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STUDIES ON BIS(N-ARYL SALICYLALDIMINATO)BERYLLIUM(II) AND N,N'-ETHYLENEBIS(SUBSTITUTED ACETOACETANILIDES)

A THESIS SUBMITTED TO
THE UNIVERSITY OF POONA FOR THE DEGREE
OF MASTER OF SCIENCE IN CHEMISTRY
(PARTLY BY PAPERS AND PARTLY BY RESEARCH)

MRS.K.K. DESHMUKH
NATIONAL CHEMICAL LABORATORY, POONA-8
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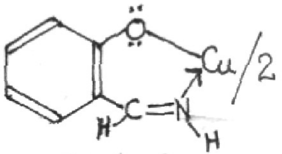
CHAPTER - I

GENERAL INTRODUCTION

Metal complexes of Schiff bases have played a significant role in the development of co-ordination chemistry. This fact is well documented by the large number of publications, ranging from purely synthetic to modern physicochemically and biochemically relevant studies of these complexes. A tremendous variety of stable compounds have been synthesized containing transition and nontransition metals, and multifarious such ligand systems. Many of these complexes are only of incidental importance in modern coordination chemistry. However, a good number of group of complexes, defined by the basic structure of their ligand systems have assumed considerable significance. The important among them are the complexes of salicylaldimines, β-ketoamines and closely related ligand systems containing O and N donor atoms. Especially, the complexes of salicylaldimines have been intensively investigated in the last thirty years and in many cases, their stereochemistry, electronic structure and many related properties are reasonably well understood. A number of reviews[1-10] have been published concerning salicylaldimines and β-ketoamines and their metal complexes, the most comprehensive being those published by Holm and coworkers[4,8].

Schiff bases are compounds which contain the azomethine group (-RC=N-) and are usually formed by the condensation of a primary amine with aldehyde or ketone. A five or six membered chelate is formed if a second group such as phenolic OH is attached ortho to azomethine group. The formation of chelate ring seems essential for the production of a stable complex with ligands containing the >C=N- group.

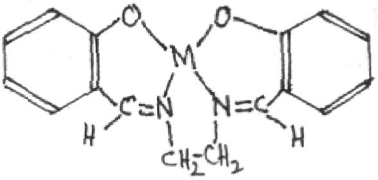
Metal complexes of Schiff's bases[11,12] have been known for over a hundred years. For instance, as early as in 1840 Ettling[13] had isolated bis(salicylaldiminato)copper(II), a dark green crystalline product, (I), from the reaction of cupric acetate, salicylaldehyde and aqueous ammonia.



(I)

Schiff[14] (1869) prepared compounds similar to (I) by substituting the amine H- with phenyl and aryl derivatives. Schiff discovered the exceedingly important synthetic technique of preparing salicylaldimine complexes by the reaction of the preformed metal salicylaldehyde compounds with primary amines. Delepine[15] (1899) prepared the complexes similar to (I) using N-methyl and N-benzyl-salicylaldimine in situ.

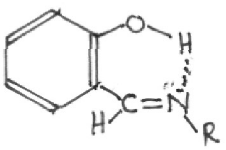
After a period of relative inactivity, Dubsky and Sokol[16] isolated N,N'-bis(salicylidene)ethylenediaminoCu(II) and Ni(II) and correctly formulated their structure (II).



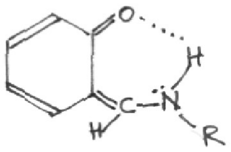
(II)

Pfeiffer and coworkers carried out ~~the~~ a systematic study of Schiff bases derived from salicylaldehyde and its substitution products, o-aminobenzaldehyde and pyrrole-2-aldehyde~~,~~ and published a series of papers[17-29].

The complexes of salicylaldimine skeleton are intensively studied. The nmr studies of these ligands show that they exist in phenolimine form[30,31]~~,~~ (IIIA) and not in keto-form (IIIB).



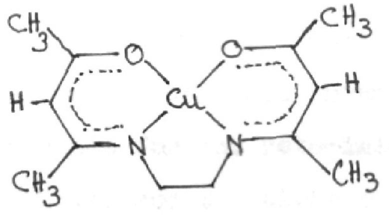
(III A) Enol form



(IIIB) Keto form

The hydrogen from phenolic OH being easily replaced by metal ions, the complexes of these ligands are comparatively easily formed. The particular advantage of the basic salicylaldimine ligand system has been the considerable flexibility of the synthetic procedure which has allowed the preparation of a variety of complexes with a given metal whose properties are often strongly dependent on the detailed ligand structure. It has been possible to affect certain stereochemical and electronic changes which can be examined in a graded series of complexes whose properties have been more or less systematically altered by structural variation of the ligand. It is this feature of these complexes which has been principally responsible for their detailed studies.

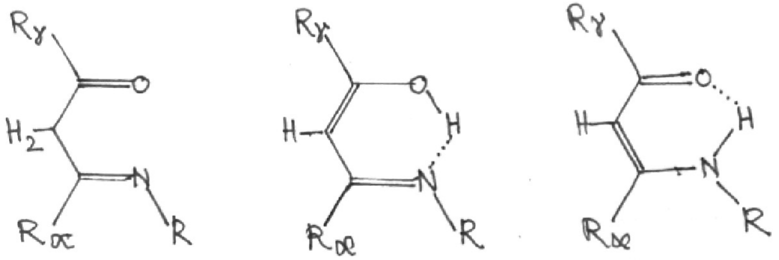
The first β-ketoamine complex was prepared by Combes[32](1889) who isolated the remarkably stable copper complex of N,N'-bis(acetylacetone)ethylenediamine (IV).



(IV)

Later, Morgan and Main-Smith[33,34] obtained a variety of analogous complexes. At that time these complexes were thought to be the complexes of Schiff base derived from acetylacetone and ethylenediamine. But the recent pmr studies[35] have proved that the free ligand exists in the β-ketoamine (VC) and not in enolimine form (VB).

The interest in the condensation products of β-diketones and primary amines is due to the possibility of the three distinct tautomeric forms.

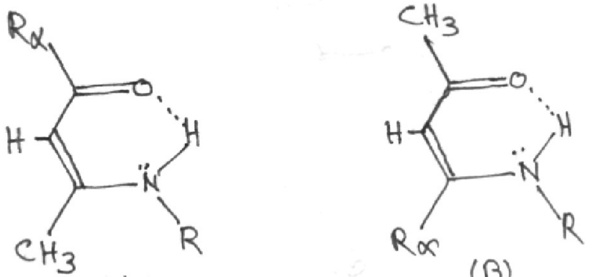


(A) (B) (C)

(V)

The tautomeric equilibria in solution has been studied by a number of physical methods including infrared[36-41], ultraviolet[38,42 pectroscopy, acidity constant measurements[42,43] and molar efraction measurements[37]. Kinetics and mechanism of hydrolysis[44] f the condensates of β-diketones with diamines have shown that hese compounds are hydrolytically more resistant than the Schiff ases of salicylaldehyde which are known to exist in the phenolimine orm[45,46]. No evidence for the keto-imine form (VA) was obtained n any of these studies and the clear evidence for the ketoamine (VC) orm has come only from the pmr studies[35,46-49].

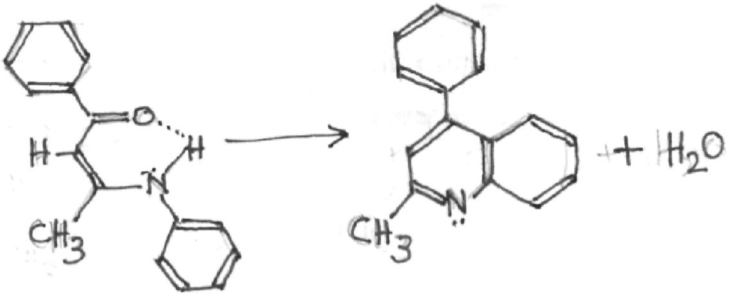
In addition to the tautomeric structures, the question of asic molecular structure arises in the case of condensation roducts of amines with unsymmetrical β-diketones which gives rise o the two possible structures (VI).



(A) (B)

(VI)

As early as 1887 Beyer[50] assigned structure (VIA) to the nilino derivative of benzoylacetone on the basis that it can ondense upon itself to form γ-phenylquinaldine as shown by the eaction.



Claisen[51] supported Beyer's assignment and gave further proof that the amine attack always occurs at the acetyl carbon. McCarthy and Martell[52] assigned the structure (VIB) to the condensation product of benzoylacetone with diamines on the basis of the dipole moment studies. Ueno and Martell[53] supported VIB structure for the reaction product of benzoylacetone and ethylenediamine on the basis of ultraviolet spectral studies. However, subsequently, Hovey and Martell[54] found evidence in favour of structure VIA as a result of dipole moment studies of similar compounds having polar groups on phenyl ring. Further work by these authors on Cu(II) and Ni(II) complexes of these ligands[55] also supported VIA structure. But the unequivocal establishment of structure VIA for the condensates of benzoylacetone with primary amines has come from pmr studies of ^{15}N-methylamine condensate by Dudek and Dudek[49]. This VIA structure is further supported by the dipole moment studies of the condensates of trifluoroacetylacetone with diamines[52,54]. The pmr spectrum of the methylamine condensate with formylacetone shows evidence[48] in favour of structure VIB. Preliminary X-ray[56] results for Cu(II) and Ni(II) bis-complexes with "3-amino-1-phenyl-2-butene-1-one" favour structure VIA, but only the heavy atoms were located.

The structure of β-ketoamines and their complexes has been a subject of several interesting studies. The complexes are not so easily formed as the very weakly acidic proton of β-ketoamines is not easily detached[57]. Compared to the salicylaldimine complexes, these complexes are less reported. Some of the β-ketoamine complexes, especially of the tetradentate ligands and Cu(II) and Ni(II) complexes of some bidentate ligands are easily formed[23,32,34,36,42,58-66]. In many other cases it became necessary to develop special synthetic procedure to overcome the hydrolytic instability of these complexes.

The direct reaction of amine with β-diketone complexes is usually unsuccessful as a preparatory method and in general no β-ketoamine complex is formed[67]. Several factors, no doubt, contribute to the stabilization of the β-diketone complexes towards nucleophil~~l~~ic attack by amines. The most important is probably the delocalization of the charge in the ligand~~,~~ with the steric hindrance due to substituents on the carbon atom next to oxygen providing the secondary contribution.

A nonaqueous chelation-reaction of the anhydrous metal salt and ligand in presence of a strong base was ~~is~~ developed by Collman and Kettleman[68] to prepare Cr(III) complexes of the type Cr(RAA)$_3$ [where R is an aromatic group; AA = $CH_3COCH{=}C(CH_3)N-$]. Everett and Holm[57] modified this procedure for preparing Ni(II) complexes of type Ni(RAA)$_2$ and Ni(RBA)$_2$ [where R is an aromatic or an aliphatic group and BA = $C_6H_5COCH{=}C(CH_3)N-$]. This general procedure requires the use of a strong base such as t-butoxide to remove the weakly acidic proton of the β-ketoamines and is useful in the preparation of hydrolytically unstable complexes derived from weakly acidic ligands. Ligand exchange reactions[61,69,70] have been reported for the preparation of complexes of the type M(RAA)$_2$, M(RBA)$_2$, M(RDBM)$_2$ (DBM = $C_6H_5COCH{=}C(C_6H_5)N-$] of Cu(II) and Ni(II), R being an aryl group. A few complexes of tetradentate ligands have also been prepared by this procedure. Template reactions, using tetrakis(ethylenediamine)-μ-dichloroNi(II)chloride as a template, are used to prepare Ni(II) complexes of tetradentate β-ketoamines and salicylaldimine complexes[71,72].

Recently, metal complexes of some tetradentate Schiff bases[5], viz. N,N'-ethylenebis(salicylaldimine) (salen) and bis(acetylacetone)ethylenediamine (bae) have been intensively studied, because of their unusual properties. Many penta- and hexa- coordinated cobalt derivatives have been prepared and investigated[73]. Because of the extra stability of the sigma Co-C bond and the overall physicochemical behaviour of such compounds,[74] they are studied as model molecules of Vitamin B_{12} group. Of particular interest are the transmethylation[75] reactions involving these complexes. The property of N,N'-ethylenebis-(salicylaldiminato)Co(II) [Co(salen)] to absorb molecular oxygen reversibly has been known for many years[11]. Recently, some oxygen adducts of formula $[Co(salen)]_2O_2L_2$[76a], $[Co(salen)](O_2)L$[76,77] and $Co(bae)(O_2)L$[78] [L = pyridine, dmf] have been reported. A review dealing with cobalt and iron complexes as inorganic oxygen carriers as models for biological system has recently been published[10].

Of all the metal complexes of Schiff bases studied, Ni(II) complexes have drawn wide attention as these complexes can exist in different structural forms[2]. A large number of copper and cobalt Schiff base complexes are reported and thoroughly studied as they can serve as biochemical models[5,10,73,74]. Iron complexes are also studied due to their biochemical importance but they are reported to a much lesser extent.

A casual survey of the literature shows that beryllium complexes of these ligands are very rarely studied[79-83]. This may be due to the belief that beryllium forms weak bond with ligands containing nitrogen as donor atom[84]. However, Martin and coworkers[85] have studied the stabilities of some β-ketoamine metal complexes and found that the stability of beryllium complexes is comparable to that of copper complexes.

In the following Chapter II of this thesis, beryllium complexes of some N-aryl salicylaldimines, isolated for the first time~~,~~ are reported. These compounds have been characterized by ir, nmr and mass spectral studies. Chapter III deals with the synthesis of eight β-ketoamines derived from acetoacetanilide and substituted acetoacetanilides by condensation with ethylenediamine. These ligands are reported for the first time along with their ir and nmr spectral studies. Our attempts to prepare metal chelates of these ligands according to the reported methods have been unsuccessful. But this does not necessarily mean that these compounds are not formed, since there have been many examples, for instance, the rare gases compounds which on theoretical and emperical grounds were believed at one time to be incapable of existence.

CHAPTER - II

STUDIES ON THE BERYLLIUM COMPLEXES OF BIDENTATE, TRIDENTATE AROMATIC SCHIFF BASES AND N,N'-ETHYLENE-BIS(SALICYLALDIMINE)

Abstract

Although bidentate, tridentate and tetradentate N-alkyl or N-aryl salicylaldimines have attracted much attention in recent years and many transition and non-transition metal complexes of such ligands have been studied, very little work, on the beryllium chelates of these ligands has been carried out. The present Chapter deals with the isolation of bis(N-salicylaldiminato)beryllium(II), bis(salicylaldoximinato)beryllium(II), bis(N-o-hydroxyphenylsalicylaldiminato)beryllium(II), mono(N-o-carboxyphenylsalicylaldiminato)beryllium(II)dihydrate and bis(N-p-aryl salicylaldiminato)beryllium(II) chelates (where p-aryl = p-tolyl, p-anisyl, p-chloro and p-nitrophenyl) and characterisation by their ir and pmr studies. The ir spectra of these ligands show a broad and weak band due to intramolecularly bonded phenolic -OH group at ~ 2700 cm^{-1} which was found to be absent in the beryllium chelates. In the ir spectra of bis(N-salicylaldiminato)beryllium(II), bis(salicylaldoximinato)-beryllium(II) and bis(N-o-hydroxyphenylsalicylaldiminato)beryllium(II), the broad medium intensity bands in the region 3300-2700 cm^{-1} are assigned to the intermolecularly bonded >NH and OH groups. The pmr spectra of these beryllium chelates also show signals due to bonded >NH or OH protons which disappeared on deuteration.

