brational frequencies $\tilde{\nu}$(V=O) are observed in the region of 940–1000 cm^{-1}.[3] The water exchange of $VO(H_2O)_5^{2+}$ was investigated[4] and found to be consistent with four equatorial water ligands exchanging at a rate of 550 s^{-1} and one weakly bound axial water exchanging too fast on the NMR time scale.

In contrast, solid titanium(IV) oxo complexes are rarely found to exhibit a true titanyl (Ti=O) moiety.[1,2,5] Some exceptions, however, exist: TiO(porphyrin),[6] TiO(phthalocyanine),[7] $(R_4N)_2TiCl_4O$,[8] $TiO(edtaH_2)(H_2O)$,[9] and salts containing $[TiOF_5]^{3-}$.[10] These compounds exhibit a Ti=O bond length of 1.62 Å for the porphyrin or $\tilde{\nu}$(Ti=O) at 972, 975, 950, and 890–920 cm^{-1}, respectively, for the remaining four.

Acidic aqueous solutions of titanium(IV) were shown[11] to contain species with a charge of 2+, TiO^{2+} or $Ti(OH)_2^{2+}$. On the basis of electron-transfer[11,12] and ligand substitution[13] reactions, Sykes and co-workers obtained evidence of the existence of TiO^{2+}. However, they[12] were not able to detect $\tilde{\nu}$(Ti=O) in 2 M $HClO_4$ by Raman solution spectroscopy. This study reports on the Raman solution spectra of titanium(IV) in aqueous $HClO_4$ and HCl and provides clear information about its structure.

Experimental Section

Preparation of the Solutions. A solution of $VO(ClO_4)_2$ (0.12 M) in $HClO_4$ (0.36 M) was prepared as described in the literature.[14] Solutions of $TiO(ClO_4)_2$ and $TiOCl_2$ in $HClO_4$ (0.2, 2.0 M) and HCl (2 M) respectively were prepared by addition of respective solutions of $Ba(ClO_4)_2$ and $BaCl_2$ to acidic solutions of titanyl sulfate (Tioxide) that was analyzed to contain 46.4% SO_4^{2-} and 19.7% Ti (gravimetry) or 19.2 ± 0.2% Ti (ICP and RFS).

Physical Measurements. The Raman spectra were measured on a Spex 1401 spectrophotometer using an argon ion laser (λ = 514.5 nm, 0.8 W).

Results and Discussion

An aqueous solution of VO^{2+} (0.12 M) in perchloric acid (0.36 M) exhibits—in addition to the modes of ClO_4^-—a polarized Raman band at 997 cm^{-1}, which is undoubtedly due to $\tilde{\nu}$(V=O) as in the solids.[1,2]

Sykes et al.[12] reported the failure to detect $\tilde{\nu}$(Ti=O) in the Raman solution spectrum of $TiO(ClO_4)_2$ (0.05 M $TiO(ClO_4)_2$ in 2 M $HClO_4$). We found, however, that the Raman spectra of similar solutions (0.08 M $TiO(ClO_4)_2$ in 2 M $HClO_4$) exhibited a weak shoulder at $\tilde{\nu}$ = 975 cm^{-1} close to the strong A_1 mode of ClO_4^-. In 0.2 M $HClO_4$ the shoulder appeared very distinctively, but colloidal TiO_2 particles were already formed and gave rise to strong Rayleigh scattering. In HCl (2 M), $\tilde{\nu}$(Ti=O) was easily detected as a broad band at 975 cm^{-1}. The $\tilde{\nu}$(Ti=O) vibration is polarized as well as the A_1 mode of ClO_4^-, and its frequency does not depend on the concentration and nature of the acid, although chloro complexes of TiO^{2+} are likely to be formed to some extent. No other bands (except those of ClO_4^-) were detected in the region of 300–1200 cm^{-1}.

A hypothetical (cis or trans) $Ti(OH)_2^{2+}$ complex is expected to give rise to $\tilde{\nu}$(Ti—OH) at ca. 500 cm^{-1}, since $\tilde{\nu}(M^{IV}—OH)$ of $Sn(OH)_6^{2-}$, $Pt(OH)_6^{2-}$, and $Pb(OH)_6^{2-}$ are reported[15] to occur around 500 cm^{-1}. Thus the vibration at 975 cm^{-1} is certainly not due to $\tilde{\nu}(Ti^{IV}—OH)$.

