The Structure of Cobalt(II) Diphenylmonothiophosphinate Polymer

By S. BRÜCKNER, M. CALLIGARIS,* G. NARDIN, and L. RANDACCIO

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

and A. RIPAMONTI

(*Istituto Chimico, Università di Napoli, Napoli, Italy*)

THE structure determination of zinc(II) and cobalt(II) thiophosphinates is part of a study of the ability of phosphinate,[1] $R_2PO_2^-$, monothiophosphinate, R_2PSO^-, and dithiophosphinate,[2] $R_2PS_2^-$, groups to act as three-atom bridging groups between metal ions of tetrahedral stereochemistry.

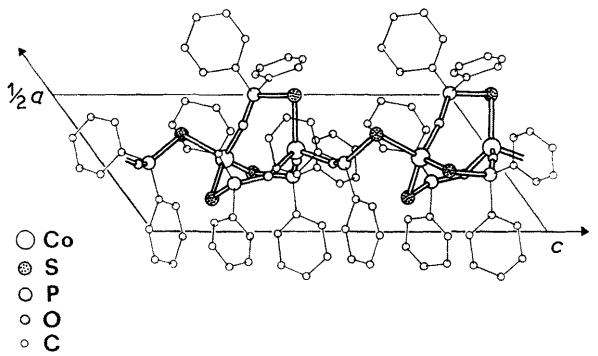

FIGURE. *The repeat unit of the chain as viewed along the* b *axis.*

Zinc(II) and cobalt(II) monothiophosphinates can be obtained as linear polymers, which undergo in solution a concentration-dependent molecular association markedly influenced by the nature of the solvent. A linear structure with double bridging monothiophosphinate groups between tetrahedral metal atoms has been postulated for these compounds.[3] On the other hand, a backbone structure with alternate single and triple bridging phosphinate groups has been established for zinc, cobalt, and beryllium phosphinate polymers.[1] Thus the same chain type could reasonably be suggested for the monothiophosphinate polymers.

X-Ray powder spectra indicate that zinc(II) and cobalt(II) diphenylmonothiophosphinates are isomorphous in the solid phase. We report here the crystal-structure analysis of cobalt(II) diphenylmonothiophosphinate, $Co(Ph_2PSO)_2$. The crystals are monoclinic with $a = 14{\cdot}96 \pm 0{\cdot}03$, $b = 23{\cdot}38 \pm 0{\cdot}04$, $c = 17{\cdot}58 \pm 0{\cdot}03$ Å $\beta = 127{\cdot}8 \pm 0{\cdot}3°$. The space group is $P2_1/n$, $Z = 8$. Three-dimensional data were recorded by the equi-inclination Weissenberg method and 2330 independent reflexions were collected using Mo-K_α radiation.

The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by isotropic block-diagonal least-squares method to the present *R*-value of **0·11.**

The crystal consists of polymeric chains with alternate single and triple bridging monothiophosphinate groups between distorted-tetrahedral cobalt atoms. Two chains, which repeat identically after four metal atoms, run through the unit cell in the [001] direction. A chain viewed along the *b*-axis is shown in the Figure. One of the two crystallographically independent cobalt atoms is surrounded by one sulphur and three oxygen atoms, whereas three sulphur and one oxygen atoms are arranged around the other cobalt atoms.

At this stage of the refinement the mean values of the skeleton bond lengths and angles are: Co–S, 2·33 (±0·02) Å; Co–O, 1·96 (±0·02) Å; P–S, 2·01 (±0·01) Å; P–O, 1·51 (±0·01) Å; S–P–O, 115·7° (±4·0)°. The values of the Co–O–P and Co–S–P angles range from 139·9° to 153·3° and from 88·7° to 106·2°, respectively. The angles around the cobalt atoms range from 96·1° to 123·0°.

We acknowledge financial assistance from the Consiglio Nazionale delle Ricerche, Roma, Italy.

(*Received, March 17th,* 1969; *Com.* 386.)

[1] F. Giordano, L. Randaccio, and A. Ripamonti, *Chem. Comm.*, 1967, 19, 1239; V. Giancotti, F. Giordano, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.* (*A*), 1968, 757; V. Giancotti, F. Giordano, and A. Ripamonti, *Makromol. Chem.*, 1968, **120**, 96.
[2] M. Calligaris, G. Nardin, and A. Ripamonti, *Chem. Comm.*, 1968, 1014.
[3] W. Kuchen and H. Hertel, *Chem. Ber.*, 1968, **101**, 1991.