

## Fluorescence Properties of Aliphatic Copper(I)–Carboxylates

P. WEBER and H.-D. HARDT

*Anorganische Chemie, Universität des Saarlandes, 6600 Saarbrücken, F.R.G.*

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Although copper(I)–acetate has been known since 1812 [1], its structure was elucidated only in 1974 [2, 3]. Today it is certainly the most investigated copper(I)–carboxylate. The fact that copper(I)–acetate fluoresces at room temperature and at the temperature of liquid nitrogen led to the discovery of a second modification, where fluorescence properties differ distinctly from those of the room temperature modification [4]. A second modification of copper(I)–butyrate has also been isolated [5]. Until today there is known no other structure of an aliphatic copper(I)–carboxylate. Since similar mass spectral fragments were found with other aliphatic copper(I)–carboxylates, the dimeric structure units are believed to exist here too [6]. We saw therefore the need to investigate the fluorescence properties of these carboxylates in order to compare their spectral behavior at room temperature and at 77 K.

Copper(I)–formiate assumes a special position among the existing aliphatic copper(I)–carboxylates. Its extraordinary sensitivity to reduction may be attributed to the aldehyde function (carbonyl activity). The method of preparation suggested by Edwards *et al.* [6] proved to be very slow. Copper(I)–formiate can best be obtained by reducing copper(II)–formiate in acetonitrile with phenyl-

hyperplanar  
spacing

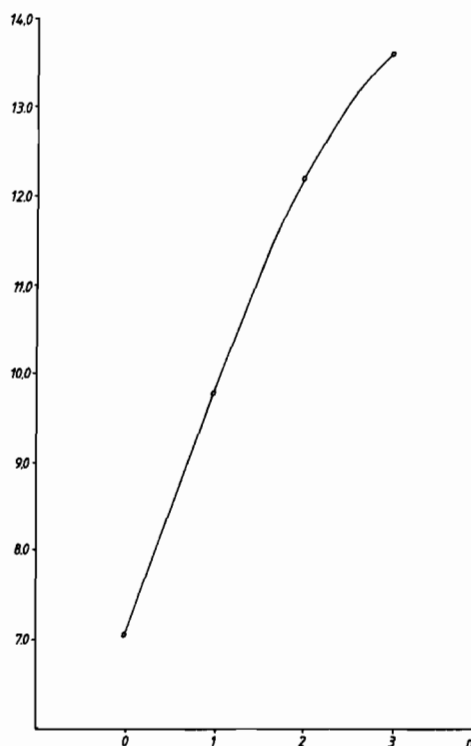


Fig. 1. Lattices bulging in function of the aliphatic rest.

hydrazine at 0 °C. The compound is then precipitated by the addition of diethylether to the colourless solution. Copper(I)–acetate, –propionate and –butyrate have been prepared by the method suggested by Hardt and Pierre [4]. Since the sensitivity to oxidation or hydrolysis decreases with

TABLE I. Excitation and Emission Maxima of Aliphatic Copper(I)–Carboxylates.

| Compound                            | T = 300 K           |                     | T = 77 K            |                     |
|-------------------------------------|---------------------|---------------------|---------------------|---------------------|
|                                     | $\lambda_{ex}$ [nm] | $\lambda_{em}$ [nm] | $\lambda_{ex}$ [nm] | $\lambda_{em}$ [nm] |
| copper(I)–formiate                  | 310                 | 535                 | 320                 | 547                 |
| copper(I)–acetate RTM <sup>a</sup>  | 350                 | 660                 | 350                 | 700                 |
| copper(I)–acetate <sup>b</sup>      | 310                 | 560                 | 307                 | 565                 |
| copper(I)–propionate                | 310                 | 560                 | 310                 | 565                 |
| copper(I)–butyrate RTM <sup>a</sup> | 305                 | 588                 | 305                 | 615                 |
| copper(I)–butyrate                  | 325                 | 620                 | 325                 | 648                 |
| copper(I)–valerate                  | 310                 | 630                 | 310                 | 600                 |
| copper(I)–hexanate                  | 310                 | 560                 | 305                 | 620                 |
| copper(I)–heptanate                 | 310                 | 590                 | 310                 | 615                 |

<sup>a</sup>RTM = room temperature modification. <sup>b</sup>A. Pierre, private communication.

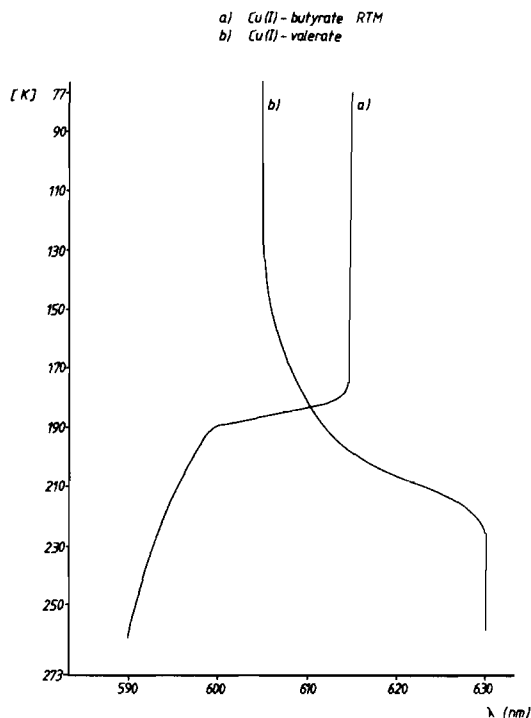


Fig. 2. Temperature dependence of emission maxima at copper(I)-butyrate and copper(I)-valerate.

increasing length of the carboxylic aliphatic rest, it is possible to prepare copper(I)-valerate by reducing copper(II)-valerate in methanol with ascorbic acid. Correspondingly, copper(I)-hexanate and copper(I)-heptanate are obtained in aqueous solutions by reduction of the respective copper(II)-salts with ascorbic acid.

