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Inorganic Coördination Polymers. III. Substitution–Addition Leading to Dimer Formation[1]

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The substitution–addition reactions of excess beryllium(II) and chromium(III) acetylacetonates with diphenylphosphinic acid carried out in melts yield the dimers $[Be(C_5H_7O_2)(OP(C_6H_5)_2O)]_2$ and $[Cr(C_5H_7O_2)_2(OP(C_6H_5)_2O)]_2$ in which the diphenylphosphinate anion acts as a catenating group, rather than a chelating ligand, forming double bridges between the central metallic atoms. Cyclic oligomers are formed in preference to linear polymers under these conditions. The thermal decomposition of these dimers proceeds *via* initial disproportionation to the respective acetylacetonates and $Be(OP(C_6H_5)_2O)_2$ or $Cr(C_5H_7O_2)(OP(C_6H_5)_2O)_2$.

Introduction

Among the ways by which coördination polymers can be made is the route classified as substitution–addition in our general discussion of the synthesis of coördination polymers.[2] This type of reaction is one in which a monomeric coördination compound is converted to a polymer by the substitution of a catenating group for the appropriate number and kind of ligands. A simple example of such a reaction is the replacement of a bidentate ligand with a catenating group. The purpose of the present study is to investigate such a reaction, the substitution of the diphenylphosphinate anion for the acetylacetonate anion. Monomeric coördination compounds selected for treatment with diphenylphosphinic acid were the acetylacetonates of beryllium(II) and chromium(III). On steric grounds it is unlikely that the diphenylphosphinate anion will act as a chelating group with beryllium because chelation would involve a four-membered ring. Four-membered rings are commonly written for octahedral coördination compounds, so there is a possibility that the diphenylphosphinate anion will chelate chromium(III).

Experimental

Reactants.—$Be(C_5H_7O_2)_2$, m.p. 112.0–112.5°, was prepared by the method of Jones.[3] $Cr(C_5H_7O_2)_3$ was in part prepared by the method of Fernelius and Blanch[4] and in part recrystallized from commercial samples procured from MacKenzie Chemical Works. $(C_6H_5)_2P(O)OH$ was prepared as follows. A mixture of 500 g. of technical grade $(C_6H_5)_2PCl$[5] (Victor Division of Stauffer Chemical Company) and 1500 ml. of water was stirred in a 4-l. beaker while 180 g. of NaOH pellets was added in small portions to prevent heating. While the milky slurry was still hot, 30 ml. of 30% H_2O_2 was added. When the temperature began to subside after its initial increase, an additional 20 ml. of 30% H_2O_2 was added, and this procedure was repeated until a clear solution resulted. The pH of the solution was checked periodically and when necessary more base was added to keep the mixture alkaline. While the clear solution was still hot, 1:1 HCl was added dropwise to a pH of 2.0. The crystalline precipitate of crude $(C_6H_5)_2P(O)OH$ (90% yield) was washed thoroughly with water, dried at 105°, and recrystallized from hot ethanol to give an over-all yield of 55% of acid melting at 194–195°; literature values range from 187 to 196°.

Anal. Calcd. for $(C_6H_5)_2P(O)OH$: C, 66.05; H, 5.08; P, 14.20. Found for the recrystallized material: C, 66.02; H, 5.08; P, 14.16.

Reactions.—Initially the reactions of $Be(C_5H_7O_2)_2$ and $Cr(C_5H_7O_2)_3$ with $(C_6H_5)_2P(O)OH$ were carried out in inert solvents, but the reactions were slow and the products did not analyze well. Subsequently the fusion reactions described next were investigated and found to give satisfactory results.

(a) **$Be(C_5H_7O_2)_2$ and $(C_6H_5)_2P(O)OH$.**—An intimate mixture of 14.3 g. (0.0687 mole) of $Be(C_5H_7O_2)_2$ and 10.0 g. (0.0458 mole) of $(C_6H_5)_2P(O)OH$ was heated at a maximum mantle temperature of 100° and 1 mm. pressure for 80 min. During this period some sublimation of $Be(C_5H_7O_2)_2$ was observed. A total of 0.040 mole of $C_5H_8O_2$ was collected in a cold trap. The reaction mass on cooling was extremely viscous and had a light lemon-yellow color. It was dissolved in acetone, and after evaporation of the solvent the residue was extracted in a Soxhlet apparatus with petroleum ether for 96 hr. to remove the excess $Be(C_5H_7O_2)_2$ and $C_5H_8O_2$.

