

In fluorolube suspension we observed $D_{III} = 1.002$ and $E_{III} < 0.002 \text{ cm.}^{-1}$, compatible with a linear molecule. Assuming $\rho_1 = \rho_5 = 0.40$, $\rho_2 = \rho_4 = -0.20$, and $\rho_3 = 0.60$, values somewhat larger than the iso-electronic carbon radical,¹² we compute $D_{III} = 0.97 \text{ cm.}^{-1}$. One reason, among others,⁹ for the larger effective spin densities in II and III is that the two π -radicals may not be independent. An exchange interaction may stabilize structures in which the two unpaired electrons are on the same atom and thus give rise to a larger D . Nitrogen, with its larger effective nuclear charge, would be particularly effective. Spin-orbit terms are also expected to give a positive contribution to the experimental values of D .⁹

In hexafluorobenzene, III gave two lines of characteristic shape⁵ and $E = 0.0033 \text{ cm.}^{-1}$. Since $E \neq 0$, the molecule is bent, presumably about the central carbon. By a procedure analogous to that used for the aromatic methylenes,^{1,13} we conclude that the deviation from linearity is not more than 10–15°. Here the crystalline matrix may be able to induce slight changes in geometry.¹⁴ With diphenylmethylenes such changes were not observed.⁸

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(13) J. Higuchi, *J. Chem. Phys.*, **39**, 1339 (1963).

(14) An alternative explanation of the apparent $E \neq 0$ is a distribution of values of D_{III} , due to different sites in the solvent, but with III still linear.

(15) Drs. A. G. Anastassiou and H. E. Simmons, of the Central Research Department, E. I. du Pont de Nemours and Co., are attempting to observe chemical reactions of I.

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Zinc(II) and Cobalt(II) Phosphinate Polymers with Low-Temperature Flexibility

Sir:

In developing the scope of tetrahedral metal phosphinate polymers,¹ we have introduced a variety of groups on the phosphorus. Preliminary results recently reported on the characterization of cobalt(II) and zinc(II) dibutylphosphinates² prompt us to present at this time some of our key observations on the polymers containing long alkyl side chains. Both of the noteworthy attributes that distinguish these materials from other cobalt(II) and zinc(II) phosphinates, namely, their surprisingly good low-temperature properties and their high intrinsic viscosities in a "good" solvent, were not described.

While many of the phosphinates we have reported in the past¹ are tractable, those that can be fabricated are brittle, glass-like solids at room temperature. We find, however, that zinc(II) and cobalt(II) phosphinate polymers containing long alkyl side chains appear to have

(1) (a) B. P. Block, S. H. Rose, C. W. Schaumann, E. S. Roth, and J. Simkin, *J. Am. Chem. Soc.*, **84**, 3200 (1962); (b) S. H. Rose and B. P. Block, paper presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, p. 11-O.

(2) V. Crescenzi, V. Giancotti, and A. Ripamonti, *J. Am. Chem. Soc.*, **87**, 391 (1965).

very low glass transition temperatures. These are the first double-bridged polymers prepared with good low-temperature properties.

In order to stabilize the amorphous form of these polymers, it is necessary to introduce disorder into their structures. We have accomplished this by making polymers containing two kinds of bridging groups—a class of copolymers which we have termed *hybrid polymers*.^{1b} The low-temperature properties of some of these double-bridged materials compare favorably with those of the better single-bridged polymers. For example, the nitroso rubbers,³ which are promising potential low-temperature elastomers, become brittle at about -50° . In comparison, films of the hybrid polymer of zinc(II) with $\text{OP}(\text{C}_4\text{H}_9)_2\text{O}^-$ and $\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}^-$ bridging groups in 1:1 ratio are flexible to below -80° .

The general procedure we have used to prepare these polymers is to reflux a mixture of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ or $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ with a solution of the stoichiometric amount of the appropriate phosphinic acid or acids in ethanol and recover the polymer by filtration.

