Crystal structures of three basic zinc carboxylates together with infrared and FAB mass spectrometry studies in solution

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Abstract

We report the X-ray crystal structures of three new basic zinc carboxylate complexes, $[Zn_4O(O_2CR)_6]$ where $R=C(CH_3)_3$ (pivalate) or C_6H_5 (benzoate) and $[Zn_5(OH)_2(O_2CCHCHCH_3)_8]_x$ (crotonate). The basic pivalate is orthorhombic, $Cmc2_1$, with $a=18.609(1)$, $b=11.027(1)$, $c=22.439(1)$ Å, $Z=4$; $R=0.042$ for 1887 unique observed reflections. The basic benzoate is monoclinic, $P2_1/m$, with $a=10.818(2)$, $b=18.527(3)$, $c=12.170(2)$ Å, $\beta=110.32(1)°$, $Z=2$; $R=0.036$ for 3633 unique observed reflections. The basic crotonate is monoclinic, $P2_1/n$, with $a=8.723(1)$, $b=21.957(2)$, $c=11.302(1)$ Å, $\beta=90.94(1)°$, $Z=2$; $R=0.058$ for 3049 unique observed reflections. The pivalate and benzoate structures possess the well-known tetranuclear structure containing a central oxygen atom, while the structure of the crotonate complex consists of a chain polymer. In solutions containing traces of water, the hydrated basic structures appear to be in equilibrium with hydrated forms of the normal 3,1 metal carboxylate structures reported previously and their interconversions have been investigated using FT-IR and FAB mass spectral data.

Introduction

Many anhydrous metal(II) carboxylate complexes are polymeric due to the bridging of metals by carboxylate groups [1–5]. A common structure for zinc carboxylates is that in which two zinc atoms are linked by three *syn–syn* [1] bridging carboxylate ligands to form a binuclear unit $[Zn_2(O_2CR)_3]^+$, R = alkyl or aryl. These units are linked to one another by a *syn–anti* bridging carboxylate ligand to produce a linear (3,1) polymer (see Fig. 1). Examples of such polymers include zinc crotonate [6], benzoate [7], methacrylate [8], 3,3-dimethylacrylate [9] and *o*-chlorobenzoate [9].

Zinc *o*-chlorobenzoate has been reported also to crystallize in the form of a linear polymer [10], in which a chain of zinc atoms is linked by pairs of *syn–syn* bridging carboxylate ligands to give a (2,2) bridged polymer structure. Crystals of this compound were produced by recrystallization of a crude product from 'dried' acetone. A basic form of zinc *o*-chlorobenzoate $[Zn_2(OH)(O_2CC_6H_4Cl)_3]_x$ has also been obtained from an acetone/water mixture and this also has a chain polymeric structure [11].

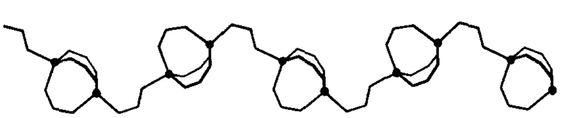

Fig. 1. Backbone of the 3,1 polymer chain. Side chains of carboxylate ligands not shown.

Currently attracting attention is the solid-state reactivity of metal carboxylate complexes by double bond overlap between unsaturated carboxylate ligands [12–15]. The general inertness of the 3,1 polymer to spontaneous solid-state reaction has led us to try and alter its structure by recrystallization to produce a possibly more reactive 2,2 or other form.

Complexes of three different types of carboxylic acid are described in this paper: an α,β-unsaturated aliphatic (crotonic acid, $CH_3CHCHCO_2H$), an aromatic (benzoic acid, $C_6H_5CO_2H$) and a saturated aliphatic (pivalic acid, $(CH_3)_3CCO_2H$)). Crotonic acid was the only one expected to produce a complex which undergoes spontaneous solid state reaction. Each zinc carboxylate salt has the 3,1 polymer structure, although this is only inferred from solid-state vibrational data in the case of zinc pivalate.

Recrystallization of zinc pivalate and zinc benzoate from acetone (dried over magnesium sulfate) yielded

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not the 2,2 polymer as intended, but the well-known tetranuclear basic structure $[Zn_4O(O_2CR)_6]$ where $R=C(CH_3)_3$ or C_6H_5 [16–18]. In contrast, zinc crotonate did not change structure on recrystallizing from dried acetone. However, on recrystallization from an ethanol/water mixture, a chain polymeric basic zinc crotonate was produced $[Zn_5(OH)_2(O_2CCHCHCH_3)_8]_x$. All three basic compounds have been isolated as crystals and their structures have been determined by X-ray diffraction.

In an attempt to understand why the 'normal' 3,1 polymer changes to a basic structure on recrystallization from moist solvents, solutions of the three normal and three basic compounds have been studied using Fourier transform infrared spectroscopy and fast atom bombardment mass spectrometry and our findings are reported here.

Experimental

Complexes

$[Zn(O_2CR_2)_x]$ where $R=CHCHCH_3$, $C(CH_3)_3$ or C_6H_5 were prepared by the action of zinc hydroxide (1 mol) on an aqueous solution of the respective carboxylic acid (2 mol).

$[Zn_5(OH)_2(O_2CCHCHCH_3)_8)_x]$ (**1**). Zinc crotonate was dissolved in the minimum amount of a 50:1 ethanol/water mixture with warming. The solution was filtered while hot and then cooled ($T<0$ °C). The product crystallized out after a short period of time.

$[Zn_4O(O_2CR)_6]$ where $R=C(CH_3)_3$ (**2**) or C_6H_5 (**3**). The zinc carboxylate was dissolved in the minimum of acetone (dried over $MgSO_4$) with warming. The solution was filtered hot and then cooled ($T<0$ °C). Crystals were produced after a short period of time (a few hours for **2** and a few days for **3**).

Analysis

C, H and N analyses were carried out on a Carlo Erba 1106 elemental analyser. Results are given in Table 1.

