

335

AWARDED Ph.D. DEGREE

VERIFIED  
INL.....

*g/ h/*  
*12-9-81*

*TH-742*

COMPUTERISE

VERIFIED  
1983  
INL.....

COMPUTERISE

NATIONAL CHEMICAL LABORATORY.  
LIBRARY  
Acc. No. .... *49488* .....  
Call. No. ....

VERIFIED  
1977  
INL.....

VERIFIED  
1981  
INL.....

STUDIES ON SOME METAL CHELATES, CHELATE POLYMERS AND  
AMMINE COMPLEXES

COMPUTERISED

111-742

A THESIS  
SUBMITTED BY  
K. K. RAMASWAMY, M.Sc.  
TO THE  
UNIVERSITY OF BOMBAY  
FOR THE DEGREE OF PH.D.

546.3:541.572.54(043)  
RAM

NATIONAL CHEMICAL LABORATORY.  
LIBRARY  
Acc. No. .... 49488  
Call. No. ....

NATIONAL CHEMICAL LABORATORY POONA 8

1966

Statement required to be submitted under Rule O.413  
of the University of Bombay

No part of this thesis has been submitted for a degree or diploma or other academic award. The literature concerning the problems investigated has been surveyed, and all the necessary references are given in the thesis. The present work has been clearly indicated separately. The experimental work has been carried out entirely by me. In accordance with the usual practice, due acknowledgement has been made wherever the work presented is based on the results of other workers.

*K. K. Ramaswamy*

(K. K. Ramaswamy)  
CANDIDATE

Poona  
July 13<sup>th</sup> 1966.

*D. N. Sen* 18/7/66.

(D. N. Sen)  
RESEARCH GUIDE

## C O N T E N T S

	<u>Page</u>
<u>CHAPTER I</u> : <u>INTRODUCTION</u>	
General ...	1
Salicylaldoxime and its metal chelates ...	2
Chelate Polymers ...	13
Ammine Complexes ...	25
<u>CHAPTER II</u> : <u>INFRARED SPECTRAL STUDIES OF SALICYLALDOXIME AND SOME OF ITS METAL CHELATES</u>	
Abstract ...	38
Introduction ...	39
Results and Discussion ...	41
Experimental ...	58
<u>CHAPTER III</u> : <u>REACTIVITY AND COLOUR ISOMERS OF BIS-(SALICYLALDOXIMATO) COPPER(II)</u>	
Abstract ...	62
Introduction ...	63
Experimental ...	65
Results and Discussion ...	69
<u>CHAPTER IV</u> : <u>STUDIES ON “CHELATE LIGANDS” AND POLYMERS OF SOME BIVALENT METALS</u>	
Abstract ...	77
Introduction & Results and Discussion ...	78
Experimental ...	100
<u>CHAPTER V</u> : <u>INFRARED ABSORPTION SPECTRAL STUDIES OF SOME WERNER TIPE COMPLEXES</u>	
Abstract ...	106
Introduction ...	107
Experimental ...	110
Results and Discussion ...	113
REFERENCES ... ..	132
ACKNOWLEDGEMENT ... ..	142

CHAPTER I

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

## INTRODUCTION

The co-ordination theory<sup>1</sup>, first conceived by the great chemist Alfred Werner in 1893 and put on an electronic basis by Sidgwick<sup>2</sup> has become one of the most useful and powerful tools of the modern chemist. While it is largely a fact that this theory finds application in almost everyday laboratory experience, it is perhaps only after Linus Pauling's work on the nature of chemical bond<sup>3</sup> that the researches on co-ordination compounds have gained the added fillip. The impact of quantum mechanics<sup>4</sup> on the one hand and the modern physical methods of investigations on the other, have brought a renaissance of co-ordination chemistry. In recent years, the use of infrared spectroscopy has become firmly established as a standard procedure in the characterization of organic compounds. Its application to the study of inorganic substances, though less widespread at present, yields information of considerable value, particularly in the study of co-ordination compounds. Although this thesis will mostly deal on such applications of infrared spectroscopy, the general theory and use of infrared spectroscopy will not be reviewed here,

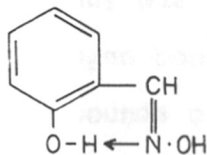
since there are available some excellent reviews<sup>5-12</sup> on infrared spectroscopy which give special emphasis to these aspects. Similarly, no review will be made on the chemistry of co-ordination compounds, since there are a large number of books<sup>12-19</sup>, reviews<sup>20-27</sup> and symposia volumes<sup>28-34</sup> on various aspect of the field. Instead, a concise account of the published informations, especially on the topics like salicylaldoxime and its metal chelates, chelate polymers and metal ammine complexes will be attempted in this chapter.

#### Salicylaldoxime and its metal chelates

Feigl<sup>35</sup> has emphatically stressed the importance to applied analytical chemistry of a clear understanding of the constitution of metallo-organic complexes, that are employed as the basis of analytical procedures. Various physical methods have been used to achieve this end. To cite an example, Tshugaeffs<sup>36</sup> reagent dimethylglyoxime, the first selective organic reagent for the analysis of metals, was known as early as 1905. However, a clear understanding of the structure of its complexes with transition metals, has been the outcome of the investigations pursued by different workers in a variety of fields, in a span of three decades. These include the X-ray diffraction<sup>37-42</sup>,

ultraviolet and infrared absorption<sup>43-48</sup>, and magnetic susceptibility studies<sup>49-52</sup>.

Salicylaldoxime has all the properties of co-ordination compound. It is sparingly soluble in water, very soluble in organic solvents and is more volatile than would be expected. On the other hand the m- and p-hydroxy benzaldoximes are readily soluble in water and moderately so in organic solvents. Salicylaldoxime, on treatment with acetic anhydride at room temperature gives a monoacetyl compound in which the oximino-hydroxyl group is acetylated, whereas p-hydroxy benzaldoxime under similar conditions gives a compound in which the phenolic group is acetylated. Hence Brady<sup>53</sup> formulated it as:



Crystallographic data of salicylaldoxime has been reported by Merrit and Schroeder<sup>54</sup>. Using hexagonal crystals, unit cell and space group have been determined. There were 8 molecules per unit cell.



The ionisation constants of salicylaldehyde have been determined<sup>55</sup> in dilute hydrochloric acid and in potassium chloride at pH 9-11. All 3 pK values have been found to obey the Debye-Huckel type equation. The results agreed with the mechanism that the phenolic hydroxyl ionises more completely than the oxime hydroxyl in alkaline conditions.

An attempt has been made by Kahovec and Kohlrausch<sup>56,57</sup> in 1942 to study the Raman spectrum of salicylaldehyde. The same authors also assigned the lowering of C=N frequency to  $1617\text{ cm}^{-1}$  in salicylaldehyde to the presence of intramolecular hydrogen bonding. In benzaldehyde the C=N Raman frequency was obtained at  $1640\text{ cm}^{-1}$ . The presence of hydrogen bonds in a number of ortho hydroxy aromatic compounds of the general type  $2\text{-HO.C}_6\text{H}_4\text{X=NY}$  where X is nitrogen or carbon and Y is carbon, nitrogen or oxygen was indicated by the absence of infrared absorption<sup>58</sup> in the hydroxyl first overtone region. Formation of hydrogen bonds was found to require the  $\text{HO-C}_6\text{H}_4$  group to have a trans configuration with respect to Y. Thus, from the absence of measurable OH absorption in oximino acetyl-salicylaldehyde, conclusions were drawn that hydrogen bonding with anti configuration

should be present in the compound. The absorption due to hydroxyl obtained for salicylaldoxime was attributed to oxime hydroxyl by comparison with that of other oximes.

Even though benzaldoxime and substituted benzaldoximes have been shown to exist in two isomeric syn and anti forms, it is noteworthy that no evidence of the existence of a second isomer has been obtained in any of the hydroxy benzaldoximes, viz. o, m or p hydroxy benzaldoxime. Attempts to prove their existence by Brady and Dunn<sup>59</sup> have not met with success. In short, salicylaldoxime exists only in one form with the oxime hydroxyl anti to the aromatic ring and there is hydrogen bonding between the phenolic hydroxyl and oxime nitrogen.

Salicylaldoxime has been also employed for the determination of copper in presence of cadmium<sup>60,61</sup> or lead<sup>62,63</sup>, zinc in presence of copper and nickel<sup>64</sup> and copper and nickel<sup>65</sup> in presence of each other. As with other selective reagents the pH of the solution is an important factor. Reif<sup>66,67</sup> has developed a method for the micro-determination of copper in presence of iron and Stengel<sup>68</sup> has reported a method for determining copper in iron and steel particularly in the presence of alloying elements. It can also be employed for the separation

of copper and cadmium in qualitative analysis<sup>69</sup>. Copper has been determined by amperometric titration by precipitation with salicylaldehyde by Neuberger<sup>70</sup>.

Salicylaldehyde has been investigated as a reagent for the polarographic determination<sup>71</sup> of small amounts of copper and from the results of the experiments it has been concluded that from 0.1516-0.6029 mg. of copper can be determined with an error of about 1-3% and 3.8-15.2 mgs. with an error of about 3%. Sodium, potassium, calcium, magnesium and ferric iron do not interfere but zinc interferes strongly. A rapid and selective method for the determination of copper and palladium polarographically<sup>72</sup> has been proposed.

The detection of iron(III) by fusion test has been reported<sup>73</sup>. The violet colour produced by heating a small specimen containing about 0.1 g. of salicylaldehyde in a microcrucible at 100°C in a steam bath has been taken as an indication. As little as 0.5  $\gamma$  of iron(III) produces a detectable violet colour. Nickel, molybdenum, vanadium, cerium and bismuth which also give highly coloured salicylaldehyde fusion products interfere.

However, salicylaldehyde is chiefly being employed for the determination of bivalent copper. The ratio of the metal ion and the reagent in the complex formed is 1:2. In the issue dealing with the possibility of the charge of the metal ion being neutralised by the acidic phenolic or the oximino hydrogen, the work of Feigl and Bondi<sup>74</sup> stands foremost. Of the isomeric oximino methyl ether and the phenolic methyl ether the former reacts with cupric acetate to form the dark brown bis-(oximinomethyl salicylaldehydato) copper(II) while the latter does not react. Thus Ephraim's assumption did not stand any cross-examination regarding the ionisation of the hydrogen of the phenolic hydroxyl function during inner complex formation. Thus the possibility of the nitron structure was ruled out.

Ephraim<sup>75</sup> has studied the reactions of a number of compounds having the same reactive groups as salicylaldehyde and has found that none of them offer any special advantage in raising analytical standards comparatively.

The substituted salicylaldoximes<sup>76</sup>

viz. 5-chloro, 3-5-dibromo and 5-nitro salicylaldoxime seems to possess no special advantages over the parent reagent regarding the analytical implications in the determination of metals.

The group  $\text{HO}-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\overset{\textstyle |}{\underset{\textstyle |}{\text{C}}}-\text{N}-\text{OH}$  which is contained in salicylaldoxime was found to be insufficient to yield a copper specific reaction. Pentanol 2-one-4-oxime  $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{C}(=\text{NOH})-\text{CH}_3$  and chloral acetophenone oxime  $\text{CCl}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{C}(=\text{NOH})-\text{C}_6\text{H}_5$  were not found to yield insoluble copper salts or colour reactions which would indicate complex formation. Thus it was concluded that differences in steric configuration and enhanced acidity of the hydroxyl group because of its linkage to the aromatic ring are duly responsible for the copper specific action of o-hydroxy benzaldoxime.

From the results of the study of the co-ordination compounds<sup>77,78</sup> of the dioximes, Brady<sup>53</sup> proposed the formula of bis-(salicylaldoximato) nickel(II) as possessive of a trans structure with free oxime hydroxyls. Complete crystal structure determinations have been conducted for the inner complexes of salicylaldoxime

with copper(II)<sup>79</sup>, nickel(II)<sup>80</sup> and palladium(II)<sup>81</sup>. It was found that each metal atom takes up two molecules of salicylaldoxime with a trans configuration. The nickel(II) complex was found to be planar and the copper(II) and palladium(II) complexes deviate slightly but significantly from total planarity.

During the studies of exchange reactions of nickel complexes Clark and Odell<sup>82</sup> observed rapid and complete exchange of the active ligands of bis-(salicylaldoximato) nickel(II) in pyridine solutions. A stepwise mechanism has been postulated for the exchange and the results are correlated with the magnetic measurements. Cox and co-workers<sup>83</sup> have found that nickel and palladium compounds of salicylaldoxime are isomorphous. The nickel compounds was found by them to be diamagnetic. However, Malatesta<sup>84</sup> has reported bis-(salicylaldoximato) nickel(II) as paramagnetic having 2.7 Bohr magnetons. As exchange occurred of the nickel<sup>85</sup> of the nickel derivative with nickel<sup>65</sup> the paramagnetic character could be explained. However, it was also known that<sup>86</sup> the compound was diamagnetic in the solid state and in benzene solution but to be paramagnetic to the extent of 1.1 and 3.1 Bohr magnetons in  $\text{CHCl}_3$  and pyridine respectively. They postulated, in the case of pyridine the formation

of an octahedral complex containing pyridine in equilibrium with planar molecules but felt that chloroform would be unlikely to form such a complex. They agreed that the differences in stability of square and tetrahedral complexes may in some cases be so small that the solvent may cause partial conversion to the tetrahedral structures as was earlier suggested by French and co-workers<sup>87</sup> in the case of bis-(formyl camphor ethylenediamine) nickel in methanol solution.

Mellor and Craig<sup>88</sup> have shown that a square co-planar configuration with strong covalent bonding is to be expected for bis-(salicylaloximato) cobalt(II). Nickel derivative has also been shown<sup>89</sup> to exist having similar configuration. Hence, if exchange were observed, it would be expected, to be slow. Rapid exchange was found to occur for nickel<sup>85</sup> and cobalt<sup>90</sup> derivatives with nickel<sup>65</sup> and cobalt<sup>60</sup>. Hence it was presumed that both the nickel and cobalt derivatives contain bonds with considerable ionic character when in solutions of methoxy ethanol and pyridine respectively.

Schweitzer and co-workers<sup>91</sup> have also observed exchange of nickel<sup>63</sup> with nickel of bis-(salicylaloximato) nickel(II) in aqueous solution. Mashima<sup>92</sup> has also found very little or partial exchange of cobalt of the cobalt derivative with

cobalt<sup>60</sup> in aqueous or pyridine solutions respectively. Zinc salicylaldoxime has been found to exchange<sup>93</sup> rapidly and completely with zinc<sup>65</sup> in about 0.8 f  $\text{HClO}_4$  and in 7 f  $\text{HCl}$ . Some magnetic measurement studies have been carried out by Lumme<sup>94</sup> on salicylaldoxime complexes of bivalent copper, cobalt and nickel. The temperature dependence of the apparent magnetic moments and absorption spectra of solutions of bis-(salicylaldoximato) nickel(II)<sup>95</sup> showed equilibrium to be existing between the planar and tetrahedral forms. Magnetic susceptibility measurements<sup>96</sup> of the pyridine solutions of bis-(salicylaldoximato) nickel(II) have confirmed the formation of paramagnetic pyridine addition compounds which contain two pyridine molecules per nickel atom. Clark and Odell<sup>97</sup> have isolated the paramagnetic pyridine adduct and from their magnetic measurement studies have concluded, that it presumably utilises the highly polar outer  $\text{Sp}^3 \text{d}^2$  octahedral configuration.

Ultraviolet and visible absorption spectral studies of alcoholic solution of salicylaldoxime and chloroform solutions of the copper, nickel, palladium and cobalt chelates have been made by Koze Sone<sup>98</sup>. The electronic



absorption spectra of bis-(salicylaldoximate) nickel(II) has been assigned<sup>99</sup> by using ligand field theory.

From the thermolysis studies<sup>100</sup>, zinc mono-(salicylaldoxime) was found to decompose very rapidly at 290°C. From these studies drying of the precipitate at 110°C was recommended during analytical estimations.

Thermal stabilities of some bivalent salicylaldoximates have been investigated by Lumme<sup>101</sup>.  $\text{CuR}_2$  decomposed explosively at 229-238°C, then slowly at 238-548°C to a CuO residue.  $\text{NiR}_2$  was stable to 259°C, decomposed explosively at 259-300°C and gradually decomposed to NiO at 300-475°C.  $\text{CoR}_2$  gradually decomposed at 400-524°C to  $\text{Co}_3\text{O}_4 \cdot \text{ZnR}_2 \cdot \text{H}_2\text{O}$  was found to be stable to 95°C, becomes anhydrous at 148°C, slowly decomposed at 148-193°C, decomposed explosively at 193-217°C, then decomposed in two stages at 400 and 536°C to ZnO.  $\text{CdR}_2$  was stable to 230°C decomposed explosively, at 230-246°C and then rapidly decomposed to CdO above 365°C.  $\text{PbR}_2$  decomposed slowly at 157-236°C, rapidly at 265°C, and finally decomposed to PbO at 350-565°C. Thermal stabilities were found to decrease in the order of  $\text{NiR}_2 > \text{CdR}_2 \geq \text{CuR}_2 > \text{PbR}_2 > \text{ZnR}_2 > \text{CoR}_2$ .

The lack of correlation with the metallic properties suggests that thermal stability is due to the organic ligand.

#### Chelate polymers

Pfeiffer<sup>102</sup> has shown that five membered chelate rings are more stable than six membered ones when there are no conjugated double bonds in the resulting chelate. It was observed in several cases that chelation with metal ions improves to a great extent the thermal stability of organic ligands<sup>103</sup>. Further, more the number of rings formed, the lower the internal energy on the formation of stable cyclic structure. This was demonstrated by Calvin and Bailes<sup>104</sup>. Thus the half wave potential of an inner complex with three chelate rings was found to be lower than that of one with two such rings. It is noteworthy that the presence of several such rings often pronounces the thermal stability of the inner complexes. Copper(II) ethylenediamine bis-acetylacetonate was found to be hardly decomposed at red heat<sup>105</sup> and copper phthalocyanine could be sublimed in vacuum at 570°C without decomposition<sup>106</sup>.

The stability of a complex depends on the type of bond formed between the metal ion and the ligand<sup>13</sup> and predominantly on the electronic configuration of the metal ion. Results of the stability constant determinations have revealed that direct relationship exist between the stability of the complex and the nature of the metal ion. Mellor and Maley<sup>107</sup> have studied the stability of salicylaldehyde complexes in 1:1 water-dioxane mixture. The metal ions could be placed in the series  $\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$  in order of decreasing stability of the complexes. Almost the same order of stability were found for the ethylenediamine, 8-hydroxyquinoline<sup>108</sup> and  $\beta$ -diketone chelates<sup>109</sup>. Thus the chemical stability of the chelates decreases with increasing basicity of the metal and the most weakly basic metals (Pd, Cu) form the most stable chelates. In other words, the chemical stability of the chelates decreases with increasing ionic character between the metal and the donor atoms of ligand.

Most of the metal chelates are distinguished by an appreciable chemical stability. The copper salt of EDTA was found to be unaffected on boiling with alkali<sup>110</sup>. The stability of chelates of alkaline earth metals are so great that the metals have not been possible to be precipitated as sulphates,

oxalates, phosphates, carbonates etc. The glycinate and alaninate of  $\text{Co}^{3+}$  dissolve in concentrated sulphuric acid without decomposition. Beryllium salicylates are only slightly decomposed by alkalies<sup>111</sup>. It is evident from the above discussions that the properties of the organic and inorganic counterparts do get definitely modified.

In view of these, it was hoped that such necessary properties as better thermal stability, flexibility etc. for practical purposes could be fostered by inorganic co-ordination polymers. Recent developments, greatly stimulated by the exacting demands of space research have enlarged to a considerable extent the field of inorganic co-ordination polymers. The optimistic requirements of space research calling forth for materials with high thermal stability and high strength/weight ratio have been a major factor in the recent rapid growth in this field. There are, however, many other potential fields where exhaustive applications can be made, as in high temperature electrical insulation, semiconductors and chemically resistant constructional materials. To nourish such requirements the development of new routes to the synthesis of polymeric materials which possess the easy workability, chemical stability and specific physico - mechanical properties characteristic of

many organic and organometallic polymers and the thermal stability, electrical conductivity, magnetic permeability etc. of metals are being worked out by various investigators. Thus, there is now a world wide interest in inorganic polymers initiated chiefly by the technological limitations of conventional organic polymers.

Two types of co-ordination polymers have been recognizable, one in which the metal ion is an integral part of the backbone and a second in which it is co-ordinated to a polymer repeating unit containing donor groups.

Where complete structural data are lacking the proof that a co-ordination compound is polymeric is generally more tenuous. Because of the non-availability of suitable solvents, the molecular weights of the polymers could be substantiated only in a relatively few cases. Because it is rather difficult to establish polymeric character of many inorganic substances, there has been a marked tendency, to ascribe any insoluble and inert or tacky and resinous appearing product as a polymer. A related approach for assigning polymeric structure has been based on elemental analysis. If the composition of the product is found to be such that there are not sufficient donor groups sterically available to a co-ordination centre to permit it to have its usual co-ordination pattern, then

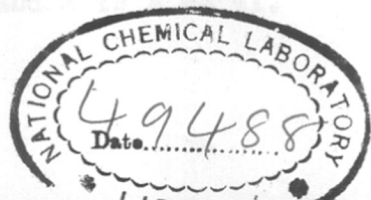
polymerisation has been assumed to have occurred, in order to enable the centre to attain its normal co-ordination number. Eventhough these points do not enlighten to any extent the polymer formation, yet totally viewed, they may be indicative of it. The variable co-ordination numbers possible for metal ions, can result in co-ordination polymers with a multiplicity of geometrical patterns. By and large, current polymer knowledge is restricted mainly to systems in which co-ordination number is 4 or 6.

It should not always be taken for granted that co-ordination polymerization yields much more thermally stable materials<sup>111,112</sup> than their corresponding monomeric analogues. It is thus necessary to investigate thermal stabilities in each system to establish the effect of co-ordination.

Survey of the work pursued in the line of inorganic co-ordination polymers indicates that the synthesis of the polymers have mainly been carried out to obtain products of appreciable thermal stability. Other fields of investigations, as their mechanism of formation, electrical conductivity or the spatial arrangement has been worked out only in minor cases. However, the outcome of the studies

546.3:541.572.54(043)

RAM

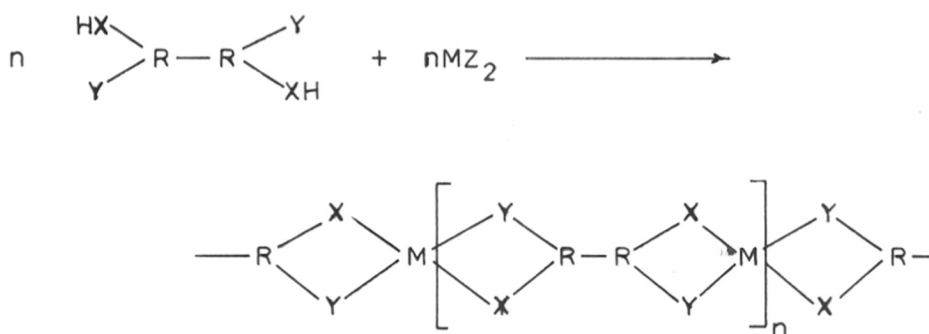


made in thermal stability measurements have crystallised the conclusion that when the metal ion is located in the main polymer chain, relatively much better thermostable materials are formed than when they are present laterally in side chains. The properties of the co-ordination polymers has been found to be dependent on the chelate loop formed.

Principal methods of synthesis of inorganic co-ordination polymers can be outlined as below:

1. Reactions of metal ions and chelate ligands

Basis of these reactions is that metal ions are polyfunctional in character capable of accepting more than one pair of electrons. A polymer from a typical reaction may be visualized as:



(A)

where x and y are donor groups and M is a metal.

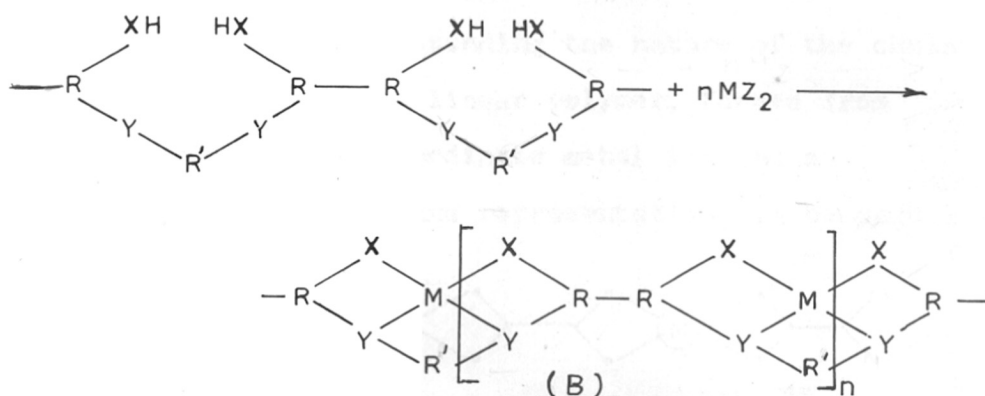
Hence, reactions between a bis-(bidentate) ligand and a tetra co-ordinate metal ion or between that of a bis-(tridentate) ligand and hexa co-ordinate metal ion will lead to linear polymers if the two bidentate functions are unable to co-ordinate to the same metal ion, whereas a bis-bidentate ligand and a hexa co-ordinate metal ion or a polyfunctional ligand with a tetra co-ordinate metal could give highly cross linked polymeric products. A hexa co-ordinate metal ion can be used to prepare linear polymers with bidentate ligands by blocking two of the co-ordination positions by unreactive groups. The degree of cross-linking in polymers is governed by the co-ordination number of the metal ion and the number and nature of disposition of the co-ordinating centres in the "chelate ligand".

Thus by employing, metals with suitable co-ordination number, and appropriate chelate ligands with polyfunctional co-ordination sites, polymers of different spatial structures viz. linear polychelates, planar and three dimensional networks can be obtained.

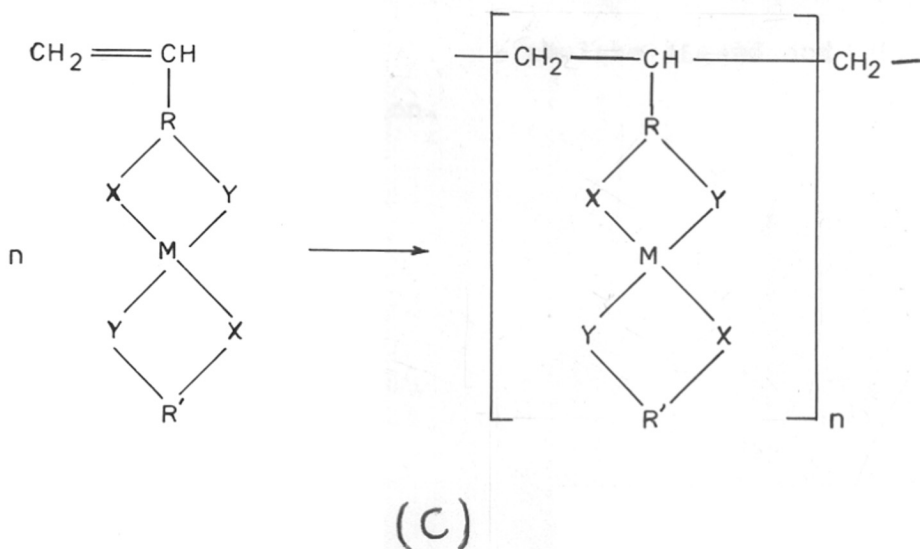


**2. Reactions of metal ions with preformed polymeric ligands having co-ordination sites**

This is by entry of the metal ion into an existing polymer in which the monomeric unit contains at least two pairs of donor groups. This can be represented as:

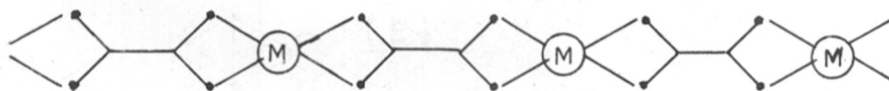


**3. Reactions in which monomers containing co-ordinated metal ions are polymerized through functional groups**

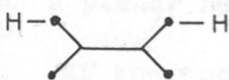


The second and the third methods of synthesising poly-chelates are usually linked with common methods for obtaining high polymers.

