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FT-IR studies on the formation of tetrazinc long straight-chain (even-numbered C_6–C_{18}) μ_4-oxo-hexa-μ-carboxylates from the corresponding bis(carboxylato)zinc compounds

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Abstract

The bis(carboxylato)zinc(II) salts of even-numbered straight-chain fatty acids (C_6–C_{18}) were successfully prepared in boiling n-octane by neutralization. The mid-FT-IR spectra of n-octane solutions of the samples were recorded at 388 K. As a consequence of the dissolution process, the coordination of the carboxylate groups changed partially from bidentate to monodentate. The influence of water added to the solution on the solute was studied by means of FT-IR spectroscopy. Formation of $Zn_4O(RCOO)_6$ was detected, confirming the general validity of the earlier proposed mechanism of formation of the tetranuclear oxo-centered complexes of aliphatic carboxylic acids. The key factor is the presence of water in the system, which shifts the following equilibrium towards formation of the tetranuclear complex: $4Zn(RCOO)_2 + H_2O \rightleftharpoons Zn_4O(RCOO)_6 + (RCOOH)_2$.

Introduction

An earlier attempt to prepare zinc complexes of long straight-chain carboxylic acids, of the type $Zn_4O(RCOO)_6$, unexpectedly failed [1]. Even the reaction between ZnO and the carboxylic acids over C_{10} to yield bis-carboxylato compounds was considered hopeless in hot toluene solution.

The method reported for $Zn_4O(RCOO)_6$ for short straight-chain (C_2–C_5) carboxylates in carbon tetrachloride was not successful either above C_5 [2]. However, the mechanism of formation proposed recently [2] does not suggest any reason for such an essential difference in the mode of formation of this type of compound.

The present paper reports the successful preparation of compounds of the type $Zn(RCOO)_2$ in n-octane, and proof of the formation of complexes of the type $Zn_4O(RCOO)_6$ for even-numbered carboxylic acids between C_6 and C_{18} in n-octane, and provides further evidence concerning the mechanism of formation proposed earlier [2].

Experimental

Materials

The n-hexanoic (H(hex)), n-octanoic (H(oct)) and n-decanoic (H(dec)) acids were Merck products of synthetic grade. The n-dodecanoic (H(dod)), n-tetradecanoic (H(ted)), n-hexadecanoic (H(hed)) and n-octadecanoic (H(ocd)) acids were Fluka products of puriss. quality. Purum grade n-octane from Fluka was employed. All other chemicals were AR grade products from Reanal. All chemicals were used as received.

Preparation of samples

The compounds $Zn(RCOO)_2$ were prepared from $Zn(OH)_2$ with a 50% excess of the corresponding carboxylic acid in boiling n-octane. The $Zn(OH)_2$ was freshly precipitated from $ZnSO_4$ solution with NaOH, washed and air-dried. The concentration of zinc in the reaction mixtures was between 10^{-1} and 10^{-2} mol dm^{-3}. The reaction mixtures were refluxed until they became transparent. The products were crystallized from the clear solution by slow cooling. Shining feathery flakes were obtained in each case. The product was filtered off and washed with n-octane.

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Elemental analyses

The zinc contents of weighed samples were determined by EDTA titration after fuming the samples twice with a 1:1 mixture of concentrated nitric and perchloric acids and once with aqua regia. Eriochrome Black-T indicator was used at pH 10.

The carbon and hydrogen contents were determined by standard methods using Körbl catalyst.

The elemental analyses showed that each compound had the composition $Zn(RCOO)_2$ (Table 1).

FT-IR study

The mid-IR spectra of the samples were recorded on a Digilab FTS-20C FT-IR spectrophotometer equipped with a high-sensitivity DTGS detector in the range 4000–400 cm^{-1}. The resolution was 2 cm^{-1}, with 128 scans in each case. The spectra of solid samples were recorded in KBr pellets. The solution samples were recorded in a SPECAC 1-100 evacuable, variable-temperature sample holder, using a liquid cell with AgCl windows with 0.125 mm pathlength. The cell temperature was maintained at 388 ± 1 K. The solution samples were taken from boiling solutions of the corresponding zinc carboxylates in n-octane. The reference spectrum of the solvent was recorded under the same conditions. Interactive subtraction was performed to achieve the optimal signal/noise ratio in the 1800–1300 cm^{-1} region of the spectra.

