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Formation and mid-FT-IR investigation of short (C_2–C_5) straight chain tetrazinc μ_4-oxo-hexa-μ-carboxylates

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Abstract

A new method for producing tetrazinc μ_4-oxo-hexa-μ-carboxylates of short straight-chain carboxylic acids in solution is reported. The complexes with C_2–C_5 chain have been prepared. Their characteristic IR bands in the mid-IR region are discussed and give a satisfactory identification method for these complexes. The formation process and the influence of the water present in the system have been monitored by FT-IR spectroscopy. A modified mechanism of formation and decomposition, based on an equilibrium and a 'feedback' step, is proposed.

Introduction

The usual method for preparation of short straight-chain $Zn_4O(RCOO)_6$ complexes, used by previous investigators, has been the vacuum distillation of the corresponding bis-carboxylato compound [1–7].

In the case of branched-chain carboxylic acids the preparation was successfully carried out in aromatic solvents by Silver and co-workers [5, 8] but the method has not proved satisfactory for straight-chain carboxylates.

Hardt and Stavenow were successful with an extraction method for the acetate complex [9].

Our investigation on the solutions of long chain zinc bis-carboxylates in non-polar solvents showed, that the previously proposed mechanism of formation [5] for these complexes is not sufficient to explain all the phenomena [10].

The present paper describes a method of preparation of $Zn_4O(RCOO)_6$ complexes for short straight-chain carboxylic acids in a non-polar solvent and suggests a modified mechanism of formation. The IR data serve as a more convincing base for identification of the $Zn_4O(RCOO)_6$ species formed.

Experimental

Materials

All acids used were of Merck 'zur Synthese' grade. The zinc oxide was prepared from zinc hydroxide, precipitated from $ZnSO_4$ solution by NaOH, by thermal dehydration after careful washing with distilled water. The carbon tetrachloride was of Fluka 'for IR spectroscopy' grade and employed without further purification.

FT-IR study

Spectra were recorded between 4000–400 cm^{-1} on a Nicolet 7199 Fourier transform infrared spectrometer using a KBr–Ge beam splitter and liquid N_2 cooled MCT detector. The spectra were recorded using KBr liquid cell with 0.1 mm thickness or as cast solid films on KBr disks. The resolution was 2 cm^{-1} and the frequencies are correct to within 1 cm^{-1}. The number of scans was 128 in each case.

Preparation of samples

The $Zn_4O(RCOO)_6$ complexes of acetic (ac), propionic (prop), n-butyric (but) and n-valeric (val) acids were prepared in boiling carbon tetrachloride by reaction of the acid with a two-fold excess of ZnO.

$$4ZnO + 6RCOOH \longrightarrow Zn_4O(RCOO)_6 + 3H_2O$$

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The progress of the reaction was monitored by FT-IR spectroscopy, taking samples from the reaction mixtures.

The samples of the reaction mixtures were filtered through a G4 sintered glass funnel using Celite as coagulating agent.

The concentrations of the samples were increased to about 0.1 mol/dm^3 zinc concentration by distilling off the solvent.

The reaction was studied in the presence of excess amount of water, added to the reaction mixture to saturate the solvent.

Solid samples were prepared by complete evaporation of the solvent.

Elemental analyses

The zinc content of the solid samples and solutions were determined by EDTA titration, using Eriochrom Black-T indicator at pH = 10. Carbon and hydrogen content were also measured for the solid samples by standard methods, and the results are given in Table 1.

Results and discussion

Characteristic bands of the $Zn_4O(RCOO)_6$ structure in the mid-IR region

The 29 atoms approach with T_d total symmetry of the $Zn_4O(RCOO)_6$ molecule predicts thirteen F_2 infrared active normal vibrations. Two of these are dominated by C–O and three by Zn–O stretching modes of the $Zn_4O(OOC)_6$ core. Both carboxylate stretching vibrations and one of the Zn–O modes, assigned to the central Zn_4O tetrahedron, have been reported in the mid-IR region [4–6].