Part II of this Chapter deals with our attempts to isolate N,N'-ethylenebis(salicylaldiminato)beryllium(II) in 1:1 metal-ligand ratio.

Part I

Introduction

Schiff bases derived from the reaction of salicylaldehyde with primary aromatic amines represent a versatile series of ligands and the metal chelates of these ligands have attracted much attention[20,24,85-94]. Schiff bases prepared from ortho-hydroxy substituted aldehyde readily form chelates with metals like copper, nickel, cobalt, zinc, iron, vanadium, uranium and titanium which are similar to the type obtained from 8-quinolinol and its derivatives. In recent years, a number of reviews[1,2,4,6-10,95] have appeared on this subject. The problem of the structure of the Schiff bases and their metal chelates has been the subject of several studies using infrared and pmr techniques[45,96-104]. The live interest in the Schiff bases and their metal chelates is undoubtedly due to the structural diversity of the complexes, the impracticability of applying normal coordinate methods to the assignment problem and the complexity of the spectra resulting from the presence of phenyl vibrations.

Even though quite a few papers[91,102-111] are concerned with the studies on bidentate, tridentate and tetradentate N-alkyl or N-aryl salicylaldimines and their metal chelates with transition and non-transition metals, very meagre work on beryllium complexes of such ligands has been carried out. The limited number of beryllium complexes of Schiff bases studied are mostly derived from N-alkyl salicylaldimine[80-82] and N,N'-ethylenebis(salicylaldimine)[79,82] or similar schiff bases using long chain alkyl amines[82].

The work presented in this chapter deals with the synthesis of some beryllium complexes of bidentate and tridentate N-aryl salicylaldimines and the ir, pmr spectral studies of these complexes.

EXPERIMENTAL

Materials and Methods

Salicylaldehyde (Sarabhai Merck, LR grade) was distilled under reduced pressure. Aniline derivatives were purified by recrystallisation from alcohol. Aniline, p-toludine, p-anisidine, p-chloroaniline, p-nitroaniline, o-aminophenol and anthranilic acid were of C.P. grade. Beryllium nitrate, $Be(NO_3)_2 3H_2O$ and beryllium sulphate, $BeSO_4 4H_2O$ were of A.R. grade. The beryllium contents of these salts was determined by standard method[112].

Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 221 equipped with sodium chloride optics. The pmr spectra were recorded on a Varian Associates, Model T-60 spectrometer operating at 60 Mc/s with TMS as an internal standard. The mass spectra were recorded on CEC 21-110B (USA) double focussing mass spectrometer at a voltage of 70 eV.

Preparation of ligands

The ligands such as N-phenylsalicylaldimine, N-p-tolylsalicylaldimine, N-p-anisylsalicylaldimine, N-p-chlorophenyl- and N-p-nitrophenylsalicylaldimine, N-o-carboxyphenyl- and N-o-hydroxyphenylsalicylaldimine were prepared according to reported methods[80,96,124,148,149]. The general procedure for these preparations consisted of mixing of equimolar quantity of salicylaldehyde and the primary aromatic amines in ethanol or methanol. The product obtained was refluxed for some time on water bath, cooled and filtered. The precipitate was washed with cold alcohol and air dried. In some cases, the reactants on mixing immediately gave the schiff base precipitate. The schiff bases were recrystallized from alcohol. The yield varied between 50 to 90%. The elemental analysis and melting point of these ligands are given below.

1. N-phenylsalicylaldimine

Bright yellow crystalline solid, yield 70% ; m.p. 51°C; soluble in most of the common organic solvents. Anal.Found: C, 78.63; H, 5.78; N, 7.24%. Calculated for $C_{13}H_{11}NO$: C, 79.15; H, 5.62; N, 7.10%.

2. N-p-tolylsalicylaldimine

Yellow needles, yield ~ 80% ; m.p. 97°C; soluble in alcohol, acetone, chloroform and carbon tetrachloride. Anal.Found: C, 78.96; H, 6.38; N, 6.16%. Calculated for $C_{14}H_{13}NO$: C, 79.62; H, 6.20; N, 6.63%.

3. N-p-anisylsalicylaldimine

Grey-green shining platelets, yield > 80% ; m.p. 89°C; soluble in hot alcohol, acetone, chloroform and carbon tetrachloride. Anal.Found: C,73.63; H,6.02; N,6.23%. Calculated for $C_{14}H_{13}NO_2$: C,73.66; H,5.76; N,6.14%.

4. N-p-chlorophenylsalicylaldimine

Dull yellow crystalline solid, yield 90% ; m.p. 110°C; soluble in alcohol, acetone, sparingly soluble in chloroform and carbon tetrachloride. Anal.Found: C,67.19; H,4.67; N,6.00%. Calculated for $C_{13}H_{10}NOCl$: C,67.39; H,4.35; N,6.05%.

5. N-p-nitrophenylsalicylaldimine

Orange,crystalline solid, yield ~ 50% ; m.p. 163-4°C;

soluble in alcohol and acetone, less soluble in chloroform and carbon tetrachloride. Anal.Found: C,64.42; H,4.41; N,11.03%. Calculated for $C_{13}H_{10}N_2O_3$: C,64.46; H,4.16; N,11.57%.

6. N-o-carboxyphenylsalicylaldimine

Orange coloured shining crystals, yield ~ 60%; m.p. 212°C; soluble in alcohol and acetone. Anal.Found: C,69.21; H,4.50; N,5.97%. Calculated for $C_{14}H_{11}NO_3$: C,69.70; H,4.60; N,5.81%.

7. N-o-hydroxyphenylsalicylaldimine

Orange-red shining plate~~s~~lets, yield ~ 90%; m.p. 194°C; soluble in alcohol and acetone. Anal.Found: C,72.17; H,5.40; N,6.53%. Calculated for $C_{13}H_{11}NO_2$: C, 73.22; H,5.20; N,6.57%.

8. N-pyridylsalicylaldimine

Deep yellow solid, yield ~ 50%; m.p. 73°C; soluble in almost all common organic solvents. Anal.Found: C,73.66; H,5.06; N,13.97%. Calculated for $C_{12}H_{10}N_2O$: C,72.71; H,5.09; N,14.13%.

Preparation of beryllium chelates

General method of preparation

N-p-substituted aryl salicylaldimine (0.02 moles) was dissolved in ethanol or methanol and to the clear solution, an aqueous alcoholic beryllium nitrate solution (0.01 mole) was added. The resulting clear yellow solution was refluxed for about an hour on water bath and then the pH of the solution was adjusted to ~ 7 with dilute ammonia (1:1) and further refluxed. The precipitated yellow solid was filtered on cooling, washed with alcohol and air or vacuum dried. In an alternative method, instead of preformed ligands, the starting reactants were mixed in required quantities using freshly prepared beryllium hydroxide. In the preparation of N-p-chlorophenyl-and N-p-nitrophenyl-salicylaldimine beryllium chelates, the preformed ligands were dissolved in a few drops of acetic acid and diluted with aqueous alcohol. The clear solution of the ligand was then reacted with an aqueous solution of beryllium nitrate. The pH of the clear, yellow solution was adjusted to ~ 7 with dilute ammonia (1:1) and the resulting yellow precipitate was digested on water bath for one hour. The crystalline precipitate was filtered while hot, washed with cold alcohol till free of ligand and air or vacuum dried. Attempts to prepare beryllium chelate of N-pyridyl-salicylaldimine by above methods failed.

Most of the beryllium chelates were insoluble or sparingly soluble in common organic solvents and have high melting points.

1. Bis(N-phenylsalicylaldiminato)beryllium(II)

Yellow crystalline solid, yield 60%; m.p., 158°C. Soluble in carbon tetrachloride and alcohol. Anal.Found: C,78.17; H,5.58; N,7.19; Be 2.18%. Required for $Be(C_{13}H_{10}NO)_2$: C,77.81; H,5.02; N,7.02 and Be 2.25%.

2. Bis(N-p-tolylsalicylaldiminato)beryllium(II)

Yellow crystalline solid, yield ~ 60%; m.p., 242°C. Anal.Found: C,79.56; H,6.02; N,6.57; Be 2.18%. Required for $Be(C_{14}H_{12}NO)_2$: C,78.30; H,5.63; N,6.59; Be 2.09%.

3. **Bis(N-p-anisylsalicylaldiminato)beryllium(II)**

Light greenish yellow, crystalline solid; m.p., 180°C. Anal.Found: C,73.77; H,5.60; N,5.92; Be 2.03%. Required for $Be(C_{14}H_{12}NO_2)_2$: C,72.88; H,5.24; N,6.07; Be,1.95%.

4. **Bis(N-p-chlorophenylsalicylaldiminato)beryllium(II)**

Yellow crystalline solid; m.p. 260°C. Anal.Found: C,66.97; H,4.11; N,5.93; Be,1.88%. Required for Be $(C_{13}H_9NOCl)_2$: C,66.38; H,3.86; N,5.96; Be,1.92%.

5. **Bis(N-p-nitrophenylsalicylaldiminato)beryllium(II)**

Orange coloured crystalline compound; m.p. 320°C. Anal.Found: C,62.69; H,4.61; N,12.52; Be,1.68%. Required for $Be(C_{13}H_9N_2O_3)_2$: C, 63.54; H,3.69; N,11.40; Be,1.83%.

6. **Bis(N-o-hydroxyphenylsalicylaldiminato)beryllium(II)**

Yellow crystalline solid, m.p. 203-5°C. slightly soluble in chloroform. Anal.Found: C,71.50; H,4.8; N,6.72; Be,2.01%. Required for $Be(C_{13}H_{10}NO_2)_2$: C,72.06; H,4.65; N,6.47; Be,2.03%.

7. **Mono-(N-o-carboxyphenylsalicylaldiminato)beryllium(II) dihydrate.**

Greenish yellow crystalline solid, soluble in alcohol; m.p. > 350°C (with decomp.). Anal.Found: C,60.15; H,5.12; N,4.55; Be,3.13%. Required for $Be(C_{14}H_9NO_3).2H_2O$: C,59.15; H,4.66; N,4.93; Be,3.17%.

8. **Bis(salicylaldoximinato)beryllium(II)**

White, needle shaped, voluminous solid, m.p. 298°C with decomposition, soluble in alcohol, chloroform, carbon tetrachloride. Anal.Found: C,60.31; H,4.93; N,10.50; Be,3.15%. Required for $Be(C_7H_6NO_2)_2$: C,59.78; H,4.40; N,9.96; Be,3.21%.

9. Bis(N-salicylaldiminato)beryllium(II)

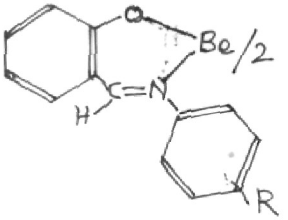
Pale yellow, crystalline solid, m.p. 250°C. Anal.Found: C,66.76; H,5.03; N,10.78; Be,3.53%. Required for $Be(C_7H_6NO)_2$: C,67.46; H,4.85; N,11.25; Be,3.62%.

Results and discussion

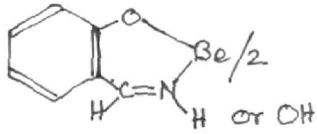
Beryllium forms a wide range of complexes in which it accepts a share in two extra lone pairs of electrons to form four tetrahedral sp^3 bonds. Beryllium cannot expand its coordination number to six due to the small size of the atom and inaccessibility of the 3d orbitals which are required for sp^3d^2 hybridization. Theoretically it should be possible for beryllium atom to form tetrahedral, trigonal planar and linear structures by employing sp^3, sp^2 and sp hybrid orbitals respectively. Although three and two coordinated beryllium compounds are known under special conditions, beryllium prefers four coordination. The beryllium complexes so far known such as $Be(acac)_2$, Be-oxyacid compound, and $[Be(NH_3)_4]Cl_2$ all are strictly four coordinated compounds[122, 150-152].

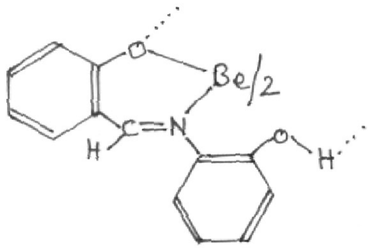
The Schiff bases studied here are found to form tetrahedral 1:2 metal-ligand complexes with beryllium. These compounds are yellow in colour and have high melting points, a few of them melt with decomposition. The solubility of these complexes in common organic solvents is quite low as expected, but most of them dissolve in DMSO to an appreciable extent. This has helped us to study their pmr spectra. Our attempts to synthesize N-salicylaldimine ligand by reported procedure[96] were a failure. However, bis(N-salicylaldiminato)beryllium(II) could be prepared by reacting bis(N-salicylaldehydo)beryllium(II) with ammonia in situ. All beryllium complexes reported here are prepared for the first time; this includes bis(salicylaldoximinato)Be(II).

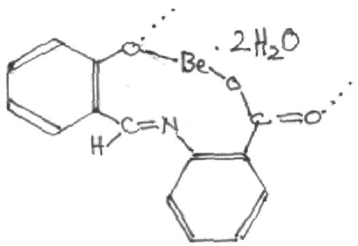
The infrared spectral data of the substituted N-aryl salicylaldimines and their beryllium chelates are presented in Fig.1-5 (Table 1-5) along with possible assignments. Reviewing the work carried out by several authors[2,41,45,89-93,102,111,123] on aromatic schiff bases, the probable structure of the beryllium chelate is shown below for bidentate and tridentate ligands.



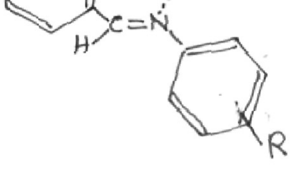
R = H, CH_3, OCH_3, Cl, NO_2.







In the ligands, it should be noted that an intramolecular hydrogen bond can form resulting in a stable six membered ring as shown below.



