Backbone Structure of Zinc(II) and Cobalt(II) Di-n-alkylphosphinate Polymers

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ZINC(II) and COBALT(II) di-n-alkylphosphinates represent an interesting class of co-ordination compounds which display polymeric properties in non-co-ordinating solvents and in the solid state.[1,2]

X-Ray fibre photographs of Zn^{II} di-n-butyl-, di-n-hexyl-, and di-n-decyl-phosphinates, which are isomorphous with the related Co^{II} compounds, show the same identity period of 9·90 Å along the fibre axis. On the basis of this value a chain model with double bridging phosphinate groups between tetrahedral metal atoms, similar to that previously suggested for Zn^{II} and Co^{II} dimethyl-, diphenyl-, and methylphenyl-phosphinates,[3] appeared to be stereochemically feasible.[1,2]

After many attempts, single crystals of Zn^{II} di-n-butylphosphinate, suitable for an *X*-ray-diffraction study, were obtained by slow evaporation of the mother liquor resulting from the preparation of the compound in ethanol.[2] From precession photographs, taken with Cu-K_α radiation, the following dimensions of the triclinic unit cell were determined: $a = 17{\cdot}84$, $b = 9{\cdot}90$, $c = 14{\cdot}33$ Å, $\alpha = 93{\cdot}8°$, $\beta = 107{\cdot}2°$, $\gamma = 86{\cdot}0°$. Four formula units, $Zn[(C_4H_9)_2PO_2]_2$ per unit cell give a calculated density of 1·166 g.cm.$^{-3}$ compared with an experimental density of 1·17 g.cm.$^{-3}$. The space group $P\bar{1}$ is consistent with the deduced structure.

The shape of the spots and the pronounced falling-off of the intensities with the Bragg angle indicated that the crystals are disordered. In spite of the poor quality of the crystals, 892 independent reflexions within a 2θ sphere of 60° could be collected using Cu-K_α radiation and their intensities were estimated visually.

Considering that the molecular chains must be parallel to the *b*-axis, which corresponds to the axis of the oriented fibres, the zinc–zinc vectors were easily discernible in the three-dimensional Patterson function. Two chains, which repeat identically after two metal atoms, run through the unit cell. The distances along the *b*-axis between pairs of consecutive Zn atoms are 3·55 and 6·35 Å. An electron-density map based upon signs for the Zn contribution revealed unambiguosly the phosphorus atoms. A near-equilateral triangular arrangement is formed by three P atoms, which are on a plane passing through the middle of the two nearest zinc atoms, whereas the projection of the fourth crystallographically nonequivalent P atom on the *b*-axis lies midway between the two zinc atoms more distant apart. These P positions clearly indicated a chain structure with alternate single and triple bridging phosphinate groups between tetrahedrally co-ordinated metal atoms.

Assuming tetrahedral angles around the zinc and phosphorus atoms and the following values of the bond lengths: Zn–O = 1·95, P–O = 1·50, P–C = 1·80 Å, the chain model, shown in the Figure, with P–O–Zn angles of the single and triple bridges of 145° and 133° respectively, was derived. The triple bridging phosphinate groups form a cage structure built from two eight-membered puckered rings fused together. The top triplet of oxygen atoms is rotated with respect to the bottom triplet. Thus, two isoenergetic enantiomorphous triple-bridged structural units are possible.

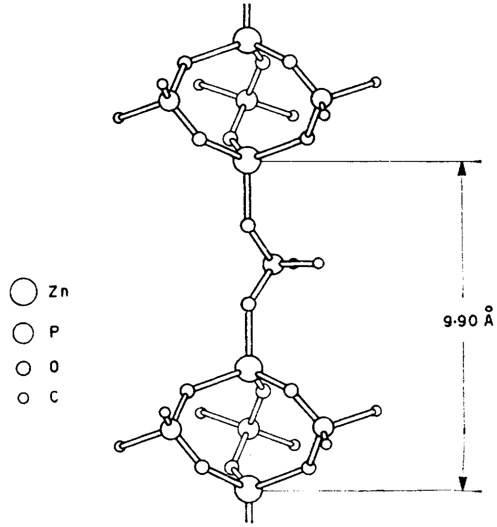

FIGURE. *Backbone structure of* Zn^{II} *di-n-butylphosphinate. Only the first carbon atoms of the alkyl side-groups are shown.*

The calculation of the structure factors for the two enantiomorphous chain models, including Zn, P, O, and the first C atoms of the side-groups with anisotropic temperature-factors for Zn and P atoms, deduced from the electron density distribution, gave almost equal *R*-values of about 0·28 for all observed reflexions. The electron-density maps did not show the location of the oxygen atoms of the triple-bridged structural unit and only slightly revealed the directions of the alkyl side-groups. The inclusion of the missing carbon atoms at calculated positions, assuming a zig-zag planar conformation of the hydrocarbon residues with standard bond angles and lengths and taking into account the best crystal packing, did not improve the agreement between observed and calculated structure factors. Since there is no steric hindrance between two successive triple-bridged units along the chain, a disordered structure with a random distribution of the two enantiomorphous units was tested. An *R*-value of 0·23 was obtained and the three-dimensional difference synthesis was satisfactorily featureless.

Although the disordered structure fits the *X*-ray data better than do the ordered models, further work will be necessary for the establishment of the possible disorder. However, the structure of the main chain with alternate single and triple phosphinate bridges between tetrahedral metal atoms is certain.

The *X*-ray fibre photographs of Zn^{II} di-n-hexyl- and di-n-decyl-phosphinate indicate that the structure of the main chain is not influenced by the length of the alkyl side-groups.[2] Furthermore the characteristic features of the fibre photographs of the copolymers of Zn^{II} containing two kinds of bridging di-n-alkylphosphinate groups, prepared according to Rose and Block,[4] are in agreement with the backbone structure established for Zn^{II} di-n-alkylphosphinates. Therefore, the molecular flexibility and the related properties of these compounds must be connected with the presence of the single bridging phosphinate group between the triple-bridged units. A similar backbone structure, instead of a double-bridged structure,[3] might be assigned to the Zn^{II} and Co^{II} methylphenylphosphinates and to the less tractable dimethyl- and diphenyl-phosphinates. In fact their properties, as compared with those of di-n-alkylphosphinates, can be accounted for reasonably well by this chain model, if one considers that the methyl groups are much less effective in screening the polar intermolecular interactions and that the chain stiffness increases as more bulky phenyl groups are introduced.

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