The IR spectra[10] of $NaK_2[M^{IV}OF_5]$ salts (M = Ti, V) are very similar. The $\tilde{\nu}$(M=O) frequencies were found to be 943 and 920 cm^{-1} for M = V and Ti, respectively. Substitution of V^{IV} by Ti^{IV} causes a shift (23 cm^{-1}) of $\tilde{\nu}$(M=O) to lower energies. Exactly the same shift is observed when V^{IV} is substituted by Ti^{IV} in aqueous $MO(H_2O)_5^{2+}$ complexes.

The solid $(NH_4)_2[TiO(C_2O_4)_2]\cdot H_2O$ is known[16] to form a tetrameric ring with cis-(–Ti–O–) units. Solutions of $K_2[TiO(C_2O_4)_2]\cdot H_2O$ (0.1 M) in $H_2C_2O_4$ (ca. 0.06 M) do not exhibit a polarized Raman band around 950 cm^{-1}. Obviously the (oxalato)titanates do not contain Ti=O moieties also in solution and, consistent with Clark's[2] statement, the Ti=O unit is observed rather exceptionally.

Acknowledgment. Titanyl sulfate (with analytical data) was donated by Dr. D. Urwin from British Tioxide UK Limited. The Raman spectra were recorded at the Department of Physics with Prof. Dr. P. Cornaz's advice. The ICP and RFS analyses were carried out by Prof. Dr. B. Magyar.

Registry No. $TiO(ClO_4)_2$, 13637-79-1; TiO^{2+}, 12192-25-5.

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Structure of Polymeric Zinc Phenoxyisobutyrate

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In an investigation of the mode of interaction of the divalent metal ions with the phenoxyalkanoic acids, which include the commercial auxin herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 4-chloro-2-methylphenoxyacetic acid (MCPA), and their 2-propionic acid analogues, the structural systematics of a number of the metal complexes have been determined by single-crystal X-ray diffraction.[1,2] So far, the zinc complexes[1,3] have been monomers unlike a number of zinc carboxylates that form polymer struc-

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Table I. Crystal Data and Details of the Data Collection for $[C_{100}H_{114}O_{32}Zn_5]_n$ at 20 °C

fw = 2154.8
a = 37.78 (1) Å
b = 13.596 (5) Å
c = 20.708 (6) Å
β = 103.90 (2)°
V = 10325 (5) Å^3
Z = 4
d_{calcd} = 1.385 g cm^{-3}
d_{obsd} = 1.37 g cm^{-3}
λ(Mo Kα) = 0.71069 Å
μ(Mo Kα) = 12.6 cm^{-1}
F(000) = 4480

monoclinic; space group $C2/c$
systematic absences: hkl for $h + k$ = odd and $h0l$ for l = odd
cryst size: 0.08 × 0.10 × 0.20 mm
no. of unique reflns: 6552
colln range: 3° < 2θ < 45°; $h,k,\pm l$
scan type, speed: θ–2θ, 2.20–8.37° min^{-1}
no. of obsd data: 2089 [$I > 2.0\sigma(I)$]

tures.[4] Diaquabis(phenoxyacetato)zinc(II) (and its isomorphous 4-chloro-substituted analogue)[1] has distorted skew-trapezoidal-bipyramidal six-coordination involving two asymmetric bidentate carboxylates and two trans-related waters. In contrast, zinc 2,4-dichlorophenoxyacetate trihydrate has both octahedral [Zn(2,4-D)$_2$(H$_2$O)$_4$] and tetrahedral [Zn(2,4-D)$_2$(H$_2$O)$_2$] metal complex centers.[3]

Preliminary X-ray analysis of the title compound, $[Zn_5(PIBA)_{10}(H_2O)_2]_n$ (**1**), prepared from 2-methyl-2-phenoxypropionic acid (phenoxyisobutyric acid: PIBAH) indicated the possibility of a polymer with 20 formula units [as Zn(PIBA)$_2$] in the unit cell. This, together with a substoichiometric amount of water in the formula, prompted a single-crystal X-ray examination. Also of interest were the comparative structural features of the PIBA ligands and those of the uncomplexed acid.[5]

