IR Studies on Mono-substituted Benzoates of Copper(II)

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IR studies on o-, m- and p- mono-substituted benzoates of copper(II) have been carried out. On the basis of asymmetric COO and symmetric COO stretching frequencies and \( \Delta E \) (difference in \( \nu_{as} \) COO and \( \nu_{s} \) COO) dimeric cage, i.e. symmetric type of structures for m-chloro-, o-methyl-, p-methyl-benzoates and polymeric, i.e. asymmetric type of structures for o-nitro-, m-nitro-, p-nitro-, o-chloro- and m-methyl-benzoates have been proposed.

A lot of interest in the binuclear copper (II) carboxylates has been generated due to their subnormal magnetic moments. Most of the workers\(^1\) have studied the magnetic moments, UV-visible spectra of these copper(II) complexes and some of them\(^2\) have proposed dimeric or monomeric structures for nitro-, chloro- and methyl-substituted benzoates. In spite of so much work reported in this field, practically no attempt has been made to study the structures of the mono-substituted benzoates of copper(II) on the basis of IR studies. We have therefore, carried out IR studies on these compounds. We have used anhydrous compounds in most of the cases because it has been observed that the impurities of basic salts are associated with the hydrated salts\(^3\).

X-ray studies\(^4\) of carboxylates show that these can exhibit different types of coordination behaviour (I-IV).

The structure (I) is fully symmetric and ionic in nature, hence its \( \nu \)COO modes are unlikely to be influenced much by a change of the metal atom. The structure (IIa) is monodentate having different C—O bond lengths and thus highly asymmetric. Structure (Iib) and (Iic), although not monodentate, are certainly more asymmetric than III, IVa and IVb. These occur in polymeric complexes. The structure (IIa) is intermediate between I and IIa. It is neither fully symmetric nor asymmetric. The structure (III) is bidentate. Here the symmetric nature of COO group should be more pronounced than that in II. Therefore, \( \nu_{as} \) COO, should decrease and \( \nu_{s} \) COO should increase compared to those for II. Structure (IVA) is symmetrically bridged and IVb is of the cage type. In these structures both \( \nu_{as} \) COO and \( \nu_{s} \) COO are shifted in the same direction on changing the metal atom\(^5\).

The free acetate ion is not fully symmetric\(^6\). It

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has a structure, $\text{H}_2\text{C} = \text{C} - \text{O}$, in which the two $\text{C} - \text{O}$

bonds are not identical and its structure lies in

between I and IIa. On similar grounds we have

assumed structure $\text{R} - \text{C}$ for the sodium salts of

benzoates.

Cu(II) can assume any of the four types of coordination with the COO group and the corresponding

$\Delta E$ values ($\Delta E = \nu_{\text{as} \text{COO}} - \nu_{\text{s} \text{COO}}$) should follow

the following sequence:\

\[ \text{IIa} > \text{IIb or IIc} > \text{IVa} > \text{III} > \text{I} \]

(bridging (bidentate) (symmetrical cage type) free ion) form.

The $\Delta E$ values for free ions of sodium salts should

lie between those for monodentate and symmetrical free ion due to their asymmetric nature.

**Materials and Methods**

All the compounds were prepared by known

methods\(^1\). IR spectra were recorded in KBr on a

Perkin Elmer instrument model 177 over the range

4000-200 cm$^{-1}$. Magnetic moment values were

taken from the literature\(^2\).

$\text{o-}, \text{m-} \text{and p-}$ Nitrobenzoic acids were obtained from Ward Benkinsop Co. Ltd,

$\text{o-}$ Chlorobenzoic acid was a Koch-Light reagent and

$\text{m-}$ and $\text{p-}$ Chlorobenzoic acids and $\text{o-}$, $\text{m-}$ and $\text{p-}$ Methylbenzoic acids were obtained from M/s Fluka AG.

NaOH and crystalline CuSO$_4$ were BDH reagents.

