uni-bivalent electrolytes are expected to have $(A + \omega B \Lambda_0)$ values in the region 460–520, while the experimental values are usually 500–600. In contrast, uni-univalent electrolytes have $(A + \omega B \Lambda_0)$ values around 240 and the values for uni-trivalent electrolytes are expected to lie above 720.[2]

The conductance data obtained in methanol (Table III) show that the new complexes XXIII and XXIV behave as uni-bivalent electrolytes, although $(A + \omega B \Lambda_0)$ for XXIV is larger than calculated or expected by analogy with similar uni-bivalent electrolytes.[2]

Relatively large deviations in this direction from the calculated values are not uncommon, however, particularly in non-aqueous solvents, and usually are ascribed to ion-pair formation. In addition, the calculated $(A + \omega B \Lambda_0)$ for XXIV behaving as a uni-trivalent electrolyte is about 720, and this can be considered a *minimum* figure, since experimental values probably will lie considerably above this (For example, see $[Co(dipy)_3][ClO_4]_3$ in Table IV.) A more highly charged structure for XXIV is also not consistent with the observed ionic weight values in acetone, which agree well with that expected for a completely ionized uni-bivalent electrolyte.

We have now extended these conductivity measurements to nitromethane solutions, and find that the methanol-insoluble tetraphenylborates give a linear relationship between Λ_c and $\sqrt{c}$ over a wider concentration range than do similar chloride, perchlorate, and picrate salts in methanol. The results are summarized in Table IV, along with data obtained for some known 1:1, 2:1, and 3:1 electrolytes. These clearly show that the complexes XXV–XXVII behave as uni-bivalent electrolytes in nitromethane. Thus, in order for palladium(II) to retain four coördination in the binuclear cation, the diethylphosphido- and diphenylphos-

phido- groups must occupy bridging positions as shown in II.

Reaction of $[PdX_2\{HP(C_2H_5)_2\}_2]$ with Strong Base.— The reactions of $[PdX_2\{HP(C_2H_5)_2\}_2]$ with NaOH in aqueous alcoholic solution have been followed potentiometrically and evidence has been found for at least two consecutive reactions, the first of which is probably

$$[PdX_2\{HP(C_2H_5)_2\}_2] + NaOH =$$
$$\tfrac{1}{2}[PdX\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2 + NaX + H_2O \quad (12)$$
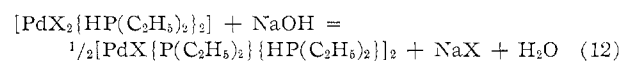
When X = Cl or Br (but not I), a second reaction, possibly (13), closely follows (12), although under the titration conditions it does not occur quantitatively.

$$\tfrac{1}{2}[PdX\{P(C_2H_5)_2\}\{HP(C_2H_5)_2\}]_2 + NaOH =$$
$$[Pd\{P(C_2H_5)_2\}_2] + NaX + H_2O \quad (13)$$
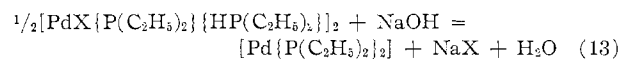
It is interesting to note that reaction 12 occurs at higher pH in the order Cl < Br < I and reaction 13 to a decreasing extent under the titration conditions in the order Cl > Br ≫ I. This behavior is similar to that qualitatively observed with $[PdX_2\{HP(C_6H_5)_2\}_2]$, which was found to become more stable with respect to loss of HX in the order Cl < Br < I. The factors which determine this order were discussed previously.[2] The diphenylphosphine complexes lose HX more readily than those of $(C_2H_5)_2PH$ and $C_2H_5C_6H_5PH$, $[PdCl_2\{HP(C_6H_5)_2\}_2]$, for example, being too unstable to be isolated, while the corresponding bromo complex, although stable in benzene, decomposes rapidly in ethanol, giving HBr and $[PdBr\{P(C_6H_5)_2\}\{HP(C_6H_5)_2\}]_2$.[2] The progressive substitution of the ethyl groups in diethylphosphine by the more electronegative phenyl probably causes an electron drift away from the ligand atom into the aromatic system. This will result in a decrease in the electron density in the P–H bond and hence in a more acidic proton.

The Donor Properties of Bis-(diisopropoxyphosphinyl)-methane and Bis-(di-N-butylphosphinyl)-methane

BY JUDITH A. WALMSLEY AND S. Y. TYREE

Some new coördination compounds containing the ligands $(C_3H_7O)_2P(O)CH_2P(O)(OC_3H_7)_2$ (designated L_1) and $(C_4H_9)_2P(O)CH_2P(O)(C_4H_9)_2$ (designated L_2) have been prepared and have been characterized by means of their infrared spectra, visible spectra, conductance measurements, and magnetic susceptibility measurements. The compounds which have been prepared are $[FeCl_2(L_1)_2][FeCl_4]$, $CoCl_2 \cdot L_1 \cdot H_2O$, $[Co(L_1)_3](ClO_4)_2$, $[Ni(L_1)_3](ClO_4)_2$, $8CuCl_2 \cdot 5L_1$, $[Cu(L_1)_2](ClO_4)_2$, $ZnCl_2 \cdot L_1$, $[Zn(L_1)_2](ClO_4)_2$, $[SbCl_4(L_1)][SbCl_6]$, $[Fe(L_2)_3][FeCl_4]_3$, $[Fe(L_2)_3](ClO_4)_3$, $[Co(L_2)_3][CoCl_4]$, and $[Ni(L_2)_3][NiCl_4]$.

Introduction

Since substituted phosphine oxides have been found to be good coördinating agents and since many complexes of them have been prepared and studied[1–4] it was decided to investigate the donor properties of ligands containing two phosphoryl groups. Compounds containing one methylene group between the two phosphoryl groups were chosen so as to permit the

(1) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 262 (1906).
(2) J. C. Sheldon and S. T. Tyree, *J. Am. Chem. Soc.*, **80**, 4775 (1958).
(3) F. A. Cotton, E. Bannister, R. Barnes, and R. H. Holm, *Proc. Chem. Soc.*, 158 (1959).
(4) E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 1873, 1878, 2276 (1960).

formation of six-membered rings with the metal ion, the ligand acting as a bidentate donor.

