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SPECTRO-STRUCTURAL STUDIES ON CARBOXYLIC ACIDS AND THEIR TRANSITION METAL COMPLEXES

A THESIS

submitted to the

UNIVERSITY OF BOMBAY

for the degree of

DOCTOR OF PHILOSOPHY

in

Physical Chemistry

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by

Anirudha Chintaman Ranade,

National Chemical Laboratory,

Poona-8,

India.

August 1967.

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A. C. RANADE
The Author

National Chemical Laboratory,
Poona-8, India.

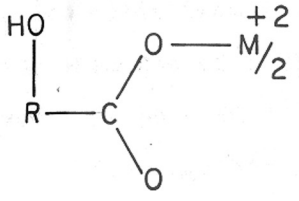
CHAPTER - I

GENERAL INTRODUCTION

Among the several physical techniques used for elucidation of the structure of coordination compounds, the infrared spectroscopic method has indeed been well-established. Based on the changes in absorption spectrum of the ligand upon complex formation, namely appearance of new bands, frequency shifts and intensity change, information regarding the relative stability, coordination sites and probable structure has been obtained for many metal complexes. However, very little attention has been paid so far to the complexes of carboxylic acids containing additional donor sites in the form of hydroxy, amide, amino groups or pyridine.

The presence of an additional donor site gives rise to two possible structures for complexes of such acids. The first type termed "salt-like" (I) would have the bonding through carboxylate group only, while the second type (II), which may be called a "chelate", would have both the carboxylate and the other group participating in the complex formation. Hydroxy acid complexes of the first row transition metal ions have indeed shown both these

possibilities. While the metal complexes of the type



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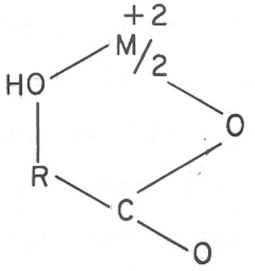

II

$M(L)_2$ where M is divalent cobalt, nickel, manganese or copper with glycolate[1] (CH_2OHCOO^-) or lactate[2] ($CH_3CHOH.COO^-$) as ligand (L) are bidentate chelates(II); those of the type M:L with tartrate ($COO^-.CHOH.CHOH.COO^-$) have indicated both type (I and II) of structures. Copper(II) tartrate[3,4] has one coordinated and one free hydroxyl groups, while cobalt(II), nickel(II), manganese(II) tartrates[4,5], which have spectra comparable with that of dipotassium tartrate, are believed to be salt-like (I). It is evident that the type of metal complex which may result, is governed by the nature of the metal ion in addition to that of the ligand. Complexes of several hydroxy acids were studied[2,5,6] by us using the infrared absorption technique. In continuation, the spectro-structural properties of benzilic and mandelic acids and their complexes have been investigated now.

N-acetylglycine($CH_3.CONHCH_2COOH$) is known to have a normal[7], (although non-dimeric) structure in the solid state

in contrast to the zwitterion structure of amino acids. Similar non-zwitterion structure has been established for many amido acids from their infrared spectra[8], which all show the presence of uncharged NH and COOH groups. Studies of several amino acid[9,10] complexes such as those of glycine[11], alanine[12,13] and valine[14], have all shown that chelate rings are formed by bonding through the carboxylate and amino groups. The nature of the complexes of amido acids do not appear to have been reported so far. In view of their peculiar structure, it was considered worthwhile to investigate several metal complexes of N-benzoyl and N-acetyl-glycines. Complexes of phenylalanine (zwitterion) which have not been studied so far are also reported along with the above.

Although some complexes of pyridine have been reported[15,16], no spectroscopic studies are available on those of pyridine carboxylic acids. Metal nicotinates and isonicotinates have, therefore, been studied here. Complexes of substituted phenoxy acetic acids have been investigated because of the unusual structure of the ligands which are also found to be antiglycemic agents[17].

The spectrum of a complex is essentially the spectrum of the ligand in which some of the vibrational modes are perturbed by complex formation. It is, therefore, clear that the

correct interpretation of the spectrum of a complex, demands a thorough understanding of the spectrum of the ligand itself.

In the present work, we have, therefore, analysed the spectrum of the ligand first. The observed infrared bands of ligands were assigned by introducing known structural changes in their molecules. For example, alkali metal salts, esters, hydrochlorides of the acids and their deuterated analogues in which active hydrogen atoms are replaced by heavy hydrogens, were studied and the structural peculiarities analysed. The vibrational coupling (interaction) between C-O stretching and OH deformation modes in alcoholic groups and between C=O stretching and NH deformation modes in amide groups, has been highlighted since coordination is likely to introduce complex changes in such coupled modes.

Following the introduction and experimental details in Chapters I and II respectively, the spectra of ligands and their complexes are described in subsequent chapters. In each case, the literature on the ligand and its complexes is reviewed. The spectra of hydroxy acids and their complexes are discussed in Chapter III. In Chapter IV studies on amido acids and their complexes are reported, followed by

DL- β -phenylalanine complexes in Chapter V. Spectral investigation of nicotinic and isonicotinic acids and their complexes forms the subject matter of Chapter VI and similar studies of several substituted phenoxy acetic acids are detailed in Chapter VII.

Magnetic and electronic spectral data are appended finally.

Since infrared spectroscopic technique has been made use of predominently in this work, a brief outline of the general principles of this method is given below:

GENERAL PRINCIPLES

The quantized energy of a molecule can be quantitatively associated with (a) the rotation of the molecule, (b) vibrations of the constituent atoms, and (c) motions of electrons as a whole, the translational energy being ignored. Interaction between the electromagnetic radiation and quantized states of the molecule will occur according to Bohr's frequency condition :

$$\Delta E = E'' - E' = h\nu$$

where ΔE is the difference in energy between the two quantized states, E'' (higher energy level) and E' (lower energy level) of the molecule, h is Planck's constant and ν is the frequency of the radiation.

The vibrational transitions in a molecule occur at frequencies $3 \times 10^{12} - 3 \times 10^{14}$ cycles/sec. and are observed in the frequency region 10000-100 cm^{-1} (1 to 100 μ) of the electromagnetic spectrum. Vibrational spectra can be observed either as Raman or as infrared spectra. Infrared spectra originate in transitions between two vibrational levels of the molecule in the electronic ground state and are usually observed as absorption and not as emission spectra.

The observable intensity of the light absorbed or emitted in any transition depends on how often this transition occurs per unit time, which in turn is proportional to the product of the intrinsic tendency of the transition to occur and the number of molecules which are in the initial state to make the transition. The ratio of the molecules in the first excited state (n_1) to the number in the ground state (n_o), according to the Boltzmann distribution law, is given by

$$n_1/n_o = \text{exp. } -(E_1 - E_o)/kT.$$

Even for a relatively low energy vibration, say 450 cm^{-1}, n_1/n_o is found to be 1/10 and for 1000 cm^{-1} it is 0.007. Thus there are not enough molecules populating the higher vibrational states to make the emission process observable under ordinary conditions. Similarly transitions between adjacent states other than 0 and 1 (1 and 2, 2 and 3, etc.) though theoretically

allowed, occur with low probability. Transition with $\Delta_n = 1$ is called the fundamental, $\Delta_n = 2$ first overtone and so on. It is found that for a sample of proper thickness and concentration to give convenient intensity to the fundamental, even the first overtone is not generally observed or is just barely seen.

Raman spectra on the other hand, originate in the electronic polarization caused by the ultraviolet or visible light and are observed as Raman shifts from the incident frequency. These Raman shifts also correspond to certain vibrational frequencies. Information on the complete vibrational spectrum can thus be obtained by studies of both the spectra.

To illustrate the nature of the vibrations of a complex molecule, a simple heteropolar diatomic molecule A-B may be considered first. The atoms in it are never stationary and the distance between them is a periodic function of time. The vibrational frequency due to periodic motion of atoms 'A' and 'B' is given by:

$$\nu = \frac{1}{c} \left[\frac{K}{4 \pi^2 \mu} \right]^{1/2}$$

where K is the force constant of the bond, and μ is the reduced mass of the system defined as:

$$\mu = \frac{M_A \; M_B}{M_A + M_A}$$

M_A and M_B being the masses of the atoms A and B respectively.

While only one vibrational mode can occur in a diatomic molecule corresponding to the periodic change in the single internuclear distance, many vibrational modes are possible in polyatomic molecules. The number of vibrational modes possible in a molecule containing "n" atoms (3n degrees of freedom) is (3n - 5) for linear and (3n - 6) for non-linear molecules. These are associated with the various modes of molecular vibrations usually described as stretching, bending, wagging, rocking, twisting, etc. This molecule is capable of absorbing all those infrared frequencies, which correspond to the frequencies of its different molecular vibrations.

The normal modes of vibration of a polyatomic molecules can be unambiguously determined by what is called a normal coordinate analysis. In this procedure a structural model for the molecule is assumed and the motions the various atoms undergo during each fundamental vibration are analysed with the help of group theory. This method is very involved and is not very practicable when the number of atoms is large. Hence for the assignment of certain observed vibrational frequencies, a greatly simplified method based on the constancy of the bond or group frequencies in different

molecules is used. This was first established experimentally and later explained theoretically on the basis of the constancy of the bond force constants.

The approximate vibrational frequency of a link A-B is determined primarily by the elasticity of the bond as measured by the force constant and by the masses of A and B. If the restoring force between the two atoms is the same in one molecule as in another, it means that the electronic structure of the bond is at least very similar in the two cases. Conversely, if the electronic structure is the same, the force constants are also same. This is indeed observed in many cases. However, on closer examination, it is found that this invariance of the force constants holds exactly only if the bond is in similar surroundings. That is, in order that the force constant of a particular linkage should be the same in different molecules, the adjacent bonds must be the same. These facts hold good not only for the stretching and bending force constants but also for the interaction constants.

The concept of group frequencies is a corollary of the invariance of bond constants. Thus many molecular groups give rise to characteristic absorption frequencies

and band intensities which are only slightly affected by the other parts of the molecule. Conversely, from the observation of such characteristic frequencies, it may be concluded that the corresponding group is present.

An explanation of the occurrence of group frequencies can easily be given by considering the cases of the C-H, O-H and N-H vibrations. Since the mass of the hydrogen nucleus is very much small as compared to those of the other nuclei, the amplitude of vibrations of the latter is much smaller than that of hydrogen atoms. As a first approximation, hydrogen nucleus may be considered to be oscillating against an infinitely large mass and therefore the vibrational frequency depends practically only on the force by which the hydrogen atom is bound to the specific atom in the molecule and will be nearly the same in different molecules with the same C-H, O-H or N-H force constants. If there are two O-H groups (as in H_2O) or more, they will, of course, all vibrate simultaneously and will be of nearly the same magnitude as for a single group, differing only by a comparatively small amount which is an indication of the strength of interaction of the equivalent groups.

Apart from the case of the end atoms, as discussed in the preceeding paragraph, bonds involving any two atoms will still have characteristic frequencies depending on the force

constants of these bonds. Thus C-C, C=C and C≡C groups have characteristic frequencies[18] 1250-1140, 1680-1600 and 2260-2100 cm^{-1}.

How well the characteristic frequencies are defined depends also on the angle between successive bonds in the molecule. If the angle is 90° there will be no transfer of vibrational energy from one bond to the next, then the characteristic frequencies are best defined. In case of a chain-like molecule having two or more equivalent bonds, there will be a resonance which leads to a splitting of the characteristic frequency. Again, the stronger the coupling between the two equivalent bonds, larger is the splitting. If there are more than two equivalent bonds there will be a splitting into more than two different frequencies and these frequencies will deviate increasingly from the frequency of a single bond.

Summarizing the preceeding discussion of group frequencies it can be said that when a particular group, if separated from the rest of the molecule, has a vibrational frequency that differs sufficiently from any vibrational frequency of the rest of the molecule, then this frequency will occur only slightly changed in the whole molecule and will roughly correspond to characteristic vibrational motions in that group only.

However, if there are several equivalent groups, the different frequencies will correspond to simultaneous motions in those groups.

The utility of infrared spectroscopy in coordination chemistry is based on the assumption that coordination only the frequencies of group coordinating to the metal ion are perturbed without affecting the vibrational modes of the remainder of the molecule. Thus it should be possible to correlate the extent to which the coordinated group is affected as measured by its vibrational frequency to the strength of the binding. In practice, however, internal (e.g. molecular geometry) or external (e.g. hydrogen bonding, change of phase or crystal form) factors are found to have appreciable effect on these absorption frequencies. Yet a comparative study of the spectra of the ligand and the complex can give interesting and useful information about the coordination sites, order of relative stability and probable geometric configuration.

REFERENCES

1. Nakamoto, K., McCarthy, P. J. and Miniatqs, B.
Spectrochim Acta, 21, 379 (1965).

2. Ranade, A. C. and Biswas, A. B.
J. Indian Chem. Soc., 44, 314 (1967).

3. Kirshner, S. and Kiesling, R.
J. Amer. Chem. Soc., 82, 4174 (1960).

4. Bolard, J.
J. Chim. Physique, 900 (1965).

5. Ranade, A. C., Srinivasan, T. K. K. and Biswas, A. B.
Indian Science Congress, January, 1965.

6. Ranade, A. C.
"Spectrochemical Properties and Thermal Stabilities of some transition metal complexes"
M. Sc. thesis, University of Bombay, October, 1964.

7. a: Carpenter, G. B. and Donohue, J.
J. Amer. Chem. Soc., 72, 2315 (1950).

   b: Donohue, J. and Marsh, R. E.,
Acta Cryst., 15, 941 (1962).

8. Micheel, F. and Schleppinghoff, B.
Chem. Ber., 88, 763 (1955).

9. Cotton, F. A. in
"Modern Coordination Chemistry" (pp. 301-393) edited by Lewis, J. and Wilkins, R. G., Interscience Publishers Inc., New York (1960).

10. Nakamoto, K.
"Infrared Spectra of Inorganic and Coordination Compounds"
John Willey & Sons Inc., New York (1963).

11. Lane, T. J., Durkins, J. A. and Hooper, R. J.
Spectrochim Acta, 20, 1013 (1964)
(and references contained therein).

12. Jose, P. and Pant, L. M.
Acta Cryst., 17, 24 (1964).

13. Dijkstra, A.,
Acta Cryst., 20, 588 (1966).

14. Nakagawa, I., Hooper, R. J., Walter, J. L.
and Lane, T. J.,
Spectrochim. Acta, 21, 1 (1965).

15. Clark, R. J. H. and Williams, C.S.
Inorg. Chem., 4, 350 (1965).

16. Duncan, J. F. and Mok, K. F.
Austr. J. Chem., 19, 701 (1966).

17. Pabrai, P. R.
"Potential Hypoglycemic Agents"
Ph.D. (Pharmacy) thesis, Banaras Hindu University, 1964.

18. Bellamy, L. J.,
"The Infrared Spectra of Complex Molecules"
Methuen and Co. Ltd., London (1956).

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C H A P T E R - II

EXPERIMENTAL

Benzilic acid, $(C_6H_5)_2COH.COOH$, (BA); Mandelic acid, $C_6H_5.CHOH.COOH$, (MA); N-benzoylglycine, $C_6H_5CONHCH\ COOH$, (BGA); Nicotinic (pyridine β -carboxylic) acid $C_5H_4N.COOH$ (NA); Isonicotinic (pyridine γ -carboxylic) acid, $C_5H_4N.COOH$, (INA); DL- β-phenylalanine, $C_6H_5CH_2CHNH_2.COOH$, (PHA); used were of 'chemically pure' grade. These were further purified by recrystallization from water. All these acids are abbreviated as given in paranthesis.

Preparation of some acids

Some of the preparative work done by us are noted in the following:

p-Bromo-N-benzoylglycine : p-$Br.C_6H_4CONHCH_2COOH$, was synthesized by the reaction of p-bromo-benzoyl chloride and glycine.

Substituted phenoxy acetic acids : The usual method was followed to synthesize this compound. It involved reaction between the appropriate phenol and monochloro acetic acid in an alkaline medium followed by acidification of the mixture and isolation of the precipitated aryloxy acid.

Purification was done by recrystallization from water.

Deuterated acids: These were prepared by two different methods:

Method 1 - The acid dissolved in dry ether was shaken with a large excess of heavy water of isotopic purity > 99.4%. Ether was then removed by pumping, resulting in the separation of the deuterated acid. The product was then dried in vacuum and subjected to repeated treatment as above, till the spectrum indicated appreciable isotope substitution.

$(C_6H_5)_2$.COD.COOD(BA-d_2) and C_6H_5CHOD.COOD(MA-d_2) were prepared by this method.

Method 2 - The acid was dissolved in hot D_2O and refluxed for 2-3 hours. On cooling the desired product separated out. The process was repeated if necessary. CH_3COND.CH_2.COOD(AGA-d_2); C_6H_5COND.CH_2COOD(BGA-d_2); p-Br.C_6H_4.CONDCH$_2$COOD(Br.BGA-d_2); C_5H_4N COOD (NA-d_1) and (INA-d_1); $C_6H_5CH_2CHND_2COOD$ (PHA-d_3) and compounds of the type X-$C_6H_4OCH_2$COOD were prepared by this method.

Alkali metal salts of acids

These were obtained by treating the respective acid with calculated amounts of the metal carbonate or hydroxide. Purification was done by recrystallization from water.

Deuterated alkali metal salts : The salts were dissolved in D_2O at elevated temperature. After refluxing for 2-3 hours the water (H_2O - D_2O) was removed by suction, yielding the desired product.

Hydrochlorides

The hydrochloride was prepared by dissolving the acid in minimum quantity of concentrated hydrochloric acid. Crystals obtained were subsequently dried in vacuum.

Nicotinic and isonicotinic acid hydrochlorides both of molecular formula $C_5H_4\overset{+}{N}.HCl.COOH$ and DL- β-phenylalanine hydrochloride, $C_6H_5CH_2CH.\overset{+}{N}H_3Cl\ COOH$ were prepared by this method.

Deuterated hydrochlorides : The acid hydrochloride when crystallized from D_2O containing a small amount of HCl (added to prevent any hydrolysis) gave the desired product.

$C_5H_4\overset{+}{N}D.Cl.COOD$ and $C_6H_5CH_2.CH\overset{+}{N}D_3COOD$ were prepared by this method.

Esters of acids

The ester was prepared by the reaction of the acid with alkaline dimethyl sulphate.

Methyl benzilate $(C_6H_5)_2.COH.COOCH_3$(MeB) was obtained by this procedure.

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Deuterated esters : The ester, dissolved in CCl_4 or $CHCl_3$, was shaken with excess D_2O. The solvent was then removed by distillation under reduced pressure when the deuterated product separated out. This was then dried in vacuum over P_2O_5. The process was repeated till the isotope substitution was achieved to the desired extent.

Deuterated methyl ester of benzilic acid, $(C_6H_5)_2C.OD.COOCH_3$(MeB-d_1) and deuterated triphenyl carbinol $(C_6H_5)_3.COD$ were prepared by this method.

Preparation of complexes

The complexes of the type $M(L)_2.n\ H_2O$ where M is divalent copper, cobalt, nickel, manganese, zinc or cadmium ions and L is the ligand, were prepared by either of the two methods:

1. The carbonate method : To an aqueous solution of the acid a little over the calculated amount of the respective metal carbonate was added gradually, while the solution was stirred continuously and maintained at 80°C on a water-bath. The excess of metal carbonate was then filtered out. The filtrate on concentration and cooling gave the complex which was purified by recrystallization from water. Complexes of N-acetyl and N-benzoylglycinates were prepared by this method.

When the complexes were insoluble in water, the following method was used:

2. Alkali metal salt method : An aqueous solution of the alkali salt of the acid and the respective metal salt solution were mixed in stoichiometric ratio; the complex separated out as precipitate was washed repeatedly with water. These were purified, whenever possible, by recrystallization from water.

Dehydration of complexes

The finely powdered compound kept in glass-boat was dried at 110° over P_2O_5 for 12 hours in vacuum (0.1 mm Hg).

Deuteration of complexes

Anhydrous compounds (prepared by the method described above) when treated with a small amount of D_2O gave the deuterated complexes of N-acetyl and N-benzoylglycine series.

Recrystallization of anhydrous compound from D_2O also yielded the deuterated product.

The methods described above are useful only when the compound to be deuterated is soluble in water/heavy water. For insoluble complexes the following method was used.

The D_2O solutions of the alkali metal salt of the acid and anhydrous metal chloride, sulphate or nitrate, were mixed in a proper ratio to get the desired product.

Deuterated complexes of the type $M(L\text{-}d)_2$ where M is the metal ion and (L-d) is the deuterated ligand such as $C_6H_5\text{-}CHOD.COO^-$, $(C_6H_5)_2COD.COO^-$, $C_6H_5.CH_2CH.ND_2.COO^-$ were prepared by this method.

The molecular formulae and purity of all the compounds were ascertained by elemental analysis, results of which are tabulated.

Instrumental

Infrared spectra : All the spectral measurements were carried out on a Perkin-Elmer Model 221, double-beam spectrophotometer equipped with sodium chloride and caesium bromide prisms or a sodium chloride prism-grating assembly. The instrument was calibrated with water vapour and carbon dioxide bands and the calibration was also checked with a polystyrene film each time before recording a spectrum. The samples were examined as Nujol and hexachlorobutadiene mulls in the 4000-650 cm^{-1} regions and as Nujol mulls in 650-300 cm^{-1} region. Alkali halide disk technique was not utilized in view of its inherent drawbacks, discussed by several workers.

TABLE - II - 1

RESULTS OF ELEMENTAL ANALYSES - BENZILIC ACID SERIES

Compound	% Found			% Calculated				M.Wt.
	C	H	Metal	C	H	Metal	For	
BA	73.6	4.90	-	73.69	4.80	-	$C_{14}H_{12}O_3$	228
Me(B)	74.2	5.61	-	74.40	5.69	-	$C_{15}H_{14}O_3$	242
K(B)	67.7	4.30	-	67.72	4.44	-	$K(C_{14}H_{11}O_3)$	266.1
$Cu(B)_2$	62.9	4.00	12.7	63.45	4.25	12.28	$Cu(C_{14}H_{11}O_3)_2$	517.5
$Co(B)_2$	65.9	4.00	11.30	65.49	4.28	11.48	$Co(C_{14}H_{11}O_3)_2$	512.9
$Ni(B)_2$	65.0	4.01	11.30	65.52	4.28	11.49	$Ni(C_{14}H_{11}O_3)_2$	512.7
$Mn(B)_2$	65.7	4.21	10.80	66.01	4.32	10.78	$Mn(C_{14}H_{11}O_3)_2$	508.9
$Zn(B)_2$	64.1	4.10	12.90	64.68	4.23	12.54	$Zn(C_{14}H_{11}O_3)_2$	519.4
$Cd(B)_2$	59.0	3.99	19.20	59.32	3.88	19.85	$Cd(C_{14}H_{11}O_3)_2$	566.4

$B = (C_6H_5)_2.COH.COO^-$, $C_{14}H_{11}O_3$.

TABLE - II - 2

RESULTS OF ELEMENTAL ANALYSES - MANDELIC ACID SERIES

Compound	% Found			% Calculated			For	M.Wt.
	C	H	Metal	C	H	Metal		
MA	63.1	5.30	-	63.17	5.26	-	$C_8H_8O_3$	152
Na $\underline{M}$	55.0	4.20	-	55.18	4.41	-	$Na(C_8H_7O_3)$	174
$Cu(\underline{M})_2$	51.9	3.95	17.00	51.34	3.83	17.38	$Cu(C_8H_7O_3)_2$	365.5
$Co(\underline{M})_2$	53.5	4.18	16.00	53.20	3.88	16.32	$Co(C_8H_7O_3)_2$	360.9
$Ni(\underline{M})_2$ *	52.9	4.20	16.00	53.22	3.88	16.32	$Ni(C_8H_7O_3)_2$	360.7
$Mn(\underline{M})_2$	53.5	3.99	15.00	53.80	3.92	15.38	$Mn(C_8H_7O_3)_2$	356.9
$Zn(\underline{M})_2$	52.0	3.98	16.90	52.29	3.81	17.8	$Zn(C_8H_7O_3)_2$	367.4
$Cd(\underline{M})_2$	46.7	3.52	27.00	46.34	3.38	27.12	$Cd(C_8H_7O_3)_2$	414.4

$\underline{M}$ = $C_6H_5.CHOH.COO^-$, $C_8H_7O_3$

(* Sample dried at 110°C was analysed).