The corresponding regions of the spectra recorded in CCl_4 are shown in Fig. 1. The frequencies and the assignments of the bands are given in Table 2.

TABLE 1. Elemental composition of the solid samples

$Zn_4O(RCOO)_6$		Zn	C	H	O
ac	found	38.25[a]	21.05	3.27	
	calc.	41.39	22.82	2.87	32.92
prop	found	35.21[a]	29.09	4.83	
	calc.	36.53	30.20	4.22	29.05
but	found	32.61	35.93	5.85	
	calc.	32.69	36.03	5.29	25.99
val	found	29.30	40.30	6.97	
	calc.	29.58	40.75	6.15	23.52

[a] The relatively large difference is due to the decomposition of the sample is solid state (see text), but the value agrees with the expected 2:3 molar ratio of Zn^{2+} and $RCOO^-$.

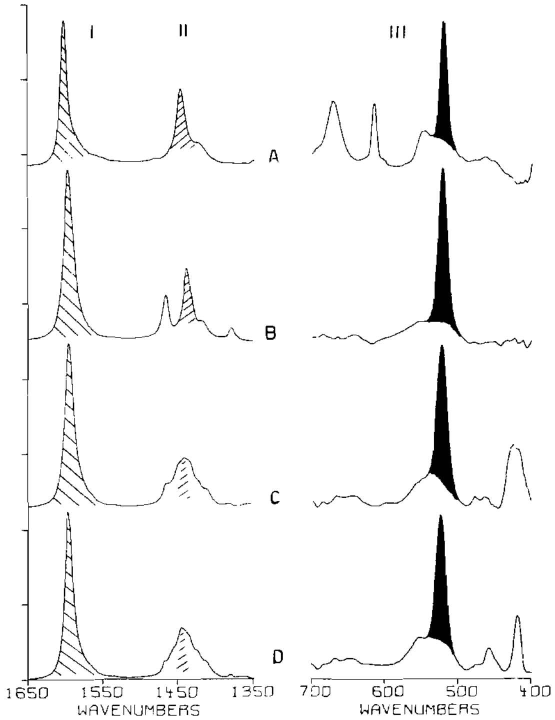


Fig. 1. Mid-IR spectra of $Zn_4O(ac)_6$ (A), $Zn_4O(prop)_6$ (B), $Zn_4O(but)_6$ (C) and $Zn_4O(val)_6$ (D) between 1650–1350 and 700–400 cm^{-1} in CCl_4. Band I = $\nu_{as}COO^-$, band II = ν_sCOO^-, band III = $\nu_{as}Zn_4O$.

TABLE 2. Characteristic bands of the tetranuclear zinc–oxo-acetate, propionate, n-butyrate and n-valerate in CCl_4 solution[a]

$Zn_4O(RCOO)_6$	$\nu_{as}COO^-$	ν_sCOO^-	$\nu_{as}Zn_4O$
acetate	1603vs	1446s	521w
propionate	1597vs	1439s	522s
butyrate	1596vs	1441m	522w
valerate	1596vs	1445m	523w

[a] vs = very strong, s = strong, m = medium, w = weak.

In addition to the analytical results, correspondence between bands reported previously at 1600, 1440 and 530 cm^{-1} for $Zn_4O(ac)_6$ gives spectroscopic support for the formulation of the compounds as the tetranuclear zinc–oxo-carboxylates of the corresponding acids.

The first remarkable difference between the previously reported $Zn_4O(ac)_6$ spectrum [6] and these spectra (Fig. 1), the sharpness of the bands, indicates the lack of intermolecular interactions and the perfect T_d symmetry of the common part of the molecules.

