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Crystal Structure and Physico-Chemical Properties of Bis(μ-Methylphenylphosphinato) Zinc(II)·Dioxane $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n \cdot nC_4H_8O_2$

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The structure of $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n \cdot nC_4H_8O_2$ *has been determined by three dimensional single-crystal X-ray techniques. This polymer crystallizes in the space group* $P4_2/m$ *with two formula units in a cell of dimensions* a = *10.725(4)* Å, c = *9.229(4)* Å, V = *1061.6* Å^3 *and* d_c = *1.45 g/ml. Least-squares refinement of 432 independent reflections gives a final* R *factor of 3.6%. The structure consists of polymeric chains of tetrahedral zinc atoms linked by double phosphinate bridges. The Zn–Zn distance is 4.614* Å. *The dioxane molecules are distributed between the chains at normal Van der Waals distances. IR and NMR evidence suggests that the amorphous form of the parent polymer* $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$ *has essentially the same backbone structure.*

Introduction

The earlier structural studies on zinc(II) bis(phosphinates), which were mostly done on fibers and disordered crystals [1–4], found them to contain linear chains of tetrahedrally coordinated metal atoms linked by alternating single and triple O,O′ symmetrically bridging phosphinate groups. A double bridge structure for zinc phosphinates with particularly bulky phosphinate groups has also been postulated based on X-ray fiber studies [5]. In more recent single crystal studies a copper(II) bis(phosphinate) [6] and a lead(II) bis(phosphinate) [7], were shown to contain double OO′ symmetrically bridging phosphinate groups.

Three forms of $\{Zn[OP(CH_3)(C_6H_5)_2O]_2\}_n$ have been isolated [8], which include one soluble amorphous form (designated α) and two insoluble crystalline forms (designated β and γ). The melt indices and the molecular weight of the soluble form indicates a polymeric structure. Both crystalline forms convert to the amorphous form upon heating above their melting points and some amorphous samples convert to the γ crystalline form on standing.

Experimental

Materials

The preparation of the three forms of $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$ has been described earlier [8]. For this study the α and β forms were both obtained as a precipitate from the reaction of two equivalents of $(CH_3)(C_6H_5)P(O)OH$ with one equivalent $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 95% ethanol. The γ form crystallized from a concentrated benzene solution of the α form which had been stored for several months. Samples of the α form were also obtained by heating the β and γ forms above their melting point.

Crystals suitable for X-ray analysis were obtained by vapour diffusing dioxane into a water solution of the amorphous form (α form) of $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$.

Physical Measurements

Infrared spectra were recorded with both Perkin-Elmer 337 and 621 spectrophotometers on Nujol mulls between KBr disks. The DSC curves were obtained with a DuPont DSC cell module and the DuPont 990 thermal analyzer. A Varian HR-60 NMR spectrometer was used for the NMR spectra.

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TABLE I. Crystal Data for $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n \cdot nC_4H_8O_2$.

a = 10.725(4) A	μ(MoKα)	=	1.89 cm^{-1}
c = 9.229(4)	Mol. wt.	=	463.75 (n = 1)
V = 1061.6 A^3	d_c	=	1.45 g/ml
Z = 2	d_m	=	1.44 g/ml
Space Group: $P4_2/m$	R	=	0.036
	R_W	=	0.039

Collection of the Intensity Data

A colourless needle with approximate dimensions 0.10 X 0.10 X 0.30 mm was selected and mounted on a Philips automatic diffractometer. The unit-cell parameters and other crystal data are reported in Table I. The 432 independent reflections with $I > 2.5\sigma(I)$, collected with the ω–2θ technique in the range $4 < 2\theta < 50°$ were used for the structure determination and refinement. The standard deviation $\sigma(I)$ of the corrected intensity I was taken as $[P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (0.01\ I)^2]^{1/2}$, where P is the total integrated peak count, B_1 and B_2 are the background counts, T_p and T_b are the count times on the peak and background respectively and 0.01 I is an empirical correction for unrealistically small standard deviations in strong reflections. Two reflections, 1 2 0 and –1 – 2 0, monitored periodically, did not show any appreciable variation in intensity during data collection, although slight efflorescence of the crystal was noted, probably due to a superficial loss of dioxane.

Intensities were corrected for Lorentz-polarization effects; absorption corrections were not applied. A ψ scan on a few reflections showed a maximum deviation of 3% in intensity.