TABLE 1. Elemental analysis for basic zinc carboxylates[a]

	C (%)	H (%)
$[Zn_5(OH)_2(O_2CCHCHCH_3)_8]_x$	36.7 (36.9)	3.9 (4.1)
$Zn_4O(O_2CC(CH_3)_3)_6$	40.6 (40.9)	6.3 (6.2)
$Zn_4O(O_2CC_6H_5)_6$	51.0 (50.0)	3.2 (3.0)

[a]Calculated values given in parentheses.

Measurements

IR spectra of KBr discs were recorded on a Perkin-Elmer model 598 spectrometer. Fourier transform IR solution spectra were recorded on Nicolet 20SXB and Nicolet 20PC IR spectrometers using KBr plates (for $CHCl_3$ solutions) and CaF_2 (for MeOH and EtOH solutions). Fast atom bombardment mass spectra were recorded on a Kratos MS 80 using xenon as fast atoms and MNBA as the matrix.

X-ray crystallography

Crystallographic data are given in Table 2. Measurements were made at room temperature on a Stoe-Siemens diffractometer with graphite-monochromated X-rays. Cell parameters were refined from 2θ values of reflections measured at $\pm\omega$. Intensity measurements were made in a ω/θ scan mode. Semi-empirical absorption corrections were applied [19], together with corrections for the observed decay in intensity of standard reflections. Reflections with $F>4\sigma_c(F)$ (σ_c from counting statistics only) were used for structure solution (by Patterson methods) and least-squares refinement [19] on F. The weighting scheme for **1** and **3** was $w^{-1}=\sigma_c^2(F)+gF_o^2$, with $g=0.0001$ for **1** and 0.00005 for **3**; for **2**, $w^{-1}=\sigma_c^2(F)+105-678G+1214G^2-195H+100H^2+539GH$ ($G=F_o/F_{max}$, $H=\sin\theta/\sin\theta_{max}$) [20]. Atomic scattering factors were taken from ref. 21. Anisotropic thermal parameters were refined for non-H atoms; H atoms were constrained to give C–H and O–H 0.96 Å, H–C–H 109.5°, olefinic and aromatic H on angle external bisectors, $U(H)=1.2U_{eq}(C)$ or $1.2U_{eq}(O)$. An isotropic extinction parameter x was refined, whereby $F'_c=F_c/(1+xF_c^2/\sin 2\theta)^{1/4}$.

The assigned space groups for **2** and **3**, not uniquely determined from systematic absences, were confirmed by successful refinement. The absolute structure of **2** was determined by refinement of $\eta=+1.14(6)$ [32].

Refined atomic coordinates are given in Tables 3–5, and selected bond lengths and angles in Tables 6–8. See also 'Supplementary material'.

Results and discussion

Crystal structure of $[Zn_5(OH)_2(O_2CCHCHCH_3)_8)_x]$ (1)

The chain polymer structure (without crotonate side chains) is shown in Fig. 2 and the structure of a single pentanuclear unit is shown in Fig. 3. This unit consists of five zinc atoms (four of which are tetrahedrally coordinated, the other being octahedrally coordinated); these are linked by two hydroxy groups and six *syn–syn* bridging crotonates. Each

TABLE 2. Crystallographic data

	1	**2**	**3**
Formula	$C_{32}H_{42}O_{18}Zn_5$	$C_{30}H_{54}O_{13}Zn_4 \cdot C_3H_6O$	$C_{42}H_{30}O_{13}Zn_4 \cdot C_3H_6O$
M_r	1041.6	942.4	1062.3
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Cmc2_1$	$P2_1/m$
a (Å)	8.723(1)	18.609(1)	10.818(2)
b (Å)	21.957(2)	11.027(1)	18.527(3)
c (Å)	11.302(1)	22.439(1)	12.170(2)
β (°)	90.94(1)		110.32(1)
V (Å^3)	2164.4	4604.6	2287.4
Z	2	4	2
D_x (g cm^{-3})	1.598	1.359	1.542
Radiation, λ (Å)	Cu Kα, 1.54184	Mo Kα, 0.71073	Cu Kα, 1.54184
μ (mm^{-1})	3.72	2.16	2.95
F(000)	1056	1960	1076
Crystal size (mm)	0.35×0.08×0.25	0.4×0.6×0.6	0.42×0.27×0.15
No. reflections for cell, 2θ range (°)	32, 20–35	32, 20–25	32, 30–40
$2\theta_{max}$ (°)	135	50	130
h range	−10 to 10	0 to 22	0 to 12
k range	−26 to 0	0 to 13	−21 to 4
l range	−13 to 13	0 to 26	−14 to 14
Intensity decay (%)	*c*. 20	*c*. 30	*c*. 20
Transmission factors	0.21–0.47	0.18–0.23	0.38–0.55
Reflections measured	7555	2156	5197
Unique reflections	3722	2156	3979
Observed reflections	3049	1887	3633
R_{int}	0.111		0.037
Extinction parameter x	$7.2(3)\times10^{-7}$	$1.4(4)\times10^{-8}$	$5.5(4)\times10^{-6}$
R	0.058	0.042	0.036
$R_w = (\Sigma w\Delta^2/\Sigma wF_o{}^2)^{1/2}$	0.088	0.026	0.047
No. of parameters	263	250	314
Mean shift/e.s.d.	0.002	0.006	0.006
Max., min. el. density (e Å^{-3})	0.89, −0.56	0.31, −0.40	0.37, −0.60

hydroxy group is bonded to three zincs. Two further crotonates link the units into a chain polymer by bridging two tetrahedral zincs in the *syn–anti* mode. The central zinc atom of the unit lies on a centre of symmetry.

As can be seen in Fig. 3 two crotonates within the monomer unit have double bonds which are almost parallel (C(22)=C(23), C(42)=C(43)). However they are not favourably aligned and too far apart (~5.1 Å) for spontaneous solid-state reaction. The compound does turn pale yellow several months after preparation; this may be due to some reaction between double bonds in adjacent polymer chains but more likely it indicates the formation of hydrolysis products.