The bands of the antisymmetric carboxylate stretching vibration (local mode B_1 of C_{2v} subgroup) are the strongest bands of the spectra, appearing in a narrow frequency range 1603–1596 cm^{-1}. The frequency shift of this band follows qualitatively the mass law of the harmonic oscillator model, and shows that the part of the chain which is above the β-carbon does not contribute to this normal vibration.

The symmetric stretching band of the carboxylate group overlaps with the CH deformation bands of the R group in the case of butyrate and valerate. Fourier deconvolution was applied to determine the number of components and their estimated frequencies [11] (Figs. 2 and 3, curve 2). Lorentzian curves were generated and fitted to the original spectra by the simplex method [12] (Figs. 2 and 3, curves 2 and 4). The data of the fitted peaks are given in Tables 3 and 4. The components with the highest intensity were assigned as symmetric carboxylate stretching vibrations. In this normal vibration the C–O stretching coordinates are strongly coupled with the internal coordinates of the whole R group.

The lowest magnitude of frequency shift with the carbon number of the R group was observed in the case of the band assigned to the central Zn_4O tetrahedron, but this shift is clearly in the opposite direction to the frequency shift of the antisymmetric carboxylate stretching vibration. This phenomenon, and the fact that this band is surprisingly strong in the case of $Zn_4O(prop)_6$, indicate that the chain has

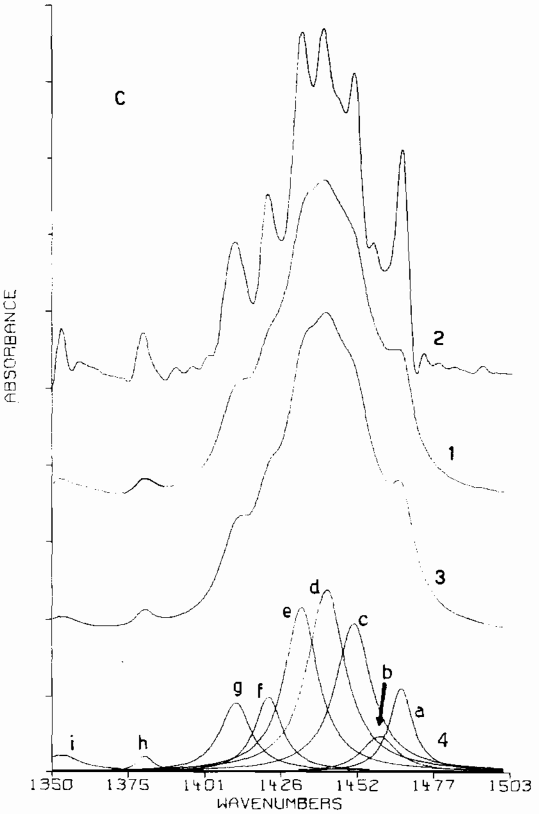


Fig. 2. Resolution enhancement of overlapping bands in the range of symmetric carboxylate stretching bands in the case of $Zn_4O(but)_6$ (C): 1, original spectrum; 2, result of Fourier deconvolution with parameters VF0 = 8 and VF1 = 2; 3, sum of generated Lorentzian curves; 4, generated Lorentzian curves, the components of the broad band. Parameters of the components are given in Table 3.