Structure Solution and Refinement

The structure was initially solved in the space group $P4_2$ by means of Patterson and Fourier syntheses which gave the positions of all the non-hydrogen atoms. During the least-squares refinement of the structure the presence of high correlation coefficients between several atomic parameters, which resulted in abnormally large standard deviations, convinced us of the existence of a mirror plane perpendicular to the fourfold screw axis at z = 0.

In $P4_2/m$ the structure quickly refined at an R factor of 0.042 with anisotropic temperature factors for all the non-hydrogen atoms. The dioxane molecules showed a disordered distribution around the $2/m$ equivalent position, with the four carbon atoms lying in the mirror plane and the oxygen atoms out of the plane with a site occupation factor of 0.5. A difference Fourier synthesis calculated at this point showed the positions of all the independent hydrogen atoms, save for one methyl hydrogen atom. Inclusion of these atoms with a temperature factor $U = 0.06$ Å^2, followed by one more least squares cycle on the non-hydrogen atoms, gave final agreement factors R and R_W of 0.036 and 0.039, respectively. R_W is defined as $[\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{1/2}$. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$ with weights $w = K/(\sigma^2(F) + 0.01\ F^2)$, with standard deviations on F from counting statistics and K a variable scale factor.

All the calculations were performed with the set of programs SHELX-76 [9] with coefficients for analytical approximation to the scattering factors and anomalous dispersion corrections from the International Tables [10]. The molecular plot and the

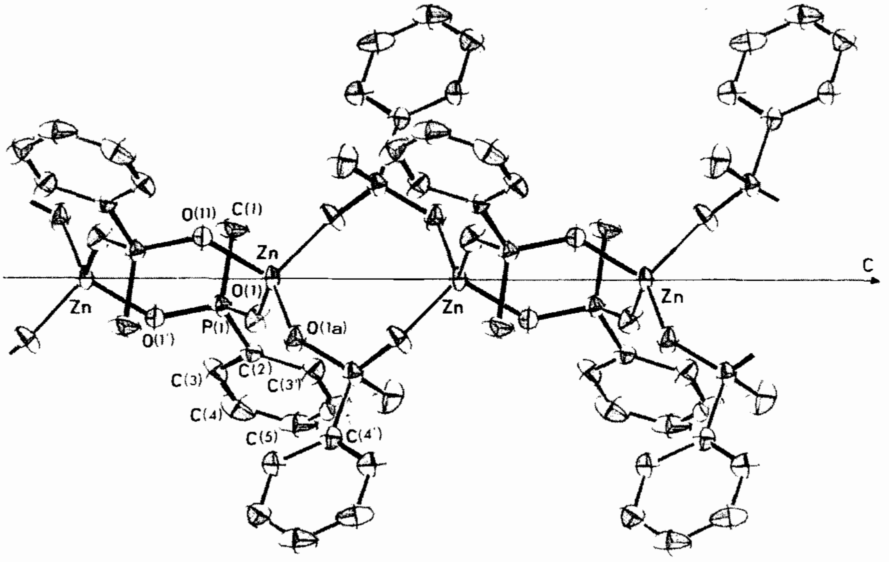

Fig. 1. ORTEP drawing showing the polymeric chain of bis(μ-methylphenylphosphinato)zinc(II)·dioxane.

TABLE II. Positional Parameters (×10^4), Thermal Parameters^a (Å × 10^3) and Estimated Standard Deviations for the Atoms of $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n \cdot nC_4H_8O_2$.

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	0	0	2500	51(1)	51(1)	24(1)	0	0	0
P(1)	667(2)	1932(2)	0	44(2)	52(2)	35(1)	–4(1)	0	0
O(1)	905(4)	1215(4)	1379(5)	65(3)	75(3)	42(3)	–18(2)	–6(2)	20(2)
C(1)	–880(10)	2497(11)	0	44(7)	102(10)	95(9)	35(7)	0	0
C(2)	1726(8)	3241(8)	0	34(5)	48(6)	48(5)	5(5)	0	0
C(3)	2138(7)	3758(6)	–1307(8)	62(5)	52(5)	61(4)	1(4)	16(4)	1(4)
C(4)	2923(8)	4778(7)	–1283(10)	78(6)	57(5)	103(7)	–5(5)	29(5)	13(5)
C(5)	3329(11)	5279(12)	0	53(8)	58(8)	154(13)	–4(6)	0	0

Atom	x/a	y/b	z/c	U	Atom^b	x/a	y/b	z/c
O(2)	–4299(10)	1128(10)	284(18)	91(4)	H(1)	–1165	3099	–737
C(6)	–5653(26)	1235(31)	0	240(14)	H(3)	1917	3176	–2354
C(7)	–3726(27)	–24(19)	0	193(9)	H(4)	3219	5080	–2439
					H(5)	3994	6059	0
					H(6)	–5590	1014	621
					H(7)	–4028	–201	1006

^{a}Anisotropic Thermal Factors are of the forms $\exp(-2\pi^2({}^3\Sigma_{i=1}{}^3\Sigma_{j=1} h_i h_j a_i^* a_j^* U_{ij}))$. ^{b}The isotropic Thermal Factor for the Hydrogen Atoms was fixed at a value of 0.06 Å^2.