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[1] Presented at the Fourth Delaware Valley Regional Meeting of the American Chemical Society, Jan. 26, 1962. Part II: B. P. Block, R. A. Florentine, J. Simkin, and G. Barth-Wehrenalp, *J. Inorg. Nucl. Chem.*, in press.

[2] B. P. Block and G. Barth-Wehrenalp, *ibid.*, in press.

[3] M. M. Jones, *J. Am. Chem. Soc.*, **81**, 3188 (1959).

[4] W. C. Fernelius and J. E. Blanch, *Inorg. Syn.*, **5**, 130 (1957).

[5] This material has a tendency to adhere to equipment, and it cannot be easily flushed away. We have found that it can be removed by soaking in concentrated nitric acid.

The extracted residue after drying under vacuum weighed 12.7 g. (calcd. 14.9 g.). *Anal.* Calcd. for $[Be(C_5H_7O_2)OP(C_6H_5)_2O]_x$: C, 62.77; H, 5.27; Be, 2.77; P, 9.52. Found: C, 62.75; H, 5.39; Be, 2.5; P, 9.2. Its molecular weight was found to be 671 in $CHCl_3$ by the thermoelectric vapor pressure lowering method[6]; calcd. for $x = 2$: 650.6. The petroleum ether extract on evaporation and drying gave 5.0 g. of impure $Be(C_5H_7O_2)_2$; calcd. excess $Be(C_5H_7O_2)_2$: 4.75 g.

A second reaction run at 75° for 3 hr. at 1.8–2 mm. pressure produced a similar reaction mass. A total of 0.039 mole of $C_5H_8O_2$ was collected. Final extraction of the residue with petroleum ether in a Soxhlet apparatus for 112 hr. gave 7.6 g. of product which analyzed: C, 62.53; H, 5.46; Be, 3.0; P, 9.2. Its molecular weight in C_6H_6 was 661. Permitting the product to stand in petroleum ether longer than the 4-day extraction time caused some dissolution of the product.

(b) **$Cr(C_5H_7O_2)_3$ and $(C_6H_5)_2P(O)OH$.**—Mixtures prepared by grinding $Cr(C_5H_7O_2)_3$ and $(C_6H_5)_2P(O)OH$ together in 1.5:1 to 2:1 mole ratios were heated to 240°. The molten mixture at first bubbled vigorously as $C_5H_8O_2$ evolved, but the rate of bubbling diminished as the reaction approached completion. When the bubbling had practically ceased and ferric nitrate test paper no longer turned red in the vapors, the melt was allowed to cool. Extraction of the cooled melt with absolute ethanol removed excess $Cr(C_5H_7O_2)_3$ and left a dark green crystalline product. *Anal.* Calcd. for $[Cr(C_5H_7O_2)_2OP(C_6H_5)_2O]_x$: Cr, 11.13; C, 56.54; H, 5.16; P, 6.63. Found: Cr, 11.0; C, 56.7; H, 5.2; P, 6.5, after recrystallization from $CHCl_3$. The molecular weight in C_6H_6 was found to be 917 by the thermoelectric vapor pressure lowering method; calcd. for $x = 2$: 934.8. This dimer melts at 275° and begins to decompose at about the same temperature. It is very soluble in $CHCl_3$, fairly soluble in C_6H_6, very slightly soluble in C_6H_6–C_2H_5OH, and insoluble in $(C_2H_5)_2O$.