Experimental Section

Compound **1** was prepared by a previously described method[1] by reacting a boiling aqueous ethanolic solution of PIBAH with excess zinc(II) carbonate. After removal of the unreacted carbonate by vacuum filtration, the solution was partially evaporated at room temperature, yielding colorless pseudo-hexagonal-prismatic crystals, suitable for X-ray examination. The IR spectrum showed a sharp maximum at 3440 cm^{-1}, consistent with coordinated water, and the elemental analysis was verified in the structure determination of the formula as $[Zn_5(PIBA)_{10}(H_2O)_2]_n$. Anal. Calcd for $C_{100}H_{114}O_{32}Zn_5$: C, 55.7; H, 5.33; Zn, 15.2. Found: C, 55.7; H, 5.36; Zn, 15.2.

A crystal specimen, mounted about the b crystal axis [perpendicular to the prism (c) axis], was used for both the preliminary X-ray examination and for the collection of intensity data. A Nicolet R3m four-circle diffractometer equipped with a graphite-monochromatized Mo Kα X-radiation source was used for data collection. Accurate cell parameters were obtained from least-squares refinement of 15 high-angle reflections. No crystal decomposition was in evidence in the intensities of three standards regularly monitored throughout the data collection period. Data were corrected for Lorentz and polarization effects but not for

Table II. Atomic Coordinates (×10^4) and Isotropic (or Equivalent Isotropic) Thermal Parameters (Å^2; ×10^3) for $[Zn_5(PIBA)_{10}(H_2O)_2]_n$ [$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$]