Zinc(II) dibutylphosphinate has a molecular weight greater than 10,000 by vapor pressure osmometry in chloroform and intrinsic viscosities in chloroform ranging from 0.35 to 0.7 dl./g. The waxy solid isolated, which gives a crystalline X-ray powder pattern, may be converted into a metastable amorphous form by melting it ($\sim 250^\circ$) and then rapidly cooling it to below room temperature. This amorphous form turns brittle at approximately -40° . On standing at room temperature it gradually turns crystalline.

Anal. Calcd. for $\text{C}_{16}\text{H}_{36}\text{O}_4\text{P}_2\text{Zn}$: C, 45.8; H, 8.6; P, 14.8; Zn, 15.6. Found: C, 45.8; H, 8.7; P, 14.9; Zn, 15.3.

Zinc(II) dioctylphosphinate is similar. Its molecular weight also exceeds 10,000 by vapor pressure osmometry in chloroform, and its intrinsic viscosity is approximately 0.6 dl./g. The waxy solid, found to be crystalline in polarized light, does not completely melt before decomposing and hence is difficult to convert to the amorphous form.

Anal. Calcd. for $\text{C}_{32}\text{H}_{68}\text{O}_4\text{P}_2\text{Zn}$: C, 59.7; H, 10.6; P, 9.6; Zn, 10.2. Found: C, 59.7; H, 10.9; P, 9.6; Zn, 10.1.

Typical samples of the hybrid polymer of zinc(II) with $\text{OP}(\text{C}_4\text{H}_9)_2\text{O}^-$ and $\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}^-$ bridging groups in 1:1 ratio have molecular weights greater than 10,000 in chloroform by vapor pressure osmometry and intrinsic viscosities in chloroform on the order of 0.4 to 0.5 dl./g. The waxy powder, also crystalline in polarized light, melts at approximately 150° to an amorphous form which appears to remain amorphous indefinitely. It can be fabricated into films and other shaped articles at 200° under slight pressure. The molded objects are transparent, very flexible, and exhibit good leathery recovery. They hold their shape at 100° and remain fairly flexible when immersed in Dry Ice.

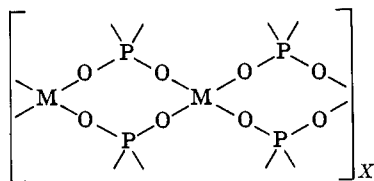
Anal. Calcd. for $\text{C}_{24}\text{H}_{52}\text{O}_4\text{P}_2\text{Zn}$: C, 54.2; H, 9.9; P, 11.6; Zn, 12.3. Found: C, 54.7; H, 10.1; P, 11.6; Zn, 11.9.

The corresponding cobalt(II) polymers are, in general, similar to their zinc(II) counterparts; they have sizable molecular weights by vapor pressure osmometry in chloroform and intrinsic viscosities in chloroform of

(3) J. C. Montermoso, *Rubber Chem. Technol.*, **34**, 1521 (1961):

about 0.4 dl./g. The hybrid polymer of cobalt(II) with $\text{OP}(\text{C}_4\text{H}_9)_2\text{O}^-$ and $\text{OP}(\text{C}_8\text{H}_{17})_2\text{O}^-$ bridging groups in 1:1 ratio may be fabricated into leathery films that remain flexible down to about -60° .

Evidence is now accumulating from X-ray studies^{2,4} to support the double-bridged structure we originally assigned to the poly(metal phosphinates). On first glance it is hard to reconcile this double-bridged structure, *i.e.*



with the low-temperature flexibility observed for the amorphous specimens reported here. However, an examination of Stuart-Briegleb models⁵ of some of these compositions reveals a high order of backbone flexibility since the alkyl side chains provide negligible steric hindrance and the basic eight-membered ring spirane struc-

(4) C. E. Wilkes and R. A. Jacobson, *Inorg. Chem.*, **4**, 99 (1965).

(5) E. Leybold's Nachfolger, Manufacturer.

ture is inherently flexible. In addition, the alkyl side chains tend to shield the polymer from any polar inter-chain attractions present in the metal phosphinates we made earlier. They, furthermore, can create a "flexible sheath around each chain molecule,"⁶ thereby reducing the resistance of the surrounding medium to movement of the polymer molecule.