Crystal structures of *$[Zn_4O(O_2CC(CH_3)_3)_6]\cdot OC(CH_3)_2$ (2) and $[Zn_4O(O_2CC_6H_5)_6]\cdot OC(CH_3)_2$ (3)*

The structure of **2** is shown in Fig. 4 and that of **3** in Fig. 5. Both compounds were recrystallized from acetone and they initially incorporated a molecule of acetone into their structures. The structures consist of a central oxygen atom tetrahedrally coordinated by four zinc atoms; the zinc atoms in turn are coordinated by six carboxylate ligands bridging in the *syn–syn* mode. Each molecule has crystallographic reflection symmetry. In both structures, acetone is placed with its oxygen atom above a triangle of zinc atoms, O...Zn distances of 2.98–3.18 Å representing only weak interactions.

Elemental analyses for all three compounds are shown in Table 1. The two tetranuclear compounds lose weight due to loss of acetone to the atmosphere. Consequently, analyses were carried out on samples which had been ground to a fine powder and heated gently to remove all of the acetone.

FT-IR solid-state spectra

The IR spectra of the six solid-state samples have been recorded (4000–200 cm^{-1}) and the results are given in Tables 9–11. We can be confident about our IR assignments for three reasons: (i) comparisons are made within a series of closely related compounds, several of which have X-ray structural data available; (ii) one of the common sources of error in the

TABLE 3. Atomic coordinates ($\times 10^4$) for basic zinc crotonate (**1**)

Atom	x	y	z
Zn(1)	5000	5000	5000
Zn(2)	2379(1)	6037(1)	5807(1)
Zn(3)	1704(1)	5045(1)	3750(1)
O(1)	2693(4)	5192(2)	5302(3)
O(11)	5958(4)	5722(1)	5997(3)
O(12)	4268(4)	6477(2)	5938(4)
C(11)	5607(6)	6272(2)	6131(5)
C(12)	6800(7)	6692(3)	6557(6)
C(13)	6531(8)	7260(3)	6837(9)
C(14)	7737(12)	7690(5)	7275(14)
O(21)	4968(4)	5554(2)	3489(3)
O(22)	2843(4)	5351(2)	2424(3)
C(21)	4179(6)	5555(2)	2552(5)
C(22)	4894(7)	5818(3)	1468(6)
C(23)	4326(8)	5771(3)	399(6)
C(24)	5053(10)	6026(4)	−692(7)
O(31)	1047(5)	6418(2)	4598(4)
O(32)	−138(6)	5604(2)	3852(4)
C(31)	−91(6)	6140(3)	4081(5)
C(32)	−1471(9)	6504(3)	3726(7)
C(33)	−1533(11)	7067(4)	3799(10)
C(34)	−2997(13)	7426(5)	3439(14)
O(41)	1612(4)	6086(2)	7444(4)
O(42)	−325(4)	5623(2)	6592(3)
C(41)	334(6)	5827(3)	7519(5)
C(42)	−395(7)	5761(3)	8665(6)
C(43)	145(9)	6006(3)	9639(6)
C(44)	−572(11)	5977(5)	10838(6)

TABLE 4. Atomic coordinates ($\times 10^4$) for basic zinc pivalate (**2**)

Atom	x	y	z
Zn(1)	851(1)	932(1)	0
Zn(2)	0	3404(1)	−199(1)
Zn(3)	0	1317(1)	−1186(1)
O(11)	1436(2)	2223(4)	353(2)
O(12)	824(2)	3938(4)	276(2)
C(11)	1325(3)	3287(6)	476(2)
C(12)	1827(3)	3882(5)	923(2)
C(13)	2564(5)	3854(16)	666(4)
C(14)	1627(6)	5172(9)	1068(5)
C(15)	1885(7)	3165(10)	1476(4)
O(21)	1470(2)	216(4)	−599(2)
O(22)	875(3)	506(4)	−1440(2)
C(21)	1401(3)	102(5)	−1148(2)
C(22)	1984(4)	−510(6)	−1500(4)
C(23)	2557(6)	−927(14)	−1132(4)
C(24)	1639(8)	−1547(11)	−1875(6)
C(25)	2216(6)	272(5)	−1996(5)
O(31)	0	4300(5)	−945(3)
O(32)	0	2828(7)	−1623(3)
C(31)	0	3934(10)	−1470(3)
C(32)	0	4908(11)	−1967(4)
C(33)	0	6050(16)	−1772(9)
C(34)	604(8)	4626(17)	−2362(7)
O(41)	600(2)	16(4)	714(2)
C(41)	0	−115(9)	959(4)
C(42)	0	−563(10)	1601(4)
C(43)	0	638(17)	1961(5)
C(44)	−656(7)	−1272(14)	1766(4)
O(5)	0	1679(4)	−338(2)
O(6)	0	−1164(7)	−462(3)
C(61)	0	−2150(9)	−245(5)
C(62)	−675(5)	−2789(8)	−138(5)

assignment of $\nu(CO_2)$ modes is the wide variations in band position due to hydrogen bonding to water molecules which are often present in the molecular structure; the present compounds are anhydrous in the solid state; (iii) no solid-state reactions with KBr have been noted.

The crystal structures of both normal zinc crotonate and benzoate show the presence of two kinds of bridging carboxylate ligand i.e. *syn–syn* and *syn–anti*, and consequently the solid-state spectra exhibit two $\nu(CO_2)_{as}$ modes (crotonate 1613 and 1547\1520; benzoate 1639 and 1531 cm^{-1}) and one $\nu(CO_2)_s$ mode (1429 and 1420 cm^{-1}, respectively).