R = H, CH_3, OCH_3, Cl, NO_2, o-OH, o-COOH

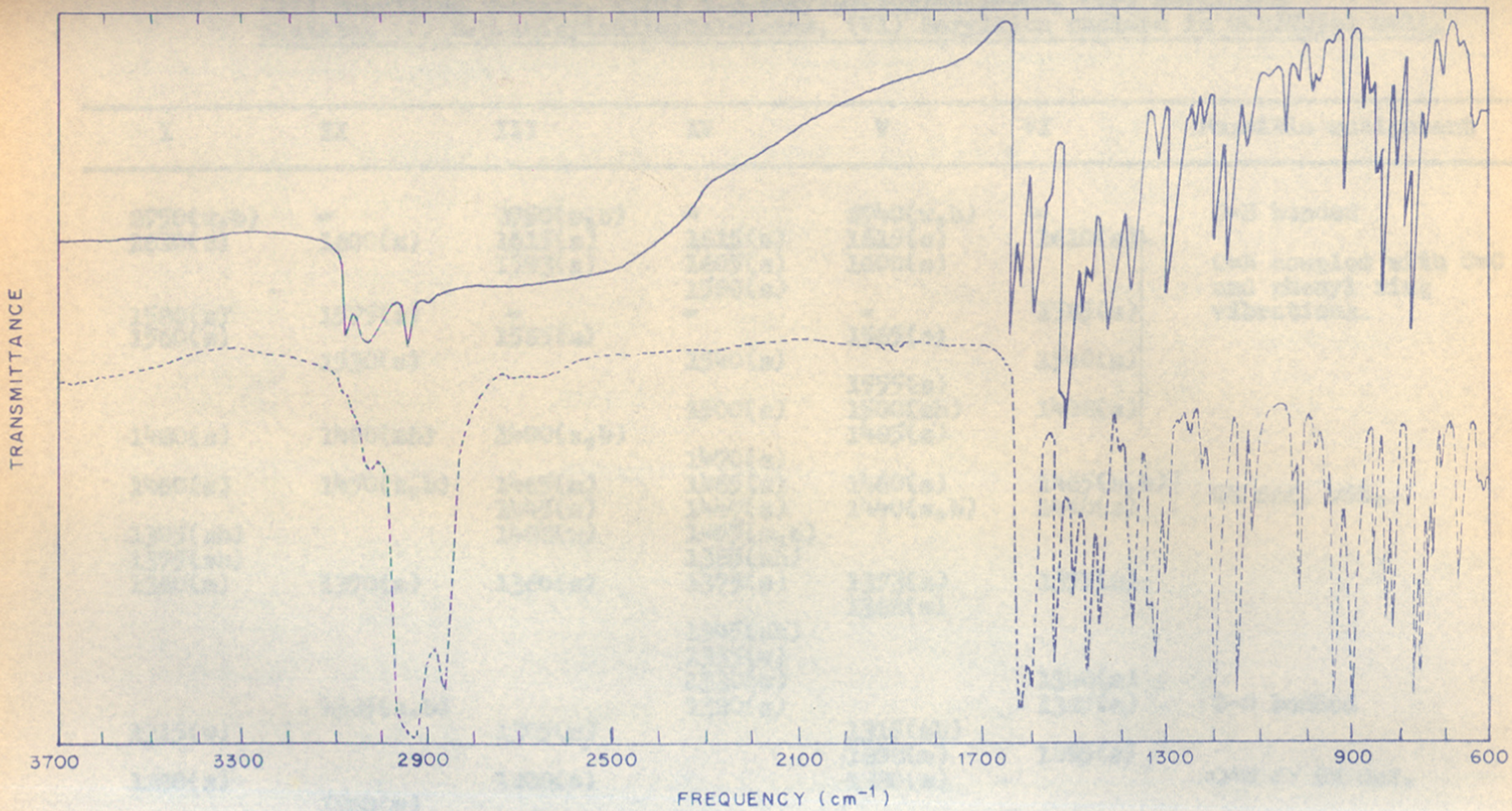


FIG. 1. INFRARED SPECTRA OF :
——— N-p-TOLYLSALICYLALDIMINE IN HCB / NUJOL MULL
------- BIS(N-p-TOLYLSALICYLALDIMINATO)BERYLLIUM (II)
IN NUJOL MULL

TABLE - I

Infrared absorption frequencies (cm^{-1}) of (I) N-phenylsalicylaldimine, (II) Beryllium chelate, (III) N-p-tolylsalicylaldimine, (IV) Beryllium chelate, (V) N-p-anisylsalicylaldimine, (VI) Beryllium chelate in HCB/Nujol mull.

I	II	III	IV	V	VI	Possible assignment
2750(w,b)	-	2750(w,b)	-	2740(w,b)	-	O-H bonded
1610(s)	1600(s)	1615(s)	1615(s)	1615(s)	1610(s)	
		1593(s)	1605(s)	1600(s)		C=N coupled with C=C
			1590(s)			and phenyl ring
1580(s)	1575(s)	-	-	-	1585(s)	vibrations.
1560(s)		1565(s)		1565(s)		
	1530(s)		1540(s)		1540(s)	
				1555(s)		
			1500(s)	1500(sh)	1498(s)	
1480(s)	1490(sh)	1490(s,b)		1485(s)		
			1470(s)			
1460(s)	1450(s,b)	1465(m)	1465(s)	1460(s)	1465(s,b)	CH def. vib.
		1445(m)	1447(s)	1440(s,b)	1440(s)	
1395(sh)		1408(w)	1405(m,b)			
1375(sh)			1385(sh)			
1360(m)	1370(s)	1360(s)	1375(s)	1373(s)	1375(s)	
				1368(w)		
			1345(sh)			
			1335(w)			
			1330(w)		1340(m)	
	1325(s.b)		1320(s)		1325(s)	C-O bonded
1315(w)		1305(m)		1315(sh)		
				1293(m)	1295(s)	
1280(s)		1280(s)		1280(s)		νC-O + δ OH def.
	1260(w)					
	1250(w)		1255(w)		1255(sh)	
				1245(s)	1243(s)	
1220(m)	1225(w)	1225(w)	1230(w)			
1185(s)	1185(s)	1190(s)	1190(s)	1185(s)	1195(s)	Aryl C-N strt.vib.
1170(m)					1168(m)	
1155(s)	1145(s)	1155(s)	1148(s)	1150(s)	1145(s)	Azomethine C-H vib.

I	II	III	IV	V	VI	Possible assignment
		1150(s)				
					1135(m)	
1120(m)	1125(m)	1116(m)	1123(s)	1110(s)	1110(m)	
1078(m)						
1036(m)	1025(m)	1030(m)	1035(w)	1030(s)	1025(s)	
			1028(m)			
			1020(s)			
	1000(sh)				1000(w)	
982(m)	980(sh)	980(m)	990(w)	982(s)	990(w)	
		978(w)	960(m)			
	940(s)		940(s)		945(s)	Be-O str.
925(s)				938(m)	935(s)	
905(m)	915(s)	910(s)	902(s)	910(s)	902(s)	
	890(s)					
				875(w)		
850(m)	860(w)	860(m)	856(s)	858(m)	852(m)	
		830(m)	825(s)	840(s)	840(m)	
					832(s)	
	818(w)	815(s)	815(s)	820(s)		
				810(m)	810(m)	C-H out of plane def.
780(s)	788(s)	785(m)	785(m)	785(m)	780(s)	
760(s,b)	760(s,b)	764(s)	765(s)	760(s)	755(s)	
		750(s)	755(s)	750(s)	750(s)	
740(sh)	730(w)	732(m)	740(m)	740(s)		
			730(m)		~~720(m)~~	
698(s,b)		700(w)	710(w)	720(m)	720(m)	
	685(w,b)		675(s,b)	660(w)	670(s,b)	

Table - 2

Infrared absorption frequencies (cm^{-1}) of (I) N-p-chlorophenyl-salicylaldimine, (II) Beryllium chelate, (III) N-p-nitrophenyl-salicylaldimine, (IV) Beryllium chelate in nujol mull.

I	II	III	IV	Possible assignment
1610(s)	1600(s)	1600(s)	1600(s)	C=N + C=C coupled vibrations.
		1590(s)		
1585(m)	1580(m)		1575(s)	
1560(m)		1560(m)		
	1540(s)			
			1525(s)	
1495(s)	1500(s)	1510(s)	1510(s)	N-O str.
		1480(m)		
1460(s)	1470(s)	1460(s)	1460(s)	
	1445(s)		1440(s)	
		1420(sh)		
1380(s)	1380(s)	1380(s)	1380(s)	
1360(m)				
	1345(s,b)			
		1340(s)	1340(s)	N-O str.
	1390(m)		1330(m)	C-O bonded
1310(w)	1310(m)	1300(sh)		
1280(s)		1280(s)		C-O + OH def.
1250(w)	1260(w)	1250(w)	1260(w)	
1238(w)	1230(w)	1230(w)	1238(w)	
1195(s)	1190(s)	1180(s)	1190(s)	Aryl C-N vib.
1180(s)				
1160(s)	1160(s)	1160(s)	1160(s)	Azomethine C-H vib.
1130(w)	1135(w)			
1100(s)	1100(s)	1120(s)	1120(s)	
1040(m)	1038(w)	1040(m)	1030(m)	
1020(m)	1018(m)			
	990(m)	990(m)	995(m)	
980(w)		980(m)		
975(m)		960(w)		
950(w)				
	945(m)		945(m)	Be-O str.
920(m)		920(m)		
	905(m,b)		905(w,b)	
		875(sh)	875(w)	
	865(w)	865(s)	860(w,b)	
850(s,b)	855(w)			
	840(m)	842(m)		
828(s,b)	820(sh)	820(m.b)		
790(m)		780(w)		
768(s,b)	770(s,b)	775(s,b)	760(s)	C-H out of plane
		745(w)		
	730(m.b)			
708(m)		695(m,b)	~~695(m,b)~~	

Table - 3

Infrared absorption frequencies (cm^{-1}) of (I) N-o-carboxyphenylsalicylaldimine, (II) Beryllium chelate, (III) N-o-hydroxyphenylsalicylaldimine, (IV) Beryllium chelate in HCB/Nujol mull.

I	II	III	IV	Possible assignment
	3380(m,b)			
			3100	O-H str.vib.
		2500(w,b)		
		1850(w,b)		
1670(m,b)				C=O str.
		1625(s)		
1612(s,b)	1600(s,b)		1605(s)	
		1610(sh)		
		1585(s)	1590(s)	
			1570(sh)	C=N coupled with
1560(s)				C=C str.vib.
	1540(s)		1545(s,b)	
		1520(s)		
1500(sh)				
		1480(m)	1490(sh)	
	1465(s)		1470(s,b)	
		1455(s)		C-H def.vib.
	1445(s)	1440(b,sh)	1440(s,b)	
		1400(m,b)		
1380(b,sh)			1375(s,b)	
1360(s)	1355(vs)	1360(s)		
1310(sh)		1300(s)		
	1302(s)		1295(s)	C-O bonded
1285(w)		1270(s)	1270(w)	C-O + O-H bending vib.
1240(s,b)	1230(s)	1240(s)	1240(m)	
		1220(s)	1210(m)	
	1190(s)			
1175(m,b)		1170(w,b)	1185(m)	Aryl C-N vib.
	1150(s)	1160(m)	1150(s)	Azomethine C-H vib.
	1122(s)	1135(s)	1125(m)	
		1115(m)	1100(m)	
		1100(sh)		
		1060(sh)		
1045(w)	1045(w)	1040(w)		
		1020(m)	1025(s)	
			995(m)	
940(w)	940(s)	940(w)	930(s)	Be-O str.
	885(m)			
870(w)	870(m)			
		850(w)	860(m)	
810(s,b)	810(w)	800(w)	800(m)	
	770(s)			
		765(s)		
752(vs)	752(s)		750(s,b)	C-H out of plane
		740(s)		
	720(w)	725(s)		
			710(w)	
700(s)			690(s)	

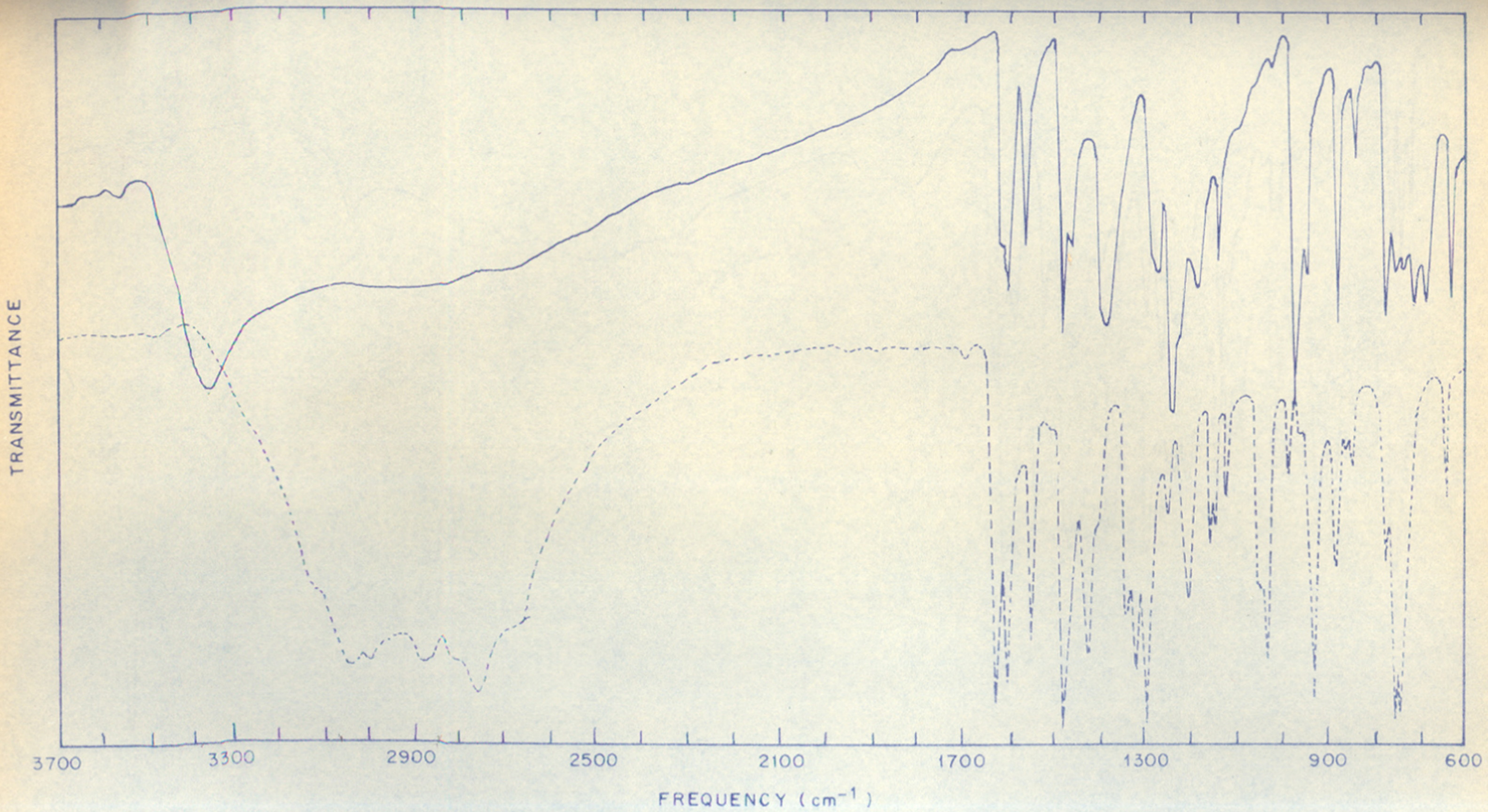


FIG. 2. INFRARED SPECTRA OF:

