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SPECTROCHEMICAL PROPERTIES AND THERMAL STABILITIES

OF SOME

TRANSITION METAL COMPLEXES

A Thesis submitted to the

UNIVERSITY OF BOMBAY

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in

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By

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P A R T - I

STUDIES ON THE SPECTROCHEMICAL PROPERTIES  
OF THE MALONATE, MALATE AND LACTATE COMPLEX SALTS

## I N T R O D U C T I O N

In the past two decades or so there has been a resurgence of world-wide interest in the study of coordination compounds and this is now a stage of rapid development in both theoretical and applied aspects. The number of publications dealing spectrostructural studies alone is very large indeed. In the present work we are particularly interested in the application of the infrared spectroscopic technique to the study of complexes of the transition metals. Two excellent reviews<sup>1,2</sup> on the subject have been published very recently, and therefore an exhaustive review of it has not been attempted. In this, instead a background of the subject is given very briefly.

The energy of a molecule can be qualitatively associated with (a) the rotation of the molecule as a whole, (b) vibration of the constituent atoms, and (c) motions of the electrons as a whole. The translational energy can be ignored. Because rotational levels are relatively close to each other, transitions between these levels occur at low frequencies in the range between  $1\text{ cm}^{-1}$  and  $10^2\text{ cm}^{-1}$ . The separation of the vibrational energy levels is greater and transitions occur at higher frequencies ( $10^2\text{ cm}^{-1}$  -  $10^4\text{ cm}^{-1}$ ) than do the rotational transitions. Lastly, the

electronic energy levels are usually far apart and the spectra are observed in the range between  $10^4 \text{ cm}^{-1}$  to  $10^5 \text{ cm}^{-1}$ .

The vibrational spectra can be observed as infrared or Raman spectra. The former originate in transitions between two vibrational levels of the molecule in the electronic ground state and are usually observed as absorption spectra in the infrared region; on the other hand the latter originate in the electronic polarization caused by ultraviolet or visible light and observed as Raman shifts from the incident frequency.

#### The physical principles of infrared absorption by molecules

The principle can be easily visualized with diatomic molecule as a model. This can then be extended to polyatomic molecules, the treatment of which is more complicated and less easy to visualize.

Consider a heteropolar diatomic molecule A-B. The atoms in it are never stationary and the distance between them is a periodic function of time (i.e. a stationary alternating electric field or an oscillating dipole). If it is exposed to infrared radiation which consists of energy packets or wave

packets of moving alternating electric field, the energy absorbed must be such that the molecule may exactly reach a higher allowed energy level. That is for a molecule

$$E_{\text{quantum}} = \Delta E_{\text{molecule}} = \left[ (1 + \frac{1}{2})hc\omega - (0 + \frac{1}{2})hc\omega \right]$$

$$= hc\omega \text{ vibration}$$

But

$$E_{\text{quantum}} = hc\omega_{\text{quantum}};$$

$$\text{hence } \omega_{\text{quantum}} = \omega \text{ vibration}$$

or in order for the quantum of radiation to be absorbed, the molecular vibration frequency ( $\omega$  vibration) must be identical to the frequency of the radiation ( $\omega$  quantum). unless the frequency of one harmonic phenomenon is equal to that of the other, they do not interact. The frequency range over which absorption occurs is generally referred to as an absorption band, for it has a finite width.

In infrared spectroscopy, we are generally concerned with the absorption and not the emission process. The observable intensity of light absorbed or emitted in any transition depends on how often the 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 the molecules which are in the initial state to make the transition. The ratio of

molecules in the first excited state to the number in the ground state according to the Boltzmann distribution law, is given by  $n_1/n_0 = \exp - (E_1 - E_0)/kT$ . Even for a relatively low energy vibration, say  $450 \text{ cm}^{-1}$ ,  $n_1/n_0$  is found to be  $1/10$  and for  $1000 \text{ cm}^{-1}$  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. The transition with  $\Delta n = 1$  is called the fundamental transition, that with  $\Delta n = 2$  the first overtone, with  $\Delta n = 3$  the second overtone etc. It is found that for a sample of the proper thickness and concentration to give a convenient intensity to the fundamental, even the first overtone is not generally observed or is just barely seen.

For a diatomic molecule the vibrational frequency is given by:

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

where  $K$  is the force constant of the bond and  $\mu$  is the reduced mass of the system, defined as  $\mu = \frac{m_A \cdot m_B}{m_A + m_B}$ ,

$m_A$  and  $m_B$  being the masses of the atoms A and B respectively.

### Vibrational spectra of polyatomic molecules

While only one vibrational mode can occur in a diatomic molecule corresponding to the periodic change in the one internuclear distance, many vibrational modes are possible in polyatomic molecules. The number of vibrational modes possible in a molecule containing 'n' atoms will be  $(3n-5)$  for linear molecule and  $(3n-6)$  for non-linear molecule. In a diatomic molecule a restoring force proportional to the force constant acts to restore the molecule from a distorted configuration to its equilibrium configuration. In a polyatomic molecule, there are a number of restoring forces corresponding to all of the various internuclear distances in the molecule. These are associated with the various modes of the molecular vibrations usually described as stretching (symmetric and asymmetric), bending, rocking, wagging, twisting, etc. frequencies. Sometimes there is considerable coupling and other disturbances (interactions) between these vibrations. The nature of the vibrations occurring in polyatomic molecules is governed by the molecular symmetry in a way which, in principle, may be formulated rigorously with the help of group theory<sup>3</sup>. Fortunately, all of these forces are not of comparable importance and the relatively weaker ones can be neglected as a good approximation to extract chemically useful and interesting informations.



### Ligand and skeletal vibrations

It is implied from the brief outline given about infrared spectra that a series of data concerning the molecular structure such as geometric properties (bond distances and bond angles) or dynamic relationships such as force constants, may be obtained.

The utility of infrared spectroscopy in determining molecular structures or correlation with other physical properties is based upon the assumption that many molecular groups give rise to characteristic absorption frequencies and intensities which are only slightly affected by the other parts of the molecule. Thus functional groups and structural units such as  $\text{OH}^-$ ,  $\text{CO}$ ,  $\text{CO}_3^{2-}$ ,  $\text{COOH}$ ,  $\text{NH}_4^+$ ,  $\text{CH}_3$  and phenyl absorb in a more or less narrow region of the spectrum. But, as indicated before, the rest of the molecule and the environment certainly do produce group frequency shifts often through the interplay of many factors such as (1) external environment (change of phase or of crystal form, solvent, hydrogen bonding etc.) and (2) internal change (molecular geometry, mass of substituent atoms to groups, mechanical coupling between vibrations, steric strains and electrical influences). Despite the large number of variables which go to determine the position, intensity and shape of an individual absorption band, it is often possible

to devise conditions for isolating one or two from the rest so that they can be studied separately. The study of carefully selected group frequency shifts enables correlation with changes in physical and structural properties.

The study of the spectra of coordination complexes can thus provide useful information, for example, on the nature of the metal-ligand bond and the stability of the complex. For such purposes it is necessary to know the spectra of simpler polyatomic cations and anions (e.g.  $\text{NH}_4^+$ ,  $\text{CO}_3^{2-}$ ,  $\text{COOH}$ ,  $\text{CN}^-$  etc.), which are commonly present as such or as ligands in complexes. Extensive compilation of such data have been given by Miller and Wilkins<sup>4</sup>, Bellamy<sup>5</sup> and also by Lawson<sup>6</sup>.

Various important types of skeletal arrangements linear, planar, tetrahedral, trigonal-bipyramidal and octahedral are found. Diagrammatic representation of the various vibrational modes have been given in the literature<sup>1</sup>. Since all these types of arrangements are found in coordination compounds, a brief mention of a few of them is made, taking specific examples as illustrations:

### Linear MX<sub>2</sub> groups

The linear cyanide complexes  $[\text{Ag}(\text{CN})_2]^-$ ,  $[\text{Au}(\text{CN})_2]^-$  and  $[\text{Hg}(\text{CN})_2]^-$  have recently been studied in detail by Jones<sup>7</sup>. The symmetric and asymmetric cyanide stretching modes,  $\nu_1$  and  $\nu_3$ , occur at frequencies intermediate between those for the free  $\text{CN}^-$  ion ( $2070\text{--}2100\text{ cm}^{-1}$ ) and covalently bound cyanides (e.g.  $\text{CH}_3\text{CN}$ ,  $2283\text{ cm}^{-1}$ ). For silver the existence of  $[\text{Ag}(\text{CN})_2]^-$ ,  $[\text{Ag}(\text{CN})_3]^{2-}$  and  $[\text{Ag}(\text{CN})_4]^{3-}$  and for gold only  $[\text{Au}(\text{CN})_2]^-$  were shown. The CN stretching frequency shifts regularly from  $2135\text{ cm}^{-1}$  in  $[\text{Ag}(\text{CN})_2]^-$ , to  $2105\text{ cm}^{-1}$  in  $[\text{Ag}(\text{CN})_3]^{2-}$  to  $2092\text{ cm}^{-1}$  in  $[\text{Ag}(\text{CN})_4]^{3-}$  towards the value for the free  $\text{CN}^-$  ion ( $2080\text{ cm}^{-1}$ ) suggesting that the bonding becomes more ionic as the number of bound  $\text{CN}^-$  groups increases.

### Planar MX<sub>4</sub> groups

This group represented by planar  $[\text{AuCl}_4]^-$ ,  $[\text{Au}(\text{Br})_4]^{2-}$  and  $[\text{Pt}(\text{CN})_4]^-$  has both in-plane and out-of-plane vibrations. In the latter<sup>8</sup> Pt-C stretch occurs at  $505\text{ cm}^{-1}$  and the C-N stretch at  $2150\text{ cm}^{-1}$ ; the metal-carbon stretching vibrations showed variations in some cases but for CN stretching the variation is rather slight. For this reason the out-

### Tetrahedral $MX_4$ groups

For a regular tetrahedral molecule of the type  $A(BC)_4$ , there are 21 vibrational degrees of freedom of which, several of them are triply and doubly degenerate modes.  $Ni(CO)_4$ ,  $Co(CO)_4^-$  and  $[Cu(CN)_4]^{3-}$  may be considered as belonging to this group. Co-C bond order has been found to be higher and the CO bond order lower<sup>9</sup> than the corresponding bonds in  $Ni(CO)_4$ .

### Octahedral $MX_6$ groups

$SF_6$ ,  $MoF_6$ ,  $[SiF_6]^{2-}$ ,  $[PtCl_6]^{2-}$ ,  $Cr(CO)_6$  and  $Mo(CO)_6$  belong to this group. Hawkin et al<sup>10</sup> described the 13 fundamental vibrations of  $A(BC)_6$  type molecules and studied the infrared spectra of the last two molecules in the gaseous state. Later studies by Danti and Cotton<sup>11</sup> suggested change in the earlier assignments.

### Carboxylic acid complexes

Carboxylic acids normally exist in dimeric form with strong hydrogen bonding between the carbonyl and hydroxyl groups of the two molecules. Some acids are capable of forming internal hydrogen bonds also. For this reason the carbonyl and O-H stretching frequencies are considerably modified.

The infrared spectra of metal carboxylates have been studied extensively. Lecompte and coworkers<sup>12</sup> examined a very large number of salts of organic acids. When ionization occurs, giving  $\text{COO}^-$  group, resonance is possible between the two C-O bonds. In consequence the characteristic carbonyl absorption in the region  $1750\text{--}1700\text{ cm}^{-1}$  vanishes and is replaced by two bands between  $1610\text{--}1550\text{ cm}^{-1}$  and  $1400\text{--}1300\text{ cm}^{-1}$ , which correspond to antisymmetrical and symmetrical vibrations of the  $\text{COO}^-$  structure. Of these bands, the former is very characteristic and more constant in frequency, while many other skeletal vibrations may occur in the range  $1400\text{--}1300\text{ cm}^{-1}$ .

If the carboxyl group is coordinated to a metal, the symmetry is lowered and splitting of the degenerate modes occurs together with the appearance of new bands. The antisymmetric  $\text{COO}^-$  stretching frequency has been found to be quite sensitive to a change in the metal and therefore, a relationship between this frequency and some physical property of the metal has been discussed by several investigators. Theimer and obtains<sup>13</sup> claimed that the radius of the metal atom is the main factor in determining the  $\text{COO}^-$  stretching frequency. Kagarise<sup>14</sup> indicated that the electronegativity of the metal is important. Recently,

Ellis, et al<sup>15</sup>, suggested that the  $\text{COO}^-$  stretching frequency in complexes of carboxylic acids may be a complicated function of the mass, radius and electronegativity of the metal.

In studies of acetylacetonate, oxalato and a few other related complexes, attention has been given to the effect of coordination on the CO stretching frequencies and its correlation with the stability constants of the complexes.

Bellamy and Branch<sup>16</sup> and Lecompte<sup>17</sup> report that the first CO absorption at about  $1580 \text{ cm}^{-1}$  is essentially constant for all metal-acetylacetonates, except Ni(II) and Mg(II). The Mg-complex may be out of line due to the small mass of the metal atom and the Ni-complex due to possible trimeric form in the crystal. The constancy of the strong C-O frequency is attributed to the operation of resonance effects within the chelate ring to minimize any variation due to the different metal atoms. Holtzclaw and Collman<sup>18</sup> on the other hand, obtained remarkable correlation between band position and the known order of the stability constants for the acetylacetonates of Na(I), Ni(II), Mg(II), Cd(II), Mn(II), Co(II), Cu(II) and Pd(II), the frequencies

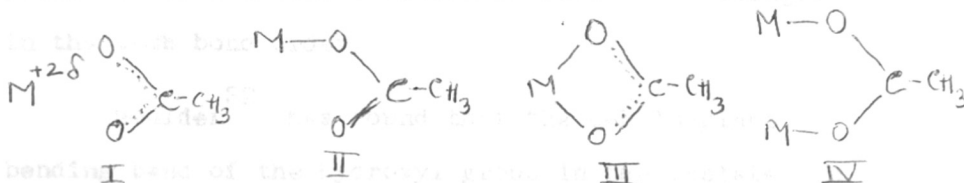
decreasing in the same order, excepting Ni(II). They explained that as the M-O bond strengthens, the bond length and hence the stretching frequency of the C-O bond decreases. However, the validity of this correlation has been questioned<sup>19</sup>, as a few workers have noticed no band above  $1600\text{ cm}^{-1}$ , to be unambiguously assigned as carbonyl stretching frequency.

Fujita et al<sup>20</sup> related the infrared data with the thermodynamic stability of oxalate complexes considering shifts of vibration modes whose assignments are not so certain. Mizushima et al<sup>21</sup> also attempted to determine the degree of covalency of metal-oxygen bonds from measured frequency shifts of the COO stretching vibrations.

Quagliano and coworkers<sup>22</sup> studied some metal complexes of glycine. Noting the shift in the N-H stretching frequency from its position in glycine, they concluded that the oxygen-metal bonds in these complexes must be essentially ionic whereas the nitrogen-metal bond is covalent. This conclusion may also be considered as rather extreme, because a band at  $3300\text{ cm}^{-1}$  is observed while there are no uncoordinated  $\text{NH}_2$  groups in these complexes.

There are no known solid state effects which could raise this frequency over that what would otherwise be in the free molecule. Svatos et al<sup>23</sup> have shown that the effects of coordination, hydrogen bonding, configuration of the complex and the solvent result in a decrease in the N-H stretching frequencies.

In examining the effect of coordination on the  $\text{COO}^-$  stretching frequency, it is important to analyse the results on the basis of the structures of these complexes, as determined by x-ray analysis. For example, the acetate ion ( $\text{ac}^-$ ) may coordinate with a metal in one of these ways:



According to x-ray analysis, the structure of sodium formate<sup>24</sup> is I, the two CO bond lengths being equal.

$\text{Li}(\text{ac}) \cdot 2\text{H}_2\text{O}$ <sup>25</sup> has structure II and it is also formed by metals of higher valency.  $\text{Zn}(\text{ac})_2 \cdot 2\text{H}_2\text{O}$ <sup>26</sup> and

$\text{Na} [\text{UO}_2(\text{ac})_3]$ <sup>27</sup> are reported to have structure III.

The structure IV was found in  $\text{Cr}_2(\text{ac})_4 \cdot 2\text{H}_2\text{O}$ <sup>28</sup>,  $\text{Cu}_2(\text{ac})_4 \cdot 2\text{H}_2\text{O}$ <sup>29</sup> and  $\text{Zn}_4\text{O}(\text{ac})_6$ <sup>30</sup>.

It will be interesting to compare the spectra of the four types of metal acetates mentioned above. In a series of salts having structure II, the antisymmetric



$\text{COO}^-$  stretching frequency will increase, as the M-O bond becomes stronger. Nakamoto and coworkers<sup>31</sup> have found that in symmetrical bridged structure IV, both the  $\text{COO}^-$  stretching bands are shifted in the same direction upon changing the metal.