Thermal Analyses.—Both $[Be(C_5H_7O_2)OP(C_6H_5)_2O]$ and $[Cr(C_5H_7O_2)_2OP(C_6H_5)_2O]_2$ were subjected to our usual thermogravimetric analysis procedure on a modified Chevenard thermobalance in a nitrogen atmosphere at a heating rate of 5°/min.[7] In addition the beryllium compound was subjected to thermogravimetric analysis in a closed-system thermobalance described in an earlier paper[8] both *in vacuo* and under nitrogen and to differential thermal analysis also at 5°/min. in all runs. The heating curves are reproduced in Fig. 1 and 2. The weight fractions remaining for curves A, B, and C in Fig. 1 at the common plateau are 0.708, 0.690, and 0.689, respectively; calcd. for conversion to $Be(OP(C_6H_5)_2O)_2$: 0.682. The weight fraction remaining at the second plateau in curve C is 0.571; calcd. for conversion to $Be_4O(OP(C_6H_5)_2O)_6$: 0.521. The weight fraction remaining at the arrest in the curve in Fig. 2 is 0.574; calcd. for conversion to $Cr(C_5H_7O_2)(OP(C_6H_5)_2O)_2$: 0.626. Composition of residue from the run shown by curve A, Fig. 1: Calcd. for $Be(OP(C_6H_5)_2O)_2$: Be, 2.0; C, 65.0; H, 4.6; P, 14.0. Found: Be, 2.5; C, 62.5; H, 3.7; P, 13.7. The composition of the residue from a run similar to that shown in Fig. 2 but stopped after 24 hr. at 272° was identified as $Cr(C_5H_7O_2)(OP(C_6H_5)_2O)_2$[9] by infrared analysis.

Discussion

The fusion reactions between diphenylphosphinic acid and excess beryllium(II) or chromium(III) acetylacetonate lead primarily to the formation of dimers. Thus the diphenylphosphinate anion does act as a catenating agent with both a tetrahedral and an octahedral central atom. The formation of rings with a tetrahedral element such as beryllium is not surprising (*cf.* $(PNCl_2)_x$ and $(R_2SiO)_x$), but the readiness with which the eight-membered Be–O–P–O–Be–O–P–O ring forms is, in view of the usual decrease in stability of coördination compounds with ring size greater than six.[10] With the octahedral element chromium the formation of a cyclic compound has steric implications. Because there has been no effective rearrangement of the configuration about the chromium atom during the reaction, any coördination-number-five intermediate that might have formed preferentially retains the *cis* relationship of the two positions vacated by the chelating acetylacetonate anion.

Although these reactions have led to dimers rather than polymers, they do support the substitution-addition concept as a potential route to coördination polymers in that bridges between atoms can be established in this fashion. They also indicate that cyclization or double-bridging is a problem which has to be overcome in order to develop linear polymers.

The first material that is volatilized when the beryllium dimer is heated is beryllium(II) acetylacetonate. It starts coming off at 170°, which is approximately the melting point observed for the dimer. The DTA curve shows a major endotherm at this temperature which we associate with the melting of the dimer. The initial reaction when the dimer is heated is a disproportionation to beryllium(II) acetylacetonate and beryllium(II) diphenylphosphinate. It is interesting to note that the DTA curve shows only a broad shallow endotherm for this process, indicating that the disproportionation takes place over an extended

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(6) A. V. Hill, *Proc. Roy. Soc.* (London), **B106**, 477 (1930); R. H. Müller and H. S. Solten, *Anal. Chem.*, **25**, 1103 (1953); and J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

(7) J. R. Soulen and I. Mockrin, *Anal. Chem.*, **33**, 1909 (1961).

(8) J. Simkin and B. P. Block, *J. Inorg. Nucl. Chem.*, **23**, 253 (1962).

(9) B. P. Block, L. R. Ocone, and J. Simkin, *J. Am. Chem. Soc.*, **84**, 1749 (1962).

(10) R. W. Parry in "The Chemistry of the Coördination Compounds," J. C. Bailar, Jr., ed., Reinhold Publishing Corporation, New York, N. Y., 1956, p. 225.

temperature range. The differences between curves A and B in Fig. 1 probably arise from the differences in apparatus for the two runs, whereas the first plateau is reached more rapidly with curve C because the beryllium(II) acetylacetonate volatilizes very readily under vacuum.

