good approximation in view of the fact that the emissions lie in the same spectral region.

Nonradiative decay rates vary considerably as X is changed, and the series in which the sixth ligand is an aliphatic amine is especially interesting. Decay rates tend to decrease as the number of hydrogen atoms attached to the nitrogen atom is decreased, *i.e.*, 1° > 2° > 3°. This is consistent with the general theory of Robinson and Frosch,[11] if we assume that N-H vibrations play an important role in the internal conversion process. The result is also reminiscent of the effect of successive substitution of methyl groups for hydrogen atoms on the nonradiative decay rates of the excited singlets[12] and triplets[13] of acetone and its derivatives. However, comparison of the results obtained with oxygen bases shows that other factors must be of importance since the longest lifetime observed with any oxy base was obtained with ethanol and there is no significant separation between the compounds which bear a hydrogen atom attached to the basic oxygen and those which do not.

In solution at room temperature the compounds all undergo photodissociation of the X ligands with high quantum yields and emission is totally quenched. The relationship between decay by chemical reaction and the fast nonradiative decay rates at low temperature is uncertain, but the processes may involve similar, or even identical, micromechanisms for internal conversion of electronic to vibrational energy.

Acknowledgment.—This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Contract No. AF OSR-71-1958), and the Army Research Office—Durham.

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A Novel Form of Cobalt(II) Dioctylphosphinate

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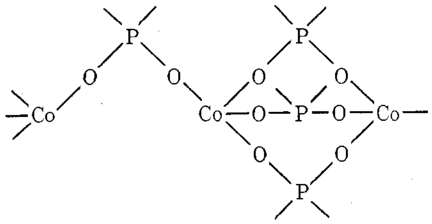
Different forms of cobalt(II) phosphinates have been studied in our laboratories[1] and elsewhere,[2] but all of the previously known compositions were reported to contain tetrahedral cobalt(II) and symmetrical bridging *O,O'*-phosphinate groups. Polymeric structures are formed, such as



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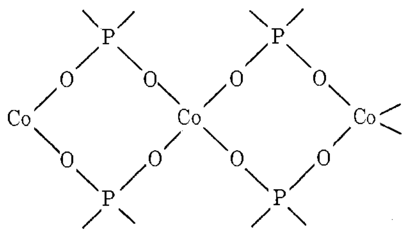

The recent synthesis in our laboratories of a new form of cobalt(II) phosphinate which probably contains six-coordinate metal centers is therefore of considerable interest. This report presents the preparation and characterization of the new form of cobalt dioctylphosphinate and compares it to the tetrahedral form of this compound.

Experimental Section

Dioctylphosphinic acid, which was supplied by Hynes Chemical Research (Durham, N. C.), was purified by recrystallization from ethanol. Other chemicals and solvents were reagent grade and were used without further purification.

$Co[OP(C_8H_{17})_2O]_2$-I.—This material was prepared using the same general procedure as described for the previously reported tetrahedral phosphinates.[1] In one experiment 2.5 g of $Co(CH_3COO)_2 \cdot 4H_2O$ (0.010 mol) in 100 ml of 95% ethanol was added with stirring to a solution containing 6.3 g of $(C_8H_{17})_2P(O)OH$ (0.022 mol) in 200 ml of 95% ethanol. A blue precipitate rapidly formed. The suspension was brought to boiling, an additional 100 ml of 95% ethanol was added, and the solvent was evaporated until the volume reached 100 ml. The suspension was then filtered, and the precipitate was dried under vacuum at 70° for 2 hr, yield 6.3 g. *Anal.* Calcd for $C_{32}H_{68}CoO_4P_2$: C, 60.27; H, 10.75; Co, 9.24; P, 9.72. Found: C, 59.71; H, 10.42; Co, 9.17; P, 10.23.

$Co[OP(C_8H_{17})_2O]_2$-II.—Anhydrous $CoCl_2$ (1.3 g, 0.010 mol) was combined with $(C_8H_{17})_2P(O)OH$ (6.09 g, 0.0217 mol) in 200 ml of absolute ethanol. The ethanol was distilled off, and the residue heated to 60° under vacuum for a short time. The residue was then washed with 95% ethanol and dried under vacuum for several hours. *Anal.* Calcd for $C_{32}H_{68}CoO_4P_2$: C, 60.27; H, 10.75; Co, 9.24; P, 9.72. Found: C, 60.36; H, 10.60; Co, 9.35; P, 9.82.