The magnitude of the intrinsic viscosities observed in chloroform for the compositions reported here is well within the range for organic high polymers. It is interesting to note, however, that in agreement with the observations of Crescenzi, *et al.*,² the intrinsic viscosity of a sample of $[\text{Zn}(\text{OP}(\text{C}_4\text{H}_9)_2\text{O})_2]_x$ in benzene is quite low, although the inherent viscosity at 0.5% is 0.25 dl./g.

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(6) A. H. Willbourn, *Trans. Faraday Soc.*, **54**, 717 (1958).

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Book Reviews

Traité de Biochimie Générale. Tome II. Les Agents des Synthèses et des Dégradations Biochimiques. Second Fascicule. Les Enzymes. By M. JAVILLIER, M. POLONOVSKI, M. FLORKIN, P. BOULANGER, M. LEMOIGNE, J. ROCHE, and R. WURMSER. Masson et Cie, 120 Boulevard Saint-Germain, Paris 6, France. 1964. 753 pp. 17 × 25.5 cm. Broché, 140 F.; cartonné toile, 155 F.

A treatise of general biochemistry is presently written by French biochemists and organic chemists, and the book "Les Enzymes," edited by P. Boulanger and J. Polonovski, is the fourth volume to be published in a series of six volumes. The text covers 714 pages, which are divided into 218 pages describing the constitution of enzymes and the nature of enzymatic reactions and 496 pages describing selected enzymes.

Whereas this book fulfills a definite need for French-speaking biochemists, it is doubtful that its usefulness to American readers will override the language barrier. The only book of similar size on the same subject written in English is the one of Dixon and Webb. In both these books the approach is, however, quite different since Dixon and Webb discuss general principles and use specific enzymes as examples, whereas the present work gives an extensive description of many enzymes. The outlook of "Les Enzymes" is more similar to the series "The Enzymes," published in 1959 by Boyer, Lardy, and Myrbäck, but the latter work covers more than 4000 pages. As judged by the only volume which has appeared at the present time, the volumes dealing with enzymes in the treatise "Comprehensive Biochemistry," edited by Florkin and Stotz, may be quite similar to "Les Enzymes," but they will show a far more extensive coverage of most enzymes.

The main criticism to be addressed to "Les Enzymes" is the excessive amount of space used for glycosidases and related enzymes, as compared to the extremely succinct treatment of the oxido-reduction enzymes. A comparison of "Les Enzymes" with "The Enzymes" shows, respectively, for glycosidases 120 pages versus 180 pages, and for phosphorylases 8 pages versus 55 pages,

but for cytochrome 15 pages versus 140 pages, and for catalase 1 page versus 65 pages. This unusual distribution greatly limits the impetus of this book as a general source of information for English-speaking readers.

The author and subject indexes are extensive, and the book is well printed and bound. The choice of references is as broad and selective as can be expected for a work of this nature, and they are well classified. In the list of important discoveries in enzyme chemistry, the reader may, however, be surprised to see the name of Rabaté as discoverer of the transglycosylation reaction, while the names of the Coris are omitted.

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Mineral Metabolism. An Advanced Treatise. Volume II. Part A. The Elements. Edited by C. L. COMAR, Cornell University, Ithaca, N. Y., and FELIX BRONNER, Hospital for Special Surgery, Cornell University Medical College, New York, N. Y. Academic Press, Inc., 111 Fifth Ave., New York 3, N. Y. 1964. xiv + 649 pp. 16 × 24 cm. \$22.00.

This is the fourth and final volume of a comprehensive, multi-author work on mineral metabolism. The first 247 pages are devoted to a review of the chemical composition of the body, first of the composition of the body as a whole and then as the composition of the organs and tissues, with a short section on distribution of minerals in the body of man. The chapter as a whole affords an exhaustive compilation of data on the composition of the body, with special reference to its mineral content from fetal to adult life, and is a rich source of information and of interpretation.

The remainder of the book deals with the mineral elements (phosphorus, calcium, magnesium, strontium, and fluoride) with special