—— SALICYLALDOXIME

----- BIS(SALICYLALDOXIMINATO)BERYLLIUM(II)

IN HCB / NUJOL MULL

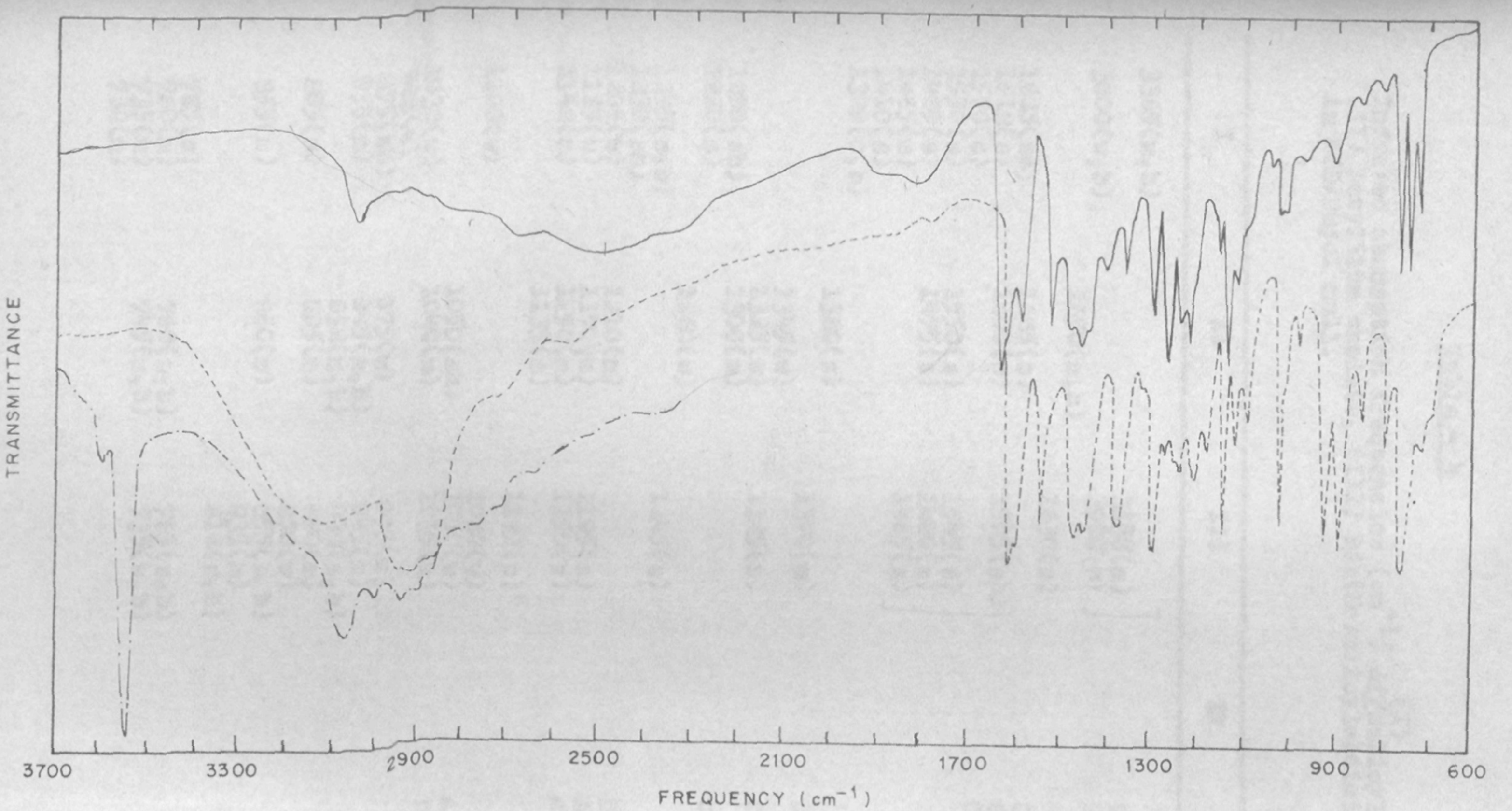


FIG. 3. INFRARED SPECTRA OF :

—— N-o-HYDROXYPHENYLSALICYLALDIMINE IN HCB / NUJOL MULL

-·-·- BIS(N-o-HYDROXYPHENYLSALICYLALDIMINATO)BERYLLIUM(II) IN NUJOL MULL

-··-··- N-o-HYDROXYPHENYLSALICYLALDIMINE IN CCl_4 SOLUTION (0·01 M)

Table - 4

Infrared absorption frequencies (cm^{-1}) of (I) Salicylaldoxime, (II) Beryllium chelate, (III) Bis(N-salicylaldiminato)beryllium(II) in HCB/Nujol mull.

I	II	III	~~IV~~	Possible assignment
3365(m,b)				
		3198(m)		O-H bonded
3000(w,b)		3095(m)		
	2650(m,b)			
		1630(s)		
1625(sh)	1625(s)			O-H def.vib.
1612(s)	1600(s)	1595(sh)		C=N coupled with
1570(s)				C=C str.vib.
1550(s)	1550(s)	1545(s)		
1485(s)	1475(s)	1480(s)		
1465(m)		1465(s)		
1410(s)				
1390(s,b)				
	1380(s)			
		1370(m)		O-H in plane bending
	1345(w)			
	1325(w)	1325(s)		C-O bonded
1290(sh)	1300(m)			
1280(s)				C-O + O-H bending vib
	1260(w)			
1245(s,b)		1245(s)		
1230(sh)				
1205(w)	1210(m)			N-O str.
1185(w)	1170(m)	1195(s)		Aryl C-N str.
1148(m)	1150(m)	1150(s)		Azomethine C-H vib.
	1135(m)			
		1122(s)		
1100(w)				
		1080(w)		
	1050(sh)	1050(w)		Aromatic C-H in
1030(w)	1040(m)	1035(m)		plane def.vib.
985(s)				
975(sh)	975(w)	975(w)		
955(m)	945(m,b)	945(m)		
	932(m,b)	930(s,b)		
895(s)	895(m)	890(m)		N-O str.
		870(w)		
855(m)	860(m)	855(s,b)		
		835(m)		
		818(s,b)		
785(s)				Aromatic C-H out
760(m)	760(m,b)	765(s,b)		of plane def.
735(m)	745(m,b)	735(s,b)		
720(m)				

Table - 5

Infrared absorption frequencies of (cm^{-1}) of C=N, C-O and O-H of N-aryl salicylaldimines along with their shift in beryllium chelates.

		C=N	Shift	C-O	O-H
1.	N-phenylsalicylaldimine	1610 1560		1280	2750
2.	Bis(N-phenylsalicylaldiminato)-beryllium(II)	1600 1530	10 30	1325	-
3.	N-p-tolysalicylaldimine	1615 1565		1280	2750
4.	Bis(N-p-tolysalicylaldiminato)-beryllium(II)	1615 1540	- 25	1320	-
5.	N-p-anisylsalicylaldimine	1615 1565		1280	2740
6.	Bis(N-p-anisylsalicylaldiminato)-beryllium(II)	1610 1540	5 25	1325	-
7.	N-p-chlorophenylsalicylaldimine	1610 1560		1280	
8.	Bis(N-p-chlorophenylsalicylaldiminato)beryllium(II)	1600 1540	10 20	1330	-
9.	N-p-nitrophenylsalicylaldimine	1600 1560		1280	
10.	Bis(N-p-nitrophenylsalcylaldiminato)-beryllium(II)	1600 1525	- 35	1300	
11.	N-o-hydroxyphenylsalicylaldimine	1625 1585		1270	2500 1850
12.	Bis(N-o-hydroxyphenylsalicylaldiminato)beryllium(II)	1605 1545	20 40	1295	3110

Table - 5 (contd.

		C=N	Shift	C-O	O-H
13.	N-o-carboxyphenylsalicylaldimine	1612 1560		1285	2950
14.	Mono(N-o-carboxyphenylsalicylaldiminato)beryllium(II)dihydrate	1600 1540	12 20	1302	3380
15.	Salicylaldoxime	1612 1570		1280	3365 3000
16.	Bis(salicylaldoximinato)-beryllium(II)	1600 1550	12 20	1300	2650
17.	Bis(N-salicylaldiminato)-beryllium(II)	1630 1545		1325	3020

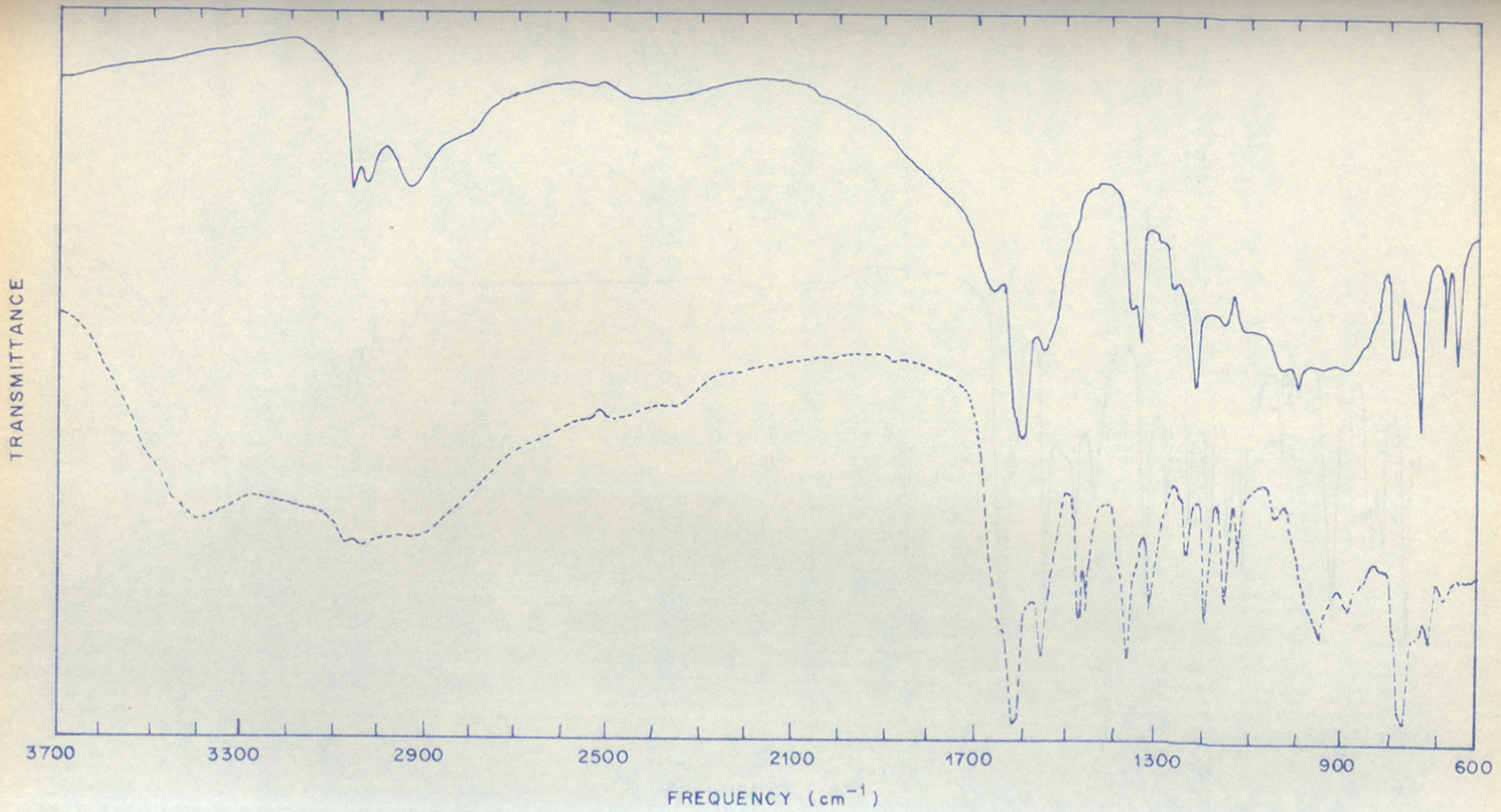


FIG. 4. INFRARED SPECTRA OF :

