INFRARED SPECTRA OF SALTS AND COMPLEXES OF CARBOXYLIC ACIDS AND SOME OF THEIR DERIVATIVES

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1. INTRODUCTION

Many of the organic reagents used for the separation and masking of metal ions are carboxylic acid derivatives. Great interest is shown in studying the structure of the compounds which are formed. Yet chemists have hardly any direct methods at their disposal which would enable them to determine with what functional groups a metal is combined. Indirect methods often do not give an unambiguous answer.

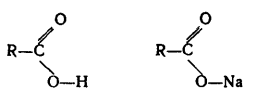
Infrared spectroscopy provides a direct method enabling the presence of a bond between a metal and a functional group to be established immediately.

The purpose of the present survey is to show, on the basis of a systematic comparison of published results, what evidence of the bonding of functional groups is provided by infrared spectra. In view of the meagre data available for comparison, only a few conclusions can be reached concerning the characteristic features of the infrared spectra of particular functional groups in different classes of acids and concerning the criteria of chelate ring formation in complexes.

Let us examine the characteristics of the infrared spectra of carboxylic acids and their salts taking the simplest representatives, monocarboxylic acids, as example.

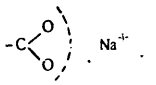
2. MONOBASIC CARBOXYLIC ACIDS AND THEIR SALTS

The characteristic functional group of carboxylic acids is the carboxyl group, the hydrogen in which is replaced by a metal on formation of a salt. Up to now chemists have held the view that such an acid and its salt can be represented quite correctly by formulae such as



However, it is assumed in several cases that the hydrogen in the carboxyl group of the acid belongs to some extent to both oxygen atoms, whereas the metal is linked to only one oxygen atom. Examination of the infrared spectra of carboxylic acids and their salts has shown that the latter view is incorrect.

According to infrared spectroscopic data, the carboxyl group has an unsymmetrical structure: the proton, owing to its small size, is located within the electron shell of one of the oxygen atoms [1]. All acids contain a band due to the carbonyl group C=O in the neighbourhood of 1700 cm^{-1}, which is present also in the spectra of aldehydes, ketones, and esters. Salts of carboxylic acids have no carbonyl band at about 1700 cm^{-1}, but contain a characteristic band in the range 1510–1650 cm^{-1} and a series of other characteristic bands due to the COO^- ion, which has a symmetrical structure in which the metal atom is associated equally with the two oxygen atoms and the O–C–O angle is 110°–130°: [1,2]



The symmetrical structure of the COO^- group is proved also by the close similarity between the spectra of carboxylates and of nitro-compounds [1,2]. Thus the Raman spectrum and the infrared absorption spectrum of disodium oxalate are very similar to those of N_2O_4, [2] while the spectrum of sodium benzoate resembles that of nitrobenzene [1].

Flett examined sixty carboxylic acids in their normal state of aggregation, solid or liquid, at room temperature [3], and found that the carboxyl group has five characteristic frequencies, at 2500–2700, ~1700, ~1400, 1200–1300, and 900 cm^{-1}, with relative intensities of 1 : 5 : 2 : 3 : 1. Table 1 gives the assignment of the frequencies. The most characteristic among them are considered to be the O–H stretching vibrations, at 2500–2700 cm^{-1}, of carboxyl groups present in dimers, and the C=O stretching band at ~1700 cm^{-1} when carboxyl-containing compounds are absent. The position of the carbonyl band may be somewhat displaced depending on the nature of the substituents in the organic radical [3–5]. Thus passage from aliphatic to aromatic acids is accompanied by a shift in the carbonyl band to longer wavelengths (1690 cm^{-1} in benzoic acid) [3].

TABLE 1. Characteristic frequencies of the carboxyl group.

Frequency, cm^{-1}	Intensity*	Assigned to	Ref.
2500–2700	w.	O–H stretching vibrations, linked into COOH dimers	3
~1700	v.s.	C=O stretching vibrations	3
~1400	m.	C–O stretching vibrations or	7,8
1200–1300	s.	O–H deformation vibrations	
~900	w.	O–H deformation vibrations (non-planar) in COOH	7

* Intensities arbitrarily denoted as: s. = strong, v.s. = very strong, m. = medium, w. = weak.

TABLE 2. Characteristic frequencies of the carboxylate ion.