atom	x/a	y/b	z/c	U or U_{eq}[a]	atom	x/a	y/b	z/c	U or U_{eq}[a]
Zn(1)	0	11210 (3)	2500	42 (3)*	Zn(3)	778 (1)	8437 (2)	5722 (1)	42 (2)*
Zn(2)	1006 (1)	9839 (2)	4592 (1)	39 (2)*	Ow	−55 (4)	10108 (12)	3188 (6)	49 (11)*
Ligand A									
C(1)	2170 (7)	10471 (17)	6245 (11)	40 (7)	C(8)	1930 (7)	8749 (18)	6073 (11)	47 (7)
C(2)	2436 (10)	11092 (26)	6151 (16)	105 (11)	C(81)	1993 (9)	7879 (23)	5591 (15)	71 (11)
C(3)	2481 (10)	12016 (27)	6440 (17)	101 (12)	C(82)	2035 (11)	8545 (27)	6848 (17)	100 (14)
C(4)	2251 (13)	12347 (31)	6808 (21)	133 (16)	C(9)	1534 (7)	9039 (19)	5750 (12)	53 (8)
C(5)	1993 (12)	11712 (31)	6901 (19)	107 (15)	O(10)	1461 (4)	9585 (11)	5287 (7)	55 (11)*
C(6)	1925 (9)	10773 (23)	6627 (14)	64 (10)	O(11)	1306 (4)	8596 (11)	6019 (7)	52 (11)*
O(7)	2171 (5)	9568 (13)	5962 (8)	52 (5)					
Ligand B									
C(1)	1171 (7)	12252 (19)	4760 (12)	42 (8)	C(8)	726 (7)	11565 (19)	5403 (12)	54 (8)
C(2)	985 (8)	12829 (21)	4247 (13)	47 (8)	C(81)	892 (8)	12283 (21)	5996 (14)	70 (9)
C(3)	1182 (9)	13578 (24)	4040 (14)	71 (9)	C(82)	347 (9)	11947 (24)	4934 (15)	79 (10)
C(4)	1534 (11)	13653 (26)	4320 (17)	87 (12)	C(9)	687 (7)	10574 (19)	5630 (12)	44 (7)
C(5)	1719 (10)	13060 (27)	4794 (16)	86 (11)	O(10)	693 (4)	9815 (10)	5273 (6)	37 (10)*
C(6)	1533 (8)	12279 (21)	5061 (13)	54 (8)	O(11)	607 (6)	10469 (16)	6193 (10)	109 (7)
O(7)	984 (3)	11423 (9)	4966 (6)	41 (9)*					
Ligand C									
C(1)	1709 (8)	9899 (22)	3979 (13)	51 (8)	C(8)	1141 (6)	10418 (16)	3214 (10)	40 (6)
C(2)	1967 (9)	10602 (23)	4160 (13)	75 (9)	C(81)	1314 (7)	11283 (20)	2906 (13)	56 (8)
C(3)	2340 (10)	10284 (27)	4250 (15)	86 (11)	C(82)	1091 (8)	9497 (21)	2750 (13)	67 (9)
C(4)	2419 (9)	9343 (26)	4125 (15)	79 (10)	C(9)	751 (6)	10696 (19)	3303 (12)	48 (8)
C(5)	2168 (12)	8695 (30)	3904 (19)	113 (14)	O(10)	662 (4)	10379 (11)	3800 (6)	51 (10)*
C(6)	1780 (9)	8928 (24)	3844 (15)	87 (10)	O(11)	562 (4)	11151 (12)	2807 (8)	44 (10)*
O(7)	1345 (4)	10202 (11)	3897 (7)	44 (10)*					
Ligand D									
C(1)	1155 (7)	6304 (19)	6379 (12)	46 (8)	C(8)	542 (6)	6654 (18)	6547 (11)	50 (7)
C(2)	1446 (8)	6289 (21)	6919 (14)	63 (9)	C(81)	641 (9)	6319 (22)	7268 (14)	90 (10)
C(3)	1746 (10)	5652 (29)	6921 (18)	128 (13)	C(82)	307 (8)	5960 (20)	6041 (13)	79 (9)
C(4)	1699 (10)	5051 (26)	6382 (17)	89 (11)	C(9)	350 (7)	7666 (19)	6566 (13)	55 (8)
C(5)	1427 (10)	4961 (27)	5873 (17)	83 (12)	O(10)	410 (4)	8400 (11)	6225 (7)	54 (11)*
C(6)	1139 (9)	5670 (24)	5838 (15)	76 (10)	O(11)	84 (4)	7642 (11)	6856 (7)	51 (11)*
O(7)	881 (4)	6978 (11)	6378 (7)	61 (11)*					
Ligand E									
C(1)	1119 (8)	6700 (21)	3516 (14)	70 (9)	C(8)	562 (7)	7029 (19)	3828 (12)	48 (7)
C(2)	1269 (10)	6602 (27)	2906 (16)	114 (12)	C(81)	174 (9)	7523 (23)	3443 (15)	97 (11)
C(3)	1635 (10)	6239 (25)	3074 (18)	111 (12)	C(82)	501 (8)	5967 (21)	4050 (13)	72 (9)
C(4)	1857 (11)	6120 (28)	3655 (21)	131 (14)	C(9)	713 (7)	7718 (18)	4343 (11)	39 (7)
C(5)	1710 (10)	6241 (24)	6261 (16)	113 (12)	O(10)	619 (5)	7630 (11)	4898 (8)	53 (12)*
C(6)	1332 (9)	6542 (23)	4096 (15)	75 (10)	O(11)	904 (5)	8427 (12)	4259 (7)	65 (13)*
O(7)	751 (5)	7031 (14)	3296 (8)	78 (6)					

[a] Asterisked values are U_{eq}.

Table III. Bond Distances (Å) and Angles (deg) (Coordination Spheres Only)