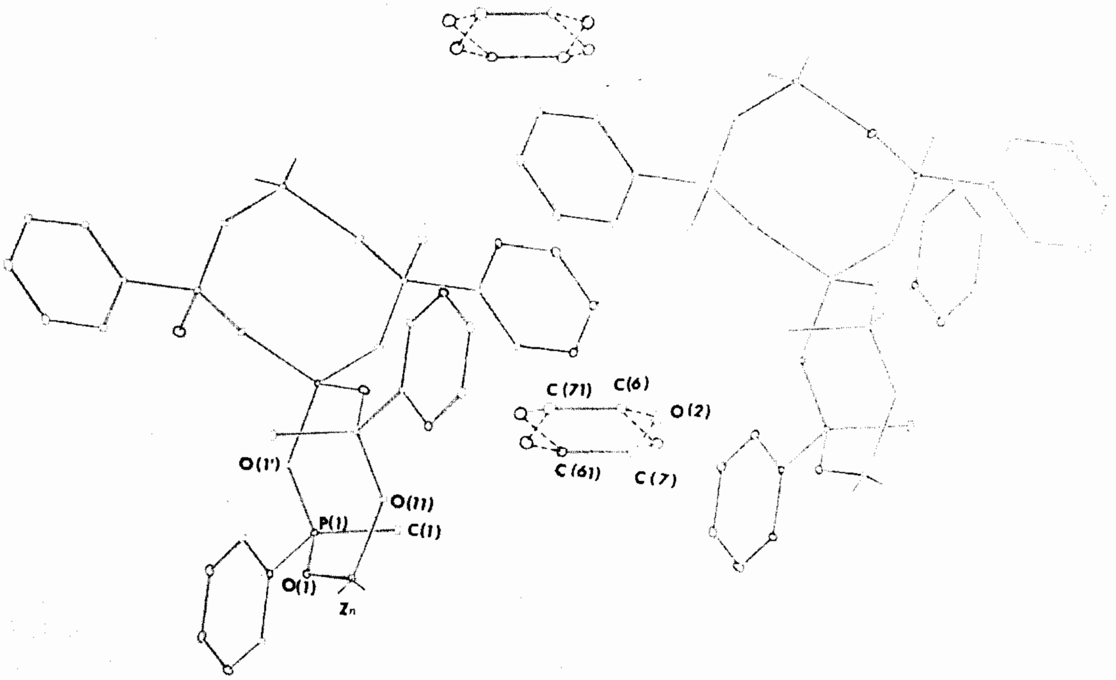

Fig. 2. Packing of the chains in bis(μ-methylphenylphosphinato) zinc(II) showing also the positions of the dioxane molecules.

packing diagram were produced by ORTEP [11]. Final atomic coordinates and thermal parameters with estimated standard deviations obtained from the least-squares calculations are reported in Table II.

Description of the Structure

The structure of bis(μ-methylphenylphosphinato)-zinc(II)·dioxane is similar to that of bis(μ-diphenylphosphinato)lead(II) [7] and bis(μ-dibutylphosphinato)copper(II) [6]. It consists of polymeric

TABLE III. Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses.

a) Phosphinate			
Zn–Zn	4.614		
Zn–O(1)	1.926(4)	O(1)–Zn–O(11)	115.0(3)
		O(1)–Zn–O(1a)	106.8(1)
		Zn–O(1)–P(1)	135.4(3)
O(1)–P(1)	1.508(4)	O(1)–P(1)–O(1′)	115.0(4)
P(1)–C(1)	1.767(10)	O(1)–P(1)–C(1)	109.5(3)
P(1)–C(2)	1.806(9)	O(1)–P(1)–C(2)	106.8(2)
		C(1)–P(1)–C(2)	108.9(5)
C(2)–C(3)	1.399(8)	P(1)–C(2)–C(3)	120.4(4)
C(3)–C(4)	1.381(9)	C(3)–C(2)–C(3′)	119.2(8)
C(4)–C(5)	1.371(10)	C(2)–C(3)–C(4)	119.5(7)
		C(3)–C(4)–C(5)	121.2(9)
		C(4)–C(5)–C(4′)	119.5(11)
b) Dioxane			
O(2)–C(6)	1.480(29)	C(6)–O(2)–C(7)	117.7(15)
O(2)–C(7)	1.404(25)	O(2)–C(6)–C(71)	120.2(37)
C(6)–C(71)	1.459(27)	O(2)–C(7)–C(61)	116.9(35)

