

The reaction of I with air, water, or halogenated hydrocarbons is quite vigorous. A controlled hydrolysis in dilute hydrochloric acid gave a mixture of II and tetramethylphosphonium chloride. The formation of the latter salt is reasonable in view of the fact that II is attacked in boiling water (very rapidly when basic) to form hexamethyldisiloxane and tetramethylphosphonium chloride.

The phosphonium salt II was obtained by heating equimolar amounts of chloromethyltrimethylsilane and trimethylphosphine in a sealed tube at 40° for several days. Traces of unchanged material were removed under vacuum to leave the pure chloride as a white crystalline solid.

Anal. Calcd. for $(\text{CH}_3)_3\text{SiCH}_2\text{P}(\text{CH}_3)_3\text{Cl}$: Cl (ionic), 17.8. Found: Cl (ionic), 17.9.

For analysis, the hexafluorophosphate salt was precipitated from an aqueous solution of the chloride and recrystallized from acidified water. It is a white crystalline solid.

Anal. Calcd. for $(\text{CH}_3)_3\text{SiCH}_2\text{P}(\text{CH}_3)_3\text{PF}_6$: C, 27.3; H, 6.5; P, 20.1. Found: C, 28.0; H, 6.6; P, 19.2.

The chloride salt was pyrolyzed at 180° under vacuum over a period of several hours, during which time the volatile material was passed through a series of traps cooled to 0, -78, and -196°, respectively. The contents of the -78° trap were transferred to a short-pass still and redistilled to give pure trimethylsilyltrimethylphosphinemethylene.

Anal. Calcd. for $(\text{CH}_3)_3\text{SiCHP}(\text{CH}_3)_3$: P, 19.1; Si, 17.3. Found⁴: P, 18.5; Si, 17.7.

A gas-phase molecular weight determination (18.5 mg. in 306.5 ml. exerted 22.6 mm. pressure at 88.4°) supported the monomeric composition, mol. wt. 165.3 (calcd. 162.3).

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(4) Carbon and hydrogen values by combustion analysis were low, apparently owing to rapid combustion. In an attempt to bring about slow combustion, the sample exploded and destroyed the combustion tube. The values found were: C, 48.6, 49.9, 50.0 (calcd., 51.8); H, 11.2, 11.8, 11.7 (calcd., 11.8).

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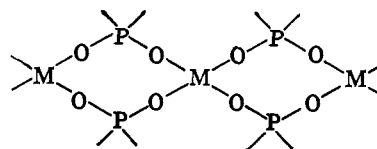
Inorganic Coordination Polymers. Cobalt(II) and Zinc (II) Di-*n*-butylphosphinates¹

Sir:

A particular class of inorganic polymers, the so-called "coordination polymers," having a skeleton formed by metal atoms interconnected by ligand molecules, has recently attracted considerable interest.² Bridged polymeric structures of the type

(1) This work was supported by the Consiglio Nazionale delle Ricerche (C.N.R.), Rome, Italy.

(2) B. P. Block, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press Inc., London, 1962, p. 447.



have been proposed for Co(II), Zn(II), and Be(II) tetrahedral complexes with dimethyl-, diphenyl- and methylphenylphosphinic acids.^{3,4} Molecular weight determinations of the zinc methylphenylphosphinate by ebulliometry in benzene have been reported.³ However, the difficulty of obtaining solutions of the dimethyl and diphenyl derivatives in solvents which do not attack the polymeric bonds has seriously impaired their physicochemical characterization.

In our laboratory di-*n*-butylphosphinates (di-*n*-BP) of Co(II) and of Zn(II), which are soluble in most organic solvents, have been prepared and display polymeric properties. We wish to report here some preliminary results on their characterization.

The di-*n*-butylphosphinate of Co (Co(di-*n*-BP)) was obtained by allowing pure sodium di-*n*-butylphosphinate to react with CoCl_2 in water at about 60°. The di-*n*-butylphosphinic acid was prepared according to Kosolapoff.⁵ On standing the blue-colored complex precipitated in an almost quantitative yield. The sample dissolved in water gives pink solutions, from which it was recrystallized on heating.

