

## The X-Ray Photoelectron Spectra of Copper(I) and Copper(II) Carboxylates

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The X-ray photoelectron spectra of the anhydrous copper(I) and copper(II) carboxylates  $\text{Cu}(\text{O}_2\text{CR})_n$  ( $R = \text{Me, Et, Pr}^n, \text{Ph; } n = 1 \text{ and } 2$ ), have been investigated and the copper  $2p_{1/2}$  and  $2p_{3/2}$  and carbon  $1s$  binding energies measured. An apparent correlation of copper  $2p$  binding energies with metal oxidation state has been found. The copper  $2p$  peak widths are much broader for the copper(II) carboxylates than for the copper(I) carboxylates, a feature attributed to multiplet splittings. Intense satellite peaks are observed only for the copper(II) compounds. Copper(II) *n*-butyrate shows evidence of X-ray photoreduction to copper(I).

### Introduction

There have been several reports of X-ray photoelectron spectroscopic measurements on copper compounds, the most extensive being that of Frost and co-workers<sup>1</sup> who examined 46 compounds. Copper(II)  $\beta$ -diketonates<sup>2</sup> and Schiff base complexes<sup>3</sup> have also been studied.

Although the copper  $2p$ ,  $3s$ , and  $3p$  binding energies were found<sup>1</sup> to be dependent not only on the metal oxidation state but also on the nature and number of ligand atoms, the binding energies of copper(I) and copper(II) compounds were generally clearly divided. However, taking the  $2p_{3/2}$  energies as an example, the lowest  $2p_{3/2}$  binding energy of the copper(II) group, that of  $\text{CuBr}_2(2,2'$ -bipyridyl), was only 0.2 eV greater than that of the highest  $2p_{3/2}$  binding energy of the copper(I) group, as shown by both  $\text{CuCN}$  and  $\text{CuI}$ .

It was felt that an examination of the X-ray photoelectron spectra of pairs of copper(I) and copper(II) compounds whose structures were as closely related as possible would provide useful data. The anhydrous carboxylates are a suitable group since in each compound the carboxylate groups bridge two copper atoms. In solid copper(I) acetate<sup>4</sup> planar binuclear eight-membered ring units are linked by alternating  $\text{Cu}_2\text{O}_2$  rings and the other copper(I) alkylcarboxylates<sup>5</sup> are thought to possess similar structures. The structures of anhydrous copper(II) propionate<sup>6</sup> and *n*-butyrate<sup>7</sup> have been determined, both essentially being of the binuclear

copper(II) acetate hydrate<sup>8</sup> type, the eight-membered rings again being linked by alternating  $\text{Cu}_2\text{O}_2$  rings. E.s.r. and magnetic susceptibility measurements<sup>9</sup> suggest a similar structure for anhydrous copper(II) acetate. The known Cu–O bond lengths<sup>4,6,7</sup> do not markedly differ. The two benzoates are probably less closely related structurally. Copper(I) benzoate is tetranuclear in the solid state<sup>10</sup> and the form of copper(II) benzoate examined<sup>11</sup> does not behave magnetically as a binuclear species but is certainly polymeric.

### Results and Discussion

None of the compounds studied here have had their X-ray photoelectron spectra reported previously, although copper(II) acetate hydrate has been examined<sup>1</sup>. This carboxylate was found to be subject to quite rapid X-ray photoreduction in the Varian spectrometer used and spectra were recorded at  $-100^\circ\text{C}$  to eliminate this effect.

In order to avoid dehydration reactions under the high vacuum conditions of the spectrometer, anhydrous carboxylates were used in this study. The only copper(II) carboxylate showing definite evidence of photoreduction to copper(I) was the *n*-butyrate whose

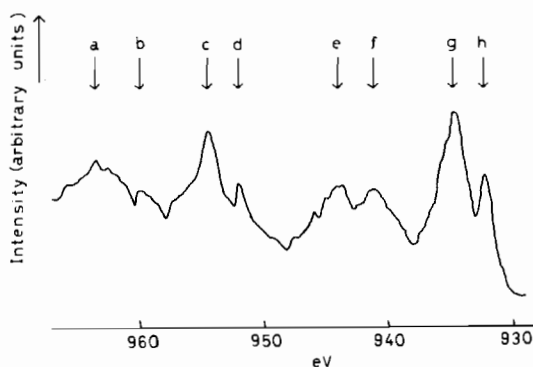


Figure 1. Photoelectron spectrum of Cu  $2p$  region of copper(II) *n*-butryate. Lines a, b, e, f: Cu(II) satellite peaks; c, g: Cu(II)  $2p_{1/2}$  and  $2p_{3/2}$  peaks; d, h: Cu(I)  $2p_{1/2}$  and  $2p_{3/2}$  peaks.