Compounds of the type $(RO)_2P(O)CH_2P(O)(OR)_2$ and $R_2P(O)CH_2P(O)R_2$ have been employed in the solvent extraction of metal ions,[5,6] but there have been no reports of the isolation and characterization of complexes of such ligands. Two compounds, $P_2O_3Cl_4 \cdot 2SbCl_5$ and $P_2O_3Cl_4 \cdot SnCl_4$, containing a similar ligand, pyrophosphoryl chloride, have been reported by Lindquist and co-workers.[7]

In this paper some complexes of bis-(diisopropoxyphosphinyl)-methane, $(C_3H_7O)_2P(O)CH_2P(O)(OC_3H_7)_2$, designated L_1, and bis-(di-n-butylphosphinyl)-methane, $(C_4H_9)_2P(O)CH_2P(O)(C_4H_9)_2$, designated L_2, are considered.

The bonding between the ligand and the metal ion is through the oxygen atoms of the phosphoryl groups. Both of the ligands exert a weak crystal field on the metal ion as shown by the magnetic properties of the complexes. In the perchlorate complexes, the first coördination sphere of the metal ion is composed of two or three ligand molecules, while in the chloride complexes of L_1 the first coördination sphere contains both the ligand and chloride ions. However, L_2 is a somewhat stronger donor than L_1, as might be expected, and it is capable of displacing all of the chloride ions from around a metal ion in its complexes with $FeCl_3$, $CoCl_2$, and $NiCl_2$.

Experimental

Reagents.—Reagent grade chemicals were used without further purification except in the cases noted.

Hydrated metal perchlorates were obtained from the G. Frederick Smith Chemical Co.

Metal chlorides used were anhydrous $FeCl_3$, anhydrous $CoCl_2$ (prepared by the dehydration of $CoCl_2 \cdot 6H_2O$), $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, anhydrous $ZnCl_2$, and anhydrous $SbCl_5$.

Metal salt solutions containing 0.1 mole/l. of metal salt or metal salt hydrate dissolved in alcohol were used for the preparation of the complexes. Isopropyl alcohol was used for all of the metal salts except $NiCl_2 \cdot 6H_2O$, which was dissolved in ethanol, and $SbCl_5$, which was dissolved in CCl_4.

Nitrobenzene used for conductance measurements was J. T. Baker "Purified" reagent and was further purified in the following manner. The nitrobenzene was partially frozen twice, each time saving the crystalline portion (about two-thirds of the total). After drying over anhydrous $CaCl_2$, it was decanted into a flask and fractionally vacuum distilled; the fraction boiling at 52–53° at 0.6 mm. was collected. The purified solvent was a light yellow liquid with a specific conductance of 1.87×10^{-8} ohm^{-1} cm.$^{-1}$ at 25°.

Triisopropyl phosphite was obtained from the Virginia-Carolina Chemical Corporation and was suitable for use without further purification.

Preparation of the Ligands.—Bis-(diisopropoxyphosphinyl)-methane was synthesized according to a method described by Kosolapoff[8] and Cade[9] except that triisopropyl phosphite[10] was

used because it led to greater yields of the diphosphonate ester. The apparatus consisted of an ordinary distillation set-up containing a 10-in. Vigreux column. A 500-ml. three-necked round bottom flask, fitted with a thermometer and nitrogen bubbler, was used as a reaction vessel. Two hundred ml. of triisopropyl phosphite (0.9 mole, 50% excess) was placed in the reaction flask and to it was added rapidly 24 ml. of methylene iodide (0.3 mole). Dry nitrogen was bubbled through the mixture to serve as a means of stirring and so that the reaction would take place in a nitrogen atmosphere. The reaction mixture was heated by means of an oil bath preheated to 150° and when the temperature reached 150–160° reaction set in with the formation and concomitant distillation of isopropyl iodide. The reaction was allowed to proceed until no more isopropyl iodide distilled over. Total heating time was 2.5–3.5 h ., and at the end of this period the reaction mixture was usually a light yellow color. Bis-(diisopropoxyphosphinyl)-methane was isolated from the reaction mixture by fractional vacuum distillation, saving the fraction boiling at 116–118° at 0.5 mm. The pure product is a colorless, essentially odorless, oily liquid; yield, 50–60%. *Anal.* Calcd. for $C_{13}H_{30}O_6P_2$: C, 45.34; H, 8.78; P, 17.99. Found: C, 44.47; H, 8.47; P, 17.70.

Bis-(diisopropoxyphosphinyl)-methane was converted to methylenediphosphonic acid, $(HO)_2P(O)CH_2P(O)(OH)_2$, by refluxing 50 g. of the former with 200 ml. of concentrated HCl for 6–8 hr. The solution was evaporated until crystals began to form in the hot solution. The white crystals were filtered, washed with copious amounts of acetone, and dried in a desiccator; m.p. 202–203°, lit.[11] 196–198°; yield, 70–80%.

The preparation of bis-(dichlorophosphinyl)-methane and bis-(di-n-butylphosphinyl)-methane was carried out by the procedure described for the n-hexyl derivative by Richard, *et al.*[12] An equimolar mixture of methylenediphosphonic acid and bis-(diisopropoxyphosphinyl)-methane was mixed with PCl_5 at room temperature to form bis-(dichlorophosphinyl)-methane, $Cl_2P(O)CH_2P(O)Cl_2$. The white needle-like crystals were very hygroscopic and melted at 100–101°.

Bis-(dichlorophosphinyl)-methane was dissolved in benzene and reacted with a twofold excess of n-butyl magnesium chloride in benzene. The organic layer from the hydrolysis of the Grignard reaction mixture was evaporated and the oily residue was purified by fractional vacuum distillation. The fraction boiling at 198–204° at 0.45 mm. was saved. Bis-(di-n-butylphosphinyl)-methane is a colorless, viscous liquid; yield, 30–40%. *Anal.* Calcd. for $C_{17}H_{38}O_2P_2$: C, 60.69; H, 11.38; P, 18.42. Found: C, 60.16; H, 11.31; P, 17.81.

Preparation of the Complexes.—The complexes generally were prepared in the following manner, with variations in individual cases. An alcoholic solution of a metal salt was mixed with the pure ligand or an alcoholic solution of the ligand. The resulting solution often was evaporated partially by bubbling nitrogen through it and then placed in a freezer at $-10°$ to crystallize. The crystals were filtered with suction on a sintered glass filter crucible, sometimes in an atmosphere of nitrogen, washed, and dried in a desiccator. Each complex was prepared at least twice and all were reproducible. It was observed that the density of bis-(diisopropoxyphosphinyl)-methane was very close to one and, therefore, the quantities used in the preparation of its complexes were measured out by volume.