The X-ray powder patterns of the aliphatic copper(I)-carboxylates show many lines so that the entire indexing process becomes difficult. Copper(I)-formate, -acetate, -propionate and -butyrate show a very intense first interference. This corresponds to the (001) copper lattice planes in copper(I)-acetate. The line width is in fact a line splitting caused by copper atoms lying out of the (001) lattice plane. Based on the assumption that aliphatic copper(I)-carboxylates may have the same structural units, a bulging in *c*-direction with increasing carboxylic rest should be expected. This is found to be the case in the order: formate, acetate, propionate and butyrate (Fig. 1).

Generally the excitation maxima of the copper(I)-carboxylates, except for the room temperature modification of copper(I)-acetate, lie between 305 and 325 nm (Table I).

Among the copper(I)-aliphatic carboxylates only copper(I)-valerate shows a blue shift in its emission spectra by cooling at the temperature of liquid nitro-

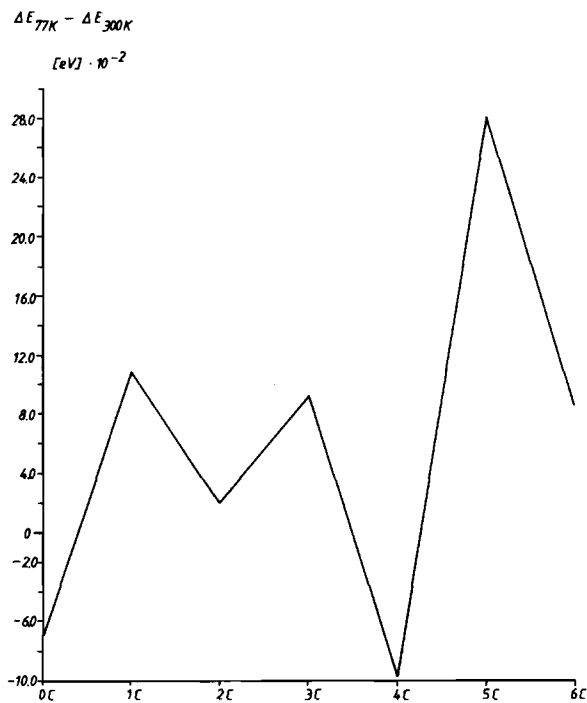


Fig. 3. Energetical difference of Stokes shifts in function of the number of C-atoms of the aliphatic rest.

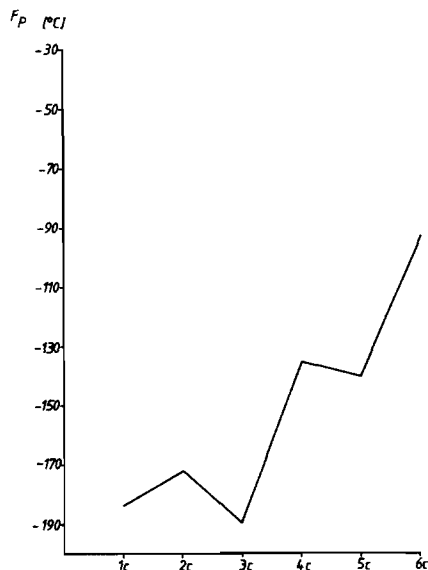


Fig. 4. Melting points of the unbranched alkanes in function of the number of C-atoms.

gen. The greatest red shift is shown by copper(I)-capronate.

The spectral shift as a function of temperature is discontinuous. A maximal shift of 15 nm is observ-

ed at temperature intervals of approximately 20 K (Fig. 2). The inductive effect (+I) increases with increasing carboxylic aliphatic rest, resulting in an increased electron density at oxygen and copper atoms. Thus the energetic position of the ground state changes correspondingly, making a comparison of the spectra impossible.

Figure 3 shows the energetic difference  $E = E_{77\text{K}}^{\text{Stokes}} - E_{300\text{K}}^{\text{Stokes}}$  as a function of the number of carbon atoms of the carboxylic aliphatic rest. The curve shows minima for carboxylic rests with even numbers of carbon atoms. A similar behaviour has been observed with the melting points of the unbranched alkanes (Fig. 4). Those alkanes with odd numbers of carbon atoms have lower melting points. The packing of these molecules is less closer, so that the Van-der-Waal forces must be smaller. We assume that this may be the reason why the energetic difference of the Stokes shifts are greater for aliphatic copper(I)-carboxylates with odd numbers of carbon atoms. A greater part of the excitation energy can

be absorbed by the system as oscillation energy. It is possible that these carboxylates exhibit other forms of oscillation.

#### Acknowledgement

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