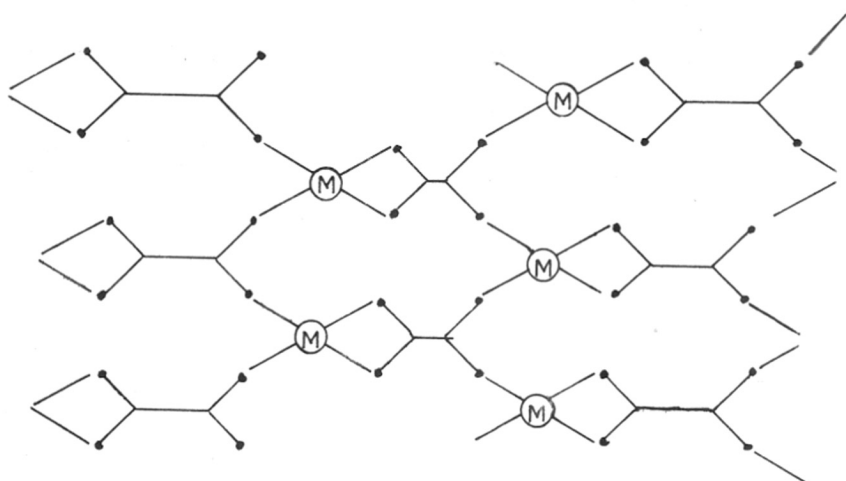
The structure of a polymer is ofcourse determined separately in each individual case. In many cases the structure of the macromolecule can be visualized by understanding the nature of the chelate loop formed. For a linear polymer, formed from a divalent four co-ordinate metal ion and a bis-(bidentate) ligand representation can be made as:



(D)

where  = chelate ligand and  
M = divalent metal ion.

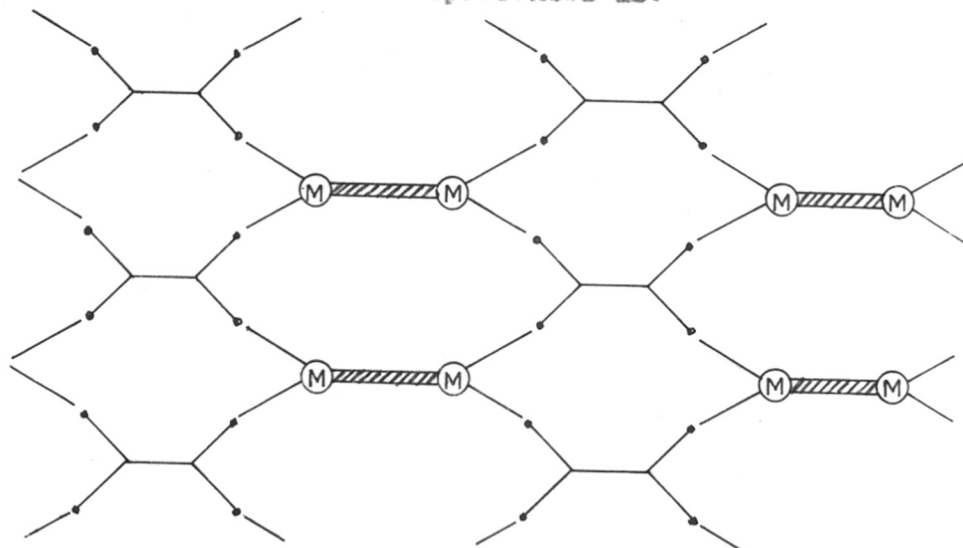
However, such a polymer can also have the structure as:




( E )

There are also several other possibilities for such a planar network.

If the chelate loops have a non-planar structure a three-dimensional network will result, one layer of which can be represented as:



( F )

where  denotes a ligand molecule "in profile". Here each chelate loop can form the basis of a new network of layer of polymer. Each of the structure (D)-(F) clearly represents in some measure an extreme case. In practice, there probably exists a definite combination of all these structures. Moreover polychelates of any particular structure have their own rules for building up of complete macromolecules and it is improper to regard chelate polymers as being completely analogous to one another. In considering the various properties of polychelates, it is probably necessary to regard that they have a network structure. As mentioned earlier only a few investigations have been directed to know the structures of chelate macromolecules. Terentev<sup>113,114</sup> and co-workers, on the basis of a series of physico-chemical properties of a large number of polychelates of different structure have arrived at the conclusion that they are mainly two dimensional and three dimensional network structures. They assume that linear macromolecules are also present, although relatively few in number.

There are a number of organic molecules which can conceivably form co-ordination polymers by acting as bis chelating agents i.e. with one part of the molecule chelating to one metal atom and the other part of the molecule chelating with another metal atom. Such systems have been observed to be possible with dicarboxylic acids and beryllium atoms and the bis cyclopentadienyl compounds between iron atoms. It may also be possible that many a compound of this category has been reported as simple ones. However, characterization of co-ordination polymers by employing bis chelating agents as bis -  $\beta$ -diketones, bis-hydroxy quinolines, bis - salicylaldehydes and other molecules possessive of donor groups capable of producing polymers as quinizarin, naphthazarin etc. have been reported.

To date, most efforts to prepare such polymers have involved the use of organic chelating agents which simultaneously satisfy charge and fill the co-ordination positions of metal ions.

### Ammine complexes

Historically, the amines of cobalt(III) and chromium(III) have influenced the entire field of co-ordination chemistry. The historical significance of these substances has been reviewed by Bailar<sup>16</sup> and the reasoning invoked may be found in Werner's<sup>1</sup> classical book or the introductory text by Grinberg<sup>14</sup>. The number of known compounds of this general class is overwhelming and relatively complete listing of the substances known in early years may be found in the standard reference works of Friend and Gmelin. Since there have been numerous investigations on the infrared spectra of ammine complexes, a concise account of the published reports will follow.

NH<sub>3</sub> stretching bands: Assignments made empirically for the bands appearing in the region 3400-3000 cm<sup>-1</sup> to NH<sub>3</sub> stretching vibrations must be undoubtedly correct as these must be due to hydrogen stretching modes. In the ammine complexes, these have been observed as broader peaks appearing at lower frequencies than those observed for free ammonia molecule. Factors responsible for the frequency shift have been accounted as co-ordination, nature of the anion or hydrogen bonding, hydration and configuration (cis, trans etc.). The broadenings of

the bands in compounds such as  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  and  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$  have been observed and reasons put forward are hydrogen bonding as well as overlapping of the individual N-H stretching bands of the whole complex ion. Most of the spectra reported in this region for such amines have been recorded as solid samples using sodium chloride optics which does not give the best possible resolution in this region. Thus, only its existence has been pointed out without much scrutiny. It should be mentioned that imperfect sample preparation for recording the spectra affects severely this region of the spectrum. It is to be expected that in the approximation of negligible interaction between the ligands, ammine complexes will exhibit two N-H stretching bands arising from the symmetric and asymmetric modes. Chatt and co-workers<sup>115,116</sup> have examined platinum and palladium complexes containing ammonia and primary and secondary amines using lithium fluoride optics. The results clearly indicate that spectra of solids are not subject to any clear interpretation because of drastic solid state effects, one of the most important, being hydrogen bonding. They have also shown that in carbon tetrachloride solutions association occurs through hydrogen bonding thus complicating the spectra. From the concentration

dependence of various bands they have determined which ones are due to unassociated molecules. In a mixed carbon tetrachloride-dioxan solvent, hydrogen bonding to the dioxan was found to have a profound effect on the spectrum. It was found that the amine hydrogen of the secondary amine ligands had only a slight tendency towards hydrogen bonding and it has been suggested that if shifts in NH stretching frequencies are to be used to diagonalise electronic effects in complexes, which must necessarily be examined as solids, secondary amine complexes should be used.

Some random observations on the effects of hydrogen bonding, hydration and solid state effects on N-H stretching frequencies have been made by Svatos and co-workers<sup>117</sup>. They have resolved two distinct bands from studies of solid materials but whether or not there are two fundamentals is uncertain. By co-ordination the N-H stretching frequencies get lowered by 100-150  $\text{cm}^{-1}$ . It has been proposed that major cause of this is the drainage of electrons from the nitrogen atom which in turn weakens the N-H bonds (analogy to ammonium ion: N-H stretch at 3125  $\text{cm}^{-1}$  where the additional bond formed must be highly covalent).



NH<sub>3</sub>-deformation and rocking bands: The assignment of the three principal absorption bands of the ammine complexes had been a subject of some controversy but uncertainties have been resolved. It had been suggested that both the 1300 and 850 cm<sup>-1</sup> absorption bands were due to skeletal modes<sup>118</sup> and specifically that the 850 cm<sup>-1</sup> absorption was due to M-N stretching<sup>119</sup>. At the same time Faust and Quagliano<sup>120</sup> proposed to assign the 1600 cm<sup>-1</sup> band to an NH<sub>3</sub> deformation. Another quite reasonable proposal<sup>121</sup> was to assign the 1600 and 1300 cm<sup>-1</sup> bands to asymmetric and symmetric NH<sub>3</sub> deformations and the 850 cm<sup>-1</sup> band either to a rocking motion of the NH<sub>3</sub> or to a metal ligand stretching frequency. The first sound evidence was presented in 1955 by Mizushima and co-workers<sup>122,123</sup>, for assigning these bands by observing the shifts resulting on complete deuteration of [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> to [Co(ND<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>. Their calculated values, assuming reasonable values of force constants of the expected shifts for symmetric and asymmetric NH<sub>3</sub> deformations and NH<sub>3</sub> rocking agreed with observed ones. Thus the assignment of the ~850 cm<sup>-1</sup> band to M-N stretching mode was ruled out as this band in the deuterated compound was found to be absent. They had not actually observed the shift. Powell and Sheppard<sup>124</sup> have reported bands at 830 cm<sup>-1</sup>

in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $665 \text{ cm}^{-1}$  in  $[\text{Co}(\text{ND}_3)_6]^{3+}$ ; while Barrow and co-workers have reported bands in these complexes at  $828$  and  $663 \text{ cm}^{-1}$  respectively in satisfactory agreement with the prediction of Mizushima for a rocking vibration. Powell and Sheppard have also reported isotopic shifts observed in several other amines such as trans-  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ ,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , and  $[\text{Ag}(\text{NH}_3)_2]_2\text{SO}_4$ . In trans-  $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$  a band at  $752 \text{ cm}^{-1}$  was found to be shifted to  $580 \text{ cm}^{-1}$  on deuteration. In  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  Barrow and co-workers<sup>125</sup> observed bands at  $826$  (m) and  $796$  (s)  $\text{cm}^{-1}$  but only one band at  $594 \text{ cm}^{-1}$  in the deuterated analogue. Thus, conclusions were drawn that metal-ligand frequencies do not occur in the rock salt region.

Metal-Nitrogen (M-N) stretching bands: These have evoked deep interest as it provides direct information about the nature of the co-ordinate bond. Because of the relatively heavy mass of the metal atom and the low bond order of the co-ordinate bond the M-N stretching vibration may appear in the low frequency region.

Many of the studies conducted with amines are in the sodium chloride prism region and studies of the caesium bromide prism region are only sporadic. The question of where the metal ligand stretching and also the N-M-N modes absorb is not yet settled. Concerning the latter, by comparison with metal carbonyls and metal cyanide complexes they may be expected to appear around  $100\text{ cm}^{-1}$ . Thus bands occurring between  $600\text{ cm}^{-1}$  and  $200\text{ cm}^{-1}$  of specific high intensity can be assigned to metal-ligand frequencies. The only reported study below  $450\text{ cm}^{-1}$  is that of Barrow and co-workers<sup>125</sup> who have scanned down to  $\sim 300\text{ cm}^{-1}$ . For a number of compounds they have observed bands between  $500$  and  $300\text{ cm}^{-1}$  for which where mention has been made intensity is strong. They have suggested the usually occurring single bands in the  $500\text{-}300\text{ cm}^{-1}$  range to be assigned to metal ammonia stretching frequencies. The essential nil shifts in these bands on deuteration substitution are in good accord with such an assignment, although the same behaviour would be expected for the N-M-N bond.

The studies conducted by Powell<sup>124,126,127</sup> for the ammine complexes upto  $\sim 450 \text{ cm}^{-1}$  brought forth proposal that the extremely weak bands near  $500 \text{ cm}^{-1}$  can be assigned to metal-nitrogen stretching frequencies. In the few deuterio analogues examined the bands in question showed only  $\sim 2\%$  shifts. He also points out that Raman lines around  $500 \text{ cm}^{-1}$  have been reported for several such complexes. For  $[\text{Pt}(\text{NH}_3)_4 \text{Cl}_2]$  Powell reports a band at  $511 \text{ cm}^{-1}$  and Barrow et al one at  $497 \text{ cm}^{-1}$ . The bands at  $\sim 507 \text{ cm}^{-1}$  in cis- and trans-  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  reported by Powell were not observed by Barrow et al.

From these, it can be visualized that much more work has to be done to understand the spectra of such complexes in the region above the rocking mode.

#### Effect of Metal-Ligand bond character on Vibrational Frequencies

Several attempts have been made to correlate the variations in the frequencies of the stretching, bending and rocking modes of the ammonia ligands with the strengths of the metal-nitrogen bonds. An early attempt was made by Kobayashi and Fujita<sup>119</sup> who have studied  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ ,  $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$  and  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  and found that the N-H stretching frequencies decreased in the above order, the  $1600 \text{ cm}^{-1}$  band showed little

variation, the 1300-1200  $\text{cm}^{-1}$  bands increased in the above order and the 800-600  $\text{cm}^{-1}$  bands increased very markedly in that order (Ni, 682, Cr, 762 and Co, 830  $\text{cm}^{-1}$ ). They have suggested that a decrease in N-H stretching frequencies can be attributable to increasing metal-nitrogen bond strength. They assigned the low frequency bands to M-N stretches, incorrectly, as revealed now. Powell and Sheppard<sup>124</sup> have pointed out using the data of Kobayashi and Fujita<sup>119</sup> along with some data of their own that plots of deformation frequencies versus free energies of formation of complexes in solution did not yield very satisfactory straight lines, although there was qualitative agreement.

Fujita and co-workers<sup>128</sup> have studied the chloride, bromide, iodide, nitrate and perchlorate salts of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and observed variations in the absorption bands which can be correlated to varying strength of hydrogen bonds to the anions. The frequencies observed for N-H stretching were found to be  $\sim 3070$ ,  $\sim 3120$  and  $\sim 3150 \text{ cm}^{-1}$  for the halides in the above order and the rocking vibrations again in the same order at 818, 797 and 792  $\text{cm}^{-1}$ . In order to compare again the frequencies in the hexamines of nickel(II), chromium(III) and cobalt(III) with minimal extraneous variations due to varying strength of hydrogen bonding in the different lattices, they examined the perchlorates. Again the stretching frequencies decreased, the

the symmetric deformation frequencies increased and the rocking frequencies markedly increased in the order of nickel(II), chromium(III), cobalt(III).

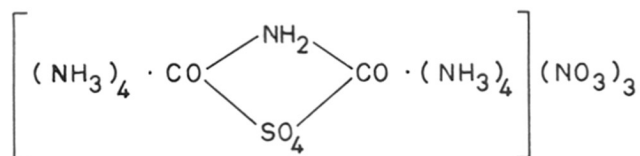
Svatos and co-workers<sup>129</sup> have examined a large variety of ammine and substituted ammine complexes. The rocking frequency was found to decrease in the order Pt(IV), Pt(II), Co(III), Pd(II), Cr(III), Cu(II), Ni(II), Co(II) although there are some inversions for the particular compounds since the salts examined were chlorides, bromides, sulphates and nitrates in which hydrogen bonding effects might be sizable and related to crystal structure. These authors have also shown, by calculations that rocking frequency is expected to depend strongly on M-N bond strength, the symmetric deformation less so and asymmetric deformation rather little and that the variations with increase of M-N bond strength should be in the directions actually found.

Powell<sup>126,127</sup> has attempted to determine whether or not the trans directing ability of various ligands can be correlated with a simple trans bond weakening effect, using compounds of the type  $[\text{Pt L}(\text{NH}_3)\text{Cl}_2]$  and observing the variation in frequency

of the Pt-N stretching vibrations. According to him these vibrations should give a more direct measure of the effect in question and will also be less affected by extraneous variations and influences such as hydrogen bonding although the procedure of Chatt<sup>115</sup> seems to be unobjectionable in the latter aspect. One objection to Powell's approach is that the Pt-N stretching will be more strongly coupled to other modes than with N-H stretches, but he feels that the great mass of platinum atom will quench this effectively. Another and more serious objection is that the assignments of Pt-N frequencies are not completely certain. On the basis of his assignments Powell finds trends in the Pt-N bond strengths paralleling those deduced by Chatt and co-workers from the N-H stretching frequencies although, the magnitude of variation is larger than Chatts' results might have suggested. Powell has concluded that for the very strongly trans directing ligands such as ethylene and diethyl sulphide, the bond weakening produced is sufficient to have a significant effect on the tendency of the trans  $\text{NH}_3$  group to dissociate although it does not necessarily imply that ability to induce dissociation is the controlling factor in determining the relative trans directing powers of the various ligands.

### Symmetry and Ligated species

Nakamoto and co-workers<sup>130</sup> have examined ammine complexes containing sulphate, carbonate, oxalate and acetate ions as ligands obtaining results which correlate well with changes in symmetry of these ions when they function as ligands. The free sulphate ion has a regular tetrahedral structure belonging to the point group  $T_d$ . When it functions as a unidentate ligand the co-ordinated oxygen is no longer symmetrically equivalent to the other three and the effective symmetry is lowered to  $C_{3v}$ . In the complex



the sulphate ion functions as a bidentate bridge and its effective symmetry is reduced to  $C_{2v}$ . The correlation has been found to be very satisfactory. A similar correlation was found to be existing in the carbonate complexes free  $\text{Co}_3^{2-}$  ( $D_{3h}$ ),  $[\text{Co}(\text{NH}_3)_5 \text{Co}_3] \text{Br}$  ( $C_{2v}$ ),  $[\text{Co}(\text{NH}_3)_4 \text{Co}_3] \text{Cl}$  ( $C_{2v}$ ), and  $[\text{Co} \text{ en}_2 \text{Co}_3] \text{Br}$  ( $C_{2v}$ ). The effects of co-ordination and concomitant lowering of the effective symmetry of the oxalate ion in oxalato amines have also been studied.



The effect of co-ordination on the symmetry and structure of carbonate and sulfate groups have been ascertained also by Drouin and co-workers<sup>131</sup> from the infra-red spectra of various crystalline cobalt(III) amines. The spectra of saturated aqueous solutions of several cobalt(III) ammine sulfates and of sulfato cobalt(III) amines have also been interpreted.

Studies of the infra-red spectra in the sodium chloride prism region has been pursued by Siebert<sup>132</sup> for 27 cobalt(III) complexes containing as ligands  $\text{NH}_3$  and anions of oxyacids which showed bands attributable to the particular anion present and relatively constant bands due to  $\text{NH}_3$ . The uncomplexed anions and cations present were found to have little effect on the spectra except for nitrate and sulfato complexes. The symmetry of the oxyanion decreased as:  $\text{CO}_3^{2-}$ ,  $D_{3h}$  to  $C_{2v}$ ;  $\text{HCO}_2^-$ ,  $C_{2v}$  to  $C_s$ ;  $\text{C}_2\text{O}_4^{2-}$ ,  $V_h$  to  $C_{2v}$ ,  $\text{NO}_2^-$ ,  $C_{2v}$  to  $C_s$  (-ONO) or unchanged (- $\text{NO}_2$ );  $\text{NO}_3^-$   $D_{3h}$  to  $C_{2v}$ ,  $\text{SO}_4^{2-}$ ,  $T_d$  to  $C_{3v}$  in the chloride salt or  $C_s$  in the nitrate or iodide salt. Comparison of these spectra with those of esters of oxyacids showed that the cobalt-oxyanion bonds are intermediate in character between pure ionic and pure covalent bonds.

Semiquantitative calculations have shown that the bonds are 20, 30, 30, 30, 30, 50 and 50% covalent for  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{ONO}^-$ ,  $\text{NO}_2^-$  and  $\text{SO}_3^{2-}$  bonds to cobalt respectively. The easy replacement of ligands containing Co-O bonds, the stability of the compounds containing Co-N or Co-S bonds and the rearrangement of  $\text{ONO}$  to  $\text{NO}_2$  compounds are discussed in terms of these findings.

CHAPTER II

INFRARED SPECTRAL STUDIES OF SALICYLALDOXIME

AND SOME OF ITS METAL CHELATES

### Abstract

The solvent-cum-deuteration infrared spectral studies of salicylaldoxime and related compounds confirmed the presence of intermolecular and intramolecular hydrogen bonding and further showed that the hydrogen bonding in salicylaldoxime is not as strong as would be expected on the basis of Freedman's findings. Moreover, salicylaldoxime diacetate, a compound synthesized for the first time, showed no absorption peak at c.  $3200\text{ cm}^{-1}$  ascribed to an C-N overtone frequency by Freedman. The salient features of the infrared spectra of salicylaldoxime and those of its chelates with bivalent metals like nickel(II), copper(II), cobalt(II), manganese(II) and palladium(II), have been brought out by comparing their spectra with those of deuterated salicylaldoxime and deuterated nickel(II) chelate.

INFRARED SPECTRAL STUDIES OF SALICYLALDOXIME  
AND SOME OF ITS METAL CHELATES

As can be seen from the review of the literature (general introduction of this thesis) published reports on the infrared spectral studies of salicylaldehyde and its metal chelates are either of casual nature<sup>133,134</sup> or non-existent. Oximes are known to be subject of association which has impeded the elucidation of their molecular structure by means of dipole moment studies<sup>135</sup>.

Infrared spectra of the fundamental or overtone transitions of the hydrogen stretching mode can be directed at discovering the nature of hydrogen bonding in molecules<sup>136,137</sup>. In our attempt to gain information concerning the nature of the hydrogen bonding in salicylaldehyde, we carried out a study of hydroxyl stretching frequencies in the fundamental region at c.  $3600\text{ cm}^{-1}$  of salicylaldehyde, deuterated salicylaldehyde, oximino acetyl-salicylaldehyde, oximino benzoyl-salicylaldehyde and salicylaldehyde diacetate in carbon tetrachloride solution.

Based on X-ray work of Merritt and Gaure<sup>80</sup> and some infrared data, Nakamoto and co-workers<sup>134</sup> proposed a badly bent hydrogen bond in nickel salicylaloxime. Recent X-ray data<sup>79</sup> on bis-(salicylaloximate) copper(II) showed that the hydrogen bond is even longer (2.58<sup>0</sup>Å) in this compound than that of the corresponding nickel chelate (2.52<sup>0</sup>Å). It is now generally agreed that very strong and short hydrogen bonds between the phenolic oxygen atom of one organic ligand and the oximino oxygen atom of the second ligand exist in such molecules of bis-(salicylaloximate) metal chelates, for instance nickel<sup>80</sup>, copper<sup>79</sup> and palladium<sup>81</sup> chelates which have distorted trans-planar configurations. An attempt to interpret the infrared spectra of such chelates has been made in the wave number range covering 1650 ~ 650 cm<sup>-1</sup>. Analysis of bands at higher frequencies and in solution was unsatisfactory owing to the broad nature of the bands and colour changes respectively.

## Results and Discussion

The  $\nu$ OH spectrum of salicylaldoxime is given in Figure 1, for different concentrations. In the curves, the bands due to free OH groups (c.  $3600\text{ cm}^{-1}$ ) and to both inter and intramolecular bonded OH groups ( $3445\text{ cm}^{-1}$  and  $3230\text{ cm}^{-1}$  respectively) can be seen. The intensity of the broad band at c.  $3445\text{ cm}^{-1}$  due to intermolecular association decreases progressively on dilution (Fig. 1b and 1c). The sharp band at c.  $3600\text{ cm}^{-1}$  can be attributed to the free oximino hydroxyl group and as expected this band is absent in the spectra of oximino acetyl and oximino benzoyl salicylaldoximes. (Fig. 3a and 3b) The broad band at c.  $3230\text{ cm}^{-1}$  is due to intramolecular hydrogen bonding of the type in which the phenolic O-H group is bonded to the nitrogen of the  $-\overset{|}{\text{C}}=\text{N}-\text{OH}$  group to give an average  $\Delta \nu$  O-H shift of about  $370\text{ cm}^{-1}$ . The half band width is several times greater than the non-associated band. The average shift of the band due to intermolecularly bonded O-H ... is c.  $170\text{ cm}^{-1}$ . Thus the intramolecular bonding is more than twice as strong as the intermolecular bonding.

On deuteration, the above mentioned bands are shifted to lower frequencies roughly as expected by a factor of  $1/\sqrt{2}$ . (Fig. 2) The peak at c.  $3070\text{ cm}^{-1}$

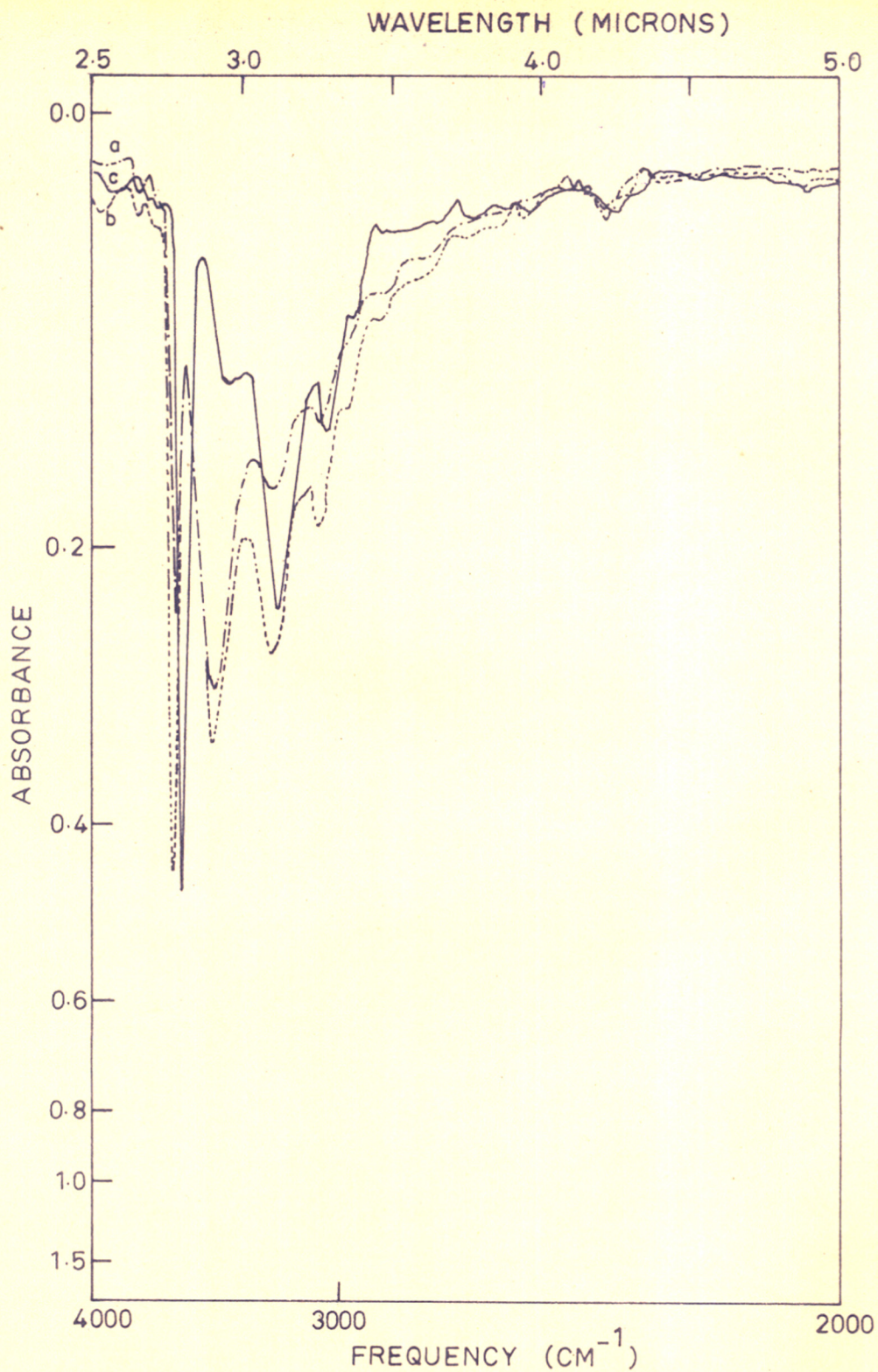


FIG. 1. INFRARED SPECTRA OF SALICYLALDOXIME IN  $\text{CCl}_4$

- a 5.8 % W/V ; 0.1 mm. CELL.
- · - · - b 1.0 % W/V ; 0.5 mm. CELL.
- c 0.2 % W/V ; 3.0 mm. CELL.