TABLE - II - 3

RESULTS OF ELEMENTAL ANALYSES - N-BENZOYLGLYCINE SERIES

Compound	Found %				Calculated %					
	C	H	N	Metal	C	H	N	Metal	For	M.Wt.
BGA	60.3	5.10	7.81	-	60.33	5.03	7.82	-	$C_9H_9O_3N$	179
Br.BGA	41.8	3.19	5.50	Br 30.20	41.88	3.10	5.43	Br 30.98	$C_9H_8O_3N$ Br	257.9
K.BG	49.3	3.50	6.20	-	49.74	3.68	6.45	-	K ($C_9H_8O_3N$)	217.1
$Cu(BG)_2.nH_2O$	44.5	5.11	6.07	12.8	43.95	4.88	5.97	12.90	$Cu(C_9H_8O_3)_2.4H_2O$	491.4
$Cu(BG)_2$	52.0	3.71	6.74	14.90	51.51	3.82	6.68	15.12	$Cu(C_9H_8O_3N)_2$	419.4
$Co(BG)_2.nH_2O$	43.7	5.29	5.60	11.8	44.19	4.91	5.73	12.10	$Co(C_9H_8O_3N)_2.4H_2O$	486.9
$Co(BG)_2$	51.9	3.99	6.50	14.00	51.82	3.84	6.75	14.20	$Co(C_9H_8O_3N)_2$	414.9
$Ni(BG)_2.nH_2O$	43.9	5.40	5.60	11.90	44.39	4.93	5.75	12.06	$Ni(C_9H_8O_3N)_2.4H_2O$	486.7
$Mn(BG)_2.nH_2O$	45.00	5.00	5.95	11.70	44.74	4.97	5.80	11.37	$Mn(C_9H_8O_3N)_2.4H_2O$	482.9
$Zn(BG)_2$	51.00	3.99	6.70	16.0	51.26	3.80	6.65	15.52	$Zn(C_9H_8O_3N)_2$	421.4

BG = $C_6H_5CONHCH_2COO$ $C_9H_8O_3N$

TABLE - II - 4

RESULTS OF ELEMENTAL ANALYSES - N-ACETYLGLYCINE SERIES

Compound	Found %				Calculated %					M.Wt.
	C	H	N	Metal	C	H	N	Metal	For	
AGA	41.0	6.01	11.90	-	41.02	5.98	11.96	-	$C_4H_7O_3N$	117
Li(AG)	38.5	5.00	11.20	-	39.05	4.88	11.40	-	$Li(C_4H_6O_3N)$	122.9
$Cu(AG)_2.nH_2O$	26.8	5.50	7.80	17.00	26.12	5.44	7.45	17.28	$Cu(C_4H_6O_3N)_2.4H_2O$	367.5
$Co(AG)_2.nH_2O$	26.4	5.62	7.51	16.10	26.45	5.51	7.72	16.18	$Co(C_4H_6O_3N)_2.4H_2O$	362.9
$Co(AG)_2$	32.7	4.45	8.99	19.7	33.10	4.13	9.63	20.24	$Co(C_4H_6O_3N)_2$	290.9
$Ni(AG)_2.nH_2O$	26.1	5.19	7.60	16.50	26.47	5.51	7.72	16.18	$Ni(C_4H_6O_3N)_2.4H_2O$	362.7
$Mn(AG)_2.nH_2O$	26.7	5.70	7.80	15.00	26.75	5.57	7.80	15.30	$Mn(C_4H_6O_3N)_2.4H_2O$	358.9

AG = $CH_3CONHCH_2COO$, $C_4H_6O_3N$

TABLE II - 5

RESULTS OF ELEMENTAL ANALYSES - DL-β- PHENYLALANINE SERIES

Compd.	% Found					% Calculated						M.Wt.
	C	H	N	Cl	Metal	C	H	N	Cl	Metal	For	
PHA	64.9	6.61	8.50	-	-	65.06	6.63	8.43	-	-	-	165
NaPH	56.6	5.86	6.80	-	-	57.76	5.35	7.32	-	-	$Na(C_9H_{10}O_2N)$	187
PHA.HCl	53.9	5.89	7.07	17.0	-	53.58	5.95	6.95	17.66	-	$C_9H_{11}O_2N\ Cl$	201.5
$Cu(PH)_2$	54.8	5.20	6.70	-	17.5	55.18	5.11	7.15	-	16.22	$Cu(C_9H_{10}O_2N)_2$	391.5
$Co(PH)_2$	55.5	5.41	7.50	-	13.0	55.84	5.19	7.24	-	13.23	$Co(C_9H_{10}O_2N)_2$	386.9
$Ni(PH)_2$	55.5	5.32	7.60	-	15.0	55.86	5.17	7.25	-	15.18	$Ni(C_9H_{10}O_2N)_2$	386.7
$Mn(PH)_2$	56.9	5.20	7.10	-	14.2	56.41	5.22	7.31	-	14.34	$Mn(C_9H_{10}O_2N)_2$	382.9
$Zn(PH)_2$	54.50	4.91	7.50	-	16.3	54.91	5.08	7.21	-	16.63	$Zn(C_9H_{10}O_2N)_2$	393.4

* PH = $C_6H_5CH.CH_2.NH_2.COO^-$ = $C_9H_{10}O_2N$

TABLE II - 6

RESULTS OF ELEMENTAL ANALYSES OF NICOTINIC ACID SERIES

Compound	% Found					% Calculated						M.Wt.
	C	H	N	Cl	Metal	C	H	N	Cl	Metal	For	
NA	58.6	4.10	11.45	-	-	58.5	4.06	11.39	-	-	$C_6H_5NO_2$	123
NA.HCl	44.7	3.70	8.70	22.6	-	44.9	3.74	8.73	22.1	-	$C_6H_6NO_2Cl$	159.5
KN	43.8	2.90	8.50	-	-	44.7	2.48	8.69	-	-	$K.C_6H_5NO_2$	161.1
$Cu(N)_2nH_2O$	42.3	3.52	8.30	-	15.0	41.9	3.49	8.15	-	14.7	$Cu(C_6H_4O_2N)_2.2H_2O$	343.5
$Co(N)_2nH_2O$	38.9	4.70	7.50	-	16.0	38.4	4.27	7.44	-	15.7	$Co(C_6H_4O_2N)_2.4H_2O$	374.9
$Ni(N)_2nH_2O$	38.9	4.50	7.65	-	16.1	38.4	4.27	7.45	-	15.7	$Ni(C_6H_4O_2N)_2.4H_2O$	374.7
$Mn(N)_2nH_2O$	39.0	4.50	7.30	-	15.0	38.8	4.31	7.55	-	14.8	$Mn(C_6H_4O_2N)_2.4H_2O$	370.9

$N = (\beta)\ C_5H_4N.COO^- = 122$

TABLE II - 7

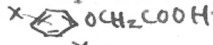
RESULTS OF ELEMENTAL ANALYSES - ISONICOTINIC ACID SERIES

Compound	% Found					% Calculated						M.Wt.
	C	H	N	Cl	Metal	C	H	N	Cl	Metal	For	
INA	58.4	4.00	11.5	-	-	58.5	4.06	11.39	-	-	$C_6H_5NO_2$	123
INA.HCl	44.8	3.30	8.51	22.0	-	44.9	3.74	8.74	22.1	-	$C_6H_5NO_2.HCl$	159.5
K(IN)	44.2	2.50	8.90	-	-	44.7	2.48	8.69	-	-	$K(C_6H_4NO_2)$	161.1
$Cu(IN)_2.nH_2O$	37.2	4.80	7.50	-	16.3	37.9	4.21	7.38	-	16.7	$Cu(C_6H_4NO_2)_2.2H_2O$	379.5
$Co(IN)_2.nH_2O$	37.9	4.11	7.60	-	15.5	38.4	4.27	7.44	-	15.7	$Co(C_6H_4NO_2)_2.4H_2O$	374.9
$Ni(IN)_2.nH_2O$	38.0	4.30	7.62	-	15.4	38.4	4.27	7.45	-	15.7	$Ni(C_6H_4NO_2)_2.4H_2O$	374.7

$IN = (\gamma)\ C_5H_4N.COO^- = 122$

TABLE II - 8

RESULTS OF ELEMENTAL MICROANALYSES - SUBSTITUTED PHENOXY ACETIC ACIDS

Compound  X=	% Found			% Calculated					M. Wt.
	C	H	Cl	C	H	Cl	For	M.P.	
H	63.10	5.20	-	63.17	5.26	-	$C_8H_8O_3$	97-8	152
2 Cl	51.31	3.80	18.75	51.47	3.75	19.03	$Cl.C_8H_7O_3$	144-46	186.5
4Cl	51.20	3.83	18.70	51.47	3.75	19.03	$Cl.C_8H_7O_3$	158-60	186.5
2,4-Cl_2	43.34	2.80	34.50	43.44	2.71	34.39	$Cl_2.C_8H_6O_3$	142	221.0
2Me-4Cl	53.70	4.60	17.80	53.87	4.49	17.70	$Cl.C_9H_9O_3$	119-20	200.5
2Me	64.80	5.89	-	64.68	5.99	-	$C_9H_{10}O_3$	148-50	167
3Me	64.75	5.88	-	64.69	5.99	-	$C_9H_{10}O_3$	102-4	167
4Me	64.91	5.89	-	64.69	5.99	-	$C_9H_{10}O_3$	136-37	167

Electronic spectra : Electronic spectra were recorded on a Perkin-Elmer Model 350 spectrophotometer using a pair of 1 cm. matched quartz cells.

Magnetic susceptibility measurements : Magnetic susceptibility measurements of powdered samples (passed through ASTM mesh 230) were carried out on a Gouy magnetic balance. Mohr's salt was used as standard. All measurements were made at room temperature and with different field strengths ranging between 3000-6000 gauss to confirm the absence of any ferromagnetic impurities. The values were reproducible within one per cent and the average of three sets of experiments were taken for each compound. Diamagnetic corrections to individual ligands were applied using Pascal's constants.

C H A P T E R - III

INFRARED SPECTRA OF SOME HYDROXY ACIDS AND THEIR METAL COMPLEXES*

INTRODUCTION

A survey of literature shows that the infrared spectra of hydroxy acids and their metal derivatives have not been adequately studied. The extensive work of Hadzi and others[1] has established the vibrational frequencies of the carboxylic acid (COOH) group, but the alcoholic ($-\overset{|}{\underset{|}{C}}-OH$) group vibrations, other than the hydroxyl stretching, in the region below 1500 cm^{-1} are neither well analysed nor understood. The difficulties in assigning these vibrational modes are due to (1) changes in hydrogen bonding with change of state, (2) presence of bands due to other groups in the same region which cannot be easily resolved, and (3) anomalous shift on dilution and deuteration arising from coupled vibrational modes. These complicating factors operative in the alcohols have led several investigators to express divergent opinions. In the case of ethanol[2], three bands viz. 1419, 1330 and 1092 cm^{-1} appear to be replaced by only one band (956 cm^{-1}) on deuteration. Krimm and coworkers[3] have found that polyvinyl alcohol absorbs

* Part of this work was presented at the International Conference on Spectroscopy, January, 1967, Bombay.

at 1446, 1326 and 1096 cm^{-1} while its deuterated analogue absorbs at 1384, 1052 and 985 cm^{-1}. It has been suggested by these workers that the OH and CH deformation modes interact, giving rise to two mixed vibrations (1446 and 1326 cm^{-1}). The 1096 cm^{-1} band is attributed to ν C-O vibration. Pitchard and Nelson[4] have observed that tert-butanol absorbs at 1380 and 1189 cm^{-1} and tert-butanol-d_1 at 1256 and 956 cm^{-1}. The isotope effect for the degree of freedom associated with the inplane bending mode of COH group is split, according to them, between two frequencies, the primary assignments of which for pure tert-butanol are δ COH (bending) at 1380 cm^{-1} and ρ_r Me (symmetrical methyl rocking mode) at 1189 cm^{-1}.

The first systematic attempt to elucidate the structure of hydroxy acid complex from its infrared spectrum was made by Kirshner and Kiesling[5]. Based on the lowering of frequency and band splitting, a structure involving three water molecules, one of the two hydroxyl groups and both the carboxylate groups coordinated to the metal ion, has been proposed for copper(II) tartrate trihydrate. Although, recently some doubt has been expressed regarding the identity of this complex by Bolard[6] who regards this to be anhydrous with the molecular formula Cu:$C_4H_4O_6$, the basic observation of Kirshner and Kiesling that one free and one coordinated hydroxyl

groups are present, is indeed, confirmed even for anhydrous compound from an examination of hydroxyl stretching frequencies.

The work on hydroxy acid complexes prior to 1963 has already been reviewed[7]; only the recent work is discussed here. Goulden[8] has found that the intensity of δ OH inplane mode follows the well known Irving-Williams order of relative stability[9]. Several metal glycolato complexes have recently been studied in detail. The infrared studies and of normal vibrational analysis by Nakamoto et al[10] propose a similar order of relative stability from ν M-O frequencies.

We undertook a programme to investigate the infrared spectra of metal complexes of hydroxy acids with a view to obtaining information regarding coordination sites, order of relative stability and probable structure. The results of such studies on tartaric[11], lactic[12] and malic acid[13] have been reported elsewhere. In what follows, the infrared spectra of benzilic (diphenyl glycolic) and mandelic (phenyl glycolic) acids have been discussed with reference to several related compounds and deuterated analogues. Further, the spectra of divalent copper, cobalt, nickel, manganese and zinc complexes have been analysed.

RESULTS AND DISCUSSION

1. Spectrum of benzilic acid $(C_6H_5)_2$-C(OH)-COOH

Infrared spectra of benzilic acid, its deuterated analogue, potassium benzilate and the deuterated salt methyl benzilate, its deuterated derivative, triphenylcarbinol and deuterated triphenyl carbinol, are shown in figures III-1 and 2, while their pertinent absorption bands along with their assignments are summarized in tables III-1 and III-2.

The alcoholic group

The band at 3390 cm^{-1} of benzilic acid is assigned to OH vibration as it is found to shift quantitatively on deuteration. In order to identify the bands below 1500 cm^{-1} due to tertiary alcoholic group of benzilic acid, a number of related compounds and their deuterated derivatives have been studied. As seen from figures III-1 and III-2 in all these compounds two bands at 1350 and 1160 cm^{-1} are replaced on deuteration by a strong band at 860 cm^{-1}. In addition to this, some minor changes in the region 1300-1200 cm^{-1} are also observed. It is, therefore, concluded that the 1350 and 1160 cm^{-1} bands represent the coupled vibrations of COH and CH (inplane deformation mode due to benzene ring). The latter may, by

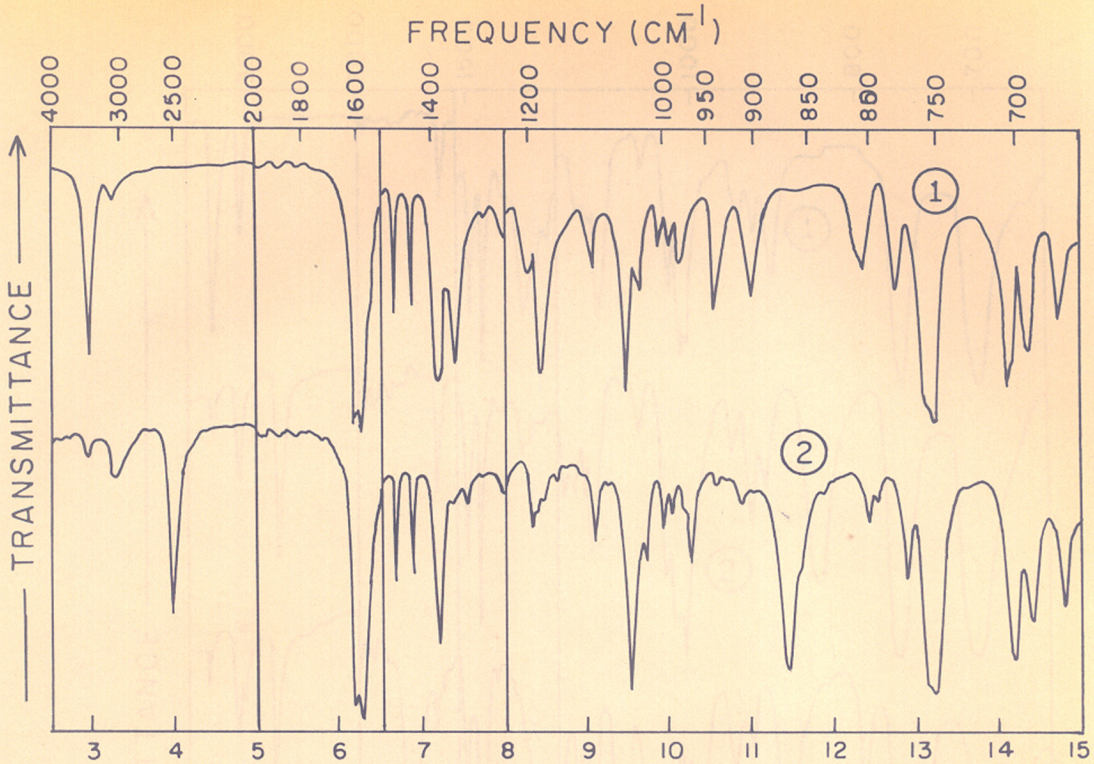


Fig. III – 1 a

1. Potassium benzilate, KB
2. Deutd potassium benzilate, KB – d_1

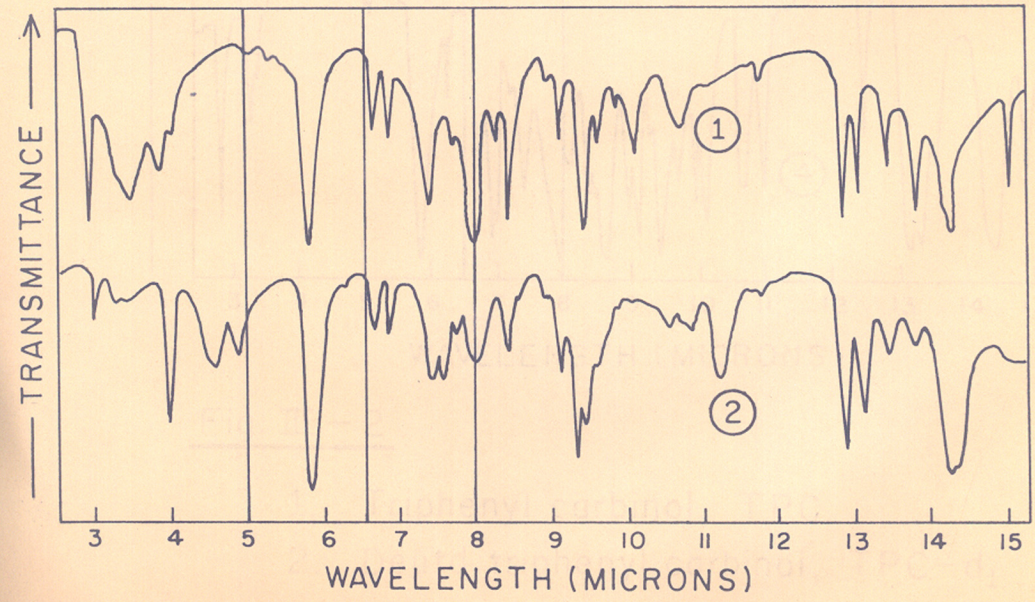


Fig. III – 1 b

1. Benzilic acid, BA
2. Deutd benzilic acid, BA – d_2

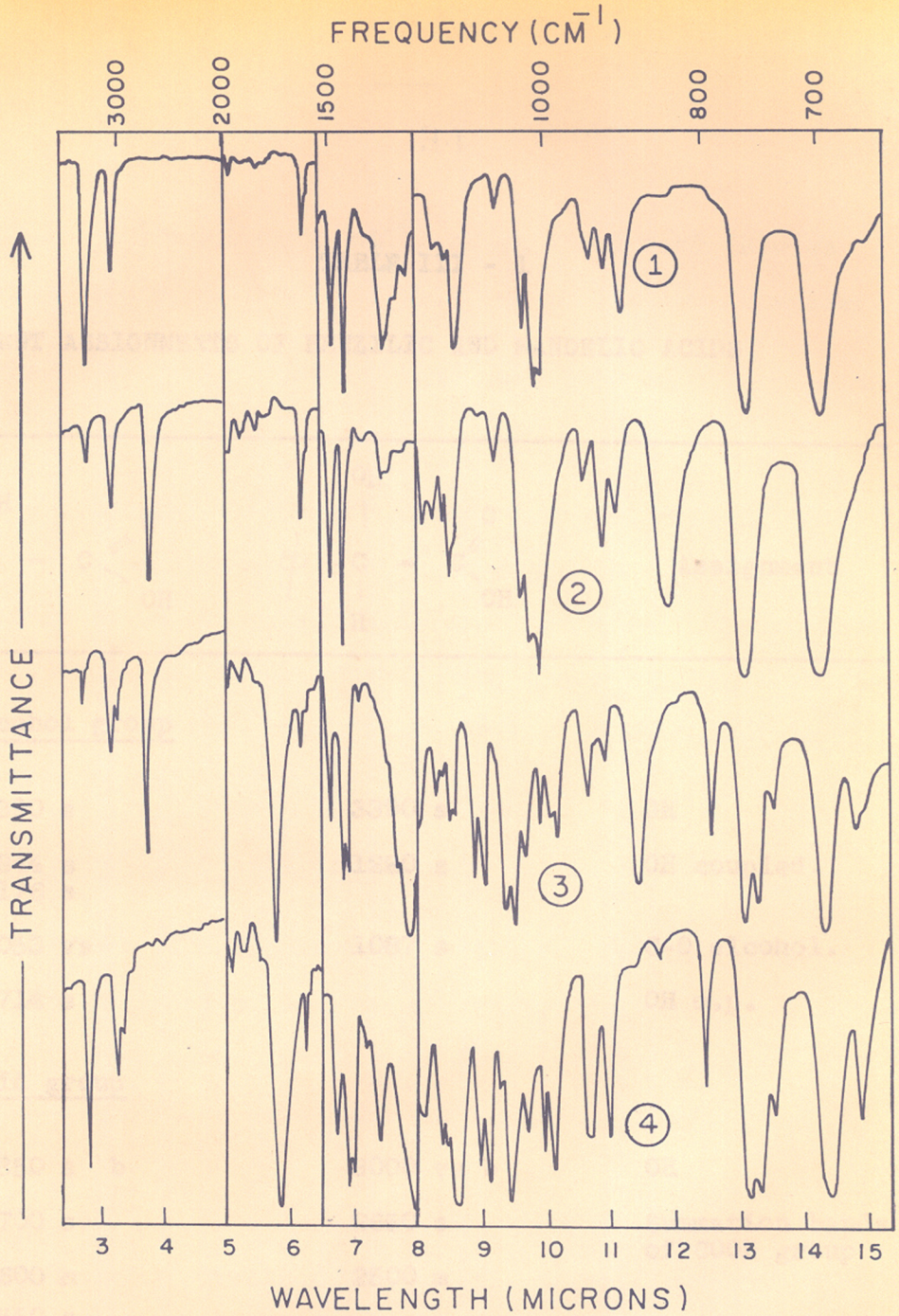
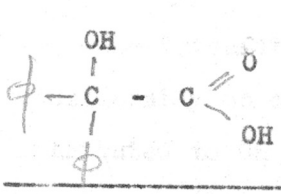
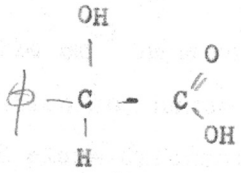


Fig. III – 2

1. Triphenyl carbinol, TPC
2. Deutd triphenyl carbinol, TPC – d_1
3. Deutd methyl benzilate, MeB – d_1
4. Methyl benzilate, MeB

TABLE III - 1

PERTINENT ASSIGNMENTS OF BENZILIC AND MANDELIC ACIDS

		Assignment
The alcohol group		
3390 s	3390 s	OH
1344 s 1176 s	1280 s	OH coupled.
1053 vs	1087 s	C-O alcohol.
714 s		OH o.p.
The acid group		
3100-2850 s b	3000 vs b	OH
2700 s	2650 s	Summation bands of COOH group
2600 m	2500 m	
2550 s		
1710 s	1705 s	C=O.
1365 s 1300 s	1425 s 1360 s	C-O + OH o.p.
915 s b	910 s b	OH o.p.
670 s	650 s	COOH

analogy to triphenyl carbinol[14], be expected near 1270 cm^{-1}, but could not be observed probably due to its low intensity.

The ν C-O vibration is found near 1050 cm^{-1} in most of the compounds studied.

The intensity of 714 cm^{-1} band of benzilic acid diminishes considerably on deuteration and hence this band may be attributed to OH out of plane deformation mode. This band, however, could not be detected in any other compounds studied. Weston and coworkers[14] have failed to locate this band in triphenylcarbinol.

The carboxylic acid group

Since the vibrational frequencies due to this group have been fully assigned by now, no discussion is given here. The pertinent assignments, which have been substantiated by deuteration studies, have been included in Table III-1.

Spectra of complexes

Complexes of divalent Cu, Co, Ni, Mn and Zn of the type $M(B)_2$ where M is the metal ion and B is the benzilate ion $(C_6H_5)_2.COH.COO^-$, and their deuterated analogues are studied. Spectra of typical complexes are illustrated in figures III-3 while their pertinent absorption bands are given in table III-2.

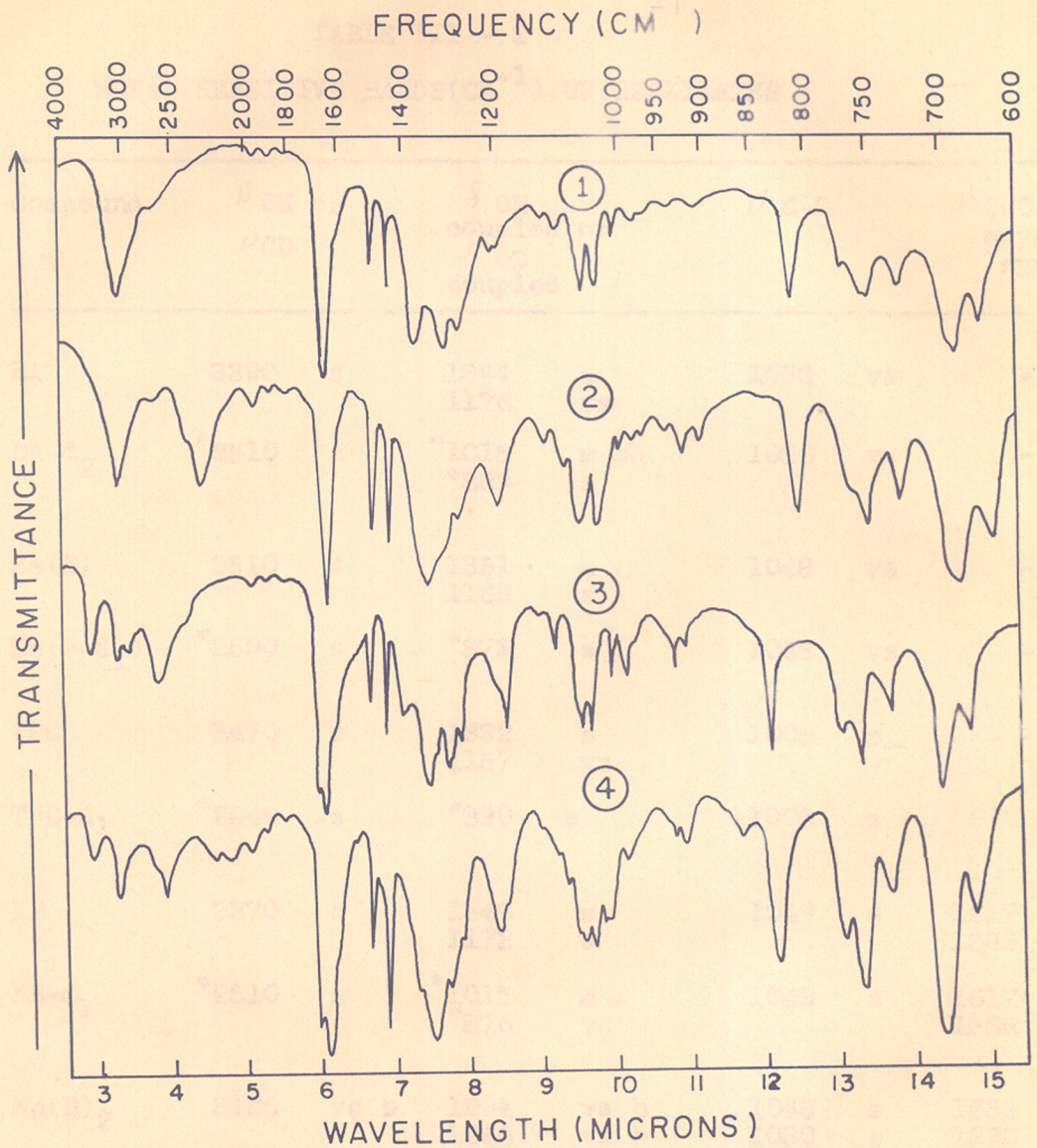


Fig. III – 3

1. Cobalt (II) benzilate, $Co(B)_2$
2. Deutd cobalt (II) benzilate, $Co(B-d_1)_2$
3. Copper (II) benzilate, $Cu(B)_2$
4. Deutd copper (II) benzilate, $Cu(B-d_1)_2$

TABLE III - 2

METAL SENSITIVE BANDS(CM^{-1}) OF BENZILATES

Compound	ν OH or ν OD		δ OH coupled or δ OD coupled		ν C-O		ν COO^- asym.		sym.	
BA	3390	s	1344	s	1053	vs	-			
			1176	vs						
BA-d_2	*2510	s	*1015	m sh	1056	vs	-			
			*889	s						
Me(B)	3510	s	1351	m	1048	vs	-			
			1168	s						
Me(B-d_1)	*2590	s	*873	s	1058	vs	-			
TPC	3470	s	1332	s	1005	s	-			
			1157	vs						
TPC-d_1	*2546	s	*890	s	1005	s	-			
KB	3370	s	1346	s	1049	s	1617	vs		
			1172	s			1385	s		
KB-d_1	*2510	s	*1015	m	1049	s	1617	vs		
			*876	vs			1385	s		
$Mn(B)_2$	3185	vs b	1294	vs b	1048	s	1652	vs		
			1266	vs b	1030	s	1370	s		
$Mn(B\text{-}d)_2$	*2390	m b	*917	m	1055	s h	1650	vs		
			*888	m b	1048	s				
					1030	s	1368	vs		
$Co(B)_2$	3070	vs b	1370	s	1049	s	1647	vs		
			1300	s b	1031		1370	s		
			1272	s						
$Co(B\text{-}d)_2$	*2290	m b	*1351	s vb	1057	s b	1647	vs		
			*1316	s sh						
			* 928	m b	1027	s	1351	s		

Table III - 2 (continued)

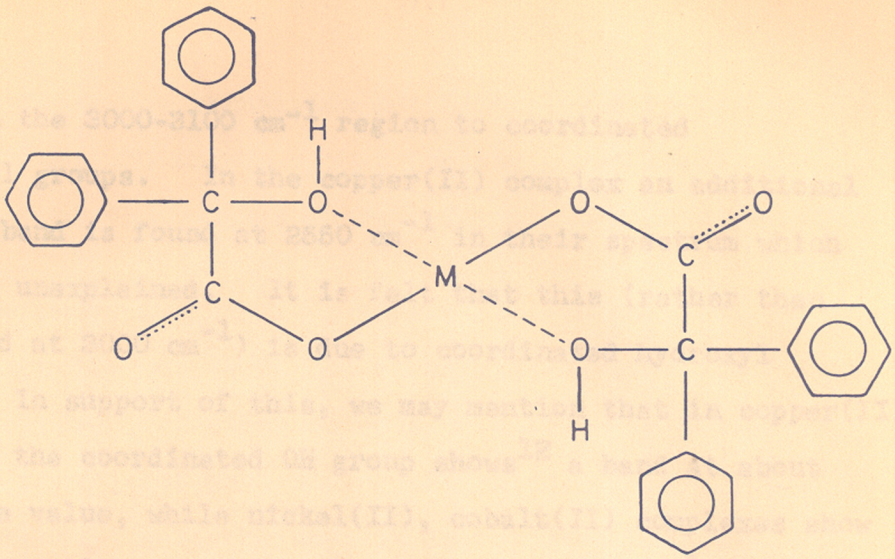
Compound	ν_{OH} or ν_{OD}			δ_{OH} coupled or δ_{OD} coupled			ν_{C-O}			ν_{COO^-} asym.		sym.
$Ni(B)_2$	3050	vs	b	1370		s	1055	s	b	1650	vs	
				1300	s	b						
				1272	s		1030	s	b	1377	s	
$Ni(B\text{-}d)_2$	*2270	m	b	*1305	vs	s	1060	s	sh	1650	vs	
				*1315	s		1055	s	b	1347	s	
				*925	s		1030	s				
$Cu(B)_2$	3380	s		1338	s		1060	s	sh	1662	vs	
	2540	s	b	1292	s	b	1055	s	b	1338	s	
				1172	s		1030	s				
$Cu(B\text{-}d)_2$	*2500	s		*1335	vs	vb	1057	m		1662	s	
	*2190	m		*908	m		1045	s		1345		
	*2090	m		*855			1064	m	sh			
							1031	s				
$Zn(B)_2$	3145	s	b	1370	vs	b	1087	m		1661	vs	
				1348	s		1067	m	sh			
							1054	s		1370	s	
$Zn(B\text{-}d)_2$	*2390	sh		*1350	s		1079	m		1661	vs	
	*2335	m	b	*1335			1051	s		1350	s	
				* 893	w	b	1028	s				

* Denotes the corresponding OD vibrational mode.