Visible spectra were recorded on a Perkin-Elmer Model 450 spectrophotometer. Solid samples were prepared as mulls with Nujol. Magnetic measurements were made on a standard Gouy balance. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. The samples were run as mulls with Nujol between KBr plates and as solutions in CCl_4. The X-ray powder patterns were obtained with a General Electric XRD-5 X-ray diffraction unit with vertical tube mount and standard General Electric 14.32 cm diameter cameras. The dsc curves were obtained on a Du Pont differential scanning calorimeter.

Results and Discussion

Previously $Co[OP(C_8H_{17})_2O]_2$ polymers (form I) were generally prepared from cobalt(II) acetate and dioctylphosphinic acid,[3] whereas the new form (form II) can be isolated from the reaction of cobalt(II) chloride and dioctylphosphinic acid. Since the substitution of potassium dioctylphosphinate for dioctylphosphinic acid has no effect on the outcome of either reaction, it appears that the cobalt salt starting material is the main factor in determining the form of the product.

The visible and near-infrared spectra of both forms are given in Figure 1. The fine structure and peak positions in the spectra of form I are quite consistent with the spectra of known tetrahedral cobalt(II) complexes

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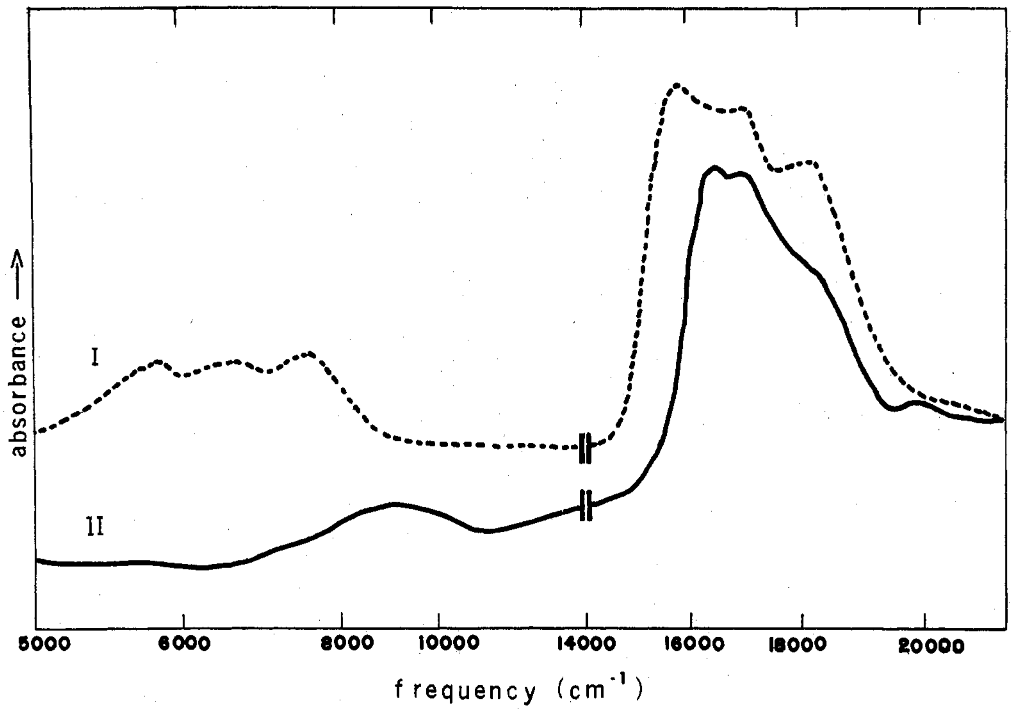

Figure 1.—Visible and near-infrared spectra of Co[OP(C_8H_{17})$_2$O]$_2$-I (dashed line) and Co[OP(C_8H_{17})$_2$O]$_2$-II (solid line), in Nujol mull. The symbol ⫲ indicates a change in the frequency scale.