Zn(1)–Ow	2.112 (15)	Zn(2)–O(10)C	1.973 (13)
Zn(1)–O(11)C	2.066 (15)	Zn(2)–O(11)E	2.045 (17)
Zn(1)–O(10)D′	2.125 (16)	Zn(3)–O(11)A	1.953 (16)
Zn(2)–O(10)A	1.989 (13)	Zn(3)–O(10)B	2.082 (14)
Zn(2)–O(7)B	2.296 (13)	Zn(3)–O(7)D	2.382 (15)
Zn(2)–O(10)B	2.045 (15)	Zn(3)–O(10)D	1.927 (17)
Zn(2)–O(7)C	2.200 (15)	Zn(3)–O(10)E	1.996 (15)
Zn(2)–Zn(3)	3.289 (4)		
Ow–Zn(1)–O(11)C	91.4 (6)	O(10)B–Zn(3)–O(7)D	172.1 (5)
Ow–Zn(1)–O(11)D	92.5 (6)	O(10)B–Zn(3)–O(11)A	94.4 (6)
O(11)C–Zn(1)–O(11)D′	97.6 (6)	O(10)B–Zn(3)–O(10)D	102.2 (6)
O(10)A–Zn(2)–O(10)C	161.4 (7)	O(10)B–Zn(3)–O(10)E	97.5 (6)
O(10)A–Zn(2)–O(10)B	92.4 (6)	O(7)D–Zn(3)–O(11)A	84.1 (6)
O(10)A–Zn(2)–O(7)C	88.5 (6)	O(7)D–Zn(3)–O(10)D	73.2 (6)
O(10)A–Zn(2)–O(7)B	90.8 (5)	O(7)D–Zn(3)–O(10)E	90.2 (6)
O(10)A–Zn(2)–O(11)E	98.0 (6)	O(11)A–Zn(3)–O(10)D	130.4 (6)
O(10)C–Zn(2)–O(10)B	101.8 (6)	O(11)A–Zn(3)–O(10)E	113.9 (7)
O(10)C–Zn(2)–O(7)C	75.1 (6)	O(10)D–Zn(3)–O(10)E	109.8 (7)
O(10)C–Zn(2)–O(7)B	82.0 (5)	Zn(2)–O(7)B–C(8)B	114.0 (12)
O(10)C–Zn(2)–O(11)E	92.1 (6)	Zn(2)–O(10)B–C(9)B	118.7 (15)
O(10)B–Zn(2)–O(7)C	167.9 (6)	Zn(2)–O(7)C–C(8)C	115.0 (12)
O(10)B–Zn(2)–O(7)B	73.1 (5)	Zn(2)–O(10)C–C(9)C	124.5 (15)
O(10)B–Zn(2)–O(11)E	97.1 (6)	Zn(3)–O(7)D–C(8)D	110.6 (12)
O(7)C–Zn(2)–O(7)B	94.8 (6)	Zn(3)–O(10)D–C(9)D	124.6 (17)
O(7)C–Zn(2)–O(11)E	94.7 (5)	Zn(3)–O(10)B–C(9)B	119.5 (14)
O(7)B–Zn(2)–O(11)E	167.2 (6)	Zn(3)–O(10)B–Zn(3)	105.7 (6)

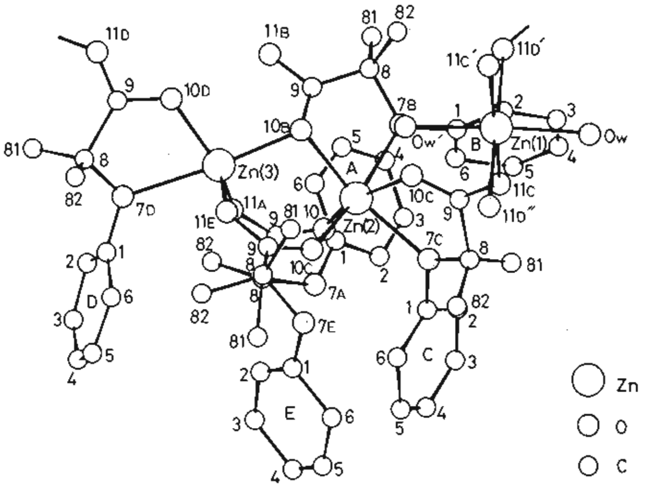

Figure 1. Molecular configuration and atom-naming scheme for $[Zn_5(PIBA)_{10}(H_2O)_2]_n$ (hydrogens omitted). The complex unit has twofold rotational symmetry coincident with Zn(1), and the primed atoms are generated by this operator. Atom-naming scheme within the ligands follows the convention employed for the phenoxyalkanoic acids.[5]

absorption. The small crystal size is considered the reason for the paucity of "observed" data [2089 with $I > 2.0\sigma(I)$].

Structure Solution and Refinement

The positions of the three independent zinc atoms in the asymmetric unit were located by using the multisolution centrosymmetric direct methods of SHELX-76[6] after hand-selection of the origin-defining symbolic phases. These coordinates were verified in a three-dimensional Patterson synthesis. The remaining 66 non-hydrogen atoms were subsequently found in several refinement/weighted difference-Fourier cycles while any located phenyl rings were maintained as rigid bodies. These constraints were released for the final cycles of refinement. Blocked-matrix least-squares refinement, with anisotropic thermal parameters for only the zinc atoms and the coordinated oxygens, reduced R [$=\sum|F_o - F_c|/|F_o|$] from an initial value of 0.58 (three zinc atoms only) to 0.105 and R_w [$=\sum w|F_o - F_c|^2/\sum w|F_o|^2)^{1/2}$] to 0.090. The value used for w was $1.9/(\sigma^2(F_o) + 6.8 \times 10^{-4}F_o^2)$. A number of hydrogens (16) were located in difference-Fourier syntheses and included in the refinement at fixed positions with their isotopic U values set invariant at 0.05 Å^2. The maximum peak in the final difference electron-density synthesis was 1.2 e Å^{-3}. Atomic scattering factors and the anomalous dispersion terms for Zn were taken from ref 7. Final atomic parameters and equivalent isotropic/isotropic thermal parameters are given in Table II while bond distances and angles about the coordination polyhedron are given in Table III.