The solid-state spectrum of zinc pivalate also shows two asymmetric carboxylate stretching modes ($\nu(CO_2)_{as} = 1612$ and 1535 cm^{-1}) and one symmetric carboxylate stretching mode ($\nu(CO_2)_s = 1429$ cm^{-1}) and hence we can deduce that the structure of normal zinc pivalate is also a 3,1 chain polymer. Assignment of the two $\nu(CO_2)_{as}$ modes to the correct bridging modes (*syn–syn* or *syn–anti*) is aided by the comparison of these spectra with that of the 2,2 polymer of zinc *o*-chlorobenzoate, which contains *syn–syn* bridging modes only ($\nu(CO_2)_{as} = 1540$ cm^{-1}, $\nu(CO_2)_s = 1410$ cm^{-1}) [10]. Therefore we assign the higher of the two $\nu(CO_2)_{as}$ modes at 1612 cm^{-1} to the *syn–anti* bridge and the lower band at 1535 cm^{-1} to a *syn–syn* bridge.

The solid-state spectra of both basic zinc pivalate and benzoate show only two carboxylate stretching modes, in support of the X-ray crystal structures and consistent with the presence of only one type of carboxylate ligand (*syn–syn*). In contrast, the solid-state spectrum of the basic zinc crotonate shows the presence of *syn–anti* (1582 cm^{-1}) as well as *syn–syn* (1530 cm^{-1}) bridges as expected from X-ray data.

Solution spectra

Acetone (which contains traces of water) solution spectra of both the normal and basic zinc pivalates are essentially identical and exhibit three carboxylate stretching modes at 1613, 1588 and 1425 cm^{-1}. The only difference is in the relative intensities of some of the bands; for example, in the basic zinc pivalate solution spectrum the 1588 cm^{-1} band is more intense than the 1613 cm^{-1} band, whereas these bands in the normal zinc pivalate solution have their relative intensities reversed. This is exactly what one would predict if two different species (i.e. normal solvated

TABLE 5. Atomic coordinates ($\times 10^4$) for basic zinc benzoate (**3**)

Atom	x	y	z
Zn(1)	3435(1)	3357(1)	5196(1)
Zn(2)	1069(1)	2500	5558(1)
Zn(3)	3962(1)	2500	7533(1)
O(11)	4036(2)	3105(1)	3909(2)
C(11)	4262(4)	2500	3542(3)
C(12)	4828(4)	2500	2577(3)
C(13)	5074(4)	3145(2)	2127(3)
C(14)	5553(4)	3135(3)	1207(4)
C(15)	5794(6)	2500	763(5)
O(21)	1863(2)	3943(1)	4429(2)
O(22)	188(2)	3328(1)	4644(2)
C(21)	668(3)	3863(2)	4286(2)
C(22)	−260(3)	4440(2)	3641(2)
C(23)	−1605(3)	4354(2)	3360(3)
C(24)	−2450(4)	4906(2)	2792(4)
C(25)	−1975(4)	5528(2)	2506(4)
C(26)	−645(4)	5617(2)	2767(3)
C(27)	216(3)	5075(2)	3344(3)
O(31)	723(3)	2500	7031(2)
O(32)	2725(3)	2500	8398(2)
C(31)	1501(4)	2500	8078(3)
C(32)	896(4)	2500	9017(4)
C(33)	1661(5)	2500	10168(4)
C(34)	1102(6)	2500	11035(5)
C(35)	−232(6)	2500	10738(5)
C(36)	−1011(6)	2500	9589(6)
C(37)	−458(5)	2500	8720(5)
O(41)	5026(2)	3363(1)	8013(2)
O(42)	4668(2)	3974(1)	6348(2)
C(41)	5258(3)	3874(1)	7420(2)
C(42)	6306(3)	4397(2)	8058(2)
C(43)	6540(3)	5005(2)	7504(3)
C(44)	7514(4)	5489(2)	8123(4)
C(45)	8251(4)	5371(2)	9264(4)
C(46)	8058(4)	4757(3)	9806(3)
C(47)	7078(4)	4271(2)	9214(3)
O(5)	2946(2)	2500	5864(2)
O(61)	6013(4)	2500	6307(4)
C(61)	6865(4)	2500	5888(4)
C(62)	7400(4)	3180(3)	5610(5)

and basic solvated zinc pivalates) are present in equilibrium in solution. We assign the band at 1424 cm^{-1} as predominantly a symmetric carboxylate stretch which has moved very slightly to lower wavenumbers on going from the solid-state spectrum of either species to the solution phase. The band at 1613 cm^{-1} corresponds to the $\nu(CO_2)_{as}$ mode of the normal species while the 1588 cm^{-1} band corresponds to the $\nu(CO_2)_{as}$ of the basic species. The $\nu(CO_2)_{as}$, 1535 cm^{-1} band from the solid-state spectrum of normal zinc pivalate is absent from the solution spectra. This suggests the formation of new species in solution which possess only one (*syn–anti*) type of carboxylate bridging ligand.

Other points to note from our solution studies are as follows.

(1) The reaction of excess pivalic acid with basic zinc pivalate in aqueous solution, followed by the removal of solvent and examination of the product by IR, produces the anhydrous normal salt. Gordon and Silver [17] also found that attempts to effect the transacidification of basic zinc carboxylates produces normal salts and water.

(2) FT-IR spectra of basic zinc pivalate in deuterated (anhydrous) acetone show bands due to the basic form only. The lack of water in the system apparently suppresses the equilibrium. Furthermore the FT-IR spectrum of the normal salt in deuterated acetone shows no basic form present.

(3) FT-IR spectrum of the anhydrous normal zinc pivalate in bench chloroform shows a substantial band at 1701 cm^{-1} due to free pivalic acid together with a band at 1584 cm^{-1} ($\nu(CO_2)_{as}$ *syn–syn*) indicating a conversion to basic zinc pivalate and pivalic acid.

(4) The addition of small amounts of water alone to basic zinc pivalate dissolved in deuteroacetone also produces IR bands which indicate the formation of anhydrous normal zinc pivalate. Presumably small amounts of free acid are generated which then react as in (1).