Anal. Calcd. for $\text{Co}[(\text{C}_4\text{H}_9)_2\text{PO}_2]_2$: C, 46.49; H, 8.78; P, 14.99. Found: C, 45.96; H, 8.84; P, 14.77.

Zinc di-*n*-butylphosphinate was prepared by stirring an aqueous solution of $\text{Zn}(\text{AcO})_2$ with a solution of di-*n*-butylphosphinic acid in benzene. The white precipitate, formed during the evaporation of the benzene layer, was collected and washed with ethanol. The reduced viscosity of both Co(di-*n*-BP) and Zn(di-*n*-BP) in benzene or carbon tetrachloride exhibits a peculiar dependence on concentration.

Typical results are reported in Figure 1, which show that the $[\eta]$ values are low, but the reduced viscosity of the solutions rises quite steeply with concentration. In the case of Zn(di-*n*-BP), gel formation occurred beyond a concentration of about 0.8% in benzene. This behavior may be explained in terms of an aggregation of relatively short chains of the coordination polymers which does not exert any influence on the absorption spectrum of Co(di-*n*-BP) in the 400-700- μ region since for a wide range of concentrations in CCl_4 no departure from Beer's law could be detected. A study is being carried out on this effect also with the aid of infrared spectra on CCl_4 solutions of both cobalt and zinc phosphinates. Crystals of Co(di-*n*-BP) were obtained by heating a water solution of the compound which appeared as twinned monoclinic prisms elongated along the *b* axis. Attempts to grow single crystals suitable for an accurate X-ray structure analysis so far have been unsuccessful.

The powder diffraction pattern of the residue obtained from evaporation of a benzene or carbon tetrachloride solution is identical with that of the crystal grown from water solutions. The Zn(di-*n*-BP) was

(3) B. P. Block, S. H. Rose, C. W. Schaumann, E. S. Roth, and J. Simkin, *J. Am. Chem. Soc.*, **84**, 3200 (1962).

(4) G. E. Coates and D. S. Golightly, *J. Chem. Soc.*, 2523 (1962).

(5) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **72**, 5508 (1950).

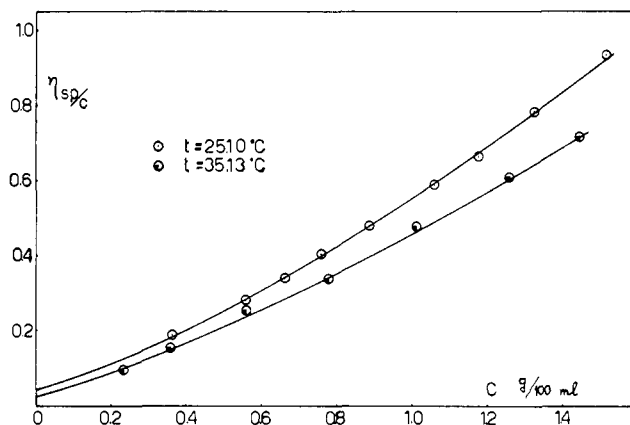


Figure 1. Reduced viscosity of Co(di-*n*-BP) in benzene as a function of concentration.

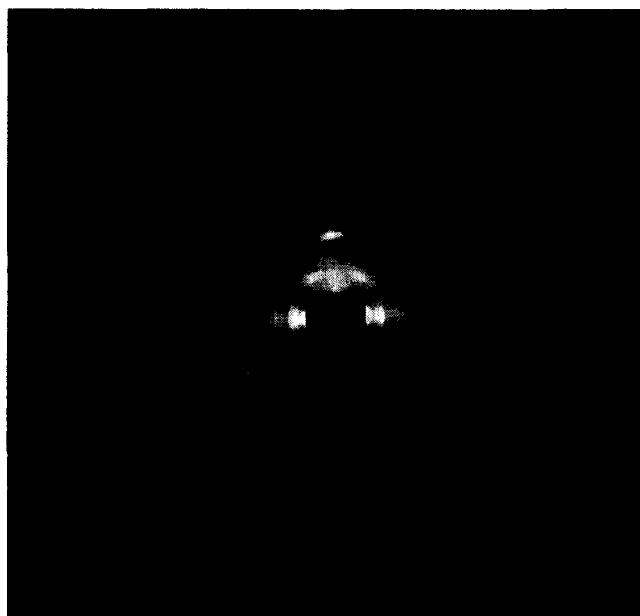


Figure 2. Fiber diagram of Zn(di-*n*-BP).

obtained as a crystalline powder isomorphous with the related Co compound.