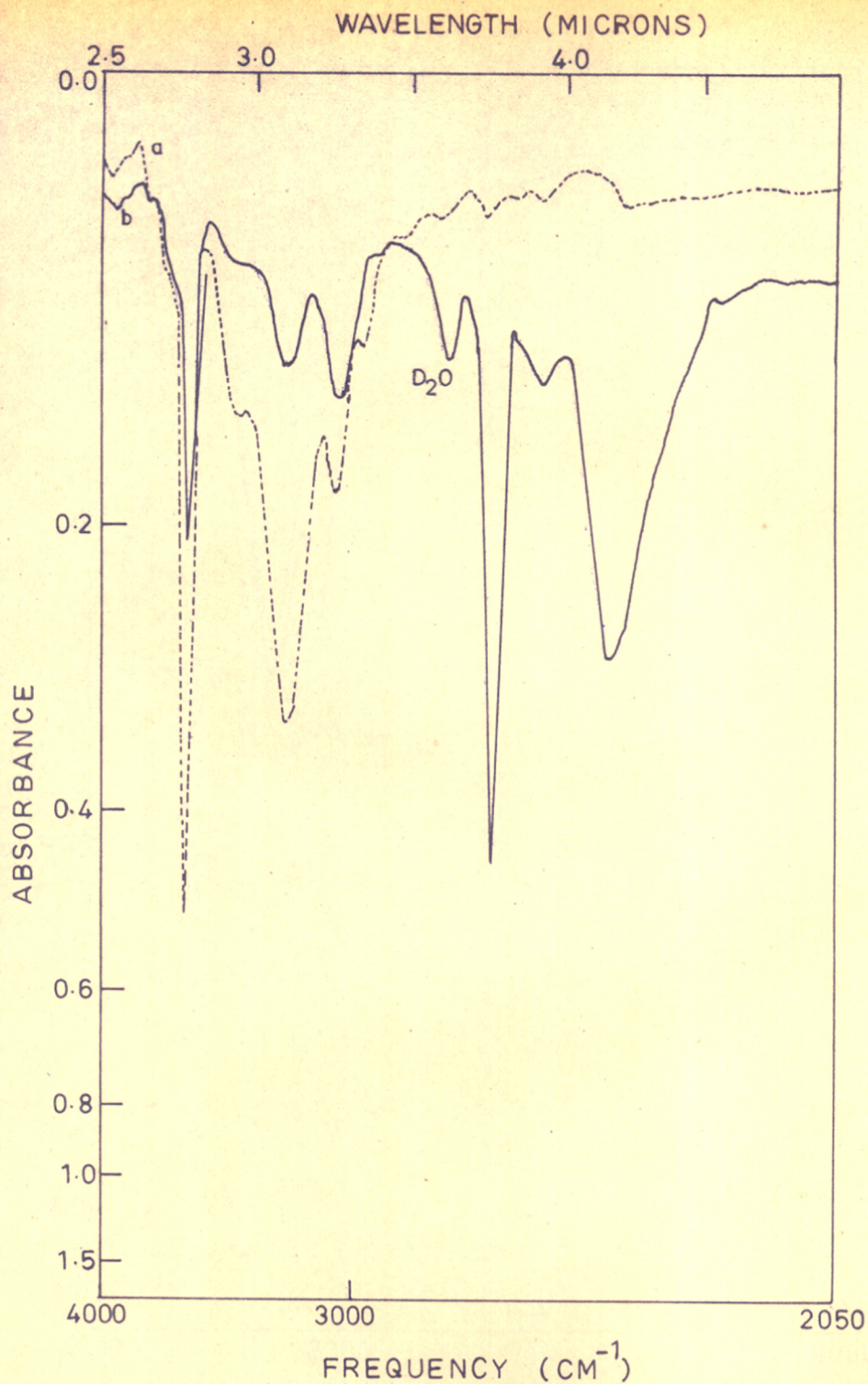


FIG. 2. INFRARED SPECTRA IN CCl<sub>4</sub> OF

- a SALICYLALDOXIME (0.08 % W/V), 1 Cm. QUARTZ CELL
- b SALICYLALDOXIME (deuterated) (0.07 % W/V) , 1 Cm. QUARTZ CELL  
in situ

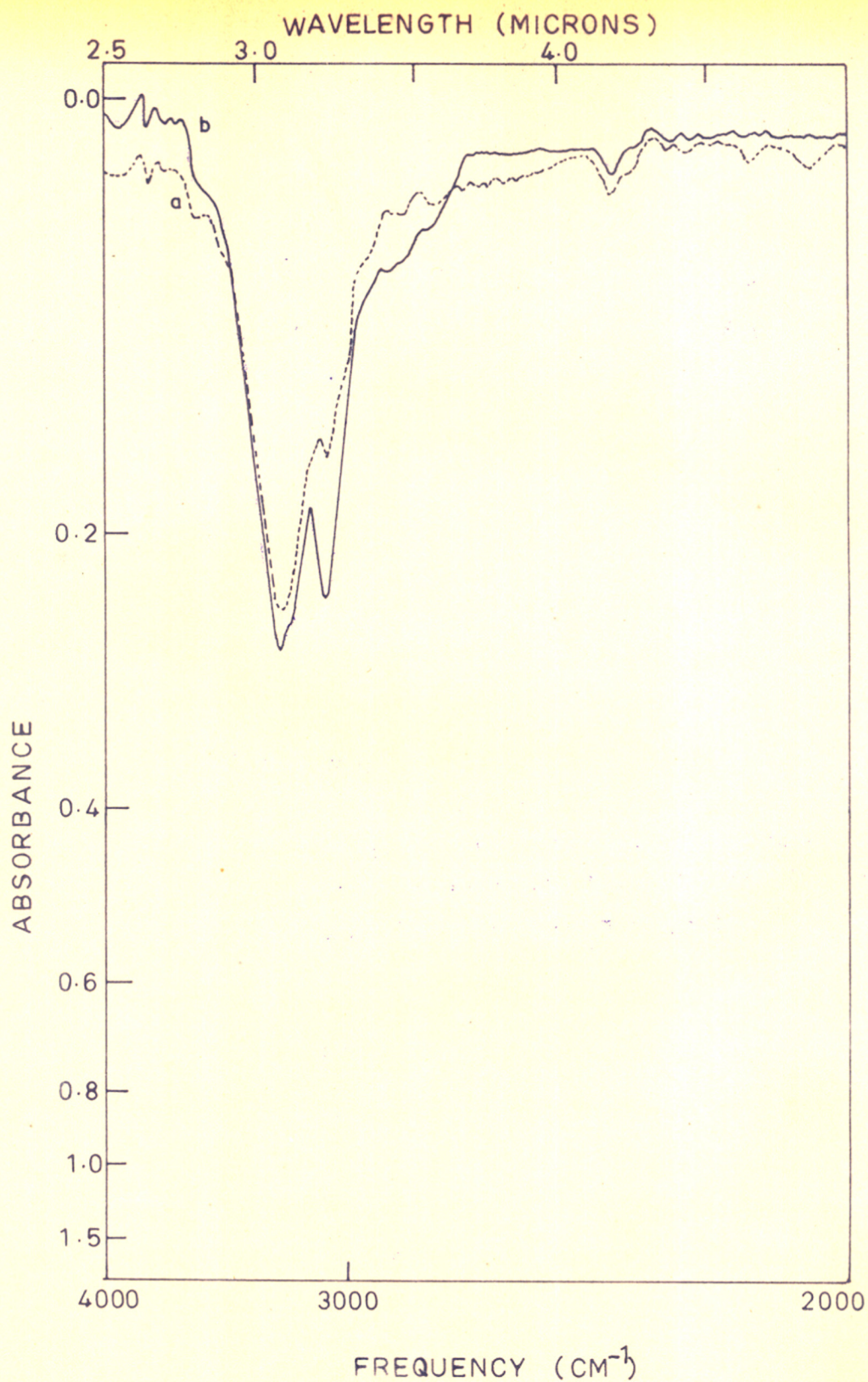


FIG. 3. INFRARED SPECTRA IN  $\text{CCl}_4$  OF

----- a OXIMINO ACETYLSALICYLALDOXIME (5.0% W/V), 0.2 mm. CELL

— b OXIMINO BENZOYLSALICYLALDOXIME (2.78% W/V), 0.5 mm. CELL

assigned to the aromatic C-H stretching vibrations, however, remain unaffected by deuteration. As expected, the spectra of oximino acetyl and oximino benzoyl salicylaldoxime showed only two bands at c.  $3230\text{ cm}^{-1}$  and c.  $3070\text{ cm}^{-1}$  due to the intramolecularly bonded hydroxyl and aromatic C-H stretching vibrations respectively. (Fig. 3)

Freedman<sup>138</sup> attributed the broad bands at c.  $2780\text{ cm}^{-1}$  and c.  $2650\text{ cm}^{-1}$  in salicylidene o-aminophenol and salicylidene o-hydroxyl benzylamine respectively to intramolecularly bonded hydroxyl groups. The ill-defined but definite absorption band at c.  $3200\text{ cm}^{-1}$  for these compounds was assigned by Freedman to the first overtone of the C=N frequency. There are no bands in the region at c.  $2800\text{ cm}^{-1}$  in the spectra of salicylaldoxime or its oximino acetyl or benzoyl derivative. Moreover, in the spectra of salicylaldoxime diacetate (Fig. 4), there is no absorption in the  $3200\text{ cm}^{-1}$  region to account for an C=N overtone frequency. Thus our results show that the hydrogen bonding in salicylaldoxime is not as strong as would be expected from Freedman's findings. Intramolecular hydrogen bonding in salicylaldoxime(I) as established in this report can be easily visualised in view of the contributions due to the polar structures,

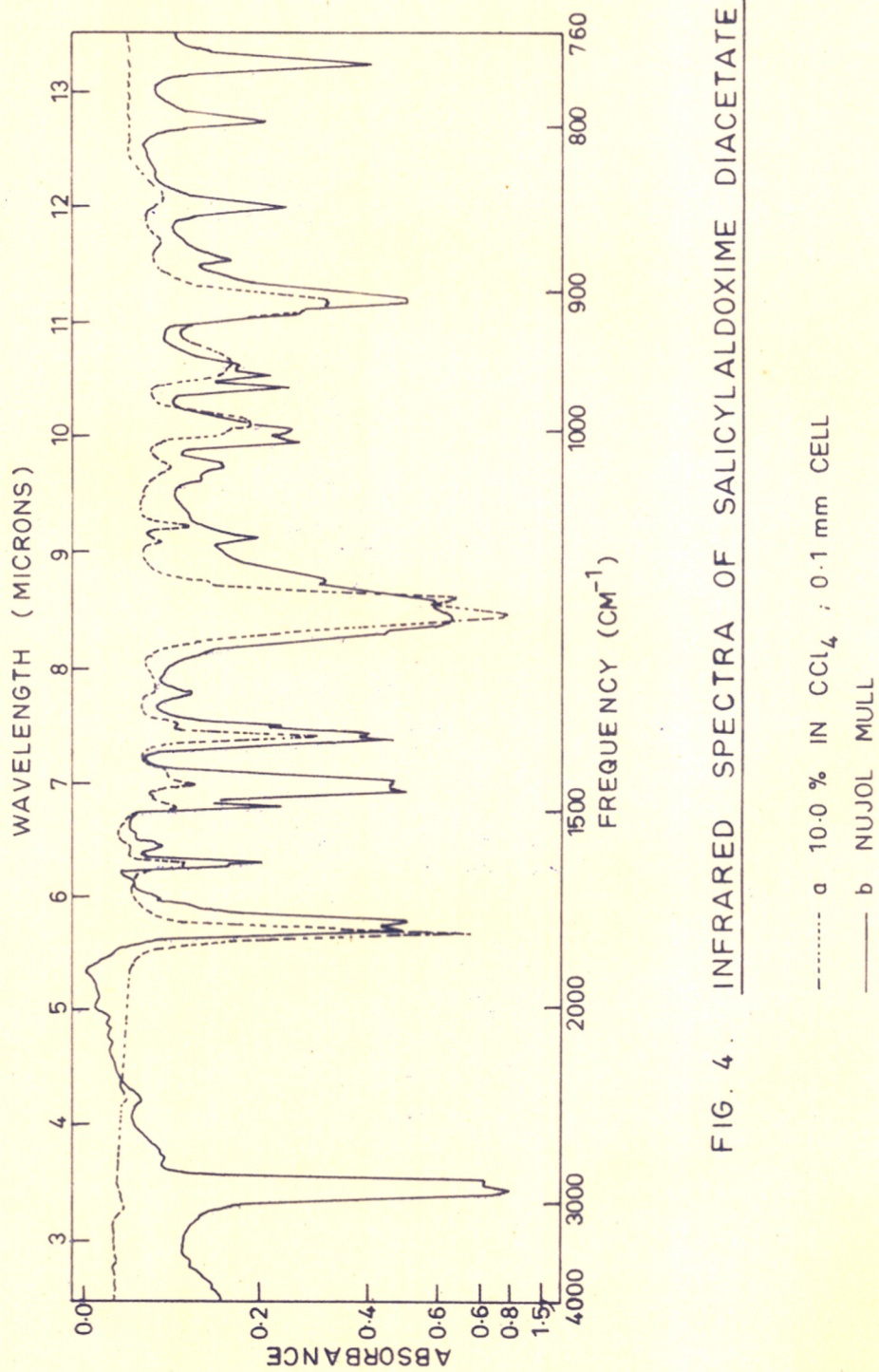


FIG. 4. INFRARED SPECTRA OF SALICYLALDOXIME DIACETATE



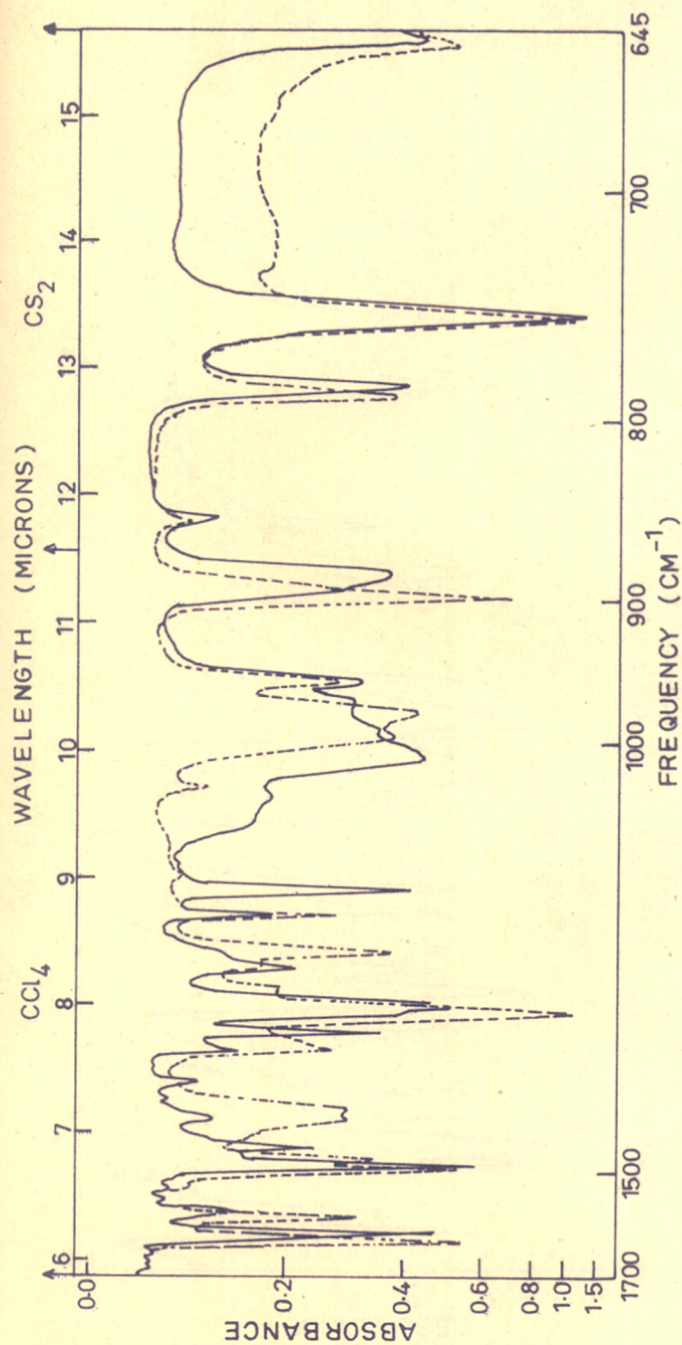


FIG. 5. INFRARED SPECTRA IN SOLUTION OF

..... a SALICYLALDOXIME  
 — b d-SALICYLALDOXIME

( both 5.56% W/V in CCl<sub>4</sub> & 5.12% W/V in CS<sub>2</sub> in 0.1 mm. cell )

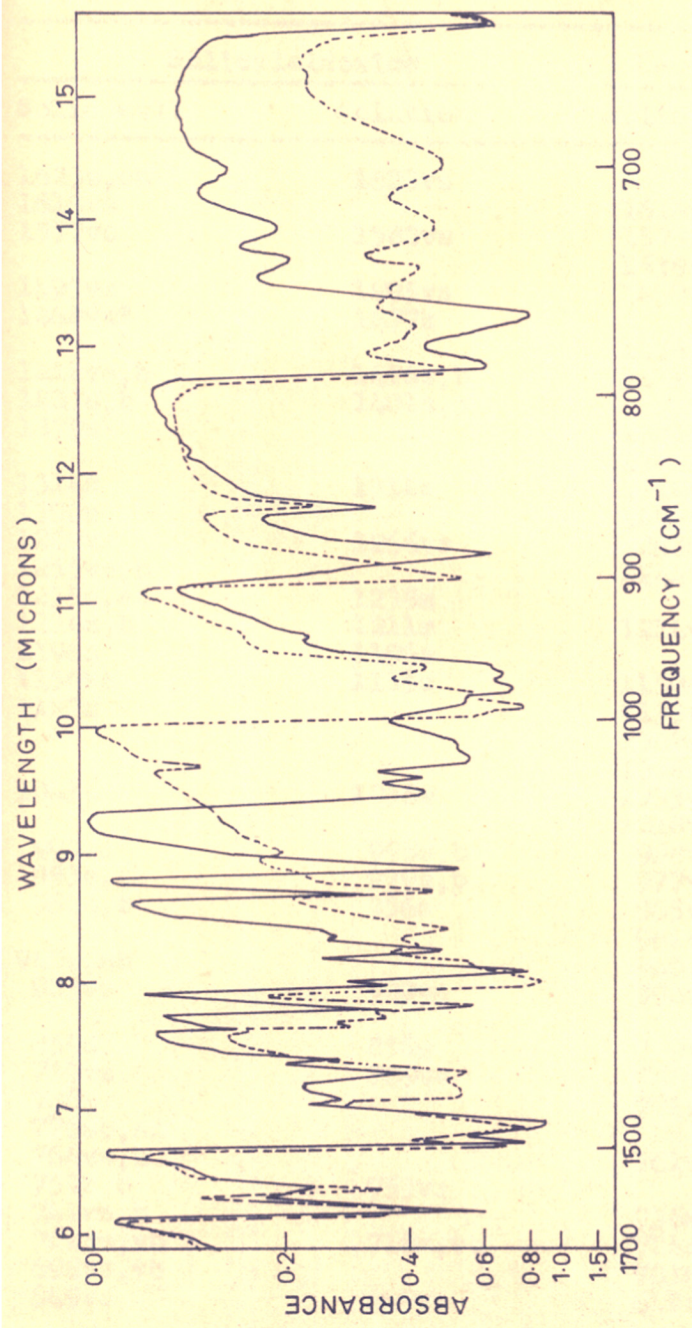


FIG. 6. INFRARED SPECTRA IN NUJOL MULL OF

- a SALICYLALDOXIME
- b d-SALICYLALDOXIME

Table II  
(in  $\text{cm}^{-1}$ )  
Absorption frequencies of salicylaldehyde and deuterated  
salicylaldehyde in nujol mull and in  $\text{CCl}_4$  and  $\text{CS}_2$  solution

Salicylaldehyde		Deuterated salicylaldehyde	
Solid mull	Solution	Solid mull	Solution
1623s, sh	1623vs		
1618vs		1616vs	1616vs
1577vs	1580vs	1572s	1570s
		1538sh, b	1524w
1495vs	1495vs	1490vs	1488vs
1468vs*	1477s		
		1456vs*	1458s
1412vs, b	1414s, b	1418s	1438m
1403s, b	1401s, b		
1379s*		1381vs*	1355m
		1364s	
1314s	1314s	1319m	1316m
1300s		1292s	
1289vs	1266vs	1263s	1289s
1255vs, b		1244vs	1259s
1235s, sh	1238m		
1214s, b	1211m	1214vs	1214s
1196s	1196s		
1156vs	1155s	1159s	1155m
1127m		1133vs	
		1062s	1062m, vb
		1048s	
1041w	1036w	1033vs, b	1043ms
		1018vs, b	1013s, b
990vs	998s, b	988vs, sh	990s, b
983s, sh	979s, b	977vs	968s, vb
962s, b	956s	965vs	956s
		961vs, sh	
940w, sh		940s	
903vs	900vs	890vs	895s, sh
			885s
859s	856w	859s	853m
789vs	789vs	786vs, sh	784s
785vs		784vs	
770sb, sh			752vs
766vs, b		761vs	
752s, b	753vs		
741vs, b		736s	
724vs, vb	718m, vb	724s	
698vs, vb		701m	
649vs	649vs	648s	647s

\* Nujol



Table III  
(continued)

Absorption frequencies of bis-(salicylaldoximate) metal(II) chelates

Nickel (deuterated)	Copper	Cobalt	Palladium	Manganese	Possible assignment
1642s (1658sh) (1642sh)	1647m	1650m	1650m	1633w	O-H def.
1610vs (1603vs)	1600s	1600s	1608vs	1600s	C=N str.
1558s (1565s, sh) (1553s)	1548s	1550s	1546s	1583s 1553w	coupled with C=C str.
1506s (1511m)	1515s	1514s	1524w 1485s, sh	1533s	O-disub. benzene ring vib.
1477vs (1477vs)	1471vs	1466vs, vb	1472vs	1548vs b	
1451vs (1453vs)	1447vs	1447 vs	1436 vs		
1381s* (1379s)*	1381m*	1381s*	1380s*	1350s*	
1346vs (1344vs)	1337vs	1335m	1343vs	1330s	C-H in plane
1297vs (1297vs, sh)	1311m	1303m	1300vs		
1256s (1266vs)	1295s, sh				
	1255w	1285m	1255w	1250s, sh	
	1220w				
1220s, b (1222vs, vb)	1193vs	1213w, s <sup>h</sup> 1198s	1220vw, vb 1187vs	1202s	N-O str.
1202s (1182vs, vb)					O-D def.
1161s	1153s	1150s	1153s	1152s	O-Disub.
1149s (1126vs)	1148s	1125s	1126s	1125s	benz. ring vib.
1039m (1092vs) (1037vs)	1042m	1040m	1044s	1042s	Benz. ring breathing
1020vs (1018vs) (993vs, vb)	1022vs	1000ms	1030vs	1021v <sup>5</sup> , b	(C-O)

Table III (continued)

924s (921s)	914vs	918s	916s	912vs	N-O str.
845w (844s)	858m	855m, b	851ms	860m, b	
830m (821s)	808m .	814m	814ms	807s	
753vs (752vs)	754s	752s	747vs	756vs, b	C-H out of- plane def.
735mb (732mb)	747vs 739vs	741s, b			
687sb (674s, b)	670mb 660m, vb	721m, vb	737s, sh	737m, sh	

Note: (a) \* Nujol  
 (b) Within  
 solution spectral data are given.

Two very strong peaks are also observed at  $1618\text{ cm}^{-1}$  and  $1577\text{ cm}^{-1}$ , one of which is due to the C-N stretching vibration and the other to the ortho disubstituted benzene ring vibration. Although these two vibrations are coupled with each other, it seems reasonable to assume that the peak at  $1577\text{ cm}^{-1}$  due to C-N stretching vibration, since in the metal chelates this frequency is lowered to 1558 (Ni II), 1548 (Cu II), 1550 (Co II), 1546 (Pd II) and  $1553\text{ cm}^{-1}$  (Mn II). Although the change in the reactivity of the C-N bond on chelation is reflected by the shift of this peak at  $1577\text{ cm}^{-1}$ , a stability order from these displacements does not appear to be feasible. Furthermore, such a large shift of this frequency from its normal value of c.  $1650\text{ cm}^{-1}$  (in open chain and non-conjugated systems) appear to be due to such factors as resonance, or conjugation, or coupling with C=C vibrations and hydrogen bonding. In fact, Hadzi<sup>139</sup> observed C-N bond of 1,4-benzoquinone monoxime at  $1555\text{ cm}^{-1}$  in the solid state.

The frequencies arising between  $1645\text{-}1633\text{ cm}^{-1}$  in these metal chelates are ascribed to O-H deformation vibrations. The fact that this absorption band is not present in the spectrum (Chapter III, Fig. 8b) of bis-(acetylsalicylaloximate)

copper(II) lends support to this assignment. Further, the infrared spectrum (from  $1675\text{ cm}^{-1}$  to  $670\text{ cm}^{-1}$ ) of the deuterated bis-(salicylaloximate) nickel(II) (Fig. 7b) clearly establishes the point. The very intense peak at  $1642\text{ cm}^{-1}$  appears only as a shoulder in the deuterated complex and a very strong and broad peak at  $1182\text{ cm}^{-1}$  appears (frequency ratio 1.39). In this region a weak shoulder appears in the spectra of salicylaloxime and this changes to an intense peak in solution spectra at  $1623\text{ cm}^{-1}$ . But a very strong band at  $1403\text{ cm}^{-1}$  due again to O-H deformation vibration appears in the ligand. These peaks completely disappear in deuterated salicylaloxime and perhaps the peaks at  $1133\text{ cm}^{-1}$  and  $1018\text{ cm}^{-1}$  can be assigned to O-D deformation vibrations (ratio, 1.43 and 1.38 respectively). This difference in O-H deformation bands is easily discernible in view of the significant difference in hydrogen bonding between salicylaloxime and its metal chelates. Again the strong peak at  $1314\text{ cm}^{-1}$  in salicylaloxime absent in the metal chelates can be assigned to the phenolic O-H deformation vibration. The very strong peak at  $890\text{ cm}^{-1}$  may be attributed to this O-D deformation vibrations (ratio, 1.47). The strong shoulder at  $1235\text{ cm}^{-1}$  in salicylaloxime absent in deuterated

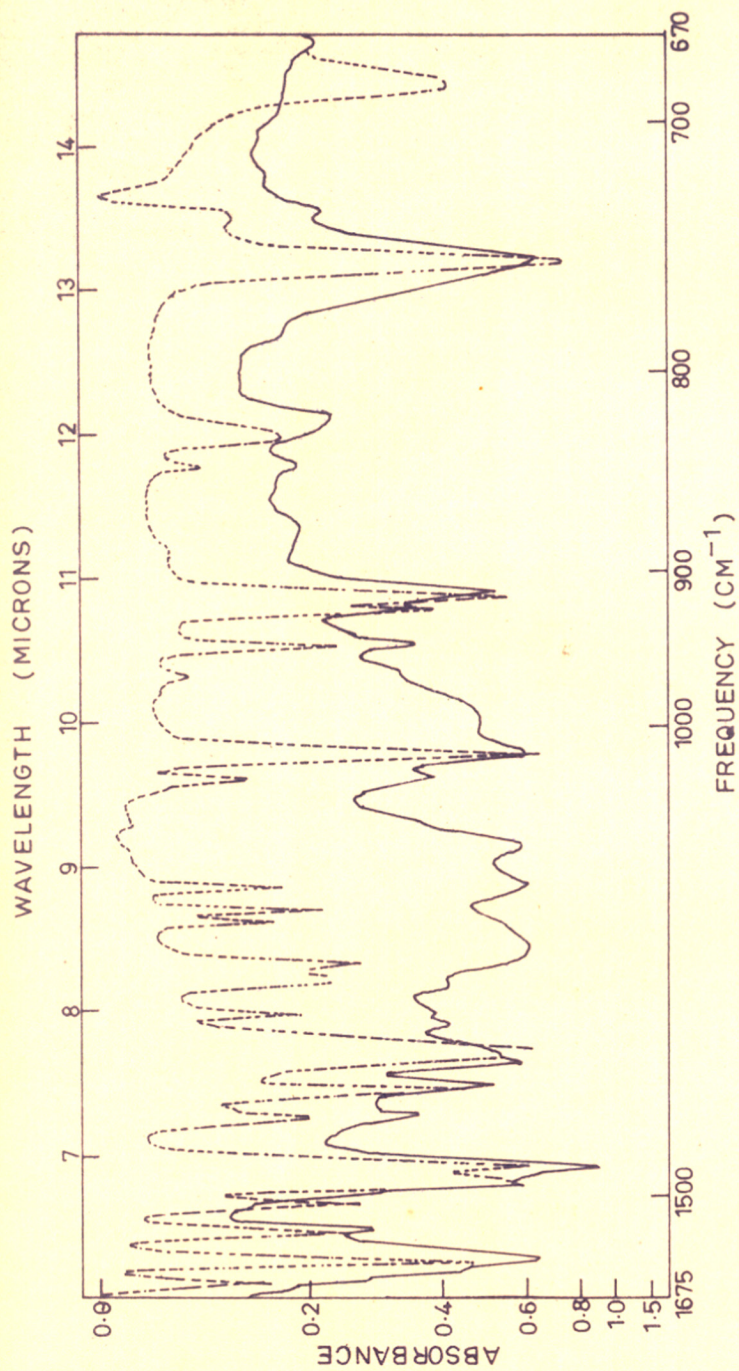


FIG. 7. INFRARED SPECTRA IN NUJOL MULL OF

- a bis - ( SALICYLALDOXIMATO ) NICKEL ( II )  
 ——— b d - bis - ( SALICYLALDOXIMATO ) NICKEL ( II )

compound and in metal chelates and a very strong peak at  $1018\text{ cm}^{-1}$  in deuterated salicylaldehyde may also be due to O-H and O-D vibrations.