The nature of the further steps in the decomposition is not as clear. The decomposition of the beryllium(II) diphenylphosphinate begins at a considerably lower temperature under vacuum than in nitrogen and takes a different course. The second plateau in curve C corresponds fairly well to the formation of $Be_4O(OP(C_6H_5)_2O)_6$, but the analysis of the residue at the third plateau does not indicate the formation of a discrete compound at that point. In addition to the beryllium(II) acetylacetonate recovered, substantial amounts of benzene, acetone, and beryllium(II) diphenylphosphinate were found among the volatile products of the vacuum decomposition. The benzene must arise from decomposition of the diphenylphosphinate anion and the acetone from decomposition of the acetylacetonate anion.

There are only two plateaus observed for the TGA run in nitrogen (curve B, Fig. 1); the second of which does not correspond to a discrete compound. The residue was obviously heterogeneous and contained much carbonaceous material. It is probable that there is not a plateau in curve B corresponding to the second plateau in curve C because $[(C_6H_5)_2P(O)]_2O$ is not volatile at low enough temperatures for it to be removed from beryllium(II) diphenylphosphinate except under vacuum. The third plateau in curve C is then lower at 700° than the second plateau in curve B because there is less diphenylphosphinate anion left to decompose to non-volatile products in the vacuum run. The major endotherm at 594° appears to correspond to the decomposition of the diphenylphosphinate anion.

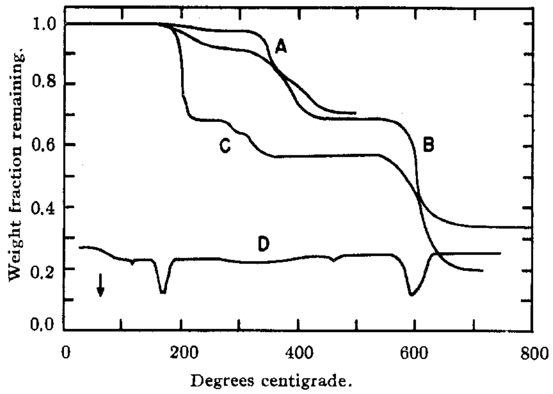

Fig. 1.—Thermal behavior of $[Be(C_5H_7O_2)(OP(C_6H_5)_2O)]_2$: curve A, TGA in closed-system thermobalance with nitrogen atmosphere; curve B, TGA in modified Chevenard thermobalance in nitrogen; curve C, TGA in closed-system thermoblance under vacuum; curve D, DTA with endothermic changes in the direction of the arrow; heating rates 5°/min.

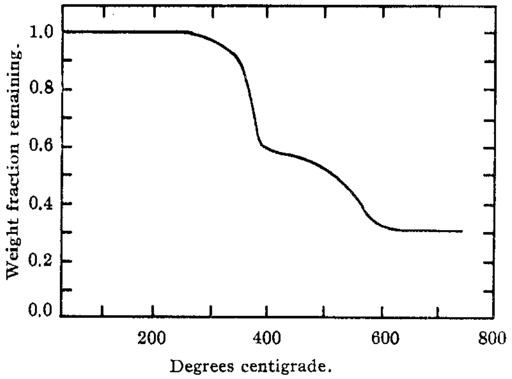

Fig. 2.—TGA of $[Cr(C_5H_7O_2)_2(OP(C_6H_5)_2O)]_2$ in modified Chevenard thermobalance in nitrogen; heating rate 5°/min.

As with the beryllium dimer, the first volatile product collected during the heating of the chromium dimer is the simple acetylacetonate. The weight loss to the first plateau, however, corresponds to the formation of $Cr(C_5H_7O_2)(OP(C_6H_5)_2O)_2$, a composition made by other reactions.[9] This conclusion is confirmed by the infrared spectra of the materials involved. The final residue has reducing power and contains less than two moles of phosphorus per mole of chromium. It is most likely a mixture containing either chromium(II) or phosphorus(III). There is no evidence for the formation of chromium(III) diphenylphosphinate during the heating of the chromium dimer. Thus, although the chromium dimer also disproportionates when heated, there is a difference from the disproportionation of the beryllium dimer in that a simple diphenylphosphinate is not formed during the disproportionation. In both disproportionations, then, the net effect is the transfer of one acetylacetonate from one metal atom in the dimer to the other, *i.e.*

$$[Be(C_5H_7O_2)(OP(C_6H_5)_2O)]_2 \longrightarrow Be(C_5H_7O_2)_2 + Be(OP(C_6H_5)_2O)_2$$

$$[Cr(C_5H_7O_2)_2(OP(C_6H_5)_2O)]_2 \longrightarrow Cr(C_5H_7O_2)_3 + Cr(C_5H_7O_2)(OP(C_6H_5)_2O)_2$$

suggesting that the process is intramolecular.

