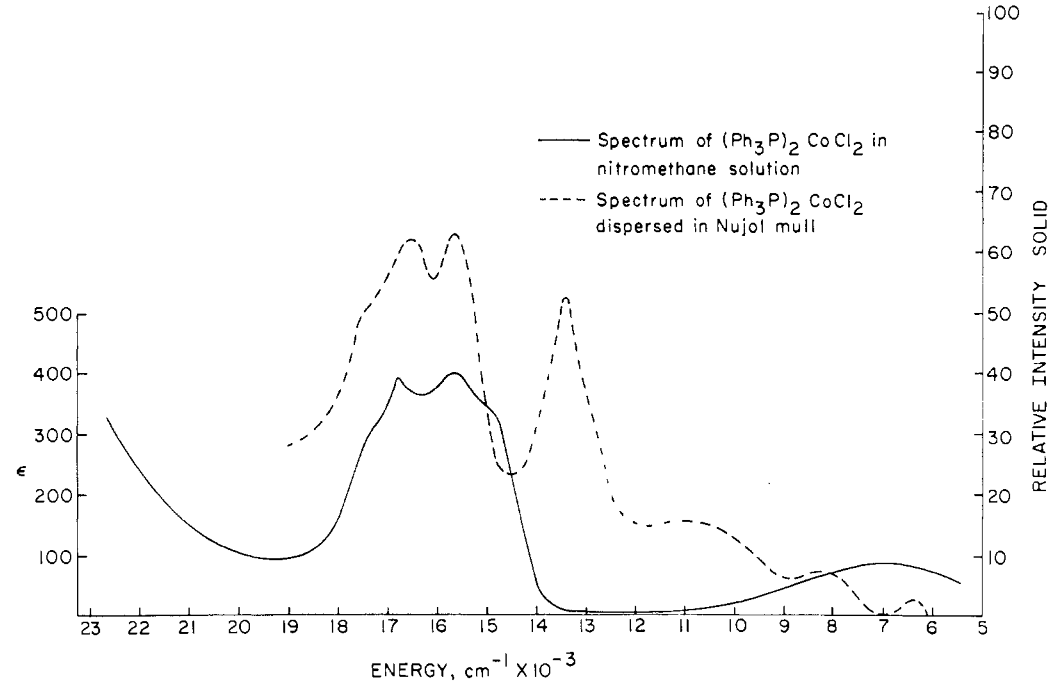

Figure 2.—The solution and mull spectra of $((C_6H_5)_3P)_2CoCl_2$.

oscillator strengths of these bands exhibit little temperature dependence over the range studied.[12–14]

In Figure 1, polarization directions are indicated by the relationship of $\vec{E}$ to the crystallographic axes *a*, *b*, and *c*. No correction was made for the fact that the *a* and *c* crystallographic axes are not orthogonal. This generally leads to incomplete polarization as the *x* and *y* molecular axes are not exactly parallel to *a* and *c*. It can be seen from Figure 1 however that mixing of polarizations is negligible.

In a tetrahedral field the ^4F ground state of Co(II) splits into $^4A_2$, $^4T_2$, and $^4T_1$ levels, while the first excited free-ion level ^4P remains degenerate, transforming as $^4T_1$. Reduction in molecular symmetry to C_{2v} further splits the $^4T_2$ term into levels of A_1, B_1, and B_2 symmetry while the $^4T_1$ state is transformed into A_2, B_1, and B_2 levels.[15]

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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 $\sim$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 $\sim$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 $\sim$16,700 cm^{-1}. It appears that a vibrational mode of $\sim$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 $\sim$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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