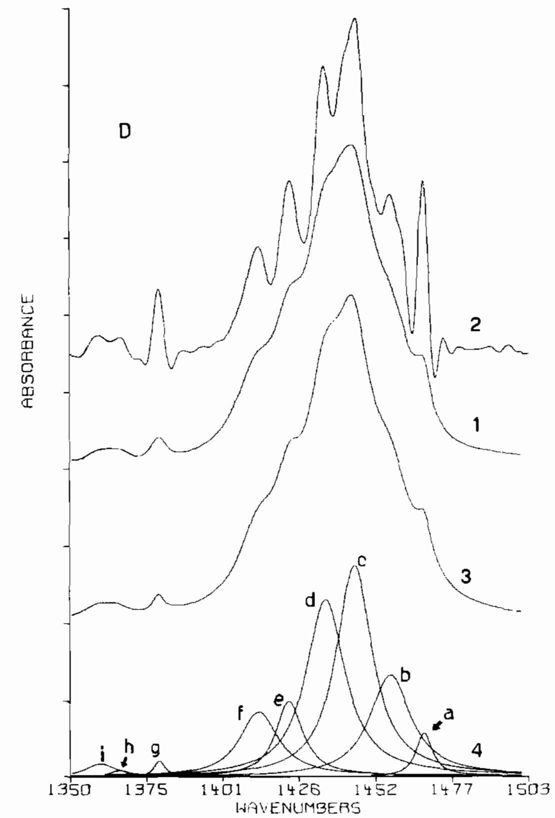


Fig. 3. Resolution enhancement of overlapping bands in the range of symmetric carboxylate stretching bands in the case of $Zn_4O(val)_6$ (D): 1, original spectrum; 2, result of Fourier deconvolution with parameters VF0 = 8 and VF1 = 2; 3, sum of generated Lorentzian curves; 4, generated Lorentzian curves, the components of the broad band. Parameters of the components are given in Table 4.

TABLE 3. Parameters of the components of the band I of $Zn_4O(but)_6$

Line	Position (cm^{-1})	Width (cm^{-1})	Intensity	Area (%)
a	1466.12	9.59	81	7.4
b	1458.92	14.47	35	4.8
c	1450.25	15.23	143	20.7
d	1441.14	15.69	175	26.3
e	1432.77	14.16	158	21.3
f	1421.90	11.42	73	7.9
g	1410.88	12.94	67	8.2
h	1380.48	7.16	15	1.1
i	1352.71	15.23	16	2.3

TABLE 4. Parameters of the components of the band I of $Zn_4O(val)_6$

Line	Position (cm^{-1})	Width (cm^{-1})	Intensity	Area (%)
a	1467.88	6.70	37	2.9
b	1456.71	17.06	85	17.1
c	1444.67	14.77	176	30.6
d	1435.12	15.99	148	27.8
e	1423.08	11.27	64	8.6
f	1412.94	15.99	55	10.4
g	1379.45	4.41	13	0.6
h	1365.67	7.16	5	0.4
i	1359.47	12.34	11	1.6

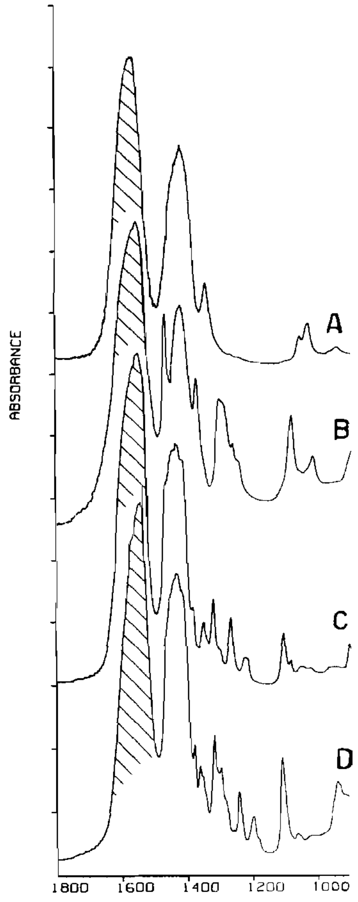


Fig. 4. Region of the carboxylate stretching bands of the solid samples, recorded as a cast film on KBr disk. A, $Zn_4O(ac)_6$; B, $Zn_4O(prop)_6$; C, $Zn_4O(but)_6$; D, $Zn_4O(val)_6$.

some influence on the normal vibration of the core.