Melting point determination

The bis(carboxylato)zinc(II) samples were studied by DSC (differential scanning calorimetry) and by visual detection using Electrothermal 9100 equipment. The reversible melting points were determined from the intercept of the extrapolated peak slope and the baseline from the DSC measurements. Both types of melting points are given in Table 2. The detailed DSC data will be published elsewhere.

TABLE 1. Elemental compositions of the solid samples

$Zn(RCOO)_2$		Zn	C	H	O
hex	found	22.17	48.85	7.52	–
	calc.	22.11	48.75	7.50	21.64
oct	found	18.61	54.68	8.52	–
	calc.	18.58	54.63	8.60	18.19
dec	found	16.08	59.05	9.42	–
	calc.	16.03	58.89	9.39	15.69
dod	found	14.15	62.30	10.02	–
	calc.	14.09	62.13	9.99	13.79
ted	found	12.60	64.44	10.43	–
	calc.	12.58	64.66	10.46	12.30
hed	found	11.38	66.68	10.84	–
	calc.	11.35	66.70	10.84	11.11
ocd	found	10.36	68.42	11.16	–
	calc.	10.34	68.38	11.16	10.12

TABLE 2. Melting points for $Zn(RCOO)_2$ prepared in n-octane, determined from DSC curves and by visual detection

$Zn(RCOO)_2$	DSC (K)	Visual detection (K)
n-Hexanoate	417	417–418
n-Octanoate	405	409–410
n-Decanoate	404	408–409
n-Dodecanoate	400	404–405
n-Tetradecanoate	398	404–405
n-Hexadecanoate	396	401–402
n-Octadecanoate	394	401–402

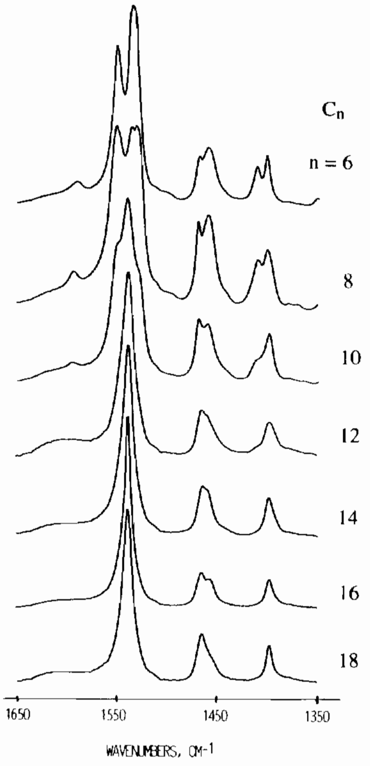

Fig. 1. The carboxylate stretching frequency region of $Zn(RCOO)_2$ prepared in n-octane (even-numbered C_6–C_{18}). The spectra were recorded in the solid state, in KBr pellets.

Results and discussion

Formation of bis(carboxylato)zinc(II) compounds in n-octane

The neutralization reactions between $Zn(OH)_2$ and the even-numbered straight-chain carboxylic acids between C_6 and C_{18} were successful at the boiling point of the solution. The zinc hydroxide dissolved readily, giving a clear solution. The IR spectra of the products which precipitated on cooling, are shown in Figs. 1 and 2. Similar series of spectra were published by Mesubi for samples prepared by metathesis in an ethanol–water mixture and recrystallized from hot benzene [3]. Comparison of these two series showed a very

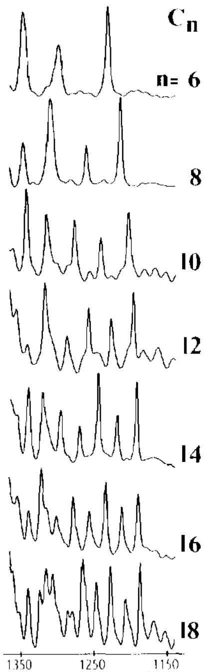

Fig. 2. The 'band progression' of $Zn(RCOO)_2$ samples prepared in n-octane (even-numbered C_6–C_{18}). The spectra were recorded in the solid state, in KBr pellets.

high degree of similarity between the corresponding spectra. In the case of Mesubi's spectra, the splitting of the $\nu_{as}(COO^-)$ bands from C_6 to C_{18} was pronounced. Our samples did not show that above C_{10}. The most obvious interpretation of this is that solid state effects — factor group splitting — vanish at higher carbon numbers. The aggregation of the two sets of samples could be altered by the different preparation methods. The frequencies of the carboxylate stretching bands are listed in Table 3. The range of 'band progression' (1375–1150 cm^{-1}) was well developed, reflecting the highly crystalline state of the samples with the alkyl chains in the all-*trans* conformation (Fig. 2).