**Results and Discussion**

$\nu_{\text{as} \text{COO}}, \nu_{\text{s} \text{COO}}$ frequencies and $\Delta E$ values of copper (II) benzoate, mono-substituted benzoates

of Cu(II) and the corresponding sodium salts are present in Table 1. The magnetic moment ($\mu$) and $pK_a$ values (taken from the literature$^{1,2}$) are also given in Table 1.

Anhydrous copper(II) benzoate is a dimeric cage type of compound which is fully symmetrical in nature$^3$. Therefore, its both the frequencies and $\Delta E$ value have been taken as a reference for cage type of compounds. Nakamoto$^{18}$ observed that $\nu_{\text{as} \text{COO}}$ and $\nu_{\text{s} \text{COO}}$ shift in the same direction on substitution in the symmetrical cage type of complexes.

Amongst the copper(II) mono-substituted benzoates the behaviour of $\text{o-}$ substituted benzoates is anomalous. Their strength is considerably greater (low $pK_a$) and accordingly they have got higher $\nu_{\text{as} \text{COO}}$ than those of $\text{m-}$ and $\text{p-}$ compounds. This may be due to (i) direct interaction of the adjacent groups and (ii) pronounced inductive effect (structure V and VI).

Greater strength (low $pK_a$) and higher $\nu_{\text{as} \text{COO}}$ of $\text{o-}$ Chlorobenzoate, may be due to molecular overcrowding. Exception to this behaviour is noted in the case of $\text{o-}$ Methylbenzoate which exhibits lower $\nu_{\text{as} \text{COO}}$ value than $\text{m-}$ and $\text{p-}$ compounds, probably due to some other factors like hyperconjugative effect of methyl group.

Both $\text{m-}$ and $\text{p-}$ Nitrobenzoates are equally acidic ($pK_a 3.47$ and $3.40$ respectively) and consequently have nearly the same $\nu_{\text{as} \text{COO}}$ values, i.e. $1598$ and $1596$ cm$^{-1}$ respectively. This is because there is a pronounced electron withdrawing inductive effect ($-I$) in $\text{m-}$ Nitrobenzoate while in $\text{p-}$ Nitrobenzoate an electron withdrawing mesomeric effect ($-\text{M}$) is present. In Chlorobenzoates there is an electron withdrawing inductive effect ($-I$) which is more pronounced

\[
\begin{array}{ccc}
\nu_{\text{as} \text{COO}} & \nu_{\text{s} \text{COO}} & \Delta E \\
\text{Benzoeate} & (\text{cm}^{-1}) & (\text{cm}^{-1}) & (\text{cm}^{-1}) \\
\text{o-Nitrobenzoate (monohydrated)} & 1550 & 1410 & 140 \\
\text{m-Nitrobenzoate} & 1575 & 1380 & 195 \\
\text{p-Nitrobenzoate} & 1600 & 1390 & 210 \\
\text{o-Chlorobenzoate} & 1585 & 1380 & 205 \\
\text{m-Chlorobenzoate} & 1570 & 1355 & 185 \\
\text{p-Chlorobenzoate} & 1555 & 1400 & 155 \\
\text{o-Methylbenzoate} & 1532 & 1378 & 134 \\
\text{m-Methylbenzoate} & 1510 & 1400 & 110 \\
\text{p-Methylbenzoate} & 1560 & 1405 & 155 \\
\end{array}
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$\begin{array}{c}
\nu_{\text{as} \text{COO}} \\
\nu_{\text{s} \text{COO}} \\
\Delta E \\
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<td>$\nu_{\text{s} \text{COO}}$</td>
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*Ref. 2; †Ref. 1
in the m-Cl derivative than in the p-Cl derivative and an electron donating mesomeric effect (+M) only in the case of p-Cl derivative. Therefore, p-chlorobenzoate is weaker (pKa = 4.05) than m-chlorobenzoate (pKa = 3.80). But both have got the same νCOO value, i.e. 1538 cm⁻¹. There appears to be some anomaly in the assignment of νCOO mode of the p-Cl compound. This has been discussed in detail later. It is observed that the pKa of m-methyl derivative is lower (4.25) than that of p-methyl (4.35) derivative and accordingly the former has got νCOO higher (1565 cm⁻¹) than the latter (1556 cm⁻¹). It may probably be due to the pronounced hyper-conjugative effect of methyl group in p-methylbenzoate.