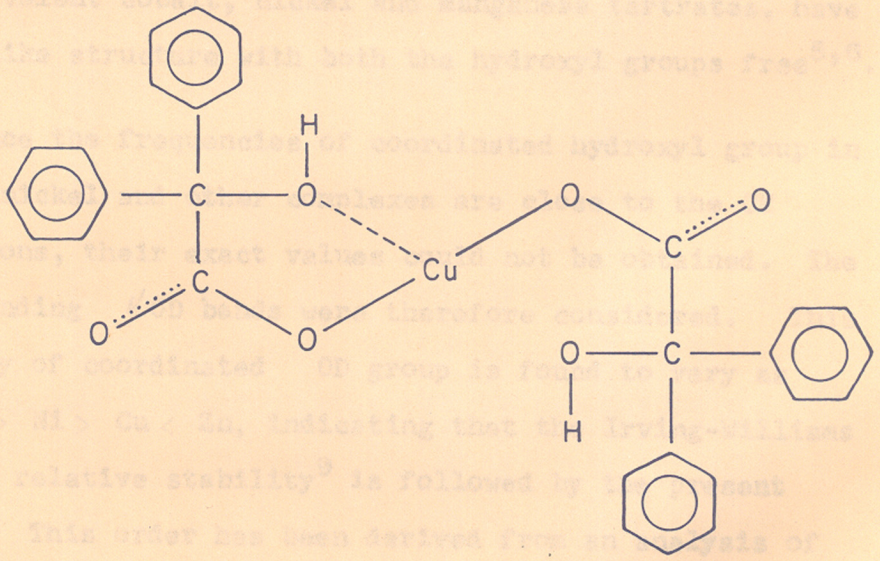
The alcoholic group

The OH stretching mode is considered the most suitable for correlation with the stability of the complex, its shift to lower frequency being considered proportional to the strength of coordination. This is because there is a pull on the electrons of oxygen atom towards the metal ion on coordination, which results in decrease of electron density around the oxygen atom, thus weakening the O-H bond. Effect of this weakening, as revealed primarily by the shift in the OH stretching frequency, may be taken to be proportional to the strength of coordination. However, the OH frequency may also be affected by hydrogen bonding and crystal field effects. The effect of hydrogen bonding may not be large in the present series of compounds since these all are anhydrous. Further the effect of coordination is considered to be strong in compounds of this type.

The νOH band (3390 cm^{-1}) of benzilic acid is replaced in all cases, except in the case of copper(II) complex, by a broad absorption pattern in the 3100-2900 cm^{-1} region. Copper(II) benzilate, however, exhibits unique spectral features of having two bands at 3390 and 2550 cm^{-1}. The former is attributed to free and the latter to coordinated hydroxyl groups. In a number of glycolato complexes including copper(II), Nakamoto et al.[10] have assigned the



Coordination behaviour of metal (divalent cobalt, nickel, manganese and zinc) benzilates.



Coordination behaviour of Copper (II) benzilate.

Fig. III – 4

band in the 3000-3100 cm^{-1} region to coordinated hydroxyl groups. In the copper(II) complex an additional strong band is found at 2550 cm^{-1} in their spectrum which is left unexplained. It is felt that this (rather than the band at 3000 cm^{-1}) is due to coordinated hydroxyl group. In support of this, we may mention that in copper(II) lactate the coordinated OH group shows[12] a band at about the same value, while nickel(II), cobalt(II) complexes show this absorption at a higher value (near 2800 cm^{-1}).Coordination of copper(II) to only one hydroxyl group is not very surprising in view of the fact that anhydrous copper(II) tartrate shows one coordinated and one free hydroxyl groups, while divalent cobalt, nickel and manganese tartrates, have a salt-like structure with both the hydroxyl groups free[5,6].

Since the frequencies of coordinated hydroxyl group in cobalt, nickel and other complexes are close to the CH absorptions, their exact values could not be obtained. The corresponding νOD bands were therefore considered. This frequency of coordinated OD group is found to vary as Mn > Co > Ni > Cu < Zn, indicating that the Irving-Williams order of relative stability[9] is followed by the present series. This order has been derived from an analysis of the extensive amount of data on the stability constants for

several first row transition metal complexes by Irving and Williams who proposed that for any given ligand the stability of the complex should vary as Mn < Co < Ni < Cu > Zn.

The bands due to δCOH appear at 1365 and 1165 cm^{-1} in benzilic acid. Since it has already been established that there is strong coupling between δOH and δCH inplane bending modes, not much diagnostic value may be attached to these modes. Nevertheless, it is observed that the 1165 cm^{-1} band of benzilic acid is shifted to 1270-1290 cm^{-1} upon coordination to a metal ion. The corresponding OD mode is found at $\sim$ 920 cm^{-1} in the deuterated complexes, as against 870 cm^{-1} in deuterated acid. In the glycolato complexes the inplane deformation mode is found at 1480 - 1470 cm^{-1} against 1250 cm^{-1} in glycolic acid[10].

The carboxylate group

The carboxylate group stretching frequencies due to the asymmetric and symmetric modes are found at $\sim$ 1650 and 1380 cm^{-1} in all the complexes studied. This is indicative of nearly the same extent of electrovalent nature of the metal to carboxylate oxygen bond.

2. Spectrum of mandelic acid $C_6H_5 - \underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}} - COOH$

In connection with the structural study of zirconium salt of mandelic acid, Stromatt[15] has reported the spectra of this compound, its deuterated analogue (MA-d_2) and the sodium salt (NaM). The author has discussed the spectra of various complexes particularly the separation between the two carboxylate stretching frequencies. However, the coupling effects of COOH and CHOH groups have not been analysed. In the present study therefore the vibrations due to the COOH and CHOH groups are discussed, the assignments being grouped in table III-1 along with those for benzilic acid.

In mandelic acid the overlapping of CHOH and COOH bands makes the precise location of the CHOH bands difficult. The specific features of CHOH group bands appearing in the region 1500-1000 cm^{-1} are therefore revealed by the study of sodium mandelate and its deuterated analogue. The latter shows new bands at 1040, 900 and 850 cm^{-1} in place of 1365 and 1090 cm^{-1} bands of sodium mandelate. The 1040 and 850 cm^{-1} bands in the deuterated analogue seem to correspond to the hydrogen modes at 1365 and 1090 cm^{-1} of the parent compounds prompting us to assign both to OH modes (namely inplane and out of plane deformations). However, the νOH

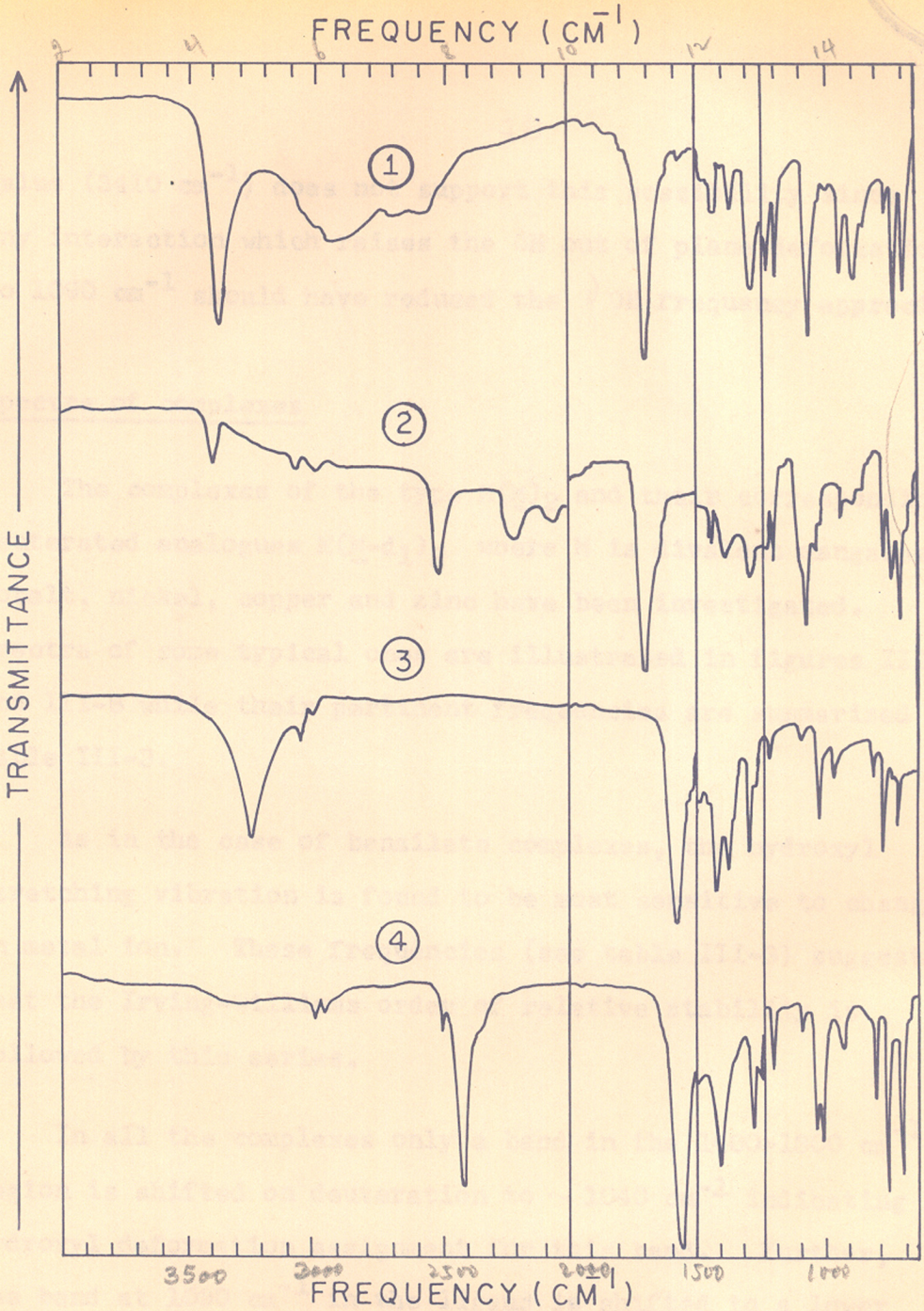


Fig. III – 5

1. Mandelic acid, MA
2. Deutd mandelic acid, MA – d_2
3. Cobalt (II) mandelate, $Co(M)_2$
4. Deutd cobalt (II) mandelate $Co(M-d_1)_2$

value (3410 cm^{-1}) does not support this possibility since any interaction which raises the OH out of plane deformation to 1090 cm^{-1} should have reduced the ν OH frequency appreciably.

Spectra of complexes

The complexes of the type $M(\underline{M})_2$ and their corresponding deuterated analogues $M(\underline{M}\text{-}d_1)_2$ where M is divalent manganese, cobalt, nickel, copper and zinc have been investigated. Spectra of some typical ones are illustrated in figures III-5 and III-6 while their pertinent frequencies are summarized in table III-3.

As in the case of benzilate complexes, the hydroxyl stretching vibration is found to be most sensitive to changes in metal ion. These frequencies (see table III-3) suggest that the Irving-Williams order of relative stability is followed by this series.

In all the complexes only a band in the 1400-1300 cm^{-1} region is shifted on deuteration to $\sim$ 1040 cm^{-1} indicating an hydroxyl deformation assignment for this band. Further, the band at 1090 cm^{-1} in the ligand is shifted to a lower frequency ($\Delta\nu \approx$ 50-90 cm^{-1}) upon coordination. This behaviour is in contrast with that of sodium mandelate, which shows two bands at 1360 and 1090 cm^{-1} which shifted on deuteration to 1040 and 850 cm^{-1}.

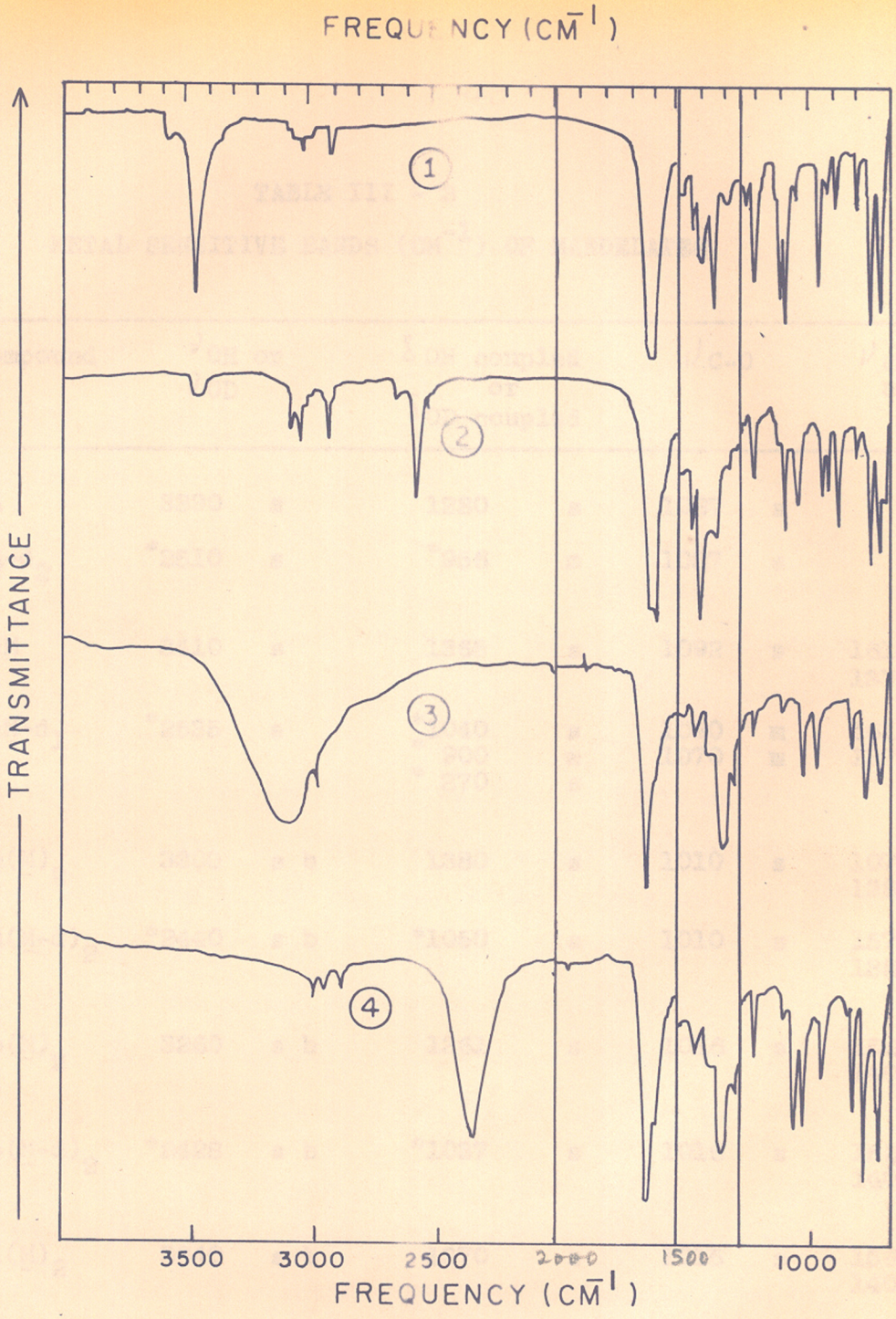


Fig. III – 6

1. Sodium mandelate, NaM
2. Deutd sodium mandelate, NaM – d_1
3. Copper (II) mandelate, $Cu(M)_2$
4. Deutd copper (II) mandelate, $Cu(M-d_1)_2$

TABLE III - 3

METAL SENSITIVE BANDS (CM^{-1}) OF MANDELATES

Compound	ν_{OH} or ν_{OD}		δ_{OH} coupled or δ_{OD} coupled		ν_{C-O}		ν_{COO^-} asym. sym.	
MA	3390	s	1280	s	1087	s	-	
MA-d_2	*2510	s	*956	m	1087	s	-	
NaM	3410	s	1365	s	1092	s	1615 1375	s s
NaM-d_1	*2535	s	*1040 * 900 * 870	s m s	1090 1070	m m	1615 1375	s s
$Mn(M)_2$	3300	s b	1380	s	1010	s	1070 1380	s b s b
$Mn(M\text{-}d)_2$	*2440	s b	*1050	s	1010	s	1570 1380	s b s b
$Co(M)_2$	3260	s b	1361	s	1016	s	1565 1408	s b s b
$Co(M\text{-}d)_2$	*2428	s b	*1037	s	1016	s	1565 1408	s b s b
$Ni(M)_2$	3240	s b	1370	s	1015	s	1566 1405	s b s
$Ni(M\text{-}d)_2$	2410	s b	1035	s			1566 1405	s b s
$Cu(M)_2$	3080	s b	1380	s vb	1010	s	1590 1380	s b s b
$Cu(M\text{-}d)_2$	*2270	s b	*1040	s	1010 1005	s s	1590 1380	s b s b
$Zn(M)_2$	3240	s b	1375	s sh	1015	s	1557 1380	s b s b
$Zn(M\text{-}d)_2$	* 2400	s b	*1047	s	1010	s	1557 1380	s b s b

The changes in the bands at 1360 cm^{-1} (δ OH) and 1000 cm^{-1} (ν C-O) in $M(\underline{M})_2$ complexes and at $\sim$ 1040 and 1000 in the deuterated analogues are not appreciable to draw coorrelative conclusions.

From the foregoing studies it is concluded that metal complexes of the type $M(L)_2$ with benzilate and mandelate ligands and divalent manganese, cobalt, nickel, copper and zinc ions, all have a bidentate chelate structure involving coordinate bonding through the oxygen atom of the alcoholic group, the strength of which is found to vary from metal to metal. The variation in the νOH frequency due to coordinated hydroxyl group indicates that the strength of this bond varies as Mn < Co < Ni< Cu > Zn, as reflected by the highest value for Mn(II) and lowest for Cu(II) complex. In contrast to νOH mode the νCOO modes (both asymmetric and symmetric) do not change very much on going from complex to complex. This indicates that the carboxylate bonding is similar in these complexes and M-O bands have nearly equal strengths.

The structure of copper(II) benzilate is unique as compared to all other metal benzilates and mandelates. The two ligand molecules are held dissimilarly in the complex, only the hydroxyl of one of the ligands being coordinated to the copper(II) ion, while the other one is free.

REFERENCES

1. a: Hadzi, D. and Sheppard, N., Proc. Royal Soc., A-216, 247 (1954).

   b: Bratoz, S., Hadzi, D. and Sheppard, N., Spectrochim. Acta, 8, 249 (1956).

2. Maclou, M. and Henry, L., Compt. Rend. acad.sc. Paris, 244, 1494 (1957).

3. Krimm, S., Liang, C. Y. and Sutherland, G.B.B.M., J. Chem. Phys., 25, 778 (1956).

4. Pitchard, J. C. and Nelson, H. M., J. Phy. Chem., 64, 795 (1960).

5. Kirshner, S. and Kiesling, R., J. Amer. Chem. Soc., 82, 4174 (1960).

6. Bolard, J., J.Chemie Physique, 900 (1965).

7. Shevchenko, L. L., Russian Chem. Reviews, 32, 201 (1963).

8. Goulden, J.D. S., Spectrochim. Acta, 16, 715 (1960).

9. Irving, H. and Williams, R. J. P., J. Chem. Soc., 3192 (1952).

10. Nakamoto, K., McCarthy, P. J. and Miniatas, B., Spectrochim. Acta, 21, 379 (1965).

11. Ranade, A.C., Srinivasan, T. K. K. and Biswas, A.B., Unpublished data. Indian Science Congress, January,1965.

12. Ranade, A. C. and Biswas, A. B., J. Ind. Chem. Soc., 44, 315 (1967).

13. Ranade, A. C., Spectrochemical properties and thermal stabilities of some transition metal complexes", M. Sc. Thesis, Bombay University, October, 1964.

14. Weston, R.E., Tsukamoto, A. and Lichtin, N. N., Spectrochim. Acta., 22, 433 (1966).

15. Strommatt, R. W., "An infrared study of zirconium tetramandelate and stabilities of metal chelates of some α-amino acids and mandelic acid" Ph.D. thesis, Kansas State University, University Microfilms, Mich. L.C. Card No: Mic.58-1268.

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CHAPTER - IV

INFRARED SPECTRA OF SOME AMIDO ACIDS AND THEIR METAL COMPLEXES*

INTRODUCTION

Infrared spectra of several ∝-amido acids R $CONHCH_2COOH$ were reported by Randall et al.[1] and certain bands arising out of carbonyl, amido and carboxyl groups, have been characterized by Fuson et al.[2]. Micheel and Schleppinghoff[3] have investigated many N-acetylamino acids and analysed some of their characteristic bands. Preliminary assignments of some bands of N-acetylglycine have been made by Newman and Badger[4] in the light of its x-ray data[5], which show the absence of either zwitterion or a dimeric carboxyl group in the crystal. On the other hand, very strong hydrogen bonding exists between the OH of COOH and C=O of the CONH group of the adjacent molecule. No other amido acid seems to have been studied in detail. In the present work, therefore, the spectra of N-benzoylglycine, its parabromo derivative and N-acetylglycine (for comparison) are analysed to obtain information regarding their structure.

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* A paper entitled 'Infrared spectra of N-benzoyl and p-bromo N-benzoyl-glycine' will appear soon in the Indian Journal of Chemistry.

In the amido acid metal complexes of the type $M(L)_2$ there are two possible donor groups; viz. the carboxylate (COO^-) and the amide (CONH). Although the coordination behaviour of the carboxylate group is well-known[6], not much information is available concerning the frequency shifts due to coordination in amides. Penland and coworkers[7] have studied the infrared spectra of urea $OC(NH_2)_2$ complexes to determine the coordination sites. Based on the amide frequency shifts it has been concluded that Pt(II) and Pd(II) coordinate through nitrogen while Fe(III), Cr(III), Zn(II) and Cu(II) coordinate through oxygen. Recently, Antonenko and Nuger[8] have reported from similar studies that in $Ca(NO_3)_2$ $C\theta(NH_2)_2$, $BaCl_2$ $C\theta(NH_2)_2$ coordination exists through oxygen, while coordination is found through nitrogen in $Hg(NO_3)_2.HgO \cdot [C\theta(NH_2)_2]_2$. The observed frequency shifts in NH out of plane deformation mode of N-methylacetamide ($CH_3CONHCH_3$) upon coordination to cadmium (II) in $Cd(CH_3CONHCH_3)Cl_2$ led Martinette and collaborators[9] to suggest coordination to the nitrogen atom. These interpretations have however been contradicted subsequently by Gerrad et al.[10] Following the study of acids, therefore, infrared spectra of divalent copper, cobalt, nickel, manganese, zinc and cadmium complexes of N-acetyl and N-benzoylglycines as hydrate, anhydrous and deuterated forms

have been discussed to establish the coordination sites and their structures.

I SPECTRA OF ACIDS

In figure IV-1 and IV-2 the spectra of $C_6H_5CONHCH_2COOH$(BGA), $C_6H_5COND.CH_2COOD$(BGA-d_2); p-Br-C_6H_4.$CONHCH_2COOH$ (BrBGA), p-Br.$C_6H_4CONDCOOD$ (BrBGA-d_2), have been illustrated; the assignments of CONH and COOH group vibrations being listed separately in tables IV-1 and IV-2. The spectra of AGA and BGA are in agreement with the reported patterns, and those of the remaining compounds do not appear to have been reported so far.