The infrared spectra of metal salts of oxyacids such as lactic and tartaric acids, have been studied by several investigators, because of the considerable interest in the assignment of the OH vibration frequencies since it is particularly sensitive to the effects of coupling, inter-molecular association, proximity of a chelated cation as well as to changes in the C-OH bond order.

Goulden<sup>32</sup> has found that the O-H in-plane bending band of the hydroxyl group in the lactate ion ( $1275 \text{ cm}^{-1}$ ) is shifted to  $1390 \text{ cm}^{-1}$  upon chelation to zinc. From the infrared spectral analysis Girard and Lecompe<sup>33</sup> proposed a structure for potassium salts of bismuth and antimony tartrates and also Kirschner and Kiesling<sup>34</sup> suggested a structure of copper tartrate.

#### Coordinated water molecules

Rather little has been reported concerning the spectra of aqua complexes. Water in inorganic salts

may be classified either as lattice water or coordinated water. The former term refers to water molecules held in the crystal lattice either by weak hydrogen bonds or by weak coordinate bonds, whereas the latter denotes water molecules held strongly in the first coordination sphere of the metal. Although x-ray and neutron diffraction analysis provide direct information concerning the geometry of the water molecules in the crystal, studies of vibrational spectra are also useful for this purpose.

In general, lattice water absorbs at  $3550-3200\text{ cm}^{-1}$  (antisymmetric and symmetric OH stretching modes) and at  $1630-1600\text{ cm}^{-1}$  (H-O-H bending mode)<sup>35</sup>. Water vapour exhibits absorption at  $3756$ ,  $3652$  and  $1592\text{ cm}^{-1}$  respectively due to the three modes mentioned above<sup>36</sup>. Lattice water also absorbs in the low frequency region ( $600-300\text{ cm}^{-1}$ ) owing to librational modes.

The absorption due to water in aquo complexes will not differ greatly from that of water molecules if the metal to oxygen bond is purely ionic. A number of new bands due to wagging, rocking and twisting motions of the  $\text{H}_2\text{O}$  molecule may be observed below  $1000\text{ cm}^{-1}$ . The vibration frequencies of these bands will be determined by the outer ion effect and the coordination effect.

Elsken and Robinson<sup>37</sup> studied the infrared spectra of alkali metal and alkaline earth halide mono and dihydrates where the distance between the metal to oxygen is pretty long. The absorption bands between  $600\text{--}300\text{ cm}^{-1}$  were ascribed to the libration modes of bound water molecules in the crystal. The values of these frequencies agree well with those of other investigators<sup>38</sup>. These frequencies are mainly determined by the outer ion effect.

Fujita and coworkers<sup>39</sup> have investigated different hydrated complexes such as copper(II) and nickel(II) glycinate and copper(II) sulphate with a view to assign certain bands of coordinated water molecules appearing in the region  $1000\text{--}800\text{ cm}^{-1}$ , depending upon the strengths of the coordinate bond and of the hydrogen bonding to neighbouring atoms. Quagliano and coworkers<sup>40</sup>, on the basis of deuteration studies have assigned the bands due to coordinated water molecules in Ni(II) and Co(II) complex of N-pyridine oxide. The bands have been observed at  $735$  and  $685\text{ cm}^{-1}$  in Co(II) and  $755$  and  $702\text{ cm}^{-1}$  in Ni(II) complex.

Blyholder and Vergez<sup>41</sup> have reported a  $820\text{ cm}^{-1}$  band in the hexaquo complexes of chromium(III).

Thus, a study of the literature shows that similar type of study has been made by Gammo<sup>42</sup>, Kolatl and Powell<sup>43</sup> have observed that the change in the

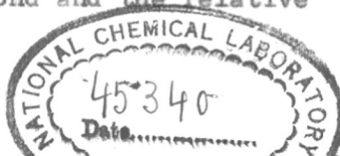
hydration number is accompanied by a change in the amino acid ligand from a pentadentate to a hexadentate configuration, which has been indicated by the infrared spectroscopic studies.

Very recently, Nakagawa and Shimanouchi<sup>44</sup> have investigated the  $\text{OH}_2$  ligand vibrations in some details. Two bands have been ascribed to the coordinated water molecules. In this the potential which governs the wagging frequency is different from that for rocking vibration, unlike in the case of  $\text{CH}_2$  wagging and rocking motion of saturated compounds. The normal vibration calculations are, therefore, not useful to distinguish these two vibration modes. It has been shown by Miyazawa<sup>45</sup> that the absorption due to libration mode about A axis (wagging) is stronger than that about C axis (rocking) for the bound water molecules in nitrogen matrix. These conclusions were drawn on the basis of approximate intensity calculations assuming the fixed dipole moments. The stronger of the two bands observed has been assigned to the wagging motion of the ligand.

Thus, a study of the literature concerning the infrared spectra of the ligands in metallic complexes, has indicated that useful information on the structure, nature of the metal-ligand bond and the relative

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stability of a complex can be obtained. However, sometime there are uncertainties in the assignment of absorption bands and conflicting interpretation of infrared data because the vibrations are affected by a variety of factors and the correlation procedures are of a semi-empirical nature. It seemed worthwhile to study more extensively the infrared spectra of coordinate complexes to provide information on their structural properties and for spectro-structural correlations in related series of compounds.

In the present investigation, the complexes of malonic, malic and lactic acid with the first row transition metals  $[\text{Cu(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Zn(II)}, \text{Cd(II)} \text{ and } \text{Mn(II)}]$ , are studied with a view to obtaining information regarding their structure, nature of the metal-oxygen bonds and the relative stabilities of the complexes. In order to help in the assignment of bands due to water of crystallisation, dehydrated and subsequently deuterated compounds have also been studied.

In Part II of the thesis studies on the thermal stabilities of these complexes in the solid state using the thermogravimetric technique have also been reported. The activation energies of dehydration and decomposition have been calculated from the mass loss kinetic data.

Further, an order of thermal stabilities observed have been compared with that obtained from infrared absorption studies.

All chemicals (metal carbonates, malic and malonic acid) used were of 'Chemically Pure' or better quality. Further purification was done by recrystallisation.

Heavy water, having isotopic purity of 99.4% was obtained from the Atomic Energy Establishment, Bombay.

Preparation of disodium or potassium salt of malonic and malic acid:

An aqueous solution of the acid was titrated to a pH 7.0 to 8.0 against sodium or potassium hydroxide. The solution was then evaporated to dryness on a water bath.

Preparation of lithium lactate:

Lithium lactate was prepared by addition of lithium carbonate to aqueous solution of the acid, till the evolution of carbon dioxide ceases, and the reaction is complete. The solution is evaporated almost to dryness.

Preparation of salts of divalent transition metals:

Various methods have been reported to prepare salts of the transition metals (Cu, Ni, Co, Mn, Zn and Cd), e.g., by reacting the carboxylic acids, with the corresponding metal hydroxide,<sup>46</sup> nitrate,<sup>34</sup> carbonate,<sup>47</sup> etc.

T A B L E - 1

However, we have found that in case of complex compounds where a possibility of a number of complexes exists, the carbonate method gave reproducible results. The product obtained is free from the anionic impurities.

#### Carbonate Method:

To an aqueous solution of an acid, excess of the metal carbonate is added. The mixture is warmed gently on a water bath till the evolution of carbon dioxide ceases and the reaction is complete. The solution is concentrated and allowed to stand in a refrigerator for 24 hours for crystallisation.

#### Purification of coordinate complexes:

The complex compounds were crystallized twice from water, whenever possible. Insoluble compounds were washed repeatedly with hot water.

These were analysed for their carbon and hydrogen contents, using the standard micro-analytical method and the results were found to be within 1% of the calculated values. These results are given in Table (1).

#### Dehydration of compounds:

Finely powdered compounds (so as to expose more



# TABLE - 1

## RESULTS OF MICRO-ANALYSIS

### Some transition metal lactates

Metal ion	% Carbon		% Hydrogen		Molecular formula
	Found	Calc.	Found	Calc.	
Cu(II)	26.7	25.9	4.84	5.05	$\text{Cu}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$
Ni(II)	25.0	24.2	5.74	5.50	$\text{Ni}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$
Co(II)	25.10	24.2	5.83	5.50	$\text{Co}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$
Mn(II)	24.3	25.1	5.47	5.58	$\text{Mn}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$
Cd(II)	24.0	24.49	3.9	3.44	$\text{Cd}(\text{C}_3\text{H}_5\text{O}_3)_2$

### Some transition metal malates

Cu(II)	18.74	19.23	3.1	4.01	$\text{Cu}(\text{C}_4\text{H}_4\text{O}_5) \cdot 3\text{H}_2\text{O}$
Ni(II)	18.7	19.62	4.62	4.09	$\text{Ni}(\text{C}_4\text{H}_4\text{O}_5) \cdot 3\text{H}_2\text{O}$
Co(II)	19.96	19.55	4.45	4.08	$\text{Co}(\text{C}_4\text{H}_4\text{O}_5) \cdot 3\text{H}_2\text{O}$
Mn(II)	19.87	19.94	4.2	4.15	$\text{Mn}(\text{C}_4\text{H}_4\text{O}_5) \cdot 3\text{H}_2\text{O}$
Cd(II)	17.0	16.1	2.49	3.36	$\text{Cd}(\text{C}_4\text{H}_4\text{O}_5) \cdot 3\text{H}_2\text{O}$

### Some transition metal malonates

Cu(II)	17.0	16.4	3.56	3.65	$\text{Cu}(\text{C}_3\text{H}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$
Ni(II)	18.36	18.3	3.42	3.04	$\text{Ni}(\text{C}_3\text{H}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$
Co(II)	18.78	18.2	3.33	3.04	$\text{Co}(\text{C}_3\text{H}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$
Mn(II)	19.58	18.8	3.53	3.13	$\text{Mn}(\text{C}_3\text{H}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$
Cd(II)	14.6	14.4	2.7	2.4	$\text{Cd}(\text{C}_3\text{H}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$

The number of water molecules were confirmed by the thermogravimetric analysis.

surface), kept in a glass-boats, were dried at  $130^{\circ}\text{C}$  over  $\text{P}_2\text{O}_5$  for 36 hours in vacuo (1 mm.Hg.). An electrically controlled oven or a Fischer-Dryer with chlorobenzene (b.p.  $130-132^{\circ}\text{C}$ ) was used for this purpose.

#### Preparation of deuterated analogues of the acids:

##### Malonic and malic acid

The acids were dissolved in a large excess (ten times) of heavy water, crystallised after seven days, dried in vacuum and used directly without any further purifications.

##### Lactic acid

Lactic acid and a ten fold excess of heavy water were refluxed on a water-bath for one hour. Water was then removed by vacuum distillation. Deuterated acid, thus formed, was distilled under reduced pressure.

##### Deuteration of the complex salts

Quagliano et al<sup>40</sup> obtained deuterated samples by crystallising the compounds from  $\text{D}_2\text{O}$ .

This method cannot be used when the compounds are insoluble in water. We have achieved the deuteration by following method:

To the dehydrated compound, a small amount of heavy water was added. The product was then dried in vacuum and used immediately.

#### SPECTRAL MEASUREMENTS

All spectra were recorded on a double pass Perkin-Elmer Spectrophotometer-Model 221. A sodium chloride prism was installed for usual records and the instrument was equipped with a diffraction grating (blazed for 3.75 microns in the first order and ruled 240 lines/mm) in place of conventional Littrow mirror, when high resolution was desired in the wavelength region 2.5 to 6.9 microns.

Calibration of the instrument was checked by a standard polystyrene film, everytime before recording the spectra.

Spectra of hydrated compounds were studied in freshly prepared potassium bromide disks and in order to check any possible changes of a substance in the disk, these were then taken in Nujol mulls.

The following procedure was used to prepare a pellet:

An intimate mixture of finely powdered (particle size 53 microns or less) alkali halide and

about 0.5% sample was evacuated to 1 mm.Hg. in a special steel die<sup>48</sup> and then subjected to a high pressure of about 10,000 lbs./in<sup>2</sup> for three minutes. The pellet then formed, was removed by applying gentle pressure.

The detailed discussion of the merits and demerits of the disk method has been given by Cotton<sup>1</sup>. However, a few of the more important points relevant to our studies are mentioned in the following:

#### Effect of moisture

Water present in the disk may cause serious interference to the sample molecules in the disk. We have observed that when dehydrated samples are studied in alkali halide disks, spectra of partially hydrated compounds are observed. Spectra of deuterated compounds are also not of good quality. This is because of the partial conversion of the deuterated compound into the original compound.

#### Chemical changes during pelleting

Maloche and Kalbus<sup>49</sup> have observed that the spectra of some inorganic compounds in disk are different from those in mulls. This difference is

mostly due to the exchange of anions of the salts with the bromide ion. These reactions are facilitated by the presence of water in the disk<sup>50</sup>. Amarkasu and Ito<sup>51</sup> observed that the spectra of some dicarboxylic acids in alkali halide disks are identical with those of the monosodium salts of these acids taken in nujol mull. However, recent works of Quagliano et al<sup>52</sup> and Hargreaves and Stevinson<sup>53</sup> do not indicate any such interactions. Our results agree with those of Quagliano et al<sup>52</sup>.

Durie and Szewczyk<sup>54</sup> have observed anomalous strong absorption in the hydroxyl region in case of compounds which do not contain such group.

Farmer<sup>55</sup> has reported anomalous spectra of carboxylic acids and phenols. These anomalies have been ascribed to the absorption of the sample molecules on the surface of the alkali halide through the hydroxy group of the compound.

Recent work of Flett<sup>56</sup> indicated that with extreme precision and precautions pellet technique can be used for quantitative work. An important result obtained by him is that the intensity of the antisymmetric vibration of the ionized carboxyl group is four times the intensity of the  $C = O$  stretching vibration of the carboxyl group.

Temperature studies can be done conveniently with the disk method. Nash et al<sup>57</sup> have studied the transition of N-N diethyl  $\alpha$ -amino propionic acid at elevated temperatures.

Because of possible uncertainties in the pellet spectra, these were always confirmed by the mull spectra. We have not used the disk technique to study the spectra of dehydrated and deuterated compounds, because of the observed changes (due to moisture) in the disks.

## RESULTS AND DISCUSSION

Assignment of infrared absorption bands

In the assignment of the absorption bands in the spectra of malonic, malic and lactic acids and their complexes, particular attention has been given to the acid and alcohol groups, since these are the ones involved in the binding with the metal ions. The results could be interpreted in terms of normal vibration or coordinate analysis, but the procedures are much involved and complicated. However, the identification and interpretation of the observed bands can be facilitated if the expected (infrared active) vibration modes and their frequencies are known on the basis of critically analysed data collected from the literature. Then a semi-empirical correlation procedure can be followed to check the final assignments.

The ranges of frequencies of carboxylic acid, COOH and alcohol groups, pertinent to our studies are compiled and listed in Tables (2) and (3).

It has been mentioned earlier that it becomes difficult to make definite assignments due to the appearance of either a large number of bands in the region of interest or by the absence of an expected band.

# TABLE - 2

## INFRARED ABSORPTION FREQUENCY RANGES OF COOH AND COOD GROUPS

Frequency (cm <sup>-1</sup> ) range	Vibrational Mode
3650-3120	O-H stretching (monomeric form)
3100-2900	O-H stretching (dimeric form)
2700-2500	Summation bands
2528-2215	O-D stretch (monomeric form)
1917-1775	O-D stretching (dimeric form)
1725-1700	C=O stretching sat. aliphatic acids
1670-1650	Acids showing internal H bonding
1620-1550	COO <sup>-</sup> stretching (antisymmetric)
1440-1390	O-H deformation and/or C-O stretching
1420-1300	COO <sup>-</sup> stretching (symmetric)
1320-1211	O-H deformation and/or C-O stretching
950-900	O-H out-of-plane deformation
674-639	O-D out-of-plane deformation



TABLE - 3

Infrared absorption frequency ranges  
of alcoholic C-OH group

Frequency ( $\text{cm}^{-1}$ ) range	Vibrational Mode
3650-3590	C-H stretching (free)
3400-3200	O-H stretching (polymeric association, bridges broken on dilution)
2591-2549	O-D stretching (free)
2414-2272	O-D stretching (polymeric association, bridges broken on dilution)
1410-1310	O-H deformation (tertiary alcohol)
1350-1260	O-H deformation (secondary and primary alcohol)
near 1150	C-O stretching (tertiary alcohol)
near 1100	C-O stretching (secondary alcohol)
near 1050	C-O stretching (primary alcohol)
1028-930	O-D deformation (tertiary alcohol)
958-895	O-D deformation (secondary and primary alcohol)

It has, therefore, been very helpful to use the process of making known structural changes in the molecule to make known changes in the spectrum. In a coordination compound the absorption bands due to the ligand are first assigned definitely. The spectrum of the complex can then be considered essentially as the spectrum of the ligand wherein some of the vibrations are perturbed by the metal ion.