——— N-o-CARBOXYPHENYLSALICYLALDIMINE

-·-·-·- MONO(N-o-CARBOXYPHENYLSALICYLALDIMINATO)BERYLLIUM (II) DIHYDRATE

IN HCB / NUJOL MULL

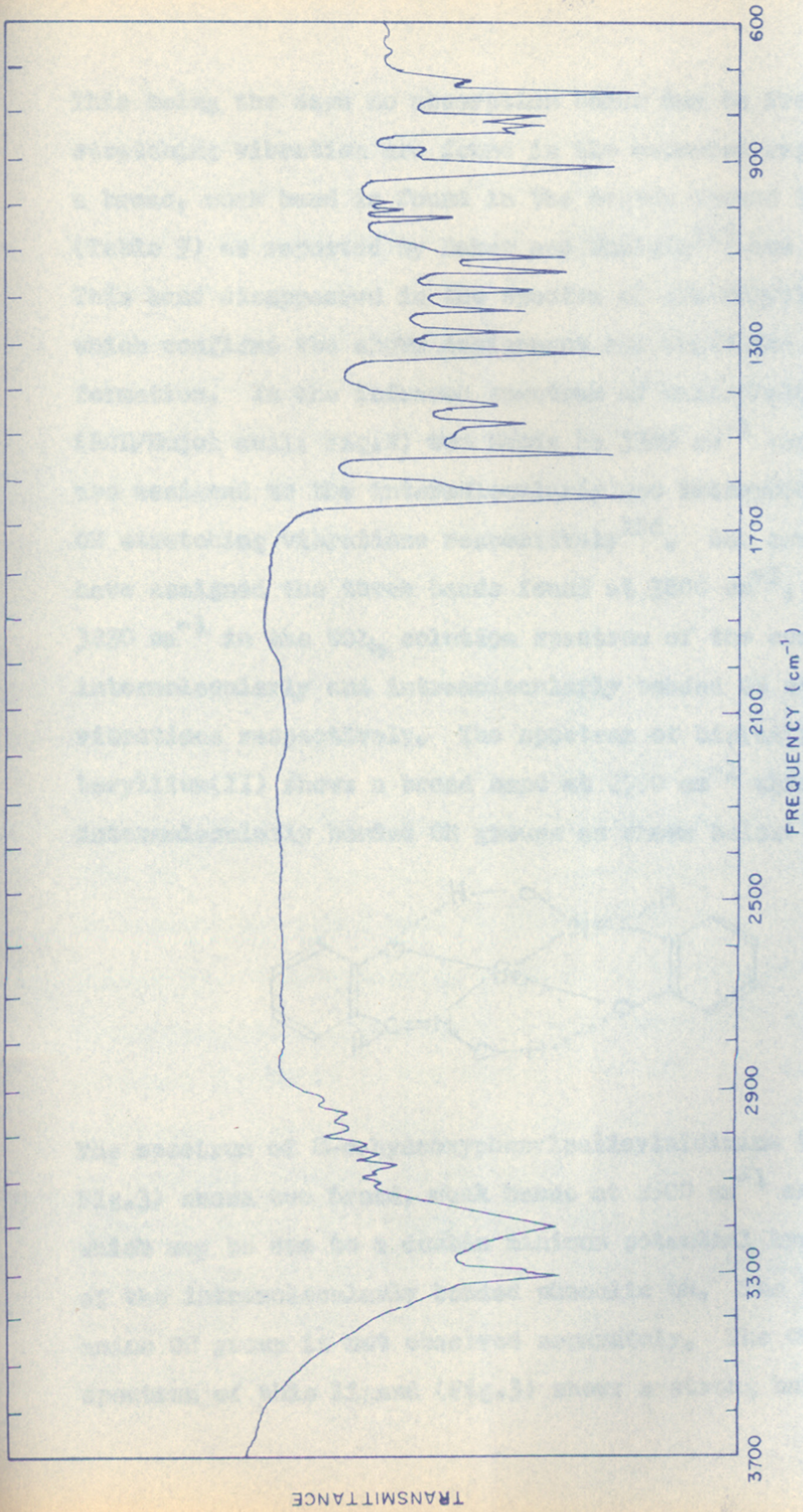
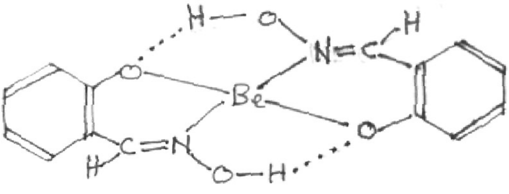
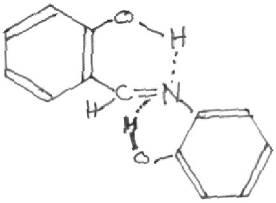


FIG. 5. INFRARED SPECTRUM OF : BIS(N-SALICYLALDIMINATO) BERYLLIUM (II) IN HCB / NUJOL MULL

This being the case no absorption bands due to free O-H stretching vibration are found in the expected region; instead a broad, weak band is found in the region around 2700 cm^{-1} (Table 5) as reported by Baker and Shulgin[113] and others[125]. This band disappeared in the spectra of all beryllium complexes which confirms the above assignment and indicates chelate formation. In the infrared spectrum of salicylaldoxime (HCB/Nujol mull, Fig.2) two bands at 3365 cm^{-1} and 3000 cm^{-1} are assigned to the intermolecularly and intramolecularly bonded OH stretching vibrations respectively[106]. Sen and coworkers[128] have assigned the three bands found at 3600 cm^{-1}, 3445 cm^{-1} and 3230 cm^{-1} in the CCl_4 solution spectrum of the compound to free, intermolecularly and intramolecularly bonded OH stretching vibrations respectively. The spectrum of bis(salicylaldoximinato)-beryllium(II) shows a broad band at 2750 cm^{-1} which is due to intermolecularly bonded OH groups as shown below:



The spectrum of N-o-hydroxyphenylsalicylaldimine (HCB/Nujol mull, Fig.3) shows two broad, weak bands at 2500 cm^{-1} and 1850 cm^{-1} which may be due to a double minimum potential hydrogen bond[127] of the intramolecularly bonded phenolic OH. The band due to amine OH group is not observed separately. The CCl_4 solution spectrum of this ligand (Fig.3) shows a strong band at 3540 cm^{-1}, associated with a weak band at 3590 cm^{-1}, and a second broad, medium intensity band at around 3000 cm^{-1}. The sharp strong band at 3540 cm^{-1} may be assigned to the O-H ... π interaction and the associated weak band at 3590 cm^{-1} to free OH stretching vibrations. The lower frequency band at ~ 3000 cm^{-1} is attributed to phenolic OH intramolecularly bonded to the nitrogen atom of the azomethine group. Such findings are reported by Baker and Shulgin[113] and they have assigned bands at 3546 cm^{-1} and 2730 cm^{-1} to O-H ... π and OH ... N intramolecular bonds respectively as shown in the figure for N-o-hydroxyphenylsalicylaldimine.



The existence of OH ... π bonds have also been reported by Oki and Iwamura[126]. These authors have assigned a band at 3566 cm^{-1} in the spectrum of 2-hydroxybiphenyl for O-H bonded to π electrons and a band at 3607 cm^{-1} to free OH stretching vibration. Very recently, Malek et al[103] have studied N-o-hydroxyphenylsalicylaldimine in halocarbon mull and DMSO and assigned the bands in the region 3500-2900 cm^{-1} to OH stretching vibration. These workers have assigned a band near 3500 cm^{-1} to phenolic OH bonded to nitrogen and the band at ~ 2900 cm^{-1} to amine OH bonded to π electrons. This appears to be contradictory to Baker and Shulgin[113] and our findings. The infrared spectrum of all other N-aryl salicylaldimines containing only phenolic OH group~~s~~ have shown only one broad, and weak band at ~ 2700 cm^{-1} which is due to intramolecular bonding. It is clear from above data that the π-bonded hydrogen bond exists as a weak bond and appears near 3600 cm^{-1} showing a little shift from free OH region. The similarity of N-o-hydroxyphenylsalicylaldimine and N-salicylaldimine to salicylaldoxime led us to expect intermolecularly bonded O-H or N-H groups in the beryllium complexes of these ligands. It is interesting to see a broad medium intensity band at 3110 cm^{-1} in the case of bis(N-o-hydroxyphenylsalicylaldiminato)beryllium(II) (Fig.3) and two weak and medium bands in bis(salicylaldiminato)-beryllium(II) (Fig.5) attributed to intermolecularly bonded OH and N-H groups respectively.

Assignment of characteristic νC=N, νC=C bands in the region of 1700-1500 cm^{-1} is difficult due to extensive vibrational coupling and the complexity of the spectra resulting from the presence of phenyl vibration and the two different metal-ligand bonds (M-O and M-N). In a nonconjugated system, νC=N normally appears in the 1690-1650 cm^{-1} region[114]; conjugation shifts it to lower frequency and it is usually found at ~ 1630 cm^{-1} for the schiff bases[98,115]. However, the reported ir spectra are generally restricted to the assignments νC=N, νC=C and νC-O bands[89-93,98,99]. Very recently ir study on ^{15}N-labelling has been reported [99,102] on the aryl Schiff bases in order to ascertain the C=N, C=C and C-O bands in these ligands and their metal chelates. Percy and Thornton[102] have found two ^{15}N-sensitive bands near 1600 cm^{-1} to occur in the spectrum of N-aryl salicylaldimines.[102] It was the higher frequency band that has been emperically assigned so far[98] to the νC=N. The lower frequency band that exhibit a greater ^{15}N-induced shift is found to be more vibrationally pure. Considering the above facts, these workers have assigned bands at 1627 cm^{-1} and 1579 cm^{-1} in N-p-anisylsalicylaldimine, 1625 cm^{-1} and 1579 cm^{-1} in N-phenylsalicylaldimine and 1613 cm^{-1} and 1573 cm^{-1} bands in N-p-chlorophenylsalicylaldimine to ν C=N frequency. Further, it was observed that the band at 1600 cm^{-1} shifts a little to lower frequency but the band at 1570 cm^{-1} shows considerable lowering (20-30 cm^{-1}) on complex formation. In the beryllium complexes we have found that these bands show shift as reported above and therefore can be assigned to C=N stretching vibration. Table 5 shows the bands assigned to C=N, C-O and O-H stretching vibrations along with their shifts on complex formation. The $\sim$1605 cm^{-1} ν C=N band occurs at higher frequency when electron donating groups such as CH_3, OCH_3, OH are attached at ortho or para position in the aniline ring and at a lower frequency when electron withdrawing groups such as chloro or nitro are attached at para position in the aniline ring. The second C=N band is found between 1560-1565 in all these ligands except in N-o-hydroxylphenylsalicylaldimine and salicylaldioxime where it occurs at 1585 cm^{-1} and 1570 cm^{-1} respectively[106]. The bands appearing in the region of 1500-1300 cm^{-1} in the ligands as well as in beryllium chelates are due to aromatic CH and =CH vibrations[45]. The characteristic strong band at 1280 cm^{-1} which is present in all the aromatic salicylaldimines is assigned to phenolic ν C-O + δ OH stretching vibration[45,102]. This band on complex formation with beryllium disappeared and a new band is found in the region of 1300-1325 cm^{-1} which is due to bonded phenolic C-O vibration. Another strong band at 1185-1190 cm^{-1} present in ligands as well as beryllium chelate may be assigned to aryl carbon-nitrogen stretching vibrations[116]. This band does not show any change even when a substituent is introduced in the p-position of aniline ring. The strong band at 1140 cm^{-1} present in both ligands and their metal chelates may be assigned to azomethine C-H stretching vibration[45,116].

The spectra in the region 1100 cm^{-1} and below is much more complicated due to the presence of phenyl ring, M-O and M-N vibrations. However, the band at 930-945 cm^{-1} in beryllium chelate is due to metal-ligand stretching[120,121] and bands in the region 800-750 are due to aromatic CH vibrations[45,89-93].

In order to get a clearer insight of these ligands, and their beryllium chelates the pmr spectral study has been carried out. The pmr spectra of these ligands and beryllium chelates are presented in Table 6 (Fig.6-12).

The strong intramolecular hydrogen bonding present in the ligands leads to very broad and weak hydroxyl absorption near 2700 cm^{-1} so that the pmr spectra are more informative than ir spectra with respect to the nature of O-H bonding. It has been shown by Dudek and Dudek[30] and Charette[31] that N-aryl salicylaldimines exists solely in the phenolimine form in non-hydroxylic solvents at normal temperatures. Any significant presence of the keto-amine form would split the signal arising from the azomethine proton. No splitting of this signal is observed in the pmr spectra of ligands studied here nor the aromatic proton signals displaced from its normal position. From these data it is assumed that the N-aryl salicylaldimines

Table - 6

The position of protons present in bidentate and tridentate Schiff bases and their beryllium chelate (ppm) δ

		CH	CH_3	OCH_3	OH	o.OH or NH	Ring
1.	Bis(salicylaldiminato)beryllium(II)	8.47	-	-	-	9.97	6.43 - 7.5
2.	N-phenylsalicylaldimine	8.42	-	-	12.9	-	6.60 - 7.40
3.	Bis(N-phenylsalicylaldiminato)-beryllium(II)	7.93	-	-	-	-	6.26 - 7.63
4.	N-p-tolylsalicylaldimine	8.44	2.34	-	12.1	-	6.70 - 7.50
5.	Bis(N-p-tolylsalicylaldiminato)-beryllium(II)	8.50	2.53	-	-	-	6.50 - 7.66
6.	N-p-anisylsalicylaldimine	8.58	-	3.80	13.20	-	6.65 - 7.50
7.	Bis(N-p-anisylsalicylaldiminato)-beryllium(II)	8.63		3.93	-	-	6.63 - 7.67
8.	N-p-chlorophenylsalicylaldimine	8.80	-	-	12.95	-	6.70 - 7.70
9.	Bis(N-p-chlorophenylsalicylaldiminato)beryllium(II)	8.60	-	-	-	-	6.57 - 7.66
10.	N-p-nitrophenylsalicylaldimine	9.20	-	-	12.84	-	7.00 - 8.65
11.	Bis(N-o-hydroxyphenylsalicylaldiminato)beryllium(II)	8.46	-	-	13.85	9.70	6.36 - 7.72
12.	N-o-carboxyphenylsalicylaldimine	8.93	-	-		5.33	6.86 - 8.30
13.	N-o-hydroxyphenylsalicylaldimine	8.9	-	-	13.35	8.30	6.70 -7.80

Table - 6 (contd.)

		CH	CH_3	OCH_3	OH	o.OH or NH	Ring
14.	(Mono-N-o-carboxyphenylsalicylaldiminato)beryllium(II) dihydrate	8.73	-	-	3.38 ($2H_2O$)	-	6.38 - 8.73
15.	Salicylaldoxime *	8.18	-	-	8.18	9.95 (oximic)	7.05
16.	Bis(salicylaldoximinato)-beryllium(II)	8.37	-	-	10.13	11.30	6.5 - 7.66

* Reported - High Resolution nmr spectra Catalog Vol. I, Varian Associates (1963).