IR data coupled with XR studies [4, 5] suggested that these carboxylate frequencies indicated the presence of bidentate carboxylate bridges between zinc ions, forming a polymeric sheet structure which is characteristic of zinc straight-chain carboxylates [6–8].

It could also be concluded that the neutralization reaction was complete in each case, as indicated by the results of elemental analyses (see Table 1).

TABLE 3. Carboxylate stretching frequencies of solid $Zn(RCOO)_2$ prepared in n-octane. Spectra were recorded in KBr pellets

$Zn(RCOO)_2$	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$
n-Hexanoate	1532bs	1399m
	1548bs	1409m
	1588vw	
n-Octanoate	1529bs	1399m
	1534bs	1409m
	1549bs	
	1592vw	
n-Decanoate	1528sh	1397m
	1539bs	1408sh
	1549sh	
	1599vw	
n-Dodecanoate	1539nvs	1399m
n-Tetradecanoate	1539nvs	1399m
n-Hexadecanoate	1539nvs	1399m
n-Octadecanoate	1539nvs	1399m

nvs = narrow and very strong, bs = broad and strong, m = medium, vw = very weak, and sh = shoulder.

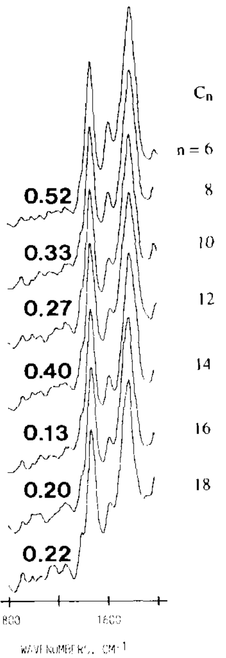

Fig. 3. The antisymmetric carboxylate stretching band region of the IR spectra for n-octane solutions of $Zn(RCOO)_2$ (even-numbered between C_6 and C_{18}) at 388 K. Intensities are given by the figures on the left-hand side.

Spectra of n-octane solutions of bis(carboxylato)zinc(II) samples at 388 K

The solid samples were dissolved in boiling n-octane, the concentration being about 10^{-2} M for zinc. Samples were taken from the boiling clear solutions and their spectra were recorded at 388 ± 1 K. Spectra in the interval 1800–1500 cm^{-1} are shown in Fig. 3. This region, representing the carboxylate stretching frequencies, shows three well-defined features with fixed positions at 1636, 1599 and 1560 cm^{-1}, as strong, weak and strong bands, respectively. Within experimental error these frequencies are practically identical for all the samples. The frequencies of the corresponding $\nu_s(COO^-)$ bands were not reliable in n-octane because of band overlapping, but after solvent subtraction they can be located in the region 1436–1431 $\mathrm{cm^{-1}}$.

It is obvious that the coordination of the carboxylate groups changed as a consequence of dissolution (see Figs. 1 and 3). A similar phenomenon was found above the melting point in a study of the thermal dependence of the IR spectra of the same series of zinc carboxylates [3]. Furthermore, the bands at 1636 and 1560 $\mathrm{cm^{-1}}$ have been established as characteristic for the bis(carboxylato)zinc(II) compounds of branched-chain acids [10–12]. Other structural data on the zinc carboxylates supported the assumption that the coordination of the carboxylate groups changed partially from bidentate to monodentate [9], with breaking-up of the polymeric sheet structure.