We have critically studied the absorption frequencies of malonic, malic and lactic acids. The alkali metal salts (Na, K or Li) of the acids were examined to assign bands of the carboxyl group. Further, the deuterated compounds were studied to assign bands involving active hydrogens. Thus, bands containing such hydrogens will either disappear or diminish considerably in intensity, depending on the extent to which the exchange has taken place. New bands of corresponding deuterium vibrations appear, the approximate frequencies of which can be calculated by using the equation of Glasstone<sup>58</sup>:

$$f_D = f_H \left( \frac{mH}{m+H} \right)^{1/2} \left( \frac{m+D}{mD} \right)^{1/2} \approx (0.71) \cdot f_H$$

where  $f_D$  is the frequency of vibration involving deuterium

$f_H$  is the frequency of vibration involving hydrogen

$H$  is the mass of hydrogen atom

$D$  is the mass of deuterium atom

$m$  is the mass of the remainder of the molecule or group.

However, this approximation is poor when hydrogen bonding is involved.

By deuteration bands of water of crystallization, especially the bands due to wagging motion of  $H_2O$  as a whole, when water is held in coordination to the metal, can be identified easily. Also, overlapping of the O-H deformation of  $H_2O$  and the antisymmetric stretching vibration of the ionized carboxyl group can be avoided by the use of deuterated analogues to facilitate correlation.

## RESULTS AND DISCUSSION

Infrared spectra of malonic acid ( $\text{HOOC} \cdot \text{CH}_2 \cdot \text{COOH}$ )  
and some metal malonates in  $4000\text{--}650\text{ cm}^{-1}$

## ASSIGNMENT OF MALONIC ACID

Infrared spectra of malonic acid, its deuterated analogue and disodium malonate are given in Figure (I) and the absorption frequencies are listed in Table (4).

Crystal structure data reported by Goedkoop and MacGillavry<sup>59</sup> have been helpful to assign some bands.

Region  $4000\text{--}2000\text{ cm}^{-1}$ 

The broad absorption peak observed in the region  $3300\text{--}2900\text{ cm}^{-1}$  can be assigned to the overtone of the  $\text{C}=\text{O}$  stretching (the fundamental appears near  $1700\text{ cm}^{-1}$ ) and the  $\text{O-H}$  stretching of the carboxylic acid in the dimer form. This vibration is expected in the range  $3100\text{--}2900\text{ cm}^{-1}$ <sup>60</sup>. In the deuterated acid (hereafter called the D-acid) a strong broad band is observed near  $2300\text{ cm}^{-1}$ , which is identified as the corresponding  $\text{O-D}$  vibration. The absence of strong broad band in the sodium salt in the  $3100\text{--}2900\text{ cm}^{-1}$  region confirms the assignment.

The broad band near  $2700\text{ cm}^{-1}$ 

Three possible assignments of this band have been

Figure (I)

INFRARED SPECTRA OF MALONIC ACID AND RELATED  
COMPOUNDS IN  $4000-650\text{ CM}^{-1}$  REGION

Upper	: Deuterated malonic acid	(Nujol mull)
Middle	: Malonic acid	(KBr disk)
Small	: Malonic acid	(Nujol mull)
portion		
Lower	: Disodium malonate n.hydrate	(KBr disk)
Small	: Disodium malonate anhydrous	(Nujol mull)
portion		

T A B L E - 4

Infrared absorption frequencies of malonic acid and related compounds

Malonic acid (KBr disk)	Malonic acid (Nujol mull)	Deutd. malonic acid (Nujol mull)	Sod. malonate $\text{XH}_2\text{O}$ (KBr disk)	Sod. malonate anhydrous (Nujol mull)
3300 s vb			3333 vb s	
2924 s vb	N	3150 vw sh	2907 m s	N
2667 s sh	2703 s b	2674 m s		
2551 s sh	2597 s sh	2257 m sh		
2247 w sh		2083 m sh		
2227 vw sh				
			1653 m sh	1640 vs s
1735 s sh	1740 s sh	1710 vs b	1587 vs s	1590 vs s
1706 vs vb	1706 s b			
1435 s s	N	N	1420 s b	N
1408 s sh		N	1377 s b	N
1395 s sh	N		1333 s s	1348 s s
1307 s s	1309 vs s	1282 s s	1259 m s	1265 s s
		1219	1176 m s	1178 m s
		1197 m b		
		1176 w sh		
1252 s b	1258 s b	1104 m s		
1212 s s	1214 vs s	1048 m s		
1170 s s	1170 w sh	1015 m sh		
			966 m s	970 m s
			956 m s	957 m s
				917 m s
	990 m sh	980 s s	917 m s	877 m s
958 m sh	935 m s	910 w sh	877 m s	787 m s
933 s sh	919 s sh	870 w b	790 s s	701 s s
919 s b	769 s s	827 w b	704 m s	
765 s s	651 s b	794 w b		
653 vs s		674 m b		

The first group of letters designates the intensity, (m - medium, w - weak, s - strong, v - very), the latter the width (s - sharp, b - broad, v - very, sh - shoulder); and N indicates Nujol bands.

discussed by Hadzi and coworkers<sup>61</sup>.

- (1) It may be the fundamental  $\nu(\text{O-H})$  of the dimeric acid.
- (2) It may correspond to a difference in the frequency of the type  $\nu(\text{O-H}) - \nu'$  i.e.  $(3000-300)\text{cm}^{-1}$  where  $\nu'$  is a fundamental having an approximate group frequency  $300\text{cm}^{-1}$ , and
- (3) It may be a summation band, the intensity of which is enhanced by the Fermi resonance effect.

The first possibility is discarded because the fundamental, which is Raman active, has been shown to appear in the range  $3100-2900\text{cm}^{-1}$  by Saksena<sup>60</sup>. The second possibility is eliminated as the experimental results do not agree with the predictions. The expected value is  $3300\text{cm}^{-1}$  and is of very much higher intensity than that of the observed for  $2700\text{cm}^{-1}$  band. It has, therefore, been concluded that the  $2700\text{cm}^{-1}$  band is a summation band of  $1440\text{cm}^{-1}$  and  $1300\text{cm}^{-1}$ , which are the coupled vibration frequencies of O-H out-of-plane deformation and C-O stretching.

In the D-acid it has appeared at  $2060\text{cm}^{-1}$  as a corresponding satellite band.

Region  $2000-1500\text{cm}^{-1}$

$1745$  and  $1705\text{cm}^{-1}$  bands are assigned to the  $\text{C}=\text{O}$

stretching of the carboxylic acid group. The values of these bands agree with those reported by Flett<sup>62</sup> and Quagliano<sup>52</sup>. Malonic acid would not be expected to be planar, as it will bring two oxygens of two carboxyl groups very near. X-ray evidence shows that one of the carboxyl groups is turned  $13^\circ$  out of plane through the carbon atoms, while the other is by about  $90^\circ$ . It has been concluded by Nyberg<sup>63</sup> that the distortion found in dicarboxylic acids with odd number of carbon atoms is mainly because of the need of efficient hydrogen bonding.

The non-planar structure may be the cause of observed doublet for  $C=O$  stretching. This doublet, as expected, vanishes in the disodium salt with appearance of new bands at 1640, 1590 and  $1390\text{ cm}^{-1}$ , first two of which represent the antisymmetric and the last symmetric stretching vibrations of ionized carboxyl,  $\text{COO}^-$  group.

#### Region $1500\text{--}1000\text{ cm}^{-1}$

The  $1440$  and  $1300\text{ cm}^{-1}$  bands are ascribed to the coupled vibrations of  $O-H$  out-of-plane deformation and  $C-O$  stretching of the carboxyl group. This is confirmed by the fact that in the D-acid, a band is observed at  $1046\text{ cm}^{-1}$ , which is the corresponding coupled



O-D out-of-plane deformation and C-O stretching vibrations. The frequency of this band is close to the expected value ( $1022\text{ cm}^{-1}$ ).

#### Bands at 1210 and 1170 $\text{cm}^{-1}$

It has been observed by Shimanouchi and coworkers<sup>64</sup> that a number of carboxylic acids having  $\text{CH}_2\text{-COOH}$  group exhibit strong absorption near  $1200\text{ cm}^{-1}$ . These investigators have concluded that this band is characteristic of the  $\text{CH}_2\text{-COOH}$  as a whole, wherein the major contribution comes from the wagging motion of  $\text{CH}_2$  and a partial contribution from C-O and C-C stretch and O-H out-of-plane deformation.

In the D-acid, these bands broaden and weaken in intensity, with the appearance of two weak bands at 870 and  $823\text{ cm}^{-1}$ , the values of which are in good agreement with calculated  $859$  and  $823\text{ cm}^{-1}$ , proving thereby the contribution of O-H deformation in 1210 and  $1170\text{ cm}^{-1}$  bands in the parent acid.

#### Region 1000-650 $\text{cm}^{-1}$

The  $918\text{ cm}^{-1}$  band observed in malonic acid vanishes in the disodium salt and in the D-acid. Further, in the latter a band at  $672\text{ cm}^{-1}$  appeared, which is in agreement with the calculated value ( $652\text{ cm}^{-1}$ ). Hadzi *et al.*<sup>61</sup> have

also observed a similar band.

The  $918\text{ cm}^{-1}$  band is assigned to the out-of-plane deformation of the COOH group.

The final assignments are summarized in Table (22).

TABLE - 5

Infrared absorption frequencies of Cu(II) and  
Ni(II) malonates in 4000-650  $\text{cm}^{-1}$  region

Cu(II) n-Hydrate (KBr disk)	Cu(II) Anhydrous (Nujol mull)	Cu(II) Deutd. (Nujol mull)	Ni(II) n.hydrate (KBr disk)	Ni(II) Anhydrous (Nujol mull)	Ni(II) Deutd. (Nujol mull)
3472 m s		3500 m s	3460 s s	3484 vw b	
3140 s b	3333 vw vb	3425 s sh	3175 s s	3195 vw b	
	N	N		N	N
		2532 s b			2564 m s
		2381 s b			2410 m s
		2278 s b			
			1660 s sh		
1590 vs b	1548 vs vb	1587 vs vb	1570 s b	1575 vs b	1575 vs vb
1429 s s	N	N	1451 m s	N	N
	N	N	1429 m sh	N	N
1370 s s			1379 s s		
1272 s s	1267 m b	1274 s s	1286 m s	1268 vw b	1282 m s
					1266 m s
					1220 m s
1181 w b		1183 m b			
1163 w b	1160 w vb	1163 m b	1178 m s	1170 vw b	1175 w b
986 w b		980 m sh	971 m s		970 w b
964 w b	952 w b	968 m s	947 m s		948 m s
933 m s		940 m b			930 w b
			889 m b		890 m s
804 m vb	803 vw vb		863 m b		868 w b
			771 s b		
736 s b	734 m vb	735 m b	727 s s	722 s s	722 s s

## INFRARED SPECTRA OF TRANSITION METAL MALONATES

The absorption frequencies of Cu, Ni, Co, Mn, Zn and Cd malonates in hydrated, dehydrated and deuterated forms are given in Tables (5), (6) and (7), and the spectra of some of them are shown in Figure (II). The spectra of cobalt(II) malonate as dihydrate, anhydrous and deuterated are given in Figure (III), to illustrate the effects of dehydration and deuteration of the parent compound.

Spectra of Co(II) and Ni(II) are more or less identical except small shifts in the frequencies. Two bands corresponding to two different water molecules in the O-H stretching region are exhibited, which as expected get shifted in deuterated compounds.

While Mn(II) and Zn(II) give comparable spectra, the spectrum of Cu(II) is unique.

Also, the spectra of all metal malonates are different from that of disodium malonate.

Coordinated water molecules

In addition to bands in the  $3400-3100\text{ cm}^{-1}$  and  $1660-1590\text{ cm}^{-1}$  regions, which disappear on dehydration and deuteration, a few which has been observed in the low frequency region below  $1000\text{ cm}^{-1}$ , are listed below:

TABLE - 6

Infrared absorption frequencies of Co(II)  
and Mn(II) malonate in 4000-650  $\text{cm}^{-1}$  region

Co(II) Hydrate (KBr disk)	Co(II) Anhydrous (Nujol mull)	Co(II) Deutd. (Nujol mull)	Mn(II) Hydrate (KBr disk)	Mn(II) Anhydrous (Nujol mull)	Mn(II) Deutd. (Nujol mull)
3460 s s			3448 s b	3333 w b	3295 w vb
3175 s s			3226 s sh		
	N	N		N	N
		2516 m s			2564 m s
		2389 m s			2410 m s
1660 s sh			1661 s sh		
1562 vs b	1570 vs vb	1562 vs b	1610 vb s	1564 vs b	1558 s b
			1554 vs b		
1449 s s	N	N	1439 m s	N	N
1373 s s	N	N	1381 m s	N	N
					1281 s s
1282 m s	1267 s s	1280 m s	1284 s s	1264 s s	
		1215 m s			1212 m sh
1171 m s	1170 m b	1170 m s	1175 b	1168 w vb	1192 m s
971 m s	972 m sh	972 m sh	971 m s	959 wb	980 m sh
943 m s	945 m vb	945 m vb	934 m s	937 w b	965 m s
1166 m s		1173 m s	1161 m s		935 m s
846 m vb	858 m vb	832 vw b	810 m b	806 w b	809 m s
769 s vb	740 m sh	737 m s		740 m b	
719 s b	722 s vb	734 s vb	720 s b	713 m vb	717 m s

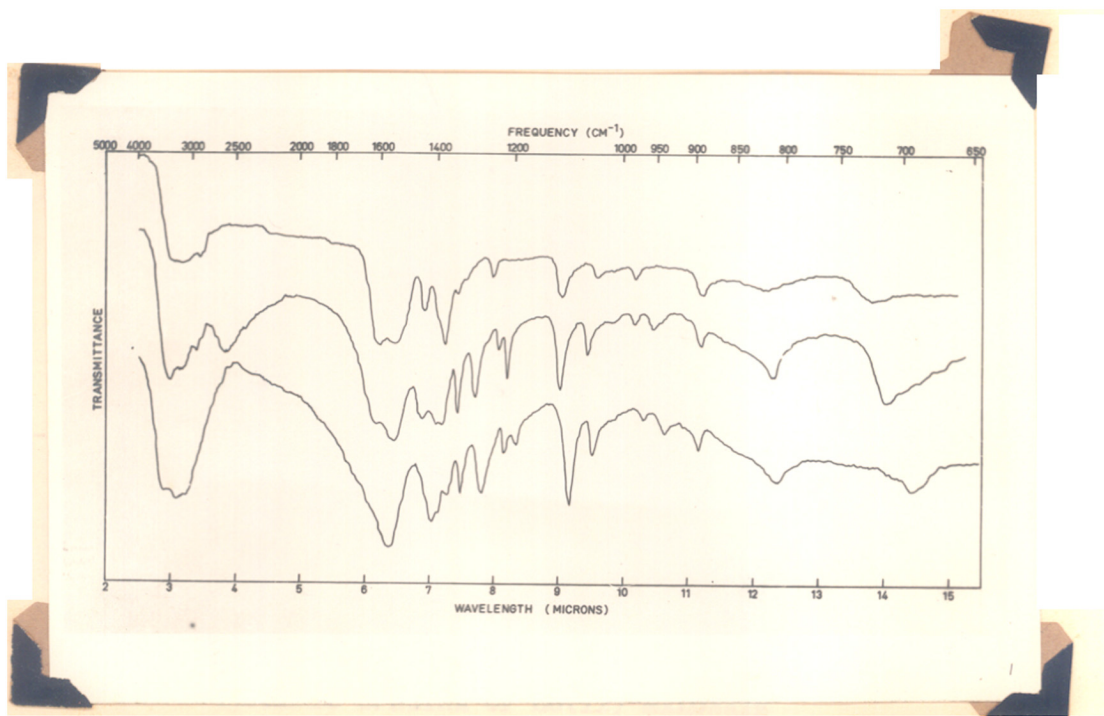


Figure (II)

INFRARED SPECTRA OF SOME TRANSITION  
METAL MALONATES IN 4000-650  $\text{CM}^{-1}$  REGION

Upper : Ni(II) malonate dihydrate (KBr disk)  
Middle : Cu(II) malonate trihydrate (KBr disk)  
Lower : Mn(II) malonate trihydrate (KBr disk)

