The Mass Spectra of Basic Zinc Carboxylates

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VOGEL AND HOBROCK[1] have recently reported on the mass spectrometry of oxohexakis(carboxylato)-tetraberyllium(II) chelates, basic beryllium carboxylates, and made brief mention of two zinc analogues, basic zinc acetate and propionate.

Studying the preparation and properties of certain basic zinc carboxylates,[2] we prepared the basic zinc 2-ethylhexanoate, $(C_7H_{15}CO_2)_6Zn_4O$, b.p. 255°/0·1 mm., n_D^{25} 1·4570, and the basic zinc 3,5,5-trimethylhexanoate, b.p. 282°/0·05 mm., n_D^{25} 1·4637. These compounds were prepared either by heating toluene solutions of the respective acids with appropriate quantities of zinc oxide or by treating zinc oxide with a stoicheiometric amount of the neutral carboxylate in boiling toluene. With an excess of zinc oxide only the stoicheiometric amount was consumed. Removal of water of reaction and solvent yielded in both cases a viscous oil which was purified by distillation. A sample of basic zinc acetate was also prepared[3] and its structure[4] as $(CH_3CO_2)_6Zn_4O$ confirmed by *X*-ray crystallography.† Mass spectra were obtained on an MS9 mass spectrometer; the samples were introduced through a direct insertion probe system at source temperatures between 150—180°.

In all cases the spectra obtained were similar to those reported for the basic beryllium carboxylates. In particular the base peak was due to the species $[(RCO_2)_5Zn_4O]^+$ and the molecular ion $[(RCO_2)_6Zn_4O]^+$ was very weak, less than 0·1 per cent of the base peak, or absent in the case of the acetate. Though Vogel and Hobrock commented on the intensity of some doubly charged ions in the spectra of the beryllium complexes they did not include them in their scheme of fragmentation. For the zinc complexes, with the exception of the 3,5,5-trimethylhexanoate, the doubly charged ion $[(RCO_2)_4Zn_4O]^{2+}$ was one of the major peaks in the spectra and gave rise to the metastable peaks described below. The 3,5,5-trimethylhexanoate derivative was different since its major fragmentation routes from the $[(RCO_2)_5Zn_4O]^+$ ion are considerably influenced by the ready loss of alkyl groups and, in consequence, the $[(RCO_2)_4Zn_4O]^{2+}$ ion was very weak.

Mixed basic zinc carboxylates were prepared, as described above, from (*a*) 5 : 1 molar mixture of 2-ethylhexanoic and crotonic acids; (*b*) 5 : 1 molar mixture of 2-ethylhexanoic and pivalic acids and (*c*) 1 : 1 molar mixture of 2-ethylhexanoic and crotonic acids. In all three cases a range of intense peaks were observed corresponding to $[(RCO_2)_{5-n}(R^1CO_2)_nZn_4O]^+$, ($R = $ 2-ethylhexyl and $R^1 = $ crotyl or pivalyl), where *n* had all values from 0 to 5. Thus like the mixed basic beryllium

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† Determined by G. W. Smith of these laboratories.

carboxylates,[1] preparation of the mixed basic zinc salts gives a range of products and not pure mixed salts.[5]

A unique feature of these basic zinc carboxylate spectra was the presence of metastable peaks at mass numbers greater than the parent ions. These arise from the transition

$$[(RCO_2)_4Zn_4O]^{2+} \rightarrow [(RCO_2)_3Zn_4O_2]^{+} + [RCO]^{+}$$

An example is illustrated in the Figure which shows the upper mass region of the spectrum of basic zinc 2-ethylhexanoate. Since the two species involved in the transition each contain four zinc atoms, they each consist of about fifteen peaks and in consequence the metastable peak is very broad, *i.e.* it covers 30 to 40 mass numbers. Similar metastable peaks were observed for the mixed salts where, because of the presence of compounds containing two acid groups in varying proportions, a number of transitions are possible. A list of the metastable peaks observed, together with the primary and secondary ions is given in the Table. Metastable transitions of doubly charged ions to single charged ions have been observed for the small molecules carbon dioxide[6] and benzene,[7] and metastable transitions involving triply charged aromatic hydrocarbons have been reported recently.[8] It is believed, however, that the results quoted here are the first examples of metastable transitions of doubly charged ions from large metal-containing compounds.