Frequency, cm^{-1}	Intensity	Assigned to	Ref.
1510–1650	s.	asymmetric COO^- stretching vibrations	1, 8, 9
~1400	s.	one of them = symmetric COO^- stretching vibrations	1, 9, 10
1280–1350	s.		
800–950	s.	COO^- deformation vibrations	1

The presence of electronegative substituents in the organic radical causes a shift to shorter wavelengths. Thus in aliphatic acids the band is usually located at 1705–1720 cm^{-1},[3] in monochloroacetic acid it is at 1735 cm^{-1},[3] and in 2-chloropropionic acid at 1730 cm^{-1}.[6]

The characteristic frequencies of the carboxylate ion are altogether different. There are four of them, at 1510–1650, ~1400, 1280–1350, and 800–950 cm^{-1}, [1,8-10] their assignment being given in Table 2.

Thus the identification of carboxylic acids and their salts from the infrared spectra presents no difficulties: the acids have a weak band at 2500–2800 cm^{-1} and an intense band due to C=O stretching vibrations at 1700 cm^{-1}; the spectra of the salts do not contain these bands, but do show an intense band due to asymmetric COO^- stretching vibrations at 1560–1600 cm^{-1}.

These characteristic frequencies can be utilised also for identifying carboxylic acids and their salts in aqueous solution[8], by placing a drop of the test solution between plates of fluorite, silver chloride, BaF_2, or As_2S_3. Since ordinary water absorbs strongly around 1600 cm^{-1}, solutions in heavy water can conveniently be employed, as they do not absorb in this region.

3. POLYBASIC CARBOXYLIC ACIDS AND THEIR COMPOUNDS WITH METALS

Polybasic carboxylic acids differ little from the monobasic acids with respect to the position of the carboxyl band[3]. Thus the C=O stretching vibrations are at 1712 cm^{-1} in acetic acid, 1690–1710 cm^{-1} in oxalic acid, 1700 cm^{-1} in succinic acid, and 1740 and 1710 cm^{-1} in malonic acid[3]. If all the carboxylic groups are combined with a metal, the carbonyl band disappears, and a band due to asymmetric stretching vibrations of the carboxylate ion appears in the range 1510–1650 cm^{-1}.[11,12] If, however, one of the carboxyl groups remains uncombined, or if the combined carboxyl groups are not equivalent, two or more bands are observed in the range 1560–1640 cm^{-1}.[11,12]

Lecomte and his collaborators carried out a detailed investigation of the infrared spectra of the oxalates of fifty metals[2]. Comparison of the infrared and Raman spectra showed that with many oxalates they have no bands in common. According to the principle of mutual exclusion, this indicates the presence of a centre of symmetry in dipotassium and diammonium oxalates and in $K_2[TiO(C_2O_4)_2]$. In the case of $K_3[Al(C_2O_4)_3]$ the same bands are present in the Raman and in the infrared spectra, and hence the molecule has no centre of symmetry[2].

Guided by the formal criterion of the presence of two different metals in the formula of a complex oxalate and of one metal in a molecule of a simple oxalate, Lecomte concludes that the characteristic features of the infrared spectra of oxalates are that simple oxalates contain two intense bands in the range 1100–1600 cm^{-1} and one in the range 700–900 cm^{-1}, whereas complex oxalates contain three and two bands respectively. The reasons for this are probably quite different. The researches of other workers on oxalates[13-15] led Fronæus and Larsson to suggest[14] that the appearance of new bands in concentrated aqueous solutions of ferric oxalate is due to the formation of polynuclear complexes, whereas the spectra of solutions containing one, two, and three $C_2O_4^{2-}$ ions per atom of iron or aluminium coincide with the bands of solid $Fe_2(C_2O_4)_3$.

All that has been stated above concerning the great similarity in the spectra of oxalates applies to molecules which are not combined with water of crystallisation. The presence of a hydrate sheath about the metal atom has a definite effect on the symmetry of the oxalate ion[11,16,17] and also on that of other anions, for example, SO_4^{2-}.[17] In the compound $U(C_2O_4)_2.5H_2O$ the oxalate ion possesses symmetry of type D_{2h}, but in $K_4[U(C_2O_4)_4].4H_2O$ its symmetry is C_{2v}.[16] The infrared spectrum of oxalates is affected not only by the number of molecules of water of crystallisation but also by differences in crystal form. For example, anhydrous calcium oxalate, the monohydrate, and the three different forms of the trihydrate have different spectra[11].

