Thermal Decomposition of Copper(II) Carboxylates: Mass Spectra of Binuclear Copper(I) Carboxylates

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As part of a study of the mass spectra of metal chelates we have investigated the behaviour of copper(II) acetate and copper(II) benzoate. Copper(II) acetate monohydrate is a binuclear complex with bridging carboxylate groups.[1] Several carboxylates have this structure in which quenching of the spin moment of the copper(II) ion occurs and the Cu–Cu distance is relatively short.[2] The benzoate is polymeric, with bridging carboxylate group, like the acetate; but the magnetic moment is normal.[2] The thermal decomposition of hydrated copper(II) acetate has been studied by differential thermal analysis and thermogravimetic analysis.[3] It was reported that dehydration *in vacuo* occurs at *ca.* 180° followed, at higher temperatures, by rapid decomposition to CuO, with water, acetone, and carbon dioxide as the major volatile products (identified mass spectrometrically). However, we have observed that volatile binuclear copper(I) carboxylates are among the decomposition products of copper(II) carboxylates. Because of the current interest in the mass spectra of inorganic

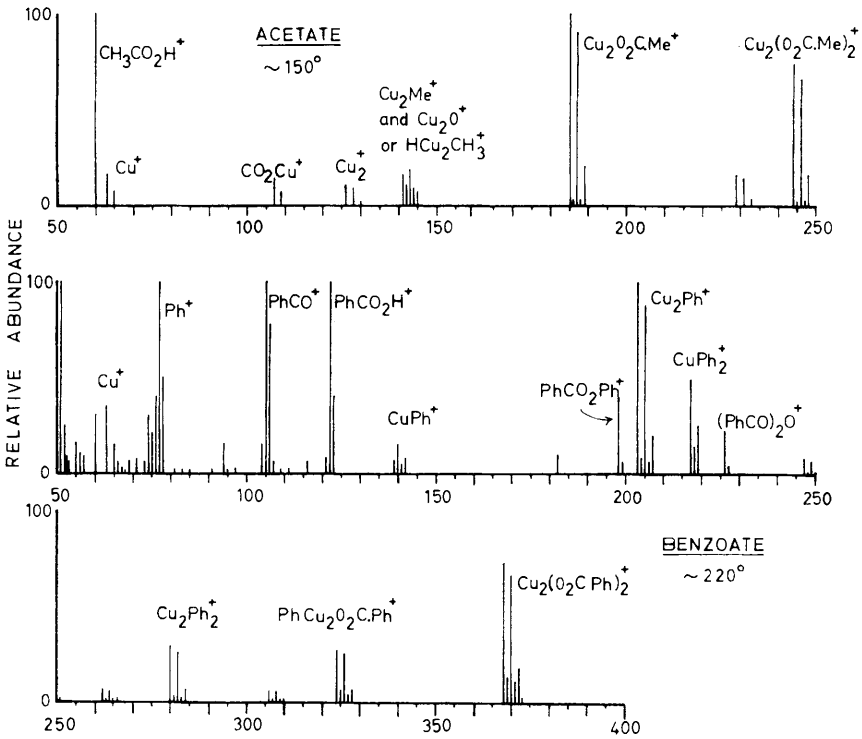

FIGURE. *Mass spectra of binuclear copper(I) acetate and benzoate. Abundances are relative to the most abundant copper-containing ion. The ions at masses* **51**, **60**, **77**, **105**, *and* **122** *were actually more than* **100** *on this scale but may arise from sources other than the parent copper ion.*

complexes, we report the mass spectra of these species.

The samples of copper(II) acetate and copper(II) benzoate were introduced *via* a vacuum lock, on a direct insertion probe, into the heated-ion source of a Hitachi RMU 6D single-focussing mass spectrometer. After the elimination of volatile decomposition products the mass spectra shown in the Figure were obtained with sample temperatures as noted, and for an electron energy of 50 v. The major peaks in the spectra are consistent with the ionization and fragmentation of binuclear copper(I) species. The interpretation of the copper acetate spectrum appears straightforward. The ions containing one copper atom could arise from a mononuclear species but this is considered unlikely since their relative intensity remained sensibly constant with variation of sample temperature. The copper benzoate spectrum contains several ions arising from migration of the phenyl group, in two cases (**368**→**324**, **324**→**280**) the process is confirmed by the presence of a metastable transition. There is also a metastable transition for the process $Cu_2Ph_2^+ \rightarrow CuPh_2^+ + Ph\cdot$, which could lead to interesting speculation concerning the structure of these ions. Other ions in this spectrum probably arise from the neutral molecules $(PhCO)_2O$, $PhCO_2Ph$, and $PhCO_2H$ which may be formed as decomposition products.

We thank the National Research Council of Canada for financial assistance.

(*Received, July 5th,* **1968**; *Com.* 905.)

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