with the band in the visible region due to the $^4A_2(F) \rightarrow {}^4T_1(P)$ transition, whereas the one in the near-infrared is due to the $^4A_2(F) \rightarrow {}^4T_1(F)$ transition. The absence of the peak associated with the $^4A_2(F) \rightarrow {}^4T_1(F)$ transition in the spectra of form II as well as the changes observed in the visible band from that of form I indicate that form II is not tetrahedral or even distorted tetrahedral.[4] Indeed, the spectrum of form II is consistent with that of six-coordinate cobalt(II) with the band at 9100 cm^{-1} due to the $^4T_1(F) \rightarrow {}^4T_2(F)$ transition and the higher energy bands due to the $^4T_1(F) \rightarrow {}^4A_2(F)$ and $^4T_1(F) \rightarrow {}^4T_1(P)$ transitions.[5,6] This is in agreement with the qualitative observation that form I has a much more intense color than form II. This evidence does not completely eliminate other structural possibilities for form II. However, the most probable structure for form II is six-coordinate since the vast majority of cobalt(II) compounds are either octahedral or tetrahedral and the spectrum of form II is clearly different from that of form I which is kown to be tetrahedral.

Since the magnetic properties of cobalt(II) complexes can sometimes be used to differentiate between four- and six-coordinate structures, the magnetic moments of both forms of Co(OP(C_8H_{17})$_2$O)$_2$ were determined. The moment of form I was found to be 4.8 BM, whereas that of form II was 4.9 BM. Unfortunately the small difference in these values is within the experimental error. Moreover, both values are in the range of those values previously reported for both four- and six-coordinate cobalt(II) complexes. Thus, these magnetic moments do not provide sufficient basis for a structural assignment.

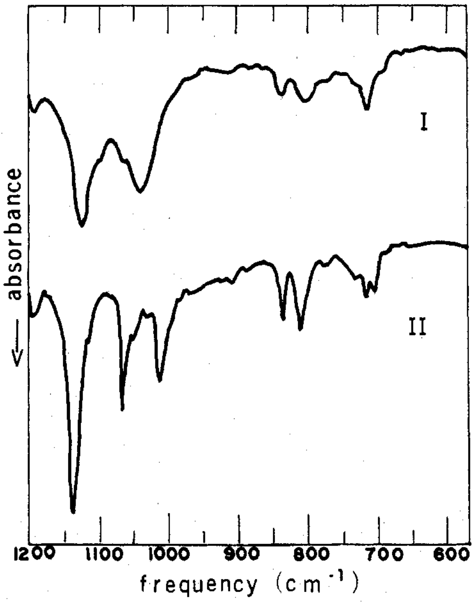

Figure 2.—Infrared spectra in Nujol mull: I, Co[OP(C_8H_{17})$_2$O]$_2$-I; II, Co[OP(C_8H_{17})$_2$O]$_2$-II.

In Co[OP(C_8H_{17})$_2$O]$_2$ the oxygens are the only apparent donor groups and there are only four oxygen atoms per cobalt atom; therefore a six-coordinate structure would require some of the oxygens to coordinate to more than one cobalt center. The infrared spectra—particularly in the PO_2 stretching region—of the six-coordinate complex would thus be expected to be considerably different from the spectra of the tetrahedral poly(metal phosphinates). The infrared absorption spectra for form I and form II in the solid state are given in Figure 2. The spectrum of form I is similar to the spectra obtained for other poly(metal phosphinates) which contain tetrahedral

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metal centers. The dissimilarity of the spectra of the two forms is consistent with form II being six-coordinate. The most striking difference between the spectra of the two forms is in the PO_2 stretching region where form I has two strong bands and form II has three. The two bands observed for form I are quite readily assigned to the antisymmetric and symmetric PO_2 stretches.[7] The intensity and position of the three bands in form II's spectra are characteristic of PO_2 stretching vibrations, but for C_{2v} or C_s symmetry of the phosphinate anion only two strong PO_2 stretching bands are expected. It may well be that form II contains more than one structural type of phosphinate.