Unfortunately the peculiarities of the infrared spectra of the simplest normal and hydrogen oxalates have not been discussed in the literature. The acid oxalate for some reason does not contain the carbonyl band, which would indicate the presence of a free carboxyl group, while in disodium oxalate the frequency of the asymmetric COO^- stretching vibrations is higher than in salts of other dicarboxylic acids[2,12].

Frequencies in compounds formed by malonic, succinic, glutaric, and other acids with metals are assigned to vibrations of the carbon chain by a comparison of the spectrum of the salt with that of the corresponding acid[12,15,18,19]. They should not be greatly displaced on passing from the acid to the salt. Like the oxalate series, the spectra of malonates[1,12,15], succinates[1,12,15], and phthalates[1] of different metals have much in common, since in each series they are due to the same anions.

In contrast to potassium hydrogen oxalate, the corresponding phthalate has a clearly defined band at 1669 cm^{-1} due to the free carboxyl group[20,21].

Comparison of the spectra of disodium malonate, succinate, glutarate, etc. shows that the succinate has a smaller number of bands than the other salts, which is due to the presence of a centre of symmetry in this molecule[12]. Rather surprisingly, the compounds formed by copper with oxalic, malonic, succinic, and other aliphatic acids have spectra which are very similar to those of the corresponding disodium salts[12,15]. It is true that, in all cases other than the malonate, the asymmetric stretching vibrations of the carboxylate ion are at shorter wavelengths in the copper salts than in the sodium salts[12]. This can be explained by the bond in the latter being ionic in character, whereas in the copper salts it is more covalent (see Table 3), by analogy with the compounds of ethylenediaminetetraacetic acid (EDTA)[22-25] and of amino-acids[26-29]. However, Kuroda and Kubo[12] have a different explanation — coupling between copper atoms in the salts of all dibasic acids other than malonic acid — as a result of which the magnetic moment associated with one copper atom is less than that

TABLE 3. Frequencies (in cm^{-1}) of acids, salts, and complexes.

	Acid					Normal salt					Complex				
	formula	stretching vibrations C=O	stretching vibrations of other functional groups	other groups	ref.	formula	stretching vibrations COO^- asymmetric	stretching vibrations of other functional groups	other groups	ref.	formula	stretching vibrations COO^- asymmetric	stretching vibrations of other functional groups	other groups	ref.
Monobasic carboxylic acids	CH_3COOH	1712			3	CH_3COONa	1600			8					
	C_6H_5COOH	1685			3	C_6H_5COONa	1600			21					
Polybasic carboxylic acids	COOH—COOH	1690—1710			3	COONa—COONa	1635			12		1665		CH_2 rock	12
	COOH—CH_2—CH_2—COOH	1700		CH_2 rock 808	3,2	COONa—CH_2—CH_2—COONa	1567		CH_2 rock 808	12				881, 893	12
		1695			3		1603			21		1608			12
Halogenated acids	$ClCH_2$—CH_2—COOH	1730			3	$ClCH_2$—CH_2—COONa	1635			6					
Hydroxy--acids	COOH—CHOH—CHOH—COOH	1750	δ1097		30							1634	1080 1063		30
		1665	3230		3,53		1603	нет		21					
EDTA	$H_2CN(COOH)_2$	1697		CH stretch. 3020 3030	25	$H_2CN(COONa)_2$	1510		C—H 2800 2810	22	$Ba[CoEDTA_2].4H_2O$	1638		CH stretch. 2900—3000	24, 25
Amino--acids	$H_3\overset{+}{N}CH_2$—COO^-	1603	3160		8	H_2NCH_2COOK	1575	3380, 3360		29		1575	3330, 3260		29
		1660	3361		3		1575	3410		26		1603	3280		26

predicted theoretically, and the band is displaced to shorter wavelengths. In copper and sodium malonates the position of the bands is the same, and the magnetic moment of the copper compound has its usual value.

The linking of two carboxyl groups in a dicarboxylic acid by a metal involves the presence of only one band due to asymmetric COO^- stretching vibrations provided that the polarity of the COO^-–M^{n+} bond and their separation in the crystal lattice are equal for the two carboxylate ions[12]. Such cases are given in Table 3 (copper oxalate and succinate).

The linking of the two carboxyl groups in succinic acid by a metal with formation of a ring results in deformation of the $-CH_2-CH_2-$ bond, causing splitting of the 808 cm^{-1} CH_2 rocking band and its displacement to shorter wavelengths[12] (see Table 3). In complexes with other dicarboxylic acids the deformation of the carbon chain is less pronounced[12].