CONH absorption

In the NH stretching region only a single band is found in all the compounds. On deuteration, however, two bands (2480, 2410 and 2450, 2400 cm^{-1}) each are found in BGA-d_2 and Br.BGA-d_2 respectively in the ND stretching region. The number of bands is not expected to change on deuteration unless the introduction of deuterium brings about a change in the symmetry of the molecule or in its crystalline form. It is evident that no change in the symmetry is involved and generally the deuterated compounds may have the same crystalline form. It is possible thus that the additional band has arisen

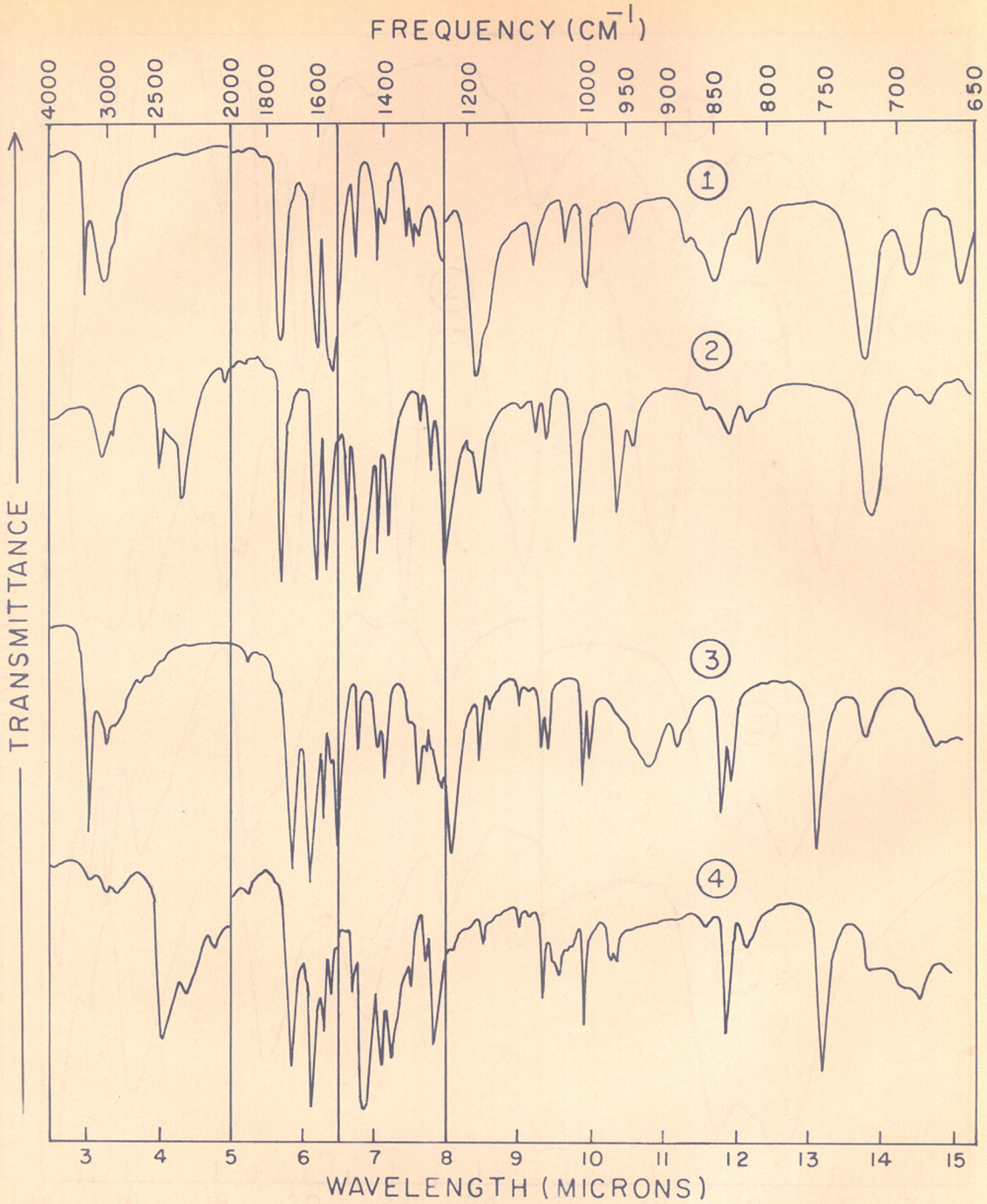


Fig. IV - 1

1. N - Benzoylglycine, BGA
2. Deutd N - benzoylglycine, BGA - d_2
3. p - Bromo - N - benzoylglycine, Br - BGA
4. Deutd p - Br - N - benzoylglycine, Br - BGA - d_2

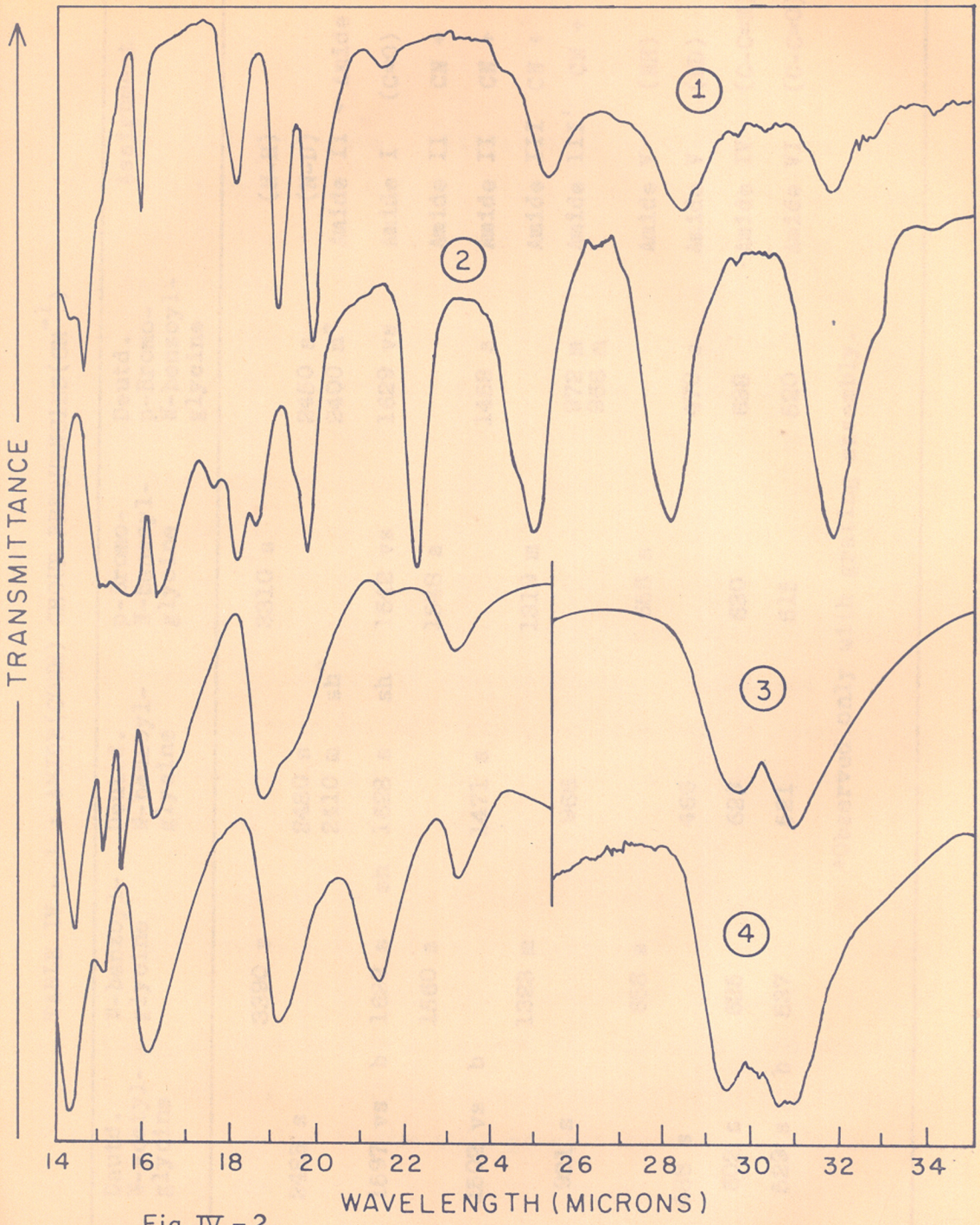


Fig. IV-2

1. Deutd p Bromo N-benzoylglycine, Br-BGA-d_2
2. p-Bromo N-benzoylglycine, Br-BGA
3. N-benzoylglycine, BGA
4. Deutd N-benzoylglycine, BGA-d_2

TABLE IV - 1 : AMIDE(CONH) GROUP FREQUENCIES(CM^{-1})

N-acetyl-glycine	Deutd. N-acetyl-glycine	N-benzoyl-glycine	Deuted. N-benzoyl-glycine	p-Bromo-N-benzoyl-glycine	Deutd. p-Bromo-N-benzcyl-glycine	Assignment
3342 s		3390 s		3310 s		(N-H)
	2488 s		2480 s 2410 m sh*		2450 s 2400 m*	(N-D) Amide II + Amide III
1580 vs b	1597 vs b	1629 s sh	1628 s sh	1642 vs	1629 vs	Amide I (C=O)
1548 vs b		1560 s		1548 s		Amide II CN + NH
	1502 vs b		1471 s		1458 s	Amide II CN + ND
1277 s		1323 m		1319 m		Amide III CN + NH
	931 s		966		972 m 966 m	Amide III' CN + ND
687 s		658 s		658 s		Amide V (NH)
	488 s		466		470 s	Amide V (ND)
602 s	602 s	625	629	630	638	Amide IV (C-C=N)
542 s b	529 s b	537	521	515	520	Amide VI (C-C=O)

*Observed only with grating assembly.

due to Fermi resonance. Vibrational perturbation of this kind can take place when two vibrational levels in a molecule have nearly the same energy and if the two vibrations are of the same species. The result of this perturbation is a shifting of one of the levels to higher energy while the other falls to a lower energy. In the present case only in the deuterated compounds appropriate fundamental bands of the proper symmetry class namely Amide II' and III' combine and get enhanced in intensity by Fermi resonance with the ν ND mole giving a doublet. Similar explanation has been offered by Fritsche[11] to account for the appearance of a doublet in ν ND region in deuterated benzimidazole. Hadzi and coworkers[12] have reported a converse case viz. a decrease in the number of bands in the 3000-2000 cm^{-1} region on deuteration of carboxylic acids.

A characteristic band at about 3100 cm^{-1} found usually in amides has been explained by Miyazawa[13] to be due to Fermi resonance of the ν NH with the overtone of the amide II band in trans and due to the resonance of ν NH with a combination band of amide I and NH in plane deformation in cis form. Due to overlapping of the COOH group vibrations it is not possible to identify this band in our acids. However, such a band could not be found in alkali metal and complex salts.

The amide I band found in secondary amides in the 1630 - 1680 cm^{-1} region, is reported at a little lower frequency range (1600 - 1630 cm^{-1}) in α-amido acids. AGA absorbs at 1580 cm^{-1}, whereas in BGA and Br.BGA there are two bands each at 1600, 1626 and 1600, 1642 cm^{-1} respectively. Bellamy[14] has assigned the 1600 cm^{-1} band to amide I and the other (1628 cm^{-1}) to aromatic ring vibration in BGA. Accordingly, the 1642 cm^{-1} band of Br.BGA will have to be assigned to aromatic ring. Since the band at 1600 cm^{-1} is common in all the compounds (BGA, BGA-d_2, Br.BGA and Br.BGA-d_2), we prefer to reverse Bellamy's assignment and ascribe the 1600 cm^{-1} band to aromatic ring and the one at higher frequency to amide I. Since amide I band is very little affected by deuteration, it is evident that it is largely a pure ν C=O mode with very little contribution from δ NH mode. In anhydrous potassium salt this band is found at 1660 cm^{-1}.

It is well established by study of several amides like N-methyl formamide[15] and N-methyl acetamide[16], that amide II and amide III bands arise out of extensive coupling between C-N stretching and NH deformation modes. The shifts in these bands on deuteration would therefore depend upon the amount of such coupling in each case. In AGA, BGA and Br.BGA the bands at 1548, 1548 and 1560 cm^{-1} (amide II) and

1277, 1319 and 1323 cm^{-1}(amide III) are shifted to 1502, 1458, 1471 cm^{-1} (amide II) and 931, 966 and 972 cm^{-1}(amide III). The amide III band showed a shift corresponding to the theoretical ratio $\nu_H/\nu_D = 1/\sqrt{2}$ (= ~ 0.71) on deuteration whereas the amide II band was shifted only by about 5%, indicating that the former has predominently NH deformation character and the latter is largely a CH stretching mode. This supports the conclusions of Mizushima et al.[17] that amide II is largely a stretching mode rather than an NH deformation mode. It may, however, be mentioned that such a situation need not be present in all amides (see for example thioamides[18]).

COOH group

In table IV-2 the bands due to COOH and COOD groups of these acids along with the expected absorption region[12] for dimeric COOH/COOD groups are given. While the carboxylic acid group frequencies of Br.BGA are found entirely in the regions found by Hadzi and coworkers[12], in the case of AGA and BGA there is considerable shift in the positions of band due to OH out of plane vibration. BGA shows this band at 850 cm^{-1} while the expected dimer range is 900-950 cm^{-1}. In addition, smaller changes in ν C=O and ν C-O + δ OH vibrations are also found. Our assignment

TABLE IV - 2 : CARBOXYLIC ACID(COOH) GROUP FREQUENCIES(CM^{-1})

N-acetyl-glycine	Deutd. N-acetyl-glycine	N-benzoyl-glycine	Deutd. N-benzoyl-glycine	p-Bromo-N-benzoyl-glycine	Deutd. p-Bromo-N-benzoyl-glycine	COOH or COOD group	Assignment
2740 s vb		3044 s b 2941 m sh	3077 m b 2941 m	3069 m 2976 m b 2890 m b	3058 w b 2924 w b	3100- 2900	(OH) + (CH)
2415 m vb 2257 m sh		2700 w b 2600 w b 2475 w b		2660 m b 2554 m b 2525 w b		2700 2600 2500	Summation bands.
	2180 s b		2320 s b		2273 s b	2300	(OD)
	2079 m sh 1976 s b 1901 s vb		2037 m		2049 m	2100	Summation bands.
1720 vs	1720 vs	1751 s	1751 s	1712 vs	1710 vs		(C=O)
1355 vs		1399 m		1422 m		1420±20	(OH) + (C-O)
	1399 m		1385 m		1379 m	1350±50	(OD) + (C-O)
1277 s		1307 m		1319 m		1300±15	(OH) + (C-O)
	1092 s		1065 m		1047 m	1050±10	(OD) + (C-O)
1036 s		848 m b		926 m b		935±15	out of plane(OH)
	750 s b		675 m b		700 m b	675±25	out of plane(OD)
385 s b	385 s b	431 s b	429 s b	450 s b	450 s b		(C-O)

of 850 cm^{-1} band of BGA to δ OH out of plane is at variance with that indicated by Bellamy[14b], who ascribed 943 cm^{-1} to this mode which we find unaffected by deuteration.

The δ OH out of plane has been found susceptible to changes by hydrogen bonding and is one of the easiest to locate in the spectrum because of its broad profile. A linear relationship between δ OH and hydrogen bond length in a large number of carboxylic acids has been demonstrated by Fischmeister[19]. This analysis further showed that very long or very short hydrogen bonded carboxylic acid groups form chains rather than dimers in the solid state. A rather low value of δ OH is, therefore, indicative of weaker hydrogen bonding compared to the dimers. The considerably higher value (1750 cm^{-1}) of ν C=O in BGA is also in agreement with the above. The νOH of COOH group expected near 3000 cm^{-1} is not well defined in BGA due to overlapping with CH and CH_2 absorptions. However, if this is calculated from the observed OD band using ν OH/ νOD = 1.35 it amounts to 3130 cm^{-1} which is higher than generally expected for dimeric species thus supporting the above conclusions. The effect of hydrogen bonding on the carboxylic group frequencies has been well brought out by the study of Bellamy and Pace[20] on the α and β forms of oxalic acid having polymeric and dimeric forms respectively. The ν OH reported for the hydrogen bonded polymeric form at 3114 cm^{-1}, the νC=O at 1756 and δ OH out of plane at 891 cm^{-1} are comparable with the bands observed for BGA.

The existence of strong hydrogen bonding between carboxylic OH and the amide C=O present in AGA gave rise to νOH at $\sim$ 2740 cm^{-1}. The corresponding δOH out of plane is not easily located probably due to strong coupling between the carboxyl, acetyl and amide groups. However, a band at 1036 cm^{-1} which shifted to 750 cm^{-1} on deuteration, may be attributed to this vibrational mode, in view of the O-H---O distance of 2.56 Å. These results show that the carboxyl group in BGA are held by weak hydrogen bonding probably as chains rather than cyclic dimers.

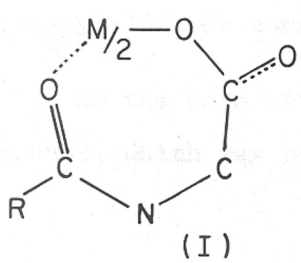
Preliminary x-ray investigation by Jose and Pant[21] is in general agreement with the above results. BGA crystallizes in orthorhombic system space group $P2_1\ 2_1\ 2_1$ with four molecules in a unit cell of dimensions a = 9.2Å, b = 10.6Å, c = 8.9Å. Para-Bromo-N-benzoylglycine belongs to a monoclinic system, space group $P2_{1/a}$ with four molecules in a unti cell of dimensions a = 40.0Å, b = 5.2Å, c = 4.9Å, β = 94°. While the long (100) spacing with approximately four times the expected molecular length and a centre of symmetry might suggest dimer formation in Br.BGA, it is unlikely in the non-centro-symmetric crystal of BGA.

The CH_2-COOH group is reported[22] to give rise to strong band near 1200 cm^{-1} in a large number of long-chain acids, which involves largely a CH_2 wagging mode and hence is not appreciably

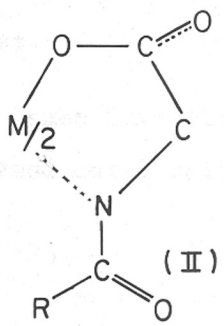
shifted on deuteration. The only band in this region at 1187 cm^{-1} in BGA and 1240 cm^{-1} in Br.BGA is, however, found to shift partially or fully on deuteration to higher frequencies (1240 and 1270 cm^{-1}) respectively. In a series of N-acetylamino acids, Mecke and Mecke[18] have observed two bands at about 1230 and 1270 cm^{-1} which were ascribed to CH_3CO vibrations. The possibility of deuteration of the CH_2 group was ruled out from the NMR spectrum of the deuterated sample. We have found that the band at 1230 cm^{-1} of AGA is shifted on deuteration to higher frequency (1265 cm^{-1}), suggesting that it is a coupled vibration. These results show the limited utility of the band near 1200 cm^{-1} to indicate the presence of CH_2-COOH group in this type of compounds.

II SPECTRA OF COMPLEXES

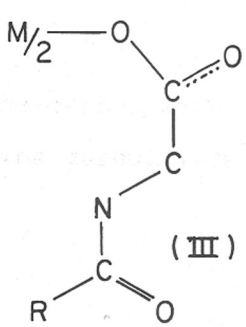
In the metal complexes of amido acid ligands, there are two types of structures possible. One involving coordination of amide as well as carboxylate groups (I and II) and the other involving linkage to only carboxylate group(III).



(I)



(II)



(III)

In the former type, the amide coordination may be either through the nitrogen(II) or oxygen(I) atom. The amide group frequencies would in this case be perturbed showing appreciable shifts in their vibrational frequencies. It has been observed in some metal-urea complexes that the nitrogen coordination results in lowering of νNH_2(at least one band) and an increase in $\nu C{=}O$ frequency (1720 cm^{-1}), compared to the value of 1680 cm^{-1} in urea itself. In the case of N-methyl acetamide complexes of Cd(II) chloride only the NH out of plane deformation has been found to be shifted on coordination, the $\nu C{=}O$ frequency being found in the same place as in the liquid ligand. Coordination to nitrogen was suggested for this complex. Gerrad et al.[10] pointed out that for postulating coordination it is necessary to compare the bands in the complex with that of the ligand in the vapour phase or in dilute solutions since the amides are highly associated in condensed states. They therefore believe that in the Cd(II) chloride N-methyl acetamide complex, the coordination is through oxygen and not through nitrogen. Coordination through oxygen should result in decrease in $\nu C{=}O$ frequency similar to that observed by Bellamy and Branch[23] in salicylaldehyde complexes.

In the case of complexes involving only the carboxylate groups, which may be termed metal salts, only the carboxylate

group frequencies would be affected and these have been well-established.

Copper(II) N-benzoylglycinate

The infrared spectra of the tetrahydrate, tetradeuterate, anhydrous products with NH as well as ND amide groups are illustrated in figure IV-3. The absorption frequencies due to amide and carboxylate groups are listed in table IV-3.

Anhydrous Cu(II) N-benzoylglycinate shows two νNH frequencies (3409 and 3354 cm^{-1}) which are not very different from those observed in N-benzoylglycine and its potassium salt (3390 cm^{-1}). The νC=O frequency (amide I band) is also very little changed and has a value 1667 cm^{-1}, which is comparable with that of potassium salt (1670 cm^{-1}). These observations, along with the COO^- group vibrations observed in this compound lead us to conclude that the CONH group is not coordinating to the metal ion and that this compound has a simple salt-like structure. As pointed out earlier, conclusions about coordination based on the comparison of the C=O frequencies in amide complexes with those of the ligands are not valid unless it is made with the values obtained in the vapour state or in dilute solutions. Since potassium salt is not likely to be associated as the free ligand the comparison is believed to be quite reasonable though the free amide I band is indeed reported[10] as high as 1720 cm^{-1}.

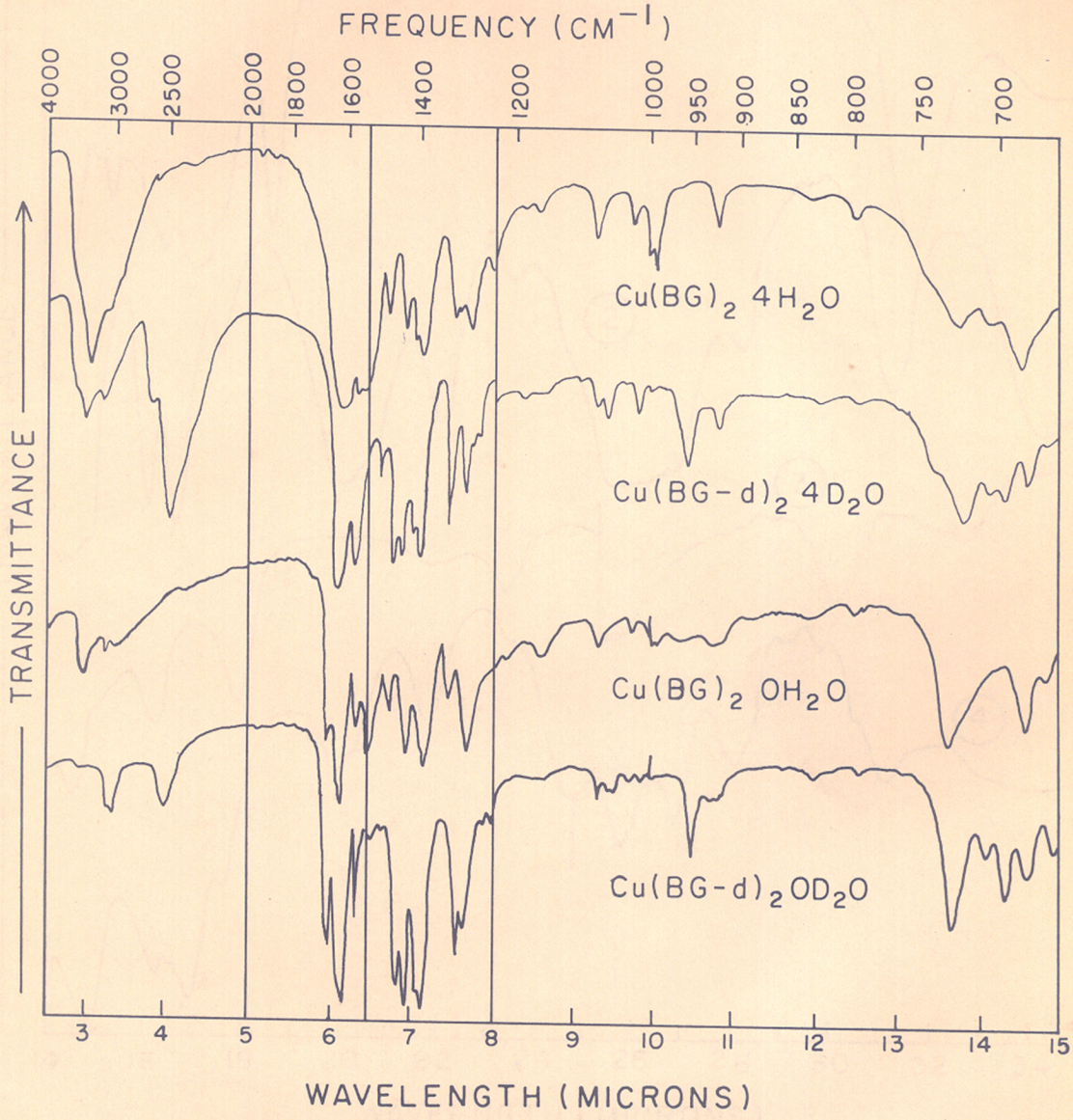


Fig. IV – 3

Copper (II) N-benzoylglycinates.

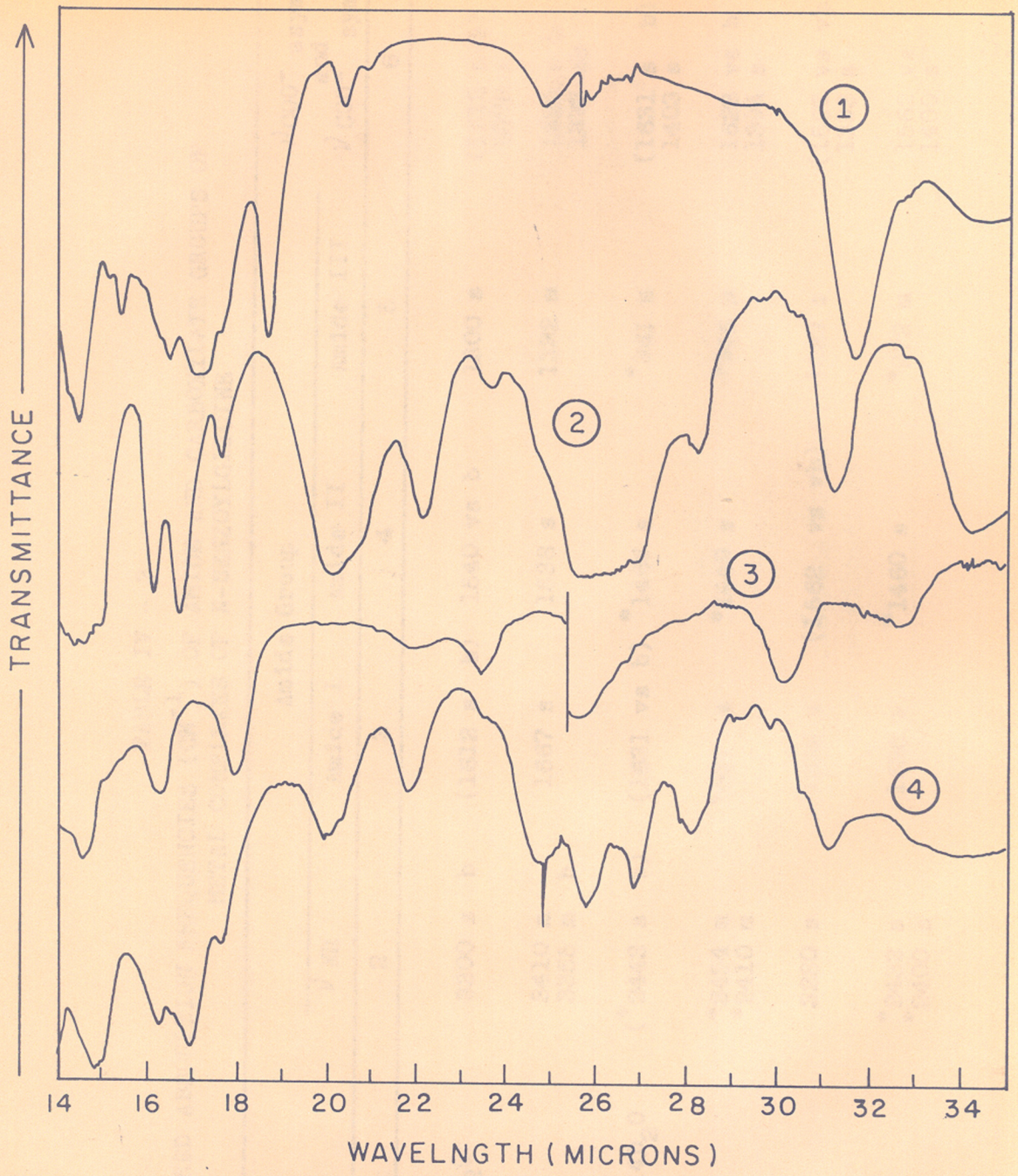


Fig. IV-4

1. Potassium N-benzoylglycinate, KB
2. Deutd copper (II) N-benzoylglycinate, $Cu(BG-d_1)_2$
3. Copper (II) N-benzoylglycinate tetrahydrate, $Cu(BG)_2 \cdot 4H_2O$
4. Copper (II) N-benzoylglycinate, $Cu(BG)_2$

TABLE IV - 3

INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF AMIDE AND CARBOXYLATE GROUPS OF METAL COMPLEXES OF N-BENZOYLGLYCINE

Compound	Amide Group				ν_{COO^-} asym. and ν_{COO^-} sym.
	ν NH	Amide I	Amide II	Amide III	
1	2	3	4	5	6
$Cu(BG)_2 \cdot 4H_2O$	3300 s b	(1612 s b)	1540 vs b	1300 s	(1612 s b) 1395 s
$Cu(BG)_2$	3410 m 3355 m b	1667 s	1538 s	1332 m	1623 s b 1395 sh
$Cu(BG\text{-}d_1)_2 \cdot 4D_2O$	(*2443 s b)	(1631 vs b)	*1466 s	*961 m	(1631 s b) 1403 s
$Cu(BG\text{-}d_1)_2$	*2454 m *2410 m	1667 s	*1449 s	*946 m	1623 vs b 1394 s
$Zn(BG)_2$	3280 s	1635 s	(1562 vs vb)	1329 s	(1562 vs vb) 1393 s
$Zn(BG\text{-}d_1)_2$	*2433 s *2400 s	1635 s	*1460 s	*972 m	1562 vs 1400 s

Table IV - 3 (continued)

1	2	3	4	5	6
$Co(BG)_2 4H_2O$	(3300 s b)	(1590 s b)	1538	1330 m	(1590 s b) 1400 s
$Co(BG\text{-}d_1)_2 \cdot 4D_2O$	(2450 vs vb)	1637 s	*1460 s	*958 m	1575 s 1400 s
$Mn(BG)_2 \cdot 4H_2O$	(3350 s b)	(1625 s b)	1570 s sh	1340 m	1600 s b 1390 s
Mn(BG-d) 4D O	(*2470 s b)	1635 s b	*1465 s	*965 m	1605 s b 1395 s
$Ni(BG)_2 \cdot 4H$ O	(3300 s b)	(1590 s b)	1538 s	1330 m	(1590 s) 1400 s
$Ni(BG\text{-}d_1)_2 \cdot 4D$ O	(*2450 s b)	1640 s	*1465 s	*960 m	1590 s 1410 s
K(BG)	3390 s	1670 s	1530 s	1333 s	1637 vs 1400 s
K(B-d)	*2450 s	1670 s	*1470 s	*950 s	1637 vs b 1400 s

Figures in parantheses indicate overlapping of bands.
* Indicates the corresponding deuterium vibrations.