$[FeCl_2(L_1)_2][FeCl_4]$.—Eight ml. of 0.5 M $FeCl_3$ solution (4 mmoles) was added to a solution of 3 ml. of L_1 (9 mmoles) dissolved in 6 ml. of isopropyl alcohol, resulting in an orange solution. Upon cooling in the freezer overnight, an orange oil separated out which crystallized on agitation. The yellow-orange crystals were filtered, washed with cold CCl_4, and dried. They were recrystallized from 10 ml. of hot isopropyl alcohol. The compound is somewhat soluble in carbon tetrachloride, ether, and

(5) T. V. Healy and J. Kennedy, *J. Inorg. Nucl. Chem.*, **10**, 128 (1959).

(6) K. Burke, H. Sakurai, J. W. O'Laughlin, and C. V. Banks, Contribution No. 1017 from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa.

(7) I. Lindquist, M. Zackrisson, and S. Eriksson, *Acta Chem. Scand.*, **13**, 1758 (1959).

(8) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 1500 (1953).

(9) J. A. Cade, *J. Chem. Soc.*, 2266 (1959).

(10) Suggested by Dr. Wendell Byrd of Virginia-Carolina Chemical Corporation.

(11) J. J. Richard, K. E. Burke, J. W. O'Laughlin, and C. V. Banks, Contribution No. 967 from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa.

(12) J. J. Richard, K. E. Burke, J. W. O'Laughlin, and C. V. Banks, *J. Am. Chem. Soc.*, **83**, 1722 (1961).

benzene; soluble in isopropyl alcohol and acetone; and is soluble or decomposed in water; m.p. 112.5–113°; yield, 0.92 g. (30%). *Anal.* Calcd.: Fe, 11.03; P, 12.23. Found: Fe, 11.01; P, 11.97.

$CoCl_2 \cdot L_1 \cdot H_2O$.—The blue crystalline substance was prepared by adding 30 ml. of 0.1 M $CoCl_2$ (3 mmoles) to 3 ml. of L_1 (9 mmoles). The solution was evaporated to 5–10 ml. by passing a stream of nitrogen through it. After remaining in the freezer for several days, dark blue crystals formed. The crystals were filtered, washed with a small amount of cold, dry benzene, and dried in a desiccator. They are soluble in acetone, isopropyl alcohol, and nitrobenzene; insoluble in benzene; and are decomposed in water; m.p. 118°; yield, 0.70 g. (47%). *Anal.* Calcd.: Co, 11.97; P, 12.59; C, 31.72; H, 6.55. Found: Co, 12.27; P, 12.45; C, 31.91; H, 6.58.

$[Co(L_1)_3](ClO_4)_2$.—Thirty ml. of 0.1 M $Co(ClO_4)_2$ (3 mmoles) was added to 3 ml. of L_1 (9 mmoles), resulting in a violet-pink solution. The solution was evaporated to approximately 10 ml. by bubbling nitrogen through it. Upon standing in the freezer overnight, large violet-pink crystals formed which were suction filtered under a rapid stream of nitrogen. The crystals were washed with a few small portions of cold isopropyl alcohol, sucked as dry as possible, and quickly transferred to a desiccator. It is necessary to filter this compound under nitrogen, otherwise it becomes sticky and gummy. When dry the crystals were ground in a mortar and pestle to be certain the last traces of isopropyl alcohol were removed. The compound is soluble in nitrobenzene and acetone, and is soluble or decomposed in water. It is somewhat soluble in isopropyl alcohol; m.p. 128.5° dec.; yield; 60%. *Anal.* Calcd.: Co, 4.57; P,1 4.40. Found: Co, 4.61; P, 14.10.

$[Ni(L_1)_3](ClO_4)_2$.—The compound was prepared by adding 30 ml. of 0.1 M $Ni(ClO_4)_2$ (3 mmoles) to 3 ml. of L_1 (9 mmoles). The resulting greenish yellow solution was evaporated to 5–10 ml. by passing a stream of nitrogen through it. Upon standing in the freezer, large yellow crystals slowly formed. These were filtered under nitrogen, washed with cold isopropyl alcohol, and placed in a desiccator to dry. Although this complex is prepared from isopropyl alcohol and is slow to crystallize from it initially, once the precipitate forms it is not very soluble in isopropyl alcohol. The compound is readily soluble in acetone and nitrobenzene and is decomposed in water; m.p. 131°; yield, 2.86 g. (74%). *Anal.* Calcd.: Ni, 4.55; P, 14.40; C, 36.29; H, 7.03. Found: Ni, 4.64; P, 14.00; C, 35.81; H, 7.13.

$8CuCl_2 \cdot 5L_1$.—Thirty-nine ml. of 0.1 M $CuCl_2$ (3.9 mmoles) was added slowly to 4 ml. of L_1 (11.6 mmoles). The solution was evaporated by passing a stream of nitrogen through it until yellow-brown crystals began to form in the flask. When this occurred, the solution was placed in the freezer to complete precipitation. The needle-shaped crystals were filtered, washed with cold CCl_4, and dried in a desiccator. They are soluble in acetone, alcohol, and N,N-dimethylformamide; slightly soluble in CCl_4 and nitrobenzene; insoluble in benzene; and are either soluble or decomposed in water; m.p. 157°; yield, 1.46 g. (14%). *Anal.* Calcd.: Cu, 18.17; P, 11.07; Cl, 20.28; C, 27.91; H, 5.41. Found: Cu, 18.05; P, 10.94; Cl, 19.97; C, 27.87; H, 5.64.

$[Cu(L_1)_2](ClO_4)_2$.—This very pale blue-green crystalline substance was prepared by mixing 45 ml. of 0.1 M $Cu(ClO_4)_2$ (4.5 mmoles) with 3 ml. of L_1 (9 mmoles). A pale blue solution resulted which was evaporated to about 30 ml. by passing a stream of nitrogen through it. It was placed in the freezer until crystallization occurred. The crystals were filtered, washed with cold benzene, and dried in a desiccator. A second crop of crystals was obtained from the filtrate upon further evaporation. The complex is soluble in acetone and nitrobenzene and is either soluble or decomposed in water. It is insoluble in CCl_4 and benzene; m.p. 131° dec.; yield, 56%. *Anal.* Calcd.: Cu, 6.68; P, 13.03. Found: Cu, 6.73; P, 13.02.