Thus the absence of the carbonyl band in the region of 1700 cm^{-1} indicates that all the carboxyl groups in a polybasic acid are combined with a metal. The presence of only one asymmetric COO^- stretching band in the range 1560–1600 cm^{-1} indicates that all the combined groups are equivalent, and the presence of more than one band that they are not equivalent or that an uncombined carboxyl group is present.

4. HALOGENATED ACIDS AND THEIR SALTS

Replacement of hydrogen by a halogen or by CN in the organic radical of an aliphatic acid increases the frequency of the carbonyl stretching vibrations. Flett points out[3] that the shift to shorter wavelengths is greater with substitution in the α-position than in the β-position. The C=O band is displaced to shorter wavelengths with increasing number of halogen atoms in the acid molecule[31,32], and the shift in the C=O stretching vibrations also increases in the sequence I^-, Br^-, Cl^-, F^-.[31,33] Analogous results for the sodium salts of chlorinated propionic acids have been published by Potts[6].

5. ETHYLENEDIAMINETETRAACETIC ACID AND ITS COMPOUNDS WITH METALS

Sawyer and his coworkers have made a detailed investigation of the infrared spectra of ethylenediaminetetraacetic acid (EDTA) and its compounds with fifteen metals[22–24,34] over the range 700–3400 cm^{-1}. In EDTA the C=O stretching vibrations occur at 1697 cm^{-1} for all four carboxyl groups. Salt formation is accompanied by the appearance of bands in the range 1550–1650 cm^{-1} (see Table 3). The C–H stretching vibrations are sensitive to the formation of chelate complexes. In the acid and its disodium salt they occur at 3020–3030 cm^{-1}, in the tri- and tetra-sodium salts at 2800–2810 cm^{-1}, and in complexes with bivalent and multivalent metals at 2900–3000 cm^{-1}. This last frequency is characteristic of chelation in EDTA compounds[22–24,34].

The position of the band due to asymmetric COO^- stretching vibrations indicates the nature of the bond between the metal and COO^-: absorption in the range 1510–1550 cm^{-1} is brought about by complexes in which the bond is predominantly ionic (Na^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Ce^{3+}, and Bi^{3+}), and in the range 1630–1650 cm^{-1} by complexes having a predominantly covalent bond (Pb^{II}, V^{III}, Cr^{III}, Fe^{III}, Co^{III}, V^{IV}, Ti^{IV}, Th^{IV}, Mo^{V}, and Mo^{VI} [34]). The difference in frequency between the asymmetric and the symmetric COO^- stretching vibrations (at 1510–1650 cm^{-1} and 1350–1450 cm^{-1} respectively) may serve as a measure of covalency. For an ionic bond Δ = 150 cm^{-1} (sodium acetate, tetrasodium salt of EDTA); the bond is covalent if $\Delta > 225$ cm^{-1} (with Cr^{III} Δ = 280 cm^{-1}).

With increasing radius of the metal the frequency of the asymmetric COO^- stretching vibrations shifts to longer wavelengths in the sequence: Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}. The ionic character of the bond becomes stronger in the same sequence (from left to right), and the complexes become less stable[24,34]. However, correlation between the position of the band and the stability of the complexes is rarely observed.

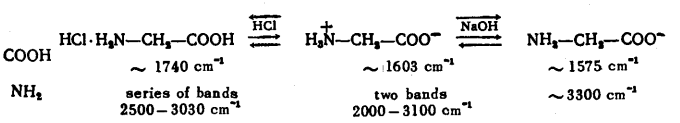
Comparison of the infrared spectra with results obtained by other physicochemical methods led Sawyer *et al.* to conclude that one narrow band in the range 1550–1630 cm^{-1} indicates a coordination number 6 with most bivalent metals[24]; a wide band in the range 1630–1660 cm^{-1} suggests that EDTA is also a sexidentate ligand in its complexes with Fe^{III}, Co^{III}, and Mo^{V}.[23] Bailar considers that in $Na[Co^{III}BrEDTA]$ the EDTA is a quinquedentate ligand[25]. In spite of the ability of EDTA to form chelate complexes and the presence of a metal–nitrogen coordinate bond (as demonstrated by X-ray structural analysis)[24], and of both Sawyer and other investigators[22-25,34-37] having obtained data on C–N vibrations, it has not yet proved possible to find criteria of metal–nitrogen bonding in the infrared spectra. It has, however, been noted that the C–N band shifts to longer wavelengths with increasing ionic radius of the metal.