The spectrum of Cu(II) N-benzoylglycinate tetrahydrate which can be obtained by crystallizing the anhydrous product from water is quite different from that of the anhydrous compound. It it interesting to note that tetrahydrate and tetradeuterate shows a single broad peak at 1612 and 1631 cm^{-1} respectively, while the anhydrous compound shows two well-resolved bands at 1667 and 1623 cm^{-1}. The water or D_2O seems to have combined both the bands and formed a broad band due to hydrogen bonding in the tetrahydrate or tetradeuterate.

Zn(II) N-benzoylglycinate

Anhydrous compound shows νNH at 3280 cm^{-1}. While the lowering of this frequency might be interpreted as coordination through nitrogen, the lowering of ν C=O to 1635 cm^{-1} cannot be understood, as coordination on amide nitrogen has been found, in many and indeed in most cases, to result in an increase in the ν C=O value. The lowering of both NH and C=O stretching modes can be explained in terms of hydrogen bonding between C=O and NH of two adjacent molecules and the coordination through amide oxygen. It should be noted that in the case of carboxylic acids, the monomer band due to νOH is ~ 3550 cm^{-1} against 3100-2900 cm^{-1} for the bonded dimer[14]. The corresponding shifts in νC=O are,

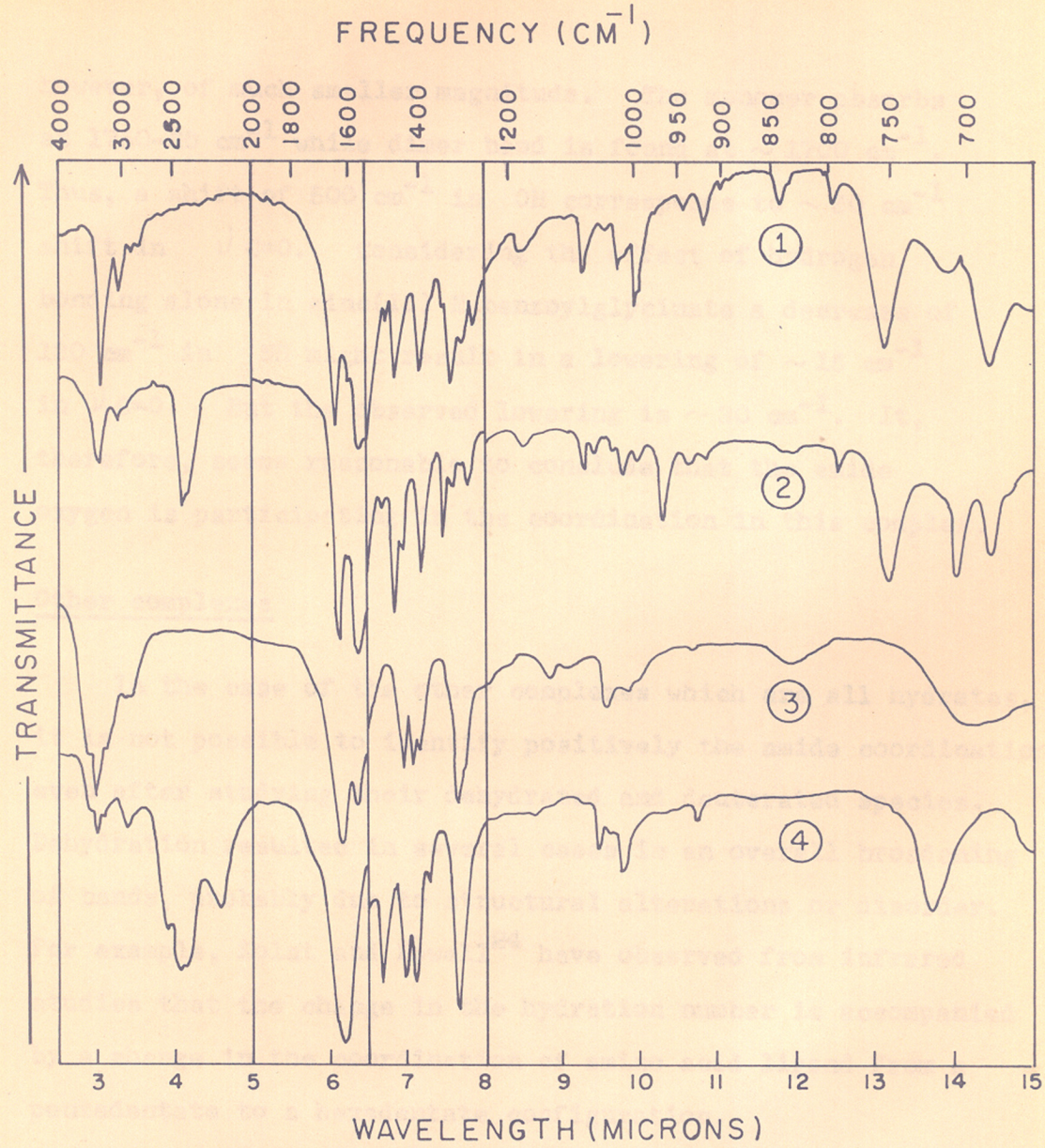


Fig. IV-5

1. Zn(II) N-benzoylglycinate, $Zn(BG)_2$
2. Deutd Zn(II) N-benzoylglycinate, $Zn(BG-d_1)_2$
3. Cu(II) N-acetylglycinate tetrahydrate, $Cu(AG)_2-4H_2O$
4. Cu(II) N-acetylglycinate tetradeuterate, $Cu(AG-d_1)_2-4D_2O$

however, of much smaller magnitude. The monomer absorbs at 1750-60 cm^{-1} while dimer band is found at $\sim$ 1700 cm^{-1}. Thus, a shift of 500 cm^{-1} in OH corresponds to $\sim$ 50 cm^{-1} shift in ν C=O. Considering the effect of hydrogen bonding alone in zinc(II) N-benzoylglycinate a decrease of 130 cm^{-1} in NH might result in a lowering of $\sim$ 15 cm^{-1} in ν C=O. But the observed lowering is $\sim$ 30 cm^{-1}. It, therefore, seems reasonable to conclude that the amide oxygen is participating in the coordination in this complex.

Other complexes

In the case of the other complexes which are all hydrates, it is not possible to identify positively the amide coordination even after studying their dehydrated and deuterated species. Dehydration resulted in several cases in an overall broadening of bands, probably due to structural alterations or disorder. For example, Kolat and Powell[24] have observed from infrared studies that the change in the hydration number is accompanied by a change in the coordination of amino acid ligand from a pentadentate to a hexadentate configuration.

In these complexes the NH and C=O stretching bands are not clearly seen due to the overlapping water bands. The ν C=O bands (in deuterated compounds also) in these complexes are found at $\sim$ 1615 cm^{-1}, overlapped with ν_{COO^-}(asym.) which is

TABLE IV - 4

INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF AMIDE AND CARBOXYLATE GROUPS OF METAL COMPLEXES OF N-ACETYLGLYCINE

Compound	Amide Group				ν_{COO^-} asym. ν_{COO^-} sym.
	~~ν~~ NH	Amide I	Amide II	Amide III	
1	2	3	4	5	6
$Cu(AG)_2 \cdot 4H_2O$	(3300 s b)	(1613 vs b)	(1565 s b)	1279 s sh	(1613 vs b) 1400 s b
$Cu(AG\text{-}d)_2 \cdot 4D_2O$	(*2440 s b)	1613 vs	*1493	1022 m b	1613 vs b 1400 s b
$Co(AG)_2 \cdot 4H_2O$	(3305 s b)	(1639 vs b)	(1556 vs b)	1327 s	(1556 vs b) 1400 s b
$Co(AG\text{-}d)_2 \cdot 4D_2O$	(*2420 s b)	1630 vs b)	*1471 vs b	*1010 s	1565 s b 1410 s b
$Ni(AG)_2 \cdot 4H_2O$	(3300 vs b)	(1640 s b)	(1550 vs b	1315 s	(1550 vs b) 1400 s b
$Ni(AG\text{-}d)_2 \cdot 4D_2O$	(*2400 s b)	1640 s b	*1470 vs b	*1015 s	1565 vs b 1405 s b

Table IV - 4 (continued)

1	2	3	4	5	6
$Mn(AG)_2 \cdot 4H_2O$	(3350 vs b)	(1635 s b)	(1570 s vb)	1310 s	(1570 s vb) 1412 s b
$Mn(AG\text{-}d)_2 4D_2O$	(*2420 s vb)	1640 s b	*1465 s b	*1005 s	1570 s b 1412 s b
Li(AG)	3226 s	1653 s	1577 s b	1294 s	1613 s b 1414 s b
Li(AG-d)	*2465 s b	1653 s	*1465 s b	*995 m	1600 s b 1414 s b
Acetanilide	3310 s	1670 s	1557 s	1266 m	
Acetanilide-d_1	*2420 s *2380 s sh	1670 s	*1404 s	*935 m	

Figures in parantheses indicate overlapping of bands.
* Indicates the corresponding deuterium vibrations.

close to the value for copper(II) N-benzoylglycinate tetrahydrate. While ruling out coordination through nitrogen in these complexes, since the NH stretching vibrations are not affected, coordination through oxygen could not be established definitely. Jain and Rivest[25] have recently reported spectra of a few complexes of group IV halides with α-cyanoacetamide ($NC.CH_2CONH_2$). While coordination through cyano(NC) group is evident from the frequency increase of ν C≡N vibration, no definite conclusions could be drawn by them regarding bonding centres in amide ($CONH_2$) group.

Summing up, it can be mentioned that copper(II) N-benzoylglycinate has a simple salt-like structure without amide coordination. The difference in the spectrum of anhydrous and tetrahydrate forms is attributed to hydrogen bonding. Zn(II) N-benzoylglycinato appears to have coordination through amide oxygen in addition to the carboxylate group. It is not possible to establish the bonding through amide group in the remaining ten compounds studied because of presence of strongly held water molecules, removal of which resulted in rather drastic changes in their structures.

REFERENCES

1. Randall, H. M., Fowler, R. G., Fuson, N. and Dangl, R., "Infrared determination of organic structures", Van Nostrand, 1949 (Chapter II).

2. Fuson, N., Josien, M. L. and Powell, R. L., J. Amer. Chem. Soc., 74, 1 (1952).

3. Micheel, F. and Schleppinghoff, B., Chem. Ber., 88, 763 (1955).

4. Newman, R. and Badger, R. M., J. Chem. Phys., 19, 1147 (1952).

5. a: Carpenter, G.B. and Donohue, J., J. Amer. Chem.Soc., 72, 2315 (1950).

   b: Donohue, J. and Marsh, R. E., Acta Cryst., 15, 941 (1962).

6. Nakamoto, K., "Infrared spectra of inorganic coordination compounds", John Willey and Sons Inc., New York (1963).

7. Penland, R. B., Mizushima, S., Curran, C. and Quagliano, J.V., J. Amer. Chem.Soc., 79, 1575 (1957).

8. Antonenko, N. S. and Nuger, Ya., A., Zh. Neorgan. Khim., 11, 1072 (1966). Chem. Abst., 65, 6517 (1966).

9. Martinnette, Sr. M., Mizushima, S. I. and Quagliano, J.V., Spectrochim. Acta., 15, 71 (1959).

10. Gerrad, W., Lappert, M.F., Pyszora, H. and Willis, J.W., J. Chem. Soc., 2144 (1960).

11. Fitsche, H., Spectrochim. Acta., 22, 1139 (1966).

12. a: Hadzi, D. and Sheppard, N., Proc. Royal Soc., A-216, 247 (1954).

    b: Hadzi, D., Bratoz, S. and Sheppard N., Spectrochim. Acta., 8, 249 (1956).

13. Miyazawa, T.,
J. Mol. Spectroscopy, 4, 168 (1960).

14. Bellamy, L. J.,
"The infrared spectra of complex molecules"
Methuen and Co., London (1958 Edn.).

a: pp. 203-247.

b: pp. 289.

c: pp. 161-177.

15. Suzuki, I.,
Bull. Chem. Soc., Japan, 35, 540 (1962).

16. Davies, M., Evans, J.C. and Jones, R. L.,
Trans. Faraday Soc., 51, 761 (1955).

17. Mizishima, S. I., Miyazawa, T. and Shimonouchi, T.,
J. Chem., Phy., 24, 408 (1956).

18. Mecke, R. Jr. and Mecke, R. Sr.,
Chem. Ber., 89, 343 (1956).

19. Fischmeister, I.,
Spectrochim. Acta., 20, 1071 (1964).

20. Bellamy, L. J. and Pace, R. J.,
Spectrochim. Acta., 19, 435 (1963).

21. Jose, P. and Pant, L. M. - Unpublished results.

22. Shimanouchi, T., Tsuboi, M., Takenishi, T. and
Iwata, N.,
Spectrochim. Acta., 16, 1328 (1960).

23. Bellamy, L. J. and Branch, R. F.,
J. Chem. Soc., 4489 (1954).

24. Kolat, R. S. and Powell, J. E.,
Inorg. Chem., 1, 485 (1962).

25. Jain, S. C. and Rivest, R.,
Can. J. Chem., 45, 139 (1967).

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CHAPTER - V

INFRARED SPECTRA OF SOME AMINO ACIDS AND THEIR COMPLEXES

INTRODUCTION

The amino acids are in general rather insoluble in all non-polar solvents and are relatively far more soluble in salt solutions. When dissolved in water they give solutions of dielectric constants much higher than that of water itself, whereas almost all polar molecules dissolved in water, decrease the dielectric constant. Their similarity to true ions had led to their being termed as dipolar or zwitter ions.

X-ray crystallography is one of the major techniques used to determine the presence of such zwitterion structure since such a structure gives a nearly tetrahedral arrangement of bonds around nitrogen and nearly equal C-O distances as illustrated by Jose[1]. Because of the involved and time consuming nature of this technique detailed structure determination of several amino acids have not been carried out.

Infrared spectroscopic technique proves to be a powerful tool to differentiate the normal and zwitterion forms since the presence of $\overset{+}{N}H_3$ and COO^- groups in the latter, instead of

NH_2 and COOH of the former gives rise to differing vibrational modes[2]. In view of this, several studies have been reported describing the vibrational mode assignments of different amino acids. Of these complete assignment of glycine[3] and alanine[4] require a special mention here. However, as seen from the recent review of such studies and subsequent publications, it is evident that there still remain several unconfirmed assignments e.g. bands arising in the 3000-2000 cm^{-1} region. Phenyl alanine is an important amino acid which is found in many proteins. Despite its importance very little attention has been paid to study its spectrochemical properties. This led us to investigate the spectrum of Dl-β-phenylalanine (PHA) along with its several related compounds.

Infrared spectral studies of metal complexes of amino acids have been a subject of interest to many workers. Special credit goes to the Notre Dame group, who have carried out several detailed studies of metal complexes of glycine[6], isoleucine[7], valine[8], etc. Cotton[9] has pointed out the difficulties in the interpretation of the results of such studies and has particularly emphasised the influence of several factors such as hydrogen bonding and crystal field effect. In view of these, we have attempted a more cautious interpretation of the observed bands of several first row transition metal complexes of DL-β-phenylalanine, which have been reported in the following.

RESULTS AND DISCUSSION

Assignment of DL- β-phenylalanine

In order to assign the bands due to PHA, the spectra of PHA-d_3, PHA.HCL, PHA-d_3-DCL have been studied. These spectra are shown in figure V-1, while their absorption bands along with the assignments thereof are listed in table V-1.

$\overset{+}{N}H_3$ group

Region 4000-2000 cm^{-1} : PHA shows a broad absorption pattern around 3000 cm^{-1}. These bands are generally attributed to asymmetric and symmetric $\overset{+}{N}H_3$ stretching modes, though the origin of the broadness is not clear. These broad band as well as some bands in the region 2900-2600 cm^{-1} are replaced quantitatively on deuteration in the present case. Most amino acids show absorption of medium to strong intensity in this region and there exists some controversy regarding the origin of these bands. In sulfamic acid[10] these have been explained in terms of Fermi resonance between the NH stretching and the overtone and combination bands involving $\overset{+}{N}H_3$ deformation and skeletal modes. In glycine and its derivatives, these are said to originate from the NH stretching modes of the various N-H...O hydrogen bonds[11]. In our opinion these bands in the present compounds are due to the reasons similar to those in the case of sulfamic acid.

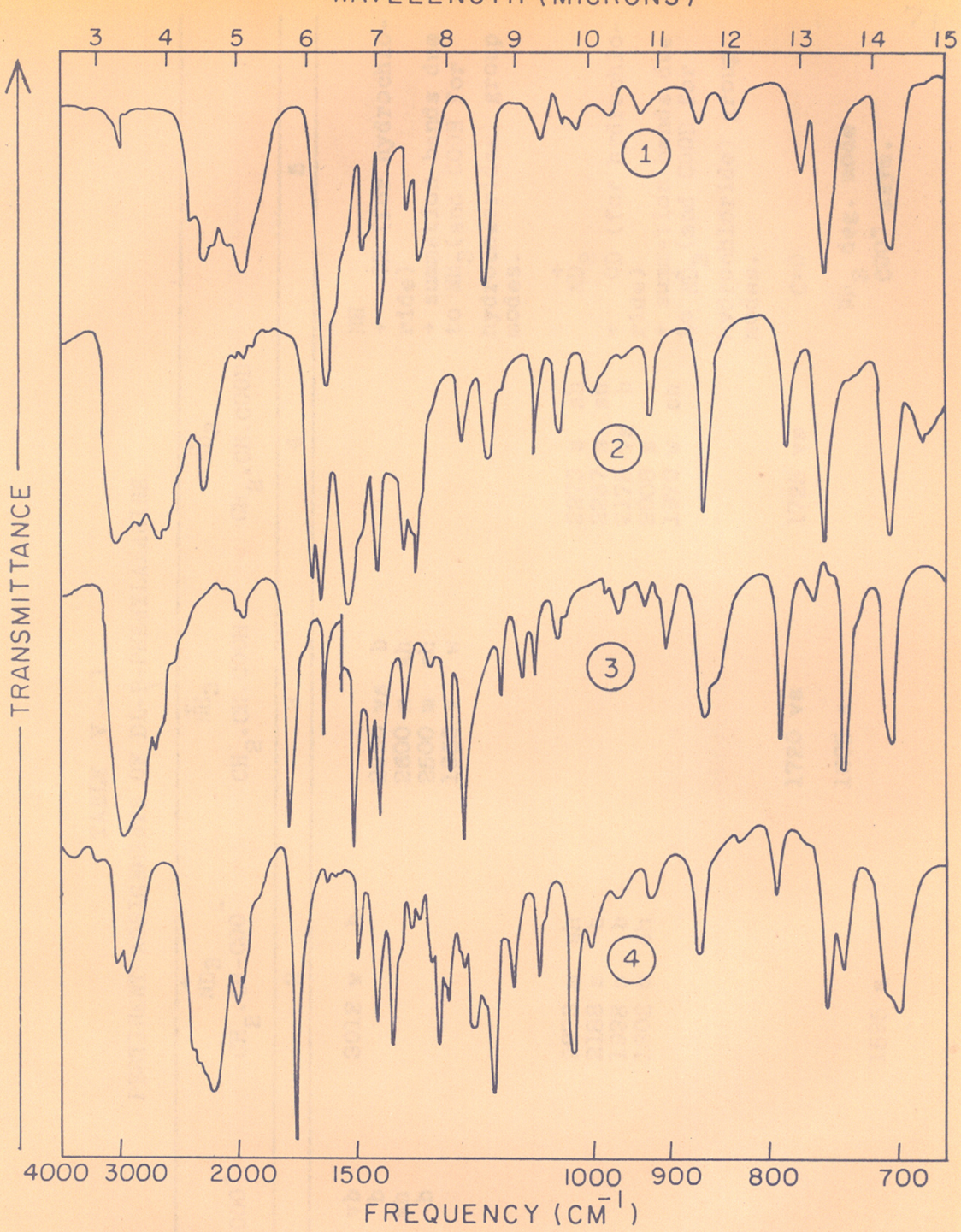

Fig. V - 1

1. Deutd DL - β Phenylalanine, PHA - d_3
2. DL - β Phenylalanine, PHA
3. DL - β Phenylalanine Hydrochloride, PHA. HCl
4. Deutd Hydrochloride, (PHA - d_3) DCl

TABLE V - 1

PERTINENT ASSIGNMENTS OF DL-β-PHENYLALANINE

$\overset{+}{N}H_3$ $CH_2.CH\text{-}COO^-$	$\overset{+}{N}D_3$ $CH_2.CH\text{-}COO^-$	$\overset{+}{N}H_3$ $CH_2.CH.COOH$	$\overset{+}{N}D_3$ $CH_2.CH.COOD$	
1	2	3	4	5
3077 s vb 2941 s b 2732 s sh 2532 s b 2175 m	3012 w b	2900 vs b 2600 m sh 2500 m sh 1960 v w		NH + OH (for hydrochloride) + summation bands due to NH_3 (and COOH for hydrochlorides) group modes.
	2273 m sh 2188 s b 1938 s b 1802 m sh		2273 s sh 2257 s sh 2178 vs b 2008 s 1970 w sh	$\overset{+}{N}D_3$ + OD (for hydrochloride) + summation bands due to $\overset{+}{N}D_3$ (and COOD for hydrochloride) group modes.
		1720 vs	1725 vs	C=O
1635 s 1595 s	1595 s	1605 s		$\overset{+}{N}H_3$ deg. mode COO^- asym.

Table V - 1 (continued)

1	2	3	4	5
1505 s		1498 s		NH_3^+ sym. mode.
		1455		C-O + OH
1325 m	1325			COO sym.
			1385	C-O + OD in plane.
		1358 s		C-O + OH in plane.
1216 m		1200 s		NH_3^+
	1166 s		1152 s	ND_3^+ deg. mode.
1162 m 1135 w sh				
	1020 m		1070	ND_3 sym. mode.
			1028 s	C-O + OD in plane.
	858 w	860 m	828 w	ND_3
		849 m b		OH out of plane.
853 s	823 m b			NH_3^+ wagging.
			699 s b	OD out of plane.
521 vs	516 vs			COO^-
		515 s	500 s	C=O

Many amino acids are known to show an additional absorption band in the 2140-2080 cm^{-1} region. A reasonable assignment of this band has so far not been made. Phenylalanine shows a sharp medium band at 2175 cm^{-1} which disappears on deuteration. The corresponding deuterium vibration is found to overlap with 1585 cm^{-1} band. It is reasonable to conclude that this is a summation band, the intensity of which is enhanced by Fermi resonance with 3000-2500 cm^{-1} band.

The situation in hydrochlorides is much more complicated by the presence of additional bands in the 3100-2300 cm^{-1} region due to the COOH group. The strong broad pattern with several submaxima in the hydrochloride which are totally replaced on deuteration by an identical pattern in the 2300-1950 cm^{-1} region contains ν_{NH^+} vibrations, ν_{OH} mode and summation bands. The hydrochlorides show an additional band (weak) near 2000 cm^{-1}. This may be attributed to the summation band of NH_3^+ and COOH group vibrational frequencies.

Region 2000-1000 cm^{-1} : In addition to the ν_{COO^-} vibration, amino acids have two characteristic bands in the 1610-1450 cm^{-1} region. The band at higher frequency is attributable to assymetric NH_3^+ deformation while the one at lower frequency is assignable to symmetrical mode. Deuterated phenylalanine shows the ND_3^+ mode at 1166 cm^{-1}. In the hydrochloride two bands (1605 and 1498 cm^{-1}) found to move to

1152 and 1070 cm^{-1} on deuteration, are also due to similar modes.

The band at 1216 cm^{-1} in the acid and 1200 cm^{-1} in the hydrochloride are also affected by deuteration. They are assigned to the $\overset{+}{N}H_3$ rocking vibrations. However, on deuteration no band of comparable intensity appears, although new weak bands at 1020 and 1010 cm^{-1} appear in the deuterated acid and its hydrochloride respectively. Similar changes in intensity on deuterium substitution have been reported by Gopal et al.[12] in m-aminobenzoic acid.

Region below 1000 cm^{-1}: Not much information is available on the bands of amino acids appearing below 1000 cm^{-1}. In many a band at $\sim$ 800 cm^{-1} has been observed. Since it is found that the 858 cm^{-1} band of the acid and 789 cm^{-1} one of the hydrochloride are shifted on deuteration, these may reasonably be assigned to $\overset{+}{N}H_3$ wagging mode.

COOH group

The vibrations due to this group are not found in the acid but are present in the hydrochloride only. These vibrational modes are found at $\sim$ 3000, 2500, 1455, 1358, 850 cm^{-1} and those for COOD at $\sim$ 2200, 2050, 1385, 1028 and 699 cm^{-1}. Their assignments are grouped in table V-1.