The strong peak at  $1412\text{ cm}^{-1}$  in salicylaldehyde possibly due to aliphatic C-H in plane deformation vibration is absent in the metal chelates. The peak at c.  $1033\text{ cm}^{-1}$  in deuterated salicylaldehyde may be interpreted as the corresponding C-D in plane deformation (ratio, 1.37). The peaks at c.  $1379\text{ cm}^{-1}$  absent in solution spectra of salicylaldehyde is due to nujol. However, some C-H deformation vibration of the complexes also appear here and a corresponding C-D deformation vibration may be located at  $993\text{ cm}^{-1}$  as a very strong and broad peak in the deuterated nickel chelate. But this absorption merged with nujol peak is shifted considerably in the manganese chelate.

The peaks at  $1039-1044\text{ cm}^{-1}$  in these compounds may be assigned to the benzene ring breathing while the peaks at  $1161-1125\text{ cm}^{-1}$  may be due to the vibrations of ortho substituted benzene ring. C-H out-of-plane deformation vibrations can be located as very strong absorption peaks at  $903\text{ cm}^{-1}$  and below.

A very strong and characteristic absorption at  $990\text{ cm}^{-1}$  in salicylaldehyde assigned to the C-O stretching vibration of the hydrogen bonded ring system and shifted to higher frequencies in the solution spectra of salicylaldehyde to  $998\text{ cm}^{-1}$  and to 1020 (Ni II), 1022 (Cu II), 1000 (Co II), 1030 (Pd II) and  $1021\text{ cm}^{-1}$  (Mn II) is noteworthy. However, here again the relationship of this shift with Mellor and Maley's stability order<sup>107</sup> is not clearly brought out. The very strong absorption bands at  $1220-1187\text{ cm}^{-1}$  and  $990-912\text{ cm}^{-1}$  in these compounds can be tentatively assigned to the N-O stretching modes. Blinc and Hadzi<sup>45</sup> had similarly assigned the bands at c. 1240 and  $1000\text{ cm}^{-1}$  to N-O stretching mode in the case of some dimethylglyoxime chelates, while Palm and Werbin<sup>140</sup> assigned the bands of various oximes at c.  $940\text{ cm}^{-1}$  to the N-O stretching vibration. According to Hadzi, the shift of N-O frequencies to higher wave numbers is because of the contribution of polar structures. Although N-O frequencies are sensitive to the electronic effect of substituents, any trend in the shift in these complexes is again difficult to find.

## Experimental

### Materials and Methods

Salicylaldoxime employed in this investigation is either of BDH quality or prepared according to Vogel<sup>141</sup> m.p. 57°C.

Oximino acetyl-salicylaldoxime was prepared according to the method of Brady and Dunn<sup>59</sup> with slight modifications. Salicylaldoxime was treated with ten-fold excess of freshly distilled acetic anhydride. The mixture was warmed gently and allowed to remain for ten minutes. The excess of acetic anhydride was decomposed by an equivalent amount of aqueous sodium carbonate solution. The mixture was stirred vigorously when the crude acetyl derivative solidified. The product was recrystallised from acetone and water to yield light pink crystals melting at 69°C. When a slight excess of sodium carbonate was employed, the first crop of crystals proved to be stable salicylaldoxime diacetate. The twice recrystallized product from acetone and water consists of white shining plates, m.p. 90°C. Salicylaldoxime diacetate has been prepared for the first time.



Oximino benzoyl-salicylaldoxime (m.p.  $117^{\circ}\text{C}$ ) was prepared by the method of Beckmann<sup>142</sup>.

Bis-(salicylaldoximate) metal(II) chelates were prepared according to known literature methods,<sup>75,143,144</sup> and the purity of the compounds were checked by elemental analysis. Elemental analyses of the compounds are summarized in Table I.

A Perkin-Elmer Model 221 infrared spectrophotometer with rock salt optics was used to obtain the spectra. The instrument was calibrated using polystyrene film. The resolution of the instrument at maximum performance was about  $15\text{ cm}^{-1}$  at  $3000\text{ cm}^{-1}$  and  $7\text{ cm}^{-1}$  at  $1600\text{ cm}^{-1}$ . For studies of hydrogen bonding by deuteration, a solution of salicylaldoxime in carbon tetrachloride was shaken with 0.2 ml. of deuterium oxide<sup>145</sup> ( $>99.4\%$ ) for five minutes. The mixture was allowed to remain for five minutes after which it was carefully syringed out without disturbing the deuterium oxide into a 1 cm. quartz cell. The spectrum was run against a blank prepared under identical conditions. The matched quartz cells were provided with tightly fitting stoppers. Solid deuterated salicylaldoxime was prepared by

Table I

Analytical data of salicylaldoxime derivatives and metal chelates

Compound	Metal		Carbon		Hydrogen		Nitrogen	
	Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found
Oximino acetyl-salicylaldoxime (C <sub>9</sub> H <sub>9</sub> NO <sub>3</sub> )			60.29	61.49	5.06	5.98		
Oximino benzoyl-salicylaldoxime (C <sub>14</sub> H <sub>11</sub> NO <sub>3</sub> )			69.69	69.00	4.59	5.00		
Salicylaldoxime diacetate (C <sub>11</sub> H <sub>11</sub> NO <sub>4</sub> )			59.71	59.95	5.01	5.45	6.33	6.22
Bis-(salicylaldoximato) Copper(II) (C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> Cu)	18.93	18.7						
Bis-(salicylaldoximato) Nickel(II) (C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> Ni)	17.74	17.7						
Bis-(salicylaldoximato) cobalt(II) (C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> Co)			50.76	50.50	3.65	4.00		
Bis-(salicylaldoximato) manganese(II) (C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> Mn)			51.4	51.9	3.7	3.68		
Bis-(salicylaldoximato) palladium(II) (C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> Pd)			44.37	44.50	3.19	3.47		

crystallization of salicylaldoxime from  $D_2O$  in dry nitrogen atmosphere. Deuteration of bis-(salicylaldoximato) nickel(II) was carried out by adding an excess of  $D_2O$  in dry nitrogen atmosphere to a solution of the chelate in pure boiling dioxane, cooling the mixture, isolating and drying the product under vacuum at  $60^\circ C$ .

CHAPTER III

REACTIVITY AND COLOUR ISOMERS OF  
BIS-(SALICYLALDOXIMATO) COPPER(II)

### Abstract

The reactivity of chelated salicylaldehyde has been demonstrated by the isolation of bis-(acetylsalicylaldehyde) copper(II) [careful acetylation of bis-(salicylaldehyde) copper(II) (decomp. pt. 204°C) with acetic anhydride]. The moisture sensitive yellowish brown acetylated chelate was also obtained by reacting copper acetate with oximino acetylsalicylaldehyde in alcoholic medium. During the course of acetylation, a new form of the parent chelate (decomp. pt. 185°C), much deeper green in colour was also isolated. Further, oximino benzoylsalicylaldehyde yielded the same new form of the parent compound. Subsequently, several other colour isomers of bis-(salicylaldehyde) copper(II) have been isolated by using different methods of preparation as described here. Diffuse reflectance and infrared spectra of these colour isomers have been recorded. X-Ray powder pattern studies of these colour isomers have established the existence of at least two separate crystal modifications of bis-(salicylaldehyde) copper(II).

REACTIVITY AND COLOUR ISOMERS OF BIS-(SALICYLALDOXIMATO)COPPER(II)

Although the colour isomers of some copper chelates are known, the existence of colour isomers of bis-(salicylaldoximato) copper(II) was reported for the first time by us<sup>146</sup>. In 1957, Suito and Sekido<sup>147</sup> prepared two forms of bis-(8-hydroxyquinolinol) copper(II) dihydrate whose X-ray powder patterns were found to be different but their infrared absorption spectra were found to be the same. Fanning and Jonassen<sup>148</sup>, recently have reported two forms of the anhydrous bis-(8-hydroxyquinolinato) copper(II) termed as alpha- and beta-forms. In methanol, the formation of the two forms of the compound seems to be related directly to the nature of the anion of the copper salt employed. The reflectance spectra of the two forms are different but the hard black beta-form when ground takes up the same colour, reflectance spectra and X-ray powder patterns as the alpha-form. Complete structure determination of only the beta-form has been reported<sup>149</sup>.

In view of the above, we have prepared bis-(salicylaldoximate) copper(II) by various procedures and have found that the compounds thus obtained show distinct differences especially in the shades of colour and perhaps in the decomposition points. Reflectance and infrared spectra have been used to characterize such compounds as individual entities. X-ray powder pattern studies have been made and the results clearly establish the existence of at least two forms of bis-(salicylaldoximate) copper(II). It is also significant to note that the so-called second colour isomer of bis-(salicylaldoximate) copper(II) was isolated by us, during the course of our acetylation studies<sup>146</sup> and in this chapter preparation of bis-(acetylsalicylaldoximate) copper(II) and its infrared spectra are also given.

## Experimental

### (a) Materials and Methods

Bis-(acetylsalicylaldoximate) copper(II) was prepared either by (a) acetylation of bis-(salicylaldoximate) copper(II) or (b) reacting oximino acetylsalicylaldoxime with copper acetate in alcohol.

(a) In a well stirred suspension of 1.679 g. of bis-(salicylaldoximate) copper(II) (0.005 mole) in 50 ml. of purified carbon tetrachloride was added 10 ml. of freshly distilled acetic anhydride. Stirring was continued for an hour when the contents of the flask turned first to dark green and then to yellowish brown. The yellowish brown compound was filtered in dry nitrogen atmosphere, washed thoroughly with  $\text{CCl}_4$  and vacuum dried. Calculated for  $\text{Cu}(\text{C}_9\text{H}_8\text{NO}_3)_2$  C, 51.48; H, 3.84. Found: C, 51.00; H, 4.01.

(b) To a solution of 0.4991 g. of copper acetate (0.025 mole) in 50 ml. of absolute alcohol was added a clear solution of 1 g. of oximino acetylsalicylaldoxime<sup>59</sup> ( $\sim$  0.005 mole) in 10 ml. of alcohol with stirring. The mixture was stirred until the formation of the yellow brown compound



was incipient (2-3 mins.). Filtered in dry nitrogen atmosphere, washed thoroughly with 100 ml. of absolute alcohol in 4 portions and dried in vacuum. (Found: C, 51.70; H, 3.80).

When the above mixture of copper acetate and oximino acetylsalicylaldoxime was stirred for an hour, a pale leaf green compound, termed by us<sup>146</sup> as the second isomer of bis-(salicylaldoximate) copper(II) resulted. The same isomer decomposing at 185°C was also isolated from copper acetate and oximino benzoyl-salicylaldoxime as follows:-

To a filtered alcoholic solution of 0.4991 g. of copper acetate (0.025 mole) was added an alcoholic solution of 1.2146 g. of oximino benzoyl-salicylaldoxime<sup>142</sup> (~ 0.005 mole) with stirring which was continued for another three hours. The colour of the mixture changed to yellowish brown and finally after two hours to dark green. After filtration and thorough washing with alcohol, the product was air dried (sample II). (Found: C, 50.74; H, 3.99).

The other colour isomers were synthesized as follows:

Sample I is dirty yellowish-green compound (decomp. pt. 204°C) prepared as described in Vogel<sup>144</sup>.

Sample III is a shining ivy green compound obtained by refluxing freshly prepared sample I (1 g.) in  $\text{CHCl}_3$  (50 ml.) for 24 hours when the colour of the parent compound changed to dark green. Filtered and washed, the product with  $\text{CHCl}_3$  (Found: Cu, 18.81). Its decomposition temperature was found to be  $199.5^\circ\text{C}$ .

Sample IV is a moss green compound decomposing at  $192^\circ\text{C}$ . To a solution of 1.705 g. (0.01 mole) of copper chloride dihydrate in 20 ml. of methanol was added with stirring a solution of 2.742 g. (0.02 mole) of salicylaldehyde in 20 ml. of methanol dropwise in 5-10 minutes. The product was filtered and washed thoroughly with methanol (Found: Cu, 18.55; C, 50.17; H, 3.90).

Sample VI is a shining peanut coloured compound decomposing at  $190^\circ\text{C}$  prepared as follows: To a well stirred clear solution of 100 ml. of methanol saturated with copper acetate monohydrate was added a saturated methanolic solution of salicylaldehyde, until precipitation was complete. The mixture was stirred for 15 minutes, filtered and washed several times with methanol. (Calculated for Cu,  $(\text{C}_7\text{H}_6\text{NO}_2)_2\text{Cu}$ , 18.93; C, 50.07; H, 3.60. Found: Cu, 18.94; C, 50.30; H, 3.76).

Sample V: Experiment in VI was repeated but the mixture was stirred for several hours (Found: Cu, 18.6). The colour of this was lighter than that of sample I and its decomposition point was over  $185^{\circ}\text{C}$ .

Infrared spectra of these compounds in nujol mull were recorded in the NaCl optics region by means of Infracord Model 137-B.

Diffuse reflectance spectra of the compounds were obtained with Unicam Spectrophotometer, SP 500 equipped with diffuse reflectance attachment using  $\text{MgCo}_3$  as internal standard. Since the samples varied appreciably in particle size and agglomeration, absolute reflectance seems to be not meaningful.

X-ray powder photographs were taken with a  $\text{Cu K}\alpha$  nickel filtered radiation ( $\lambda = 1.542\text{\AA}$ ). The camera used for this purpose was of the Debye-Scherrer type with diameter 14.32 cms. This gave the Bragg angle,  $\theta$  in degrees directly by the relation  $2D_{\text{cms}} = \theta \text{ deg.}$  where D was the diameter of the rings in the powder photographs. The value of angle  $\theta$  were obtained from the diameters of the different powder rings measured with the help of an illuminator and 'd' values were obtained from standard tables. The 'd' values were calculated

by using the expression giving the spacing of the various planes for monoclinic system.

$$d = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} + \frac{k^2}{b^2} \sin^2 \beta}}$$

Unit cell dimensions of Jarski and Lingafelter<sup>79</sup> ( $a = 13.98 \pm 0.03$ ,  $b = 6.08 \pm 0.01$ ,  $c = 8.00 \pm 0.01 \text{ \AA}$ ,  $\beta = 97^\circ 35'$ ) and of Cox and Webster<sup>150</sup> ( $a = 27.61$ ,  $b = 6.00$ ,  $c = 7.86 \text{ \AA}$ ,  $\beta = 98^\circ 13'$ ) were employed along with suitable hkl values selected to correspond with the obtained 'd' values.

### Results and Discussion

Although the reactivity of co-ordinated ligands has attracted much current attention<sup>151</sup>, the isolation of the yellowish brown moisture sensitive bis-(acetylsalicylaldoximate) copper(II) appears to be the only example demonstrating the reactivity of chelated salicylaldoxime. Further, this appears to be of special significance in view of the fact that attempts to acetylate other chelates of salicylaldoxime did not lead to the isolation of acetylated chelates. The infrared spectra of bis-(acetylsalicylaldoximate) copper(II) and oximine acetylsalicylaldoxime are given in Fig. 8. Comparison of these spectra

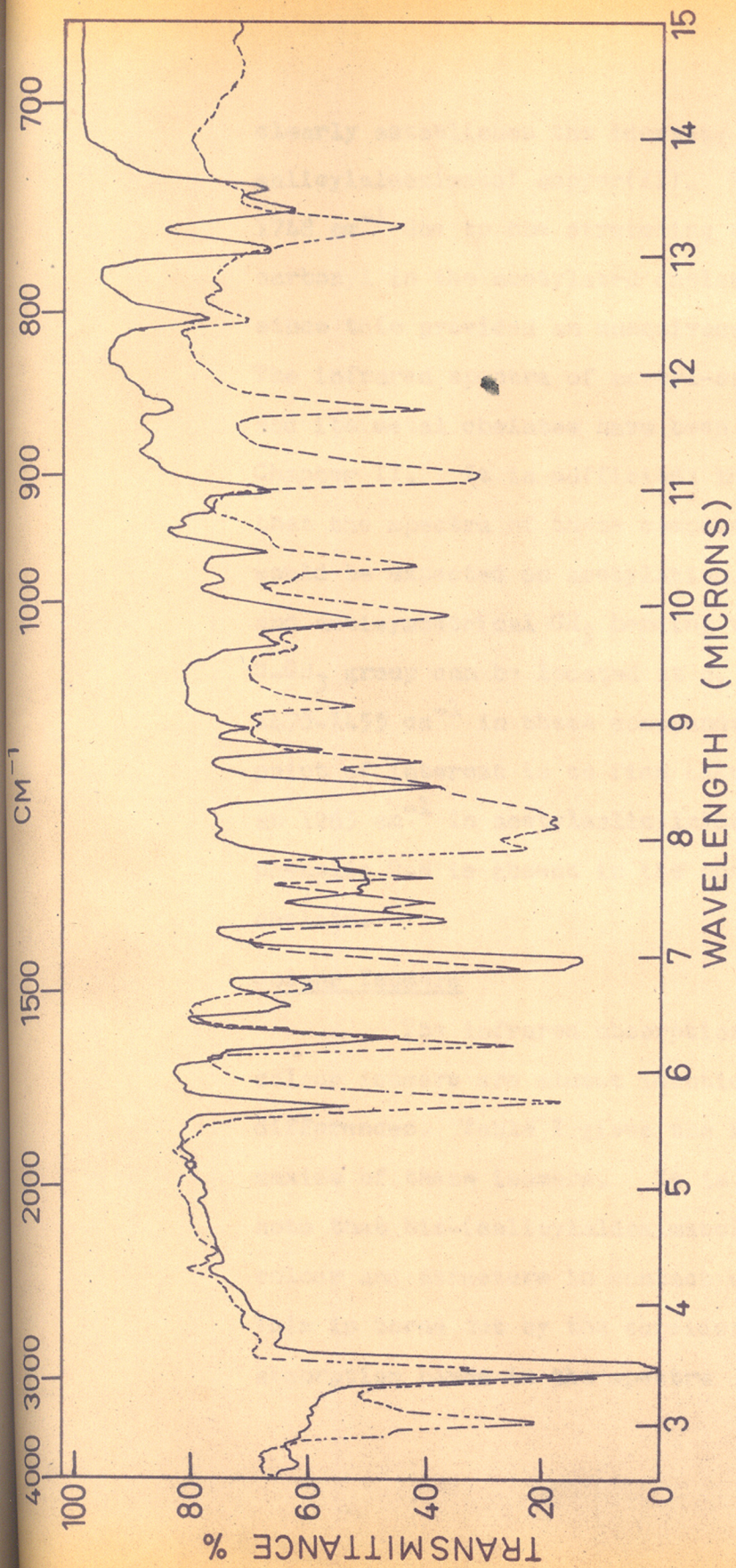


FIG. 8. INFRARED SPECTRA OF

- a. OXIMINO ACETYL - SALICYLALDOXIME
- b. BIS-(ACETYL - SALICYLALDOXIMATO)  
COPPER (II)

clearly establishes the identity of bis-(acetyl-salicylaldoximate) copper(II). The sharp peak at  $1748\text{ cm}^{-1}$  due to the stretching vibration of the carbonyl in the acetylated chelate is noteworthy since this provided an unequivocal proof of acetylation. The infrared spectra of acetyl-salicylaldoxime and its metal chelates have been discussed in Chapter II. It is sufficient therefore to note that the spectra of these compounds are exactly what would be expected on acetylation. The symmetrical and antisymmetrical  $\text{CH}_3$  bending vibrations of the  $\text{C}-\text{CH}_3$  group can be located at c.  $1325-1350$  and  $1470-1455\text{ cm}^{-1}$  in these compounds. A further point of interest is to find that the strong peak at  $1265\text{ cm}^{-1}$  in acetylsalicylaldoxime due to the phenolic O-H is absent in the spectrum of the chelate.

#### Colour Isomers

The infrared absorption spectra of these colour isomers are almost identical with minor differences. Table I gives the infrared absorption maxima of these isomers. It is perhaps worthy to note that bis-(salicylaldoximate) copper(II) changes colour and structure in contact with solvents. This is borne out by the considerably less sharper absorption bands in the spectra of the chelate modified

Table I  
Infrared absorption maxima ( $\text{cm}^{-1}$ ) of colour isomers of  
bis-(salicylaloximate) copper(II) in the region  $4000 \text{ cm}^{-1}$  to  $650 \text{ cm}^{-1}$ .

I	II	III	IV	V	VI
2950vs	2965vs	3000vs, b	3000vs, b	3000vs	
1640s	1643m	1643w	1650s	1642w	1650d
1600vs	1600s	1600m	1600s	1600s	1600vs
1545s	1540s	1516m	1550vs 1520s	1540m	1550s
1505s	1570m	1445s	1475vs	1512w	1475vs
1472vs	1464s, b	1370w	1450sh, sh	1440s	1342s
1440vs	1375s	1325w	1370s	1375w	1305s
1400w	1330s	1280w	1338s	1325s	1255s
1375m	1295w	1188s	1300b, s	1290m	1195vs
1332vs	1190s	1146s	1258w	1190s	1155s
1302s	1152s	1010s	1220w	1145s	1125s
1280m, sh	1120m	958s	1195vs	1120w	1040s
1250w	1040m	910wb 860s, b	1162s	1020s	1025vs
1182s	1020s	805s, b	1132m	962s	963s 930m 919s
1152s	961s	747s, b	1040s	915s	860s
1145sh	910m	735s	1020s	860m	810, sb
1122s	853w		963s	807m	752vs
1040 m	802w		918s	750s	742s
1020s	750s		<del>862s</del> 740s	740s	
960s	738s		806s		
914s			754v, s		
858m			740s		
806s					
753sh					
750s					
739s					

by refluxing with chloroform (sample III). The appearance of an additional absorption peak at  $930\text{ cm}^{-1}$  in the peanut coloured compound which is definitely different from the parent chelate is also noteworthy.

The diffuse reflectances spectra of these colour isomers shown in Fig. 9 are, perhaps, characteristic of trans-planar copper(II) chelate and show some differences characterizing the individual entities. The reflectance spectra contains absorption bands characteristic of divalent copper in the solids. Since the ligand field theory predicts a four fold splitting of the 'd' energy levels in a tetragonal field, one expects to find three d - d transitions represented by three absorption bands. The spectra of the isomers can perhaps be resolved into Gaussian components. However, no such attempt will be made in view of the limited value of the reflectance spectra of solids for making unambiguous resolution and assignments.

The X-ray powder pattern data along with calculated 'd' values are listed in Table II. It is evident from these data that the sample used by Jarski and Lingafelter<sup>79</sup> for crystal structure determination is the same as the dirty yellowish-green compound (sample I). These authors have reported that



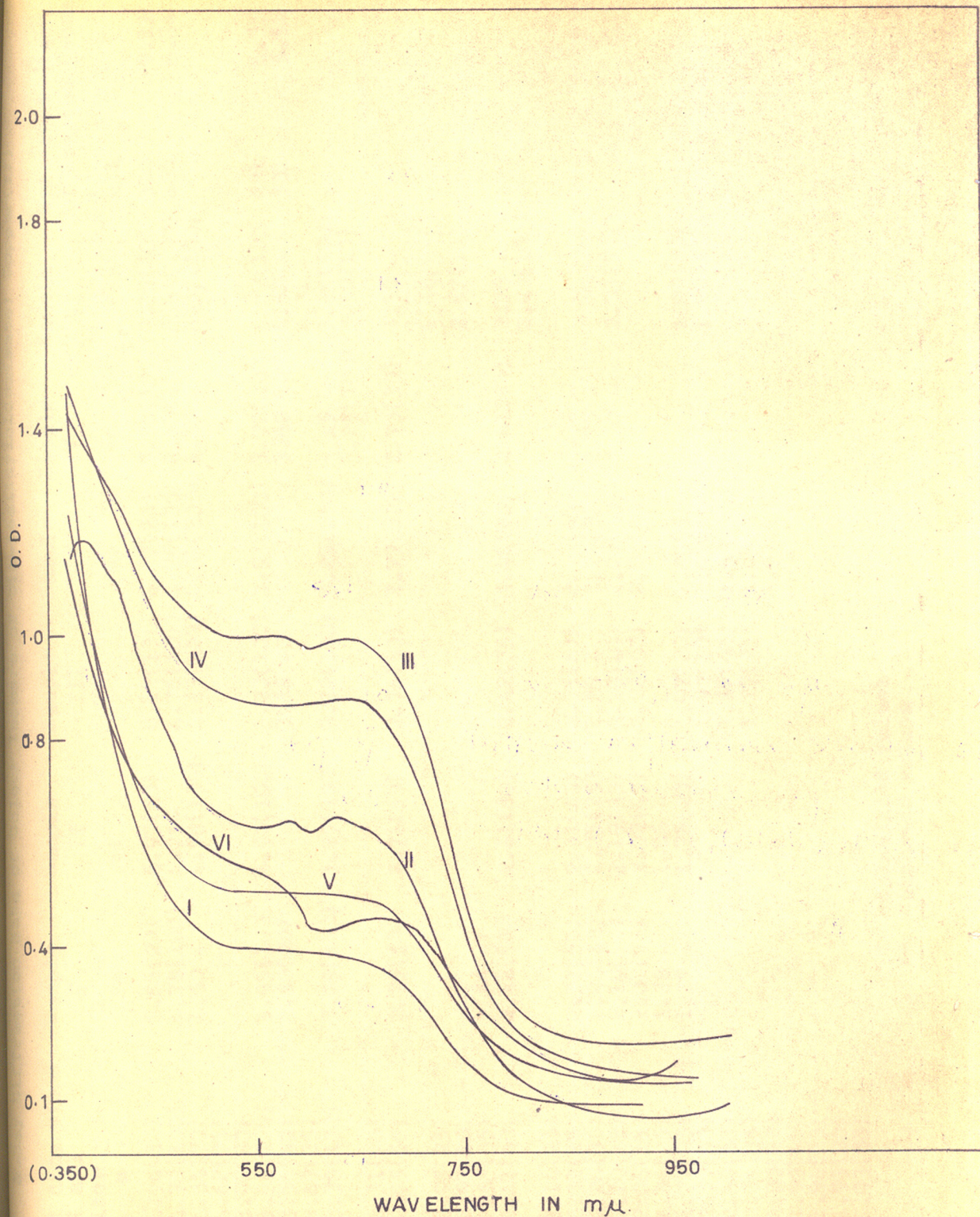


FIG. 9. DIFFUSE REFLECTANCE SPECTRA OF THE COLOUR ISOMERS OF BIS-(SALICYLALDOXIMATO) COPPER (II)

Table II

X-Ray Diffraction data of Colour Isomers of bis-(salicylaldoximate) Copper(II)

Unit cell dimensions of Jarski and Linga/felter #	Sample I **	Sample II **	Sample III **	Sample IV **	Sample V **	Sample VI **	Unit cell dimensions of Cox and Webster
hkl							hkl
200	6.86(20)	6.97(20)	8.14(10)	6.87(20)	5.30(10)	9.36(60)	300
011	4.78(100)	4.75-	4.76(100)	4.79(100)	4.80(100)	6.61(100)	400
111	4.60 -	4.58(100)	4.63(100)	4.64(100)	4.58 -	6.37(100)	
300							
002							
102	3.95(100)	3.90(100)	3.93(100)	3.93(100)	3.92(100)	4.67(100)	201
211	3.80(20)		3.80 -		3.62(10)	4.62 -	301
400						4.34 -	
112	3.29(100)	3.27(100)	3.29(100)	3.29(100)	3.45 -	3.88(100)	
					3.28(100)	3.50(10)	
012							
220	2.75(50)	2.74(50)	2.74(50)	2.77(50)	2.73(30)	3.33 -	
						3.28(100)	
120						3.03(50)	
411						2.87(10)	
221	2.56(35)						
013	2.41(60)					2.76 -	
						2.40(100)	
112							
222	3.14(20)						
313	2.32(50)	2.31(40)	2.33(40)	2.31(40)	2.32 -		
322	2.24(40)	2.25(25)	2.26 -	2.26(5)	2.25 -		
210	2.20(15)	2.19(30)	2.20(40)	2.22(10)	2.20 -		
210	2.06(15)	2.01(75)	2.02(40)	2.03(40)			
214	1.88(25)	1.86 -					
331	1.77(25)	1.76(20)	1.97(20)	1.98(5)		1.99(50)	
500	2.77(60)		1.92(10)	1.93(5)		1.93 -	
213	2.40(50)		1.87(50)	1.89 -			
313	2.04(35)		1.77(25)	1.85 -			
104	2.00(20)			1.77(10)			
123	1.99(45)						
123	1.94(20)						
131	1.93(20)						
104	1.93(30)						

\* Calculated values

\*\* Observed values

they could not get any evidence for doubling of the length 'a' as was previously reported by Cox and Webster<sup>150</sup>. A glance at the table will show that 'd' values calculated by employing Cox and Webster's unit cell dimensions agree with the 'd' values for the peanut coloured compound (sample VI). It is noteworthy that although the method of preparation of this compound is different from that of Cox and Webster, this investigation showed that Cox and Webster's observation is correct.