The presence of one narrow band in the region of the asymmetric COO^- stretching vibrations indicates that all the carboxyl groups are linked with the metal. Thus $Ba[CoEDTA_2].4H_2O$ has one band at 1638 cm^{-1}, and hence all the carboxyl groups are equally linked with the metal; $Na[Co(NO_2)EDTA].H_2O$ has bands at 1628 and 1723 cm^{-1}, *i.e.* one free carboxyl group[25]. The presence of three bands in the titanium compounds of EDTA allows us to accept for it the formula $TiOEDTA.H_2O$ with two uncombined groups[23,24]. With the titanium compound the bands are observed at 1700–1720 cm^{-1}, so that they can be confidently assigned to a free carboxyl group; in the case of the Mo^{V}, Mo^{VI}, Th^{IV}, and other compounds, more than one band is observed below 1650 cm^{-1}, so that they can be assumed to contain either a free carboxyl group or non-equivalent combined carboxyl groups[24,25,34].

Other studies have been made[25,36] of compounds formed by Co^{III} with EDTA, including the effect of water of crystallisation on the infrared spectrum[38], and also of the Cu^{II},[30] Pt^{II}, and Pd^{II} [37] compounds. Thus the linking of the carboxyl groups in EDTA by a metal produces similar changes in the infrared spectrum to those with the other acids. Formation of a chelate ring is accompanied by a shift in the C–H stretching vibration to the 2900–3000 cm^{-1} range.

6. AMINO-ACIDS AND THEIR COMPOUNDS WITH METALS

Amino-acids are usually in the form of zwitter-ions, and therefore do not exhibit the bands due to the free carboxyl group at ~1740 cm^{-1} or the free NH_2 at 3300 cm^{-1}.[8,29,39] If sodium hydroxide is added to an aqueous solution of an amino-acid[8], bands due to the carboxylate ion and free NH_2 appear; addition of hydrochloric acid at first causes the appearance of NH_3^+ bands in the range 2000–3000 cm^{-1} and the associated COO^- band at 1603 cm^{-1}, whereas a high concentration of hydrochloric acid produces a band at ~1740 cm^{-1} due to the free carboxyl group and an almost continuous series of bands in the range 2500–3030 cm^{-1}, characteristic of compounds formed by amines with hydrochloric acid[8,29]. With glycine this equilibrium can be represented thus:



Quagliano and his collaborators examined the infrared spectra of the compounds formed by about ten metals with glycine and its derivatives, alanine, sarcosine, and other amino acids[9,10,26-29,40-42]. They showed that the complexes contain an ionic bond between the metal and the carboxylate ion (band in the range 1550–1630 cm^{-1}) and a coordinate link with the amino-group, the corresponding band being displaced to longer wavelengths compared with the sodium salt (see Table 3)[26,29]. As with the EDTA compounds, the frequency of the asymmetric COO^- stretching vibrations gives a measure of the covalency of the bond with the metal: for a purely ionic bond the frequency is 1570–1580 cm^{-1} (Zn^{2+}, Co^{2+}, Cu^{2+}, and Ni^{2+} diglycinates), and for a covalent bond above 1610 cm^{-1} (with Pt diglycinate 1640 cm^{-1})[26,29]. A characteristic sign of a coordinate link between a metal and an amino-group is a sharp increase in intensity of the NH stretching band at 3300 cm^{-1}.[9] An increase in the number of coordinated ligands containing NH_2, and in particular an increase in the number of coordinated ammonia molecules in ammines, shifts this band to longer wavelengths[9].

If the spectra of the solids are determined, the form of the N–H stretching bands may give information on the structure of the complex[9]. Thus one narrow band in complexes containing two molecules of amino-acid combined with one atom of copper indicates that these molecules have a *trans*-coplanar configuration. A wide band given by the bis(salicylideneimine) complex of zinc indicates a tetrahedral configuration; and an intense narrow band at 3297 cm^{-1} and a broad band at 3160 cm^{-1} indicate that the tris(salicylideneiminato)iron(III) complex has an octahedral configuration[9]. In the case of a *cis*-coplanar configuration, the narrow NH stretching band is split into two. The splitting of bands into two in the case of the *cis*- compared with the *trans*-configuration is a general characteristic of the infrared spectra of such compounds.

The relation between the position of the NH band and the stability of the complexes is a matter of controversy. Thus in the glycinato-complexes the NH frequency diminishes in the sequence K^+, Cu^{2+}, Co^{3+}, Pt^{2+}, H^+,[9] and in the salicylideneimine complexes in the sequence Zn^{2+}, Be^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+},[9] it being assumed that a shift to a longer wavelength corresponds to strengthening of the M → N bond. However, this is not always confirmed by other methods.