All of these observations, together with the intensity variations observed for the three solution bands, depending on whether the solution species have been generated from the solid-state normal or basic compounds, suggest the presence of an equilibrium in solution between normal and basic zinc pivalate (see eqn. (1)).

$$\begin{tikzcd}
4ZnA_2(s) + \text{solvent}^* \arrow[r] & 4ZnA_2\ (\text{hydrated}) \arrow[d, shift right, "\substack{H_2O \\ -2HA}"'] \\
{[Zn_4OA_6(s)]} + \text{solvent}^* \arrow[r] & {[Zn_4OA_6\ (\text{hydrated})]} \arrow[u, shift right, "\substack{H_2O \\ +2HA(\text{solv})}"']
\end{tikzcd}$$

*the solvents were not dried before use and hence invariably contained traces of water.

$A = O_2CR$ where $R = (CH_3)_3C$ or C_6H_5.

Zinc benzoate and basic zinc benzoate

FT-IR spectra of both normal and basic zinc benzoate in bench chloroform solutions showed free benzoic acid at 1710 cm^{-1}, and solvated basic zinc benzoate, inferred from the presence of an asymmetric carboxylate stretching mode at 1570 cm^{-1}, which has moved from the solid-state value of 1562 cm^{-1}. The two asymmetric carboxylate stretches of the normal salt have been replaced by a single $\nu(CO_2)_{as}$ stretch at 1607 cm^{-1} in chloroform solution as has already been noted for solutions of normal zinc pivalate. Thus the overall indication is that the benzoate system exhibits the same equilibrium in solution as pivalate.

TABLE 6. Selected bond lengths (Å) and angles (°) for **1**

Zn(1)–O(1)	2.089(3)	Zn(1)–O(11)	2.110(4)
Zn(1)–O(21)	2.097(4)	Zn(2)–O(1)	1.963(4)
Zn(2)–O(12)	1.914(4)	Zn(2)–O(31)	1.965(5)
Zn(2)–O(41)	1.981(4)	Zn(3)–O(1)	1.969(3)
Zn(3)–O(22)	1.933(4)	Zn(3)–O(32)	2.027(4)
Zn(3)–O(42b)	1.932(4)		
O(1)–Zn(1)–O(11)	97.8(1)	O(1)–Zn(1)–O(21)	90.9(1)
O(11)–Zn(1)–O(21)	89.9(1)	O(1)–Zn(2)–O(12)	112.1(2)
O(1)–Zn(2)–O(31)	106.5(2)	O(12)–Zn(2)–O(31)	109.7(2)
O(1)–Zn(2)–O(41)	111.9(2)	O(12)–Zn(2)–O(41)	101.8(2)
O(31)–Zn(2)–O(41)	115.0(2)	O(1)–Zn(3)–O(22)	114.2(2)
O(1)–Zn(3)–O(32)	100.7(2)	O(22)–Zn(3)–O(32)	104.6(2)
O(1)–Zn(3)–O(42b)	124.4(2)	O(22)–Zn(3)–O(42b)	115.8(2)
O(32)–Zn(3)–O(42b)	88.8(2)	Zn(1)–O(1)–Zn(2)	112.2(2)
Zn(1)–O(1)–Zn(3)	103.3(1)	Zn(2)–O(1)–Zn(3)	110.7(2)

Symmetry operator: (b) $-x$, $1-y$, $1-z$.

TABLE 7. Selected bond lengths (Å) and angles (°) for **2**

Zn(1)–O(11)	1.959(4)	Zn(1)–O(21)	1.938(4)
Zn(1)–O(41)	1.951(4)	Zn(1)–O(5)	1.939(3)
Zn(2)–O(12)	1.959(4)	Zn(2)–O(31)	1.945(5)
Zn(2)–O(5)	1.927(5)	Zn(3)–O(22)	1.943(5)
Zn(3)–O(32)	1.935(7)	Zn(3)–O(5)	1.944(4)
O(11)–Zn(1)–O(21)	104.2(2)	O(11)–Zn(1)–O(41)	100.2(2)
O(21)–Zn(1)–O(41)	120.1(2)	O(11)–Zn(1)–O(5)	107.6(2)
O(21)–Zn(1)–O(5)	112.8(2)	O(41)–Zn(1)–O(5)	110.2(2)
O(12)–Zn(2)–O(31)	108.4(2)	O(12)–Zn(2)–O(5)	112.6(1)
O(31)–Zn(2)–O(5)	111.2(2)	O(12)–Zn(2)–O(12a)	103.1(2)
O(22)–Zn(3)–O(32)	104.3(2)	O(22)–Zn(3)–O(5)	112.5(1)
O(32)–Zn(3)–O(5)	108.6(2)	O(22)–Zn(3)–O(22a)	113.8(3)
Zn(1)–O(5)–Zn(2)	110.9(2)	Zn(1)–O(5)–Zn(3)	107.2(2)
Zn(2)–O(5)–Zn(3)	111.2(2)	Zn(1)–O(5)–Zn(1a)	109.5(2)

Symmetry operator: (a) $-x$, y, z.

TABLE 8. Selected bond lengths (Å) and angles (°) for **3**

Zn(1)–O(11)	1.949(3)	Zn(1)–O(21)	1.960(2)
Zn(1)–O(42)	1.937(2)	Zn(1)–O(5)	1.940(2)
Zn(2)–O(22)	1.939(2)	Zn(2)–O(31)	1.955(3)
Zn(2)–O(5)	1.932(3)	Zn(3)–O(32)	1.969(4)
Zn(3)–O(41)	1.938(2)	Zn(3)–O(5)	1.945(2)
O(11)–Zn(1)–O(21)	103.1(1)	O(11)–Zn(1)–O(42)	112.7(1)
O(21)–Zn(1)–O(42)	106.5(1)	O(11)–Zn(1)–O(5)	110.9(1)
O(21)–Zn(1)–O(5)	109.6(1)	O(42)–Zn(1)–O(5)	113.5(1)
O(22)–Zn(2)–O(31)	108.2(1)	O(22)–Zn(2)–O(5)	112.6(1)
O(31)–Zn(2)–O(5)	110.3(1)	O(22)–Zn(2)–O(22a)	104.5(1)
O(32)–Zn(3)–O(41)	106.4(1)	O(32)–Zn(3)–O(5)	108.4(1)
O(41)–Zn(3)–O(5)	112.1(1)	O(41)–Zn(3)–O(41a)	111.2(1)
Zn(1)–O(5)–Zn(2)	109.9(1)	Zn(1)–O(5)–Zn(3)	107.5(1)
Zn(2)–O(5)–Zn(3)	112.1(2)	Zn(1)–O(5)–Zn(1a)	109.9(1)

Symmetry operator: (a) x, $\frac{1}{2}-y$, z.