It is apparent from the table that the 'd' values of the other isomers more or less agree with either Jarzski and Lingafelters' or Cox and Websters'. Furthermore, matching of the intensities of some of the principal X-ray lines of these are also noteworthy. Thus it is established that at least two separate crystal modifications of bis-(salicylaloximate) copper(II) exist. The other isomers show minor differences only, presumably due to the fact that during the process of crystallization, the molecules have packed in a slightly different way. Assuming that the crystal field effect is not limited to the near neighbour interactions only, the splitting of the electronic levels  $t_{2g}$  and  $e_g$  may be somewhat different from compound to compound leading to this difference in colour or shades of colour.

CHAPTER IV

STUDIES ON "CHELATE LIGANDS" AND POLYMERS  
OF SOME BIVALENT METALS

The "chelate ligand" resorcinol dialdehyde has been shown to be actually resorcinol 2:4 dialdehyde from its NMR spectrum. The NMR and deuteration substitution cum infrared spectral studies, of resorcinol 2:4 dialdehyde and salicylaldehyde crystallized the conclusion that intramolecular hydrogen bonding is stronger in the former, obviously due to extended conjugation. Leaning on the weight of evidence from infrared spectroscopic studies, it appears that intramolecular hydrogen bonding in resorcinol 2:4 dialdehyde and 4:6 diacetyl resorcinol are of comparable strength.

Of special significance was the isolation of "chelate polymers" of resorcinol 2:4 dialdehyde with copper(II), nickel(II), cobalt(II) and zinc(II), of resorcinol 2:4-dialdoxime with copper(II) and of 4:6 diacetyl resorcinol with copper(II), nickel(II) and cobalt(II). Nickel and cobalt polymers of both the chelate ligands appear to be dihydrates.

TGA studies in vacuum of the polymers of resorcinol 2:4 dialdehyde have been reported and the relation between the temperature of accelerated weight loss and atomic number has been pointed out.

STUDIES ON "CHELATE LIGANDS" AND POLYMERS OF SOME  
BIVALENT METALS

As can be seen from the literature review (the general introduction of this thesis) the synthesis and study of chelate polymers formed from "chelate ligands", possessive of poly-functional co-ordination sites have gained considerable importance in recent years. The distinctive characteristic feature of such "chelate ligands" has been employed for obtaining linear polychelates and planar and three dimensional networks.

Resorcinol-2:4-dialdehyde, resorcinol-2:4-dialdoxime and 4:6-diacetyl resorcinol can conveniently be included in the above category of "chelate ligands" and have been chosen for the study reported here. The preparations of chelate polymers of resorcinol-2:4-dialdehyde with copper(II), nickel(II), cobalt(II) and zinc(II), resorcinol 2:4-dialdoxime with copper(II) and 4:6-diacetyl resorcinol with copper(II), nickel(II) and cobalt(II) have been carried out for the first time. However, some of their properties are yet to be

determined and whatever work has already been done are being reported in this section.

It may be mentioned that resorcinol 2:4-dialdoxime will have similar constitution as the dialdehyde from which it was synthesized according to the method of Kuhn and Staab<sup>152</sup>. The compound turns red and melts with decomposition at 207-209°C. The parent chelate ligand, however, was first prepared by Tiemann and Lewy<sup>153</sup> in 1877, but it was only in 1932 that Baker and co-workers<sup>154</sup> termed this compound as resorcinol 2:4-dialdehyde from chemical evidence. The results of the nuclear magnetic resonance and infrared spectral studies of these compounds are given below.

The NMR spectrum of the dialdehyde in  $\text{CDCl}_3$  (Fig. 11) shows signals at 399.5 cps and 465.5 cps (doublet,  $J=9$  cps) which can be assigned to aromatic C-H in positions 5 and 6. The signals at 757.5 cps and 761 cps represent protons of the two phenolic functions and the signals at 587 cps and 628 cps can be attributed to the two aldehydic groups. As the starting material was resorcinol, NMR spectrum clearly establishes that this chelate ligand is indeed 2:4-dialdehyde and this is in agreement with the findings of Baker and co-workers<sup>154</sup>.

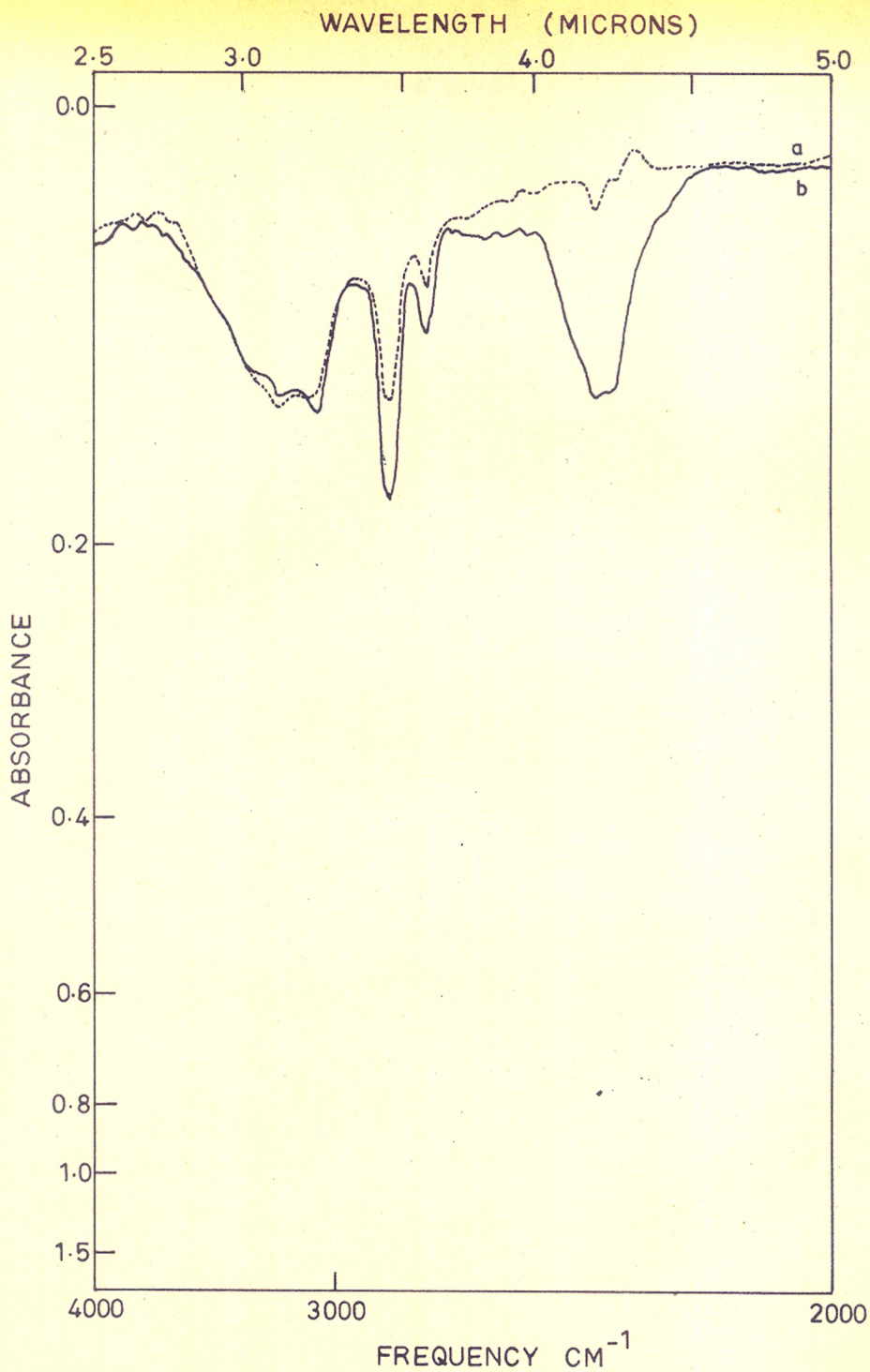


FIG. 10. INFRARED SPECTRA OF

- a SALICYLALDEHYDE (LIQUID FILM)
- b d-SALICYLALDEHYDE (LIQUID FILM)



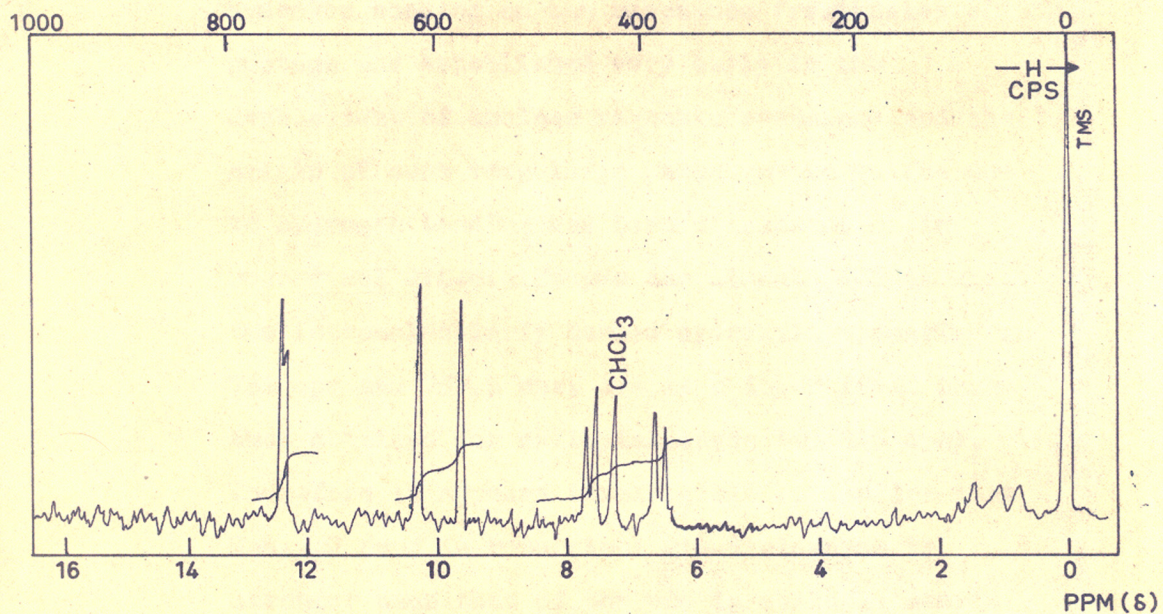


FIG. 11. PMR SPECTRUM OF RESORCINOL 2:4 DIALDEHYDE  
IN CDCl<sub>3</sub>

Changes in the electron distribution in the neighbourhood of a hydrogen atom occur when it takes part in hydrogen bonding and so proton NMR technique can detect and have been used to detect and study hydrogen bonding. The marked effect of hydrogen bonding on the resonance frequencies of protons was established very early in the development of nuclear magnetic resonance and the origin of such very large paramagnetic shifts due to hydrogen bonding has been discussed. In resorcinol 2:4-dialdehyde the signals due to the two intramolecularly bonded hydroxyls appearing at 761 cps and 757.5 cps. are at a lower field than that obtained for salicylaldehyde (at 645 cps). Therefore it appears intelligible to confirm that O-H...O bond in resorcinol 2:4-dialdehyde is stronger than that of the one in salicylaldehyde. The infrared spectral studies also lead to the same conclusions. The band due to intramolecularly bonded O-H lies between  $3160\text{ cm}^{-1}$  to  $3030\text{ cm}^{-1}$  in resorcinol 2:4-dialdehyde (Fig. 13a,b) while the intramolecular hydrogen bonding in salicylaldehyde gives rise to a broad band<sup>155</sup> with a centre at  $3150\text{ cm}^{-1}$ .

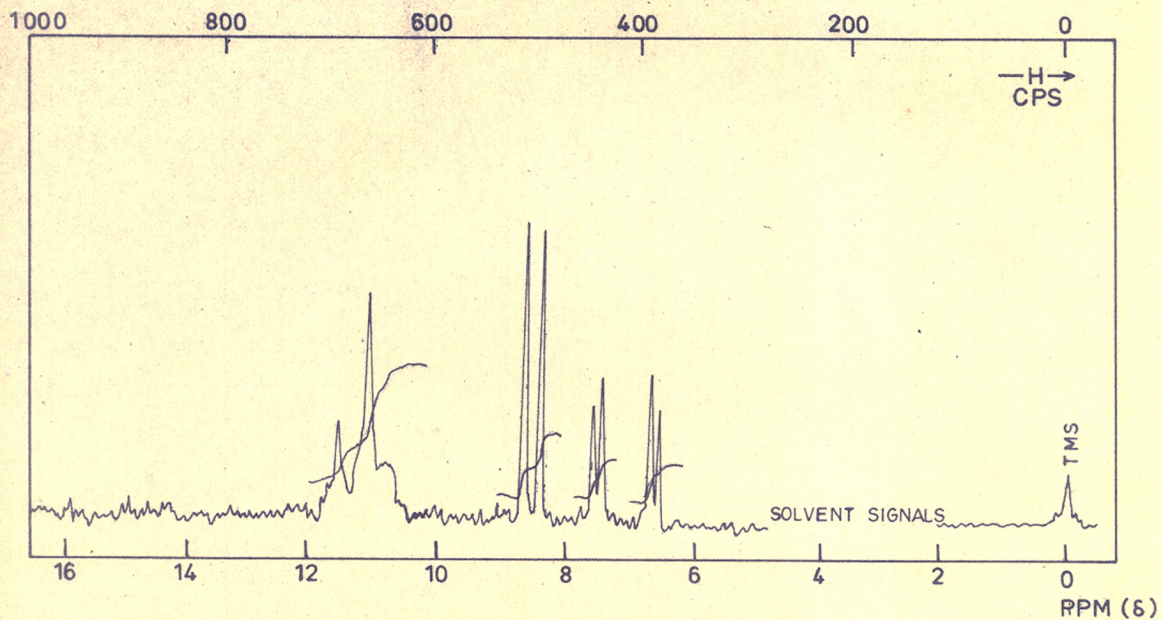
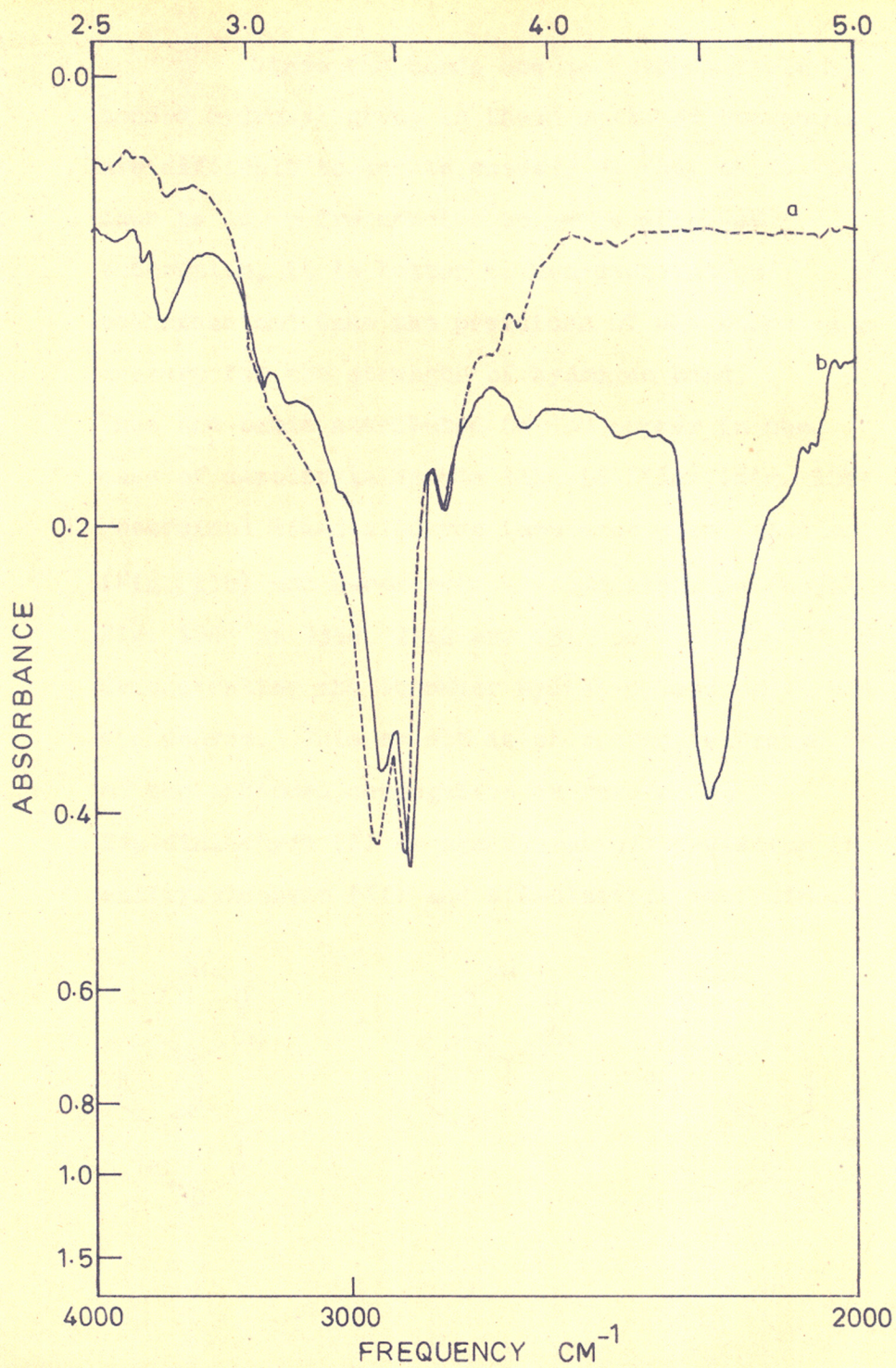
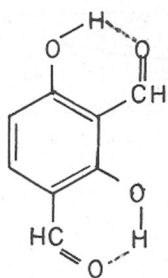


FIG. 12. PMR SPECTRUM OF RESORCINOL 2:4 DIALDOXIME  
IN DMSO

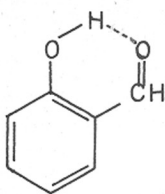
FIG. 13. INFRARED SPECTRA OF

- a RESORCINOL 2:4 DIALDEHYDE (0.08 % W/V), 1 CM. QUARTZ CELL  
 ——— b RESORCINOL 2:4 DIALDEHYDE (deuterated) (0.08 % W/V), 1 CM. QUARTZ CELL  
 in situ

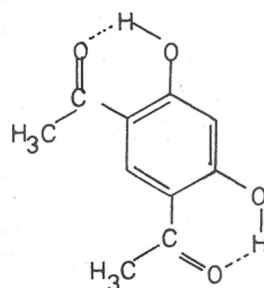
Since the bands due to intramolecularly bonded hydroxyl group in these chelated compounds are difficult to locate exactly as they shift far down to lower frequencies to merge with C-H absorption, it is better to use deuteration technique and take the positions of O-D bands as a measure for the strength of hydrogen bond. Thus the bands attributed to O-D appear in the case of d-salicylaldehyde (liquid film) (Fig. 10b) resorcinol 2:4-dialdehyde (deuterated in solution) (Fig. 13b) and d-resorcinol 2:4-dialdehyde (nujol mull) (Fig. 13d) at 2358, 2212 and 2310  $\text{cm}^{-1}$  respectively demonstrating the stronger hydrogen bonding in the dialdehyde. This result is of course, expected in view of the extended conjugation in resorcinol 2:4-dialdehyde (I) as against single chelation in salicylaldehyde (II) and 4:6-diacetyl resorcinol (III).



I



II



III

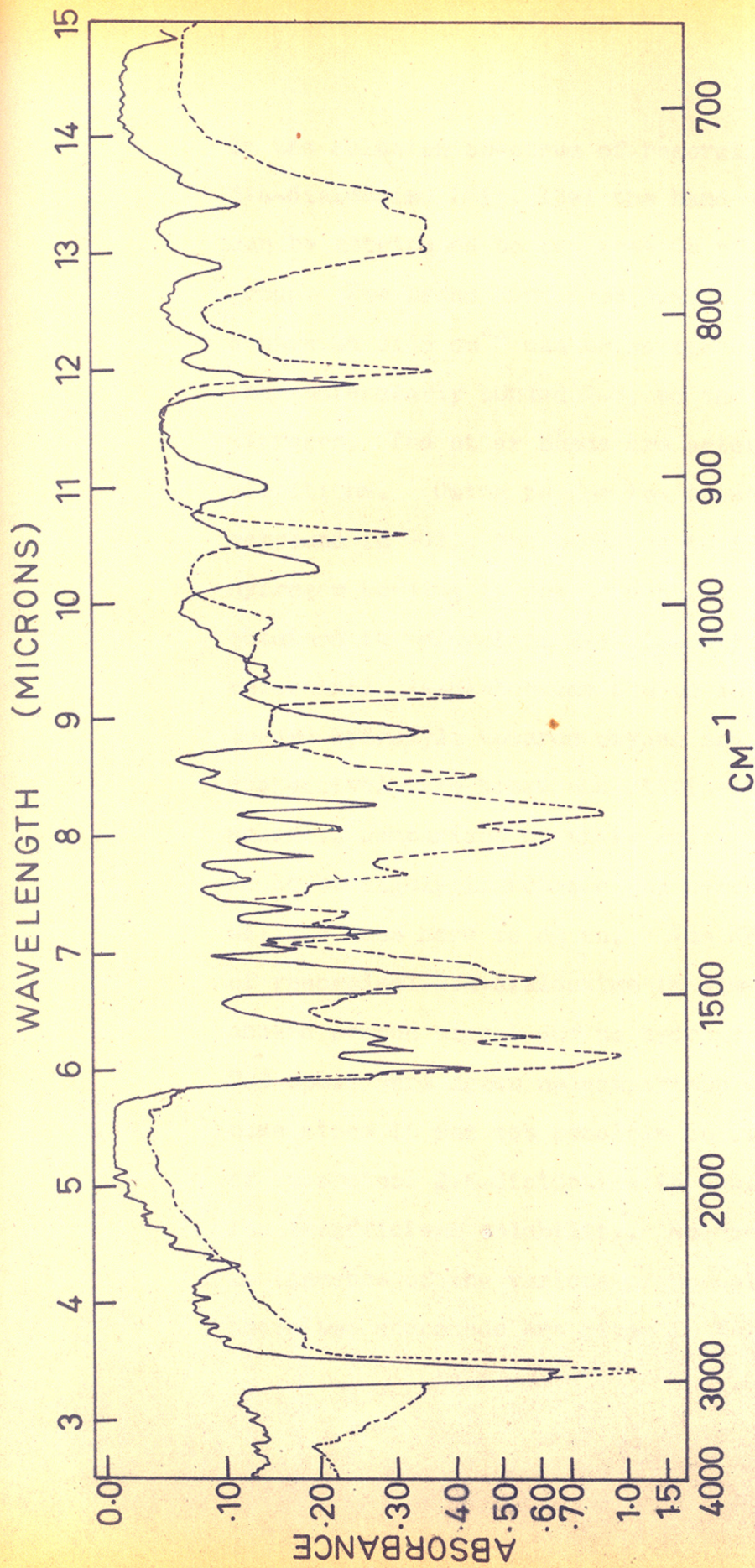


FIG. 13. INFRARED SPECTRA IN NUJOL MULL OF

- C. RESORCINOL 2:4 DIALDEHYDE
- d. d-RESORCINOL 2:4 DIALDEHYDE

In the solution spectrum of resorcinol 2:4-dialdoxime (Fig. 13e) the band at  $3585\text{ cm}^{-1}$  can be attributed to the free OH of the oxime group. The broad band from  $3280\text{--}3050\text{ cm}^{-1}$  with the centre at  $3165\text{ cm}^{-1}$  can be assigned to the intramolecularly bonded O-H, to the oximino nitrogen. The other bands are arising from C-H vibrations. Owing to the low concentration of the compound in  $\text{CCl}_4$ , the band due to intermolecular hydrogen bonding is not present. Since the bands obtained in resorcinol 2:4-dialdehyde and resorcinol 2:4-dialdoxime due to intramolecular bonded hydroxyls towards oxygen and nitrogen respectively are broad and difficult to locate exactly, comparison of their relative strengths would be highly improbable and hence no such attempt will be made here to do so. The NMR spectrum of resorcinol 2:4-dialdoxime in dimethylsulfoxide showed proton signals due to hydroxyls, at 670 cps and 700 cps. Here again no comparison will be made since it was not possible to obtain NMR spectrum of resorcinol 2:4-dialdoxime in  $\text{CDCl}_3$  owing to its insufficient solubility. However, the assignments of the various proton signals of these two compounds are given in Table I and II.