Anthranilic acid behaves similarly to other amino-acids[9,26,43]. Thus in copper anthranilate the NH band is at longer wavelengths (3280 cm^{-1}) than in sodium anthranilate (3410 cm^{-1})[9] (see Table 3). Anthranilates have the advantage over other complexes formed by metals with organic reagents that, for Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+}, Hg^{2+}, Ag^{+}, Pb^{2+}, Na^{+}, and Ba^{2+}, it has proved possible to find[43] specific bands from which one metal can be conveniently determined quantitatively in the presence of another. However, the error in such a determination is 2–3%.[43]

Thus the linking of a carboxyl group with a metal in amino-acids shows the same features as in the other acids. The presence of a coordinate bond with the amino-group is characterised by a strengthening of the NH stretching vibration in the region of 3300 cm^{-1}.

7. HYDROXY-ACIDS AND THEIR COMPOUNDS WITH METALS

The presence of a hydroxyl group in a hydroxy-acid produces only a slight displacement of the carbonyl band to shorter wavelengths[44], the stretching vibrations of the C=O group in glycollic and the isomeric hydroxypropionic and hydroxybutyric acids lying between 1700 and 1725 cm^{-1}. The presence of a hydroxy-group in an acid is most readily established by means of an intense band in the region of O–H stretching vibrations at about 3440 cm^{-1}, and also from weak bands at 6700 cm^{-1} (first overtone) and 5150 cm^{-1} (combination frequency)[44]. The region of O–H deformation vibrations at ~1050 cm^{-1} is convenient for determining the relative positions (α, β, or γ) of the hydroxyl and carboxyl groups. Ordinary acids, too, show a band in this range, due to O–H deformation vibrations in the COOH group, but in hydroxy-acids the band is more intense, being displaced to shorter wavelengths by an α-hydroxyl group but not shifted by a β-hydroxyl[44]. Thus O–H deformation vibrations are located at 1040 cm^{-1} in butyric acid, 1060 cm^{-1} in lactic acid, and at 1042 cm^{-1} in 3-hydroxybutyric acid[44].

Interesting data on the structure of copper tartrate trihydrate $CuC_4H_4O_6.3H_2O$ have been obtained by Kirschner[45], who has shown that one narrow band at 1634 cm^{-1} proves that the two coordinated carboxyl groups are completely equivalent. In the complex the band at 1097 cm^{-1} due to deformation vibrations of the equivalent free hydroxyl groups in free tartaric acid is split into two (1080 and 1063 cm^{-1}), which indicates their non-equivalence. Although the hydrogen in them has not been replaced by copper, one of the hydroxyl groups is more closely linked with the copper atom than is the other. The influence of the water of crystallisation on the spectrum of Rochelle salt has been studied by Bernard[46].

Some work has been done on the salts of pyruvic acid, most of which show a band due to stretching vibrations of the carbonyl group, both in the solid state and in aqueous solution, *i.e.* they are derivatives of the keto-form $CH_3.CO.COOM$.[47,49] The lithium salt in the solid state, and according to some investigators also the sodium salt[49], show no band corresponding to C=O, but are derived from the diol form of the acid, $CH_3.C(OH)_2.COOLi.nH_2O$.[47–49] Contradictory data have been obtained concerning the presence of a band due to C=O in aqueous solutions of lithium pyruvate.

Goulden has investigated aqueous solutions of salts having the composition $M^{2+}\{HO.CR_2.COO^-\}_2$ formed by Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, and Cu^{2+} with glycollic, lactic, and 2-hydroxy-2-methylpropionic acids[50–52]. Owing to the strong absorption by water, the region of the asymmetric COO^- stretching vibrations was not examined; the deformation vibrations of the hydroxy-group were investigated. Goulden assigned the band at 1390 cm^{-1} in compounds formed by bivalent metals with glycollic and lactic acids to vibration of the hydroxy-group combined in a chelate complex[50]. This band increases in intensity as the complex becomes more stable in the sequence $Sr^{2+} < Ca^{2+} < Mg^{2+} < Zn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} \ll Cu^{2+}$, while the band at 1275 cm^{-1}, assigned to the hydroxy-group in a free lactate ion, and the band at ~1080 cm^{-1} diminish. All the lactates investigated, including those of lithium, sodium, and potassium, have bands at 1390, 1275, and 1080 cm^{-1}, and all conclusions concerning chelation were made merely from a comparison of the intensities of these bands, which is unconvincing[51]. It is also not clear why Goulden assigned the shoulder of the 1360 cm^{-1} band in calcium and strontium 2-hydroxy-2-methylpropionates to an uncombined hydroxy-group (1330 cm^{-1}), while the 1360 cm^{-1} band itself, observed in calcium and copper 2-hydroxy-2-methylpropionates, was assigned to a hydroxy-group linked to copper in a chelate complex.