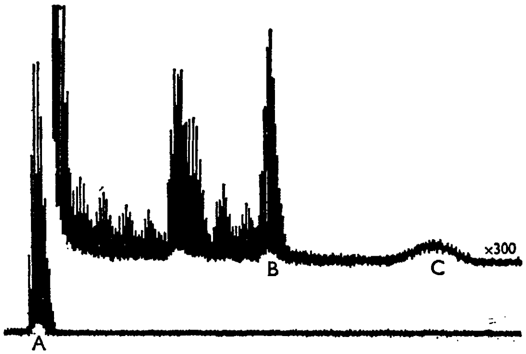

FIGURE. *Partial mass spectrum of basic zinc 2-ethylhexanoate.* (A) *Base peaks centred at* 993 m/e *due to* $[(RCO_2)_5Zn_4O]^+$ $R = C_7H_{15}$; (B) *Parent peaks centred at* 1136 m/e *due to* $[(RCO_2)_6Zn_4O]^+$; (C) *Metastable peak centred at* 1229 m/e *due to transition*

$$\underset{849\cdot7\ m/e}{[(RCO_2)_4Zn_4O]^{2+}} \rightarrow \underset{722\cdot7\ m/e}{[(RCO_2)_3Zn_4O_2]^{+}} + [RCO]^{+}$$

$$m^* = 2 \times (722\cdot7)^2/849\cdot7 = 1229\cdot4$$

Doubly charged metastable transitions observed in the mass spectra of basic zinc carboxylates

$$m^* = 2\ m_1{}^2/m_0$$

Compound	Primary ion m_0	Secondary ion m_1	Metastable ion m^* position (calculated)
(2-Ethylhexanoate)$_6$Zn$_4$O	$[(C_7H_{15}CO_2)_4Zn_4O]^{2+}$	$[(C_7H_{15}CO_2)_3Zn_4O_2]^{+}$	1229·4
†(2-Ethylhexanoate)$_5$-(pivalate) Zn$_4$O ..	$[(C_7H_{15}CO_2)_4Zn_4O]^{2+}$	$[(C_7H_{15}CO_2)_3Zn_4O_2]^{+}$	1229·4
	$[(C_7H_{15}CO_2)_3(C_4H_9CO_2)Zn_4O]^{2+}$	$[(C_7H_{15}CO_2)_2(C_4H_9CO_2)Zn_4O_2]^{+}$	1148·0
	$[(C_7H_{15}CO_2)_2(C_4H_9CO_2)_2Zn_4O]^{2+}$	$[(C_7H_{15}CO_2)_2(C_4H_9CO_2)Zn_4O_2]^{+}$	1211·1
	$[(C_7H_{15}CO_2)_2(C_4H_9CO_2)_2Zn_4O]^{2+}$	$[(C_7H_{15}CO_2)(C_4H_9CO_2)_2Zn_4O_2]^{+}$	1065·5
	$[(C_7H_{15}CO_2)(C_4H_9CO_2)_3Zn_4O]^{2+}$	$[(C_7H_{15}CO_2)(C_4H_9CO_2)_2Zn_4O_2]^{+}$	1128·1
†(2-Ethylhexanoate)$_5$-(crotonate) Zn$_4$O ..	$[(C_7H_{15}CO_2)_4Zn_4O]^{2+}$	$[(C_7H_{15}CO_2)_3Zn_4O_2]^{+}$	1229·4
	$[(C_7H_{15}CO_2)_3(C_3H_5CO_2)Zn_4O]^{2+}$	$[(C_7H_{15}CO_2)_2(C_3H_5CO_2)Zn_4O_2]^{+}$	1116·1
(Acetate)$_6$Zn$_4$O	$[(MeCO_2)_4Zn_4O]^{2+}$	$[(MeCO_2)_3Zn_4O_2]^{+}$	862·6

† Nominal composition (see text).

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[2] U.S. Pat., 3367869.
[3] V. Auger and I. Robin, *Compt. rend.*, 1924, **178**, 1546.
[4] H. Koyama and Y. Saito, *Bull. Chem. Soc. Japan*, 1954, **27**, 112.
[5] *Cf.* S. Tanatar, *Ber.*, 1910, **43**, 1320, who reported a number of apparently pure mixed basic beryllium carboxylates.
[6] A. S. Newton and A. F. Sciamanna, *J. Chem. Phys.*, 1964, **40**, 718.
[7] W. Higgins and K. R. Jennings, *Chem. Comm.*, 1965, 99.
[8] K. R. Jennings and A. F. Whiting, *Chem. Comm.*, 1967, 820.