Zinc crotonate and basic zinc crotonate

The FT-IR spectrum of normal zinc crotonate in methanol shows a band at 1702 cm^{-1} due to free crotonic acid. There is also a broad band at 1556 cm^{-1} with a shoulder at *c.* 1600 cm^{-1}. As in the case of zinc benzoate, the higher frequency band is equivalent to the solid-state band of zinc crotonate at 1613 cm^{-1} but it has moved down in frequency on going into solution. The hydroxy stretching mode observed in the solid-state spectrum of basic zinc

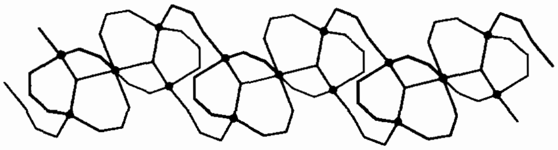

Fig. 2. Backbone of the basic zinc crotonate polymer. Side chains of crotonate not shown.

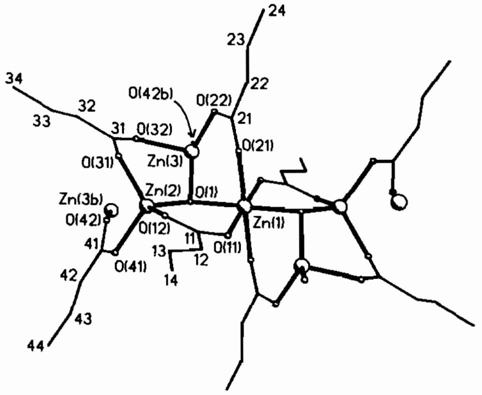

Fig. 3. The basic zinc crotonate unit with the atom numbering scheme (C atoms by number only) and connections to adjoining units. H atoms not shown.

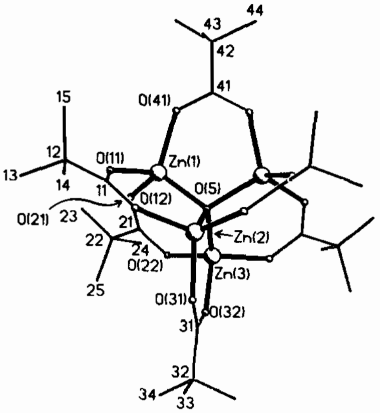

Fig. 4. The basic zinc pivalate structure with the atom numbering scheme. Acetone of crystallization not shown.

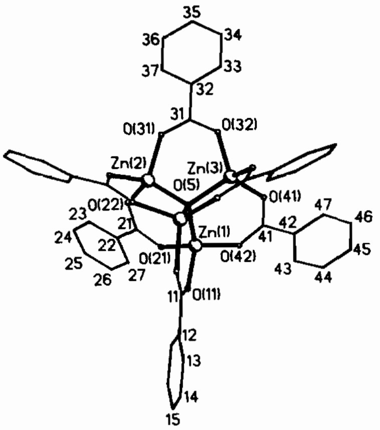

Fig. 5. The basic zinc benzoate structure with the atom numbering scheme. Acetone of crystallization not shown.

crotonate (3465 cm^{-1}) [22] is not observed in the solution spectrum of normal zinc crotonate, indicating that the hydroxy basic zinc crotonate structure is not produced.

The FT-IR spectrum of basic zinc crotonate in methanol produced a peak at 1571 cm^{-1} which lies between the 1556 and 1600 cm^{-1} bands observed in the normal zinc crotonate spectrum. There are no ν(O–H) or free acid bands and no normal zinc crotonate bands, suggesting that basic zinc crotonate has been converted to a new species, possibly $[Zn_4O(O_2CCHCHCH_3)_6]$. The lack of free acid and normal zinc crotonate would suggest a different series of events occurring in solution to that observed for pivalate and benzoate. The hydroxy basic species is not believed to form due to the presence of a different equilibrium. The hydroxy basic species is also quite unreactive towards carboxylic acids [22]. Thus the evidence suggests that a hydrated salt acts as a precursor to the formation of the hydroxy basic species [23].

Fast atom bombardment (FAB) mass spectrometry

The high ionization energy involved in electron impact (EI) mass spectrometry is likely to drive the equilibrium of eqn. (1) to the right, producing a fragmentation pattern of the tetranuclear basic species. The spectra were obtained using the lower ionization energies involved in FAB mass spectrometry, however; this technique is more likely to show both the normal and the tetranuclear species found in solution by IR measurements.

FAB mass spectra were recorded for solutions of the normal and basic zinc carboxylates. The presence of three major isotopes for zinc (^{64}Zn, ^{66}Zn, ^{68}Zn) make assignment of m/z for some peaks difficult, alleviated somewhat by characteristic isotope patterns for Zn_4, Zn_3, and Zn_2 clusters.

Zinc pivalate and basic zinc pivalate

FAB mass spectra were recorded in acetone and chloroform; deuterated acetone was used for normal zinc pivalate, see Table 12. Each spectrum was obtained using a matrix of metanitrobenzylalcohol (MNBA).