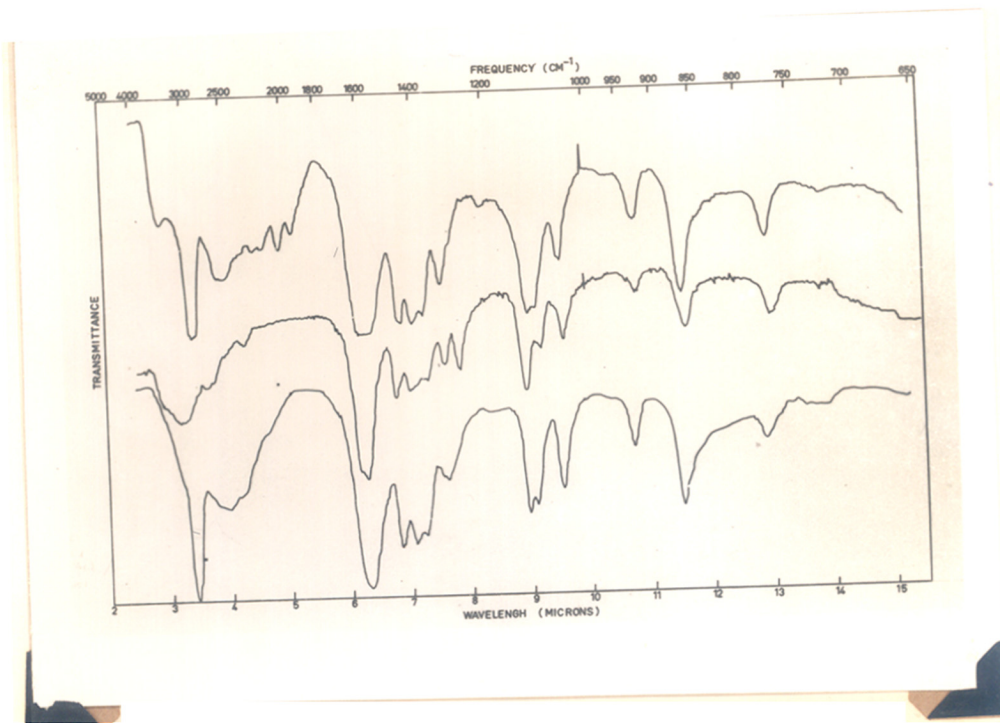


Figure (III)

INFRARED SPECTRA OF CO(II) MALONATE  
IN 4000-650 REGION

Upper : Anhydrous Co(II) malonate (Nujol mull)  
Middle : Co(II) malonate dihydrate (KBr disk)  
Lower : Deuterated Co(II) malonate (Nujol mull)

Co(II)	860	and	770	cm <sup>-1</sup>
Ni(II)	860	and	760	cm <sup>-1</sup>
Zn(II)	870			cm <sup>-1</sup>
Cd(II)	860			cm <sup>-1</sup>
Cu(II)	804			cm <sup>-1</sup>
Mn(II)	810	(?)		cm <sup>-1</sup>

These bands are assigned to the coordinated water molecules. As they cannot be due to the stretching or bending of O-H in the water molecule, they are assigned to some sort of wagging or twisting motion of whole H<sub>2</sub>O ligand itself. Following Fujita <sup>39</sup> et al, the nature of binding of the water molecules can be described as:

- (1) Water exists in the substance as a ligand as opposed to any other types of water of crystallization.
- (2) The metal to oxygen bond is fairly strong, and
- (3) The water molecule so bound forms strong or moderately strong hydrogen bond with the neighbouring atoms.



# THE STRUCTURE AND RELATIVE STABILITIES OF TRANSITION METAL MALONATES

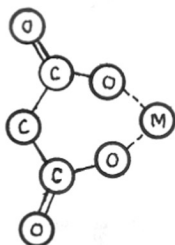
Since the frequencies of the carboxyl group would be related to some physical properties of the metal, a brief discussion of their behaviour is made here. The non-ionized carboxyl group may be represented as



(3100-2900  $\text{cm}^{-1}$ ), C = O stretching (1725-1650  $\text{cm}^{-1}$ ) and two coupled vibration frequencies of C-O stretching and O-H out-of-plane deformation (1450-1290 and 1300  $\text{cm}^{-1}$ ).

The ionized carboxyl group is considered to be a resonance structure and has two independent modes of vibrations, the antisymmetric  $\begin{array}{c} \nearrow \text{O} \\ \text{C} \begin{array}{c} \nwarrow \nearrow \\ \nwarrow \nearrow \end{array} \searrow \text{O} \end{array}$  (1650-1550  $\text{cm}^{-1}$ ) and the symmetric  $\begin{array}{c} \nearrow \text{O} \\ \text{C} \begin{array}{c} \nwarrow \nwarrow \\ \nearrow \nearrow \end{array} \searrow \text{O} \end{array}$  (1430-1290  $\text{cm}^{-1}$ ). On ionization the electron density in the C = O is lowered as a result of which the antisymmetric  $\text{COO}^-$  stretching is found at lower frequency than the C = O frequency in the acid.

Infrared spectra of Cu(II), Ni(II), Mn(II), Zn(II) and Cd(II) do not have any absorption bands of the COOH group. The structure of these malonates may be postulated as:



In this type of structure the carboxyl groups are greatly affected by the metal ion. The antisymmetric and symmetric frequencies of the  $\text{COO}^-$  group will then be sensitive to the change in the metal. The band of the symmetric  $\text{COO}^-$ , is in some cases overlapped by the  $\text{CH}_2$  group vibrations. However, considering the antisymmetric  $\text{COO}^-$  vibrations in the metal complexes, it may be seen in Table (8) that these are appreciably shifted to lower frequencies than that observed in the corresponding Na-salt. It may be explained thus; as a result of the metal-ligand interaction electrons from the  $\text{COO}^-$  group have been pulled towards the metal ion, thereby weakening the C-O bond strength. This will lower the force constant or the  $\text{COO}^-$  vibration frequency as we indeed observe in all the metal complexes. This in turn prompts us to conclude that the metal-oxygen bond is at least partially covalent in nature.

T A B L E - 8

Antisymmetric  $\text{COO}^-$  stretching frequencies, stability constants of some transition metal malonates

and some physical constants of the metal ions

Metal ion	Zn(II)	Cu(II)	Ni(II)	Co(II)	Mn(II)	Cd(II)	Na(I)
Radius $\text{\AA}$	0.72	0.72	0.73	0.74	0.78	0.99	
Second ionization potential e.v.	17.89	20.34	18.2	17.3	15.7	16.84	
Stability constant* $\log K_1$	3.68	5.75	4.01	3.72	3.29		
Antisym. $\text{COO}^-$ stretch. freq. $\text{cm}^{-1}$	1562 1565 1575	1590 1548 1587	1590 1575 1575	1562 1570 1562	1554 1564 1558	1558 1563 1585	1640/1590

\* J. Chem. Soc., 297, 1953.

It has been pointed out by Irving and Williams<sup>65</sup> that there is a relationship between the stability constant, the second ionization potential, and the reciprocal of ionic radii. The second ionization potential is a measure of electron affinity for a process  $M_{(gas)} \longrightarrow Me^{2+} + 2e^{-}$  and the strength of coordinate bond may be related to the loss in potential energy, when electrons are donated from high energy levels of the ligand to the low energy levels of the metal ion. On the basis of the above, they established an order of stability in a series of metal complexes containing the same ligand.

The antisymmetric stretching may be correlated with the change in metal. The frequency  $1590\text{ cm}^{-1}$  of this vibration is found high in Cu(II) malonate trihydrate and low ( $1554\text{ cm}^{-1}$ ) in Mn(II) malonate dihydrate. The order according to the value of this band is  $Mn < Co < Ni \ll Cu > Zn, Cd$  which is identical with that reported by Irving and Williams<sup>66</sup> for relative stabilities of the complex, based on the evaluation of their pK values.

Infrared spectra of malic acid ( $\text{HOOC} \cdot \text{CH}_2\text{CHOH} \cdot \text{COOH}$ ) and some metal malates in  $4000\text{-}650\text{ cm}^{-1}$  region

#### ASSIGNMENT OF MALIC ACID

Infrared spectra of malic acid, its deuterated analogue and thiomalic acid are given in Figure (IV) and the absorption frequencies are listed in Table (9).

The assignment of absorption bands in malic acid has been made with attention focused on the frequencies arising from carboxylic acid and alcohol groups. A comparison with the spectrum of thiomalic acid has provided a confirmation for the bands due to the alcoholic group.

#### Region $4000\text{-}2000\text{ cm}^{-1}$

A strong sharp band is observed at  $3448\text{ cm}^{-1}$ . This is assigned to the O-H stretching frequency of the secondary alcoholic group. On deuteration it should either disappear or diminish in intensity, depending on the extent to which the exchange has taken place. In the D-acid, a sharp band observed at  $2597\text{ cm}^{-1}$  is sufficiently close to the expected range of  $2590\text{-}2550\text{ cm}^{-1}$ . A band of medium intensity remains in the D-acid at  $3510\text{ cm}^{-1}$  because of incomplete deuteration. Further, the value of this band has

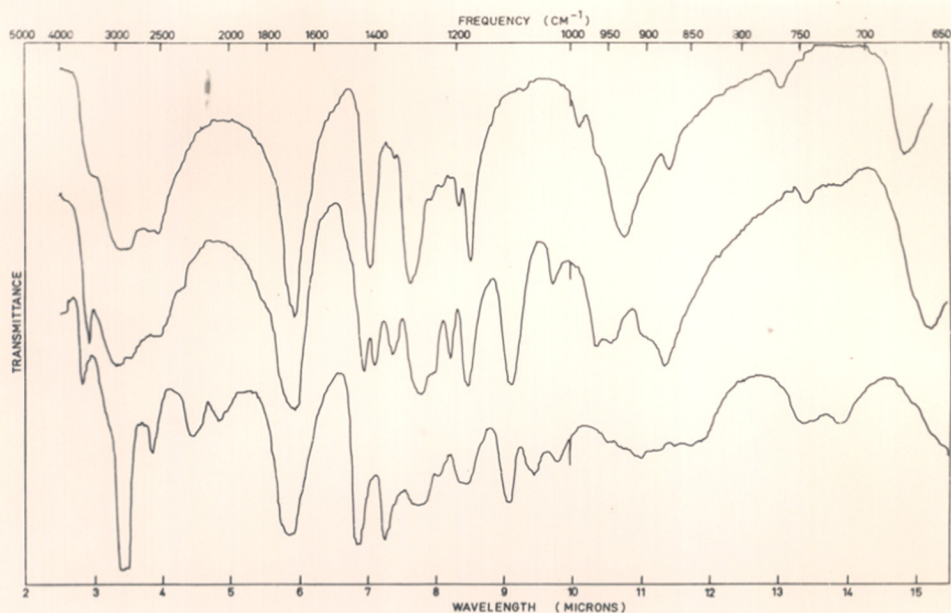


Figure (IV)

INFRARED SPECTRA OF MALIC ACID AND RELATED  
COMPOUNDS IN  $4000\text{-}650\text{ CM}^{-1}$  REGION

Upper	:	Thiomalic acid	(KBr disk)
Middle	:	Malic acid	(KBr disk)
Lower	:	Deuterated malic acid	(Nujol mull)

TABLE - 9

Infrared absorption frequencies of malic acid  
and related compounds in 4000-650  $\text{cm}^{-1}$  region

Malic acid (KBr disk)	Deuterated malic acid (Nujol mull)	Thiomalic acid (KBr disk)	Disodium malate (KBr disk)
3448 s s	3510 s s	3333 m sh	3510 s s
2985 s b	N	2899 m b	3150 s b
2591 m sh	2597 m s	2625 s b	3086 s b
	2247 m b	2535 s s	
	2066 m b		
1709 vs b	1709 vs b	1709 vs sh	1585 vs vb
		1684 s s	
1439 m sh	N	1418 vs s	1462 m b
1408 s s			1421 m b
1359 m s	N	1334 w s	1409 s s
			1379 s b
			1342 s b
			1323 s s
	1290 s vb		1293 s s
1272 s sh	1242 m b		1252 s s
1220 s s	1198 s b	1214 vs s	1224 s s
1178 s s	1178 s b	1198 s s	1212 m sh
		1172 s s	
1100 s s	1101 s s		1104 s s
	1058 s b		
1030 m s	1020 m b		1043 s s
968 m sh		990 m s	952 m s
948 m b		967 m sh	
907 m sh	909 m b	930 s b	911 m s
	869 m vb	876 m s	876 s sh
	859 m vb		
746 w b	749 s b	766 w b	790 m b
661 s b	719 s b	672 s b	689 m b

increased from  $3448\text{ cm}^{-1}$  to  $3510\text{ cm}^{-1}$ ; this may be due to the formation of weaker hydrogen bond in the D-acid.

This band at  $3448\text{ cm}^{-1}$  is, as expected, absent in the spectrum of thiomalic acid. The corresponding S-H stretching vibration is observed at  $2535\text{ cm}^{-1}$ .

O-H stretching vibration of the carboxylic acid group:

This is expected in the range  $3100\text{-}2900\text{ cm}^{-1}$  and the corresponding O-D would appear in the range  $2200\text{-}1959\text{ cm}^{-1}$ . Malic acid exhibits very broad absorption peak with  $2985\text{ cm}^{-1}$  as the centre of maxima. The absorption due to  $\text{CH}_2$  and CH stretching modes also appears in this region. The band due to O-H stretching vibration cannot, therefore, be identified exactly. The appearance of a band at  $2247\text{ cm}^{-1}$  in the D-acid confirms the presence of O-H stretching absorption band in the range  $3100\text{-}2900\text{ cm}^{-1}$ .

The  $2591\text{ cm}^{-1}$  band observed in the malic acid is most probably a summation band of  $1439$  and  $1272\text{ cm}^{-1}$  and in the D-acid a corresponding band is observed at  $2066\text{ cm}^{-1}$ .



Region 2000-1500  $\text{cm}^{-1}$

Malic acid exhibits very strong and broad absorption band with  $1709 \text{ cm}^{-1}$  as the centre of maximum, which indicates that the two carboxyl groups have slightly different environments.

Region 1500-1000  $\text{cm}^{-1}$

The O-H deformation frequency (coupled) of the acid group is expected in the range  $1440-1399 \text{ cm}^{-1}$  (corresponding O-D in  $1010-977 \text{ cm}^{-1}$ ). The band observed at  $1439 \text{ cm}^{-1}$  is assigned to this deformation frequency, the corresponding (O-D) being observed at  $1058 \text{ cm}^{-1}$  in the D-acid.

O-H deformation frequency of the alcoholic hydroxy group appears in the region  $1350-1260 \text{ cm}^{-1}$ . The absorption of the acid C-O (coupled) also appears near  $1300 \text{ cm}^{-1}$ . The band observed at  $1272 \text{ cm}^{-1}$  in the malic acid may be assigned to these two vibrations.

Shimanauchi T. et al<sup>64</sup> have studied a large number of carboxylic acids having  $\text{CH}_2\text{-COOH}$  and concluded that the band observed near  $1200 \text{ cm}^{-1}$  is

a characteristic of  $\text{CH}_2\text{-COOH}$  group, wherein the major configuration comes from  $\text{CH}_2$  rocking motion and some contribution is made by C-C stretch, C-O stretch and O-H deformation vibrations. 1220 and 1178  $\text{cm}^{-1}$  bands in the dl-malic acid may be assigned to the  $\text{CH}_2\text{-COOH}$  group. The changes observed in the disodium salt, deuterated analogue and thiomalic acid may be attributed to the loss of contribution from ~~one~~ vibration or the other.

Band observed at 1104  $\text{cm}^{-1}$

According to Bellamy<sup>5</sup> this is due to O-H deformation and/or C-O stretching vibration of the secondary alcoholic group. This band, as expected, remains unchanged on disodium salt formation and on deuteration. In the D-acid no new band is observed near 780  $\text{cm}^{-1}$  which could correspond to O-D deformation frequency. Also, thiomalic acid does not absorb in this region. We, therefore, conclude that the band at 1104  $\text{cm}^{-1}$  is of the C-O stretching mode of the alcoholic (secondary) group.

Region 1000-650  $\text{cm}^{-1}$

Out-of-plane deformation of the O-H group in carboxylic acid appears in the region  $960 \text{ cm}^{-1}$  to  $900 \text{ cm}^{-1}$ . The observed  $948 \text{ cm}^{-1}$  band in the dl-malic acid can thus be assigned to this vibration. The corresponding O-D deformation observed at  $779 \text{ cm}^{-1}$  is in approximate agreement with the calculated value  $675 \text{ cm}^{-1}$ .

In-plane deformation of the acid group is assigned the  $661 \text{ cm}^{-1}$  band in malic acid, which is absent in disodium salt as well in the deuterated analogue.

THE STRUCTURE AND RELATIVE STABILITIES  
OF TRANSITION METAL MALATES

Hydroxy acids readily form complexes with transition metal ions. A potentiometric study of malic acid and cupric ion in aqueous solution led Wanda and Pani<sup>67</sup> to conclude that several complexes are formed in solution under varying conditions of pH. These workers report the formation of a neutral complex at lower pH. The most probable structure postulated is one involving two ionised carboxyl groups (as evidenced by the release of two protons) and the alcoholic hydroxyl group.