The thermograms for both forms were recorded by dsc, and the results are given in Table I. The temperatures of the transitions were found to vary with the thermal history of the sample as well as its size and heating rate, so that the values given are only approximate. The transition temperatures and energies of form I are in the range of those previously observed for $Zn[OP(C_8H_{17})_2O]_2$[8] which is isomorphous with form I. The assignment for the endothermic transformation at 54° for form I is based on that made for the isomorphous $Zn[OP(C_8H_{17})_2O]_2$ polymers, whereas the assignment of the transition at 111° was made after a careful study with a light polarizing microscope. The higher temperature transition for $Zn[OP(C_8H_{17})_2O]_2$ was previously assigned as a melting. However, even well above 170° birefringence was observed for both $Co[OP(C_8H_{17})_2O]_2$ and $Zn[OP(C_8H_{17})_2O]_2$. Thus the high temperature transition is most probably a transition from a crystalline form to a paracrystalline form, similar to that described for other zinc and cobalt phosphinates.[2] The thermogram of form II shows one transition which corresponds to its conversion to form I and which was found to be irreversible.

TABLE I

DSC ENDOTHERMS FOR $Co[OP(C_8H_{17})_2O]_2$

Form	Approx transition temp, °C	ΔH, cal/g	Assignment
I	54	5.1	Solid state transition from one crystalline form to another
	111	5.8	Transition from crystalline form to paracrystalline form
II	68	24.9	Transition from form II to form I

Although both forms are soluble in nonpolar solvents, infrared spectra indicate that form II converts irreversibly to form I upon dissolution and consequently no molecular weight data could be obtained for form II. Form II is crystalline with a considerably different X-ray powder pattern than form I which can be either crystalline or amorphous. The *d* spacings for both forms are given in Table II.

This appears to be the first example of a poly(metal phosphinate) which exists both in four- and six-coordinate forms. However the two isomers have some similarities to the well known α and β forms of $Co(py)_2Cl_2$.[9] In both systems the six-coordinate form converts to the four-coordinate form on heating or dissolution; on the other hand, the conversion in the $Co(py)_2Cl_2$ system is reversible, whereas in the $Co(OP(C_8H_{17})_2O)_2$ system it is not.

TABLE II

X-RAY POWDER PATTERNS OF $Co[OP(C_8H_{17})_2]O_2$[a]

Form I		Form II	
d, Å	I[b]	*d*, Å	I[b]
16.07	100	14.04	100
10.07	40	10.32	30
9.10	30	8.81	80
8.42	100	4.71	60
7.09	30	4.35	90
6.24	10	4.06	20
4.94	60	3.63	50
4.58	5		
4.27	50		

[a] Cu Kα radiation was used. [b] Relative intensities estimated visually.

Acknowledgment.—The author wishes to acknowledge B. B. Wayland for the use of his Gouy balance. This investigation was supported in part by the Office of Naval Research.

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Ab Initio Self-Consistent Field Calculation of the Energies of Formation of B_2H_6 and $B_2H_7^-$

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Accurate binding energies cannot usually be obtained from Hartree–Fock (HF) calculations because the changes in correlation energy are often of the same orders of magnitude as the corresponding changes in the HF energy.[1] The HF binding energies are still of interest, however, when some estimate of the sign and magnitude of the correlation energy changes can be made. We report in this note *ab initio* self-consistent field (SCF) calculations[2] of the energies of formation, ΔE_f, for B_2H_6 and $B_2H_7^-$.

An extensive calculation of the ΔE_f for the reaction

$$2BH_3(g) \longrightarrow B_2H_6(g) \qquad (1)$$

has been reported by Gelus, Ahlrichs, Staemmler, and Kutzelnigg (GASK).[3] This calculation employed a large Gaussian basis set and the correlation energy corrections were estimated using the independent electron pair approximation.[3,4] The total ΔE_f was estimated to be −36.0 ± 5 kcal/mol. These authors attributed −11.5 kcal to the HF energy changes, and −24.5 kcal to changes in the correlation energy; these values included estimates of −3.0 kcal/mol and −7.7

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