All four spectra show peaks due to basic zinc pivalate; however, one peak in each spectrum corresponds to the normal zinc pivalate $[Zn_2(O_2CC(CH_3)_3)_3]^+$ (m/z 433), the binuclear unit of the zinc pivalate polymer. The appearance of this ion in all of the spectra supports the idea that basic zinc pivalate does not need excess pivalic acid to

TABLE 9. Vibrational data[a] for zinc pivalate and basic zinc pivalate

Normal zinc pivalate (cm^{-1})			Basic zinc pivalate (cm^{-1})			
Acetone	Acetone-d^6	KBr	KBr	Acetone-d^6	Acetone	
1615(s)	1615(s)	1612(s)			1613(s)	$\nu(CO_2)_{as}$*syn–anti*
1587(s)[a]			1586(s)	1594(s)(br)	1588(s)	$\nu(CO_2)_{as}$*syn–syn*
		1535(s)				$\nu(CO_2)_{as}$*syn–syn*
1485(s)	1485(s)	1484(s)	1488(s)	1485(s)	1485(s)	δ(C–H)
1459(m)	1459(m)	1457(m)	1462(m)	1459(m)	1459(m)	δ(C–H)
1423(s)	1426(s)	1429(s)	1429(s)	1424(s)	1424(s)	$\nu(CO_2)_s$

[a] Range 1750–1400 cm^{-1}, carboxylate area only. s = strong, m = medium, br = broad.

TABLE 10. Vibrational data[a] for normal and basic zinc benzoate

Normal (cm^{-1})		Basic (cm^{-1})		
$CHCl_3$	KBr	KBr	$CHCl_3$	
1710(m)			1710(m)	benzoic acid
	1639(s)			$\nu(CO_2)_{as}$*syn–anti*
1607(s)			1607(s)	$\nu(CO_2)_{as}$*syn–syn*
	1594(s)	1600(s)		ring breathing
	1578(s)			ring breathing
1570(s)		1562(s)	1570(s)	$\nu(CO_2)_{as}$
	1531(s)			$\nu(CO_2)_{as}$*syn–syn*
1494(m)	1493(m)	1493(m)	1494(m)	ring breathing
N.O.	N.O.	1449(sh)	N.O.	ring breathing
1417(br)	1420(br)	1410(br)	1417(br)	$\nu(CO_2)_s$

[a] Range 1750–1400 cm^{-1}. br = broad, sh = shoulder. N.O. = not observed.

drive the equilibrium towards the normal species (see eqn. (1)).

The most intense peak in each spectrum is due to the $[Zn_3O(O_2CC(CH_3)_3)_3]^+$ (*m/z* 514) ion, the stability of which, in solution, is matched by the stability of the same species (with different carboxylate ligands) in both solid [24, 25] and gaseous state [26] spectra. Higher *m/z* species were found in two spectra only — zinc pivalate in chloroform and basic zinc pivalate in acetone. The most important of these ions are (i) $[Zn_5O_2(O_2CC(CH_3)_3)_5]^+$ (*m/z* 863) produced possibly by the fusion of normal and basic zinc pivalate followed by loss of pivalic anhydride, (ii) $[Zn_5O(O_2CC(CH_3)_3)_5]^+$ (*m/z* 846) produced by fusion of normal and basic zinc pivalate with loss of two pivalate ligands, (iii) $[Zn_4O(O_2CC(CH_3)_3)_5]^+$ (*m/z* 781) and (iv) $[Zn_4O_2(O_2CC(CH_3)_3)_4]^+$ (*m/z* 695) produced by loss of pivaldehyde from ion (iii). All of the spectra show smaller ions due to fragmentation of these species, especially the successive loss of pivalate ligand from these species. The fragmentation pathway of basic zinc pivalate in solution is very

TABLE 11. Vibrational data[a] for normal and basic zinc crotonate

Normal (cm^{-1})		Basic (cm^{-1})		
Methanol	KBr	KBr	Methanol	
1702(m)				Crotonic acid
1662(s)	1662(s)	1662(s)	1662(s)	ν(C=C)
	1613(s)			$\nu(CO_2)_{as}$*syn–anti*
1600(s, sh)				$\nu(CO_2)_{as}$
		1582(s, sh)		$\nu(CO_2)_{as}$*syn–anti*
			1571(s, br)	$\nu(CO_2)_{as}$
		1567(s)		$\nu(CO_2)_{as}$
1556(s, br)				$\nu(CO_2)_{as}$
	1547(s)			$\nu(CO_2)_{as}$*syn–syn*
		1530(s)		$\nu(CO_2)_{as}$*syn–syn*
	1520(s)			$\nu(CO_2)_{as}$*syn–syn*
		1512(s)		$\nu(CO_2)_{as}$
1450(s)	1441(sh)	1430(sh)	1450(m)	$\nu(CO_2)_s$
1422(s, br)	1429(s, br)	1418(s, br)	1422(s, br)	$\nu(CO_2)_s$
1400(sh)	1400(sh)	1400(sh)	1400(sh)	$\nu(CO_2)_s$

[a] Range 1750–1400 cm^{-1}: br = broad, sh = shoulder, s = strong, m = medium.

TABLE 12. FAB mass spectra for normal and basic zinc pivalates

Ions ($R = C(CH_3)_3$)	Normal in acetone-d^6	Basic in acetone	Normal in $CHCl_3$	Basic in $CHCl_3$
$Zn_5O_2(O_2CR)_5{}^+$		862(40)		
$Zn_5O(O_2CR)_5{}^+$		846(33)		
$Zn_4O(O_2CR)_5{}^+$		781(72)		
$Zn_4O(O_2CR)_6$–$2R^+$		768(22)		
$Zn_5O_2(O_2CR)_4{}^+$		761(26)		
$Zn_4O(O_2CR)_5$–R^+		724(33)		
$Zn_4O_2(O_2CR)_4{}^+$		696(19)		
$Zn_4O(O_2CR)_4{}^+$		680(18)		
$Zn_4O_2(O_2CR)_4$–H_2O^+		677(18)		
$Zn_4O(O_2CR)_3{}^+$		595(56)	595(28)	
$Zn_4O(O_2CR)_3{}^+$			579(34)	
$Zn_4O(O_2CR)_3$–$(R$–$CH_3)^+$		537(26)		
$Zn_4O(O_2CR)_3$–R^+			522(66)	
$Zn_3O(O_2CR)_3{}^+$	514(100)	514(100)	514(100)	514(100)
$Zn_3O(O_2CR)_3$–$CH_2{}^+$			500(38)	
$Zn_3O(O_2CR)_3$–CH_3OH^+			482(44)	482(48)
$Zn_2(O_2CR)_3{}^+$	433(44)	433(25)	433(75)	433(43)
$Zn_3O(O_2CR)_2{}^+$		413(15)	413(142)	

similar to that which takes place in the gas phase. For all of the spectra obtained, basic zinc pivalate seems to dominate in solution, suggesting that for the pivalates, the equilibrium of eqn. (1) lies to the right.