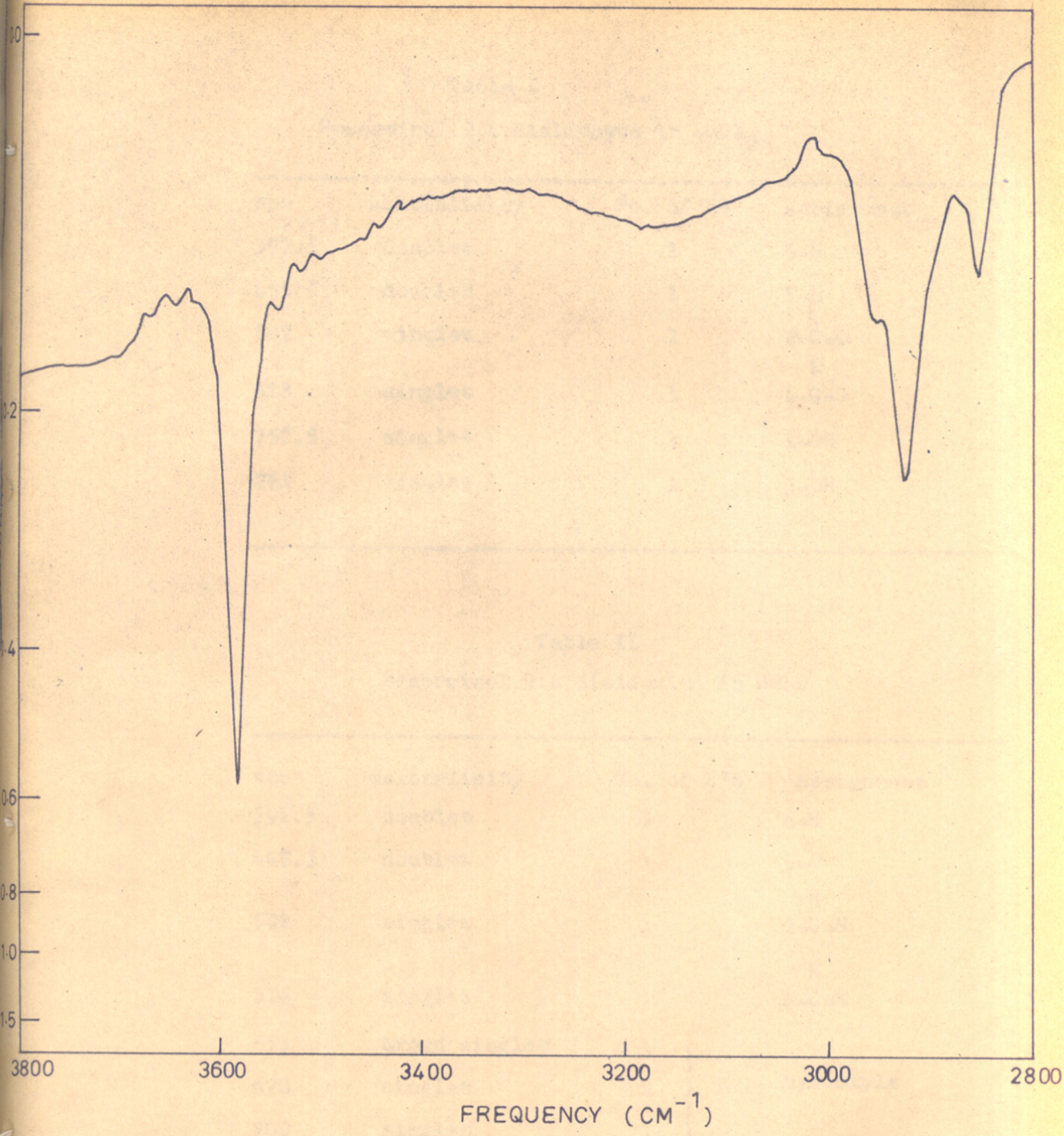


FIG. 13 e INFRARED SPECTRUM OF RESORCINOL-  
2:4 DIALDOXIME

(SATURATED SOLUTION IN CCl<sub>4</sub>; ~10<sup>-4</sup>M)  
2 Cm. QUARTZ CELL.  
(PRISM GRATING ASSEMBLY)



Table I  
Resorcinol 2:4 dialdehyde in  $\text{CDCl}_3$

cps	multiplicity	No. of H's	Assignment
397.5	doublet	1	6-H
465.5	doublet	1	5-H
587	singlet	1	<sup>H</sup> 2-C=O
628	singlet	1	<sup>H</sup> 4-C=O
757.5	singlet	1	1-OH
761	singlet	1	3-OH

Table II  
Resorcinol 2:4 dioxime in DMSO

cps	multiplicity	No. of H's	Assignment
391.5	doublet	1	6-H
448.5	doublet	1	5-H
502	singlet	1	<sup>H</sup> 2-C=N
516	singlet	1	<sup>H</sup> 4-C=N
653	broad singlet	1	hydroxyls
670	singlet	2	
700	singlet	1	

It is perhaps appropriate here to refer to the investigations of Badilescu and Badilescu concerning the strength of the hydrogen bonds in the diacetyl resorcinols<sup>156</sup>. They obtained for  $\nu$  C=O, values of 1631 and 1652  $\text{cm}^{-1}$  for 2:4 and 4:6-diacetyl resorcinol respectively. The O-D bands of d/-2:4 and 4:6 diacetyl resorcinol appear at 2075 and 2212  $\text{cm}^{-1}$  while that of resorcinol 2:4 dialdehyde appear at 2212  $\text{cm}^{-1}$  (Fig. 13b) and  $\nu$  C=O appear at 1650  $\text{cm}^{-1}$ . Although in view of this, it seems probable that the strength of hydrogen bonding and the extent of conjugation in 2:4-resorcinol dialdehyde and 4:6-diacetyl resorcinol are comparable, it is not rigidly correct to make such a commitment since the systems are somewhat different.

The absorption maxima of the chelate ligands together with those of their polymers with some divalent metals are presented in Table III and IV.

Table III

Infrared absorption maxima (in  $\text{cm}^{-1}$ ) of resorcinol 2:4-dialdehyde and its chelate-polymers with copper(II), nickel(II), cobalt(II) zinc(II) and of resorcinol 2:4 dialdoxime and its copper(II) chelate polymer.

Resorcinol 2:4-dialdehyde	Copper(II) Resorcinol 2:4-dialdehyde	Nickel(II) Resorcinol 2:4-dialdehyde dihydrate	Cobalt(II) Resorcinol 2:4-dialdehyde dihydrate	Zinc(II) Resorcinol 2:4-- dialdehyde	Resorcinol 2:4-- dialdoxime	Copper(II) Resorcinol 2:4-- dialdoxime
3250s, vb	3500s, b	3250s, b	3300s, br	3400s, br	3510s	3200s, v, br
2950v, s	2980v, s.	2950v, s.	2900v, s.	3440vs 2950v, s.	3440vs 2970v, s	2950s
1640v, s.		1636v, s.	1625v, s, b	1630v, s	1630s	
	1580v, s, b	1575v, s	1575v, s	1558v, s, b	1600m	1585v, s. 1550s, sh
1600vs		1520v, s, sh 1516v, s	1525v, s, sh			
1480v, s	1482v, s	1480v, s	1495v, s b	1478v, s	1510s	
1462s, sh	1466v, s	1460v, s	1474v, s, b		1457s	1464vs
	1440s, sh	1435s		1440s, sh		
1408m	1400s, b, sh	1410v, s	1406v, s	1400s, sh	1410v, w	
1400m						
1370m	1375vs, b	1387s	1398v, s	1375v, s	1375s	
1330m, sh		1345s	1380v, s		1366s	1350s, sh 1345s
1300s			1336s		1312m	1330s, sh, b 1313m, sh, b 1303s

Table III (continued)

1250v.s	1280s, b	1284s	1280s	1290m	1280s
	1265s				
	1230v.s	1235v.s	1228s	1225s	1245w, sh 1228w, sh 1213m
1225v, s				1250w	
1175s	1184m	1170s	1165m	1175s	1173m
1158m, sh	1123s	1127	1127m	1112m	1128s
	1110s, sh	1094s	1090s	1084s	1090m
1088vs		1063s	1055s		1072s
1016m, bf	1016w, br			1025s	1040s
					1996s, bf
945s	975m		970w, bf	998s	956w
	946w			969m	
				953m	
832s	833s, sh, b	834s	830m	937m	860m
	823s				806s
816m, bf, sh	787, m, bf	793m, br	790s	834m, sh, br	806s
				816s	775s
				792m	764m
767b, s	740m, br	727m, v, br	730m, br	768m, br	
753s, b					732w, bf
739s					

Table IV

Infrared absorption maxima (in  $\text{cm}^{-1}$ ) of 4:6-diacetyl resorcinol and its co-ordination polymers with copper(II), nickel(II) and cobalt(II).

4:6-Diacetyl Resorcinol	4:6-Diacetyl Resorcinol Copper(II)	4:6-Diacetyl Resorcinol Nickel(II) dihydrate	4:6-Diacetyl Resorcinol Cobalt(II) dihydrate
3600w, sh	3450m	3400s, vb	3350m, vb
2900vs	2950*vs	2950*vs	2985*vs
1666vs	1660w	1635vs, b	1632vs
1600s	1604s	1600vs, sh	1600s, sh
1575s, sh	1575vs, sh	1554vs	1560s
1500s	1500vs		1510m, sh
1475*m	1480vs	* 1480vs	* 1480s
1440w, sh	*	1465vs	1470s
1380s	1390s	1395vs	1460s
		1380vs*	1390s
1360m, sh	1360w		1380s*
1350s		1345vs	1340s
1320s	1328s	1298m	1295w
1270vs	1280vs	1275vs	1275s
		1265vs	1260s, sh
1250m	1232vw	1220m	1210w
1190m			
		1090w	1085w
1055m	1066m	1065m	1065m
1040w	1030w	1044w	1040w
976vw	978m	980w	980w
		965m	965w
950w			
912w	929vw	920m	918w
	904vw		
880w, sh	865m	862s	865m
850s		845s, b	840m, b
	823m	810s	810w
800v, w		770m, b	770vw, b
	751m		
742w			
730v, w, b	730, vw, b	730m, b	730vw, b
	716m	690m, vb	688vw, b

\* Nujol peaks appear here.

In the spectrum of d-resorcinol 2:4-dialdehyde (Fig. 13d) several new bands appear. As the system is one in which strong intramolecular hydrogen bonding has been made evident and in addition, as the vibrations due to carbonyl and hydroxyl groups couple, it is difficult to make any tentative assignments for the bending modes of hydroxyl. Like the chelate polymers of 2:4 resorcinol dialdehyde, the chelate polymer of 4:6-diacetyl resorcinol with copper(II) seems to be anhydrous, while those of nickel(II) and cobalt(II) of both the chelate ligands are dihydrates. Perhaps this is borne out in the case of 4:6 diacetyl resorcinol chelates by the fact that the medium intensity absorption peak at  $1350\text{ cm}^{-1}$  presumably due to the OH bending vibration of the chelate ligand is absent in the copper polymer while the other two polymers show strong absorption bands at  $1340$  and  $1345\text{ cm}^{-1}$  possibly due to such vibrations due to the presence of water.

In many cases co-ordination polymerization has been found to yield relatively thermostable materials. Bearing in mind this modern trend of interest the thermogravimetric analysis of the chelate polymers of resorcinol 2:4 dialdehyde with

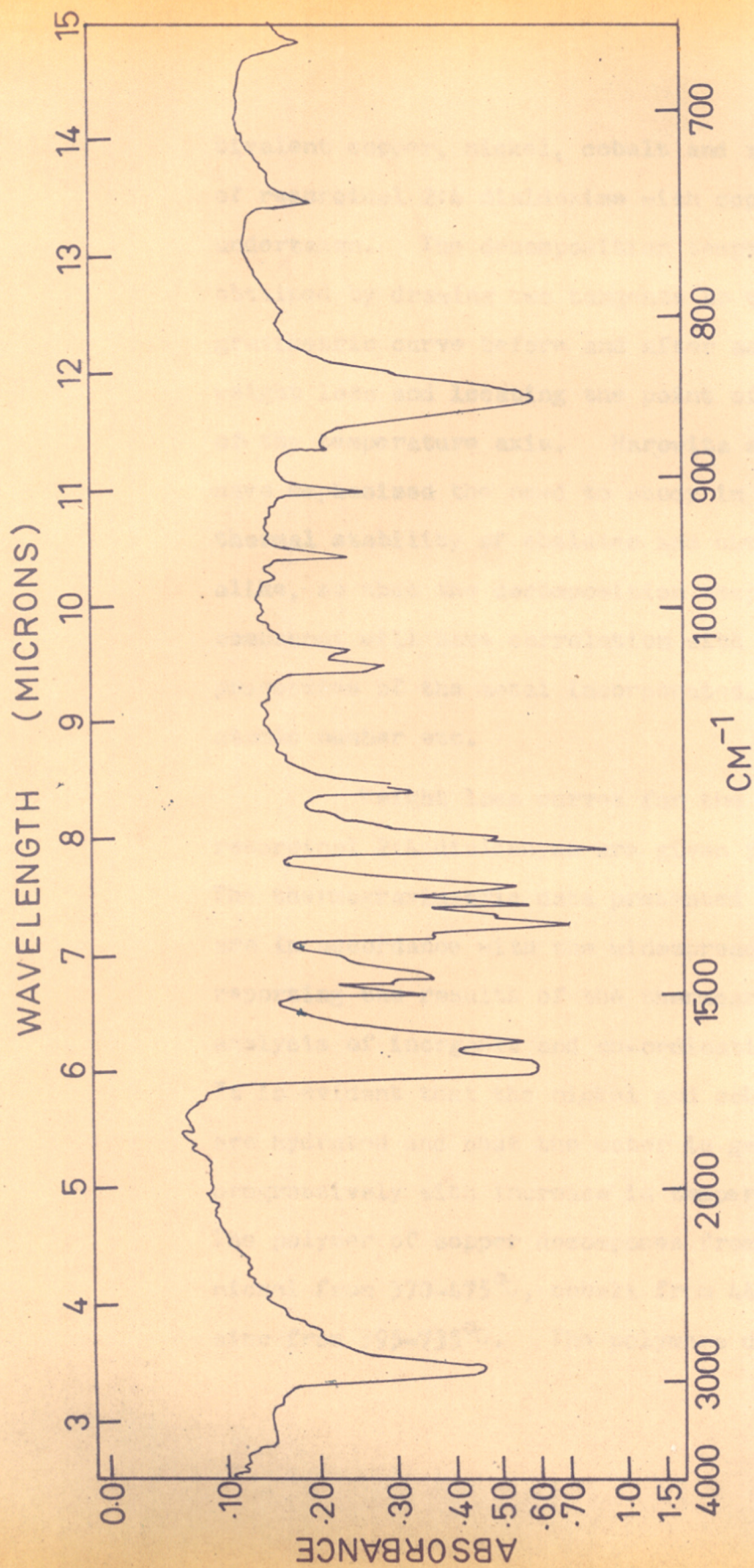


FIG. 13f INFRARED SPECTRUM IN NUJOL MULL OF  
4:6 DIACETYL RESORCINOL

bivalent copper, nickel, cobalt and zinc and that of resorcinol 2:4 dialdoxime with copper(II) were undertaken. The decomposition temperature was obtained by drawing two tangents to the thermal gravimetric curve before and after accelerated weight loss and locating the point of intersection of the temperature axis. Harowitz and Perros<sup>157</sup> have emphasised the need to study in vacuum the thermal stability of chelates and chelate polymers alike, so that the decomposition temperature of the compounds will have correlation with the periodic properties of the metal incorporated, such as atomic number etc.

Weight loss curves for the polymers of resorcinol 2:4 dialdehyde are given in Fig. 14. The thermogravimetric data presented in the figure are in accordance with the widespread practice of reporting the results of the thermogravimetric analysis of inorganic and co-ordination compounds. It is evident that the nickel and cobalt polymers are hydrated and that the water is getting removed progressively with increase in temperature. The polymer of copper decomposes from 240-450°C, nickel from 370-475°C, cobalt from 440-625°C and zinc from 395-735°C. The polymers do not completely



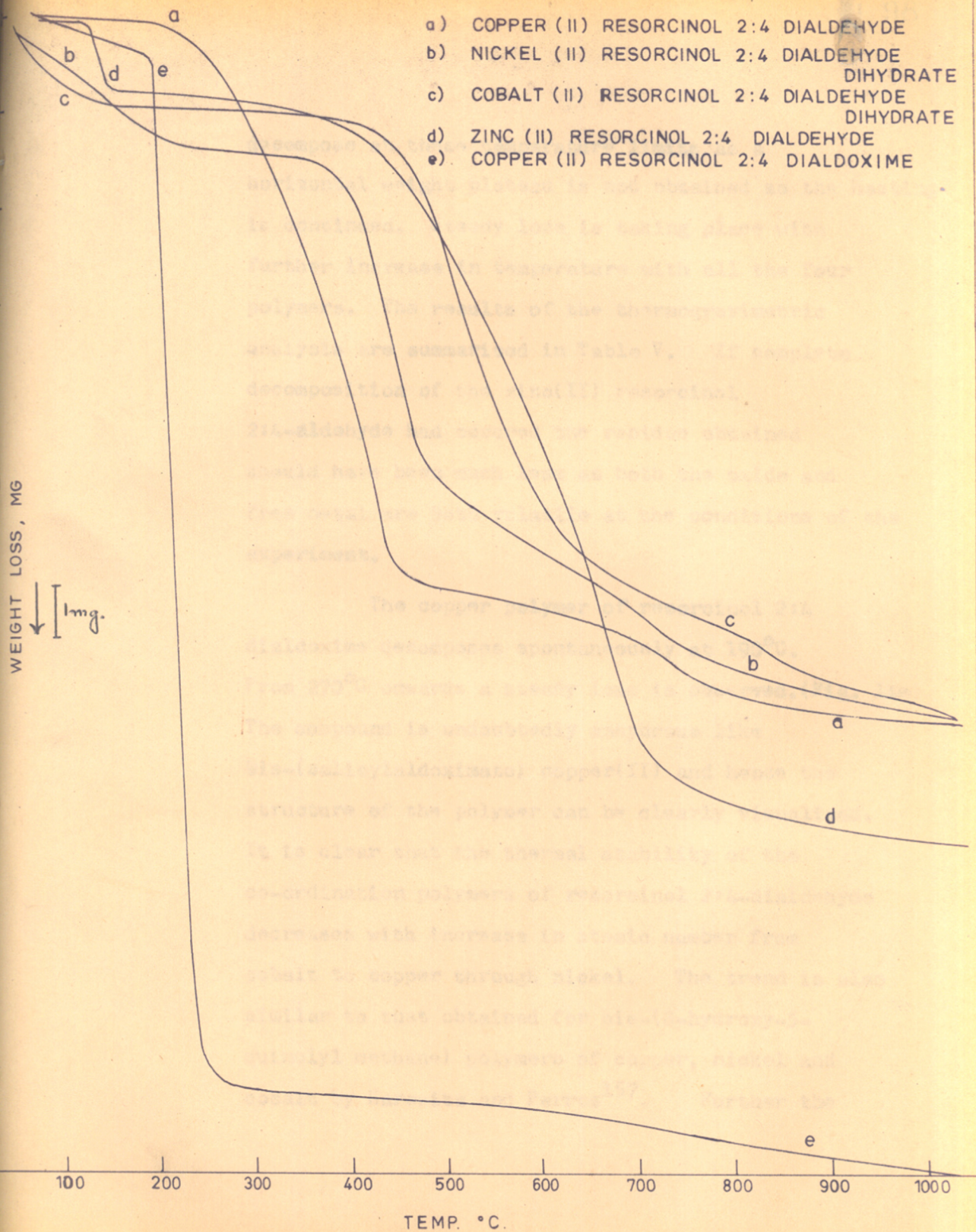


FIG. 14. THERMOGRAMS FOR THE 'CHELATE POLYMERS'

decompose at these temperature limits as a horizontal weight plateau is not obtained as the heating is continued. Steady loss is taking place with further increase in temperature with all the four polymers. The results of the thermogravimetric analysis are summarized in Table V. If complete decomposition of the zinc(II) resorcinol 2:4-aldehyde had occurred the residue obtained should have been much less as both the oxide and free metal are both volatile at the conditions of the experiment.

The copper polymer of resorcinol 2:4 dialdoxime decomposes spontaneously at 190°C. From 270°C onwards a steady loss is observed. (Fig. 14e) The compound is undoubtedly anhydrous like bis-(salicylaldoximate) copper(II) and hence the structure of the polymer can be clearly visualized. It is clear that the thermal stability of the co-ordination polymers of resorcinol 2:4-dialdehyde decreases with increase in atomic number from cobalt to copper through nickel. The trend is also similar to that obtained for bis-(8-hydroxy-5-quinolyl methane) polymers of copper, nickel and cobalt by Harowitz and Perros<sup>157</sup>. Further the

Table V

Decomposition temperature and total percentage of sample volatilized after pyrolysis at 1000°C to constant weight of the "chelate polymers".

Chelate polymer	Decomposition Temperature °C	Elemental Analysis Metal (%)	Calc. C, H, O (%)	After pyrolysis at 1000°C Residue(%)	Volatilized (%)
Copper(II) resorcinol 2:4 dialdehyde	240	27.92	72.08	40.64	59.36
Nickel(II) resorcinol 2:4 dialdehyde dihydrate	370	22.68	77.32	39.91	60.09
Cobalt(II) resorcinol 2:4 dialdehyde dihydrate	440	22.75	77.25	26.9	73.1
Zinc(II) resorcinol 2:4 dialdehyde	395	28.48	71.52	26.77	73.23
Copper(II) resorcinol 2:4 dialdoxime	190	24.67	75.33	3.23	96.77

decomposition temperatures reported<sup>158</sup> for the salicylaldehyde chelates of copper (190°C) nickel (300°C) and cobalt (230°C) in static air atmosphere do not bear any such relationship with the atomic number of the metal. As the decomposition temperatures of the corresponding chelate polymers with resorcinol 2:4-dialdehyde are high and as thermogravimetric data <sup>in vacuum</sup> are lacking for the metal salicylaldehyde chelates, it is reasonable to conclude that co-ordination polymerization yields much more thermally stable compounds.

### Experimental

#### Materials and Methods

Resorcinol 2:4-dialdehyde was prepared essentially according to literature methods<sup>152,153</sup> with slight modifications.

To a mechanically stirred solution of 15 g. of resorcinol in 1200 ml. of 20% sodium hydroxide, 240 g. of chloroform was added dropwise at room temperature (34-36°C), in a minimum of 3 hours, care being taken to maintain the temperature. The mixture was refluxed for 26 hours acidified with 9N H<sub>2</sub>SO<sub>4</sub> and steam distilled immediately to obtain the dialdehyde as voluminous white needles. m.p. 130°C.

Resorcinol 2:4-dialdoxime was prepared by the method of Kuhn and Staab<sup>152</sup>.

To an alcoholic solution containing 1.66 g. (0.01 mole) of resorcinol 2:4 dialdehyde was added a strong aqueous solution of 2.8 g. (0.04 mole) of hydroxylamine hydrochloride. The solution was made alkaline with a clear five per cent sodium carbonate solution and left aside for 15 hours. The separated product was collected by filtration and recrystallized from water. m.p. 207-209°C. Calculated for  $C_8H_8N_2O_4$ : C, 49.00; H, 4.11. Found: C, 48.83; H, 4.13.

Deutero chloroform was prepared according to the method of Gopakumar and Madhavan Nair<sup>159</sup>.

d-Salicylaldehyde was prepared according to the method given by Murray and Williams<sup>160</sup>.

To 25.7 g. of anhydrous aluminium chloride was added 23.54 g. of freshly distilled salicylaldehyde. The yellow complex of  $(OC_6H_4CHO)_2Al_2Cl_4$  was suspended in peroxide free sodium dry ether and treated with heavy water (> 99.4%). After complete decomposition of the product, it was extracted with ether. Ether was removed under reduced pressure and the residual liquid was fractionated at 2.7 mm. The fraction collected at 50°C was used for spectral purposes. All the operations were performed in a dry box.

Chelate polymers of resorcinol 2:4 dialdehyde:

The metal "chelate polymers" were prepared by "solution polymerization" by the dropwise addition of aqueous metal acetate solutions to mechanically stirred alcoholic solutions of the chelate ligand in the mole ratio of 1:1. Precipitation was instantaneous and almost quantitative in all the cases. All the polymers were washed first with absolute ethanol, followed by dry ether and air dried. The copper(II) polymers of the dialdehyde and dialdoxime were of colloidal nature.

A typical preparation can be outlined thus:

A clear solution of 0.3992 g. (0.002 mole) of cupric acetate monohydrate (A.R.) in 10 ml. of water was added dropwise to a filtered magnetically stirred solution of 0.3222 g. (0.002 mole) of resorcinol 2:4 dialdehyde in 25 ml. of absolute ethanol. Precipitation was instantaneous and quantitative. Collected the product by filtration and washed first with absolute ethanol followed by dry ether. Air dried the dark green product.

The colours and elemental analysis of single unit for different polymers isolated are given below:

- 1) Copper(II) resorcinol 2:4 dialdehyde (dark green)  
 calculated for Cu ( $C_8H_4O_4$ ) C, 42.24; H, 1.77  
 Found: C, 42.85; H, 2.74.
- 2) Nickel(II) resorcinol 2:4 dialdehyde dihydrate  
 (pale green)  
 Calculated for Ni ( $C_8H_8O_6$ ) C, 37.15; H, 3.12  
 Found: C, 37.95; H, 3.65.
- 3) Cobalt(II) resorcinol 2:4 dialdehyde dihydrate  
 (yellowish orange)  
 Calculated for Co ( $C_8H_8O_6$ ) C, 37.13; H, 3.12  
 Found: C, 36.63; H, 3.36.
- 4) Zinc(II) resorcinol 2:4 dialdehyde (yellow)  
 Calculated for Zn ( $C_8H_4O_4$ ) Zn, 28.5  
 Found: Zn, 29.3.
- 5) Copper(II) resorcinol 2:4 dialdoxime (brownish black)  
 Calculated for Cu ( $C_8H_6N_2O_4$ ) C, 37.31; H, 2.35.  
 Found: C, 37.74; H, 3.7.

4:6-Diacetyl resorcinol was prepared essentially  
 by the method of Dean and Robertson<sup>161</sup>, m.p. 182°C.

Calculated for  $C_{10}H_{10}O_4$  C, 61.84; H, 5.19  
 Found: C, 60.94; H, 5.31.

Chelate polymers of 4:6 diacetyl resorcinol were isolated exactly in the same way as the chelate polymers of resorcinol 2:4 dialdehyde. All the three polymers are of colloidal nature.

The colour and elemental analysis of a single unit for the polymers isolated are given below:

1) Copper(II) 4:6 diacetyl resorcinol (dark green)

Calculated for Cu ( $C_{10}H_8O_4$ ) C, 46.97; H, 3.15

Found: C, 45.28; H, 4.13.

2) Nickel(II) 4:6 diacetyl resorcinol dihydrate

(colourless)

Calculated for Ni ( $C_{10}H_{12}O_6$ ) C, 41.85; H, 4.22

Found: C, 42.85; H, 5.15.

3) Cobalt(II) 4:6 diacetyl resorcinol dihydrate

(colourless)

Calculated for Co ( $C_{10}H_{12}O_6$ ) C, 41.82; H, 4.21

Found: C, 42.85; H, 5.15.

Procedures for the determination of infrared spectra of solutions of the chelated compounds and for the deuteration in situ were described earlier in Chapter II. Solid samples were deuterated in the usual way by recrystallisation of the samples from heavy water (>99.4%) in dry nitrogen atmosphere. Infrared



spectra of the "chelate polymers" were run in infra-red spectrophotometers as nujol mulls.

NMR spectra were recorded on a Varian Associates A-60 spectrometer using TMS (tetramethyl silane) as internal standard.

#### Thermogravimetric Analysis

The thermograms were taken on a vacuum spring thermobalance built by A.E.E.T. The sensitivity of the spring was 0.5 mm/mg. The changes in length of the spring corresponding to the changes in weight were observed on a cathetometer capable of reading upto 1/100 mm. The sample under study was carefully weighed in the 25 mg. range in a platinum crucible. The pressure in the system was maintained at  $30\mu$  by continuous evacuation throughout the experiment. Starting at room temperature the sample was heated to  $1000^{\circ}\text{C}$  and then to constant weight, if necessary, at the rate of  $6^{\circ}/\text{min}$ . the heating being manually controlled. The temperature measuring thermocouple was situated very close to the sample in the reaction tube. The reaction tube of the thermobalance was of Mullite, joined to the rest of the glass assembly by means of adhesives, elastomer and araldite.

CHAPTER V  
INFRARED ABSORPTION SPECTRAL STUDIES OF  
SOME WERNER TYPE COMPLEXES.

### Abstract

Since the infrared spectra of ammine complexes are of great significance for assigning metal-ligand stretching vibrations the  $\text{C}_6\text{Br}$  spectra of a large number of Werner type complexes have been recorded. Besides ammonia some of these complexes reported in this chapter contain inorganic groups or radicals whose original symmetries are modified as a result of co-ordination. Hence infrared spectral data for these compounds are given from  $4000$  to  $\sim 300 \text{ cm}^{-1}$  in order to locate such perturbations as well as various metal ligand vibrations. Further, it can be seen from the data given that at least in some instances there are small but significant differences between the position of the absorption peaks depending on whether the spectra was taken using nujol mull or KBr pellet. Although, assignment of most of the absorption peaks appear to be reasonable, some of these assignments may be regarded as speculative especially in view of lack of theoretical calculations.

INFRARED ABSORPTION SPECTRAL STUDIES OF SOME  
WERNER TYPE COMPLEXES

Infrared spectra of Werner type complexes, for instance, the metal amines are of considerable interest in the study of the co-ordination bond, although the band assignments for the metal-nitrogen stretching mode was a subject of some controversy in the past. Thus, the band at  $\approx 300 \text{ cm}^{-1}$  in the spectra of cobalt ammine complexes once assigned to the M-N stretching mode is now believed to be due to the N-M-N bending mode<sup>162,163</sup>.

As can be seen from the general introduction, the infrared spectra of metal ammine complexes have already been a subject of numerous investigations. However, as a part of our programme on the study of the infrared spectra of co-ordination compounds, we have recorded the spectra of a number of Werner type complexes in the NaCl prism as well as in the CsBr prism regions. It was of interest to carry out such measurements for the following purposes (a) to find out the metal ligand stretching vibrations in the complexes, (b) to observe any changes in the infrared spectra associated to such factors as crystallinity of the sample (i.e. depending on whether a nujol mull or

potassium bromide disk was used) and the extent of hydration, (c) whether there is any significant difference traceable for compounds having geometrically different configurations (cis-trans isomers) and (d) to examine the effect of co-ordination or the perturbing crystalline field on the symmetry of groups inside and outside the co-ordination sphere. .

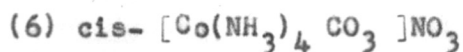
The infrared spectral studies of the following cobalt complexes are given here.

- (1) cis-  $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl}$ .
- (2) trans-  $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{HSO}_4$ .