Discussion

The title compound is best described as a one-dimensional polymer with a pentameric repeating unit $[Zn_5(PIBA)_{10}(H_2O)_2]$ (Figure 1). The pentamer has crystallographically imposed twofold rotational symmetry about axes at $z = {}^1/_4, {}^3/_4$ in the cell (Figure 2), which contain one of the three independent zinc atoms [Zn(1)]. The coordination about Zn(1) is distorted octahedral [mean Zn–O = 2.101 (16) Å] and involves the two trans-related water molecules. The stereochemistry about Zn(2) is also distorted octahedral [Zn–O: range, 1.973 (13)–2.296 (13) Å; mean, 2.091 (14) Å]. Between Zn(2) and Zn(3) are two carboxylate-*O,O′* bridges (ligands A and E) and a single carboxylate-*O* bridge [O(10) of ligand B]. Ligand B also acts as a five-membered chelate group with Zn(2) [via carboxylate and ether oxygens [O(7)]] while another chelate ring involving ligand C completes the Zn(2) coordination sphere. Similarly, ligand D completes the five-coordination about Zn(3). Ligands C and D provide the bridging carboxylate oxygens to Zn(1).

The bidentate chelate mode observed in this compound is known for the copper(II) phenoxyalkanoates (copper phenoxyacetate dihydrate,[8] anhydrous copper phenoxyacetate,[9] copper 4-nitrophenoxyacetate dihydrate,[10] copper 4-methoxyphenoxyacetate,[10]

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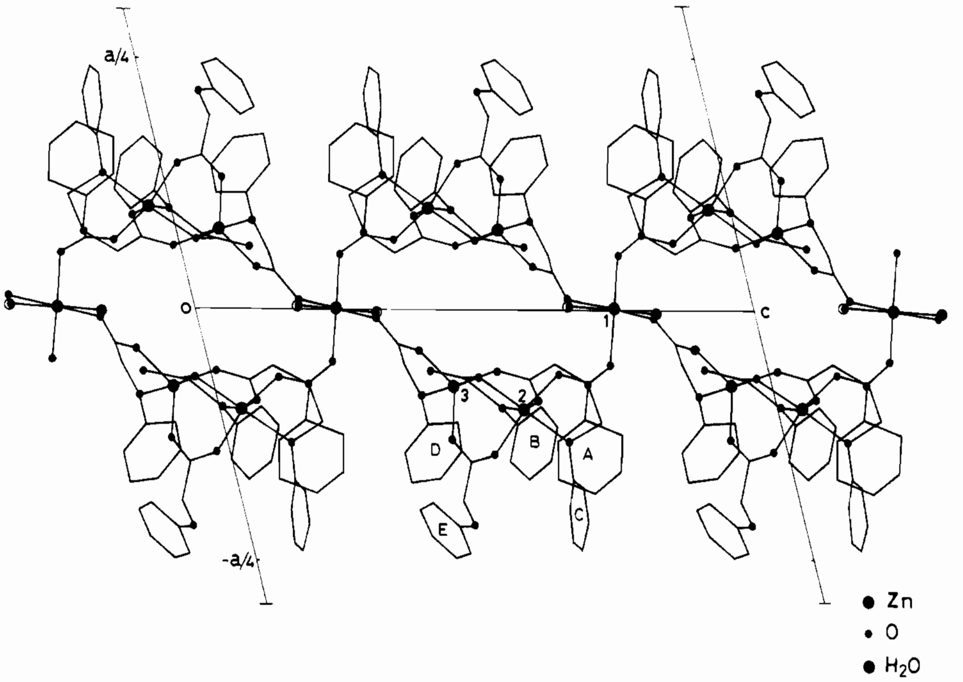

Figure 2. Packing of the complex polymer in the cell viewed perpendicular to *ac*. Crystallographic twofold axes at $z = {}^1/_4, {}^3/_4$ are coincident with molecular symmetry. The methyl carbons [C(81), C(82)] have been omitted for clarity.