In the solid state, there are two most probable types of bonding involved in the complexes of transition metals with hydroxy acids. The compound may be either a salt or a chelate. If the compound is salt-like, its spectrum will be similar to that of the sodium salt of the acid and the vibrations of the alcoholic group will remain more or less unchanged (except for changes due to decrease in hydrogen bonding). In a chelate, however, the vibrations of alcoholic group will be

perturbed, because of covalent bonding. Stromatt<sup>68</sup> has reported a band centred at  $2540\text{ cm}^{-1}$  in the spectrum of zirconium tetramandelate. This band has not been observed in the parent acid and also in its sodium salt. Also, the complex does not show any prominent absorption in the region for alcoholic O-H stretching frequency ( $3400\text{--}3200\text{ cm}^{-1}$ ). The  $2540\text{ cm}^{-1}$  broad band has been ascribed to the strongly bonded hydroxyl group.

We have studied the spectra of mandelic acid and copper(II) mandelate with a high resolution instrument. The frequency of the alcoholic hydroxy group is shifted to a value of  $3190\text{ cm}^{-1}$  from the  $3340\text{ cm}^{-1}$  in the acid.

In the present investigation, we have attempted to correlate the vibration frequency of the alcoholic group with the probable site of coordination, as we are inclined to believe that this is more sensitive to the coordination effect.

The malate complexes contain water of crystallization. The appearance of very broad absorption band with various sub-maxima in the hydroxy stretching region may be ascribed to the presence of

water molecule. This absorption, as expected, disappears or diminishes very much in the dehydrated and deuterated compounds.

Typical spectra of malate complexes are given in Figure (V) as an illustration.

The dehydrated copper malate does not take up heavy water. The spectra of dehydrated and deuterated compound to which excess  $D_2O$  was added, do not show any sharp band in the hydroxyl stretching region. All other metal malates also have no prominent absorbance in the anhydrous state. It is thus clear that the hydroxyl group is coordinated to the metal ions. Comparing the spectrum of sodium salt with the spectra of the metal malates it is found that, in the region  $1350-1250\text{ cm}^{-1}$ , the spectra differ considerably from the alkali salts.

Since the sharp O-H stretching frequency has disappeared from the usual O-H vibration region and also, in some cases a small shift in the C-O stretching vibration to a lower frequency seem to occur, it has been concluded that the malic acid forms chelate types of complexes with Cu, Ni, Co, Zn, Mn and Cd.

Figure (V)

INFRARED SPECTRA OF SOME TRANSITION  
METAL MALATES IN  $4000-650\text{ CM}^{-1}$  REGION

Upper : Cu(II) malate trihydrate (KBr disk)  
Middle : Zn(II) malate trihydrate (KBr disk)  
Lower : Mn(II) malate trihydrate (KBr disk)

TABLE - 10

Infrared absorption frequencies of Cu(II)  
and Ni(II) malates in 4000-650  $\text{cm}^{-1}$  region

Cu(II) n.Hydrate (KBr disk)	Cu(II) Anhydrous (Nujol mull)	Cu(II) Deutd.	Ni(II) n.Hydrate (KBr disk)	Ni(II) Anhydrous (Nujol mull)	Ni(II) Deutd. (Nujol Mull)
3175 s b	3300 s vb	Same as dehydrated. Does not take up water	3448 s b	3460 m sh	
3500 s b	3135 s vb			3300 m sh	3500 to 3100 m vb
	N			N	N
2899 s s					
2841 m sh	2610 m sh			2700 m b	2560 s vb
			1656 s b		
1655 vs sb	1550 vs vb		1563 s b	1575 vs vb	1570 s vb
1602 s s					
1547 s b					
	N			N	N
1441 s s	1438 s s		1445 s s	1440 s b	1440
1399 s sh	N		1382 s b	N	N
1379 s s	1310 m sh		1351 m sh	1300 s sh	1300
1342 w b	1340 m sh				
1318 m s					
1251 m s	1250 m s		1290 s vb	1200 m b	1198 m b
1291 s s	1210 s s		1236 m b		
			1208 m b		
1104 s s	1108 m s		1099 s s	1070 m s	1073 s b
1042 m s	1045 m s		1042 s s	1032 m s	1030 m sh
982 m b	985 m s		957 s s	960 w b	
	899 s s		946 m b		
889 m s	830 m s		897 s sh	880 m b	
819 m vb			800 s b	840 m b	840 m s
723 s b	760 m sh			720 s b	720 s b
	720 s s		703 s b	690 s b	690 s b



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Infrared absorption frequencies of Co(II)  
and Mn(II) malates in 4000-650  $\text{cm}^{-1}$  region

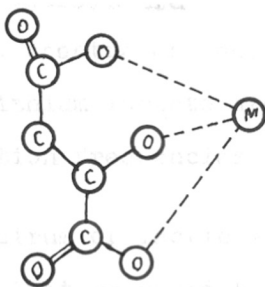
Co(II) n.Hydrate (KBr disk)	Co(II) Anhydrous (Nujol mull)	Co(II) Deutd. (Nujol mull)	Mn(II) n.Hydrate (KBr disk)	Mn(II) Anhydrous (Nujol mull)	Mn(II) Deutd. (Nujol mull)
3500 s vb	3440 w b	3530 m sh	3448 s b	3440 m vb	3455 s b
		3390 s sh	3226 s b	3160 m b	3280 s b
3330 s vb		3198 s b	3077 s b		3150 s b
	N			N	
	2700 w sh	2720 w b	2381 vw b	2715 m s	2615 vs b
		2606 m b		2650 m b	2530 s b
		2490 m b			2440 s b
		2400 s b			2305 s b
1656 s b			1656 s sh		
1565 vs b	1570 s b	1580 vs vb	1569 s b	1580 vs vb	1565 vs vb
	N	N		N	N
1391 s sh	1440 s b	1426 s b	1418 s s	1431 s s	1410 s b
	N	N	1403 s s	N	N
	1340 m sh		1376 s s		
1311 s s		1310 m sh		1300 m sh	1333 s s
	1300 m b	1298 m sh	1368 s s		1320 m sh
1291 s s	1250 m b	1200 m s	1280 s s	1190 m b	1280 m b
1209 m s	1200 m sh		1227 s s		1200 m s
1073 s s	1082 m s	1081 s s	1198 m s	1080 m b	1090 s s
1031 m s		1058 s s	1091 s s	1040 m b	1053 s s
			1048 m s		
966 m s	970 w b	960 w b	969 m s	910 m vb	950 m s
					920 m b
911 m b		910 w s	939 m s	880 m vb	804 s s
881 m sh		860 w b	895 s s		
862 m sh		840 vw s	807 s b		
833 s b		810 ms s			
725 m vb	720 m b	720 m sh	692 s b	720 s s	690 s s
702 s b		701 s s			

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Infrared absorption frequencies of Zn(II)  
and Cd(II) malates in 4000-650  $\text{cm}^{-1}$  region

Zn(II) n.Hydrate (KBr disk)	Zn(II) Anhydrous (Nujol mull)	Zn(II) Deutd. (Nujol mull)	Cd(II) n.Hydrate (KBr disk)	Cd(II) Anhydrous (Nujol mull)	Cd(II) Deutd. (Nujol mull)
3333 s b	3250 m s	3430 s b	3401 s b	3430 w b	
3175 s b		3280 m sh	3195 s b	3170 m b	
2941 s b	2980 m vb	2520 s b		2700 w sh	2420 m vb
	2597 s b	2355 m sh	2151 vw b		
1621 s s			1653 m sh		
1550 s b	1568 vs b	1568 vs b	1563 s b	1570 vs b	1555 vs vb
			1520 s b		
1450 s s	N	N	1460 s s	N	N
1408 s s	1430 s s	1430 s s	1449 s s	1440 s sh	1440 s s
			1422 s s		
1389 s s	N	1400 s s	1406 s s		
		N	1377 s s	N	N
		1350 m sh		1300 s s	1300 m b
		1320 m b	1342 s s		
1297 s s	1290 m s				
1238 m s			1274 s s		
1222 m s	1210 m s	1300 m s	1225 m s	1200 s s	1200 m s
	1100 m b	1200 m s	1211 m s		
1106 s s	1040 m sh	1081 m s	1087 s s	1080 s s	1080 m b
1058 m s		1054 s s	1054 s s	1032 m s	
1015 vw b					
	910 m vb	957 w s		960 w b	
982 m b	897 m vb	920 w s	972 m s	910 w sh	
955 m b	812 m s	810 m s	939 m s	880 w s	
892 m b		720 m sh	892 w b	840 m s	840 m s
812 s b	738 m sh		860 s b	800 m sh	
776 s b	718 s s	700 s s	815 w b	720 s sh	720 s s
712 s b			693 s b	690 s b	690 m vb

Since the presence of coordinated alcoholic group has been observed and as there are no bands of COOH group, the structure of transition metal malates may be written as:



Spectra of Cu(II), Co(II) and Ni(II) are more or less alike, having two (or one broad) bands of  $\text{COO}^-$  antisymmetric stretching vibration. On the other hand Mn(II) has only one relatively sharper band.

The determination of the order of stabilities of these complexes has not been attempted as the carboxylic group frequencies are complicated and the bonded O-H stretching vibration of C-OH group overlaps nujol bands.

## RESULTS AND DISCUSSION

Infrared spectra of lactic acid ( $\text{CH}_3\text{CHOHCOOH}$ ) and some metal lactates in  $4000\text{-}650\text{ cm}^{-1}$  region

## ASSIGNMENT OF LACTIC ACID

Infrared spectra of lactic acid, its deuterated analogue and lithium lactate are given in Figure (VI) and the absorption frequencies are listed in Table (13).

The spectrum of lactic acid observed by us is identical with that reported by Barr and Horton<sup>69</sup>.

Region  $4000\text{-}2000\text{ cm}^{-1}$ 

Lactic acid exhibits a strong, broad absorption band centered at  $3333\text{ cm}^{-1}$ . This band is assigned to the O-H stretching vibration of the alcohol group. The broadness of the band is indicative of the strong hydrogen bonding. This band is relatively unchanged in the ethyl ester of lactic acid, value of the absorption frequency being  $3420\text{ cm}^{-1}$ . This increase in the value may be attributed to decrease in hydrogen bonding.

In the deuterated analogue this is diminished in intensity (due to incomplete deuteration) and a new band is observed at  $2475\text{ cm}^{-1}$  (calculated value  $2366\text{ cm}^{-1}$ ).

Figure (VI)

INFRARED SPECTRA OF LACTIC ACID AND RELATED  
COMPOUNDS IN 4000-650  $\text{CM}^{-1}$  REGION

Upper	:	Deuterated lactic acid	(Liquid film)
Middle	:	Lactic acid	(Liquid film)
Lower	:	Lithium lactate n.hydrate	(KBr disk)

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Infrared absorption frequencies of lactic acid  
and related compounds in 4000-650  $\text{cm}^{-1}$  region

Lactic acid	Deuterated lactic acid	Lithium lactate (KBr disk)	Lithium lactate Anhydrous (Nujol mull)	Ethyl <sup>*</sup> lactate
3333 s b	3390 m b	3390 m sh		3448 s s
	2990 m s	3175 s s	3175 s s	3030 s s
2980 s s	2941 m sh	2963 m s	N	2978 s sh
2597 s b	2475 s b			
2326 vw b	2283 s sh			
	2062 m s			
1718 vs b	1724 vs s			
1639 m sh		1587 vs s	1585 vs s	1715 vs s
1444 m s	1456 s s	1467 s b	N	1451 s s
1399 m sh		1425 vs s	1429 s sh	1370 s s
	1380 s b	1361 s s	N	
1370 m b	1318 s b	1310 m s	1307 m s	
	1258 s b	1286 m s	1283 m s	
1280 m sh				1263 s s
1212 s b	1217 s s			1211 s s
	1156 s sh			
1124 s s	1129 s b	1122 vs s	1120 vs s	1124 s s
				1099 m s
1093 s sh	1099 s sh	1087 m s	1087 m s	1043 s s
1042 m s	1042 m vb	1052 s s		1015 m s
926 w b	952 m b	933 m b	930 w s	925 m s
820 m b		861 m b	862 m s	855 m s
	794 m b	781 m s	780 m s	794 m sh
		690 s vb	690 s vb	758 m b

\* NBS compound Card No.422

In anhydrous lithium lactate, this band of the O-H stretching vibration is observed at  $3175\text{ cm}^{-1}$ . Lithium lactate, in hydrated form, has an additional band at  $3400\text{ cm}^{-1}$ , which is assigned to water of crystallization as it disappears on dehydration. The  $3175\text{ cm}^{-1}$  band is comparatively sharp, which is probably due to weaker hydrogen bonding. It is interesting to note that the value of this frequency is considerably lowered from that in the acid.

X-ray crystallographic studies by Tavale et al<sup>70</sup> have shown that, in the case of sodium  $\alpha$ -keto butyrate, there are six short distances ( $2.5 \pm 0.2\text{ \AA}$ ) between sodium atom and the neighbouring oxygens, five of these belong to the carboxylic group and the remaining belongs to the keto group. Structure of sodium pyruvate is also similar<sup>71</sup>. It has been observed in our laboratory that the C=O stretching frequency of the keto group is at  $1789\text{ cm}^{-1}$  in the parent acid (pyruvic acid spectrum in  $\text{CCl}_4$ ) and is observed at  $1708\text{ cm}^{-1}$  in sodium pyruvate. Accordingly, the structure, similar to that of sodium pyruvate, may also be postulated in the case of lithium lactate.

A strong, broad absorption peak is observed in the region  $3100\text{--}2900\text{ cm}^{-1}$ .  $\text{CH}_3$ , CH and O-H (carboxylic acid in dimer form) stretching vibrations occur in this region.

The strong, broad band of O-H stretching mode overlaps with the other bands and hence it cannot be unambiguously assigned. Deuterated acid shows a shoulder of strong intensity at  $2283\text{ cm}^{-1}$ . This band is within the expected range ( $2341\text{--}2060\text{ cm}^{-1}$ ).

Spectrum of lithium lactate is cleaner in this region. The bands observed in this spectrum are attributed to  $\text{CH}_3$  and CH stretching modes.

The complex absorption pattern, with a number of submaxima, characteristic of dimeric association, is observed in the spectrum of lactic acid. This is absent in the lithium salt and the ethyl ester. The deuterated acid absorbs at  $2062\text{ cm}^{-1}$ . As discussed earlier in the case of malonic acid, the band in lactic acid is assigned to the summation bands of coupled vibrations of C-O stretching and O-D out-of-plane to the deformation vibrations of the carboxylic group.

#### Region $2000\text{--}1500\text{ cm}^{-1}$

$1718\text{ cm}^{-1}$  band of lactic acid is assigned to C-O stretching frequency of the carboxylic group. This value lies well within the range  $1725\text{--}1700\text{ cm}^{-1}$ , reported for aliphatic acids<sup>5</sup>. This band remains unaffected on deuteration but vanishes in the lithium salt in which two new bands of asymmetric and symmetric



stretching vibrations of ionised carboxyl group,  $\text{COO}^-$ , appear at  $1585$  and  $1425 \text{ cm}^{-1}$  respectively.

Region  $1500\text{-}1000 \text{ cm}^{-1}$

$1466$  and  $1364 \text{ cm}^{-1}$  bands in lithium lactate are assigned to asymmetric and symmetric deformation vibrations of  $\text{CH}_3$  group.

Lactic acid has a broad absorption band at  $1400 \text{ cm}^{-1}$ , which can be assigned as a coupled vibration. In the D-acid a band at  $1157 \text{ cm}^{-1}$  is observed. The band at  $1280 \text{ cm}^{-1}$  in lactic acid can be assigned to the combined vibrations of C-O stretching and O-H deformation of carboxylic group plus alcohol O-H deformation. The D-acid shows an additional band at  $958 \text{ cm}^{-1}$  which is close to the expected value ( $909 \text{ cm}^{-1}$ ).

The band observed at  $1124 \text{ cm}^{-1}$  is ascribed to the C-O stretching mode of the alcoholic group. As expected, this band is relatively unchanged on salt formation and on deuteration.

Region  $1000\text{-}650 \text{ cm}^{-1}$

$926 \text{ cm}^{-1}$  band is assigned to the out-of-plane deformation of carboxylic acid group. Earlier investigators<sup>62</sup> have also made the same assignment. This is confirmed by the  $794 \text{ cm}^{-1}$  band observed in the D-acid. In the deuteration

The final assignments of the vibrational frequencies of the lactic acid are made as given in Table (22).

THE STRUCTURE AND RELATIVE STABILITIES  
OF SOME TRANSITION METAL LACTATES

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Goulden<sup>32</sup> has investigated a number of lactates in aqueous solutions. The attention was centered to the band of alcohol O-H deformation vibration. The band at  $1275\text{ cm}^{-1}$  diminishes in intensity and a new band is observed near  $1395\text{ cm}^{-1}$  in the chelated ions. The band due to C-OH vibration was chosen as the one sensitive to the effect of vibration coupling, intermolecular association and to the changes in the C-OH bond order. Increase in stability leads to the increase in the relative proportions of chelated to free ions, the respective bands being observed at  $1395$  and  $1275\text{ cm}^{-1}$ .

