Dimeric Structure of Zinc(II) and Cobalt(II) Diethyldithiophosphinates in the Solid State

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DIETHYLDITHIOPHOSPHINATES of some divalent ions show in solution a concentration-dependent molecular association process.[1,2] In order to study the structural nature of this association, we have undertaken the crystal structure analysis of zinc(II) and cobalt(II) diethyldithiophosphinates. These compounds are isomorphous in the solid phase.[2] A three-dimensional X-ray analysis has been carried out for the zinc(II) derivative.

The crystals are monoclinic with $a = 10{\cdot}67 \pm 0{\cdot}02$, $b = 31{\cdot}93 \pm 0{\cdot}04$, $c = 12{\cdot}50 \pm 0{\cdot}02$ Å, $\beta = 126{\cdot}7^\circ \pm 0{\cdot}3^\circ$. These data correspond to those previously reported[2] after suitable transformation of axes. For $Z = 8$, $D_c = 1{\cdot}444$ g.cm.$^{-3}$ and $D_m = 1{\cdot}46$ g.cm.$^{-3}$. The possible space groups are $P2_1$ or $P2_1/m$; the former was chosen on the basis of the vector distribution on the Patterson map. This choice was later verified by the successful refinement of the structure.

The structure, based on 3997 independent reflexions collected on equi-inclination Weissenberg photographs with Cu-K_α radiation, was solved with the aid of a Buerger minimum function, which allowed us to locate the Zn atoms and many P and S atoms. A three-dimensional Fourier synthesis phased on these atoms was used to locate the remaining atoms. The refinement to R 0·12 was then carried out by isotropic block-diagonal least-squares analysis.

The results showed that the crystal structure consists of discrete dimeric molecules with distorted-tetrahedral zinc atoms double-bridged by two dithiophosphinate groups. The co-ordination polyhedron of the zinc atoms is completed by dithiophosphinate groups, which behave as chelate ligands to form planar four-membered rings. The two crystallographically non-equivalent dimers viewed along the a-axis are shown in the Figure. At this stage of the refinement the bond lengths and angles in the eight-membered cycles are: Zn–S, 2·33; P–S, 2·03 Å; S–Zn–S, 121·0°; S–P–S, 115·5°; Zn–S–P, 103·6°; and in the four-membered cycles are: Zn–S, 2·42; P–S, 2·02 Å; S–Zn–S, 86·0°; S–P–S, 109·5°; Zn–S–P, 82·1°. If the conformation of the ethyl groups is neglected the dimers have very nearly a two-fold symmetry axis passing through the middle of the two zinc atoms and of the two phosphorus atoms of the eight-membered ring.

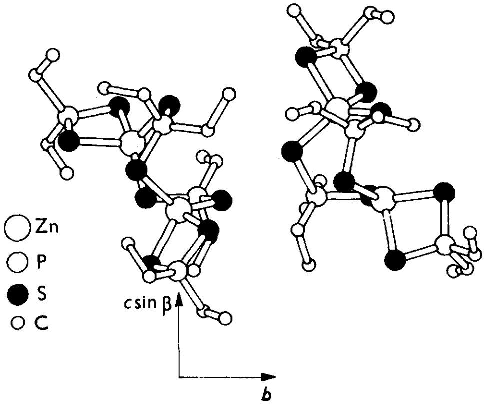

FIGURE. *The two crystallographically independent dimers viewed along the* a*-axis.*

Phosphinate,[3] $R_2PO_2^-$, and monothiophosphinate,[4] R_2PSO^-, groups, in contrast to dithiophosphinate groups, give linear polymers containing alternate triple and single three-atom bridging groups between tetrahedral zinc(II) and cobalt(II) ions. This different behaviour might be due to the ability of the dithiophosphinate groups to act as chelate ligands with tetrahedral metal ions because of the ease with which sulphur undergoes valency-angle deformation relative to oxygen. A similar suggestion was proposed by Coates and Mukherjee[5] to explain the differences in the reaction products of phosphinic, monothiophosphinic and dithiophosphinic acids with trimethyl-gallium and -aluminium.

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