$ZnCl_2 \cdot L_1$.—Forty-five ml. of 0.1 M $ZnCl_2$ (4.5 mmoles) was added to 3 ml. of L_1 (9 mmoles) and the solution was evaporated to 5–10 ml. The crystals were slow to form and the solution

remained in the freezer several days before precipitation occurred. The white crystals were filtered under nitrogen and washed with two small portions of cold isopropyl alcohol. Care must be taken in handling this compound as it exhibits some sensitivity to moisture, especially when it is wet with solvent. The compound is soluble in isopropyl alcohol and acetone and is soluble or decomposed in water; m.p. 134–134.5° dec.; yield, 0.97 g. (47%). *Anal.* Calcd.: Zn, 13.60; P, 12.89; C, 32.48; H, 6.29. Found: Zn, 13.55; P, 12.28; C, 32.73; H, 6.57.

$[Zn(L_1)_2](ClO_4)_2$.—Thirty ml. of 0.1 M $Zn(ClO_4)_2$ (3 mmoles) was added to 2 ml. of L_1 (6 mmoles) and the resulting colorless solution was evaporated to 10 ml. It was placed in the freezer and white crystals slowly formed in clusters. The crystals were filtered in an atmosphere of nitrogen, washed with a small amount of cold isopropyl alcohol, and dried in a desiccator. This compound is hygroscopic and must be handled in the absence of moisture. It is difficult to obtain the compound completely free of solvent. The complex is soluble in acetone, isopropyl alcohol, and nitrobenzene and either dissolves or decomposes in water and benzene. Melting point in a sealed capillary: about 114°; yield, 2.32 g. (81%). *Anal.* Calcd.: Zn, 6.86; P, 13.00. Found: Zn, 6.80; P, 12.51.

$[SbCl_4(L_1)][SbCl_6]$.—One ml. of L_1 (3 mmoles) was dissolved in 25 ml. of reagent grade carbon tetrachloride and cooled in an ice bath. Another solution composed of 1 ml. of $SbCl_5$ (8 mmoles) dissolved in 25 ml. of carbon tetrachloride was prepared. The $SbCl_5$ solution was added very slowly to the ligand solution with swirling, and when approximately half of the $SbCl_5$ solution had been added a white precipitate began to form. The mixture was cooled in an ice bath for about 10 min., filtered under nitrogen, washed thoroughly with cold CCl_4, and placed in a desiccator to dry. The white product is stable in air and is insoluble in water. It also is insoluble in CCl_4, benzene, ether, and concentrated H_2SO_4, but it is readily soluble in acetone. It is decomposed in hot aqueous ammonia; m.p. 110.5–111° dec.; yield, 2.67 g. (94%). *Anal.* Calcd.: Cl, 37.62; C, 16.57; H, 3.21. Found: Cl, 37.75; C, 16.74; H, 3.48.

$[Fe(L_2)_3][FeCl_4]_3$.—Five ml. of 0.5 M $FeCl_3$ (2.5 mmoles) was added to 2.38 g. of L_2 (7.1 mmoles) which had been weighed into a small flask. A yellow oil or precipitate started to form as the $FeCl_3$ solution was added, but it disappeared quickly and a red-brown oil formed in its place. A few ml. of isopropyl alcohol was added to increase the volume of the solution and it was heated on a steam bath for 5–10 min., during which time the oil redissolved. Evaporation and cooling of the solution did not induce crystallization, but the addition of a large excess of $FeCl_3$ caused a yellow crystalline precipitate to form. The crystals and some oil which had formed also were allowed to stand overnight at room temperature so that the oil would crystallize. The substance was filtered, washed with cold isopropyl alcohol, and dried in a desiccator. The compound is insoluble in isopropyl alcohol and benzene. It is soluble in acetone and nitrobenzene and is either soluble or decomposed in water; m.p. 238° dec.; yield, 3.44 g. (87%). *Anal.* Calcd.: Fe, 13.47; P, 11.21; Cl, 25.66; C, 36.94; H, 6.93. Found: Fe, 13.33; P, 10.59; Cl, 25.49; C, 36.65; H, 6.76.

$[Fe(L_2)_3](ClO_4)_3$.—Seventeen ml. of 0.1 M $Fe(ClO_4)_3$ was added to 5 ml. of 0.74 M L_2. A yellow-brown oil formed immediately. A few drops of this oily mixture were removed and to it were added two drops of water, resulting in the immediate formation of a precipitate. This was returned to the original mixture and by allowing it to stand for several days at room temperature most of the oil crystallized. The straw-colored crystals and the remaining oil were filtered on a coarse porosity filter crucible which allowed the oil to pass through while retaining the crystals. The crystals were washed with cold isopropyl alcohol and recrystallized from 20 ml. of warm methanol. They are insoluble in water and only slightly soluble in alcohol and nitrobenzene, but readily soluble in acetone; m.p. 215–216° dec.; yield, 0.33 g. (7%). *Anal.* Calcd.: Fe, 4.10; P, 13.63; C, 44.92; H, 8.43. Found: Fe, 4.34; P, 12.93; C, 43.43; H, 7.94.

[Co(L₂)₃][CoCl₄].—When 25 ml. of 0.1 M CoCl₂ (2.5 mmoles) was added to 4 ml. of 1 M L₂ (4 mmoles), a blue solid precipitated at once. The solution was cooled in an ice bath, and the precipitate was filtered and washed with diethyl ether. The precipitate was recrystallized from a warm solution composed of 15 ml. of isopropyl alcohol and 5 ml. of absolute ethanol. Upon cooling lovely violet-blue crystals formed. These were filtered and washed with diethyl ether. This compound is soluble in alcohol, acetone, and slightly soluble in nitrobenzene. It is insoluble in diethyl ether and is decomposed in water; m.p. 224–226°; yield, 1.01 g. (64%). *Anal.* Calcd.: Co, 9.29; P, 14.65; C, 48.27; H, 9.05. Found: Co, 9.31; P, 14.38; C, 47.87; H, 8.84.