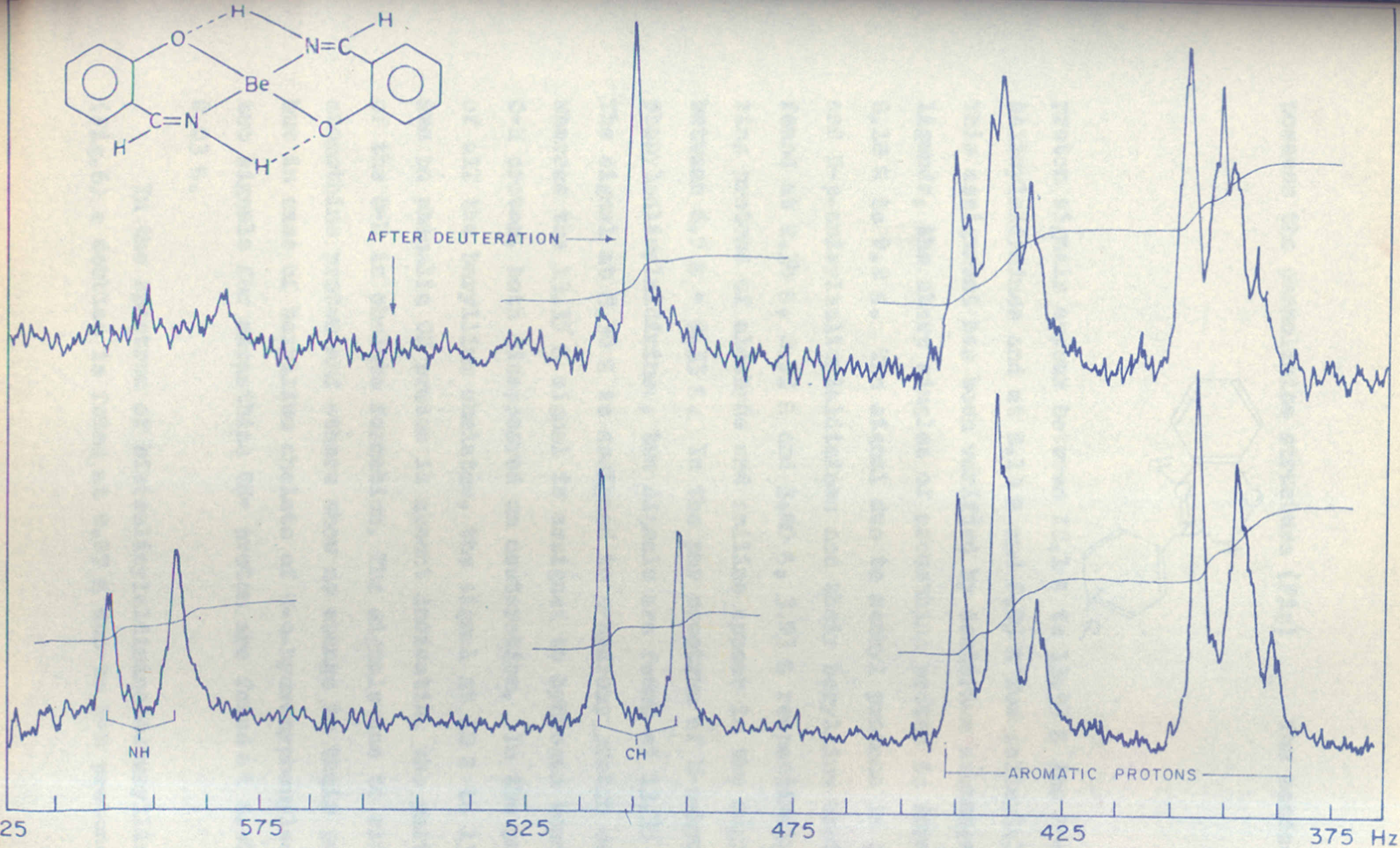
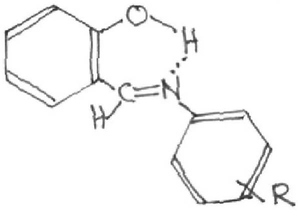


FIG. 6. PMR SPECTRUM OF BIS(N-SALICYLALDIMINATO)BERYLLIUM(II) IN DRY DMSO.

possess the phenolimine structure (Fig).). The bonded O-H



proton signals appear between 12.1 δ to 13.35 δ for N-aryl salicylaldimines and at 8.18 δ and 9.95 δ for salicylaldoxime[117]. This assignment has been verified by deuterium exchange. In ligands, the sharp singlet of azomethine proton is found between 8.18 δ to 9.2 δ. The signal due to methyl protons in N-p-tolyl and N-p-anisylsalicylaldimines and their beryllium chelate is found at 2.34 δ, 2.53 δ and 3.80 δ, 3.93 δ respectively. The ring protons of aldehyde and aniline appear in the region between 6.5 δ - 8.33 δ. In the pmr spectrum of N-o-hydroxyphenylsalicylaldimines, two signals are found at 13.35 δ and 8.30 δ. The signal at 8.30 δ is assigned to o-hydroxy proton of aniline, whereas the 13.35 δ signal is assigned to hydrogen bonded aldehyde O-H proton, both disappeared on deuteration. In the pmr spectra of all the beryllium chelates, the signal at 12 δ to 13.85 δ due to phenolic OH proton is absent indicating the participation of the O-H in chelate formation. The signals due to ring protons, azomethine proton and others show no change in their position, but in case of beryllium chelate of N-o-hydroxyphenylsalicylaldimine two signals for azomethine CH- proton are found at 8.40 δ and 9.03 δ.

In the spectrum of bis(salicylaldiminato)beryllium(II) (Fig.6) a doublet is found at 9.97 δ due to N-H protons. This is

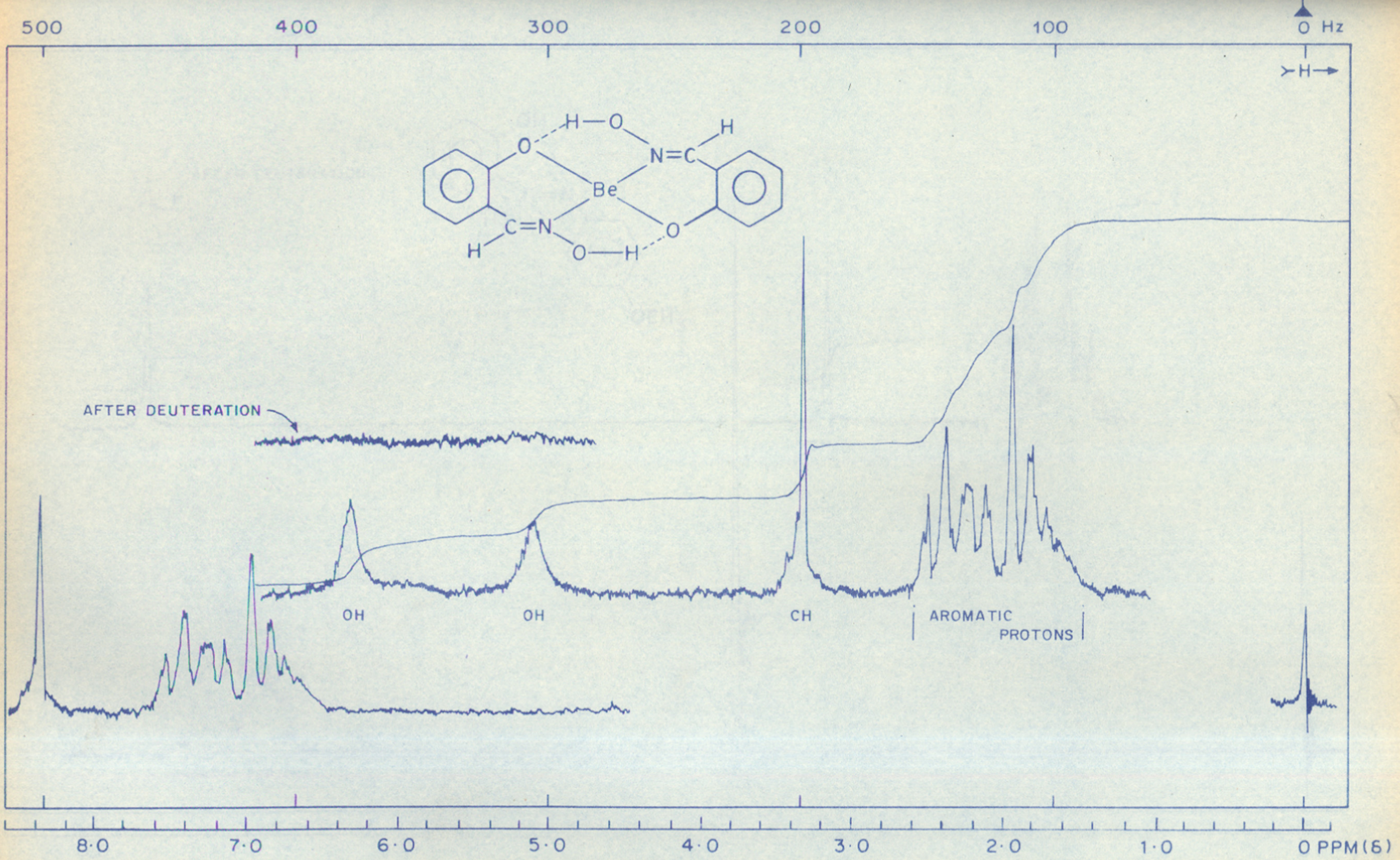


FIG. 7. PMR SPECTRUM OF BIS(SALICYLALDOXIMINATO)BERYLLIUM(II) IN DRY DMSO.

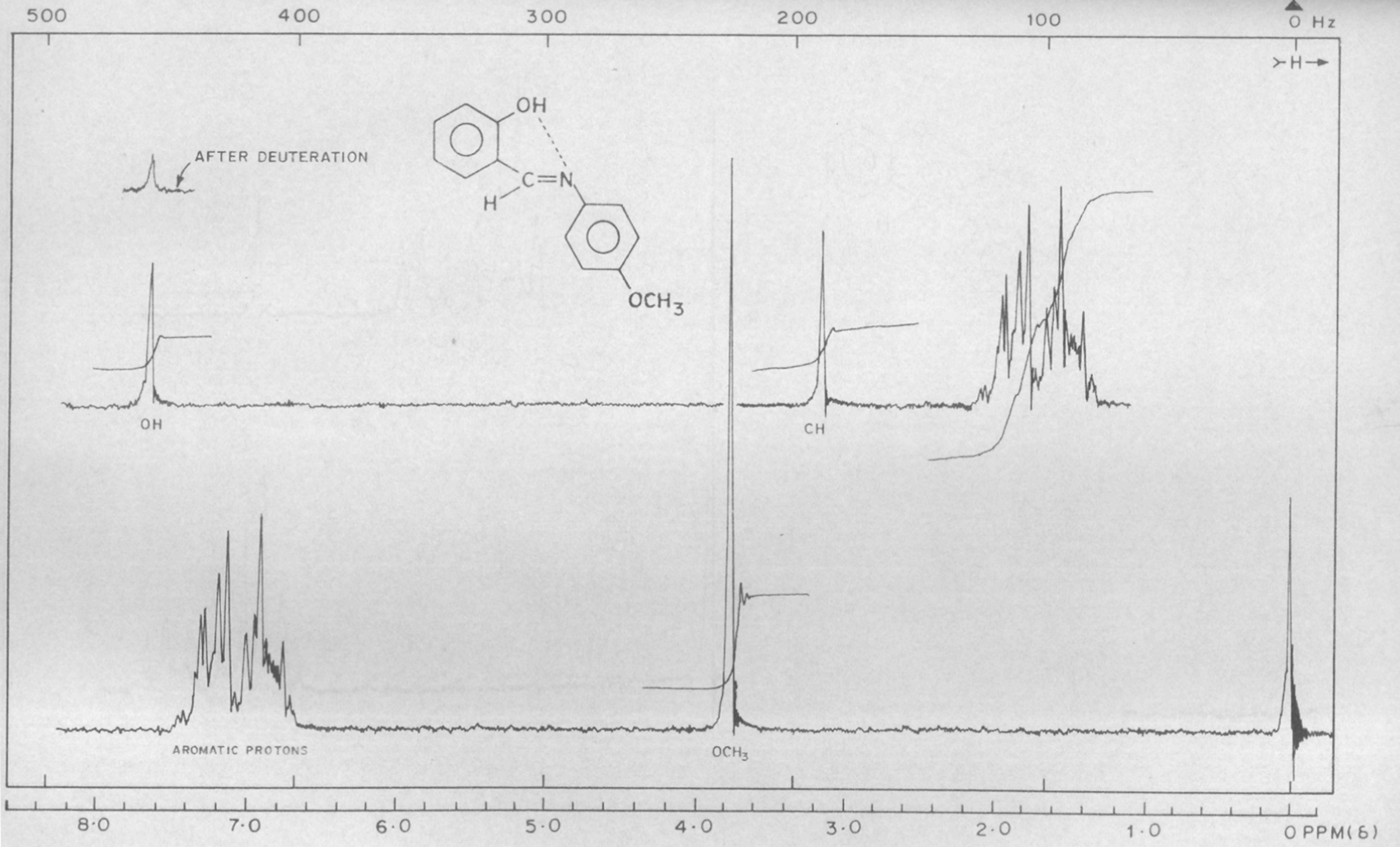


FIG. 8. PMR SPECTRUM OF N-p-ANISYLSALICYLALDIMINE IN CCl_4.