Highly oriented fibers were drawn from the gel obtained by wetting the Zn(di-*n*-BP) powder with benzene. The fiber diagram, recorded with a cylindrical camera (diameter 57.3 mm.) using Cu K α radiation, is shown in Figure 2. From this diagram a value of 9.90 Å. may be deduced for the identity period along the fiber axis which corresponds to the *b* axis of the twinned crystals of Co(di-*n*-BP). This indicates that the two polymers are isostructural and consist of molecular chains oriented along the *b* axis. The 9.90-Å. value for the *b* axis and a strong meridional reflection on the second layer of the fiber photograph strongly suggest that the structure repeats identically after two metal atoms along the chain. Assuming reasonable values of bond angles and bond lengths, a chain model with double phosphinate bridges between tetrahedrally coordinated metal atoms appears to be stereochemically feasible.

In conclusion these preliminary results give strong indication that cobalt(II) and zinc(II) di-*n*-butylphosphinates exist as linear chains in the solid state and in

solution, the metal atoms forming part of the repeating units of these chains through stable coordination linkages, as previously proposed^{3,4} for the dimethyl, diphenyl, and methylphenyl derivatives. Further studies on this interesting class of inorganic polymers are in progress in our laboratory.

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Field-Dependent Conductance in Sodium-Liquid Ammonia Solutions

Sir:

We wish to report an unexpectedly large and complex influence of electrical field on the conductance of dilute solutions of sodium in liquid ammonia. At -33° and concentrations from 3 to $7 \times 10^{-3} M$ (well below the equivalent conductance minimum at $0.04 M$), two distinctive effects are noted.¹ One is time dependent and may constitute a relaxation phenomenon. It is present under pulse conditions at the lowest fields we are currently able to observe experimentally,¹ 2.5 v./cm. On application of so small a field, the conductance increases within $1 \mu\text{sec.}$ to a value 2–3% larger than that observed on a commercial bridge at a field less than one-tenth as large and at audiofrequency, 0.2 v./cm. and 1592 c.p.s. After about $10 \mu\text{sec.}$ this time-dependent increase of conductance has diminished to near zero, and conductances comparable within 0.1% to the 0.2 v./cm.–1592 c.p.s. values are observed. It is not yet certain that we have conducted measurements at fields which are sufficiently low to assure constant conductance with changing field, nor has the frequency dependence of the conductance been further investigated, especially at the lower frequencies.

A second effect is even more striking. As the field is increased by factors of ten from the lowest value practical for measurement, the conductance, measured at a given time following the application of the pulse, increases abruptly and quickly reaches a near-limiting value. The effect is many times larger than observed in any previous electrolytic measurements, with the possible exception of studies on certain polyelectrolytes, and is larger than can be accounted for by change in dielectric constant or equivalent conductances of the conducting species using any currently accepted theory for the influence of high fields. The following figures are representative: field, 5×10^0 v./cm.; conductance quotient $\Delta\lambda/\lambda$ (measured at 0.2 v./cm. and 1592 c.p.s.), 2%; 5×10^1 v./cm., 5.2%; 5×10^2 v./cm., 8.5%; 5×10^3 v./cm., 9.8%; 8×10^3 v./cm., 9.9%. These latter measurements employ a constant product of oscilloscope sensitivity and applied pulse voltage. Under these circumstances the first-mentioned time-

(1) Since the bridge employed was designed for fields 10^3 larger than those evidently required in the present studies (see J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, **56**, 999 (1952)), practical limitations on pulse rise time, impedance level, and electrical noise level narrow the range of the present investigation. All of these limitations could be overcome in equipment designed specifically to study the newly observed phenomena.