It is, however, interesting to note that the OH out of plane deformation mode is found at a lower frequency (850 cm^{-1}) whereas the normal dimeric acids absorb in 950-900 cm^{-1}.

Similar lowering has been reported for glycine hydrochloride and alanine hydrochloride[5]. This lowering is considered to be due to the interaction of the HCl group with cyclic dimer. It may, however, be pointed out that several compounds with non-dimeric structure like that of oxalic acid dihydrate[13] absorb at about this frequency.

Spectra of complexes

Since it is well-established that when an amino acid forms a transition metal complex, $\overset{+}{N}H_3$ changes to NH_2 due to the loss of one proton, as in the case of alkali metal salt. Hence the effect of coordination on NH_2 and COO^- groups will be discussed.

NH_2 stretching vibrations

The NH_2 group is known to give rise to two vibrational frequencies in the 3500-3200 cm^{-1} region. The higher band is attributed to the assymetric NH stretching mode while the lower one is due to the symmetric mode. However, more than two bands have indeed been found in a number of amino complexes of the type $M(L)_2$. Springer and Curran[14] mention that in the case of metal(II) halide complexes of ethyl and methyl glycinates a third band of relatively weak intensity is found in the 3 micron region. This band is considered to be the overtone of the δ NH_2 band, the intensity of which is enhanced and frequently lowered by Fermi resonance. The absorption

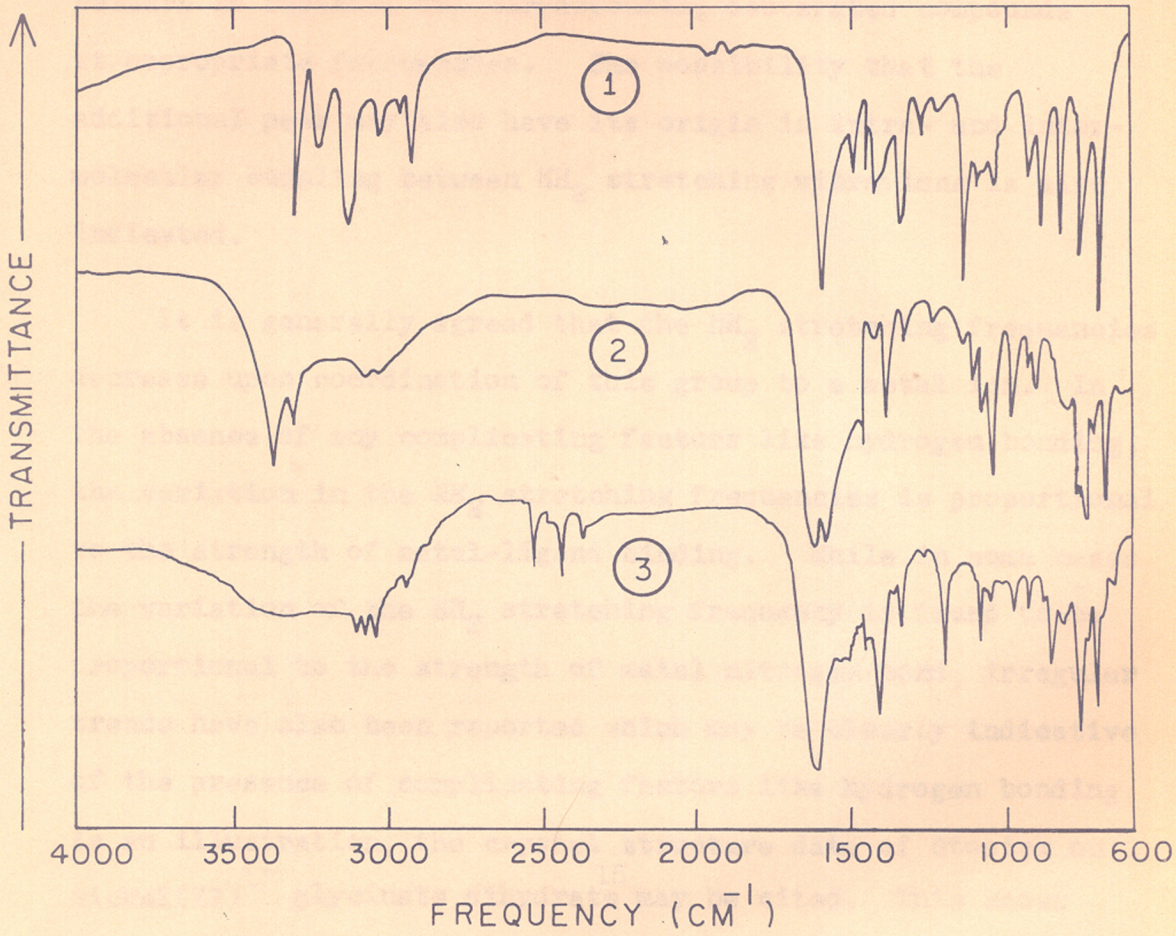

Fig. V – 2

1. Copper (II) Phenylalaninate (anhydrous), $Cu(PH)_2$
2. Cobalt (II) Phenylalaninate, $Co(PH)_2$
3. Deutd. Cobalt (II) Phenylalaninate $Co(PH-d_2)_2$

pattern is repeated for corresponding deuterated compounds at appropriate frequencies. The possibility that the additional peak may also have its origin in intra- and intermolecular coupling between NH_2 stretching vibrations is also indicated.

It is generally agreed that the NH_2 stretching frequencies decrease upon coordination of this group to a metal ion. In the absence of any complicating factors like hydrogen bonding, the variation in the NH_2 stretching frequencies is proportional to the strength of metal-ligand binding. While in some cases the variation of the NH_2 stretching frequency is found to be proportional to the strength of metal nitrogen bond, irregular trends have also been reported which may be clearly indicative of the presence of complicating factors like hydrogen bonding. As an illustration, the crystal structure data of Stosick on nickel(II) glycinate dihydrate[15] may be cited. This shows that all amino hydrogens are involved in fairly strong hydrogen bonds and that the uncoordinated carboxyl oxygen atoms are linked by fairly strong hydrogen bonds to water molecules and NH_2 groups of the adjacent molecules.

Summing up, it appears that when the hydrogen bonding is strong the correlation would be affected. Whether such effects are operative in a given case or not would depend on the structure of the complex in the solid state.

As seen from table V-2, sodium salt absorbs at 3350 cm^{-1} with a shoulder at higher frequency side (3400 cm^{-1}). Methyl ester of phenylalanine is reported[16] to absorb at 3370 and 3290 cm^{-1} due to assymetric and symmetric stretching modes of NH_2. Copper(II) salt shows maximum shifts, indicative of strongest bonding in this compound.

Our results are comparable to those by Sen et al.[16] on metal glycinato complexes. The sodium salt is indeed found to absorb at a lower frequency than that of zinc(II) complex. It is known that there are no solid state effects which would raise the frequency of stretching vibration. The most plausible explanation for the observed facts would therefore be that in the sodium salt (and also in the methyl ester) hydrogen bonding is much stronger nature than in the transition metal salts.

NH_2 deformation

It has been found that in general there is lowering in the frequency of this band upon coordination to a metal ion. Such is the case with several anthranilate complexes[18]. The utility of this band is indeed not considerable because of relatively smaller shifts upon changes in the metal ion and also because of its "crowded" location (1600-1500 cm^{-1}) where

TABLE V- 2

AMINO AND CARBOXYLATE GROUP FREQUENCIES OF METAL COMPLEXES OF DL-β-PHENYLALANINE

Compound	ν NH_2 asym. sym.	δ NH_2 asym. sym.	NH_2 wagging	NH_2 rocking	ν_{COO^-} asym. sym.
$Mn(PH)_2$	3330 s b	(1600 vs b)	1090 m b	780 s	(1600 s vb) 1400 s b
$Co(PH)_2$	3360 s 3298 s	1582 s	1102 m 1052 s	769 s	1620 vs b 1398 s
$Co(PH\text{-}d)_2$	*2500 s *2412 m *2320 m b	*1180 s	*845 m		1612 vs b 1398 s
$Ni(PH)_2$	3360 s 3300 s	1590 s	1110 m 1070 s	774 s	1630 vs b 1400 s
$Cu(PH)_2$	3290 s 3220 s b 3122 s	1580 vs b	1125 s 1088 s	828 s	1580 vs b 1400 s
$Cu(PH\text{-}d)_2$	*2435 s *2390 s b *2260 s	*1185 s	860 m		1585 vs b 1400 s b
$Zn(PH)_2$	3350 s 3290 s	1580 s b	1102 m 1062 m	838 s	1635 s b 1400 s b

* Indicates corresponding deuterium vibrations.

Figures in parentheses indicate overlapping bands.

several overlapping bands like those due to νCOO^- asym., H_2O, aromatic ring vibration are likely to be present. Although the "location" problem can, to some extent, be simplified by deuteration, no diagnostic importance has been found.

In our series of complexes bands due to aromatic ring, antisymmetric COO^- vibration are expected near 1600 cm^{-1} in addition to NH_2 deformation band. It has not been possible to resolve this band from the remaining, but the corresponding ND_2 vibration has been located near 1180 cm^{-1}.

NH_2 wagging

This vibrational mode also appears to be affected by coordination to a metal ion. In the metal halide complexes of aniline, of the type $MX_2(aniline)_2$, Jungbauer and Curran[19] have observed appreciable enhancement of intensity and large spread in their frequencies. It may be mentioned that although the frequencies are found to vary from 1010 cm^{-1} in Mn(II) complex to 1100 cm^{-1} in cobalt(II) complex, the variation is not found to vary regularly with the strength of metal-nitrogen bond. However, it may at times be difficult, as in the case of complexes of metal halides with methyl and ethyl esters of glycine, to identify these bands.

The complexes studied by us show two bands which may be attributed to this mode. Of these, the low frequency band is

found at 1088 cm^{-1} in copper(II) complex and at 1052 cm^{-1} in cobalt(II) complex. Mn(II) shows only the one band (at about 1080 cm^{-1}) instead of doublet. With the exception of Mn(II) (where bands are not split) the variation in frequency of the lower band (see table VI-2) varies uniformly with the strength of the metal-nitrogen bond.

NH_2 rocking

In contrast to the NH_2 stretching and scissoring modes which decrease in their frequencies in a manner which may correspond to the strength of the metal-nitrogen bond, NH_2 rocking mode has indeed been found to increase in frequency with the strength of M-N bond. Such behaviour has been reported by Nakagawa et al.[8] in metal valine chelates and by Springer and Curran[13] in metal(II) halide complexes of esters of glycine. The latter group of investigators have observed the isotopic substitution ratio of 1.24 - 1.27.

Although variation in frequency is observed as the metal ion is changed, no definite trend of such variation is evident in our series of compounds.

From the foregoing discussion of the amino acid complexes following conclusions may be drawn.

DL- β-phenylalanine forms with first row transition metal ions chelates giving a five membered ring structure. The NH_2 frequency shift is maximum in copper(II) complex indicative

of maximum stability or strength of hydrogen bonding. In all other metal complexes NH_2 bands are found at nearly the same value (~3360, 3300 cm^{-1}) indicating that hydrogen bonding plays major role thus making it difficult to study any relative stability order from these frequencies. Likewise, the NH_2 deformation and rocking modes show influence of the metal ion in a complicated way. The NH_2 wagging mode varies in such a way as to indicate that in the present series of complexes the Irving-Williams order of relative stability is followed.

The spectra of complexes below 400 cm^{-1} in region where the vibrational modes involving the metal ion may be expected are too complex to gain any useful information.

REFERENCES

1. Jose, P.,
"The crystal structures of -alanine and some of its metal complexes" (p.48) - A Ph.D. Thesis, Poona University, India, (1964).

2. Bellamy, L. J.,
"Infrared spectra of complex molecules", Methuen and Co. Ltd., London (1956).

3. Tsuboi, M., Onishi, K., Nakagawa, I., Shimanouchi, T. and Mizushima, S. I.,
Spectrochim. Acta, 12, 253 (1958).

4. Fukushima, K., Onishi, T., Shimanouchi, T. and Mizushima, S. I.,
Spectrochim. Acta, 15, 236 (1959).

5. Tsuboi, M., Takenishi, T. and Nakamura, A.,
Some characteristic frequencies of amino acids,
Spectrochim. Acta, 19, 271 (1963).

6. Lane, T. J., Durkin, J. A. and Hooper, R.J.,
Spectrochim. Acta, 20, 1013 (1964).

7. Hooper, R. J., Lane, T. J. and Walter, J. L.,
Inorg. Chem., 3, 1568 (1964).

8. Nakagawa, I., Hooper, R. J., Walter, J. L. and Lane, T. J.,
Spectrochim. Acta, 21, 1 (1965).

9. Cotton, F. A. in
"Modern Coordination Chemistry", edited by Lewis, J. and Wilkins, R. G., Interscience Publishers Inc., New York (1960).

10. Vuagnat, A. M. and Wagner, E. L.,
J. Chem. Phys., 26, 77 (1957).

11. Khanna, R. K., Horak, M. and Lippincott, E. R.,
Spectrochim. Acta, 1757, 1801 (1966).

12. Gopal, L., Jose,C. I. and Biswas, A. B., Spectrochim. Acta., 23A, 513 (1967).

13. Bellamy, L. J. and Pace, R. J., Spectrochim. Acta, 19, 435 (1963).

14. Springer, M. P. and Curran, C., Inorg. Chem., 2, 1270 (1963).

15. Stosick, A. J., J. Amer. Chem. Soc., 67, 365 (1945).

16. Hay, R. W. and Porter, L. J., Austr. J. Chem., 20, 675 (1967).

17. Sen, D. N., Mizushima, S. I., Curran, C. and Quagliano, J. V., J. Amer. Chem. Soc., 77, 211 (1955).

18. Uhlig, E., Z. anorg. allgemeine. chemie, 343, 204 (1966).

19. Jungbauer, M. A. J. and Curran, C., Spectrochim. Acta, 21, 641 (1965).

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C H A P T E R - VI

INFRARED SPECTRA OF SOME PYRIDINE CARBOXYLIC ACIDS AND THEIR METAL COMPLEXES

INTRODUCTION

In spite of the fact that pyridine carboxylic acids ($C_5H_5N.COOH$) and their derivatives have been found to play an important role in biological systems, it is rather surprising that very little work is reported concerning their structure. Among the few studies, crystal structure determinations of nicotinic (β -pyridine carboxylic) acid[1] and picolinic (α -pyridine carboxylic) acid hydrochloride[2], should be mentioned. A brief infrared study of nicotinic acid and its hydrochloride has been made by Yoshida *et al.*[3] In the present work, infrared spectra of nicotinic and isonicotinic acids and their hydrochlorides have been discussed, with particular reference to $\overset{+}{N}H$ and COOH group vibrations.

Very few attempts have been made to establish the coordination of pyridine nitrogen from the infrared spectral data. Recently, the effect of coordination on a few characteristic bands (1587, 601 and 403 cm^{-1}) of the pyridine ring has been reported[4]. Coordination through nitrogen in methyl ester of pyridine acetic acid($-CH_3COOCH_3$) has

been taken for granted by Uhlig[5]. A number of first row transition metal complexes of nicotinic and isonicotinic acids have therefore been studied to see whether coordination through nitrogen and carboxylate groups takes place in these compounds or only one of the two sites is involved.

RESULTS AND DISCUSSION

Spectra of acids

The infrared absorption spectra of nicotinic, isonicotinic acids and their hydrochlorides along with their deuterated analogues are illustrated in figures VI-1, 2. Their absorption frequencies are listed in tables VI-1, 2. The assignments of the COOH, NH^+ and pyridine ring vibrations are discussed. Frequencies in the acids and their hydrochlorides are considered here.

The spectra of nicotinic acid and its hydrochloride are identical with those reported in the literature. The spectrum of nicotinic acid in potassium bromide disk indicated interaction with the matrix[6]. Recently, presence of *cis* and *trans* forms have been identified[7] in very dilute solutions (carbon tetrachloride) of nicotinic acid.

Carboxylic acid group : The structure of nicotinic acid revealed by x-ray structure analysis indicates strong intermolecular hydrogen bonding ($r_{N-H\ldots O} = 2.56\text{Å}$) between the

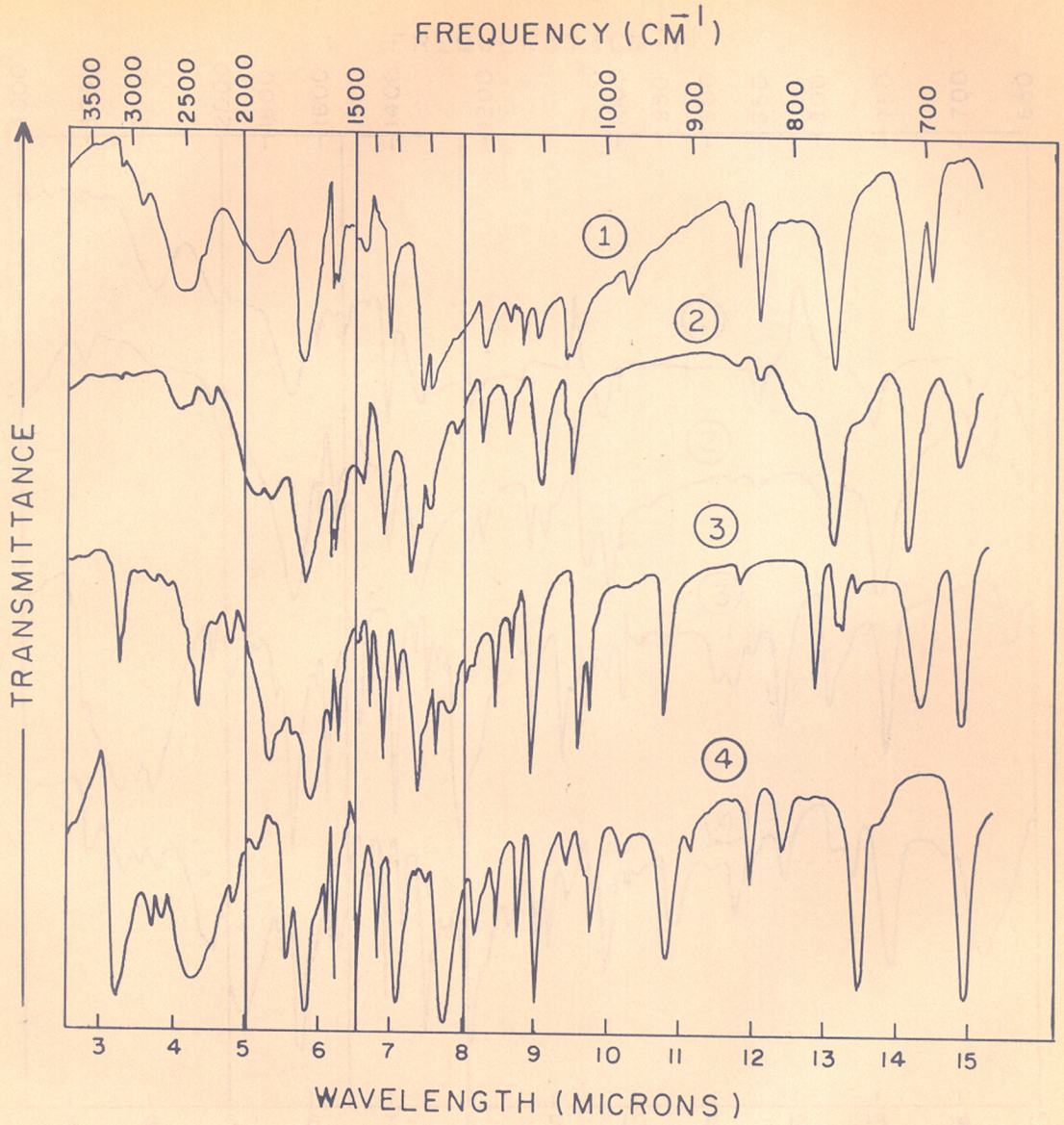


Fig. VI – 1

1. Nicotinic acid, NA
2. Deutd nicotinic acid, NA – d_1
3. Deutd hydrochloride (NA – d_1) DCl
4. Nicotinic acid hydrochloride NA. HCl

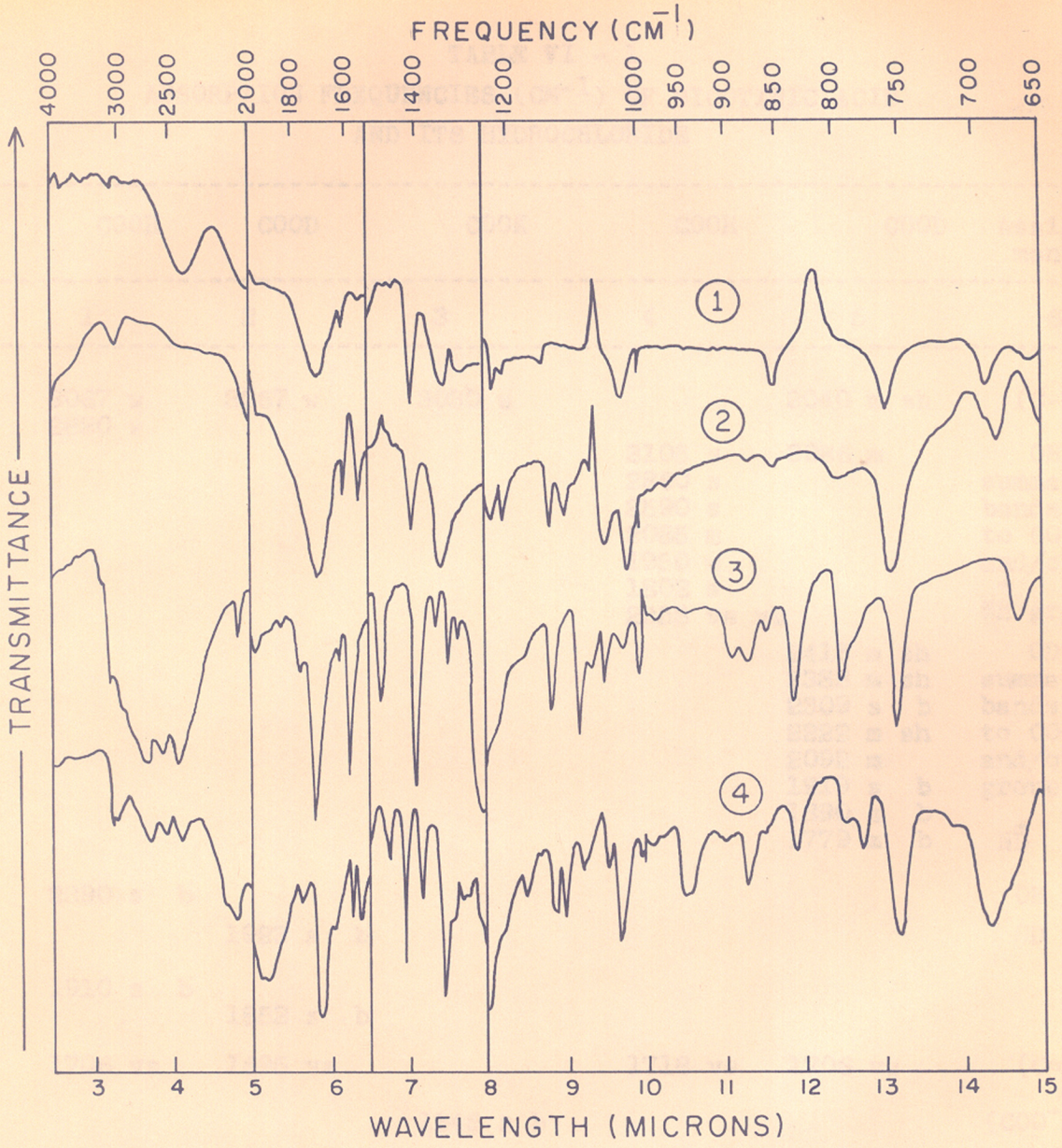


Fig. VI – 2

1. Isonicotinic acid, INA
2. Deutd isonicotinic acid, INA – d_1
3. Isonicotinic acid hydrochloride, INA – HCl
4. Deutd hydrochloride, (INA – d_1) DCl

TABLE VI - 1

ABSORPTION FREQUENCIES (CM^{-1}) OF NICOTINIC ACID AND ITS HYDROCHLORIDE

COOH	COOD	COOK	COOH	COOD	Assignment
1	2	3	4	5	6
3067 w 2820 w	3067 w	3030 w		3040 m sh	(C-H)
			3105 s 2860 s 2590 s 2085 m 1950 w 1802 s 2358 vs vb	3086 m	OH + summation bands due to COOH and/or $\overset{+}{N}H$ groups.
				2415 m sh 2388 m sh 2309 s b 2222 m sh 2092 m 1919 s b 1890 s b 1779 m b	OD + summation bands due to COOD and/or $\overset{+}{N}D$ groups.
2390 s b					OH
	1923 s b				OD
1910 s b					
	1852 s b				
1706 vs	1695 vs		1718 vs	1706 vs	(C=O)
		1545 s b			(COO^-)asym.
1597 m 1582 m	1597 m 1582 m	1589 s			I and II 16
			1535 m 1608 m	1632 m 1602 m	
			1529 m		$\overset{+}{N}H$
1482 m	1482 m	1475 m 1401 sh			III and IV 13
		1385			(COO^-)sym.
1422 sh 1437 s			1412 s 1412 s		(C-O) + OH

TABLE VI - 1 (continued)

1	2	3	4	5	6
1325 vs					
	1348 vs			1408	(C-O) + OD
1302 vs			1298 vs		C-O + OH
	1244 w				
				1182	ND^+
1185 s	1189 s	1196 s			(C-H)
1138 s	1139 s	1149 s	1145 m	1151 m	XIII, XIV,
1125 s	1124 sh	1120 w	1119 m	1115 m	XV.
1115 s					
	1081 m			1042 m	(C-O) + (OD)
1042 vs b			980 m b		OH out of plane, ring breathing XVI
	1041 m	1036 m	1033 m	1026 m	
1035 sh	1031 s	1020 s	1025 m		
	983 vw				CC, CN C^+N
956 m	956 vw	979 w	925 s	926 s	skeletal modes.
840 sh	833 w	840 m	895 m	840 w	
832 m	812 w	820 m	830 m		
812 s			803 m		
	781 s sh			695 m b	OD out of plane.
748 vs	746 vs	756 vs	740 vs	777 s	Skeletal mode(8)
	730 sh				
693 vs					
	667 sh				
680 s			670 s		COOH
	661 s			670 s b	COOD
637	635 s	621 s	625 s	641 s	Skeletal mode CC, CN.
495 s b	490 s b		521 s b	518 s b	C=O
		510 m b			COO^-
386 m b	389 m b	425 m b			Pyridine ring deformation (0)

TABLE : VI - 2 : INFRARED ABSORPTION FREQUENCIES(CM^{-1}) OF CARBOXYLIC ACID GROUP AND $\overset{+}{N}H$ GROUP IN SOME PYRIDINE CARBOXYLIC ACIDS

NA	$NA-d_1$	NAHCl	$NAHCl-d_2$	INA	$INA-d_1$	INA.HCl	$INA\ HCl-D_2$	Assignment
2390 s b	1923 s b	3105 s	3086 m	2352 m b	1923 m	3115 m sh	3115 m s	OH/ OD
	1852 s b	2860 s	2415 m sh			3077 sh	3000 sh	Summation
1910 s b		2590 s	2388 m sh	1960 s	1923 m	2860 sh	2800 w	bands
		2358 s b	2309 s b			2705 s	2705 w	+
		2085 m	2222 m sh			2565 s	2565 w	NH
		1950 w	2090 m			2450 s	2450 w	
		1802 s	1919 b				2125 s sh	
			1890 s b				2100 s	
							1950 s	
							1790 w	
1706 vs	1695 vs	1718 vs	1706 vs s	1695 vs b	1700 vs b	1724 s	1715 s	C=0
1437 s				1299 m b	1342	1408 s	1350 s	C-0 + OH*
1325 vs	1348 vs	1412 s	1408 m	1230 s	1050 s	1259 vs	1036 s	C-0 + OH
1302 vs	1081 m	1294 vs	1042 m					
1042 vs	781 s sh	980 m	695 m b	858 m	654 s	1055 m	690 s b	OH
680 s		670 ?				658		COOH
								+
		1529 s	1182 m			1603 s	1185 m	NH

* Corresponding deuterium vibration is given for deuterated compounds.

pyridine nitrogen and hydrogen atom of COOH group of an adjacent molecule. The usual cyclic dimer structure is thus not present in nicotinic acid in the crystalline state. The structure of picolinic acid hydrochloride, which is also non-dimeric, shows yet another type of hydrogen bonding between OH and Cl (with $r_{O-H\cdots Cl}$ = 3.00Å). In view of these interactions the carboxylic acid group frequencies would be expected to be modified appreciably.