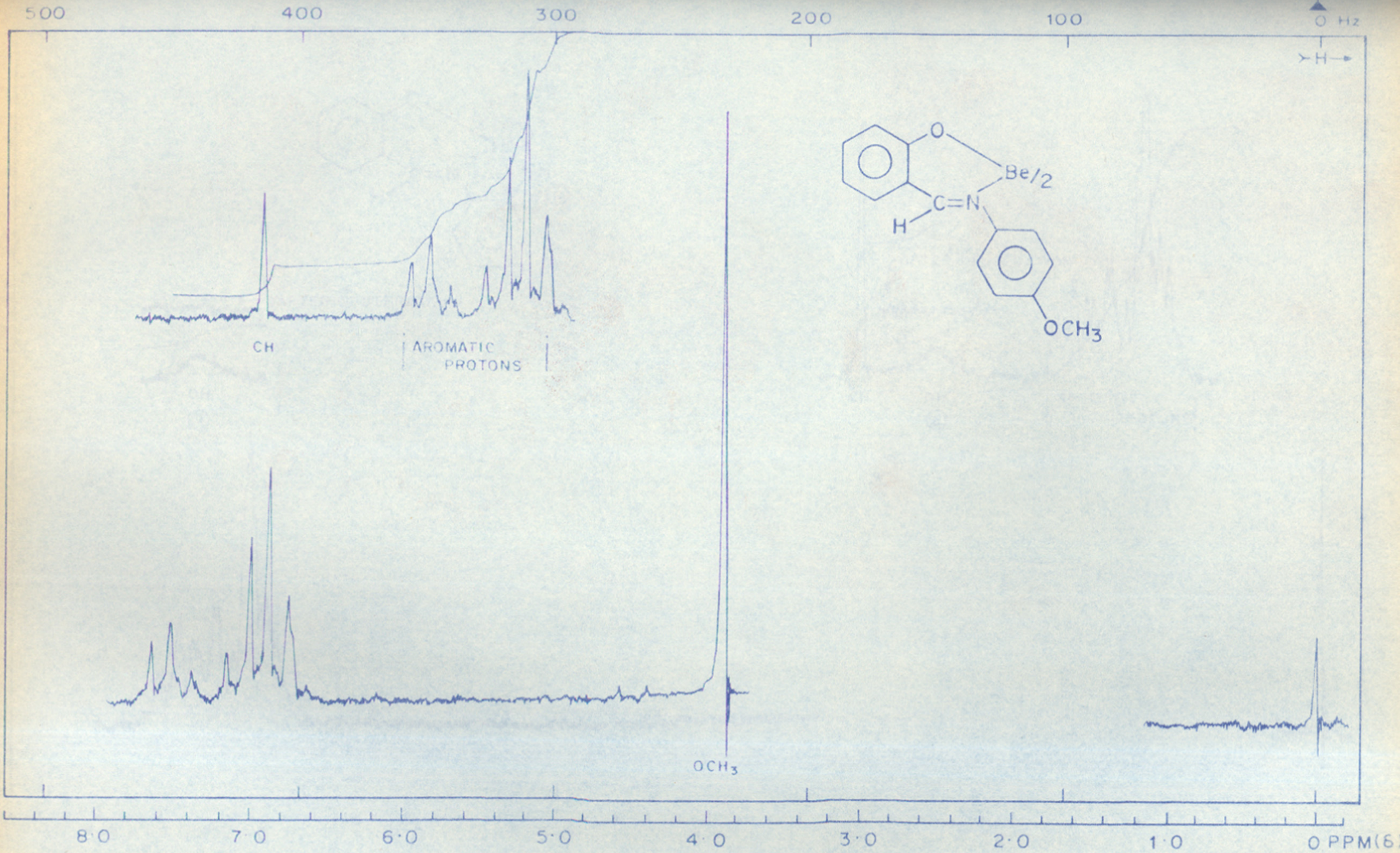


FIG. 9. PMR SPECTRUM OF BIS(N-p-ANISYLSALICYLALDIMINATO)BERYLLIUM(II) IN DRY DMSO

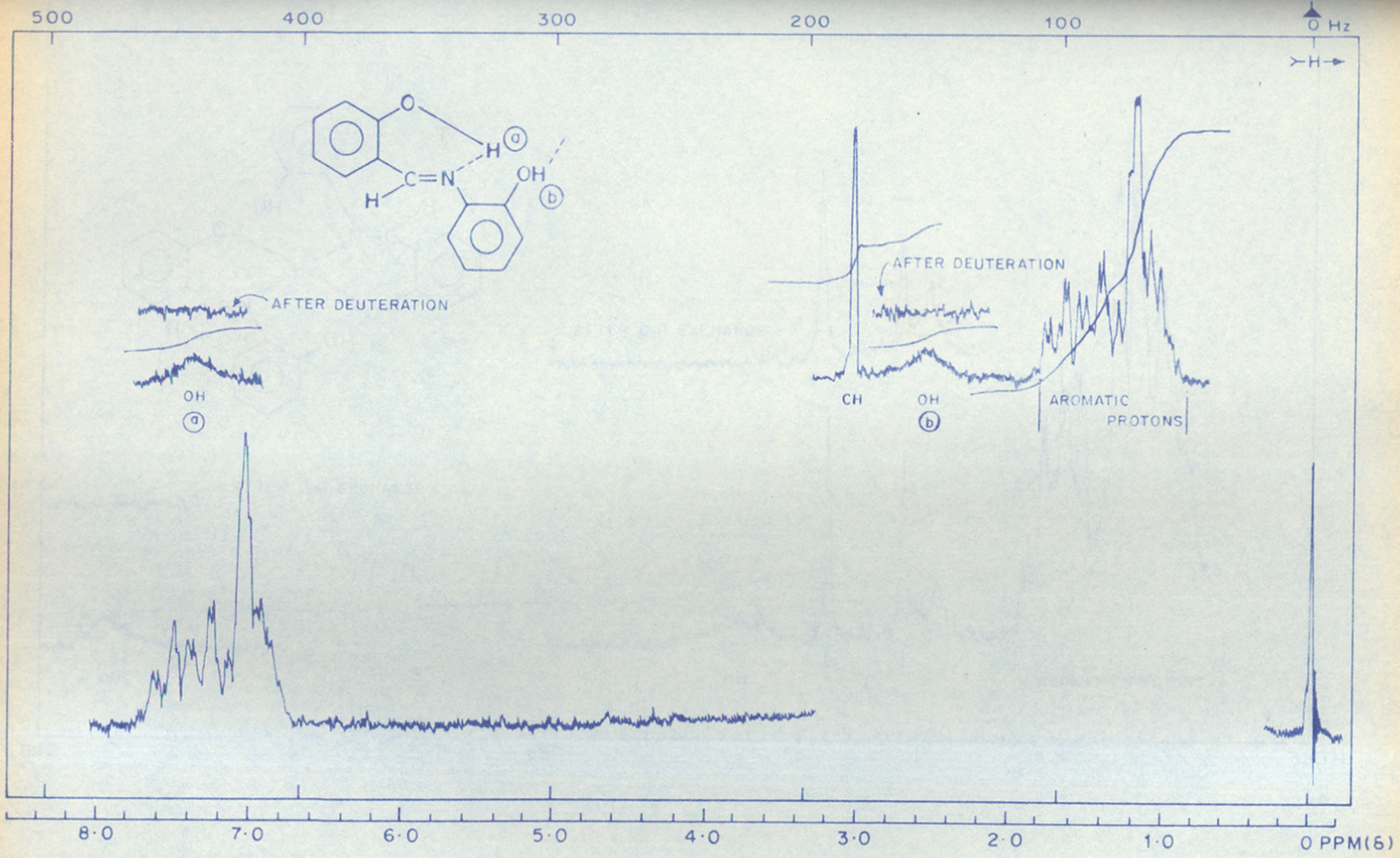


FIG. 10. PMR SPECTRUM OF N-o-HYDROXYPHENYLSALICYLALDIMINE IN ACETONE.

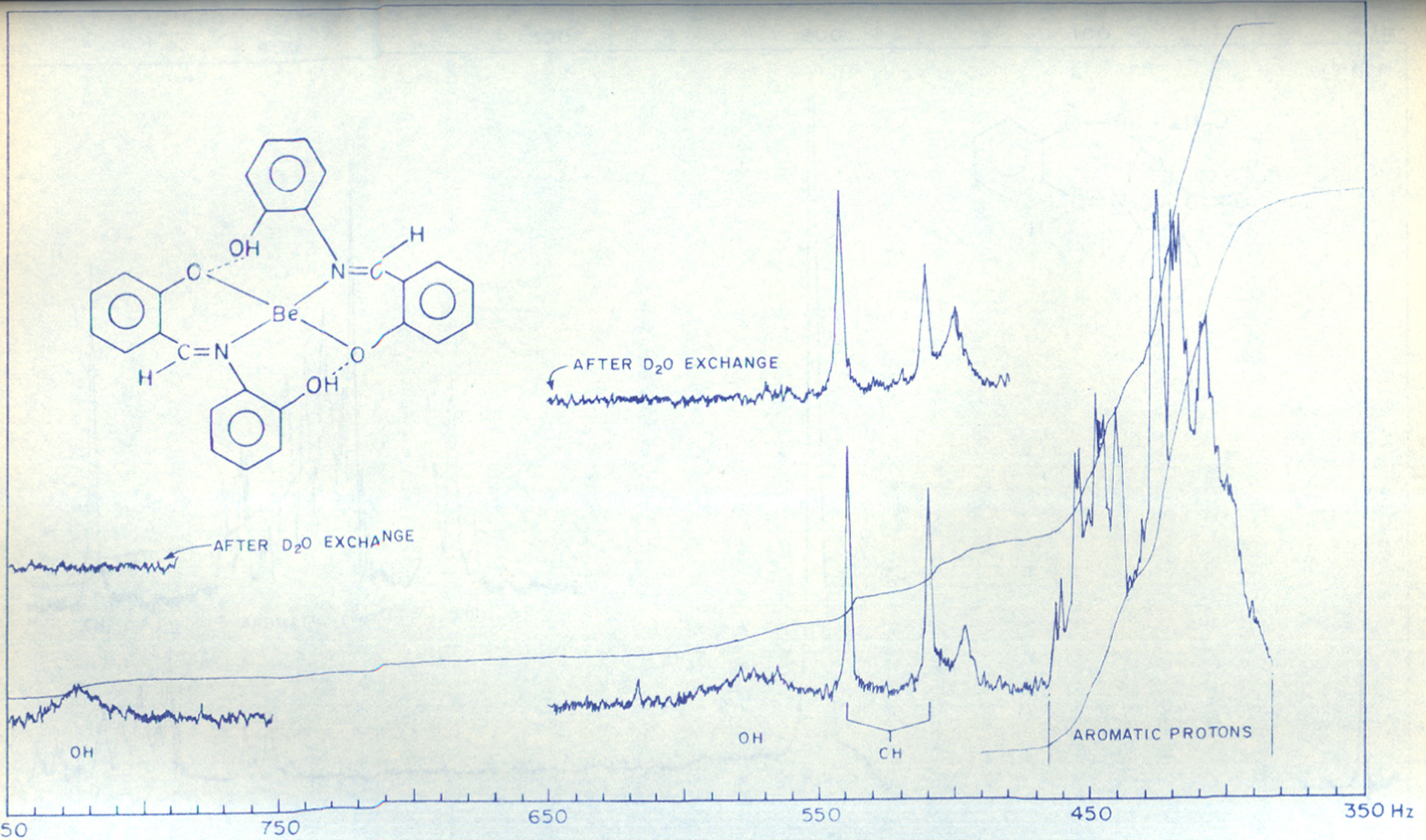


FIG. 11. PMR SPECTRUM OF BIS(N-o-HYDROXYPHENYLSALICYLALDIMINATO)BERYLLIUM(II) IN DRY DMSO.

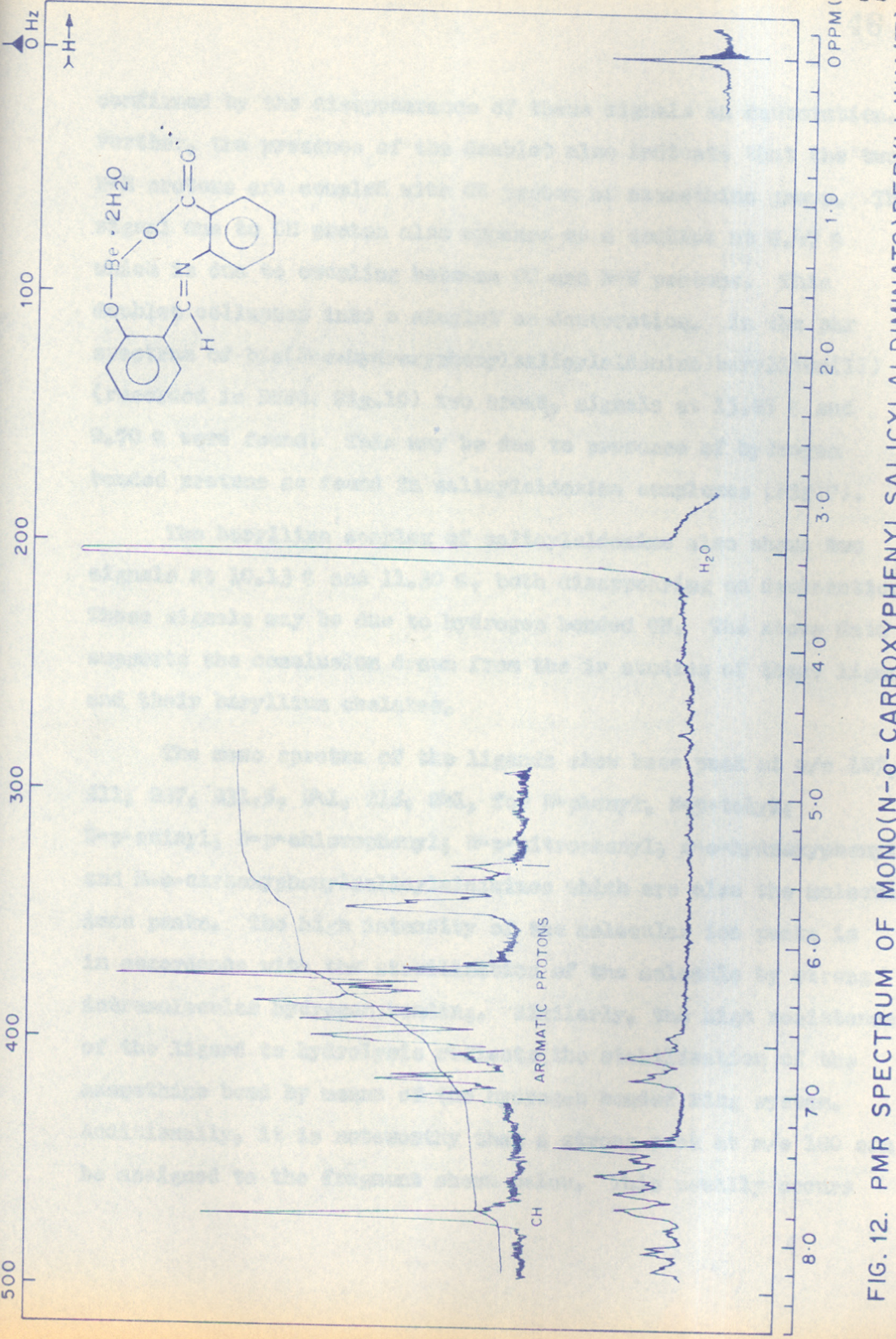
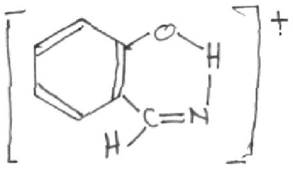


FIG. 12. PMR SPECTRUM OF MONO(N-o-CARBOXYPHENYLSALICYLALDIMINATO)BERYLLIUM(II) DIHYDRATE IN DRY DMSO.

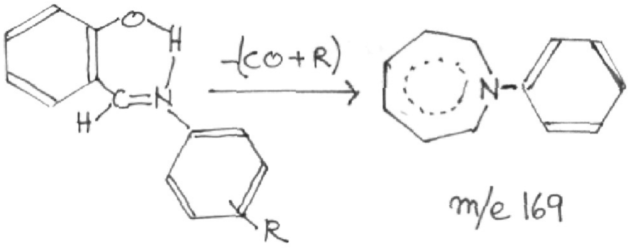
confirmed by the disappearance of these signals on deuteration. Further, the presence of the doublet also indicate that the two N-H protons are coupled with CH proton of azomethine group. The signal due to CH proton also appears as a doublet at 8.47 δ which is due to coupling between CH and N-H protons.[154] This doublet collapses into a singlet on deuteration. In the pmr spectrum of bis(N-o-hydroxyphenylsalicylaldimine)beryllium(II) (recorded in DMSO, Fig.10) two broad, signals at 13.85 δ and 9.70 δ were found. This may be due to presence of hydrogen bonded protons as found in salicylaldoxime complexes (Fig.7).

The beryllium complex of salicylaldoxime also shows two signals at 10.13 δ and 11.30 δ, both disappearing on deuteration. These signals may be due to hydrogen bonded OH. The above data supports the conclusion drawn from the ir studies of these ligands and their beryllium chelates.

The mass spectra of the ligands show base peak at m/e 197, 211, 227, 231.5, 241, 213, 241, for N-phenyl, N-p-tolyl; N-p-anisyl; N-p-chlorophenyl; N-p-nitrophenyl; N-o-hydroxyphenyl- and N-o-carboxyphenylsalicylaldimines which are also the molecular ions peaks. The high intensity of the molecular ion peaks is in accordance with the stabilization of the molecule by strong intramolecular hydrogen bonding. Similarly, the high resistance of the ligand to hydrolysis reflects the stabilization of the azomethine bond by means of the hydrogen bonded ring system. Additionally, it is noteworthy that a strong peak at m/e 120 can be assigned to the fragment shown below. This usually occurs with hydrogen transfer resulting in a cluster of peaks at m/e 121, 120, 119.


m/e 120

The formation of such stable heterocyclic species is characteristic of the mass spectra of ortho substituted aromatic Schiff bases[118,119]. The spectra of N-p-tolyl, N-p-anisyl, N-p-chloro-ligands show loss of the p-substituted groups resulting in a metastable ion[119]. Similarly, the spectra of N-o-hydroxyphenyl and N-o-carboxyphenylsalicylaldimines show loss of water and carbon dioxide from molecular ion. Another characteristic feature of these Schiff bases is the formation of a species of m/e 168-169. The formation of such a fragment may be due to the loss of CO and the p-substituent with proton transfer.[119].



m/e 169

Apart from these major peaks, these spectra also show a peak at m/e 77 corresponding to $C_6H_5^+$ ion formed by the breakdown of the parent ion. These spectra show that fission at the ring-nitrogen bond is more facile than at the ring carbon-bond. The mass spectra of para substituted schiff bases show essentially the same features, sometimes complicated by the effects of substituents.