The observed intensity of the  $1395\text{ cm}^{-1}$  band may not be its own intensity completely. The stretching vibration due to the  $\text{COO}^-$  group may in some cases overlap. We have therefore chosen a different band (the hydroxyl stretching vibration) to study the order of stability of the metal lactates.

Cu(II) lactate dihydrate,  $\text{Cu}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$

Spectra of this compound are given in Figure (VII).

This compound shows a broad band centred at  $2550\text{ cm}^{-1}$  which remains unaffected on dehydration. In the deuterated

Figure (VII)

INFRARED SPECTRA OF CU(II) LACTATE  
IN 4000-650  $\text{CM}^{-1}$  REGION

Upper	: Deuterated Cu(II) lactate	(Nujol mull)
Middle	: Cu(II) lactate dihydrate	(KBr disk)
Lower	: Anhydrous Cu(II) lactate	(Nujol mull)

Figure (VIII)

INFRARED SPECTRA OF SOME TRANSITION  
METAL LACTATES IN 4000-650  $\text{CM}^{-1}$  REGION

Upper : Ni(II) lactate trihydrate (KBr disk)  
Middle : Co(II) lactate trihydrate (KBr disk)  
Lower : Zn(II) lactate trihydrate (KBr disk)

T A B L E - 14

Infrared absorption frequencies of Cu(II) and  
Co(II) lactates in 4000-650  $\text{cm}^{-1}$  region

Cu(II) n.hydrate (KBr disk)	Cu(II) Anhydrous (Nujol mull)	Cu(II) Deutd. (Nujol mull)	Co(II) n.hydrate (KBr disk)	Co(II) Anhydrous (Nujol mull)	Co(II) Deutd. (Nujol mul
3378 s b		3390 m s	3460 m sh		3503 w sh
3009 s b			3279 s b		3300 m b
2963 s b	N	N	3130 s b	3077 s sh	3175 m sh
2551 s b	2500 s vb	2545 s vb	2899 s s	N	N
		2326 m sh	2714 b sh	2703 s sh	2577 m s
			2315 w b	2347 w sh	2463 s b
					2353 s b
2326 m sh	2353 m sh	2227 m s			2247 m sh
		2160 m s			2174 m s
		2040 m s			2062 m s
		1942 m s			1957 w s
			1653 s sh	1626 vs b	
1653 w sh	1582 vs vb	1582 vs b	1583 vs b		1587 vs b
1585 vs b					
1460 m s	N	N	1460 m b	N	N
		1449 s b			1429 s sh
1393 s b	1410 s b	1409 s b	1418 s s		
1372 m sh	N	N	1389 m sh	N	N
			1361 m s	1346 s sh	
1316 m s	1307 s b	1321 m s	1327 m s	1311 s s	1329 w s
			1304 m s		1303 m s
1290 m sh		1205 w b	1281 s s	1274 s s	1276 m s
				1117 s sh	1205 w b
					1130 s b
1112 s s	1115 s s	1117 m sh	1111 s s	1105 s s	1118 s s
		1111 s s	1081 m s		1102 s s
1093 s s	1099 s s	1094 s sh			
1046 m s	1047 m s	1047 m s	1042 m s	1045 m s	1053 m s
935 m b	931 m s	935 w b	926 w b	926 w b	943 w b
869 s b	867 s s	869 m s	862 m s	862 s b	930 w b
					859 m s
775 m b	775 m b	775 w b	769 m b	769 m s	768 m b

T A B L E - 15

Infrared absorption frequencies of Ni(II)  
and Mn(II) lactates in 4000-650  $\text{cm}^{-1}$  region

Ni(II) n.Hydrate (KBr disk)	Ni(II) Anhydrous (Nujol mull)	Ni(II) Deutd. (Nujol mull)	Mn(II) n.Hydrate (KBr disk)	Mn(II) Anhydrous (Nujol mull)	Mn(II) Deutd. (Nujol mull)
3509 s sh		3460 m sh	3430 s sh		3390 m sh
3185 s b	3030 s sh	3226 s b	3175 s b	3125 s sh	3125 m s
	N	N		N	N
2740 s sh	2703 s sh	2564 s sh	2703 m sh	2706 s sh	
2331 vw b		2381 vs b	2317 w b	2353 vw b	2516 s s
		2174 m sh			2326 s b
		2062 m s			2151 m sh
		1961 w b			2043 m s
					1942 w b
	1639 vs s	1575 vs vb	1667 s sh	1582 vs b	1575 vs b
1587 vs b			1600 vs vb		
1471 m b			1472 m s		
	N	N	1460 m sh	N	N
1425 s b		1449 s b	1418 s sh		1418 s s
		1425 s s	1404 s b		
1370 m s	N	N	1361 m s	N	N
1318 m b	1312 m s	1326 m s	1315 s b	1309 m b	1325 s s
1280 m s	1279 m s	1307 m sh	1266 s s	1266 m b	1290 s s
		1276 m s			1266
					1205 w b
1117 s s	1115 m s	1205 vw b	1111 s s	1111 s s	
		1117 s s			1114 s s
1093 m sh	1105 m s	1100 s sh	1086 s s	1082 s sh	1099 s s
					1075 s s
1046 m s	1043 m s	1050 m s	1042 m s	1041 m s	1041 m s
		952 w b	930 w b	929 m s	971 w b
935 w b		930 w b			924 w b
869 m b	858 m s	858 m b	865 m b	857 m b	857 m b
775 w b	769 vw b	763 m b	766 m vb	767 m b	767 m b

T A B L E - 16

Infrared absorption frequencies of Zn(II)  
and Cd(II) lactates in 4000-650  $\text{cm}^{-1}$  region

Zn(II) n.H <sub>2</sub> O (KBr disk)	Zn(II) Anhydrous (Nujol mull)	Zn(II) Deutd. (Nujol mull)	Cd(II) (KBr disk)	Cd(II) Deutd. (Nujol mull)
3378 s sh		3448 w sh		
3125 s b		3175 vs s b	3175 m b	3175 m b
	N	N	2925 m s	N
			2890 m b	
2740 s sh	2740 s sh	2564 m s		2555 m b
		2326 s b		
2326 m sh	2355 w sh	2237 m b		2200 w b
		2119 m s		
		2045 w s		
		1942 w b		1950 vw b
1613 vs sh				
1590 vs vb	1639 s b	1585 vs vb	1590 s b	1585 s b
1471 m s	N	N	1470 m s	N
1420 m s	1418 m s	1449 vs b	1413 m s	1415 m s
		1429 s sh		
1399 m sh	1377 vs b	1400 m s		
1362 m s	1351 s s	1360 m s		N
		1325 m s		
1316 m s	1314 m s	1302 m s	1320 m s	1315 m s
1274 m s	1274 m s	1274 w s	1270 m s	1270 m s
		1198 w b		1200 vw b
1117 s s	1116 s s	1130 m sh	1110 s s	1100 s s
		1119 s s	1090 m sh	1095 m sh
1087 m s	1093 m sh	1099 s s		
1044 m s	1047 m s	1052 m s	1045 m s	1045 m s
935 w b	930 w b	930 w b	930 w b	930 w b
862 m b	858 m s	859 m s	870 m b	870 m b
862 m b				
775 m b	769 m b	767 m b	765 m b	765 m b
		719 w b		

compound, in addition to this original band, two new bands are observed at 2027 and 1950  $\text{cm}^{-1}$ .

The 2550  $\text{cm}^{-1}$  band in Cu(II) lactate is assigned to the coordinated hydroxyl group.

The spectra of Cu(II), Ni(II), Co(II), Zn(II), Mn(II) and Cd(II) lactates do not show any absorption due to O-H stretching of the H-C-OH group, in the usual range of 3450-3300  $\text{cm}^{-1}$ . The observed bands in this range are ascribed to the water molecules as these disappear in deuterated and dehydrated compounds.

A critical examination for locating the bands of bonded C-OH group, using the high resolution set-up of the prism-grating assembly, revealed that these bands do appear in the region 2800-2500  $\text{cm}^{-1}$  confirming thereby the covalent bonding of metal to the alcoholic group.

This interaction of the alcoholic group and the absence of COOH group suggest the formulation of structure for the metal lactate:





The O-H stretching frequency of H-C-OH group is greatly perturbed by the metal ion. Due to covalent bonding, the electron density of the OH group is reduced. As a result, the O-H stretching vibration is appreciably changed. The lowest frequency is observed in the case of Cu(II) lactate dihydrate at  $2550\text{cm}^{-1}$ , wherein the metal-oxygen bond is likely to be most strong. It has the highest value of  $2740\text{ cm}^{-1}$  in the case Mn(II) lactate trihydrate. The value of this frequency decreases as  $\text{Mn} > \text{Co} > \text{Ni} > \text{Cu}$  and in the case of Zn(II) it is found to be  $2770\text{ cm}^{-1}$ , as indicated in Table (17).

In the case of similar metal complexes with amino acids, it has been observed<sup>72</sup> that there are two N-H frequencies, one of which increases and the other decreases as a result of complex formation. Both have been shown to be related to the stability constant of the complexes. Accordingly, we can also in the present case, considering the change in the O-H frequency, suggest an order of stability of these complexes as:

$$\text{Mn} < \text{Co} < \text{Ni} \ll \text{Cu} > \text{Zn}, \text{Cd}$$

which again is in agreement with the Irving-William series.

It is interesting to observe that, in contrast with the metal-malonate complexes, the carboxyl frequencies in the lactates are little affected due to its interaction with the metal ion. Similar observation has also been made in the case of metal-amino acid complexes.

T A B L E - 17

Metal sensitive bands of some metal lactates

Metal ion	Frequency $\text{cm}^{-1}$ .	
	Antisym. $\text{COO}^-$ stretching	Alcoholic O-H stretching*
Mn(II)	1600	2740
Co(II)	1583	2725
Ni(II)	1587	2715
Cu(II)	1585	2550
Zn(II)	1590	2770
Cd(II)	1590	3175
Na(I)	-	-
Li(I)	1587	3175

\* Obtained with the high resolution NaCl prism-Grating assembly.

P A R T - II

STUDIES ON THE THERMAL STABILITIES  
OF THE MALONATE, MALATE AND LACTATE COMPLEX SALTS

## I N T R O D U C T I O N

In order to assign the bands of water molecules, dehydration of the compounds was necessary. It was then thought worthwhile to study the relative thermal stabilities for dehydration and decomposition of these complexes for comparison with the results obtained from infrared absorption studies.

The compound may contain:

- (1) adsorbed water, present on all solid surfaces in amounts depending on the humidity of the atmosphere;
- (2) occluded water, present in solid solution or cavities within the crystals,
- (3) sorbed water, associated with substances having a large internal surface developments e.g. hydrous oxides, and
- (4) essential water, present as water of hydration or crystallization or as water of constitution.

Thermogravimetric analysis, within its limitations, can throw some light on the nature of binding of the water molecules.

Thomas and Paris<sup>73</sup> have studied the quinaldates of divalent transition metals. An order of thermal stability, which obviously corresponds to the decomposition temperatures, has been given. It is interesting to note

that the order of thermal stability is different from that of Irving and Williams<sup>66</sup>. Similar type of work on 2-quinoline carboxylates of divalent metals is reported by Lumme<sup>74</sup>. Charles et al<sup>75</sup> have studied the divalent metal chelates of 8-quinolinol. The order of thermal stability observed by these workers is comparable with that by Thomas and Paris<sup>73</sup>. Thermolysis of 2( o-hydroxy phenyl) benzoxazole chelates by Wendlandt<sup>76</sup> suggested the order of decomposition temperatures as:  $\text{Cd} > \text{Ni} > \text{Co} > \text{Cu}$

Dhar and Bosolo<sup>77</sup> have attempted to correlate the activation energies of the solid decomposition with crystal field energies by thermogravimetric and isothermal studies of tris (2,2'-bipyridine) complexes. Results obtained for Cu(II) and Ni(II) were reproducible; Mn(II), Co(II) and Zn(II) complexes did not give reproducible results.

Some cobalt(II) and nickel(II) salts of some aliphatic acids have been investigated both isothermally and at increasing temperatures in air, nitrogen and vacuum. This study by Leicester and Redman<sup>78</sup> gives valuable information regarding the end products obtained under various experimental conditions. A thorough study of cobalt(II) oxalate dihydrate in air, nitrogen, hydrogen and a mixture of nitrogen with 25%

hydrogen, by Amiel and Paulmier<sup>79</sup>, illustrated the effects of different atmospheres on the decomposition process.

In the present investigation, we have studied the transition metal (Cu, Co, Ni, Zn, Mn and Cd) complexes of malonic, malic and lactic acids, with a view to elucidate the dehydration and thermal decomposition processes. Some of the malonates have also been studied in nitrogen, hydrogen and carbon dioxide atmospheres.

## EXPERIMENTAL

An apparatus, designed and constructed in our laboratory, was used to study the pyrolytic behaviour.

A known weight (approximately 25 mg.) of the substance in a finely powdered form (230 mesh) was taken in an aluminium bucket and hung from a calibrated quartz spring balance. The balance had a sensitivity (elongation) of 40.67 cms./gm. The spring was suspended at the top of a pyrex tube of 40 mm. diameter and 45 cms. long. The support of the spring at the top was a pyrex rod with a hook at the bottom. The top was a ground glass plug with a lateral outlet and vacuum stopcock. At the bottom there was another outlet with a stopcock. The whole assembly could be evacuated to  $10^{-3}$  mm. of mercury or any gas atmosphere could be maintained. The sample was carefully adjusted on the central axis of the furnace.

A thermocouple well was kept in the close vicinity of the sample, so that its temperature could be measured. A calibrated chromel-alumel thermocouple was used by us. For the measurements the temperature was raised at a linear rate of  $2^{\circ}\text{C}$  per minute, using a temperature regulator and a variac.

A travelling microscope having least count 0.1 mm. was used to measure the change in length of the spring.

### Purification of gases

**Nitrogen:** The oxygen contents were removed by bubbling the gas through an alkaline solution of pyragallol (prepared by dissolving 15 gms. pyragallol in 100 mls. concentrated KOH solution ). The gas was then dried over concentrated  $H_2SO_4$ .

**Hydrogen:** The gas was purified by passing through a heated ( $310^{\circ}C$ ) platinized asbestos gauze, cooled by passing through a cold trap and finally dried over anhydrous calcium chloride, silica gel and soda asbestos.

Carbon dioxide was used without any purification.

The purified gas was flushed through the system atleast for 30 minutes before starting the experiment.

The percent loss in weight was plotted against temperature.



## RESULTS AND DISCUSSION

Thermogravimetric Analysis of some  
Metal Malonates in various atmospheres

The pyrolysis curves of Co(II), Ni(II), Zn(II), Mn(II) and Cd(II) are shown in Figure (IX) and the results are presented in Table (18).

Copper(II) malonate trihydrate  
Cu.  $C_2H_2O_4 \cdot 3H_2O$ 

Thermogravimetric analysis curves of this compound are shown in Figure (X) and the results are summarized in Table (18).

In air, the dehydration begins at  $50^\circ$  and is almost complete at  $170^\circ$ . The portion of the curve between  $170^\circ$  and  $230^\circ$  is not strictly horizontal. The compound decomposes quickly at  $241^\circ$ . The loss of water at  $50^\circ$  suggests a loosely bound water molecule.

In the nitrogen atmosphere, as evident from the curve, dehydration temperatures remain unaffected. However, the decomposition, unlike that in air, is very sluggish and extends over the temperature range  $241-305^\circ$ .

In a current of hydrogen, the decomposition begins at  $230^{\circ}$  and this is very rapid at  $240^{\circ}$ .

In carbon dioxide, the decomposition begins at  $246^{\circ}$ , which proceeds fast in the beginning and then slowly till at  $297^{\circ}$  when the horizontal level begins.