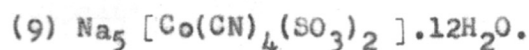
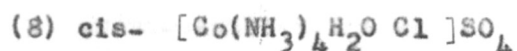
The infrared spectra of these two compounds have been recorded for the first time, although the infrared spectrum of trans- $[\text{Co}(\text{NH}_3)_4 \text{Cl}_2] \text{Cl}$  has been recorded previously and discussed.

- (3) cis-Na  $[\text{Co}(\text{NH}_3)_4 (\text{SO}_3)_2] \cdot 4\text{H}_2\text{O}$
- (4) trans-Na  $[\text{Co}(\text{NH}_3)_4 (\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$
- (5) cis-NH<sub>4</sub>  $[\text{Co}(\text{NH}_3)_4 (\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ .

The spectra of these compounds were recorded for the first time with a view to determine the effect of co-ordination on the vibrations of the sulphite groups in the cis and trans configurations of the complexes.

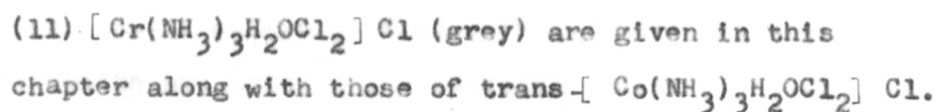


The spectra of these two cis compounds have been recorded also for the first time in the CsBr prism region, although there have been some mention and discussion about spectra of similar complexes in the NaCl prism region in the literature.



The spectra of these two compounds have also been recorded for the first time.

Also the infrared spectral data of the two isomeric chromium complexes, namely,



Since we have not made a detailed normal co-ordinate analysis in which the vibrations in the  $\text{NH}_3$  ligand as well as those for the skeletal part are taken into consideration, the assignments made here may be regarded as tentative. However, many of these assignments are based on the previous work reported in the literature on similar compounds and are presumed to be correct.

ExperimentalMaterials and MethodsPreparation of compounds

(1) Cis-dichloro-tetrammine cobalt(III) chloride was prepared essentially according to the method given by Merritt and Wiberly<sup>166</sup>. Calculated for  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ : Co, 25.25. Found: Co, 25.34.

(2) Trans-dichloro-tetrammine-cobalt(III) hydrogen sulphate. This compound was prepared according to the prescription of Palmer<sup>167</sup>.

Calculated for  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{HSO}_4$ , Co, 19.97.

Found: Co, 20.45.

(3) and (4) Sodium cis-disulfito-tetrammine cobaltate(III) tetrahydrate and sodium trans-disulfito-tetrammine cobaltate(III) dihydrate. These compounds were prepared by slight modification of the method of Hoffmann and Jenny<sup>168</sup>. Calculated for

$\text{Na}[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 4\text{H}_2\text{O}$ ;  $\text{NH}_3$ , 17.82.

Found:  $\text{NH}_3$ , 17.68. Calculated for

$\text{Na}[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$ : Co, 17.02; S, 18.52.

Found: Co, 17.65; S, 18.15.

- (5) Ammonium cis-disulfito tetrammine cobaltate(III) trihydrate was prepared by the method of Bailer and Peppard<sup>169</sup>. Calculated for  $\text{NH}_4[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$ : S, 17.83. Found: S, 17.70.
- (6) Cis-carbonato-tetrammine cobalt(III) nitrate was prepared according to the method described in "Inorganic Syntheses"<sup>170</sup>. Calculated for  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$ :  $\text{NH}_3$ , 27.36. Found:  $\text{NH}_3$ , 27.01.
- (7) Cis-oxalato-tetrammine cobalt(III) chloride was prepared according to the directions given by Palmer<sup>167</sup>. Calculated for  $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{Cl}$ :  $\text{NH}_3$ , 27.19. Found:  $\text{NH}_3$ , 27.25.
- (8) Cis-chloro aquo tetrammine cobalt(III) sulphate was prepared according to the directions given in "Inorganic Syntheses"<sup>170</sup>. Calculated for  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O Cl}]\text{SO}_4$ :  $\text{NH}_3$ , 24.62. Found:  $\text{NH}_3$ , 24.60.
- (9) Sodium disulfito tetracyano cobaltate(III) dodecahydrate. This compound was prepared according to the method of Ray and Chakraborty.<sup>171</sup> Calculated for  $\text{Na}_5[\text{Co}(\text{CN})_4(\text{SO}_3)_2] \cdot 12\text{H}_2\text{O}$ . Co, 9.01. Found: Co, 9.12.



(10) and (11) Dichloroaquatriammine chromium(III) chloride. The red-violet and grey forms of the compound were prepared according to the method of Bhatnagar<sup>172</sup> et al. Calculated for

[Cr(NH<sub>3</sub>)<sub>3</sub>H<sub>2</sub>OCl<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O. Cr, 22.88; NH<sub>3</sub>, 22.46%.  
 Found: (red-violet); Cr, 22.67; NH<sub>3</sub>, 22.01.  
 Found: (grey): Cr, 22.28; NH<sub>3</sub>, 21.75.

(12) Trans-dichloroaquatriammine cobalt(III) chloride was prepared according to the method of Palmer<sup>167</sup>. Calculated for [Co(NH<sub>3</sub>)<sub>3</sub>H<sub>2</sub>OCl<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O. Co, 25.15. Found: Co, 25.1.

#### Measurement of spectra

The infrared spectra of the compounds were recorded by using a Perkin-Elmer Model 221 infrared spectrophotometer equipped with NaCl and CsBr optics. The instrument was calibrated for the NaCl prism region by a standard polystyrene film and for the CsBr prism region, water vapour and carbon dioxide bands were used. The spectra of all the compounds were run in KBr disks in the NaCl optics region and in nujol mulls in the CsBr optics region. The spectra of some of the compounds were recorded in nujol mulls in the NaCl optics region and some in KBr disks in the CsBr optics region to examine the differences in the KBr and mull spectra.

### Results and Discussion

The infrared absorption maxima of  
 cis-  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , trans-  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{HSO}_4$ ,  
 cis-Na  $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2]4\text{H}_2\text{O}$ ,  
 cis-NH<sub>4</sub>  $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$  and  
 trans- Na  $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$ , (Table I);  
 cis-  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$  and cis-  $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{Cl}$   
 (Table III); Na<sub>5</sub>  $[\text{Co}(\text{CN})_4(\text{SO}_3)_2] \cdot 12\text{H}_2\text{O}$  and  
 cis-  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OCl}]\text{SO}_4$  (Table II),  
 $[\text{Cr}(\text{NH}_3)_3\text{H}_2\text{OCl}_2]\text{Cl}$ , red violet and grey isomers  
 and trans-  $[\text{Co}(\text{NH}_3)_3\text{H}_2\text{OCl}_2]\text{Cl}$  (Table IV) are given.  
 A glance at these tables shows that there are some  
 differences between the mull spectra and KBr pellet  
 spectra. Such differences may be attributed to  
 various causes like crystallinity of the sample,  
 modification of KBr spectra due to use of pressure  
 during pelleting, etc. The KBr pellet spectra in  
 the CsBr prism region is unreliable beyond  $25\mu$ .  
 Compared to the mull spectra the former gives very broad  
 and diffuse bands and hence these have not been  
 listed, beyond  $25\mu$ . The mull spectra for all  
 the compounds (except one) in the CsBr prism region  
 are presented in figures (15-19).

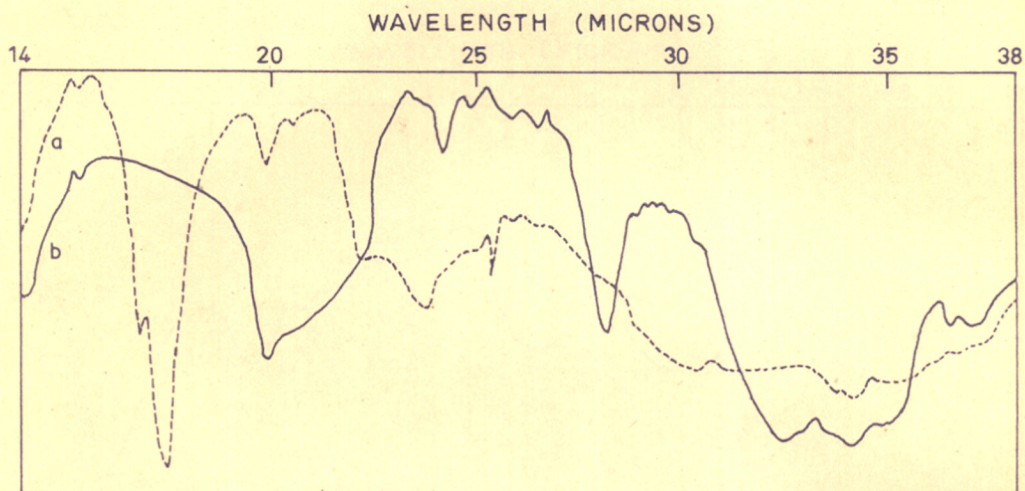


FIG. 15. INFRARED SPECTRA IN THE CsBr PRISM REGION  
IN NUJOL MULL OF

- a     $\text{cis-} [\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{Cl}$   
 ————— b     $\text{trans-} [\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{HSO}_4$

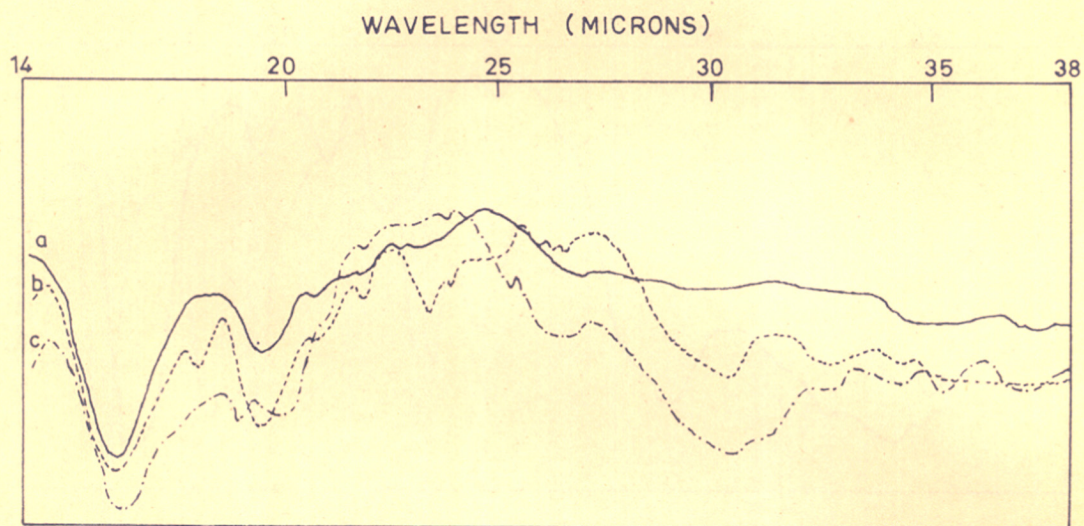


FIG. 16. INFRARED SPECTRA IN THE CsBr PRISM REGION OF

- a cis - Na  $\left[ \text{Co}(\text{NH}_3)_4(\text{SO}_3)_2 \right] \cdot 4 \text{H}_2\text{O}$  (KBr PELLET)
- ..... b trans - Na  $\left[ \text{Co}(\text{NH}_3)_4(\text{SO}_3)_2 \right] \cdot 2 \text{H}_2\text{O}$  (NUJOL MULL)
- - - c cis -  $\text{NH}_4 \left[ \text{Co}(\text{NH}_3)_4(\text{SO}_3)_2 \right] \cdot 3 \text{H}_2\text{O}$  (NUJOL MULL)

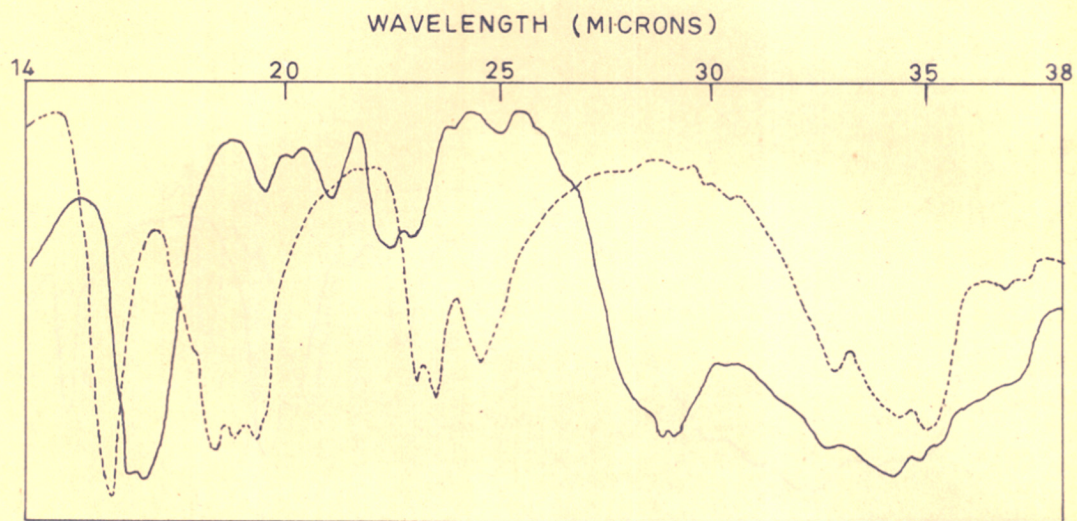


FIG. 17. INFRARED SPECTRA IN THE CsBr PRISM REGION  
IN NUJOL MULL OF

- a  $\text{cis-} [\text{CO}(\text{NH}_3)_4 \text{H}_2\text{O Cl}] \text{SO}_4$   
 - - - b  $\text{Na}_5 [\text{CO}(\text{CN})_4 (\text{SO}_3)_2] \cdot 12 \text{H}_2\text{O}$

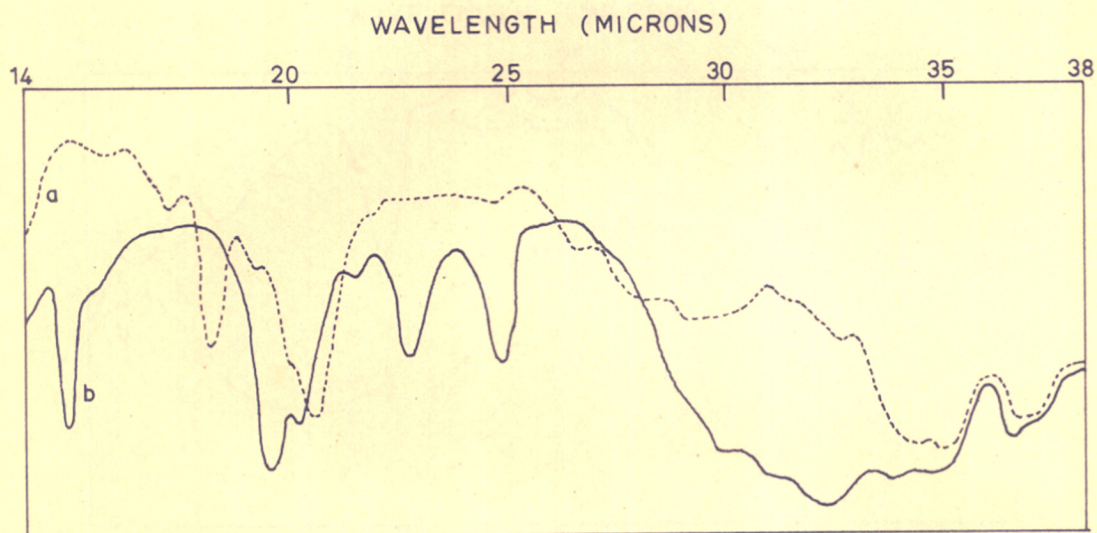


FIG. 18. INFRARED SPECTRA IN THE CsBr PRISM REGION  
IN NUJOL MULL OF

----- a cis -  $[\text{CO}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$

———— b cis -  $[\text{CO}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{Cl}$

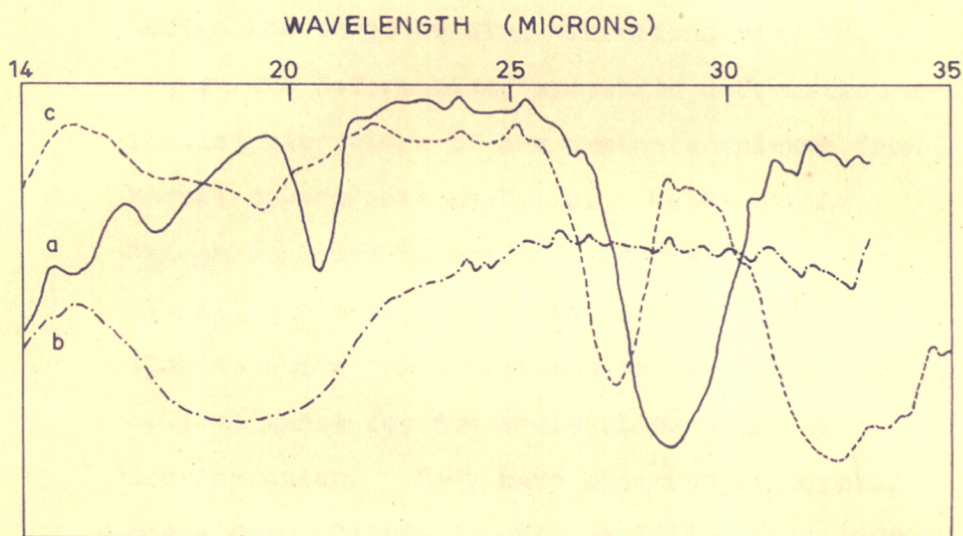


FIG. 19. INFRARED SPECTRA IN THE CsBr PRISM REGION  
IN NUJOL MULL OF

- a  $[\text{Cr}(\text{NH}_3)_3 \text{H}_2\text{O Cl}_2] \text{Cl}$  (RED VIOLET)
- - - b  $[\text{Cr}(\text{NH}_3)_3 \text{H}_2\text{O Cl}_2] \text{Cl}$  (GREY)
- · - · c trans-  $[\text{Co}(\text{NH}_3)_3 \text{H}_2\text{O Cl}_2] \text{Cl}$

Although the structure of the ammine complexes as a whole is highly complicated, the vibrational spectrum can be understood if a 1:1 model (i.e.  $M-NH_3$ ) is used. Based on such a model, Mizushima and co-workers<sup>122</sup> were the first to assign the three bending vibrations viz.  $NH_3$  degenerate deformation, symmetric deformation and rocking vibrations of the ammine complexes from a normal co-ordinate analysis. Subsequently, Shimanouchi and Nakagawa<sup>163</sup> have made normal co-ordinate analysis of the infrared active species where the vibrations in the  $NH_3$  ligand as well as those for the skeletal part are taken into consideration. They have observed absorption peaks for  $Co[(NH_3)_6]Cl_3$  at 3240, 3170, 1600, 1325, 820, 503, 325  $cm^{-1}$  for  $\nu(NH)_a$ ,  $\nu(NH)_s$ ,  $\delta(NH_3)_d$ ,  $\delta(NH_3)_s$ ,  $\delta(NH_3)_\gamma$ ,  $\nu(M-N)$  and  $\nu(NMN)$  vibrations respectively; their calculated values being 3240, 3164, 1615, 1323, 830, 501 and 326  $cm^{-1}$ . However, we have taken the spectra of more complicated ammine complexes which besides ammonia, contain some inorganic radicals whose group frequencies also appear. Furthermore, the presence of water (water of crystallisation as well as co-ordinated water) may lead to some modifications of the absorption frequencies.



There can be seen one or more strong absorption bands in the region  $3550-3100\text{ cm}^{-1}$  in these compounds, evidently due to the anti-symmetrical and symmetrical modes of  $\text{NH}_3$ . However, it should be noted that lattice water also absorbs in this region ( $3559-3200\text{ cm}^{-1}$ ). The higher frequency peaks like  $3550\text{ cm}^{-1}$ ,  $3350\text{ cm}^{-1}$  may therefore be attributed to lattice water, while the lower ones are due to N-H stretching vibrations or bound water. Similarly, though the  $\text{NH}_3$  degenerate deformation in these compounds appear near about  $1600\text{ cm}^{-1}$ , the strong and broad absorption band near  $1630\text{ cm}^{-1}$  in  $\text{cis-}[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O Cl}]\text{SO}_4$  is presumably due to  $\text{OH}_2$  scissors. However, a strong peak at  $1610\text{ cm}^{-1}$  in the compound can be easily attributed to  $\text{NH}_3$  degenerate deformation. But in compounds like  $\text{cis Na}[(\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 4\text{H}_2\text{O}$ , the  $1620\text{ cm}^{-1}$  medium broad peak though predominantly due to  $\text{NH}_3$  degenerate deformation seems to have been modified to some extent due to the presence of water vibration. The symmetrical  $\text{NH}_3$  deformation, vibrations in these compounds can be traced without much difficulty at  $c. 1300\text{ cm}^{-1}$  region.

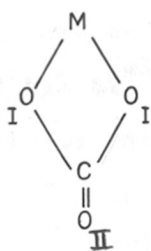
In cis- $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O Cl}] \text{SO}_4$ , the broadness of the peak at  $880\text{-}840 \text{ cm}^{-1}$  is noteworthy. This is, perhaps, due to overlapping of  $\text{NH}_3$  rocking mode with a vibration characteristic of co-ordinated water. However, according to Fujita and co-workers,<sup>128</sup> the characteristic bands of co-ordinated water in the  $\text{NaCl}$  prism region are observable only when the water molecule are linked to the metal by fairly covalent bonds and also to the outer ion by strong hydrogen bonds. While the  $\nu_{3a}$ ,  $\nu_{3b}$ ,  $\nu_{3c}$  vibrations due to  $\text{SO}_4$  in this compound can be traced at  $1134$ ,  $1103$ ,  $1043 \text{ cm}^{-1}$  and  $\nu_1$  vibration at  $924 \text{ cm}^{-1}$ , the  $\nu_{4a}$  and  $\nu_{4b}$  vibrations appear at  $617$  and  $629 \text{ cm}^{-1}$ , being somewhat affected by the presence of  $\text{H}_2\text{O}$ . The peak at  $629 \text{ cm}^{-1}$  is, perhaps, merged with  $\text{OH}_2$  rocking or wagging vibration, a definite assignment of  $\text{H}_2\text{O}$  vibrations being not possible.

The bands due to  $\text{HSO}_4^-$  ion was deduced by comparing the spectra of trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{Cl}$  and trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2] \text{HSO}_4$  and also by comparing the spectrum of the latter compound with the characteristic frequencies compiled by Miller and co-workers<sup>8,9</sup>.

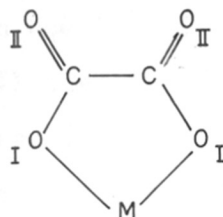
In  $[\text{Co}(\text{CN})_4(\text{SO}_3)_2]^{5-}$ , the very sharp peak at  $2125 \text{ cm}^{-1}$  is due to  $\text{C}\equiv\text{N}$  stretching vibration and the peak at  $543 \text{ cm}^{-1}$  can be attributed to the  $\text{M}-\text{C}$  stretching mode. All the four fundamental vibrations of the pyramidal sulphite ion (having approximately  $\text{C}_{3v}$  symmetry) were observed in this compound at  $966 \text{ cm}^{-1}$  (sym. str.),  $518 \text{ cm}^{-1}$  (sym. bend),  $1120 \text{ cm}^{-1}$  and  $1064 \text{ cm}^{-1}$  (asym. str.) and  $623 \text{ cm}^{-1}$  (asym. bend). The presence of asymmetric stretching vibrations in this compound as well as in the sulphitoammine complexes examined shows that the Co-ligand bonding in these compounds is through sulphur and the sulphite behaves as a monodentate ligand. As shown in Table II eight bands are attributed to the  $\text{SO}_3$  vibrations. However, this cannot be interpreted on the basis of the lower symmetry ( $\text{C}_s$  symmetry) for the co-ordination through oxygen. Even in the co-ordination through sulphur (approximately  $\text{C}_{3v}$  symmetry)  $\text{SO}_3$  asymmetric (degenerate) stretching vibration may be observed as a doublet or multiplet by a perturbation in the solid state. The assignments given in the table for  $\text{SO}_3$  vibrations are therefore reasonable.

In the CsBr prism spectra, it is possible to locate metal-nitrogen stretching modes, metal-chlorine stretching modes as well as N-M-N bending modes. For trans-  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ , Nakagawa and Shimanouchi<sup>162,163</sup> have reported the weak band near  $500\text{ cm}^{-1}$  and the strong band near  $300\text{ cm}^{-1}$  to be due to the Co-N stretching and N-Co-N bending modes. Theoretically, the trans-  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  complex should show only one Co-N stretching vibration, while the corresponding cis compound should show four Co-N stretching modes. The absorption bands at  $504$ ,  $479$  and  $423\text{ cm}^{-1}$  in cis  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  are presumably due to the Co-N stretching vibrations. The infrared spectra of cis-  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  have not been reported in the literature. The strong absorption peaks at  $330$  and  $297\text{ cm}^{-1}$  in this compound may be attributed to Co-Cl stretching and out of plane deformation modes, since similar assignments can be made for  $356$  and  $294\text{ cm}^{-1}$  peaks in the trans  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{HSO}_4$ . However, an additional strong peak at  $317\text{ cm}^{-1}$  can be attributed to the Co-Cl stretching mode in the cis compound. But the case of cis and trans isomers of the sulphito complexes is found to be less clear. While the weak peaks at  $\sim 480\text{ cm}^{-1}$  can be attributed to the Co-N stretching modes,

the trans-isomer showed larger number of peaks in this region than the cis-compound. Furthermore, the electronic absorption spectra of both the cis- and trans- compounds showed the "third band", contrary to the observation of Shimura<sup>164</sup>. The three very strong peaks at 490, 488 and 484  $\text{cm}^{-1}$  in the cis-  $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]\text{Cl}$ , again, can be attributed to the four possible Co-N stretching vibrations of the cis-amine. But the similar carbonate complex  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$  shows only one strong peak at 495  $\text{cm}^{-1}$  assigned to Co-N stretching vibration. The symmetry of carbonate ( $D_{3h}$ ) and oxalate ( $V_h$ ) are lowered by complex formation (as shown below, structure I and II) to  $C_{2v}$ .

BIDENTATE CARBONATE ( $C_{2v}$ )

I

BIDENTATE OXALATE ( $C_{2v}$ )

II

and the infrared spectral assignments given in Table III are mainly based on previous work done on some oxalato- and carbonato- complexes. The appearance of  $\nu_3$  and  $\nu_2$  vibrations of  $\text{NO}_3^-$  at  $1380 \text{ cm}^{-1}$  and  $832 \text{ cm}^{-1}$  are in agreement with ionic nature of the nitrate ( $D_{3h}$  symmetry) in the complex  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$ .

The Co-N stretching frequency of  $[\text{Co}(\text{NH}_3)_3\text{H}_2\text{O Cl}_2]\text{Cl}$  which has a trans-configuration<sup>173</sup> appears at  $517 \text{ cm}^{-1}$  while the Cr-N stretching frequencies in the similar Cr(III) complexes appear at c.  $480 \text{ cm}^{-1}$ . This is in agreement with the recent observation of Tanaka and co-workers<sup>165</sup> that the stretching band due to Cr-N in the Cr(III) ammine complexes appear at a lower frequencies by about  $40 \text{ cm}^{-1}$ . The weak and broad bands at c.  $440 \text{ cm}^{-1}$  in the Cr(III)-isomers and at  $431 \text{ cm}^{-1}$  in the Co(III) complex can be tentatively assigned to the metal-oxygen stretching modes. The assignment of the bands further down is rather difficult. It appears that the strong band at  $365 \text{ cm}^{-1}$  is due to the Co-Cl stretching vibration and band at  $330 \text{ cm}^{-1}$  is due to N-Co-N deformation vibration. The strong band at  $348 \text{ cm}^{-1}$  in the red violet Cr(III) isomer may be assigned to the Cr-Cl stretching mode, but no such band appear in the grey isomer. Again, corresponding to the very strong bands at  $307 \text{ cm}^{-1}$  and  $296 \text{ cm}^{-1}$  presumably

due to the N-Co-N deformation and N-Co-O deformation vibrations, the bands in the Cr(III) isomers are either weak or absent presumably due to the greater ionic character of the chromium complexes. The appearance of the rocking frequency at  $818\text{ cm}^{-1}$  for the Co(III) compound and at  $722\text{ cm}^{-1}$  for the grey Cr(III)-isomer and its absence in the red-violet isomer again point to the greater ionic character of the Cr(III) complexes. However, such conclusions are only tentative and need confirmation from studies of the corresponding deuterated compounds.