When the frequencies of mono-substituted copper (II) benzoates are compared with those of copper (II) benzoate (anhydrous), it is found that the increase in νCOO and decrease in νCOO occur in the cases of m-nitro-, o-chloro- and m-methyl-substituted benzoates indicating asymmetric structures of these compounds. In the other hand shifting of νCOO and νCOO in the same direction in m-chloro- and o-methyl-substituted benzoates indicates their symmetric nature. νCOO of o- and p-nitro-benzoates are raised by about 40 cm⁻¹ compared to the value for anhydrous copper (II) benzoate which is indeed a remarkable increase in frequency while νCOO of these derivatives remain in the same range. In fact νCOO is not a pure vibration because of the possible mixing of νCOO and νC=C vibrations. Therefore, an expected decrease could not be observed. Thus, in view of the much higher νCOO modes observed, o- and p-nitro-compounds are assumed to have, asymmetrically bonded COO group or monomeric or polymeric nature.

In p-chlorobenzoate the νCOO is decreased by 22 cm⁻¹ while the νCOO remains almost unchanged. These frequencies give anomalous ΔE value, i.e. 128 cm⁻¹ which is much lower than that for the cage type of compounds. There remains only one possibility, i.e. this compound may be of ionic type. But for ionic type of compounds both the frequencies should move in the same direction. Thus the assignment of νCOO appears virtually doubtful. In the IR spectra there exists another band at 1580 cm⁻¹, which can give a reasonable value of ΔE (170 cm⁻¹) but normally this frequency is assigned to benzene ring vibration. This convinced us to consider only the band at 1538 cm⁻¹ to be due to νCOO. However, with this assignment no definite conclusions could be drawn about its structure. Our conclusions about o- and m-chlorobenzoates can further be justified on the basis of the magnetic moment values (Table 1). The νCOO and νCOO values of p-methylbenzoate remain almost in the same range as those of copper (II) benzoate (anhydrous). Therefore, a structure similar to that of copper (II) benzoate (anhydrous) is indicated. Our conclusions about o-, m- and p-nitro-, chloro- and methyl-substituted benzoates can further be justified on the basis of magnetic moment values shown in Table 1.

Since the ΔE values of m-chloro-, o-methyl-, and p-methyl-benzoates are 153, 150 and 151 cm⁻¹, respectively (comparable to the value of ΔE = 155 cm⁻¹ for dimeric cage type reference, anhydrous copper benzoate) dimeric cage structures can be proposed for these compounds. The only exception is p-chlorobenzoate with its anomalous behaviour as mentioned earlier. ΔE values of o-nitro-, m-nitro-, p-nitro-, o-chloro- and m-methylbenzoates are 202, 208, 186, 20, 0, 180 cm⁻¹ respectively which are remarkably higher than those for the cage type of compounds. According to the sequence proposed, these compounds should have the structures IIa (nonodentate) or IIb or IIc (polymeric). But if the ΔE values of their corresponding sodium salts are taken into consideration, it is obvious that ΔE values of o-nitro-, o-chloro- and m-methyl-benzoates of Cu(II) are higher by 7, 15 and 25 cm⁻¹ respectively. The ΔE values of copper compounds are not much higher than those of the corresponding sodium salts (which are not monodentate). Thus monodentate structures cannot be assigned. These should have either IIb or IIc type of structures. m-Nitrobenzoate of Cu(II) has got slightly lower ΔE value than that of the sodium salt indicating that the copper complex has got a more pronounced symmetric character as compared to the sodium salt. Therefore, the structure for this compound cannot be monodentate (since the sodium salt itself does not have monodentate structure) and should have IIb or IIc type of (polymeric) structure.

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References