The carboxylate stretching region of the IR spectra of the solid samples are shown in Fig. 4. The antisymmetric carboxylate stretching bands are shifted to the 1560–1540 cm^{-1} range which corresponds to the zinc bis-carboxylato compounds [13]. The bands at about 520 cm^{-1} completely disappeared, but new bands turned up in the OH stretching region and their intensity increased in time as shown in the case of $Zn_4O(ac)_6$ (Fig. 5).

These results are in agreement with the reported instability of $Zn_4O(ac)_6$ and $Zn_4O(prop)_6$, but it is inconsistent with the supposed moisture sensitivity [2, 14].

The decomposition must consist of two steps. The first is the rearrangement into a zinc bis-carboxylate type structure.

$$Zn_4O(RCOO)_{6(s)} \longrightarrow 3Zn(RCOO)_{2(s)} + ZnO_{(s)}$$

The second is the reaction of the finely dispersed ZnO with the atmospheric moisture.

$$ZnO_{(s)} + H_2O_{(g)} \longrightarrow Zn(OH)_{2(s)}$$

This mechanism of decomposition is supported by the observation of Gordon and Silver [5]; in several cases they have found that the zinc–oxo-carboxylates behave as mixtures of zinc bis-carboxylate and zinc oxide.

On the basis of these data, it is obvious, that the convincing identification of the existence of the $Zn_4O(RCOO)_6$ structure is possible in the case of alkyl carboxylates on the basis of the antisymmetric carboxylate stretching vibration appearing at a relatively high frequency about 1600 cm^{-1} and the appearance of the antisymmetric stretching band of the central Zn_4O tetrahedron at about 530–520 cm^{-1} in the mid-IR spectrum.

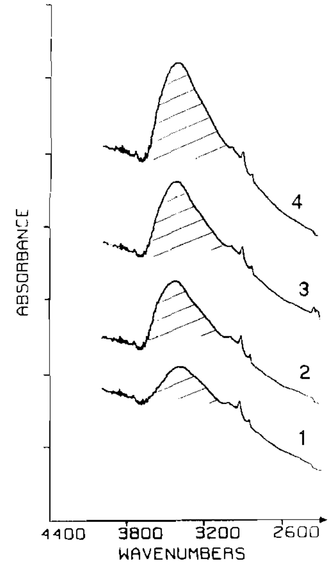
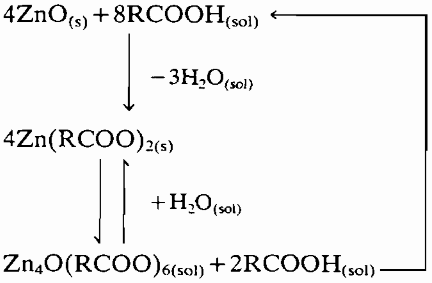


Fig. 5. Intensity change of the νO–H stretching band during the decomposition of $Zn_4O(ac)_6$ in film phase. The spectra were recorded at 10 min intervals in 1–4 sequence.

Mechanism of formation of $Zn_4O(RCOO)_6$ complexes in CCl_4

The carbonyl stretching band of the dimeric carboxylic acid disappeared very quickly from the spectra of the samples taken from the reaction mixtures, and there was no detectable solute in the solvent at that stage. This gives further support to the conclusion that the first step of the reaction is the formation of the bis-carboxylato compound [5]. On refluxing the reaction mixture for a longer period of time (6–24 h), a new band appeared in the filtrate at about 1600 cm^{-1}, indicating the formation of the tetranuclear zinc–oxo-carboxylate complex. Addition of water to the reaction mixture sharply increased the rate of this reaction and the yield of the basic carboxylate. These observations suggest a modified mechanism of formation, containing a 'feedback' step.



The presence of solute water in the reaction mixture is the most important condition for the formation of the $Zn_4O(RCOO)_6$ complexes. The second step of the reaction is reversible and leads to equilibrium, on the basis of our previous studies on the dissolution process of branched-chain zinc carboxylates in non-polar solvents [15, 16].

Acknowledgements

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