chains running parallel to the fourfold screw axis with the phosphinato groups forming double bridges between the zinc atoms (Fig. 1). The dioxane molecules are distributed in cavities between the chains and at normal Van der Waals distances (Fig. 2). Owing to disorder around the 2/*m* equivalent positions. It cannot be stated whether they assume the boat or the chair conformation. The coordination around the zinc atom is an almost regular tetrahedron with S_4 crystallographic symmetry. The planes of symmetry normal to the fourfold screw axis pass through the phosphorus atoms and the methyl carbon atoms, bisecting the phenyl rings. Bond lengths and angles in the structure are in agreement with the values from analogous metal phosphinates (Table III) [6, 7].

The Zn–Zn distance along the fourfold screw axis is 4.614 Å which is somewhat shorter than the Cu–Cu distance in bis(μ-dibutylphosphinato)copper(II) (4.938 Å). Since bond lengths and angles in the phosphinato bridge are essentially unaltered in the two structures, the shortening of the metal–metal distance along the chain must be attributed to the increased values of the O–M–O angles which are much closer to the tetrahedral values in the present structure.

Previous workers have suggested [3] a structure containing alternating single and triple phosphinato bridges for $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$; however, this work clearly shows that it is possible to have a double bridged structure. It is also possible for the various modifications of the pure polymer to have structures that differ from each other and from that of the dioxane adduct. The X-ray powder patterns of the β and γ forms of the pure polymer are clearly different from one another [8] and from that of the dioxane adduct, but it cannot be said whether this difference is due to single triple *vs.* double bridging or to chain packing such as in the orthorhombic and monoclinic forms of $\{Zn[OP(CH_3)(C_4H_9)O]_2\}_n$ [2]. In our opinion the IR spectra which will be discussed below suggest that the dioxane adduct and amorphous form have the same backbone structure.

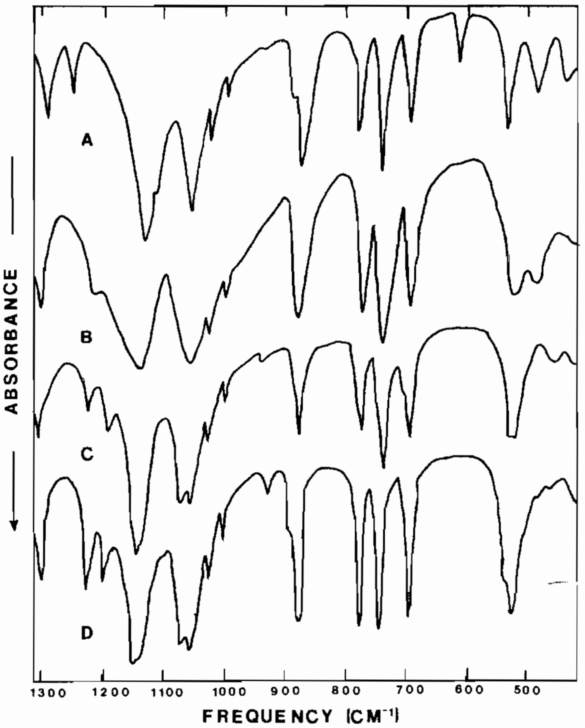

Fig. 3. Infrared spectra of $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$ in Nujol mull. (A) Dioxane adduct: (B) Amorphous α form; (C) Crystalline γ form; (D) Crystalline β form.