TABLE I. Carbon 1s and Copper 2p Binding Energies (eV).

Compound	C 1s	Cu 2p <sub>1/2</sub>	Satellites	Cu 2p <sub>3/2</sub>	Satellites
CuO <sub>2</sub> CMe	287.6, 283.9	951.3		931.4	
Cu(O <sub>2</sub> CMe) <sub>2</sub>	287.5, 283.8	953.6	6.0, 8.3	934.1	7.0, 8.9
CuO <sub>2</sub> CEt	287.4, 284.0	951.9		932.2	
Cu(O <sub>2</sub> CEt) <sub>2</sub>	287.5, 283.9	953.6	6.3, 8.5	934.0	5.8, 9.6
CuO <sub>2</sub> CPr <sup>n</sup>	287.5, 284.0	951.9		932.0	
Cu(O <sub>2</sub> CPr <sup>n</sup> ) <sub>2</sub>	287.8, 284.3	953.9	5.9, 9.4	934.4	5.9, 9.9
CuO <sub>2</sub> CPh	287.7, 283.8	952.3		932.4	
Cu(O <sub>2</sub> CPh) <sub>2</sub>	287.5, 283.3	953.7	5.4, 8.0	934.0	5.3, 8.8

spectrum (Figure 1), generated after a 20 minute data accumulation period in the spectrometer, exhibited small additional copper 2p<sub>1/2</sub> and 2p<sub>3/2</sub> peaks which could be assigned to the formation of copper(I) n-butyrate.

Since copper(I) carboxylates are subject to atmospheric oxidation to copper(II), the spectra of these compounds were examined carefully, but no additional 2p or satellite peaks were found which could be associated with the presence of copper(II) on the surface of the well-ground samples used.

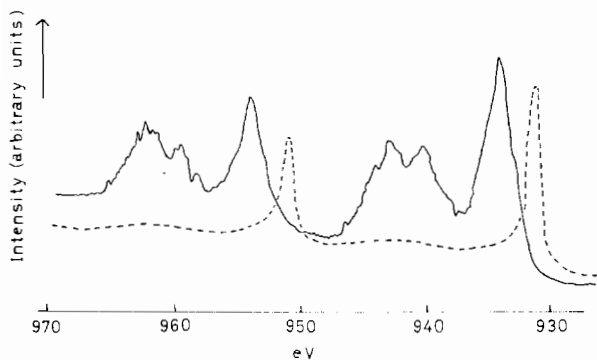


Figure 2. Copper 2p binding energy region of copper(II) acetate (—) and copper(I) acetate (---).

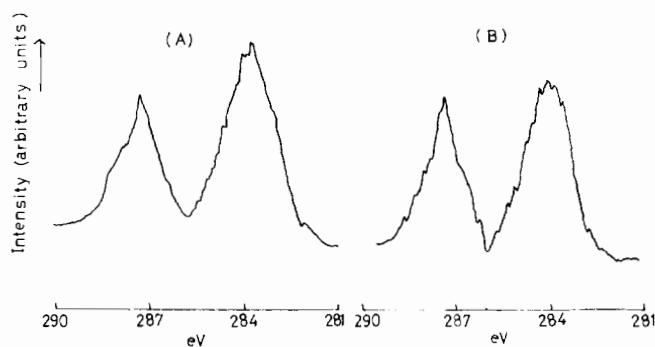


Figure 3. Carbon 1s binding energy region of copper(II) acetate (A) and copper(I) acetate (B).