Nickel(II) malonate dihydrate,

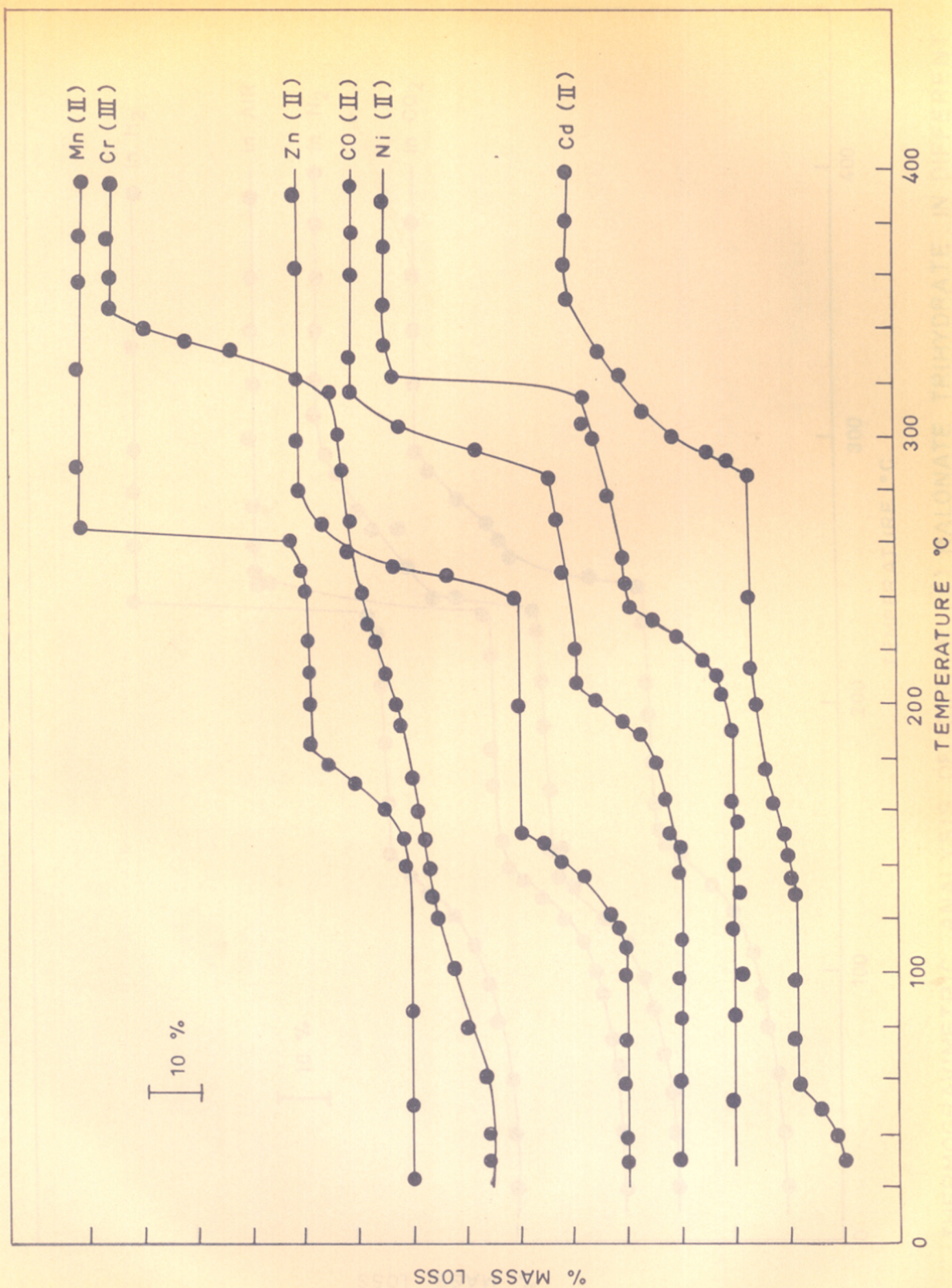
Ni.  $C_3H_2O_4 \cdot 3H_2O$

The dihydrate is stable till  $200^{\circ}$ , when the water of crystallization begins to get removed. The dehydration is complete at  $240^{\circ}$ . The decomposition occurs rapidly at  $323^{\circ}$ .

In nitrogen, the decomposition is slow and is complete at  $350^{\circ}$  while the dehydration temperature remains, as expected, unaffected.

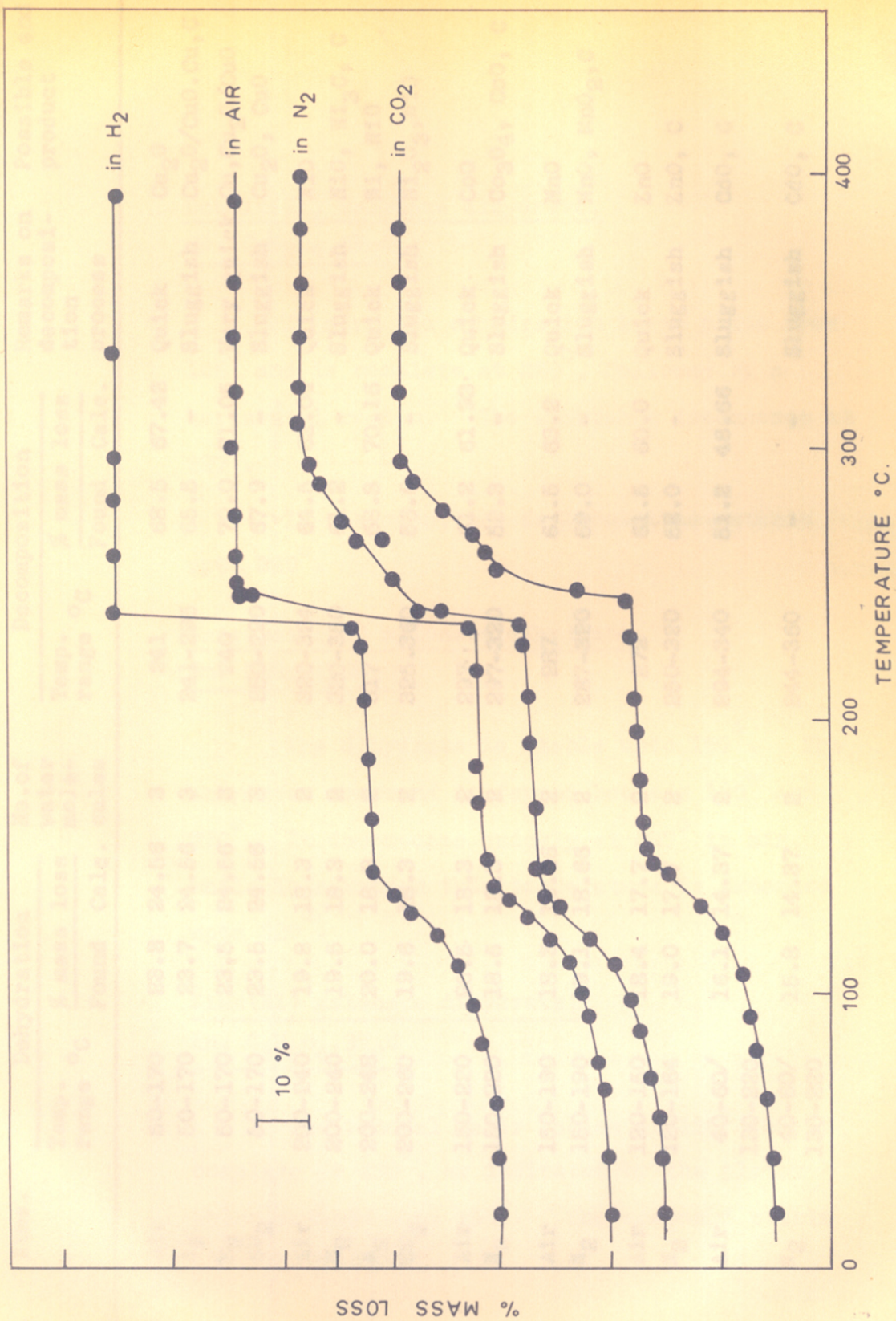
In hydrogen, the compound decomposes rapidly at  $317^{\circ}$ .

In carbon dioxide, the decomposition range observed is  $315^{\circ}$  to  $360^{\circ}$ . The mass of the residue corresponds to that of NiO.



THERMOGRAVIMETRIC ANALYSIS OF METAL MALONATES IN AIR



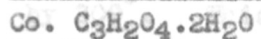


THERMOGRAVIMETRIC ANALYSIS OF COPPER (II) MALONATE TRIHYDRATE IN DIFFERENT

ATMOSPHERES

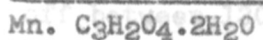
TABLE 18 - THERMOGRAVIMETRIC ANALYSIS OF SOME MALONATES IN VARIOUS ATMOSPHERES

Compd.	Atms.	Dehydration			No. of water molecules	Decomposition			Remarks on decomposition process	Possible end product
		Temp. range °C	% mass loss			Temp. range °C	% mass loss			
			Found	Calc.			Found	Calc.		
Cu(II)	Air	50-170	23.8	24.56	3	241	68.5	67.42	Quick	Cu <sub>2</sub> O
	N <sub>2</sub>	50-170	23.7	24.56	3	241-295	65.5	-	Sluggish	Cu <sub>2</sub> O/CuO, Cu, C
	H <sub>2</sub>	50-170	23.5	24.56	3	240	70.0	71.05	Very quick	Cu, Cu <sub>2</sub> O/CuO
	CO <sub>2</sub>	50-170	23.5	24.56	3	250-290	67.9	-	Sluggish	Cu <sub>2</sub> O, CuO
Ni(II)	Air	200-240	19.8	18.3	2	320-324	64.5	62.04	Quick	NiO
	N <sub>2</sub>	200-240	19.5	18.3	2	320-350	61.2	-	Sluggish	NiO, Ni <sub>3</sub> C, C
	H <sub>2</sub>	200-248	20.0	18.3	2	317	68.8	70.16	Quick	Ni, NiO
	CO <sub>2</sub>	200-260	19.6	18.3	2	325-360	56.5	-	Sluggish	Ni <sub>2</sub> O <sub>3</sub> , NiO
Co(II)	Air	150-220	20.5	18.3	2	297	61.2	61.93	Quick	CoO
	N <sub>2</sub>	150-220	18.5	18.3	2	297-320	52.3	-	Sluggish	Co <sub>3</sub> O <sub>4</sub> , CoO, C
Mn(II)	Air	150-190	18.3	18.66	2	287	61.5	63.2	Quick	MnO
	N <sub>2</sub>	150-190	19.1	18.66	2	287-320	59.0	-	Sluggish	MnO, MnO <sub>2</sub> , C
Zn(II)	Air	120-150	18.4	17.7	2	272	61.5	60.0	Quick	ZnO
	N <sub>2</sub>	120-164	19.0	17.7	2	250-320	58.0	-	Sluggish	ZnO, C
Cd(II)	Air	40-60/ 130-220	16.1	14.37	2	294-340	51.2	48.66	Sluggish	CdO, C
	N <sub>2</sub>	40-60/ 130-220	15.8	14.37	2	244-360	-	-	Sluggish	CdO, C

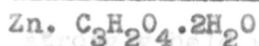
Cobalt(II) malonate dihydrate,

In air, the dehydration takes place from  $158^\circ$  and is complete at  $220^\circ$ , followed by a horizontal region. The substance decomposes at  $297^\circ$ .

In nitrogen, the decomposition extends upto  $320^\circ$ .

Manganese(II) malonate dihydrate,

The dihydrate is stable upto  $150^\circ$ . The anhydrous compound is formed between  $190^\circ$  and  $270^\circ$ . It decomposes quickly at  $287^\circ$  in air, while in nitrogen this temperature is extended upto  $320^\circ$ .

Zinc(II) malonate dihydrate,

The removal water begins at  $120^\circ$  and is complete at  $230^\circ$ , as indicated by the plateau which extends upto  $250^\circ$ . The compound starts

decomposing quickly first at  $252^{\circ}$  and is complete by  $300^{\circ}$ . This temperature is extended upto  $320^{\circ}$  in nitrogen. The weight of the residue, in air, agrees with that calculated for  $ZnO$ .

Cadmium(II) malonate dihydrate,  
 $Cd \cdot C_3H_2O_4 \cdot 2H_2O$

Dehydration takes place in two well defined stages. One of the water molecules is lost between  $40^{\circ}$  and  $60^{\circ}$ . The other water molecule is driven off between  $130^{\circ}$  and  $220^{\circ}$ . The overall dehydration range may be taken as  $40-220^{\circ}$ . Its decomposition is rather sluggish; commencing at  $294^{\circ}$  and ending at  $340^{\circ}$ , with the formation of  $CdO$ . In nitrogen, the oxide level starts at  $360^{\circ}$ .

As seen from the pyrolysis curves, the water of crystallization is very strongly held in  $Co(II)$  and  $Ni(II)$  malonates. According to Lumme<sup>74</sup> strongly held water eliminates the possibility of tetrahedral configuration.

The order of thermal stability for this series of compounds is comparable with that of Thomas and Paris<sup>73</sup>.

Thermogravimetric Analysis in air  
of some metal malates in air

Compound      Decomp.

With the exception of Cu(II) malate trihydrate, in all other compounds the dehydration and decomposition stages overlap. It is for this reason the number of water molecules and the exact temperatures at which the decomposition commences cannot be unambiguously evaluated.

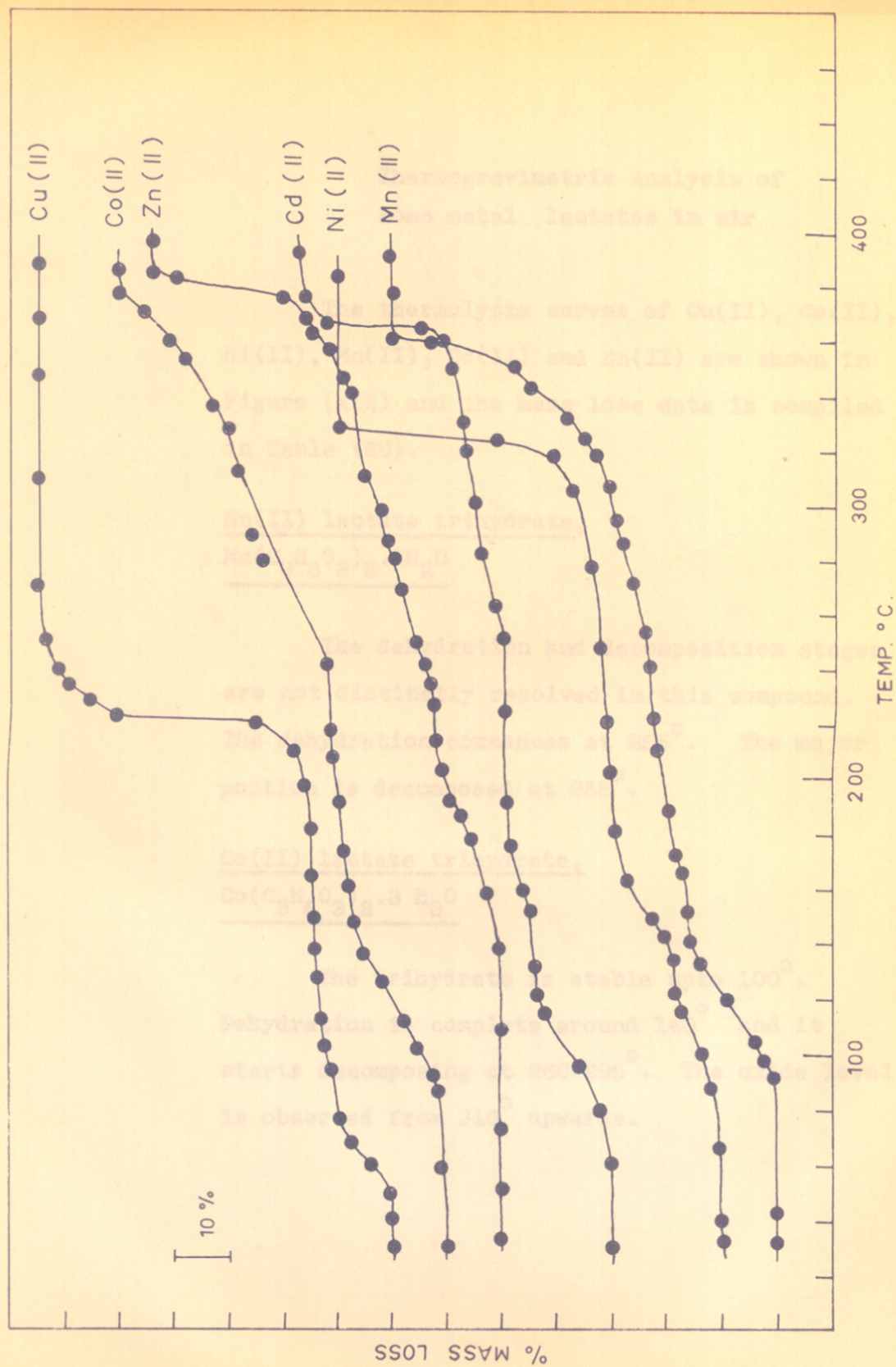
The temperature at which the decomposition is found to have increased is taken as mean decomposition temperature. Results of decomposition temperature and mass loss data are summarized in Table (19).



T A B L E - 19

Thermal decomposition of malates in air

Compound	Decomp. temp. °C	Total loss in weight		
		% Found	Calculated %	for
Cu(II)	224	65.5	68.1	CuO
Ni(II)	320	64.0	66.19	Ni <sub>2</sub> O <sub>3</sub>
Co(II)	345	60.0	67.2	Co <sub>3</sub> O <sub>4</sub>
Mn(II)	360	70.0	70.65	MnO
Zn(II)	382	64.0	68.63	ZnO
Cd(II)	364	52.2	51.1	CdO

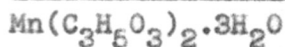


THERMOGRAVIMETRIC ANALYSIS OF METAL (II) MALATES IN AIR

Thermogravimetric Analysis of  
some metal lactates in air

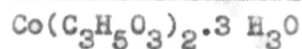
The thermolysis curves of Cu(II), Co(II), Ni(II), Mn(II), Cd(II) and Zn(II) are shown in Figure (XII) and the mass loss data is compiled in Table (20).