[Ni(L₂)₃][NiCl₄].—A yellow solution resulted when 27 ml. of 0.1 M NiCl₂ (2.7 mmoles) was added to 4 ml. of 1 M L₂ (4 mmoles). The solution was evaporated considerably and acetone was added to it until the solution turned blue-green in color and blue-green crystals began to precipitate. The crystals were filtered, washed with cold acetone, and dried in a desiccator. The filtrate was evaporated further and by adding more acetone to it another crop of crystals was obtained. The complex is soluble in alcohol, giving a yellow solution, slightly soluble in acetone, giving a blue solution, and readily soluble and probably decomposed in N,N-dimethylformamide. It is slightly soluble in nitrobenzene, soluble in acetonitrile, and decomposed in water and methylene chloride; m.p. 276–278°; yield, 1.10 g. (65%). *Anal.* Calcd.: Ni, 9.25; P, 14.65; C, 48.29; H, 9.06. Found: Ni, 9.30; P, 13.69; C, 48.07; H, 8.92.

Conductance measurements have been described in a previous publication.[13] All of the compounds were sufficiently soluble in nitrobenzene to give 10^{-3} to 10^{-4} M solutions except the compound 8CuCl₂·5L₁, which was insufficiently soluble to obtain a measurement.

Magnetic susceptibility measurements were made on the compounds using the Gouy method. A Variflux permanent magnet made by the Laboratory for Science, Oakland, California, equipped with 5-cm. diameter pole faces was used. The pole gap was 1.11 cm. and the shunt rings were set at position 8. These settings produced a field strength of approximately 2900 gauss. Hg[Co(CNS)₄], having a gram susceptibility of 16.44 × 10^{-6} c.g.s. unit at 20°,[14] was used as a standard to calibrate the sample tube.

Infrared spectra were obtained as paraffin oil mulls on a Baird-Atomic recording spectrophotometer, serial No. AB2-193. They were obtained also as KBr pellets on a Perkin-Elmer Infracord, Model 137. Pellet spectra were not obtained for [Cu(L₁)₂](ClO₄)₂ and [Zn(L₁)₂](ClO₄)₂ due to decomposition of these compounds in the pellet. The P–O stretching frequencies given in Table I were obtained from mull spectra except where otherwise noted.

Visible spectra were obtained on a Cary recording spectrophotometer, Model 14. The compounds were run as acetone solutions, except for [Ni(L₂)₃][NiCl₄], which was run in acetonitrile.

Results

The magnetic, conductance, and infrared spectral data are summarized in Table I.

The concentrations of the solutions used for conductance measurements ranged from 10^{-3} to 10^{-4} M, depending on the nature of the solute. In the cases of the 2:2 electrolytes low conductance values, which have been ascribed to molecular association in solution, were obtained even at concentrations as dilute as 10^{-4} M. It was not practicable to go to more dilute solutions. From the conductance study of a number of

(13) D. J. Phillips and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 1806 (1961).
(14) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

TABLE I

Compound	P–O stretching frequency (mull), cm.⁻¹	μ_{eff}, B.M. at 20°	Conductance Λ at 25°, cm.² ohm⁻¹ mole⁻¹	Concn. × 10⁻³, M
(C₃H₇O)₂P(O)CH₂P(O)(OC₃H₇)₂[a]	1250			
(C₄H₉)₂P(O)CH₂P(O)(C₄H₉)₂[a]	1168			
Cl₂P(O)CH₂P(O)Cl₂	1260			
[FeCl₂(L₁)₂][FeCl₄]	1212	6.06	28.9	0.34
	1165			
[Fe(L₂)₃][FeCl₄]₃	1077	6.02	82.5	0.96
[Fe(L₂)₃](ClO₄)₃	1080	6.14	69.7	0.26
CoCl₂·L₁·H₂O	1213	5.07	2.5	1.04
[Co(L₁)₃](ClO₄)₂	1205	5.26	59.7	0.99
[Co(L₂)₃][CoCl₄]	1147	5.08	10.0	0.59
[Ni(L₁)₃](ClO₄)₂	1206	3.35	59.3	0.98
[Ni(L₂)₃][NiCl₄]	1150	3.71	20.8	0.34
8CuCl₂·5L₁	1193	2.06		
[Cu(L₁)₂](ClO₄)₂	1200	2.05	48.6	0.46
ZnCl₂·L₁	1230		0.1	1.13
	1212			
	1198			
[Zn(L₁)₂](ClO₄)₂	1205		58.3	0.39
[SbCl₄(L₁)][SbCl₆]	1220		35.9	0.48
	1135			

a CCl₄ solution.

triphenylarsine oxide complexes,[13] from conductance data on a series of tetra-substituted ammonium picrates,[15] and from the data observed by these authors, it has been concluded that in nitrobenzene at 25° 1:1 electrolytes exhibit molecular conductance values from 25–35 and 2:1 electrolytes from 44–60. Little work seems to have been done on 3:1 electrolytes in nitrobenzene, but from the values observed for 1:1 and 2:1 electrolytes it appears reasonable to anticipate a value in the vicinity of 80.

The P–O stretching frequency in the infrared is found at a lower frequency in the complexes of L₁ and L₂ than it is in the uncoördinated ligands. The formation of a metal–oxygen bond causes the electron density between the phosphorus and the oxygen to be decreased, thereby decreasing the P–O bond order and causing the stretching frequency to be lowered.

It has been observed before[13,16] while working with donor–acceptor complexes such as these that in certain circumstances the band attributed to the X–O stretching frequency (where X = As, P, or N) is split into several bands upon coördination. The splitting usually is observed when the metal is coördinated with two or more ligands (or one or more bidentate ligands) and some other kind of atom or atoms. If the metal is completely surrounded by the ligand and has no other kind of atoms in its first coördination sphere, the splitting does not occur. If only one monodenate ligand plus some other kinds of atoms are in the coördination sphere of the metal, splitting does not occur either. The infrared spectra of the ligands, in thin film between NaCl windows, are shown in Fig. 1.