The weak band at 1599 $\mathrm{cm^{-1}}$ showed the presence of a small amount of another species, the $\mathrm{Zn_4O(RCOO)_6}$ form. The recently-reported mechanism of formation of compounds of the type $\mathrm{Zn_4O(RCOO)_6}$ contained a key step: the reaction between $\mathrm{Zn(RCOO)_2}$ and the water present in the system [2].

$$\mathrm{4Zn(RCOO)_2 + H_2O \rightleftharpoons Zn_4O(RCOO)_6 + (RCOOH)_2} \qquad (1)$$

In order to confirm this reaction, water at a concentration of 10^{-2} mol $\mathrm{dm^{-3}}$ was added to the hot solutions and new samples were taken for IR study. The recorded spectra in the region 1800–1500 $\mathrm{cm^{-1}}$ are shown in Fig. 4. The carboxylate bands at 1599 $\mathrm{cm^{-1}}$ indicate the formation of $\mathrm{Zn_4O(RCOO)_6}$. The $\nu_{as}(\mathrm{Zn_4O})$ band was the most significant proof of its formation for the short straight-chain carboxylates [2]. Unfortunately, in the present case the signal/noise ratio was poor in the 700–400 $\mathrm{cm^{-1}}$ range of the spectra under these circumstances, due to the low concentration and the very low relative intensity of the band. However, further support for $\mathrm{Zn_4O(RCOO)_6}$ formation is given by the presence of the $\nu(\mathrm{C{=}O})$ bands of the uncomplexed dimers of the acids $\mathrm{(RCOOH)_2}$, as eqn. (1) predicted. There was a slight shift in the frequencies of the carbonyl bands with increasing carbon number of the alkyl group. Their rounded values were 1718 $\mathrm{cm^{-1}}$ for $\mathrm{C_6}$, $\mathrm{C_8}$ and $\mathrm{C_{10}}$, 1717 $\mathrm{cm^{-1}}$ for $\mathrm{C_{12}}$ and $\mathrm{C_{14}}$, and 1716 $\mathrm{cm^{-1}}$ for the $\mathrm{C_{16}}$ and $\mathrm{C_{18}}$ acids.

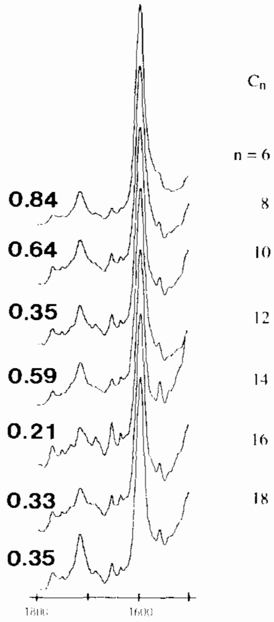

Fig. 4. The antisymmetric carboxylate stretching band region of the IR spectra for n-octane solutions of $\mathrm{Zn(RCOO)_2}$ after water treatment (even-numbered between $\mathrm{C_6}$ and $\mathrm{C_{18}}$) at 388 K. Intensities are given by the figures on the left-hand side.

On the above basis, we were able to add an extra step to the mechanism of formation of $\mathrm{Zn_4O(RCOO)_6}$: the dissolution equilibrium of the bis(carboxylato)-zinc(II).

The mechanism for the reactions of the aliphatic carboxylic acids with $\mathrm{Zn(OH)_2}$ can therefore be characterized by the following scheme:

$$\begin{tikzcd}
\mathrm{4Zn(OH)_2\ (s) + 4(RCOOH)_2\ (sol)} \arrow[d, "\mathrm{-4H_2O\ (sol)}"] \\
\mathrm{4Zn(RCOO)_2\ (s)} \arrow[d, shift left, harpoon] \\
\mathrm{4Zn(RCOO)_2\ (sol)} \arrow[u, shift left, harpoon] \arrow[d, shift left, harpoon, "\mathrm{+H_2O\ (sol)}"] \\
\mathrm{Zn_4O(RCOO)_6\ (sol) + (RCOOH)_2\ (sol)} \arrow[u, shift left, harpoon] \arrow[uuu, bend right=90]
\end{tikzcd}$$

It can be stated, that the formation of $\mathrm{Zn_4O(RCOO)_6}$ is a general feature of the zinc carboxylates, but the conditions of formation are dependent on the structure of the alkyl group in the carboxylic acid. Branched-chain acids readily give this type of compound in organic solvents [1, 13]. The short straight-chain carboxylic acids yield the complex at a slightly elevated temperature [2]. Their formation from higher fatty acids requires an even higher temperature, although the presence of water in all systems is the most important requirement for the formation of $\mathrm{Zn_4O(RCOO)_6}$.

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