Zinc benzoate

FAB mass spectra of zinc benzoate were recorded in acetone and ethanol solutions with an MNBA matrix (see Table 13). Basic zinc benzoate is not sufficiently soluble in the common solvents to record adequate FAB mass spectra.

The most intense peak in each spectrum was due to $[Zn_2(O_2CC_6H_5)_3]^+$ (*m/z* 493), in marked contrast to the pivalate case. In ethanol, three other normal ions were observed: $[Zn_2(O_2CC_6H_5)_3 \cdot C_2H_5OH]^+$ (*m/z* 539), $[Zn_3(O_2CC_6H_5)_5$–$2C_6H_5]^+$ (*m/z* 645) and $[Zn_3(O_2CC_6H_5)_5]^+$ (*m/z* 800). The presence of these ions may explain why trinuclear [27–29] and binuclear [30, 31] adducts of zinc form so readily. The presence of the ethanol in one of the above ions suggests that the FAB technique really does produce ions which correspond closely to species found in solution. No basic ions were found in ethanol.

TABLE 13. FAB mass spectra for zinc benzoate

Ions ($R = C_6H_5$)	Acetone	Ethanol
$Zn_4O(O_2CR)_5{}^+$	882(1)	
$Zn_3(O_2CR)_5{}^+$		800(1)
$Zn_3O(O_2CR)_5$–$2R^+$		646(27)
$Zn_3O(O_2CR)_3{}^+$	574(37)	
$Zn_2(O_2CR)_3$–$C_2H_5OH^+$		539(23)
$Zn_2(O_2CR)_3{}^+$	493(100)	493(100)
$Zn_2(O_2CR)_3$–$2R^+$		339(24)
$Zn_3O(O_2CR)^+$	332(24)	
$Zn_2O(O_2CR)^+$	267(17)	

In acetone solution, two major basic zinc carboxylate ions occurred. The heavier species was in relatively low abundance compared with the normal species present — $[Zn_4O(O_2CC_6H_5)_6]^+$ (*m/z* 882) and $[Zn_3O(O_2CC_6H_5)_3]^+$ (*m/z* 574). The domination of the two spectra by the normal species indicates that the equilibrium of eqn. (1) lies to the left for benzoate.

Zinc crotonate and basic zinc crotonate

FAB mass spectra of normal zinc crotonate in chloroform and basic zinc crotonate in methanol were recorded with an MNBA matrix (see Table 14). The normal salt produced three ions due to normal zinc crotonate: $[Zn_3(O_2CCHCHCH_3)_5]^+$ (*m/z* 620), $[Zn_2(O_2CCHCHCH)_3]^+$ (*m/z* 385) and $[Zn_2(O_2CCHCHCH_3)_2$–$CHCHCH_3]^+$ (*m/z* 255). No ion appeared which could have arisen from the basic zinc crotonate polymer $[Zn_5(OH)_2(O_2CCHCHCH_3)_8]_x$; instead the tetranuclear basic species was represented by $[Zn_4O(O_2CCHCHCH_3)_5]^+$ (*m/z* 701) and $[Zn_3O(O_2CCHCHCH_3)_3]^+$ (*m/z* 466).

The FAB mass spectra of the basic zinc crotonate polymer produced the normal ion $[Zn_2(O_2CCHCHCH_3)_3]^+$ (*m/z* 385) and ions of higher *m/z* due to the basic tetranuclear zinc crotonate. One ion had *m/z* greater than 1000, ($[Zn_6O_2(O_2CCHCHCH_3)_7]^+$, *m/z* 1017), possibly formed due to the fusion of normal zinc crotonate

TABLE 14. FAB mass spectra for normal and basic zinc crotonate

Ions ($R=CHCHCH_3$)	Normal $CHCl_3$	Basic methanol
$Zn_6O_2(O_2CR)_7^+$		1017(2)
$Zn_4O(O_2CR)_6^+$		786(14)
$Zn_4O(O_2CR)_5^+$	701(30)	701(32)
$Zn_3(O_2CR)_5^+$	620(18)	
$Zn_4O(O_2CR)_4^+$		616(17)
$Zn_3(O_2CR)_5–H_2O$	602	
$Zn_4O(O_2CR)_4–C_3H_2O_2^+$		546(18)
$Zn_3O(O_2CR)_3^+$	466(95)	466(100)
$Zn_3O(O_2CR)_3–H_2O$	450	
$Zn_2(O_2CR)_3^+$	385(82)	385(82)
$Zn_3O(O_2CR)_2–CO_2^+$	337(32)	
$Zn_3O(O_2CR)_2^+$	296(26)	
$Zn_2(O_2CR)_2–CO_2^+$	256(22)	

and tetranuclear basic zinc crotonate followed by (or preceded by) loss of crotonaldehyde.

Both of these spectra indicate that zinc crotonate takes part in the equilibrium in eqn. (1).

It is interesting to note that the FAB mass spectrum of $[Zn_5(OH)_2(O_2CCHCHCH_3)_8]$ shows peaks which are apparently due to both normal zinc crotonate and $[Zn_4O(O_2CCHCHCH_3)_6]$ whereas the solution FT-IR spectrum of the hydroxy species is dominated by absorption bands which can be assigned to $[Zn_4O(O_2CCHCHCH_3)_6]$ only, although the presence of other species cannot be entirely ruled out.

Supplementary material

Complete tables of geometry, thermal parameters, H atom parameters and structure factors are available from the authors.

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