The λ_{max} of the visible absorptions of the complexes

(15) E. G. Taylor and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1731 (1947).
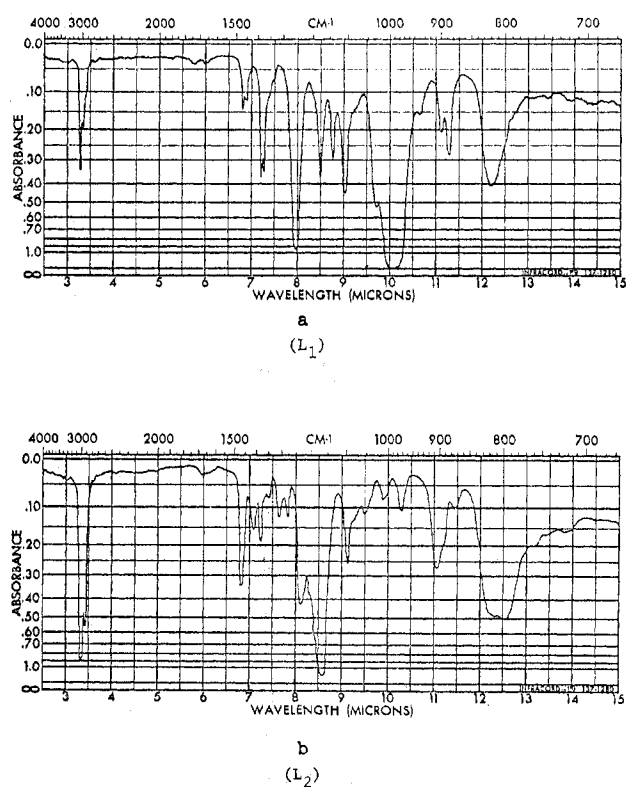(16) S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **1**, 122 (1962).

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a
(L_1)

b
(L_2)

Figure 1.

Compound	λ_{max} in mμ (cm.$^{-1}$)	$\sim\epsilon$
$[FeCl_2(L_1)_2][FeCl_4]$	525	Shoulder
	445	416
	362	12,000
$[Fe(L_2)_3][FeCl_4]_3$	527	10
	447	139
	362	7,300
$[Fe(L_2)_3](ClO_4)_3$	423	74
	337	379
$CoCl_2 \cdot L_1 \cdot H_2O$	675	313
	640	222
	577	152
$[Co(L_1)_3](ClO_4)_2$	538 (18,600)	13
	476 (21,000)	4
$[Co(L_2)_3][CoCl_4]$	677 (14,800)	793
	632 (15,800)	407
	583 (17,150)	305
	525 (19,000)	21
	480 (20,800)	6
$[Ni(L_1)_3](ClO_4)_2$	1180 (8,470)	$\sim$2
	796 (12,600)	4
	678 (14,800)	2
	477 (21,000)	2
	422 (23,700)	11
$[Ni(L_2)_3][NiCl_4]$	1158 (8,640)	$\sim$2
	854 (11,700)	7
	682 (14,700)	88
	660 (15,200)	97
	613 (16,300)	140
	580 (17,200)	105
	427 (23,400)	11
$8CuCl_2 \cdot 5L_1$	850	134
	475	444
$[Cu(L_1)_2](ClO_4)_2$	875	17

are listed in Table II, along with the approximate molar extinction coefficients.

Discussion

An attempt was made to prepare L_2 directly by the action of a Grignard on L_1 but it was unsuccessful. It appears that the Grignard reacts only with the somewhat acidic methylene hydrogens, which upon hydrolysis of the reaction mixture leads to the re-formation of the starting material.

Recently Kosolapoff[17] has reported the preparation of L_2 by a completely different method, obtaining an extremely low yield. He reports a melting point of 174° for this compound. Although we had difficulty crystallizing L_2, due probably to the formation of small amounts of impurities during distillation, one preparation which was crystallized from ether melted below room temperature. Since bis-(di-*n*-hexylphosphinyl)-methane melts at 33–35°,[12] it is reasonable that the *n*-butyl compound have a melting point near or below room temperature.

From a consideration of the over-all picture presented by the analytical, magnetic, conductance, and spectral data, it has been possible to deduce the structure of a majority of the complexes. In a few cases, the data appear to be ambiguous or contradictory and no structure has been postulated for these compounds.

Perchlorate Salts.—The compounds are somewhat sensitive to moisture, especially during filtration and washing, but $[Zn(L_1)_2](ClO_4)_2$ is the only one which is decidedly hygroscopic. All of the perchlorate salts

are electrolytes, as indicated by the conductance data. The compounds containing Fe(III), Co(II), and Ni-(II) have three molecules of ligand occupying the first coördination sphere of the metal, forming octahedral cations. On the other hand, Zn(II) and Cu(II) perchlorates form complexes containing only two molecules of L_1, even when prepared in the presence of excess ligand. Several of the perchlorate compounds, in particular $[Ni(L_1)_3](ClO_4)_2$, $[Cu(L_1)_2](ClO_4)_2$, and $[Zn(L_1)_2](ClO_4)_2$, decompose slowly after standing several months.

$[Fe(L_2)_3][FeCl_4]_3$.—L_2 forms a series of analogous compounds with $FeCl_3$, $CoCl_2$, and $NiCl_2$ in which the cation consists of a metal ion octahedrally surrounded by ligands and the anion consists of a tetrachlorometallate ion.

The conductance value of 82.5 cm.^{2} ohm^{-1} mole^{-1} for $[Fe(L_2)_3][FeCl_4]_3$ in nitrobenzene is indicative of a 3:1 electrolyte. The visible spectrum of the $[FeCl_4]^-$ ion has been studied by various workers[18,19] and the main characteristic absorptions of this ion are a weak, but well defined peak at about 535 mμ and several extremely weak band systems in the 600 to 725 mμ region. There is an intense shoulder around 450 mμ

(17) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 2423 (1961).

(18) M. Baaz, V. Gutmann, and L. Hubner, *Monatsh.*, **92**, 135 (1961).

(19) H. L. Friedman, *J. Am. Chem. Soc.*, **74**, 5 (1952).

which apparently also is present in the spectra of other iron(III) species. The solution spectrum of [Fe-$(L_2)_3$][$FeCl_4$]$_3$ exhibits a weak band at 527 mμ and two extremely weak bands in the 600–700 mμ region. The general shape of the spectrum observed and the approximate molar extinction coefficients are in agreement with those known for the [$FeCl_4$]$^-$ ion.

