

The Structure of Zinc(II) n-Butylphenylphosphinate Polymer

By F. GIORDANO, L. RANDACCIO, and A. RIPAMONTI*

(Istituto di Chimica, Università di Trieste, Trieste, Italy)

THE nature and order of organic side-chains have a marked influence on the properties of the coordination polymers containing three-atom bridging phosphinate groups between tetrahedral metal atoms.¹⁻³ Our X-ray analysis of crystals of $[\text{Zn}(\text{Bu}^n\text{PO}_2)_2]_n$ ⁴ and of the mixed ligand species $\{\text{Zn}[(\text{Bu}^n\text{PO}_2)(n\text{-C}_6\text{H}_{13})_2\text{PO}_2]\}_n$ ² has established that these compounds have a backbone structure with alternate single and triple phosphinate bridges between tetrahedral metal atoms. The

same chain-type has been suggested for beryllium phosphinates³ and for the insoluble and high-melting zinc(II) and cobalt(II) diphenylphosphinate polymers.^{2,4} Zinc copolymers, $\{\text{Zn}[(\text{Bu}^n\text{PO}_2)_{2-2x}(\text{Ph}_2\text{PO}_2)_{2x}]\}_n$, richer in diphenylphosphinate groups, have been found to have a basic crystal structure similar to that of the γ -form of $[\text{Zn}(\text{Ph}_2\text{PO}_2)_2]_n$ and of a monoclinic form of $[\text{Zn}(\text{Bu}^n\text{PhPO}_2)_2]_n$.⁵ The crystal structure of the latter compound may provide further insight into the

backbone structure of the less tractable phosphinate polymers.

Crystal data: $C_{20}H_{28}P_2O_4Zn$, $M = 459$, *monoclinic*, $a = 10.16$, $b = 14.08$, $c = 32.59$ Å, $\beta = 96.8^\circ$, $U = 4628$ Å³, $D_m = 1.32$ g.cm.⁻³, by flotation, $Z = 8$, $D_c = 1.32$ g.cm.⁻³. Space group $P2_1/c$ by systematic absences. The structure analysis was based on 2212 Weissenberg intensity data collected with Cu- K_α radiation. The co-ordinates of the zinc and phosphorus atoms were obtained from conventional Patterson technique. The oxygen atoms were located in subsequent three-dimensional Fourier syntheses. However, the carbon atoms of the organic side-chains were revealed only in part because of the disorder due to a random occupation of n-butyl and phenyl groups. Therefore the remaining carbon atoms were located assuming a statistical occurrence of the two different side groups with standard bond angles and lengths. Co-ordinates and anisotropic temperature factors of the atoms of the main chain were then refined by least squares, while positional and isotropic thermal parameters of the carbon atoms were held constant. At present $R = 0.16$ for all observed reflexions. Further refinement is in progress in order to improve the location of the carbon atoms.

The mean values of the skeleton bond lengths and angles calculated at this stage of the refinement are: Zn-O 1.92 (± 0.04) Å; P-O 1.50 (± 0.03) Å; $\angle O-Zn-O$, 109.5 ($\pm 4^\circ$); $\angle O-P-O$, 116.5 ($\pm 2^\circ$); $\angle Zn-O-P$ (single bridge), 151 ($\pm 2^\circ$); $\angle Zn-O-P$ (triple bridge), 137 ($\pm 2^\circ$). The structure consists of polymeric chains parallel to the a axis. Single and triple bridging phosphinate groups alternate between tetrahedral zinc atoms in a similar way to that found in zinc(II) and cobalt(II) di-n-alkylphosphinate polymers.^{2,4} The variation of the identity period along the chain axis from 9.90 to 10.16 Å, when a phenyl group replaces a n-alkyl group bonded to the phosphorus atom, is related to different conformation of the triple-bridged unit. In fact, as shown in the Figure, where the backbone structures established for zinc(II) di-n-alkylphosphinates^{2,4} and phenyl-n-butylphosphinate are compared, the top triplet of oxygen atoms is rotated or not with respect to the bottom triplet. This effect is essentially due to interchain forces, which in turn remove, in the phenyl-n-butyl derivative, the possibility of a

disordered distribution of the two enantiomorphous triple-bridged units of zinc(II) di-n-alkylphosphinates.^{2,4} Thus the crystals of $[Zn(Bu^iPhPO_2)_2]_n$ are more ordered at room temperature than those of $[Zn(Bu^iPO_2)_2]_n$,⁵ in spite of the disorder introduced with the asymmetry of the phosphinate groups in relation to the organic side-chains.

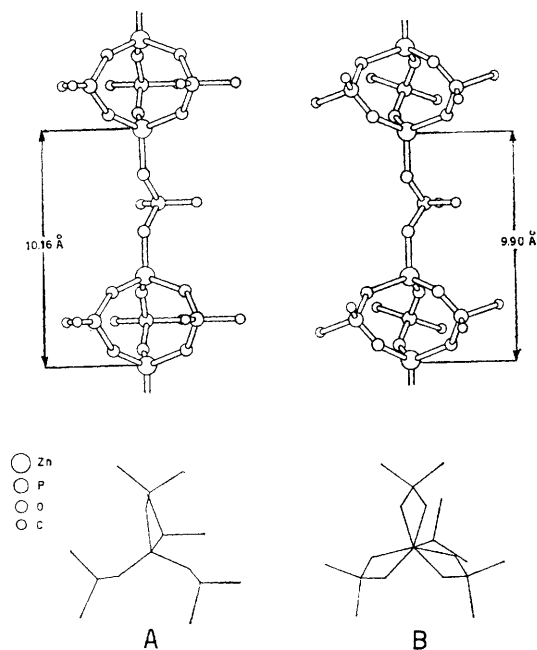


FIGURE. (A), Backbone structure of zinc(II) phenyl-n-butylphosphinate; (B) Backbone structure of zinc(II) di-n-alkylphosphinates. (Only the first carbon atoms of the organic side-groups are shown.)

These results substantiate the earlier hypothesis^{2,4} that the main chains of phenyl derivatives have the same basic structure of zinc(II) and cobalt(II) di-n-alkylphosphinate polymers, the differences in properties being related to the influence of the more bulky phenyl side-groups on the chain flexibility.

We thank the Consiglio Nazionale delle Ricerche, Italy, for financial support.

(Received, October 23rd, 1967; Com. 1133.)

¹ V. Crescenzi, V. Giacotti, and A. Ripamonti, *J. Amer. Chem. Soc.*, 1965, **87**, 391; S. H. Rose and B. P. Block, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1966, **4**, 573; S. H. Rose and B. P. Block, *ibid.*, p. 583; S. H. Rose and B. P. Block, *J. Amer. Chem. Soc.*, 1965, **87**, 2076; V. Giacotti and A. Ripamonti, *Chimica e Industria*, 1966, **48**, 1065.

² V. Giacotti, F. Giordano, L. Randaccio, and A. Ripamonti, *J. Chem. Soc. (A)*, in the press.

³ F. Gemit, V. Giacotti, and A. Ripamonti, *J. Chem. Soc. (A)*, in the press.

⁴ F. Giordano, L. Randaccio, and A. Ripamonti, *Chem. Comm.*, 1967, 19.

⁵ V. Giacotti and A. Ripamonti, to be published.