Carbon 1s and copper 2p binding energies are listed in Table I, and as examples the spectra of the two acetates are shown in Figures 2 and 3. Two well separated carbon 1s peaks are observed for each carboxylate at binding energies comparable to those found<sup>12</sup> for other carboxylates. The highest binding energy peak in each case is associated with the carboxylate carbon atom and the lower energy peak with the alkyl or aryl carbon atoms. The peak area ratios are of the correct order for each compound, indicating that decarboxylation does not occur to any detectable extent in the spectrometer.

Some of the compounds showed surface charging effects but these were effectively eliminated by use of an electron "Floodgun" which bathed the sample surface with a flux of "zero" volt electrons. With the knowledge that charging effects can be discounted, the results listed in Table I show that for pairs of copper(I) and copper(II) carboxylates there is an apparent correlation of copper 2p<sub>3/2</sub> and 2p<sub>1/2</sub> binding energies with metal oxidation state. The copper(I) 2p<sub>3/2</sub> and 2p<sub>1/2</sub> binding energies fall in the ranges 931.4–932.4 and 951.3–952.3 eV respectively whereas the corresponding copper(II) ranges are narrower, being 934.0–934.4 and 953.6–953.9 eV respectively. Although the copper(I)–copper(II) binding energy differences are moderate in magnitude (*ca.* 2 eV) there is no overlap of the binding energy ranges.

The copper(II) carboxylate  $2p_{3/2}$  and  $2p_{1/2}$  peaks are significantly broader than those of the copper(I) analogues, a feature attributable to multiplet splitting<sup>13</sup> associated with paramagnetic copper(II). As an example, the full width at half maximum of the copper(II) acetate  $2p_{3/2}$  peak is 2.5 eV compared with 1.6 eV for the corresponding copper(I) acetate peak.

A further difference between the X-ray photoelectron spectra of the copper(I) and copper(II) carboxylates is the observation for the copper(II) compounds only of intense satellite peaks at some 5–10 eV higher ionisation energy than the main  $2p$  peaks. This is in agreement with the general observation that compounds of the first transition series with less than ten  $3d$  electrons display satellite structure in the metal  $2p$  binding energy region, whereas  $3d^{10}$  compounds do not. The satellites shown in Figure 2 for copper(II) acetate are representative, each copper(II) carboxylate showing at least two strong satellites on both the  $2p_{3/2}$  and  $2p_{1/2}$  peaks. Several explanations<sup>14</sup> of the origin of copper(II) satellites have been proposed. Initially it was suggested<sup>15</sup> that the satellites arose from copper  $3d \rightarrow 4s$  or  $4p$  transitions. However, assignments based on ligand  $\rightarrow$  metal charge transfers are now favoured<sup>16</sup>. Frost *et al.*<sup>17</sup> have suggested that for copper(II) square planar complexes the lower-energy satellite associated with a particular  $2p$  peak can be assigned to a ligand  $\sigma \rightarrow$  copper  $3d$  transition and the higher energy satellite to a ligand  $\rightarrow$  ligand transition (either  $\sigma \rightarrow \sigma^*$  or  $\pi \rightarrow \pi^*$ ). Since at least two satellites are associated with each copper(II)  $2p$  peak in the carboxylates, similar assignments may be reasonable.

## Experimental

Copper(I) carboxylates were prepared as before<sup>5</sup>. Anhydrous copper(II) carboxylates were obtained by dehydration of the hydrates *in vacuo* at 110°C, the benzoate being prepared by Method I of Lewis and Mabbs<sup>11</sup>.

The X-ray photoelectron spectra were recorded using the Hewlett-Packard 5950A ESCA spectrometer of the Department of Chemistry, Purdue University, Indiana, U.S.A. The aluminium  $K\alpha_{1,2}$  line (1486.6 eV) was used as the X-ray excitation source and binding energies calculated from the expression  $E_b = E_x - E_k - \Phi_s$ , where  $E_x$  is the incident X-ray energy,  $E_k$  is the kinetic energy of the emitted electrons, and  $\Phi_s$  is the spectrometer work function. Well-powdered samples

were dispersed on a gold-plated copper surface, excess material not in good electrical contact with the surface being subsequently removed. Surface charging effects were eliminated by use of an electron "Floodgun" which bathes the sample surface in a flux of "zero" volt electrons. The spectra were referenced to the 1s line of graphite at 284.0 eV. The precision in location and accuracy of measurement of the photolines was better than  $\pm 0.2$  eV.

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