Both nicotinic and isonicotinic acids absorb strongly at about 2350 and 1900 cm^{-1}. It is interesting to note that in both these compounds there is no band above 2400 cm^{-1} which can be attributed to the hydroxyl stretching vibration. The 2350 cm^{-1} band shifts quantitatively ($\sim$1900 cm^{-1}) on deuteration and may therefore be assigned to the hydroxyl stretching mode. The shifting of 1900 cm^{-1} band is not clearly seen since 2350 cm^{-1} band shifts to about this value upon deuteration.

The low value of 2350 cm^{-1} for bonded hydroxyl stretching vibration is not very surprising. N-acetyl glycine which also possesses a non-dimeric structure, having a very short hydrogen bond shows νOH band at 2750 cm^{-1}. Several other N-acetyl amino acids are also found to absorb near 2700 cm^{-1}. In view of the strong basic character of the pyridine nitrogen,

it may be surmised that a stronger hydrogen bonding interaction has occurred along with charge transfer which is responsible for lowering of the ν OH band.

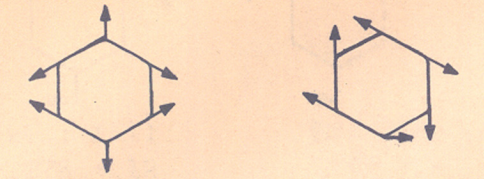
Inorder to explain the observed two bands 2350 - 1900 cm^{-1} in nicotinic acid Hadzi[8] has suggested the possibility of proton transfer, similar to that indicated by Bellamy and Rogasch[9] in several compounds containing NH. A number of other causes have also been reported for the observed multiplicity of bands. Fermi resonance is considered to be responsible for the multiplicity of bands in dimeric carboxylic acids[10]. The various bands in the region 3000-2500 cm^{-1} in glycine have been ascribed to different hydrogen bond lengths[11]. Presence of two geometric isomers[7] have also been considered to give rise to additional bands.

The 1042 cm^{-1} band of nicotinic acid is shifted to 780 cm^{-1} upon deuteration and assigned to OH out of plane deformation mode. The high value (1042 cm^{-1}) is not unexpected since the corresponding stretching mode is found at a very low value (2350 cm^{-1}). It may be noted that Yoshida et al.[3] have not reported the occurrence of this band.

Pyridine ring vibrations Pyridine molecule behaves like monosubstituted benzene with C_{2v} symmetry. As a consequence, monosubstituted pyridines behave as disubstituted benzenes. The vibrational modes of the ring along with those of hydrogens

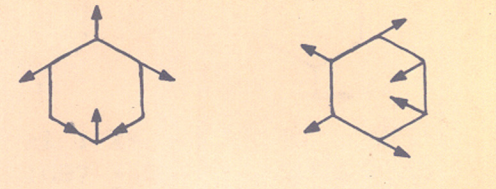
are depicted in figures VI-3, 4. The assignments for nicotinic acid have been given in table VI-1, following Katrizky[12], without further discussion.

$\overset{+}{\text{NH}}$ group - Very little has been reported on the absorption due to NH group which is found in pyridine hydrochlorides. Nicotine, its mono- and di-hydrochlorides have been investigated[13] to identify the bands due to this group. These studies have indicated that the "ammonium band" due to $\overset{+}{\text{NH}}$ group occurs as a strong, broad band at 2500-2325 cm^{-1}. The "immonium bands" which are characteristic of salts of open and cyclic imines(including heterocyclics like pyridine) are found in the 2275-1820^{-1} region and are attributable to $\overset{+}{\underset{H}{N}}$ group. These are shifted quantitatively on deuteration. A number of additional summation bands having their intensity enhanced by Fermi resonance appear in deuterated compounds. Spectra of some methyl ammonium iodides have been reported by Ebsworth and Sheppard[14]. The abnormal changes upon deuteration have led to some confusion regarding the ND mode, while NH and CN modes have been definitely assigned. In the hydrochlorides of nicotinic and isonicotine acids there is no absorption attributable to $\overset{+}{\underset{H}{N}}$ in the region 2275-1820 cm^{-1}. However, a strong band at 2360 cm^{-1} is found in both which may be assigned to the $\overset{+}{\text{NH}}$ stretching mode. It is possible that the interaction with chloride is responsible for the upward shift and the



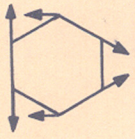
E_{2g} ν_{16} 1585 cm^{-1}

I II



E_{1u} ν_{13} 1485 cm^{-1}

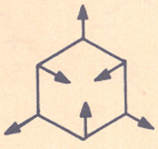
III IV



B_{2u} (ν_9)

1310 cm^{-1}

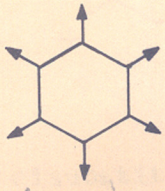
V



B_{1u} (ν_6)

1008 cm^{-1}

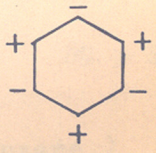
VI



A_{1g} ν_2

984 cm^{-1}

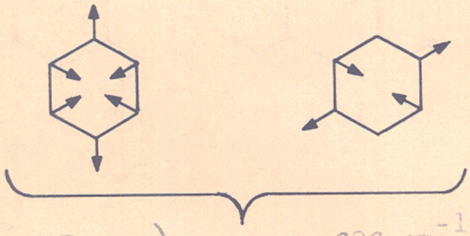
VII



B_{2g} (ν_8)

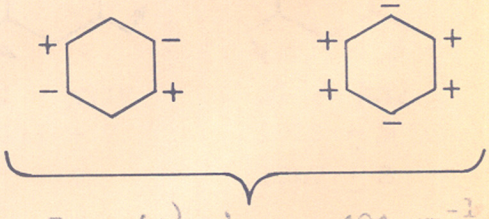
538 cm^{-1}

VIII



E_{2g} ν_{18} 606 cm^{-1}

IX X



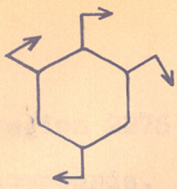
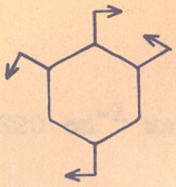
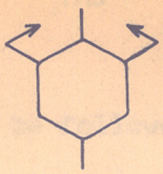
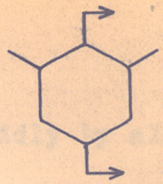
E_{2u} (ν_{20}) 404 cm^{-1}

XI XII

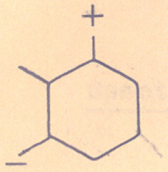
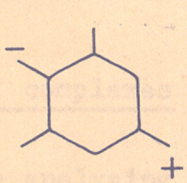
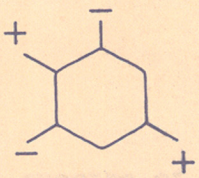
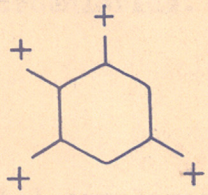
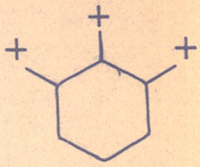
Degenerate modes are bracketed together. ν_{13} is infrared active, ν_{16}, ν_2 and ν_{18} are Raman-active; ν_9, ν_6, ν_8 and ν_{20} are totally inactive (obtained by indirect means, e.g. deuteration).

FIG. VI - 3 : SKELETAL MODES OF BENZENE

A : FOUR H-ATOMS (1,2,3,5) POSITIONS

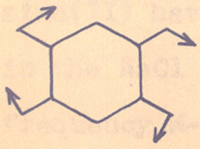
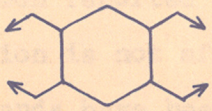
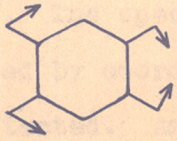
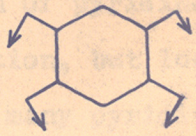
INPLANE	B1 : XIII	B1 : XIV	A1 : XV	B1 : XVI
m.B	1278 ± 12	1157 ± 5	1097 ± 7	1076 ± 7
3-Py	Ca. 1190?	1124 ± 5	1103 ± 5	1038 ± 7

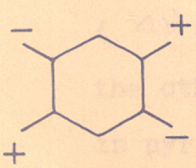
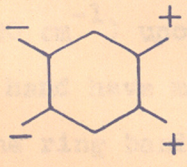
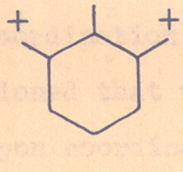
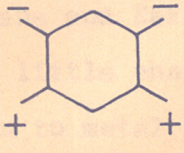
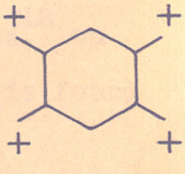
(A2) : XVII B2 : XVIII B2 : XIV B2 : XX B2 : XXI

(3-Py, 3-substituted pyridine; m.B, meta disubstituted benzene.)

B : FOUR H-ATOMS (1,2,4,5) POSITIONS

INPLANE	B1 : XXII	A1 : XXIII	B1 : XXIV	A1 : XXV
p.B	1258 ± 11	1176 ± 6	1111 ± 7	1013 ± 5
4-Py	1220	?	?	1067 ± 3

(A2) : XXVI (A2) : XXVII B2 : XXVIII B2 : XXIX B2 : XXX

(4-Py, 4-substituted pyridine; p.B, para disubstituted benzene)

A2 modes forbidden in C_{2v} compounds in infrared spectrum.

FIG. VI - 4 : HYDROGEN DEFORMATION MODES

region 2275 - 1820 cm^{-1} may not be followed rigidly by all compounds.

The presence of a charged nitrogen has also significant effect on the ring breathing mode. The band near 380 cm^{-1} of nicotinic acid disappears in the hydrochloride.

Spectra of complexes

While analysing the spectra of metal complexes of pyridine carboxylic acids, it is necessary to examine the spectrum of the pyridine ring and the carboxylate group. A few studies reported in the literature indicated the effect of coordination on the pyridine ring vibration. Spectra of tris complexes of 1,10,phenanthrone and 2,2'bipyridine with Fe(II) through zinc(II) have been reported[15,16]. The spectrum of pyridine ring in the NaCl region is not affected by coordination, but low frequency M-N bands have been detected. Among many pyridine complexes[16] that have been investigated a number of pyridine complexes of the type $Fe(X)_2Py_4$ where Py is the pyridine molecule which have been recently studied[4,17]. The 1587, 601 and 403 cm^{-1} bands appear to shift to higher frequency ($\Delta\nu$ = 20 cm^{-1}) upon coordination. Lane and Nakagawa[18] on the other hand have mentioned that very little change is found in pyridine ring bands upon coordination to metal ion.

Nicotinic acid absorbs at 1587, 1600, 625 and 385 cm^{-1}. These bands are found in the several complexes as shown in table VI-3. While there seems to be only minor changes (if any) in 1587, 1600, 625 cm^{-1} bands, the 385 band does indeed indicate some significant shift.

The carboxylate group frequencies found in all the complexes, indicate absence of free COOH group. The COO^- wagging mode indeed found to vary as Mn Co Ni Cu indicating that the Irving-Williams[19] order of stability is followed.

Complexes of isonicotinic acid gave a blurred spectrum below 650 cm^{-1} and hence no information could be obtained. No characteristic bands are found for substituted pyridines[20] in 650 - 350 cm^{-1} region.

Since only the carboxyl group frequencies are noticeably affected a simple salt-like structure by interaction with the metal ions may be suggested for nicotinic acid (and also isonicotinic acid) complexes.

TABLE VI - 3

INFRARED FREQUENCIES (CM^{-1}) OF SOME METAL NICOTINATES

K.N.	$Mn(N)_2 \cdot nH_2O$	$Co(N)_2 \cdot nH_2O$	$Ni(N)_2 \cdot nH_2O$	$Cu(N)_2 \cdot nH_2O$	Me	Assignment
621 m	635 m	645 s 602 s	599 s	640 s	617 s	Pyridine ring.
510 m	552 m	529 s	532 m	581 m		COO^- wagging
					476 m	CO
425 m	418 m	445 w 410 m	448 w 413 m	445 m	427 m	Pyridine ring deformation

REFERENCES

1. Wright, W. B. and King, G. S. D.,
Acta Cryst., 6, 305 (1953).

2. Laurent, A.,
a: Compt. rend., 256, 916 (1963).
b: Acta Cryst., 18, 799 (1965).

3. Yoshida, S. and Asai, M.,
Chem. Pharm. Bull (Tokyo), 7, 162 (1959).

4. Duncan, J.F. and Mok, K. F.,
Austr. J. Chem., 19, 701 (1966).

5. Uhlig, E. and Keil, D.,
Z. anorg. allgemeine chemie, 332, 69 (1964).

6. Taylor, L. D.,
J. Org. Chem., 4064 (1962).

7. Oki, M., Hirota, M. and Morimoto, Y.,
Bull. Chem. Soc., Japan, 39, 1620 (1966).

8. Hadzi, D., Vestnik. Slov. Kem. Drustva., 21 (1958).
Chem. Abst., 54, 10515 h (1960).

9. Bellamy, L. J. and Rogasch, P.E.,
Proc. Royal. Soc., A-257, 98 (1960).

10. a : Hadzi, D. and Sheppard, N.,
Proc. Royal Soc., A-216, 247 (1954).
b : Bratsz, S., Hadzi, D. and Sheppard, N.,
Spectrochim. Acta, 8, 249 (1956).

11. Khanna, R. K., Horak, M. and Lippincott, E. R.,
Spectrochim. Acta, 22, 1757, 1801 (1966).

12. Katrizky, A. R.,
Quart. Review, 13, 353 (1959).

13. Witkop, B.,
Experimentia, 10, 422 (1954).

14. Ebsworth, E. A. V. and Sheppard, N.,
Spectrochim. Acta., 13, 261 (1959).

15. Schilt, A.A. and Taylor, R. C.,
J. Inorg. Nucl. Chem., 9, 211 (1959).

16. Inskeep, R. G.,
J. Inorg. Nucl. Chem., 24, 763 (1962).

17. Gills, N. S., Nuttalle, R. H., Scaife, D. E. and
Sharp., D. W. A.,
I J. Inorg. Nucl. Chem., 18, 79 (1961).

18. Lane, T. J., Nakagawa, I., Walter, J. L. and
Kandathil, A. J.,
Inorg. Chem., 1, 261 (1963).

19. Irving, H. and Williams, R. J. P.,
J. Chem. Soc., 3192 (1952).

20. Issac, R., Bentley, F. F., Steinglanz, H. and
Coburn, W. C., Stephenson, C. V. and Wilcox, W. S.,
Appl. Spectry. 17, 90 (1963).

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C H A P T E R - VII

INFRARED SPECTRA OF SOME SUBSTITUTED PHENOXYACETIC ACIDS AND THEIR COMPLEXES

INTRODUCTION

The extensive amount of infrared data available on the carboxylic acid (COOH) group has, indeed, been restricted to those having dimeric structures in the solid state as indicated by x-ray crystal structure studies[1]. In solution and in the gaseous state, however, non-dimeric (either monomeric or polymeric) forms are present. Information on the non-dimeric COOH compounds in the solid state is very scanty in the literature. With a view to analyse the vibrational frequencies of COOH group in this unusual form, we have investigated the spectra of compounds such as N-acetylglycine, nicotinic acid, the structures of which are known from x-ray evidence to have a non-dimeric COOH group. Subsequent search for carboxylic acids showing unusual spectral features led us to the present series of compounds. Incidentally, it may be mentioned that these compounds are known to have potential pharmacological utility as hypoglycemic agents[2].

Spectra of metal complexes of a few of them have also been recorded in order to find whether they are simple salt as

in normal carboxylic acid complexes or chelates coordinating in addition to the ether oxygen.

RESULTS AND DISCUSSION

The band assignments of the COOH group for the various phenoxyacetic acids as well as their deuterated analogues (COOD) are compiled in table VII-1. Spectra of phenoxyacetic acid and its deuterated analogue are illustrated in figure VII-1. The most striking feature of the spectra is the splitting of the bands due to C=O stretching and the OH or OD out of plane deformations and C=O deformation modes. In the normal monocarboxylic acids the splitting of the C=O stretching, OH and OD out of plane deformation and C=O deformation is not common in the solid state, though in solution due to the presence of both the monomeric and associated species two bands each for these modes may be found. Splitting of the bands in the solid state, however, can arise either from the crystal field effects or the different surroundings of the molecules in the unit cell. An example of the former is found in the case of octadecanoic acid[3,4] which crystallizes in monoclinic and triclinic forms. In the monoclinic form splitting of ν C=O is reported with probably doubling of the OH deformation modes also. X-ray evidence is cited to show that the C=O groups of the molecules in the unit cell have similar surroundings so that the splitting is not caused by

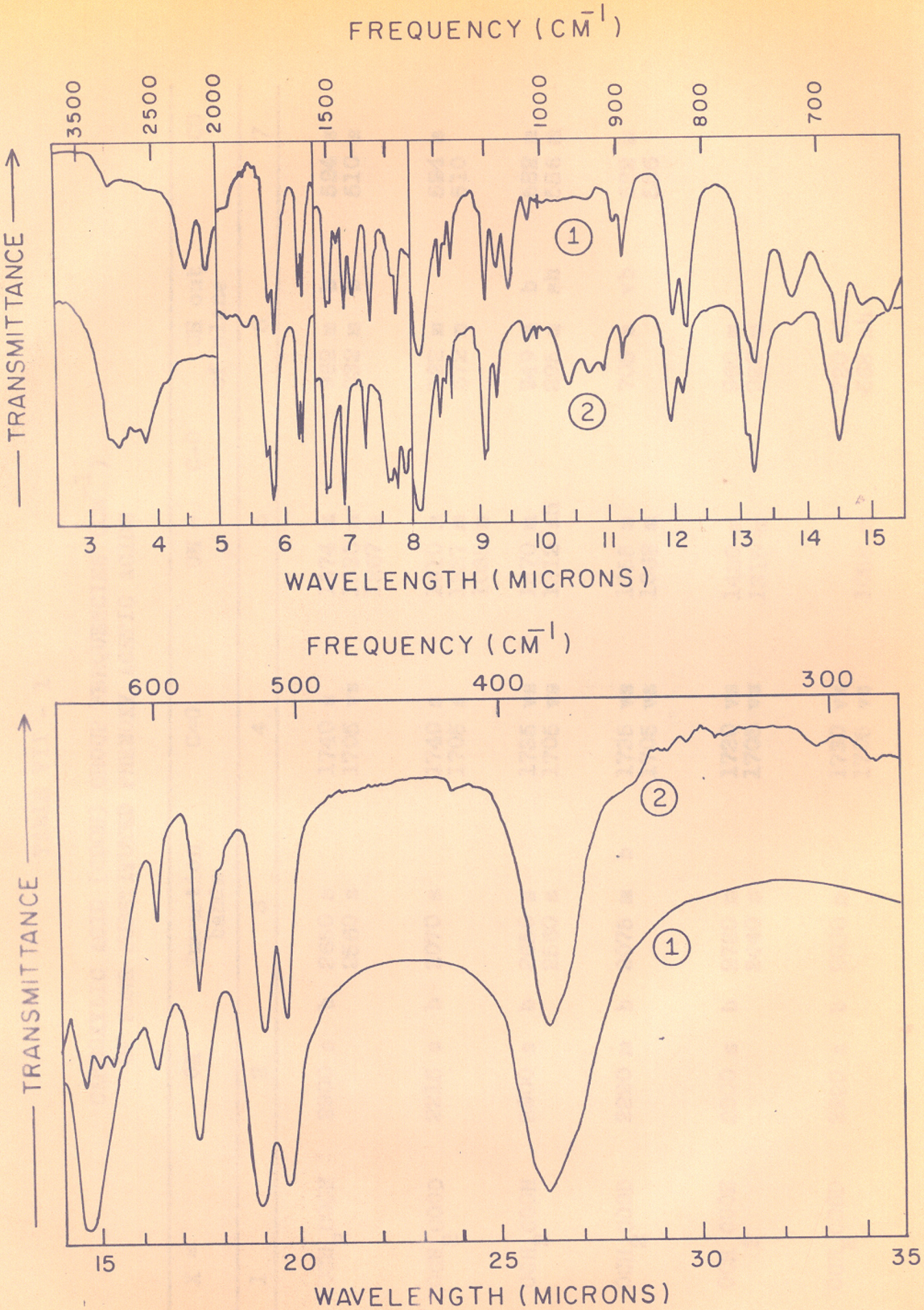


Fig. VII – 1

1. Phenoxy acetic acid
2. Deutd phynoxy acetic acid

TABLE VII - 1

CARBOXYLIC ACID (COOH) GROUP FREQUENCIES (CM^{-1})
OF SOME SUBSTITUTED PHENOXY ACETIC ACIDS

	X =	OH	Summation bands	C=O	OH + C-O	OH out of plane	CO
	1	2	3	4	5	6	7
	OCH_2COOH	2900 s b	2650 s 2560 s	1740 s 1705 vs	1374 m 1330 m 1267 m	962 m b 932 m b	524 s 510 s
I							
	OCH_2COOD	2215 s b	2070 s	1740 s 1705 s	1410 m 1337 m 1035 m	722 m 672 m	524 s 510
	OCH_2COOH	2900 s b	2650 s 2560 s	1735 vs 1705 vs	1370 m 1312 sh	949 m b 895 m sh	582 m 556 m
II							
	OCH_2COOD	2220 m b	2075 m b	1735 vs 1705 vs	1355 m 1062 m	705 s vb	582 m 556
	OCH_2COOH	2900 s b	2780 m 2440 s	1730 vs 1705 vs	1420 m 1315 m	960 m 920 m	
III							
	OCH_2COOD	2220 s b	2030 m	1730 vs 1705 vs	1056 m	720 sh 668 sh	

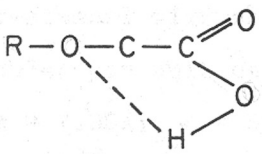
Table VII - 1 (continued)

1	2	3	4	5	6	7
OCH_2COOH	2900 s b	2650 m	1725 s	1427 m	914 s b	
		2550 m	1705 s sh	1310 m		
				1255 m		
IV						
OCH_2COOD	2240 s b	2083 s	1725 s	1405 m	680 s b	
			1705 s sh	1057 m		
OCH_2COOH	2900 s b	2660 s	1740 vs	1480 s	957 m b	571 m
		2550 s	1705 m	1300 m	914 s b	552 s
V						
OCH_2COOD	2230 s b	2085 s	1740 vs	1350 s	685	570 m
			1705 m	1060 m		550 s
OCH_2COOH	2900 s b	2650 s	1335 vs	1553 m	966 m b	592 m
		2550 s sh	1705 s	1320 m	920 m b	564 s
				1269 m		
VI						
OCH_2COOD	2230 m	2080 m	1735 vs	1408 m	694 m b	542 m
			1705 s	1062 m		564 s
OCH_2COOH	2900 s b	2653 m b	1735 vs	1486 m	964 m	538 s
		2560 s	1705 vs	1312 m	912 m	508 s
VII						
OCH_2COOD	2200 m	2075 m	1735 vs	1351 m	664 s	538 s
			1705 s	1057 m		508 s

Table VII - 1 (continued)

	1	2	3	4	5	6	7
	ϕCH_2COOH	2885 m b	2675 m b 2565 m b	1730 s 1705 s	1441 m 1319 m 1312 m	965 m b 934 m	513 s 504 s
VIII							
	OCH_2COOD	2220 m b	2070 m b	1730 s 1705 s	1405 m 1054 m	724 664	513 s 504 s
	OCH_2COOH	2900 m b	2825 m b 2650 m b 2560 m b	1735 s 1705 s	1460 m 1377 s	938 m b 915 m b	515 s 505 s
IX							
	OCH_2COOD	2211 m b 2075 m b 1951 w		1730 s 1705 s	1412 m 1049 s	700 s b	515 s 504 s
	OCH_2COOH	3000 s	2700 m 2600	1730 s 1705 s	1408 m 1316 m	935 m 920 m b	532 s 512 s
X							
	OCH_2COOD	2217 m b	2080 m b	1730 s 1705 s	1357 m 1050 m	921 m 670 sh	532 s 502 s

it. The infrared spectra of the solutions of some of the present compounds such as phenoxyacetic acid in dilute carbon tetrachloride have been reported by Oki and Hirota[5]. They found two hydroxy and two carbonyl stretching bands which have been attributed to two rotational isomers of the carboxylic acid group. In one case the hydroxy of the COOH group forms hydrogen bond with the ether oxygen(I) forming a five membered ring, while in the other(II), there is a cis, structure for the acid group



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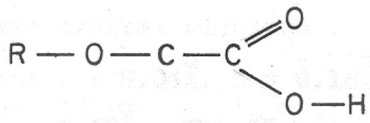
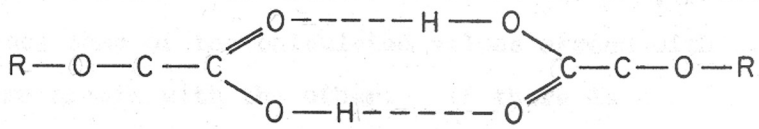


II

In addition to these two forms, the usual dimeric form(III) is also present.



III

These results cannot, however, be translated for the case of solids for obvious reasons.

One of the common explanations offered for the present of additional bands is Fermi resonance. The anomalous band splitting in carboxylic acids[6], imidazole derivatives[7], amido acids (Chapter IV), has been explained on the basis of this phenomenon. This argument does not appear to be valid

in the present series of compounds since summation bands of very low frequencies will have to be present to give rise to the splitting of δ CO mode at ~ 500 cm^{-1}.

In order to get an idea of the structure in the solid state, the preliminary structural analysis was carried out for one of them, the p-chloro-phenoxyacetic acid, by the x-ray group of this laboratory[8]. Their results are as follows: p-chloro-phenoxyacetic acid crystallized from water-ethanol mixture forms triclinic crystal with two molecules per unit cell of dimensions a = 8.94Å, b = 6.16Å and c = 7.93Å; $\alpha = 93^{\circ}$, $\beta = 89^{\circ}$, $\gamma = 60^{\circ}$. The IR spectrum of this sample was not different from the one crystallized from water.

Attempts to establish whether it is $P\bar{1}$ or $P1$, proved futile, since some of the calculated values agreed with one symmetry and others with the other. If there is a $P\bar{1}$ symmetry as is generally found in the case of triclinic long-chain acid, then the splitting of the bands would not be possible on crystal field effect since they are related by a centre of symmetry and each molecule is similarly located as the other. If, however, the two molecules are not related to each other, by any symmetry as in $P1$, then the surroundings of the two molecules would be different and hence the doubling of the bands might take place. There are

very few cases of two different environments for the same type of molecules in the unit cell and hence detailed x-ray crystallographic studies of this type of compound would be interesting.