[Co(L_2)$_3$][$CoCl_4$].—In the visible solution spectrum of the compound it is possible to identify absorption bands associated with the octahedral Co(II) ion and those associated with the tetrahedral Co(II) ion. The visible spectrum of the complex [Co(L_1)$_3$](ClO_4)$_2$, which is known to contain an octahedral cation, has a weak band at 538 mμ (18,600 cm.$^{-1}$) with a shoulder at 476 mμ (21,000 cm.$^{-1}$). The former corresponds to the transition $^4T_{1g} \rightarrow {}^4A_{2g}(F)$, usually appearing in the 16,000–18,000 cm.$^{-1}$ region in octahedral cobalt, and the latter corresponds to the transition $^4T_{1g} \rightarrow {}^4T_{1g}(P)$, observed in the 20,000–21,000 cm.$^{-1}$ region.[20] The bands at 525 mμ (19,050 cm.$^{-1}$) and 480 mμ (20,800 cm.$^{-1}$) in [Co(L_2)$_3$][$CoCl_4$] have extinction coefficients of the same order of magnitude as the corresponding bands in [Co(L_1)$_3$](ClO_4)$_2$, and likewise can be assigned, respectively, to the transitions $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)$.

A comparison of the ligand fields created by L_1 and L_2 may be obtained from the absorption spectra of the octahedral Co(II) species. The transition in the 19,000 cm^{-1} region is $^4T_{1g} \rightarrow {}^4A_{2g}(F)$, a two-electron transition which corresponds to the promotion of two electrons from the t_{2g} level to the e_g level. Since the ligand field splitting is the energy separation of the t_{2g} and e_g orbitals, one-half of the energy of such a transition should correspond to 10 Dq. In a spin-allowed transition, no correction for pairing energy is involved. 10 Dq is found to be 9300 cm.$^{-1}$ in the L_1 complex, as compared with a value of 9525 cm.$^{-1}$ in the L_2 complex. These values for the ligand field splitting indicate that, while L_2 gives rise to a slightly greater ligand field, both ligands are in the weak field class.

Because of the lower symmetry of a tetrahedral field, the bands arising from transitions involving the $CoCl_4{}^{2-}$ species should be of considerably higher intensity than those associated with octahedral Co(II). The bands which occur at 677, 632, and 583 mμ (15,000–17,000 cm.$^{-1}$ region) in [Co(L_2)$_3$][$CoCl_4$] are observed to have extinction coefficients on the order of 10^2 times those of the octahedral species, and correspond to absorptions of the tetrahedral Co(II) ion.[21] Such bands are due to transitions in $CoCl_4{}^{2-}$ which are essentially $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, and are generally observed in the 15,000 cm.$^{-1}$ region.[22] The visible spectrum of the compound in a KBr pellet showed peaks at 727, 697, 667, 638, and 613 mμ, the peak at 697 mμ being the most intense. This corresponds quite well

with the KBr pellet spectrum of Cs$_2$[$CoCl_4$] at liquid nitrogen temperature observed by Katzin.[23]

The magnetic data give further support to the spectral evidence. The magnetic moment per metal ion of such a complex should be the square root of the mean of the squares of the moments of the tetrahedral Co(II) ion and the octahedral Co(II) ion. Unfortunately the magnetic moment of the [Co(L_2)$_3$]$^{2+}$ ion is not available, but we feel that its moment should be near the moment of the [Co(L_1)$_3$]$^{2+}$ ion due to the similarity of the ligands. Cotton[24] reports the magnetic moment of [$CoCl_4$]$^{2-}$ as 4.69 B.M., and the moment for [Co(L_1)$_3$]$^{2+}$ measured in this Laboratory is 5.26 B.M. The magnetic moment of 5.08 B.M. for the compound [Co(L_2)$_3$][$CoCl_4$] is in fair agreement with the root mean square value of the [Co-(L_1)$_3$]$^{2+}$ and the [$CoCl_4$]$^{2-}$ ions, 4.99 B.M.

The conductance value of 10.0 cm.^{2} ohm^{-1} mole^{-1} is considerably low for a 2:2 electrolyte. Although no known 2:2 electrolytes were available as standards, it is believed that a 2:2 electrolyte would have a value similar to that for a 1:1 electrolyte. The low value which was obtained can be explained on the basis of appreciable molecular association in the solvent. Indeed, the solubility of [Co(L_2)$_3$][$CoCl_4$] in nitrobenzene is quite small and its rate of dissolution very slow.

[Ni(L_2)$_3$][$NiCl_4$].—As in the case of the [Co(L_2)$_3$]-[$CoCl_4$] compound, it is possible to identify absorption bands due to the d–d transitions of octahedral and tetrahedral Ni(II) species in the visible spectrum of this compound. The assignments for the bands observed in [Ni(L_1)$_3$](ClO_4)$_2$ are[25]: 8470 cm.$^{-1}$, $^3A_{2g} \rightarrow {}^3T_{2g}(F)$; 12,550 cm.$^{-1}$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$; 14,800 cm.$^{-1}$, $^3A_{2g} \rightarrow {}^1E_g(D)$; 21,000 cm.$^{-1}$, $^3A_{2g} \rightarrow {}^3A_{1g}(G)$; and 23,700 cm.$^{-1}$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. A comparison of the extinction coefficients as well as the position of the bands observed in [Ni(L_2)$_3$][$NiCl_4$] indicates that the bands at 8640, 11,700, and 23,400 cm.$^{-1}$ are absorptions of the octahedral Ni(II) species, and correspond, respectively, to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The value of 10 Dq for both compounds may be obtained directly from the spectra. Since the transition $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ corresponds to the promotion of one electron from the t_{2g} level to the e_g level, the ligand field splitting is equal to the energy of the band in the 8500 cm.$^{-1}$ region. As in the case of the Co(II) complexes, 10 Dq is slightly larger in the L_2 complex, with a value of 8640 cm.$^{-1}$ as compared with 8470 cm.$^{-1}$ for the L_1 complex. Again, both complexes are clearly of the weak field variety.

The transitions in the lower symmetry tetrahedral field are less forbidden than in the octahedral case. The bands in the 600–700 mμ region of the [Ni(L_2)$_3$]-[$NiCl_4$] spectrum are much more intense than those discussed above as arising from octahedral Ni(II), and are transitions associated with the $NiCl_4{}^{2-}$ ion. Absorption bands in the 600–700 mμ region have

(20) T. M. Dunn, "The Visible and Ultra-Violet Spectra of Complex Compounds," in "Modern Coordination Chemistry," Lewis and Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 290.

(21) L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, **72**, 5464 (1950).

(22) T. M. Dunn, ref. 20, p. 245.