Other salts of hydroxy-acids have been studied by Parker[53].

Thus the previous generalisations relating to the carboxyl group remain valid for the compounds formed by hydroxy-acids with metals. The stretching vibrations and overtones of the hydroxy-group have not been investigated, while the deformation vibrations do not always show marked differences in chelate complexes and in simple salts having an uncombined hydroxy-group.

Salicylates

The band corresponding to C=O stretching vibrations in salicylic and 3-hydroxy-2-naphthoic acids is at longer wavelengths (down to 1660 cm^{-1})[3,54,55] than in acetic acid (1712 cm^{-1}) and benzoic acid (1685 cm^{-1})[3], while the hydroxyl stretching band is in the neighbourhood of ~3200 cm^{-1} owing to the presence of a strong intramolecular hydrogen bond[54–57]. In methoxybenzoic acid, where a hydrogen bond is impossible, the O–H stretching vibration occurs at 3400 cm^{-1}.[21] The reason for the unusual stability of this bond, which has been termed a "chelate and conjugate hydrogen bond", has formed the subject of much detailed investigation[54–57]. It is due to the superposition of three effects: ring formation (chelation), the presence of the conjugated bond O=C–C=C, and hydrogen bond formation –O–H...O=C– between hydroxyl and carboxyl groups located close to one another.

Lecomte and coworkers[1] examined the compounds formed by salicylic acid with six metals over the range 650–1500 cm^{-1}, and showed the great similarity in the infrared spectra of the salicylates of different metals. The compounds formed by salicylaldehyde and methyl salicylate with Na^+, Cu^{2+}, Ti^{4+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Cd^{2+} have been investigated by Yamada[58], Yamamoto and Kambara[59], and Bellamy and Branch[60]. They showed that the presence of a coordinate link with the C=O group produces a shift in the corresponding band to longer wavelengths compared with free salicylaldehyde and methyl salicylate, together with a considerable increase in its intensity. In contrast to many other complexes (with acetylacetone[60], benzoylacetone[60], tropolone[61]) the position of the C=O stretching band (1668 cm^{-1}) and its shift to longer wavelengths in the salicylaldehyde complexes vary linearly with the logarithm of the instability constant of the complex. The frequency of the C=O stretching vibrations falls in the sequence $Mg^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Ti^{4+} > Cu^{2+} > Cd^{2+}$,[58,60] while the stability increases from left to right. The frequencies in this sequence are 1681, 1659, 1656, 1652, 1637, 1608, and 1585 cm^{-1} respectively. Ayers and Land have identified

the Nb=O band in the sulphosalicylic complex of niobium[62]. Hales *et al.*[21] showed that, in monosodium and disodium salicylates, the band due to asymmetric vibrations of the carboxylate ion is located at 1603 and 1590 cm^{-1} respectively, which is similar to what is found with the salts of all carboxylic acids. They suggested[21] that the monosodium salicylate will differ from the disodium compound in the O–H stretching band in the range 3100–3400 cm^{-1}. However, with neither salt was any band detected in this range[21]. The reason for the absence of bands due to the hydroxy-group in monosodium salicylate is completely obscure. Cardinaud considers[63] that the absence of O–H stretching vibrations in *o*-nitrophenol is due to a strong hydrogen bond between the OH and NO_2 groups, as a result of which the O–H band disappears from the 3100–3400 cm^{-1} range. He observed that dissolution of the compound in dioxan considerably increases the intensity of the 3200 cm^{-1} band[63], which can therefore be assigned to vibrations of the hydroxyl group. Since the spectrum of *o*-hydroxynitrobenzene should be similar to that of sodium salicylate, the latter would be expected to have a band at 3200 cm^{-1}, but this is not the case. An interesting fact in this connection is that the very stable hydrogen bond formation in 5-hydroxyflavones is accompanied by the disappearance of the band due to O–H stretching vibrations, whereas a less stable hydrogen bond in 3-hydroxyflavones gives a weak band at 3200 cm^{-1}.[64]

Thus the infrared spectra of metal salicylates have been little investigated. Judging from the spectra of the sodium salicylates, the asymmetric COO^- stretching vibrations have the usual frequency, but the disappearance of the hydroxyl band from the range 3100–3400 cm^{-1} has not been explained in the literature.