Physical Properties and Structural Isomerism

The infrared spectra of the three forms of $\{Zn[OP(CH_3)(C_6H_5)O_2\}_n$ and its dioxane adduct are presented in Fig. 3. All contain two strong PO_2 stretching bands at *ca.* 1135 and 1060 cm^{-1}. The position and separation of these bands is indicative of symmetrical O,O′ bridging phosphinate groups [12, 13]. In the spectrum of the amorphous form these bands are very broad whereas they are sharp in the spectra of the crystalline forms. Some differences in the spectra of the various forms occur in the 1200–1300 cm^{-1} region; however, these bands are very weak and are probably overtones or combination bands. The most significant differences in these spectra are in the M–O stretching region. The amorphous form and the dioxane adduct both have

TABLE IV. NMR Results for $CH_3(C_6H_5)P(O)OH$ and $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$ in Chloroform.

Compound	Nuclei	δ (PPM)[a]	J(CPS)
$(CH_3)(C_6H_5)P(O)OH$	^1H	1.61^b 7.49^c 7.84^c	14.3^b
$\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$	^1H	1.32^b 7.21^c 7.7^c	14.6^b
$(CH_3)(C_6H_5)P(O)OH$	^{31}P	-43.5^d	14.5 ± 0.5
$\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$	^{31}P	-36.0^e	14.5 ± 0.5

[a] Relative to $(CH_3)_4Si$ (internal) and 85% H_3PO_4 (external). [b] Doublets due to CH_3. [c] Overlapping doublets due to C_6H_5. [d] Quartet. [e] Quartet slightly broader than in spectrum of free acid.

TABLE V. Transition Temperatures and Energies of $\{Zn[OPRR'O]_2\}_n$.

$\{Zn[OPRR'O]_2\}_n$			Endotherm Transition Temp. °C	Type of Transition[a]	ΔH Kcal/Mole	Ref.
Form	R	R'				
α	CH_3	C_6H_5	90	A → M	⩽0.9	
β	CH_3	C_6H_5	185	C → M	5.6	
γ	CH_3	C_6H_5	210	C → M	5.3	
Dioxane Adduct	CH_3	C_6H_5	113	C → M + Dioxane	133	
	C_4H_9	C_4H_9	170	C → M	3.3	14
	C_8H_{17}	C_8H_{17}	145	C → P	3.0	14
α	C_4H_9	C_6H_5	168	C → P	5.2	15
γ	C_4H_9	C_6H_5	167	C → P	3.1	15

[a] A-Amorphous; C-Crystalline; M-Melt; P-Paracrystalline melt.

two bands in this region, one at 525 cm^{-1} and one at 485 cm^{-1}. On the other hand the γ form of $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$ has only one symmetrically split band centered at 525 cm^{-1} and the β form has an unsymmetrical band at the same frequency. The similarities of the spectra of the amorphous form and the dioxane adduct suggest a similar structure for these two forms.

The ^{31}P and proton magnetic resonance spectra for $(CH_3)(C_6H_5)P(O)OH$ and the amorphous form of $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$ were recorded and the results appear in Table (IV). Except for the chemical shifts the only other difference between the spectra of the acid and the zinc polymer is a slight broadening of the ^{31}P resonance in the spectrum of the polymer. One would expect that if the polymer had two types of bridging phosphinate groups, as in the single triple bridged structure, additional splitting of the ^{31}P resonance would be observed. Unfortunately, the absence of this splitting does not prove double bridging.

The DSC thermograms of the three forms of $\{Zn[OP(CH_3)(C_6H_5)O]_2\}_n$ were each found to contain one irreversible endotherm (see Table V). The initial heating of the α form produced one weak endotherm at 90 °C, whereas reheating this sample as well as samples of the α form obtained from melting β and γ samples, produced barely detectable endotherms at similar temperatures. This transition may be due to the transformation of small regions of crystallinity into the amorphous form, since in the initial heating the transition energy differed drastically from sample to sample.

As expected the β and γ form melt at much higher temperatures and with greater enthalpy than the α form. No paracrystalline form was observed for either the β or γ forms as has been found in a number of other zinc phosphinates [14, 15]. It was not possible to crystallize either form from the melt, even with extremely slow cooling (*i.e.* 1°/hr). Some transition energies and temperatures which have been observed for other zinc phosphinates also appear in Table V for the purpose of comparison. The transition energies for the fusion of the crystalline forms of the methyl phenyl polymer are higher than any previously reported fusion enthalpy, however, the α form of $\{Zn[OP(C_4H_9)(C_6H_5)O]_2\}_n$ converts to a paracrystalline form with only slightly lower ΔH_f.

The dioxane adduct has one endotherm at 113 °C and its TGA shows a weight loss of 18% at this temperature. This corresponds to the loss of one dioxane per $Zn[OP(CH_3)(C_6H_5)O]_2 \cdot$dioxane at this temperature.

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