Mn(II) lactate trihydrate,



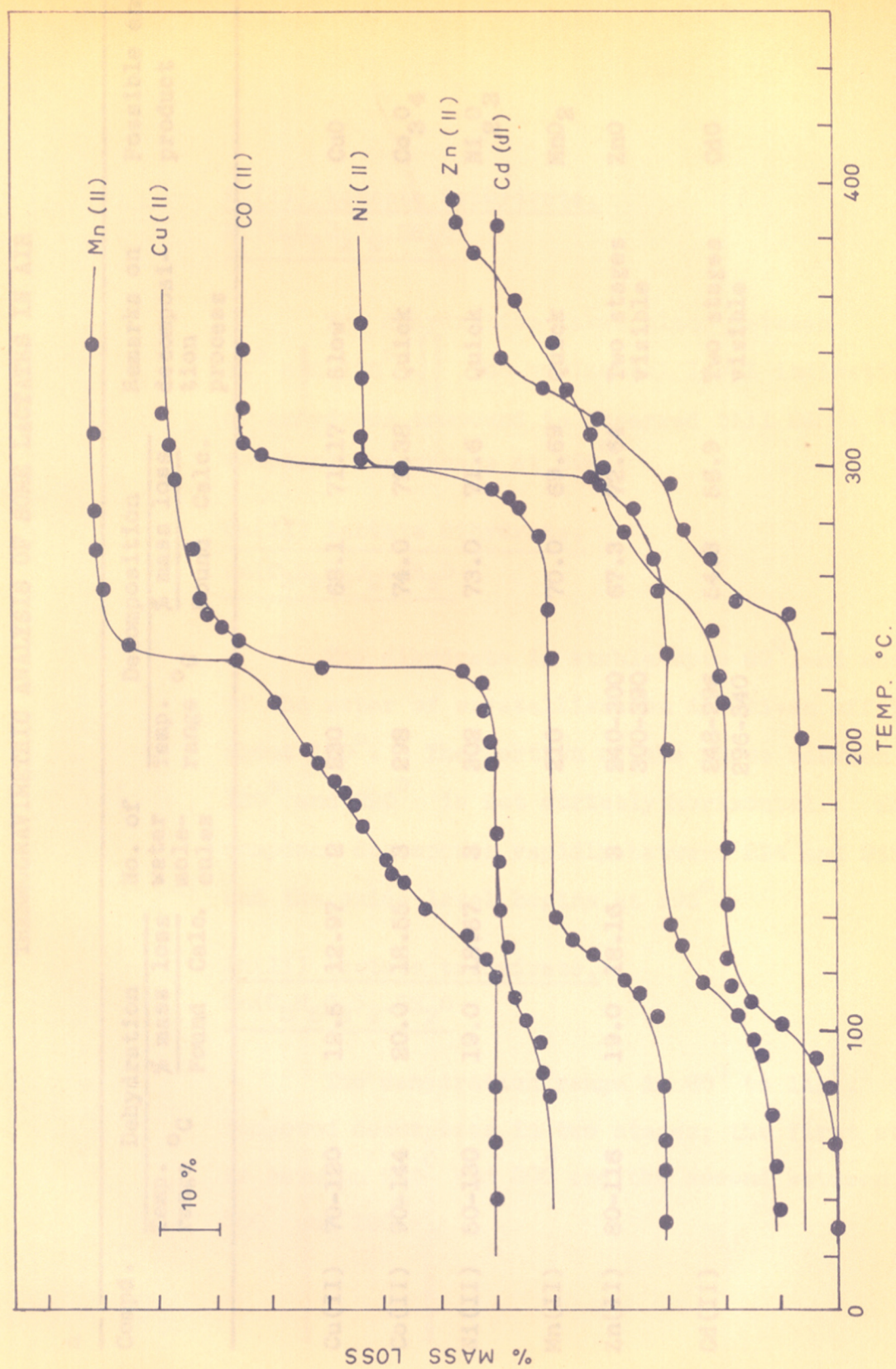
The dehydration and decomposition stages are not distinctly resolved in this compound. The dehydration commences at  $255^\circ$ . The major portion is decomposed at  $255^\circ$ .

Co(II) lactate trihydrate,



The trihydrate is stable upto  $100^\circ$ . Dehydration is complete around  $140^\circ$  and it starts decomposing at  $260-295^\circ$ . The oxide level is observed from  $310^\circ$  upwards.



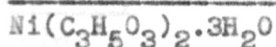


THERMOGRAVIMETRIC ANALYSIS OF METAL LACTATES IN AIR

## THERMOGRAVIMETRIC ANALYSIS OF SOME LACTATES IN AIR

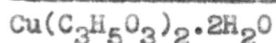
Compd.	Dehydration		No. of water molecules	Decomposition		Remarks on decomposition process	Possible end product
	Temp. range °C	% mass loss Found    Calc.		Temp. range °C	% mass loss Found    Calc.		
Cu(II)	70-120	12.5    12.97	2	230	68.1    71.17	Slow	CuO
Co(II)	90-144	20.0    18.55	3	298	74.0    72.38	Quick	Co <sub>3</sub> O <sub>4</sub>
Ni(II)	50-130	19.0    18.57	3	302	73.0    71.6	Quick	Ni <sub>2</sub> O <sub>3</sub>
Mn(II)				210	70.0    69.69	Quick	MnO <sub>2</sub>
Zn(II)	80-116	19.0    18.16	3	240-300 300-390	67.3    72.64	Two stages visible	ZnO
Cd(II)				243-296 296-340	54.3    56.9	Two stages visible	CdO

Ni(II) lactate trihydrate,



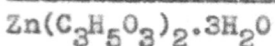
The dehydration takes place between  $80^\circ$  and  $138^\circ$ . The horizontal level indicative of anhydrous compound is observed till  $260^\circ$ . The compound decomposes at  $298^\circ$ .

Cu(II) lactate dihydrate,



The dihydrate is stable upto  $80^\circ$  and most of the water of crystallisation is driven off by about  $120^\circ$ . The portion of the curve between  $120^\circ$  and  $220^\circ$  is not strictly horizontal. The compound decomposes rapidly between  $226^\circ$  and  $245^\circ$  and the oxide level begins at  $295^\circ$ .

Zn(II) lactate trihydrate,



The dehydration range is  $80^\circ$  to  $115^\circ$ . The compound decomposes in two stages; the first stage is between  $240^\circ$  and  $300^\circ$  and the second between  $300^\circ$  and  $380^\circ$ .

Cd(II) lactate,

$\text{Cd}(\text{C}_3\text{H}_5\text{O}_3)_2$

The decomposition process of this compound is similar to the zinc lactate. The first stage extends from  $246^\circ$  to  $296^\circ$  and the second till  $340^\circ$ .

### Calculation of Energy of Activation for a solid state reaction

The kinetics of a solid state reaction has been a subject of interest to many workers<sup>80,81</sup>.

In a solid state decomposition of the type  $A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}}$ , the onset of the reaction involves the formation of a new phase B, at special points in the lattice of A. Local deformation of the lattice must occur to cause this which is referred to as "strain". The potential nucleation sites are generally associated with some type of lattice imperfections, for example, lattice defects, dislocations, smekel cracks. Therefore, the reaction rate, dependent on the rate of nucleus formation, is a function of the particular crystal structure and surface conditions of the solid.

The activation energies of solid state reactions using mass loss kinetic data have been calculated by the method of Coates and Redfern<sup>81</sup>. Results of the calculations are summarized in Table (21).



T A B L E - 21 A

Activation energies 'E' (Kcal/mole) and temperature ranges  
for dehydration of some  
transition metal malonates, malates and lactates in air

Metal ion	Malonate		Malate		Lactate	
	Temp. range °C	E when n = 0.66	Temp. range °C	E when n = 0.66	Temp. range °C	E when n = 0.66
Cu(II)	50-170	15.5	40-80	15.5	70-120	12.9
Co(II)	150-220	32.0	* * *	* * *	90-144	22.2
Ni(II)	200-240	30.0	* * *	* * *	50-130	17.9
Mn(II)	150-190	31.8	* * *	* * *	* * *	* * *
Zn(II)	120-150	29.9	* * *	* * *	80-116	22.5
Cd(II)	40-60	30.5	* * *	* * *	* * *	* * *
Cd(II)	130-220	19.3				

\* \* \* : Cannot be evaluated, as the dehydration and decomposition stages are submerged.

\* \* : Indicates anhydrous compound.

TABLE - 21 B

Activation energies 'E' (Kcal/mole) and temperature ranges  
for decomposition of some  
transition metal malonates, malates and lactates in air

Metal ion	Malonate		Malate		Lactate	
	Temp.range °C	E when n = 1.0	Temp.range °C	E	Temp.range °C	E when n = 1.0
Cu(II)	241	125	224	*	230	65.15
Co(II)	297	82	345*	*	298	84.2
Ni(II)	320-324	213	320*	*	302	62.1
Mn(II)	287	154	360*	*	210*	* * *
Zn(II)	272	73	382*	*	240-300 300-390	37.3 27.6
Cd(II)	294-340	197.8	364*	*	248-296 296-340	25.3 69.0

\* \* \* : Cannot be evaluated, as the dehydration and decomposition stages are submerged.

\* : Mean temperatures are given as the exact temperature at which the decomposition commences, cannot be established.

Garner<sup>82</sup> has compiled the reported values of the activation energies of dehydration. The lowest value reported for  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  is 15.6 kcal. while the highest is 38-49 kcal. for  $2\text{KHC}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

Values obtained by us lie within the reported range.

Comparing the thermal decomposition data which can be considered as proportional to the thermal stabilities of these compounds, the order of stabilities is formed as:  $\text{Ni}(322^\circ)$ ,  $\text{Cd}(317^\circ) > \text{Co}(297^\circ) > \text{Mn}(287^\circ) > \text{Zn}(272^\circ) > \text{Cu}(241^\circ)$  in malonates. However, due to several uncertainties, determination of such order has not been attempted in the case of malates and lactates at this stage.

One may be tempted to correlate the activation energies for dehydration of the various metal-complexes with the vibration frequencies of the  $\text{OH}_2$  ligand. However, neither of the two could be determined with certainty. As a very rough approximation, our data (see p. 36) indicate that in  $\text{Cu(II)}$  where the activation energy for dehydration (15.5 kcal/mole) was found to be lowest, the corresponding  $\text{OH}_2$  group frequency ( $804 \text{ cm}^{-1}$ ) was also the lowest.

## SUMMARY AND CONCLUSIONS

## SUMMARY AND CONCLUSIONS

I Infrared Spectroscopic Studies

The final assignments of the absorption bands of malonic, malic and lactic acid, made with the help of the data available from the literature and by the study of known structural changes, such as the alkali-metal salt formation and deuteration, are summarized in Table (22).

## Studies of Metal Complexes:

## Coordinated water molecules:

Of the three series (malonate, malate and lactate) investigated, only Cu(II), Co(II), Ni(II), Mn(II)(?), Zn(II) and Cd(II) malonates exhibit the bands of coordinated water molecules in the region  $900-750\text{ cm}^{-1}$ . These bands are ascribed to the wagging or rocking motion of  $\text{OH}_2$  ligand as a whole.

The absence of this type of bands in malates and lactates leads to the conclusion that the structure of the aquo malonates is different from those of the malates and lactates.

## Coordination sites:

Spectra of the malates and lactates do not have any absorption bands due to the alcoholic group,  $\text{CHOH}$ , in its usual range  $3450-3300\text{ cm}^{-1}$ . Its absence indicates that the oxygen of this group is covalently bound to the metal atom. In the bidentate lactate complexes both the oxygens of two alcoholic groups are coordinated.

TABLE - 22 - The final assignments of malonic, malic and lactic acids.

Frequency cm <sup>-1</sup> .			Assignment
Malonic acid	Lactic acid	Malic acid	
3300-2900 m b	3333 s b	3448 s s	Alcoholic O-H stretching.
	3100-2900 syb	3000-2850s vb	C = O (acid) overtone
			O-H stretching, carboxylic acid (dimer)
			C-H stretching
2900-2600 m b	2800-2600 m b	2800-2500 s b	Summation band of coupled vibrations of C-O stretching and O-H deformation of carboxylic acid group (satellite bands).
1745 vs sh	1714 vs s	1709 vs b	Acid C = O stretching.
1705 vs b			
1440 s s	1400 s b	1408 s s	Coupled vibrations of C-O stretching and O-H deformation of carboxylic group.
1300 m s			
	1280 s b	1272 s sh	Alcoholic O-H deformation and coupled vibrations of C-O stretching and O-H deformation of carboxylic group.
1210 s s		1220 s s	CH <sub>2</sub> -COOH group.
1170 s s		1178 s s	
	1125 s s	1100 s s	Alcoholic C-O stretching.
918 m b	926 m b	948 m b	Acid O-H out-of-plane deformation.

### Relative stabilities of complexes:

In the case of malonates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), the antisymmetric stretching frequency of the  $\text{COO}^-$  group is found to be most sensitive to the changes in the metal ion. The value of this frequency increases with the increasing stability of the complex i.e. highest value of  $1590\text{ cm}^{-1}$  is observed in the Cu(II) compound and the lowest in Mn(II) complex.

In the lactate complexes, however, the asymmetric  $\text{COO}^-$  stretching frequency values do not alter markedly. All the metal complexes studied by us have this vibration near  $1585\text{ cm}^{-1}$ . Lithium lactate, which is probably a weak chelate, has also the same value. It is, therefore, concluded that the extent of covalent character of the bond between the metal ion and the oxygens of carboxyl groups is identical in all the complexes.

In malate complexes, the carboxyl group frequencies behave differently. Cu(II) and Zn(II) show a doublet, Co(II) and Ni(II) a very broad band (the doublet is not observed because of complications of O-H deformation of  $\text{OH}_2$ ). Mn(II) on the other hand shows a relatively sharp single peak. This appearance of doublet in some cases and a single peak in the other, may be attributed to the influence of steric environments.

Copper(II) complexes of malonic, malic and lactic acid:

In copper(II) malonate trihydrate the possible coordination sites are the oxygens of two carboxyl groups and those of the water molecules.

The structure of these compounds cannot be similar to that of Cu(II) oxalate dihydrate which comprises infinitely extending two dimensional net-work involving coordination links, rather than the separate molecules as the turning of the chains at the central carbon atom renders such net-work structure improbable.

The structure of Cu(II) malonate trihydrate may be postulated to consist of a single molecule in which the six coordination sites are comprised of : two by two carboxyl groups, three by three water molecules and the remaining by the non-coordinated oxygen of the neighbouring molecule.

In the case of Cu(II) malate trihydrate, three coordination sites are filled by three water molecules, one by the alcohol group oxygen and remaining two by oxygens of two carboxyl groups.

Bidentate Cu(II) lactate must be having its octahedron filled by one oxygen each from two carboxyl groups, one each from two alcoholic oxygens and remaining two by water molecules.



Infrared spectra of these compounds support the proposed structures, as firstly no free COOH group is detected and secondly in the malate and lactate complexes the coordination of the alcoholic, C-OH group is established.

Ni(II) and Co(II) complexes:

Spectra of these two compounds of each series are comparable. Assuming an octahedral configuration, the coordinating atoms may be said to be identical to those in the corresponding copper(II) compounds.

Mn(II) and Zn(II) complexes:

Spectra of the two are comparable in the malonates. Two bands of O-H deformation of water are found in both these compounds, while all other compounds of this series have only one band, indicating the difference in structures.

Spectrum of Mn(II) malate trihydrate is also different from the Cu(II), Co(II) and Ni(II) malates.

## II Thermogravimetric analysis

The decomposition of a compound is found to be sluggish in carbon dioxide and in nitrogen atmospheres; the dehydration temperatures being very little affected.

The order of thermal stability, which obviously corresponds to the decomposition temperatures, is found to be:  
$$\text{Ni} > \text{Cd} > \text{Co} > \text{Mn} > \text{Zn} > \text{Cu} \quad , \text{ in the case of malonate}$$

complexes. This order is comparable with that of other workers' results. However, due to several uncertainties, determination of such order has not been attempted at this stage, in the case of malates and lactates.

The activation energies for the dehydration are found to be 30 (or more) Kcal/mole for Co(II), Ni(II), Zn(II), Mn(II) and Cd(II) malonates and 15.5 Kcal/mole for Cu(II) malonate.

It is interesting to note that in Cu(II) where the activation energy for dehydration is found to be the lowest, the corresponding  $\text{OH}_2$  group frequency ( $804\text{ cm}^{-1}$ ) is also the lowest. Whereas the order of relative stability found from the metal sensitive band frequencies is in agreement with that of the Irving and Williams series (viz.  $\text{Mn} < \text{Co} < \text{Ni} \ll \text{Cu} > \text{Zn}, \text{Cd}$  ), the order of thermal stability is different.

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