Since all the compounds of the series have the phenoxyacetic acid group and all of them show doubling, it appears that it is connected with the presence of the ether oxygen, suitably placed for an intramolecular hydrogen bonding with OH of COOH group. If the doubling is due to two different rotational isomers as found in the solution then it is one of the unusual cases of two isomers existing in the solid. We have found in the case of long chain alkoxy ethanols[9], again having an ether oxygen conveniently situated to form an intramolecular hydrogen bonded five member ring($-OCH_2CH_2OH$) that in the solid state, there are two types of molecules, one having a gauche (favouring intramolecular hydrogen bonding) configuration and the other a trans configuration of the OCH_2CH_2O group. Certain long chain alcohols have the end $CH_2CH_2CH_2O$ group in trans and gauche forms and give rise to two types of hydrogen bonds as shown by x-ray crystallography[10].

A strong band near 1200 cm^{-1} has been assigned by Shimanauchi et.al[11] to CH_2 -COOH group, involving largely a

CH_2 wagging mode along with OH in plane deformation and ν(C-O) modes. The band 1240-1200 cm^{-1} in the present type of compounds is not at all affected on deuteration indicating that the δ OH contribution is insignificant. The band may be said to arise from C-O stretching and CH_2 wagging modes.

Spectra of complexes

Spectra of copper(II), nickel(II), manganese(II), cobalt(II), complexes of phenoxyacetic acid and its substituted derivatives viz. p-chloro, p-methyl-o-chloro, have been recorded. These spectra show presence of COO^- group and unperturbed ν C-O vibration leading us to propose salt-like structure for these complexes.

REFERENCES

1. Nyberg, S. C.,
"X-ray analysis of organic structures",
Academic Press Inc., New York, London (1961).

2. Pabrai, P. R.,
"Potential hypoglycemic agents",
A Ph.D.(Pharmacy) thesis, Banaras Hindu University, 1964.

3. I. E. Von Sydow,
Acta Chem.Scand., 9, 119 (1955).

4. Holland, R.E. and Nielson, J.Rvd.,
J. Mol. Spectroscopy, 9, 436 (1962).

5. Hirota, M. and Oki, M.,
Bull. Chem. Soc., Japan, 34, 374 (1961).

6. Hadzi, D., Bratoz, S., Sheppard, N.,
Spectrochim. Acta, 8, 249 (1956).

7. Fritsche, H.,
Spectrochim. Acta, 22, 1139 (1966).

8. Pant, L. M. and Dhaneshwar, D. D.,
Unpublished data.

9. Srinivasan, T. K. K., Jose, C. I. and Biswas, A. B.,
Bull. Chem. Soc., Japan, 37, 1770 (1974).

10. Tasumi, M., Shimanouchi, T., Watanabe, A. and Gato, R.,
Spectrochim.Acta, 20, 629 (1964).

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APPENDICES

APPENDIX - I

VISIBLE SPECTRA AND COORDINATION OF COBALT(II), N-ACETYL AND N-BENZOYL-GLYCINES IN NON-AQUEOUS SOLVENTS

It is known that salts of transition metals, when dissolved in non-aqueous solvents may undergo structural changes. Such changes occurring in cobalt(II) salts are visibly evident because of the distinct color changes from pink (octahedral) to blue (tetrahedral). In recent years a number of ligands have been exploited to obtain the unusual tetrahedral configuration of cobalt(II) ions[1-3]. A review of the literature reveals that most of these complexes having tetrahedral symmetry have smaller ions especially the halogen (Cl, Br or I) or pseudo-halogen(CNS) as anions. Very few tetrahedral complexes of cobalt(II) are known with no anions[4,5] or with a very large anion[6,7]. Cobalt(II) (dipivaloylmethane) complex having molar extinction 40 is an example of the former type. On the other hand, $Co(NO_3)_2$ (hexamethyl phospharamide)$_2$ is described as pseudo-tetrahedral complex by Drago and Donohue[8].

In what follows, the spectra of cobalt(II), N-acetyl and N-benzoylglycinates in dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF) solutions are discussed.

The color of the compounds in various solvents are given in table I-1. Some typical spectra in DMSO are shown in figure I-1 and the absorption frequencies and molar extinction coefficients are listed in table I-2. Similar spectral data of a few related compounds from the literature are also included in table I-2 for comparison.

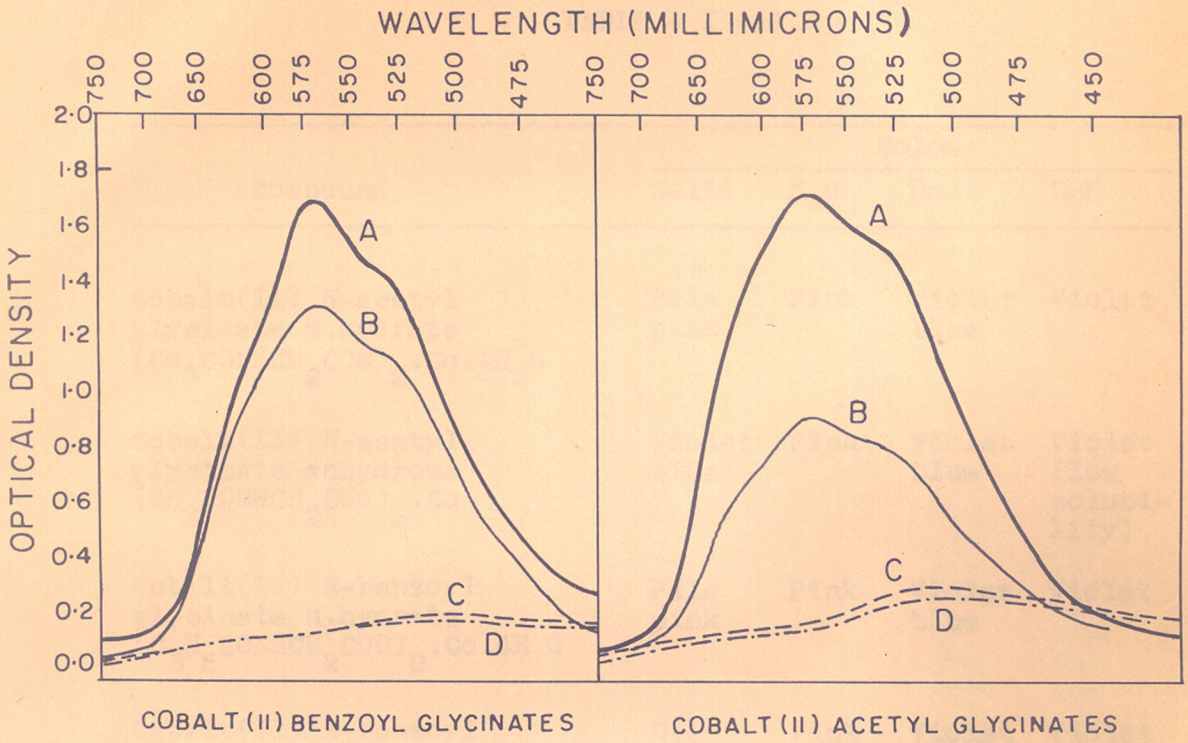
Cobalt(II) ion having an octahedral symmetry has a molar extinction of 4.8[9]. The value for a tetrahedral species[10] ranges from 600-2500 and lower values have also been reported for compounds having distorted structure[8,11].

Our DMSO and DMF solution spectra indicate that the metal ion exists predominantly in the distorted tetrahedral or at least partially tetrahedral (along with octahedral) form. In the hydrated complexes, the amount of tetrahedral species is smaller, as indicated by lower molar extinction coefficients.

The composition of the complex may be represented by a general formula:

$$Co(BG)_{4-n}(DMSO)_n) \qquad Co(BG)_n(DMSO)_{6-n}$$

when n = 0 to 4. All the structures except n = 2 are improbable since they require removal of at least one BG^-



VISIBLE SPECTRA IN WATER AND DMSO

Fig. I - (1)

Co(II) benzoyl glycinates

A - 0.018 M anhydrous and B - 0.0205 M hydrate in DMSO

C - 0.0207 M anhydrous and D - 0.0203 M hydrate in H_2O

Co(II) acetyl glycinates

A - 0.0228 M hydrate and B - 0.0096 M anhydrous in DMSO

C - 0.0224 M anhydrous and D - 0.0215 M hydrate in H_2O

TABLE - I - 1

Compound	Colour			
	Solid	H_2O	DMSO	DMF
Cobalt(II) N-acetyl glycinate n.hydrate $(CH_3CONHCH_2COO)_2.Co.4H_2O$	Pale pink	Pink	Violet blue	Violet
Cobalt(II) N-acetyl glycinate anhydrous $(CH_3CONHCH_2COO)_2.Co$	Violet blue	Pink	Violet blue	Violet (low solubility)
Cobalt(II) N-benzoyl glycinate n.hydrate $(C_6H_5CONHCH_2COO)_2.Co.4H_2O$	Pale pink	Pink	Violet blue	Violet
Cobalt(II) N-benzoyl glycinate anhydrous $(C_6H_5CONHCH_2COO)_2.Co$	Deep pink	Pink	Violet blue	Violet blue

On addition of excess of chloride ion to the DMSO and DMF solutions a blue solution is obtained.

TABLE - I - 2

ELECTRONIC SPECTRAL DATA OF SOME COBALT(II) COMPLEXES

Compound	Medium	max	max	After adding excess LiCl		Ref.
				max	max	
$Co(BGl)_2$	Water	506 458	4.7 -			Our work
$Co(BGl)_2 4H_2O$	Water	506 458	4.1 -			
$Co(BGl)_2$	DMSO	615 570 535	61.4 96.0 80.0	696 670 638 618 602	633 567 405 255 101	
$Co(BGl)_2 4H_2O$	DMSO	615 570 535	44.8 59.4 51.6	698 670 638 618 602	564 534 356 237 119	
$Co(BGl)_2$	DMF	612 593 565	75.2 85.4 68.8	698 673 638 618 600	599 558 395 224 129	
$Co(BGl)_2 4H_2O$	DMF	605 560 535	42.0 44.5 45.2	698 673 638 618 600	590 544 394 394 103	
$Co(AGl)_2$	Water	510 460	5.6 -			
$Co(AGl)_2 4H_2O$	Water	510 460	5.4 -			

Table - I - 2 (continued)

Compound	Medium	Max	max	After adding excess LiCl		Ref.
				max	max	
$Co(AGl)_2$	DMSO	615 570 535	71.7 93.4 80.4	698 673 638 618 602	635 560 400 282 115	
$Co(AGl)_2 4H_2O$	DMSO	615 570 535	56.1 71.9 64.9	698 673 638 618 602	607 566 393 270 120	
$Co(AGl)_2 4H_2O$	DMF	605 560 535	43.1 44.5 45.2	685 640 620	543 369 205	
$(CoCl_4)^{2-}$	Nitro-methane	693 668 635 613 593	653 580 419 - 122			10
$Co(OH_2)_6^{2-}$	Water	513 454	4.8 -			10
$(C_6H_5)_3AsCH_3 \cdot Co(NO_3)_4$	Nitro-methane	538	107			12
$Co(NO_3)_2 \cdot 2HMPA$	Nitro-methane	568	170			4
Co(dipivaloy-methane)$_2$			40			6

group from coordination. Hence $Co(BG)_2(DMSO)_2$ is considered to be the most probable species giving rise to the observed absorption.

On addition to excess chloride ion (LiCl) to these solutions, the truly tetrahedral species $(CoCl_4)^{-2}$ is formed as shown by the position of the absorption bands and the enhanced values of ε_{max} (last column table I-2), which are well comparable with the spectral data reported by Gill and Nyholm[9].

The reactions involved may be indicated as:

$$\underset{\text{tetrahedral}}{(CoCl_4)^{-2}} \xrightarrow{LiCl} Co(DMSO)_2(BG)_2 \xrightarrow[H_2O]{\text{Excess}} \underset{\text{octahedral}}{Co(OH_2)_n(DMSO)_{4-n}(BG)_2}$$

where $n = 4$.

Similar behaviour is observed for N-acetylglycine ligand and DMF solvent. Buffagni and Dunn[12] have suggested a similar explanation for the spectra of anhydrous cobalt(II) chloride in nitromethane.

Several attempts to isolate a solid product from the non-aqueous solutions, have so far been unsuccessful, resultant product being in every case an oily substance.

A P P E N D I X - II

MAGNETIC SUSCEPTIBILITIES OF SOME FIRST ROW TRANSITION METAL CARBOXYLATES*

In recent years, magnetochemical studies of coordination compounds have been made extensively to determine their stereochemistry. Magnetic susceptibility data on a few first row transition metal carboxylates is reported here.

The data on copper(II) complexes is given in table I-3 while those on cobalt(II), nickel(II) and manganese(II) are presented in table I-4.

Copper(II) salts:

A large amount of magnetic data on copper(II) salts are available[13]. Copper(II) ion (d^9) with one unpaired electron has theoretical spin-only moment 1.73 BM. From the point of view of magnetic properties copper(II) complexes fall into two broad classes. First there are those having essentially temperature independent magnetic moments in the vicinity of 1.8 BM owing to quenched orbital coupling. Those

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* A paper with this title has been published by us in Indian J. Chem., 4, 42 (1966).

TABLE I - 3

MAGNETIC SUSCEPTIBILITY DATA FOR SOME COPPER(II) CARBOXYLATES

Ligand	Mol.formula	Molar suscep-tibility $M \times 10^6$	Effective magnetic moment $\mu_{eff.}$ BM	T
Lactate	$Cu(CH_3CHOHCOO)_2.2H_2O$	1388	1.83	297
Malonate	$Cu\ H_2C.(COO)_2\ .3H_2O$	1411	1.84	297
Tartrate	$Cu\ OOC.(CHOH)_2.COO$	1393	1.83	297
Mandelate	$Cu(PH.CHOH.COO)_2$	1199	1.69	295
Benzilate	$Cu\ (Ph)_2.COH.COO$	1150	1.67	303
N-acetyl-glycinate	$Cu(CH_3CONHCH_2COO)_2.4H_2O$	1410	1.85	303
N-benzoyl-glycinate	$Cu(Ph.CONHCH_2COO)_2.4H_2O$	1416	1.85	300
N-benzoyl-glycinate	$Cu(Ph.CONHCH_2.COO)_2$	1105	1.63	300
Phenoxy-acetate	$Cu(Ph.OCH_2COO)_2.H_2O$	1430	1.86	300
o-chloro-phenoxy-acetate	$Cu(o\text{-}Cl\text{-}Ph.OCH_2COO)_2$	1005	1.56	302
p-chloro-phenoxy-acetate	$Cu(p\text{-}Cl\text{-}Ph.OCH_2COO)_2 2H_2O$	1100	1.64	303
p-CH_3-phenoxy-acetate	$Cu(p\text{-}CH_3\text{-}Ph.OCH_2COO)_2.2H_2O$	1056	1.60	300

exhibiting such moments are mononuclear complexes having no major interaction between the unpaired electrons on different copper atoms. The malonate, lactate, tartrate, N-acetylglycinate tetrahedrate, N-benzoylglycinate tetrahydrate, belong to this group.

The second class of compounds have magnetic moment much below the spin-only value (1.73 BM) for an unpaired electron. A review on such compounds has recently been published by Kato and others[14] who divide such compounds into two types. Those with direct copper-copper interaction as found in dimeric copper(II) acetate monohydrate[15] $Cu_2(CH_3COO)_4 2H_2O$ wherein δ bonding has been postulated. In the second group, interaction by a superexchange mechanism is said to be responsible for the lowering of magnetic moment.

Copper(II) complexes of N-benzoylglycine (anhydrous) substituted phenoxy acetic acids, mandelic and benzilic acids are found to have sub-normal magnetic moment. This may be attributed to exchange interaction between copper(II) ions by a superexchange mechanism. Such results have been reported b for copper(II) formate tetrahydrate[16] and copper(II) formate bisurea dihydrate[17] and substituted phenoxy acetates[18].

Nickel(II) salts :

Nickel(II), a d^8 system, forms a large number of complexes which belong to one or another of three structural types, namely six coordinate octahedral with $^3A_{2g}$ ground term, associated with low orbital contribution to the magnetic moment (2.9 - 3.3 BM), four-covalent square planar diamagnetic with spin singlet ground term. From table I-4 it is evident that the values of the moments of Ni(II) in the complexes range from 3.0 to 3.3 BM. Hence a six-covalent octahedral structure may be ascribed to the three complexes studied. No structural assignment is attempted for Ni(II) mandelate dihydrate at this stage.

Cobalt(II) salts :

Cobalt(II) ion with d^7 has either octahedral or tetrahedral ligand field. The high spin octahedral complexes with $^4T_{2g}$ ground term possesses moments in the range 4.7 - 5.2 BM corresponding to three unpaired electrons, whereas the rarely occurring low spin complexes having ^2E_g ground term will have moment corresponding to only one unpaired electron (1.73 BM). In a high-spin tetrahedral complex the ground term is $^4A_2$ and the moment expected is between 4.4 and 4.8 BM. The magnetic moment values for cobalt(II) mandelate, malonate tartrate suggest that these complexes will have high spin

TABLE I - 4

MAGNETIC SUSCEPTIBILITY DATA FOR SOME FIRST ROW TRANSITION METAL CARBOXYLATES

Compound	Mol.formula	Molar suscep -tibility M x 10^6	Effec- tive magne- tic moment $\mu_{eff.}$ BM	T
Ni(II)lactate	$Ni(CH_3HOH.COO)_2.2H_2O$	3883	3.04	295
Ni(II)malonate	$NiCH_2(COO)_2.2H_2O$	4499	3.27	295
Ni(II)mandelate	$Ni(C_6H_5.CHOHCOO)_2.2H_2O$	5122	3.49	296
Ni(II)tartrate	Ni(OOC.CHOH.CHOH.COO)	4707	3.35	295
Co(II)lactate	$Co(CH_3.CHOH.COO)_2.2H_2O$	9616	4.79	295
Co(II)malonate	$CoCH_2(COO)_2.2H_2O$	11406	5.22	296
Co(II)mandelate	$Co(C_6H_5.CHOH.COO)_2$	10895	5.10	297
Co(II)tartrate	Co(OOC.CHOH.CHOH.COO)	10472	5.00	296
Mn(II)lactate	$Mn(CH_3.CHOH.COO)_2 3H_2O$	14932	5.97	297
Mn(II)malonate	$MnCH_2(COO)_2 2H_2O$	14993	6.00	298
Mn(II)mandelate	$Mn(C_6H_5.CHOH.COO)_2$	15630	6.14	295
Mn(II)tartrate	Mn(OOC.CHOH.CHOH.COO)	14730	5.93	298

octahedral symmetry. The value 4.79 BM for cobalt(II) lactate cannot rule out the possibility of tetrahedral configuration. The octahedral symmetry of this compound is indeed confirmed from the position and intensity of the absorption maxima of the electronic spectrum.

Mangenese(II) salts :

Compounds of bivalent manganese having d^5 electrons show both high and low spins. The high spin octahedral complexes are expected to show the magnetic moments very close to the spin-only value (5.92 BM) since the orbital contribution is negligible[19]. All the compounds are found to have values around this value, suggesting that they belong to the high spin category.

REFERENCES

1. Cotton, F. A., Faut, O. D. and Mague, J. T., Inorg. Chem., 3, 17 (1964).

2. Cotton, F. A. and Dunn, T. G., J. Amer. Chem. Soc., 84, 2013 (1962).

3. Cotton, F. A., Goodgame, D. M. L., Goodgame, M., and Haas, T. D., Inorg. Chem., 1, 565 (1962).

4. Dannister, E. and Cotton, F. A., J. Chem. Soc., 1878 (1960).

5. Ramsay, C. A. and Fergusson, J. E., J. Chem. Soc., 5222 (1965).

6. Cotton, F. A. and Sonderberg, R. H., J. Amer. Chem. Soc., 84, 872 (1962).

7. Cotton, F. A. and Wood, J. J., Inorg. Chem., 3, 245 (1964).

8. Drago, R. S. and Donohue, J. T., Inorg. Chem., 2, 572 (1963).

9. Gill, N. S. and Nyholm, R. S., J. Chem. Soc., 3997 (1959).

10. Orgel, L. E., J. Chem. Phys., 23, 1004 (1955).

11. Straub, D. K., Drago, R. S. and Donohue, J. T., Inorg. Chem., 1, 848 (1962).

12. Buffagni, S. and Dunn, T. M., J. Chem. Soc., 5105 (1961).

13. Figgis, B. N. and Lewis, J.,
cited in "Progress in Inorganic Chemistry"
edited by Cotton, F. A., Interscience
Publishers, New York (1964).

14. Kato, M., Jonassen, H. B. and Fanning, J. C.,
Chem. Rev., 64, 99 (1964).

15. Van Niekerk, J. N. and Schoening, F. R. L.,
Acta Cryst., 6, 227 (1953).

16. Martin, R. L. and Waterman, H.,
J. Chem. Soc., 1359 (1959).

17. Kishita, M., Inoue, M. and Kubo, M.,
Inorg. Chem., 3, 237 (1964).

18. Haffield, W. E., McGuire, H. M., Paschal, J. S.
and Whyman, R.,
J. Chem. Soc., A, 1194 (1966).

19. Cotton, F. A. and Wilkinson, G.,
"Advanced Inorganic Chemistry" (2nd Edn.), p.635,
Interscience Publishers, New York (1966).

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SUMMARY

S U M M A R Y

1. As part of our programme of spectro-structural studies of hydroxy acids and their metal complexes, the infrared spectra of benzilic acid (BA), mandelic acid(MA) and their several first row transition metal complexes with OH as well as OD groups have been investigated here.

In order to identify the bands due to alcoholic (C – $\overset{|}{\underset{|}{C}}$ — OH) group spectra of several related compounds along with their deuterated analogues have been examined. In the benzilate series having a tertiary alcoholic group two bands at ~1350 and ~1160 cm^{-1} are replaced on deuteration by a strong band near 860 cm^{-1}. Strong coupling between δ COH mode and δ CH (inplane ring) is considered to be the cause for the observed anomalous shift on deuteration. Similar anomaly is observed in mandelate series as well. The bands at 1365 and 1090 cm^{-1} of sodium mandelate (Na$\underline{M}$) are replaced on deuteration by 1040, 900 and 850 cm^{-1} bands in the deuterated product (Na$\underline{M}$-d_1). Strong coupling between δ COH and ν C-O modes is believed to be the reason.

Assignments of all the bands likely to be affected by coordination to a metal ion are tabulated. Based on the shifts in alcoholic group frequencies in general and

especially by an examination of OH mode, bidentate chelate structure involving both the hydroxy and carboxylate groups is proposed for all the complexes of the type $M(L)_2$, where M is divalent manganese, cobalt, nickel, copper and zinc and 'L' is benzilate or mandelate ion. The notable exception is copper(II) benzilate which shows one free and one coordinated hydroxyl groups. Further, the OH frequency is found to vary with the metal ions and the frequency of the coordinated hydroxyl group is indeed found to change as Mn > Co > Ni > Cu < Zn, suggesting that the Irving-Williams order of relative stability is followed by the present series of compounds.

The band at 1176 cm^{-1} (δ C-OH) of benzilic acid is shifted to 1270 - 1290 cm^{-1} upon coordination to a metal ion. The corresponding OD mode is also found at higher frequency ($\sim$ 920 cm^{-1}) in benzilate complexes on compared to the ligand (KB, $\sim$ 870 cm^{-1}) and near 1040 cm^{-1} in mandelate complexes against 850, 900 cm^{-1} in the ligand (NaM). This mode, however, does not show any pronounced sensitivity to changes in the metal ion.

2. Infrared spectrum of N-benzoylglycine (BGA), which exists in the usual (non-zwitterion or non-polar) form has been investigated and compared with its para- bromo derivative and N-acetylglycine. While studying the characteristic bands due to the amide (CONH) group by the

study of deuterated compounds, it was found that the Amide II band was to predominently ν CN mode while the Amide III band was chiefly the δ NH vibration. Further, while a single band was found for ν NH mode, a doublet is seen in the corresponding ND region. Fermi resonance of ν ND and a summation band of Amide II' and III' is considered to be the cause of this splitting.

From an examination of COOH group frequencies (ν OH, ν C=O, δ OH out of plane) a structure involving polymeric chains of COOH group is proposed for N-benzoylglycine, while its p-bromo derivative exists as a cyclic dimer. These results have been substantiated by preliminary x-ray analyses.

Several complexes of N-acetyl and N-benzoylglycines are studied in the hydrate, anhydrous and deuterated forms. Based on ν NH and Amide I, II and III bands a salt-like structure without any amide coordination is proposed for copper(II) N-benzoylglycinate. The differences in the spectra of the tetrahydrate and the anhydrous product are attributed to hydrogen bonding between the amide group and water molecules, resulting in lowering of ν C=O (Amide I). In contrast to copper(II) salt, zinc(II) N-benzoylglycinate indicates coordination through the amide oxygen. Spectral data of other metal complexes (about ten) were complicated by strongly held water of crystallization and hence could not be utilized fruitfully.

3. Assignments of bands due to $\overset{+}{N}H_3$ and COO^- groups of DL-β-phenylalanine and those of $\overset{+}{N}H_3$ and COOH groups of its hydrochloride were made by the study of their deuterated analogues as well. The low frequency (850 cm^{-1}) of δ OH out of plane is explained as arising out of interaction of the chlorine atom with the bonded COOH groups.

Spectra of its first row transition metal complexes indicate a chelate ring involving coordination through both the NH_2 and COO^- groups. Shifts in the NH_2 mode are found to be maximum in the copper(II) complex. NH_2 stretching modes in the remaining complexes are found at $\sim$3360, 3300 cm^{-1}. NH_2 deformation and rocking modes are also affected by coordination. However, these frequencies do not indicate any definite order. The NH_2 wagging mode in complexes however changes in such a manner upon change of metal ion, as to follow the Irving-Williams order of relative stability.

4. Spectra of nicotinic acid(NA) isonicotinic acids(INA) and their hydrochlorides along with the deuterium substituted products have been analysed. The COOH frequencies are indicative of non-dimeric structure for the acids. The possibility of proton transfer is suggested to explain the two strong bands at $\sim$2350 and $\sim$1900 cm^{-1}, ascribable to ν OH a modes considering the basic nature of nitrogen. The characteristic modes of $\overset{+}{N}H$ group and the variation in pyridine

ring bands upon formation of pyridimium ion are mentioned.

Spectra of several complexes have been studied. Changes observed primarily in bands at 650 - 400 cm^{-1} region have been discussed in order to suggest probable structure for the nicotinate complexes. The COO^- wagging modes in these complexes follow Irving-Williams order of relative stability.

5. Spectra of eight substituted phenoxyacetic acid along with the deuterated analogues are investigated. These spectra showed splitting of bands due to ν C=O, δ CO, δ OH out of plane (and also in some cases ν C-O + δ OH modes). Several possible causes have been discussed; of which presence of two forms in the crystal is considered the most likely one, and arguments in favour of this are presented.

Spectra of complexes of some of these have been analysed which all indicate uncoordinated ether oxygen atom.

6. Electronic spectra of cobalt(II) N-benzoyl and N-acetyl-glycinate in DMSO and DMF indicated presence of Co^{+2} ion at least in part in the tetrahedral (pseudo) configuration.

7. While presenting magnetic data for several cobalt(I), nickel(II), manganese(II) and copper(II) complexes, and stereochemistry thereof, the causes for subnormal magnetic moments of copper(II) complexes are discussed.

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