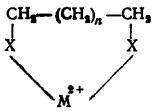
8. CRITERIA OF THE LINKING OF FUNCTIONAL GROUPS AND OF CHELATE RING FORMATION

From the results obtained by several investigators the changes in the infrared spectrum occurring when hydrogen in a carboxyl group is replaced by a metal can be attributed to a change in symmetry of the carboxyl group. The bands due to the carboxyl group, located at 2500–2700, ~1700, ~1400, 1200–1300, and ~900 cm^{-1},[8] are replaced by bands due to the carboxylate ion, at 1510–1630, ~1400, 1280–1350, and 800–950 cm^{-1}.[8,16] In order to demonstrate the linking of the carboxyl group with a metal it is sufficient to establish the disappearance of the C=O stretching band at ~1700 cm^{-1} and the appearance of the asymmetric COO^- stretching band in the range 1510–1630 cm^{-1}.[8] In several cases the position of the band due to asymmetric stretching vibration of COO^- depends on the nature of the metal, and several investigators explain this by different degrees of polarity of the metal–COO^- bond[22,24-26,29].

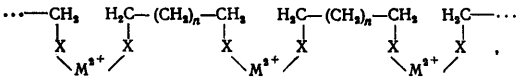
From all that has been said it follows that the linking of a carboxyl group with a metal produces the same spectral changes compared with the acid irrespective of the acid chosen, whether a monocarboxylic acid, an amino-acid, a hydroxy-acid, etc. Splitting of the band due to asymmetric stretching vibration of the carboxylate ion is observed when the molecule contains more than one carboxyl group, forming bonds of different polarity[22,26,29,34].

The presence of other functional groups in an acid results in the appearance of the corresponding bands in the infrared spectrum, while interaction of these groups with the metal (replacement of hydrogen, formation of coordinate bonds) results in corresponding changes in the spectrum.

If a carboxylic acid can act as a bidentate ligand, the linking of both functional groups by a bivalent or a multivalent metal indicates formation of a chelate ring:



where the X are functional groups. Theoretically, compounds can be formed in a different way:



but the existence of such chains has not yet been demonstrated among the compounds which we have been discussing. The formation of chelate rings is proved partly by chemical methods, in particular by the considerable stability of such compounds, in many cases by the formation of intensely coloured compounds, etc.

Summarising the information available in the literature, we can conclude that the infrared spectra give no criterion which is valid for all cases of chelate ring formation. In individual cases chelation can be assessed on the following basis:

1. In all cases in which a carboxylic acid may act as a bidentate ligand, combination of both functional groups with one metal atom may indicate formation of a chelate ring. In particular, this is shown in the infrared spectrum as follows: (a) in a dicarboxylic acid by the presence of only one band due to asymmetric stretching vibration of COO^- at 1510–1630 cm^{-1};[12,21] (b) in a monocarboxylic hydroxy--acid by the disappearance of the C=O stretching vibration at ~1700 cm^{-1} and appearance of the asymmetric COO^- stretching vibration at 1510–1630 cm^{-1}, a shift in the deformation vibration of the hydroxy-group at ~1090 cm^{-1};[8,30] (c) in monocarboxylic amino-acids by the disappearance of the C=O stretching vibration at ~1700 cm^{-1} and appearance of the asymmetric COO^- stretching vibration at 1510–1630 cm^{-1}, an intense band due to NH_2 coordinated with the metal at ~3300 cm^{-1}.[28,29]

2. Direct proof of the formation of a chelate ring may be provided by deformation of the carbon chain of the acid, which in the particular case of the succinates appears in a shift in the CH_2 rocking oscillations at ~808 cm^{-1} to shorter wavelengths[12], and in the case of EDTA complexes a displacement to longer wavelengths of the CH stretching vibrations at 3020 cm^{-1}.[22,24,25] However, an increase or a decrease in the number of carbon atoms in a dicarboxylic acid is accompanied by a smaller displacement of the CH_2 rocking oscillations compared with succinic acid (the shift may even be absent). This may indicate less deformation of the chain[12].

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THE ELECTROCHEMISTRY OF SEMICONDUCTORS

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