(23) L. I. Katzin, *J. Am. Chem. Soc.*, **76**, 3089 (1954).

(24) F. A. Cotton and R. Francis, *ibid.*, **82**, 2986 (1960)

(25) T. M. Dunn, ref. 20, p. 288.

been assigned previously to the tetrahedral Ni(II) species.[26]

The magnetic moment of 3.71 B.M. which was observed is in fair agreement with the root mean square value (3.63 B.M.) of the moments for $[Ni(L_1)_3]^{2+}$ and the value of 3.89 B.M.[27] reported for $[NiCl_4]^{2-}$ in $[(C_6H_5)_3AsCH_3]_2[NiCl_4]$.

The conductance value is lower than anticipated, but not nearly as low as in the case of $[Co(L_2)_3][CoCl_4]$. Molecular association in solution is believed to account for the low value in this case also.

$[FeCl_2(L_1)_2][FeCl_4]$.—The compound exhibits a stoichiometry corresponding to $FeCl_3 \cdot L_1$. The conductance value calculated considering the compound to be a 1:1 adduct is 14.5 cm.^{2} ohm^{-1} mole^{-1}, which is about one-half the value expected for a 1:1 electrolyte and is extremely high for a non-electrolyte, even assuming partial decomposition in nitrobenzene. If the compound is actually dimeric, $(FeCl_3 \cdot L_1)_2$, then the conductance value obtained is 28.9 cm.^{2} ohm^{-1} mole^{-1}, which is in the range for a 1:1 electrolyte. On the basis of this and other data, particularly the infrared spectral evidence, the salt-like structure cited above has been proposed.

The P–O stretching vibration is shifted from 1250 cm.$^{-1}$ in the free ligand and is split into two bands occurring at 1212 and 1165 cm.$^{-1}$, in agreement with the expected splitting for the proposed structure in which the cation contains two chloride ions and two ligand molecules in the first coördination sphere of the Fe(III).

The visible spectrum of an acetone solution of the compound does not yield further information. There is a slight shoulder at about 525 mμ, but it is not very distinct, probably because of broadening of the intense charge transfer band which has occurred, and cannot be assigned definitely to a $[FeCl_4]^-$ as yet. There are several very weak bands in the 600–700 mμ region which may be due to $[FeCl_4]^-$ absorptions.

$CoCl_2 \cdot L_1 \cdot H_2O$.—The presence of stoichiometric H_2O is indicated by absorptions in the infrared at 3330 and 3280 cm.$^{-1}$, corresponding to the O–H stretching mode, and at 1650 cm.$^{-1}$, corresponding to the H_2O bending mode. The visible spectrum of an acetone solution shows fairly intense bands at 675, 640, and 577 mμ, the region where tetrahedral Co(II) species absorb, but no bands around 525 mμ, where octahedral Co(II) species absorb. This latter evidence appears to preclude the existence of a species such as $[Co(H_2O)_2(L_1)_2][CoCl_4]$.

The conductance value of 2.5 cm.^{2} ohm^{-1} mole^{-1} indicates that the compound is a non-electrolyte. The magnetic moment of 5.07 B.M. is almost the same as the moment for $[Co(L_2)_3][CoCl_4]$, which might mean that there is a similarity in their structures. The only conclusions which can be reached in view of this data are that the compound is probably tetrahedral and a non-electrolyte.

$8CuCl_2 \cdot 5L_1$.—The magnetic moment of the compound, 2.06 B.M., is very similar to that of $[Cu(L_1)_2](ClO_4)_2$ and is a normal value for a compound containing Cu(II). It is unfortunate that the complex is insufficiently soluble in nitrobenzene to obtain a conductance measurement as this might have been very helpful. The P–O stretching vibration occurs at 1193 cm.$^{-1}$ with the possibility that this vibration is split in the complex. The P–O stretching frequency is lowered in such a manner that it partially overlaps another band in the spectrum and it is impossible to determine with certainty whether or not splitting occurs. It seems likely that this compound is some complicated bridged structure.

$ZnCl_2 \cdot L_1$.—In nitrobenzene the compound behaves as a non-electrolyte, having a conductance of 0.1 cm.^{2} ohm^{-1} mole^{-1}. The infrared spectrum shows that the P–O stretching vibration is split into three bands, occurring at 1230, 1212, and 1198 cm.$^{-1}$, upon coördination. This indicates that the L_1 molecule and the two chlorides are coördinated to the zinc ion. There are two possible structures which would satisfy the data. One of these is the monomer $[ZnCl_2L_1]$, and the other is a dimer having ligand bridges

$$\begin{bmatrix} Cl & L_1 & Cl \\ & Zn \quad Zn & \\ Cl & L_1 & Cl \end{bmatrix}$$
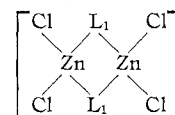
$[SbCl_4(L_1)][SbCl_6]$.—At first it was anticipated that the compound possessing the stoichiometry $2SbCl_5 \cdot L_1$ would be a non-electrolyte, but the conductance value of 35.9 cm.^{2} ohm^{-1} mole^{-1} is very indicative of a 1:1 electrolyte. On the basis of this data, which also is supported by the infrared spectral data, the salt structure

$$[R_2PCH_2PR_2][SbCl_6]$$
$$\begin{array}{c} O \quad O \\ SbCl_4 \end{array}$$
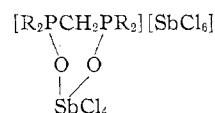
has been proposed. The infrared spectrum shows that the P–O frequency is split into two bands occurring at 1220 and 1135 cm.$^{-1}$. Splitting is expected for the ionic structure because one antimony (V) has a bidentate ligand and chloride ions coördinated to it.

Attempts were made to enolize L_1 and to form neutral chelate complexes analogous to the acetylacetonates. It is possible to remove an acidic hydrogen from the methylene carbon atom by using a reagent such as Na^0, K^0,[8] or NaH.[28] However, reaction of the diphosphonate anion with a metal salt led to the formation of oils or amorphous solids. The metal ions generally used were Cr(III) and Fe(III). To date none of the methods tried has been successful and we strongly suspect the formation of polymers in some cases.

(26) D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, **63**, 393 (1959).
(27) N. S. Gill, R. S. Nyholm, and P. Pauling, *Nature*, **182**, 168 (1958).
(28) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).