Table 1  
Absorption maxima (in  $\text{cm}^{-1}$ ) of Tetramine cobalt(III) Complexes.

Cis- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$		Trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{HSO}_4$		Cis-Na $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 4\text{H}_2\text{O}$		Cis-NH <sub>4</sub> $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 3\text{H}_2\text{O}$		Trans-Na $[\text{Co}(\text{NH}_3)_4(\text{SO}_3)_2] \cdot 2\text{H}_2\text{O}$		Assignment
Nujol mull	KBr pellet	Nujol mull	KBr Pellet	Nujol Mull	KBr Pellet	Nujol Mull	KBr Pellet	Nujol Mull	KBr Pellet	
3320vs 3200vs 2960*vs	3230s 3100s	3290s 3175s		3350s 3250s 2950*s 1635m,b	3350s 3160s 1620m,b	3300sb 2960*s 1600m,b	3300s 1410m	3300s 3320m,sh 2955*s 1710m,vb	3255s 3150s 1605m	H <sub>2</sub> O (symm.& antisym.)str NH <sub>3</sub> (symm.& antisym.str)
1600s,b 1470*s	1530s,b 1400w	1620s 1400w		1450*s 1400m	1450*s 1400m	1450*s 1400w,sh	1427m,sh 1405s	1450*s	1460w 1400w	NH <sub>3</sub> deg.def. (+H <sub>2</sub> O scisso)
1380*s 1320s	1310s	1295s		1375*s 1305m	1310m	1370*s 1315m	1330s 1300s,vb	1370*s 1300mb	1320s 1280sh 1260w 1213w	NH <sub>3</sub> sym.def.
1300s,sh	1294s	1270s,sh		1270w	1278w				1205w	
		1205vs,b 1070vs,vb		1095s,b 1075s,sh 1037s	1090s,b 1070sh 1034s	1220w 1085s,vb	1220w 1100s,vb	1093s 1085s 1070s 1030m,b	1090s 1070s,sh 1042m,b	SO <sub>3</sub> asym.str.
1020w,b		1080m 1050m,b,sh 1022vs	**	930s 953s,b 840w,b	937m 955s 834vw,b	970s	970s	932m 950s,b	935w 970-956s,b	** Bands due to HSO <sub>4</sub> SO <sub>3</sub> sym.str.
855s,b 827m,b,sh	846s	855vs 790w,b		717w,b		840m,b 780vb	836s,b 703mb	840w,b 720w,vb	833w,b	NH <sub>3</sub> rock
		597s 575vs	599m,sh 578s	533sh 525s	533sh 525s	564s,sh,b 564s,sh,b 531s	605s 578w 515s	633vs 621vs	632s 591w 588w	SO <sub>3</sub> asym.bend SO <sub>3</sub> sym.bend
504v,s.	501s	504w 486vw	505v,w	481w	481w	500s,sh,b		553s 518s 513s	481w	Co-N str.
479s,sh	478m,sh 463s	452s 413w	450w 413w	429v,w,b		461vw		492m 461m 431m 423m		
423s,b 330s,b		356s				437vw 421w		405w,vb		
317s,b 297v,s,v 294v,s,b		308v,s,b				386m,b 373m,vb 331v,s,vb 306s,b		379w,vb 331s,vb 306s,vb		
270s,b		294v,s,b 286v,s,b 276s,b				286s,b				
						270s,v,b.				



Table II

Infrared absorption maxima (in  $\text{cm}^{-1}$ ) of sodiumdisulphito tetracyano cobaltate(III) dodecahydrate and cis-chloroquo tetrammine cobalt(III) sulphate.

$\text{Na}_5 [\text{Co}(\text{CN})_4 (\text{SO}_3)_2] \cdot 12\text{H}_2\text{O}$	Assignments	$\text{Cis} [ (\text{Co}(\text{NH}_3)_4 \text{H}_2\text{OCl} ] \text{SO}_4$	Assignments
Nujol mull	KBr pellet	KBr pellet	
3550vs	3550s	3255s	H-H str.
3200m, sh, b		3150s	
2900*s	2125vs		
2100vs	2125vs		
1602s	1610m	1630s, b	$\text{OH}_2$ scissors
		1610s	$\text{NH}_3$ deg.def
1450*s		1562sh	
1375*s		1385m	$\text{NH}_3$ sym.def.
		1334s	
1118vs	1120vs	1134vs	Bands due to $\text{SO}_4$
1100s, sh		1100vs, vb	
1063vs, b	1063vs	1093vs, b	( $\nu_3$ a, $\nu_3$ b, $\nu_3$ c)
		1043vs	
960vs, b	966vs, b	924s	$\text{SO}_4^{2-} (\nu_1)$
		888w, vb	$\text{H}_2\text{O}$ rock
		840w	$\text{NH}_3$ rock
635vs	623vs	629vs	$\text{H}_2\text{O}$ wagg.
568s, sh	543s	610vs	$\nu_4$ of $\text{SO}_4^{2-}$
535s	532s		
521vs	518s	516w	Co-N str.
		478w	
		448m, b	
		438m	



Table III

Infrared absorption maxima (in  $\text{cm}^{-1}$ ) of carbonate and oxalato tetrammine cobalt(III) complexes.

Cis- $[\text{Co}(\text{NH}_3)_4\text{CO}_3]$	$\text{NO}_3$	Assignments	Cis- $[\text{Co}(\text{NH}_3)_4\text{C}_2\text{O}_4]$	Cl	Assignments
KBr pellet			Nujol mull	KBr pellet	
3250s	)	$\text{NH}_3$ antisymm. &	3300s	3255s	$\text{NH}_3$ str.
3190s	)	symm.str.	3100s, b	3100s	
3130s	)		2900*s		
1595v.s.		C=O symm.str. overlapped by $\text{NH}_3$ deg.def.	1650s, b	1600v.s ) 1560m, sh )	v (C=O) ) $\text{NH}_3$ deg.def. )
1380v.s.		v <sub>3</sub> of $\text{NO}_3$	1448*s	1403v.s.	
1320sh		$\text{NH}_3$ symm.def	1380*s	1375sh	v (C-O) + v (C-C)
1278vs		v (C-O) + $\delta$ (OCO II)	1365sh		$\text{NH}_3$ symm.def.
850b, sh		$\text{NH}_3$ rock.	1310w, sh 1302m.	1313vs	
832vs		v 2 of $\text{NO}_3$	1270m, sh	1280m, sh	
763s		Ring def. + v(CO-O)	1253s	1266vs	v (C-O)
667s, b		$\delta$ (O(CO)O) ) CO <sub>2</sub> + v(C-O) ) symm. + v(CO-O) ) bend.	1015w, b		+ $\delta$ (CO-O)
495s		Co-N str.	861m, b	862w, b	$\text{NH}_3$ rock.
433m, b		v(CO-O) Nujol peaks	845s, b	843s, b	
			795s	794s	Ring def. v(CO-O)
			723w, b	720w, vb 656vw.	
				582m ) 552vs ) 524w, b ) 490s ) 488s ) 444s )	v (Co-O) + v(C-C) Co-N stretch.

Table IV

Infrared absorption maxima (in  $\text{cm}^{-1}$ ) of Dichloroquo trisamine chromium(III) chloride-red violet and grey forms and trans-dichloroquo trisamine cobalt(III) chloride.

[ $\text{Cr}(\text{NH}_3)_3\text{H}_2\text{OCl}_2$ ] Cl		[ $\text{Co}(\text{NH}_3)_3\text{H}_2\text{OCl}_2$ ] Cl		Assignment
Red-violet isomer		Grey isomer		
Nujol Mull	KBr pellet	Nujol mull	KBr pellet	Nujol mull
3275s	3260s	3300s	3245s	3230s, b
3200s	3200s	3225s	3180s	
2875*s	3115s	3180s	3135s	2950*s
1575s	1600s	2900*s	1652sh	1600s
1435*s		1620s	1600s	1455*s
1355*s		1450*s	1418sh	1370*s
		1400w		
		1370*s		
		1300s, sh		
1267s	1286s	1285s	1284vs	1288s
1012w		1266s		
671mb	654wb	1016w	722s, b	1016
662mb		725s, vb	654wb	818w, b
485m	481s	526vs, vb	478s, b	743w, vb
	444wb		446wb	517m, vb
377vw		377v wb	417wb	431w, vb
348vs, b		330w		365vs, b
317wb		317wb		346vw
306wb		305wb		305vs, vb

\*Nujol peaks

Sym. & Antisym.  
Str. of  $\text{NH}_3$  &  $\text{H}_2\text{O}$  $\text{NH}_3$  deg. def. &  $\text{OH}_2$   
scissor $\text{NH}_3$  symm.def. $\text{NH}_3$  rock and  $\text{OH}_2$   
wag.M-N str.  
M-O str.M-Cl str.  
N-M-N def.

O-M-N def.

REFERENCES

1. Werner, A., "New Ideas on Inorganic Chemistry" Longmans Green and Company, London, (1911).
2. Sidgwick, N.V., "Electronic Theory of Valency", Clarendon Press, Oxford, (1927).
3. Pauling, L., "Nature of Chemical Bond", 3rd Edition, Cornell University Press, (1960).
4. Orgel, L.E., "Transition-Metal Chemistry - Ligand Field Theory", John Wiley and Sons, New York, (1960)
5. Herzberg, G., Molecular Spectra and Molecular Structure II, "The Infrared and Raman spectra of Polyatomic Molecules", D. Van Nostrand Company, New York, (1949).
6. Lawson, K.E., "Infrared absorption of Inorganic substances", Reinhold Publishing Co. New York, (1961).
7. Bellamy, L.J., "The Infrared spectra of Complex Molecules", 2nd Edition, Methuen, London, (1958).
8. Miller, F.A. and Wilkins, C.H., Anal.Chem., 24 (1952), 1253.
9. Miller, F.A., Carlson, G.L., Bentley, F.F. and Jones, W.H., Spectrochim.Acta, 16 (1960), 135.
10. Ferraro, J.R., J.Chem.Ed., 38 (1961), 201.
11. Willis, J.B., Rev. Pure Appl.Chem., 8 (1958), 101.
12. Cotton, F.A., "Modern Co-ordination Chemistry", Edited by Lewis, J. and Wilkins, R.G., Interscience (1960).
13. Martell, A.E. and Calvin, M., "Chemistry of chelate Compounds", Prentice-Hall, Inc., New York (1952).
14. Grinberg, A.A., "Einführung in die chemie der komplex verbindungen" Verlag Technik, Berlin (1955).
15. Basolo, F. and Pearson, R.G., "Mechanisms of Inorganic Reactions", John Wiley and Sons (1958).

16. Bailer, J.C., "Chemistry of Co-ordination Compounds" Reinhold Publishing Corp. (1956).
17. Bjerrum, J., Schwarzenback, G. and Sillen, L.G. "Stability Constants" Vol. I, Organic Ligands; Vol II Inorganic Ligands, Chem.Soc., London, Special Pub., No.7 (1958)
18. Yatsimirsku, K.B. and Vasilov, V.P., "Instability Constants of Complex Compounds", Pergamon Press, New York (1960).
19. Rossotti, F.J.C. and Rossotti, H.C., "The determination of stability constants, McGraw-Hill, New York (1961).
20. Bailer, J.C., Jr., "Stereochemistry of Complex Inorganic Compounds", Chem.Revs., 19 (1936), 67.
21. Keller, R.W., "Co-ordination Compounds of Olefins with metallic salts", Chem.Revs., 28 (1941), 229.
22. Mellor, D.P. "Stereochemistry of square Complexes", Chem.Revs., 33 (1943), 137.
23. Bjerrum, J., "Tendency of metal ions towards Complex formation", Chem.Revs., 46 (1950), 381.
24. Taube, H., "Reactivity of metal Complexes", Chem.Revs., 50 (1952), 69.
25. Quagliano, J.V. and Schubert, L. "Trans effect in metal Complexes", Chem.Revs., 50 (1952), 201.
26. Basolo, F., "Stereochemistry and Reaction mechanisms of hexaco-ordinated Complexes", Chem.Revs., 52 (1953), 459.
27. Nyholm, R.S., "Stereochemistry and Valence states of Nickel", Chem.Revs., 53 (1953), 263.
28. Second International Conference on Co-ordination Chemistry, Danish Chem.Soc. (1953).
29. Third International Conference on Co-ordination Chemistry, Amsterdam, Rec.Travaux Chim.Pays-Bas. 75 (1955).

30. Fourth International Conference on Co-ordination Chemistry, Rome, J.Inorg.Nucl.Chem., 3 (1958), 1.
31. Fifth International Conference on Co-ordination Chemistry, London Special Pub.No.13, Chem.Soc. (1959).
32. Sixth International Conference on Co-ordination Chemistry, Detroit, McGraw-Hill (1961)  
(also Seventh and Eighth International Conference on Co-ordination Chemistry).
33. "Transition Metal Chemistry", Dublin, Faraday Soc.Disc.No.26 (1958).
34. "Electron transfer Reactions", New Castle, Faraday Soc.Disc., No.29 (1960).
35. Feigl, F., Anal.Chem., 21 (1949), 1298.
36. Tshugaeff, L., Z.anorg.Chem., 46 (1905), 144.
37. Godycki, L.E. and Rundle, R., Acta.Cryst., 6 (1953), 487.
38. Williams, D.E., Wohlauer, G. and Rundle, R.E. J.Amer.Chem.Soc., 81 (1959), 755.
39. Frasson, E., Panattoni, C. and Zannetti, R. Acta.Cryst. 12 (1959), 1027.
40. Frasson, E., Bardi, R. and Bezzi, S., Acta.Cryst., 12 (1959), 201.
41. Frasson, E. and Panattoni, C. Acta.Cryst., 13 (1960), 893.
42. Viswanathan, K.S. and Kunchur, N.R. Acta.Cryst., 14 (1961), 675.
43. Rundle, R.E. and Parasol, M., J.Chem.Phys., 20 (1952) 1487.
44. Fujita, J., Nakahara, A. and Tsuchida, R., J.Chem.Phys., 23 (1955), 1544.
45. Blinc, R. and Hadzi, D., J.Chem.Soc (1958), 4536.

46. Blinc, R. and Hadzi, D., Spectrochim. Acta, 16 (1960), 852.
47. Gillard, R.D. and Wilkinson, G., J. Chem. Soc. (1963) 6041.
48. Burger, K., Ruff, I. and Ruff, F.  
Jour. Inorg. Nucl. Chem., 27 (1965), 179.
49. Cambi, L. and Szeo, L., Ber. (1931), 2591.
50. Sugden, S., J. Chem. Soc., (1932), 246.
51. Fereday, R., Proc. Phys. Soc., London, 44 (1932), 274.
52. Willis, J.B. and Mellor, D.P.  
J. Amer. Chem. Soc., 69 (1947), 1237.
53. Brady, O.L., J. Chem. Soc., (1931), 105.
54. Merritt, L.L. and Schroeder, E., Acta Cryst., 2 (1956), 194.
55. Lumme, P.O. Suomen Kemistilehti, 30B (1957), 194.
56. Kahovec, L. and Kohrausch, <sup>K.W.F.</sup><sub>A</sub> Ber, 75B (1942), 1541.
57. Kahovec, L. and Kohrausch, <sup>K.W.F.</sup><sub>A</sub> Montash, 83 (1952), 614.
58. Hendricks, S.B., Wulf, O.R., Hilbert, G.E.  
and Liddel, U. J. Amer. Chem. Soc., 58 (1936) 1991.
59. Brady, O.L. and Dunn, F.P., J. Chem. Soc., (1914), 821.
60. Ishibishi, M. and Kishi, H., J. Chem. Soc., Japan,  
55 (1934), 1060.
61. Ishibishi, M. and Kishi, H. J. Chem. Soc. Japan,  
55 (1934), 1065.
62. Ligett, W.B. and Biefeld, L.P., Ind. Eng. Chem., Anal.  
Ed., 13 (1941), 813.
63. Biefeld, L.P. and Howe, D.E., Ind. Eng. Chem., Anal.  
Ed., 11 (1939), 251.
64. Ducret, L., Bull. Soc. Chim. (1946), 392.
65. Riley, H.L., J. Chem. Soc., (1933), 895.



66. Reif, W. and Mikrochemie, N.S., 3 (1931), 424.
67. Reif, W., Z.anal.Chem., 88 (1932), 38.
68. Stengel, F. Tech.Mitt.Krupp. Forsch., Ber. 2 (1939), 87.
69. Biefeld, L.P. Jour.Chem.Ed., 18 (1941), 525.
70. Kolthoff, I.M. and Lingane, J.J.  
"Polarographic Analysis and Voltammetry Amperometric titrations", Interscience, New York, (1941), 472.
71. Carruthers, C., Industrial and Eng.Chem.,  
Anal.Ed., 17(1945), 398.
72. Cihalik, J., Sunek, J. and Ruzicka, J.  
Chem.Listy, 51 (1957) 1663.
73. J. de Oliveira Meditsch, Chemist Analyst., 46 (1957),  
69.
74. Feigl, F. and Bondi, A., Ber., 64 (1931), 2819.
75. Ephraim, F., Ber., 64 (1931), 1210, 1215.
76. Flagg, J.F. and Furman, N.H.,  
Industrial and Eng-Chem., Anal.Ed., 12 (1940), 529.
77. Hieber, W, and Leutert, F., Ber., 62 (1929), 1839.
78. Brady, O.L. and Muers, M.M. J.Chem.Soc (1930), 1599.
79. Jarski, M.A. and Lingafelter, E.C.,  
Acta.Cryst., 17 (1964) 1139.
80. Merrit, L.L., Guare, C. and Lessor, A.E.  
Acta.Cryst., 2 (1956), 253.
81. Pfluger, C.E., Dissert.Abstr., 18 (1958), 1644.
82. Clark, H.C. and Odell, A.L., J.Chem.Soc.(1955), 3435.
83. Cox, E.G., Pinkard, F.W., Wardlaw, W. and Webster, K.C.,  
J.Chem.Soc.(1935), 459.
84. Malatesta, L. Gazz.Chim. ital., 68 (1938), 319.
85. Johnson J.E. and Hall, N.F.  
J.Amer.Chem.Soc., 70 (1948), 2344.

86. Willis, J.B. and Mellor, D.P.  
J.Amer.Chem.Soc., 69 (1947), 1237.
87. French, H.S. Magee, M.Z. and Sheffield, E.,  
J.Amer.Chem.Soc., 64 (1942), 1924.
88. Mellor and Craig, J.Proc.Roy.Soc., N.S.W.,  
74 (1940), 495.
89. West, B., Jour.Proc.Roy.Soc. N.S.W., 74 (1940), 475.
90. West, B., J.Chem.Soc., (1952), 3115.
91. Schweitzer, G.K. and Baum, P.B.  
J.Amer.Chem.Soc., 74 (1952), 6131.
92. Mashima, M., Nippon Kagaku Zasshi, 78 (1957), 1413.
93. Garner, C.S., Brookhaven Conf.Rept. BNL-C-8,  
Isotopic exchange reactions and chemical kinetics,  
No.2 (1948), 94.
94. Lumme, P.O., Suomen Kemistilehti 32B (1959), 203.
95. Fujii, S. and Sumitani, M., F.Ishikawa Anniversary Vol.  
I, Science Repts. Tohoku Univ., 37 (1953), 49.
96. Basolo, F. and Matoush, W.R.  
J.Amer.Chem.Soc., 75 (1953), 5663.
97. Clark, H.C. and Odell, A.L.  
J.Chem.Soc., (1955), 3431.
98. Kozo Sone, J.Amer.Chem.Soc., 75 (1953), 5207.
99. Maki, G., Jour.Chem.Phys., 29 (1958), 1129.
100. Rynasiewicz, J. and Elagg, J.F., Anal.Chem., 26  
(1954), 1506.
101. Lumme, P., Suomen Kemistilehti, 32B (1959), 261.
102. Pfeiffer, P., Angew.Chem., 53 (1940), 93.
103. Pokras, L. Jour.Chem.Edu., 33 (1956), 152, 223, 282.
104. Calvin, M. and Bailes, R.H. J.Amer.Chem.Soc., 68  
(1946), 949.
105. Mogan, G.T. and Smith, J.D.M., J.Chem.Soc., 127 (1925)  
2030.

106. Dent, G.B. and Linstead, R.P.  
J.Chem.Soc., (1934), 1027.
107. Mellor, D.P. and Maley, L., Nature, 159 (1947), 370.
108. Pfeiffer, P., Thickert, H. and Glaser, H.  
Jour.Prakt.Chem., 152 (1939), 145.
109. Van Uitert, Jour.Amer.Chem.Soc., 75 (1953),  
451, 455, 2736, 2739, 3577.
110. Ley, H. and Winkler, H., Ber., 42 (1909), 3894.  
42 (1912), 372.
111. Rosenheim, A. and Lehmann, F., Ann., 440 (1926), 153.
112. Marvel, C.S. and Tarkoy, N.,  
J.Amer.Chem.Soc., 79 (1957), 6000.
113. Terentev, A.P., Rode, V.V. and Rukhadze, E.G.,  
Vysokomol Soed., 5 (1963), 1658.
114. Rode, V.V., Candidate Thesis (Ph.D.Equivalent)  
Moscow State University, Moscow, 1961.
115. Chatt, J., Duncanson, L.A. and Venanzi, L.M.  
J.Chem.Soc. (1955), 4461.
116. Chatt, J., Duncanson, L.A. and Venanzi, L.M.  
Suomen Kem., (1956), 75.
117. Svatos, G.F., Curran, C. and Quagliano, J.V.  
J.Amer.Chem.Soc., 77 (1955), 6159.
118. Hill, D.G. and Rosenberg, A.F.,  
J.Chem.Phys., 22 (1954) 148.
119. Kobayashi, M. and Fujita, J.  
Jour.Chem.Phys., 23 (1955), 1354.
120. Faust, J.P. and Quagliano, J.V.,  
Jour.Amer.Chem.Soc., 76 (1954), 5346.
121. Duval, R., Duval, C. and Lecompte, J., C.R.  
Acad.Sci.Paris, 224 (1947), 1632.
122. Mizushima, S., Nakagawa, I. and Quagliano, J.V.,  
Jour.Chem.Phys., 23 (1955), 1367.
123. Nakagawa, I. and Mizushima, S., Bull.Chem.Soc., Japan,  
28 (1955), 589.

124. Powell, D.B. and Sheppard, N.  
J.Chem.Soc. (1956), 3108.
125. Barrow, G.M., Krueger, R.H. and Barolo, F.,  
Jour.Inorg.Nucl.Chem., 2 (1956), 340.
126. Powell, D.B.  
Chem. and Ind. (1956), 314.
127. Powell, D.B.  
J.Chem.Soc. (1950), 4495.
128. Fujita, J., Nakamoto, K. and Kobayashi, M.  
Jour.Amer.Chem.Soc., 78 (1956) 3963.
129. Svatoys, G.F., Sweeny, D.M., Mizushima, S.  
Curran, C. and Quagliano, J.V.  
Jour.Amer.Chem.Soc., 79 (1957) 3313.
130. Nakamoto, K., Fujita, J. Tanaka, S. and  
Kobayashi, M., Jour.Amer.Chem.Soc., 79 (1957), 4904.
131. Drouin, M., Mathieu, J.P. and Poulet, H.  
Jour.Chim.Phys., 58 (1961), 322.
132. Siebert, H., Z.anorg.U.allegem.Chem., 298 (1959), 51.
133. Duychaerts., J., Bull.Soc.Roy.Sci.Liege, 21 (1952)  
196.
134. Nakamoto, K., Margosches, M. and Rundle, R.E.,  
Jour.Amer.Chem.Soc., 77 (1956), 6480.
135. Sutton, L.E. and Taylor, T.W.J.  
J.Chem.Soc., (1931), 2190.
136. Pimental, G.V. and McClellan, A.L.  
"The Hydrogen bond", W.H. Freeman & Co.,  
San Francisco, Calif. (1960).
137. Hadzi, D. and Thompson, H.W., "Hydrogen bonding",  
Pergamon Press, New York, 1959.
138. Freedman, H.H., Jour.Amer.Chem.Soc., 83 (1961), 2900.
139. Hadzi, D., Trans.Farad.Soc., 52 (1956), 464.
140. Palm, A. and Werbin, H., Can.Jour.Chem., 31 (1953), 4536.
141. Vogel, A.I., "A text book of practical Organic  
Chemistry" including qualitative analysis, Longmans  
Green and Co. (1956), 958.

142. Beckmann, E., Ber., 26 (1893), 2621.
143. Ephraim, F., Ber., 63B (1930), 1928.
144. Vogel, A.I., "A Text book of quantitative inorganic analysis", Longmans, Green and Co., (1962), 498,526.
145. Hoyer, H., Montash, 90 (1959), 351.
146. Ramaswamy, K.K. and Sen, D.N.  
Indian J.Chem., 3 (11) (1965), 516.
147. Suito, E. and Sekido, E., Proc.Japan Acad., 33 (1957), 196.
148. Fanning, J.C. and Jonassen, H.B. Jour.Inorg.Nucl. Chem., 25 (1963), 29.
149. Palenik, G.J., Acta.Cryst., 17 (1964), 687.
150. Cox, E.G. and Webster, K.C., J.Chem.Soc. (1935), 731.
151. Reactions of Co-ordinated Ligands and Homogenous Catalysis, Advances in Chemistry Series 37, Amer.Chem. Soc. (1963).
152. Kuhn, R. and Staab, H.A., Ber., 87 (1954), 272.
153. Tiemann, F. and Lewy, L., Ber., 10 (1877), 2211.
154. Baker, W., Kirby, A.W.W. and Montgomery, L.V., J.Chem.Soc. (1932), 2876.
155. Brooks, C.J.W. and Morman, J.F.  
J.Chem.Soc. (1961), 3372.
156. Badilescu, S. and Badilescu, I.,  
Rev.Roum.de Chim., 10 (1965), 103.
157. Harowitz, E. and Perros, T.P.,  
Jour.Inorg.Nucl.Chem., 26 (1964), 139.
158. Wendlandt, W.W., Iftikar, Ali, S.I. and Stenbridge, C.H., Anal.Chim.Acta., 30 (1), (1964), 84.
159. Gopakumar, G. and Nair, P.M., Indian J.Chem., 2 (1964), 128.
160. Murray, A. and Williams, D.L.,  
"Organic Synthesis with Isotopes" (Part II)  
Interscience, New York, (1958), 1367.
161. Dean, F.M. and Robertson, A.,  
J.Chem.Soc. (1953), 1241.

162. Shimanouchi, T. and Nakagawa, I.  
Spectrochim. Acta, 18 (1962), 89.
163. Nakagawa, I. and Shimanouchi, T.,  
Spectrochim. Acta., 22 (1966), 759.
164. Shimura, Y. Bull. Chem. Soc. Japan, 25 (1952), 46.
165. Tanaka, N., Kamada, M., Fujita, J. and Kyuno, E.  
Bull. Chem. Soc. Japan, 37 (1964) 222.
166. Merrit, P. T. and Wiberley, S. E.  
Jour. Phys. Chem., 59 (1955), 55.
167. Palmer, W. G., "Experimental Inorganic  
Chemistry" (Cambridge) (1954).
168. Hoffmann, K. A. and Jenny, A., Ber., 34 (1901), 3855.
169. Bailer, J. C. and Peppard, D. F., Jour. Amer. Chem. Soc.,  
62 (1940), 105.
170. Rochow, E. G., Inorganic Syntheses, Vol. VI.  
McGraw-Hill, New York (1960);
171. Ray, P. R. and Chakraborty, S. C.  
J. anorg. allegem. Chem., 211 (1933), 173.
172. Bhatnagar, S. S., Prakash, B. and Hamid, A.  
J. Chem. Soc., (1938), 1428.
173. Tanito, Y., Saito, Y. and Kuroya, H.,  
Bull. Chem. Soc. Japan, 25 (1952), 328.

ACKNOWLEDGEMENT

I wish to express my deep sense of gratitude to Dr. D. N. Sen, Scientist, National Chemical Laboratory, for his guidance and supervision of the work reported here. It is a pleasure to record my thanks to Dr. C. I. Jose for his ungrudging help in running the infrared spectra of our samples and the group working with Dr. M. D. Karkhanwala at A.E.E.T. for thermogravimetric analysis. Thanks are also due to Dr. P. M. Nair for NMR spectral work, to Mr. J. S. Gujral for X-ray diffraction patterns and to the microanalytical group for the microanalytical data reported.

I am grateful to the Director, N.C.L. for his permission to submit the thesis and to the Council of Scientific and Industrial Research for the award of a Junior Research Fellowship.

July 18<sup>th</sup>, 1966.



CANDIDATE