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Phosphorus Complexes of Group III Acids. II. Infrared Spectra of Boron Complexes of Polycyclic Phosphites

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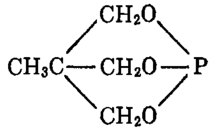
The infrared spectra from 650 to 5000 cm.$^{-1}$ of the polycyclic phosphites, 4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane ($C_5H_9O_3P$) and 1-phospha-2,8,9-trioxaadamantane ($C_6H_9O_3P$) as well as trimethylphosphite and some complexes of these ligands with BF_3, BH_3, BD_3, B_3H_7, and $B(CH_3)_3$ are reported and compared. The boron-phosphorus stretching frequency for these compounds falls in the region from 750 to 870 cm.$^{-1}$. It appears that the polycyclic ligands are better donors toward a BH_3 group than trimethylphosphite.

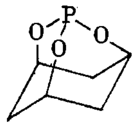
Introduction

While typical stretching modes have been reported for a variety of bond types, only one B–P stretching frequency has appeared in the literature, that of F_3PBH_3.[1] It was felt, therefore, that the following spectral study of some complexes of BH_3, BD_3, B_3H_7, BF_3, and $B(CH_3)_3$ would be of interest. The principal ligands used have been the polycyclic phosphites shown below.



$C_5H_9O_3P$

(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)



$C_6H_9O_3P$

(1-phospha-2,8,9-trioxa-adamantane)

Experimental

The preparation of the BH_3, BD_3, and B_3H_7 complexes of $C_5H_9O_3P$ are described elsewhere.[2] Details of the preparation of the corresponding adducts of $C_6H_9O_3P$ will be reported later.[3]

The boron trifluoride and boron trimethyl complexes were prepared by condensing a stoichiometric quantity of the acceptor onto a frozen 5–10% solution of the ligand in the appropriate solvent.[2,3] The mixtures so prepared were thawed, stirred, and scanned in the spectrometer. In the case of the $B(CH_3)_3$ complex with $C_5H_6O_3P$, a second solution, containing a tenfold excess of the acceptor, was scanned. Boron trimethyl was prepared as described by Brown.[4] Commercially available boron trifluoride from cylinders was purified after the fashion of Brown and Johannesen.[5]

The compound, $(CH_3O)_3PBH_3$, first reported by Reetz,[6] was prepared by the direct combination of diborane and trimethyl phosphite followed by vacuum distillation. A similar procedure was used for the preparation of $(CH_3O)_3PBD_3$.

Spectral grade solvents were used in all cases. For the BF_3 and $B(CH_3)_3$ complexes, the solvents were dried over P_4O_{10} and distilled *in vacuo* into the mixing vessel.

Spectra were scanned with a Perkin-Elmer Model 21 infrared spectrometer in the rock salt region. Where improved resolution was warranted, duplicate spectra were taken with a Beckman IR-7. The compound $C_5H_9O_3$-PBH_3 also was examined with potassium bromide optics in a Perkin-Elmer Model 13 instrument.

Results and Discussion

It is significant that the vibrational frequencies of the polycyclic phosphites are relatively constant in their positions for the derivatives described here. This perhaps is due to the constraint imposed on the configuration of the skeleton in such polycyclic systems. The constancy of the bands of the ligand greatly facilitates the assignment of the new bands due to the acceptor moieties and to the B–P stretching mode. This point is illustrated in the spectra of $C_5H_9O_3P{=}O$ and $[Cu(C_5H_9O_3P)_4]NO_3$, which are shown in

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(1) R. C. Taylor and T. C. Bissot, *J. Chem. Phys.*, **25**, 780 (1956).
(2) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).
(3) J. G. Verkade and C. W. Heitsch, to be published.
(4) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).
(5) H. C. Brown and R. B. Johannesen, *ibid.*, **72**, 2934 (1950).
(6) T. Reetz, *ibid.*, **82**, 5039 (1960).