Table IV. Comparative Torsion Angles (deg) for the Oxoalkanoate Side Chains of Ligands A–E in **1** Compared with Those for the Parent Acid 2-Methyl-2-phenoxypropionic Acid (PIBAH)[5]

	A	B	C	D	E	PIBAH
C(2)–C(1)–O(7)–C(8)	+172.8	−79.5	+97.4	−100.8	+172.4	+167.7
C(1)–O(7)–C(8)–C(9)	+66.8	−164.6	+178.4	+173.1	+65.2	+65.6
O(7)–C(8)–C(9)–O(10)	+27.6	−34.1	−23.5	+27.2	+20.1	+29.2

copper 4-chlorophenoxyacetate dihydrate,[1] and the copper 4-fluorophenoxyacetate dihydrate–4-fluorophenoxyacetate adduct[11]) but has not previously been found among the zinc complexes. With these copper complexes, the bidentate chelate formation is accompanied by asymmetry in the Cu–O bond lengths, the longer (weaker) bond being directed toward the ether oxygen, invariably in the tetragonally elongated position in the coordination sphere (range 2.41–2.48 Å for the examples considered). In the present example, distortion also appears, but to a lesser extent [2.200 (15) Å, ligand C (octahedral); 2.296 (13) Å, ligand B (octahedral); 2.382 (15) Å, ligand D (trigonal bipyramidal). The causative factor for this mode of complexation is probably the maintenance of a discrete O(ether)–O(carboxylate) interactive distance in the oxoalkanoate side chain, irrespective of any conformational differences. The regularity of this distance is also a feature of the uncomplexed acids[5] [range 2.605–2.775 Å, mean 2.711 Å (19 examples)]. The value found for phenoxyisobutyric acid (2.723 Å)[5] compares with 2.710, 2.595, 2.549, 2.595, and 2.714 Å for ligands A, B, C, D, and E, respectively. The side-chain conformations are compared in Table IV. The torsion angle most sensitive to conformational change in the phenoxy acid side chain is C(1)–O(7)–C(8)–C(9) (β). In the parent acid (PIBAH), the side chain is synclinally related to the ring system (β ca. 90°), which is the only conformation known for the 2-phenoxy-substituted propionic and 2-methylpropionic acids.[5] This contrasts with the phenoxyacetic acids where the planar conformation is preferred (β ca. 180°). With the complexed example **1**, the basic conformation is preserved in all the ligands, irrespective of their bonding mode, i.e. unidentate, bidentate, and bidentate bridging. Therefore, it is highly likely that since the structural features found for **1** have not been previously observed, the dimethyl substitution at C(8) plays an important role in the stabilization of this structure.

The infinite polymer chains of the pentamer unit extend along the *c* direction of the cell at $a = 0, {}^1/_2$ and are stabilized within the chain by both intra- and intermolecular hydrogen-bonding associations involving the coordinated waters and the carboxylate oxygens. The only carboxylate oxygen not involved in coordination is O(11)B, which has an interunit hydrogen bond (2.807 Å) to a water while a second (2.915 Å) is directed to O(11)D within the unit. Other interactions exist across the twofold axis ($-x, y, {}^1/_2 - z$): Ow···O(11)C, 2.833 Å; Ow···Ow′, 2.977 Å; O(11)D···O(11)D′, 2.886 Å; O(11)D···O(11)C, 2.850 Å. Ow is also linked to O(11)D′ (2.807 Å; $-x, 2 - y, 1 - z$). The polymer chains appear to have voids in the regions of the cell about 0, 0, 0 and 0, 0, $^1/_2$ (Figure 2). This is possibly responsible for the hardness but relatively low density (1.385 g cm^{-3}) of the compound. Although the possibility exists that solvent molecules could fit into these channels in the structure, there is no evidence, either in the elemental analysis or from the present structure analysis, to support this contention.

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Registry No. **1**, 96213-10-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, intraligand bond distances and angles, hydrogen atom coordinates, and observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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