It is concluded from the above studies that beryllium forms strong bonds with oxygen and nitrogen containing ligands. It was found by Martin et.al.[35] that the beryllium complexes have the same stability as copper complexes which contradicts the apparent belief that beryllium bonds weakly with ligands containing ~~oxygen and~~ nitrogen donor atoms. It is also found that N-aryl salicylaldimine beryllium complexes are as stable as the N-alkyl salicylaldimine complexes. The tridentated dibasic ligand, N-o-hydroxyphenylsalicylaldimine acts as a monobasic, bidentate ligand towards beryllium, where the amino -OH group takes part only in hydrogen bonding as is found in case of salicylaldoxime. It is interesting to note that N-o-carboxyphenylsalicylaldimine acts as dibasic ligand with beryllium. The elemental analyses, ir and nmr spectra and the thermal analysis of this beryllium chelate confirm the composition given here.

Part II

As a part of our general programme of work on Schiff base complexes of beryllium, our attention was drawn to the beryllium complex of N,N'-ethylenebis(salicylaldimine), 'salen', since there appears to be some controversy about the structure of this compound. Green et al[79] prepared beryllium complex of 'salen' and assigned the formula $Be(C_{16}H_{15}N_2O_2)_2.H_2O$ to the yellow, insoluble precipitate in which the ligand is bidentate towards beryllium. Bately et al[82] studied a number of beryllium complexes using quadridentate Schiff bases derived from ethylenediamine, 1,3-trimethylenediamine and with four or six methylene group in the amine bridge. These workers were unable to get 1:1 beryllium-salen complex but obtained instead 1:2 complex having the formula $C_{32}H_{33}BeN_4O_{5.5}$. These authors did not get the monohydrate as reported by Green et al. They, however, assigned a hydrogen-bonded structure to the compound on the basis of the ultraviolet absorption spectra in solid

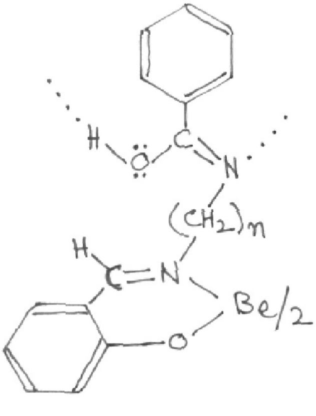


Fig. I

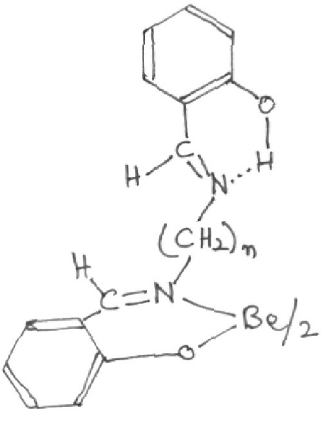


Fig. II

$n = 2, 3.$

state. The reflectance spectra of beryllium-salen complex showed a band at 430 nm attributable to intermolecular hydrogen bonding which was found to disappear in non-hydrogen bonding solvents probably due to the replacement of intermolecular bonds by intramolecular bonds as shown in the Figs. I,II.

Singh et al [83] have used 'salen' as a gravimetric reagent for beryllium and tentatively assigned a structure (Fig1 III) to the precipitate obtained from sodium potassium tartarate buffer solution at pH ~ 8.5. The composition of the weighable form

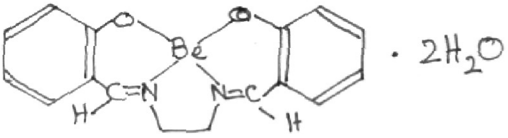


Fig III.

of the complex is reported to be $C_{16}H_{14}N_2O_2Be.2H_2O$. Further, it is stated that the complex possesses constant weight on drying at any temperature between 100° to 150°C. According to these authors the compound isolated is a dihydrate and no elemental analysis of the compound is reported by them.

In order to throw light on this complex, we adopted the methods of Green et al as well as Singh et al. However, the beryllium complex prepared according to both the methods gave almost identical values of carbon, hydrogen, nitrogen and beryllium which correspond nearly to 1:1 molarity (Table 7). Our finding is that the compound does not contain any water molecule of crystallization. This was verified by repeating the precipitation

Table - 7

Elemental analysis

			C	H	N	Be(%)
1.	N,N'-ethylenebis(salicylaldimine) $C_{16}H_{16}N_2O_2$, m.p. 115°C	Found	70.81	6.17	11.71	
		Cal.	71.65	5.97	10.45	
2.	N,N'-ethylenebis(salicylaldiminato)-beryllium(II) $Be(C_{16}H_{14}N_2O_2)$, >300°C	Found	70.05	5.45	9.94	3.20
		Cal.	69.81	5.09	10.19	3.28

Table - 8

Positions of the protons present in N,N'-ethylenebis(salicylaldimine) and its beryllium chelate. (ppm) δ

		CH_2	CH	Ring	OH. (δ)
1.	N,N'-ethylenebis(salicylaldimine).	3.77	8.30	6.66-7.66	13.13
2.	N,N'-ethylenebis(salicylaldiminato)beryllium(II)	4.63	9.66	7.16-8.11	-

of the complex ~~several~~ a number of times and studying their ir, pmr spectra and thermogravimetric analysis.

The ir spectra of 'salen' and its beryllium chelate is given in Fig.13 and Table 9 with possible assignments[45,125]. The ir spectrum of beryllium chelate does not show the presence of OH stretching frequency in 3700 cm^{-1} - 2000 cm^{-1} region either free or bonded. However, there appears to be a small peak at 1272 cm^{-1} which has been presumed to be due to the presence of phenolic CO coupled with OH bending vibrations. Therefore, the presence of the water molecule in the complex is in doubt. Furthermore, the pmr spectra of the complex does not show any signal corresponding to water or hydroxyl protons (Tab. 8). It is interesting to see (Fig.14) that the thermogravimetric curve of the beryllium complex does not show any loss in weight upto 200°C. Progressive loss in weight occurs only on further heating. This clearly shows that the complex does not contain any water of crystallization.

Bately et al[82] have carried out model studies to justify their assumption to show that even though 'salen' is a quadridentate ligand, it behaves as bidentate towards beryllium which does not tolerate even slight departure from tetrahedral stereochemistry. To verify this, we have also studied the model of beryllium-salen complex taking the bond distance of Be-O = 1.7 Å[153] and it was found that three bonds could easily be formed. When the fourth bond is forced to form with the metal, the aromatic ring hydrogens are twisted out of the plane increasing strain on the rings and consequent

Table - 9

Infrared absorption frequencies (cm^{-1}) of (I) N,N'-ethylenebis(salicylaldimine), (II) Beryllium chelate in HCB/Nujol mull.

I	II	Possible assignment
	2900(vs)	
2650(m,b)		O-H bonded.
	1635(s)	C=N coupled with C=C str.vib.
1625(v,s)	1625(s)	
1610(s)	1600(sh)	
1570(s)	1580(sh)	
1550(sh)		
	1540(s)	
1485(s)		
	1465(sh)	=CH in plane vib.
1455(m)	1460(s)	
1448(m)	1440(s)	
1400(s,b)		
	1385(w)	
1360(m)	1370(m)	
	1330(s)	C-H def.vib.
	1315(s)	C-O bonded str.
1305(w,sh)	1300(s,b)	
1272(vs)		CO+OH bonding vib.
	1270(m)	
	1250(w)	
1240(m)		
	1215(s)	
1210(m)		
1192(m)	1200(s)	
1142(s)	1140(s)	Azomethine C-H vib.
	1120(s)	
1105(m)	1100(sh)	
	1052(m)	
1038(s)		
	1035(sh)	Aromatic C-H in plane def. vib.
1018(s)	1022(m)	
	985(w)	
975(s,b)		
968(s,b)		
	938(v,s)	Be-O str.
930(m)		
895(m)	883(m)	
855(m)	852(s)	=CH out of plane vib.
770(s)		
755(sh)	758(v,s)	
745(s)		
740(v,s)	735(v,s)	C-H out of plane
	675(m,b)	
638(m)	640(m)	

ethylenic C-C bond rupture (IV).

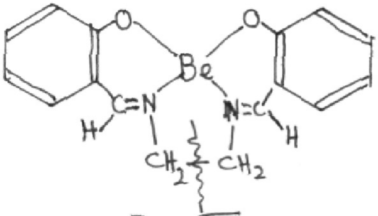
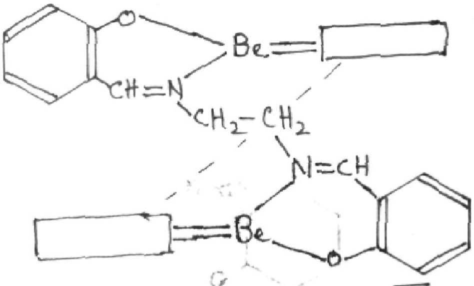
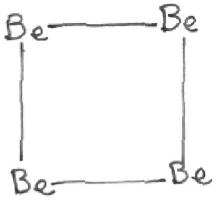


Fig. IV.

Considering the above facts, the beryllium complex may be thought to have polymeric structure in which 1:1 metal-ligand molarity is maintained. This may happen when two or four metal-ligand molecules are bonded (V) maintaining strictly the tetrahedral spacing between beryllium and the ligand.



V



The mass spectrum of the compound showed molecular ion peak at m/e 275 confirming presence of a molecule in which beryllium and salen are in 1:1 molar ratio. This, however, does not rule out the polymeric structure proposed by us, since under drastic condition of high vacuum and high temperature the polymeric units can break up and give rise to monomers. Therefore in the condensed solid state the polymeric structure still seems to be feasible. This is also revealed by the departure of the analytical data slightly from the theoretical values. If we presume that the compound is polymeric, then we can account for all the four coordination number of beryllium; however, in the monomeric compound, the fourth coordination number remains unsatisfied and in this case, one is allured to invoke the presence of a water molecule in order to have four coordinated beryllium. At any rate, our data is not conclusive in deciding between these two alternatives. It is possible that both these compounds are present in different proportions and the physical data obtained can be explained partially by both the structures. We therefore feel that the composition and structure of beryllium-salen ~~is~~ are not straight forward and the use of salen in gravimetric estimation of beryllium is not desirable. and safe.

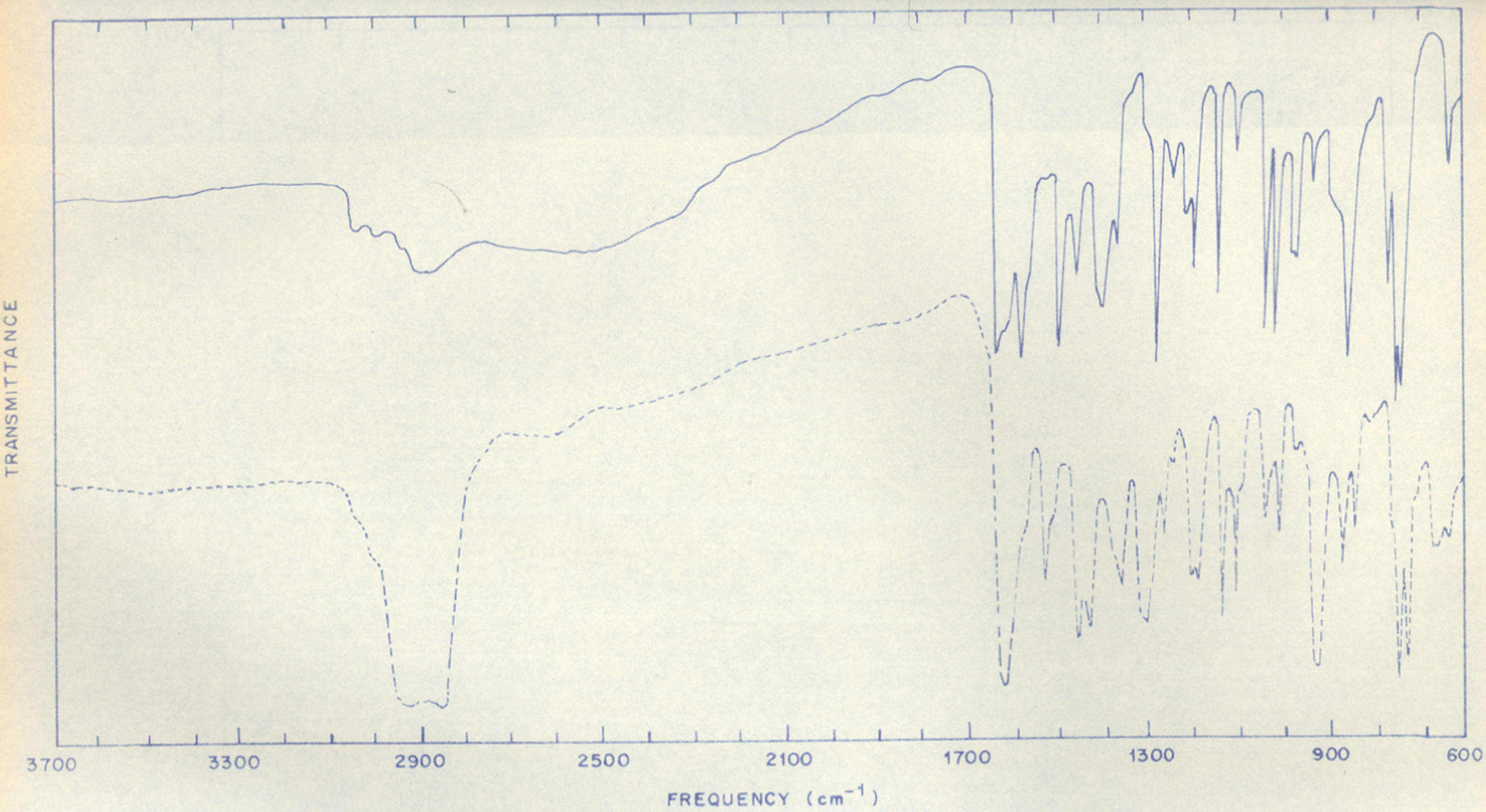


FIG. 13. INFRARED SPECTRA OF:

——— N,N'-ETHYLENEBIS(SALICYLALDIMINE) IN HCB / NUJOL MULL

------- N,N'-ETHYLENEBIS(SALICYLALDIMINATO)BERYLLIUM(II) IN NUJOL MULL

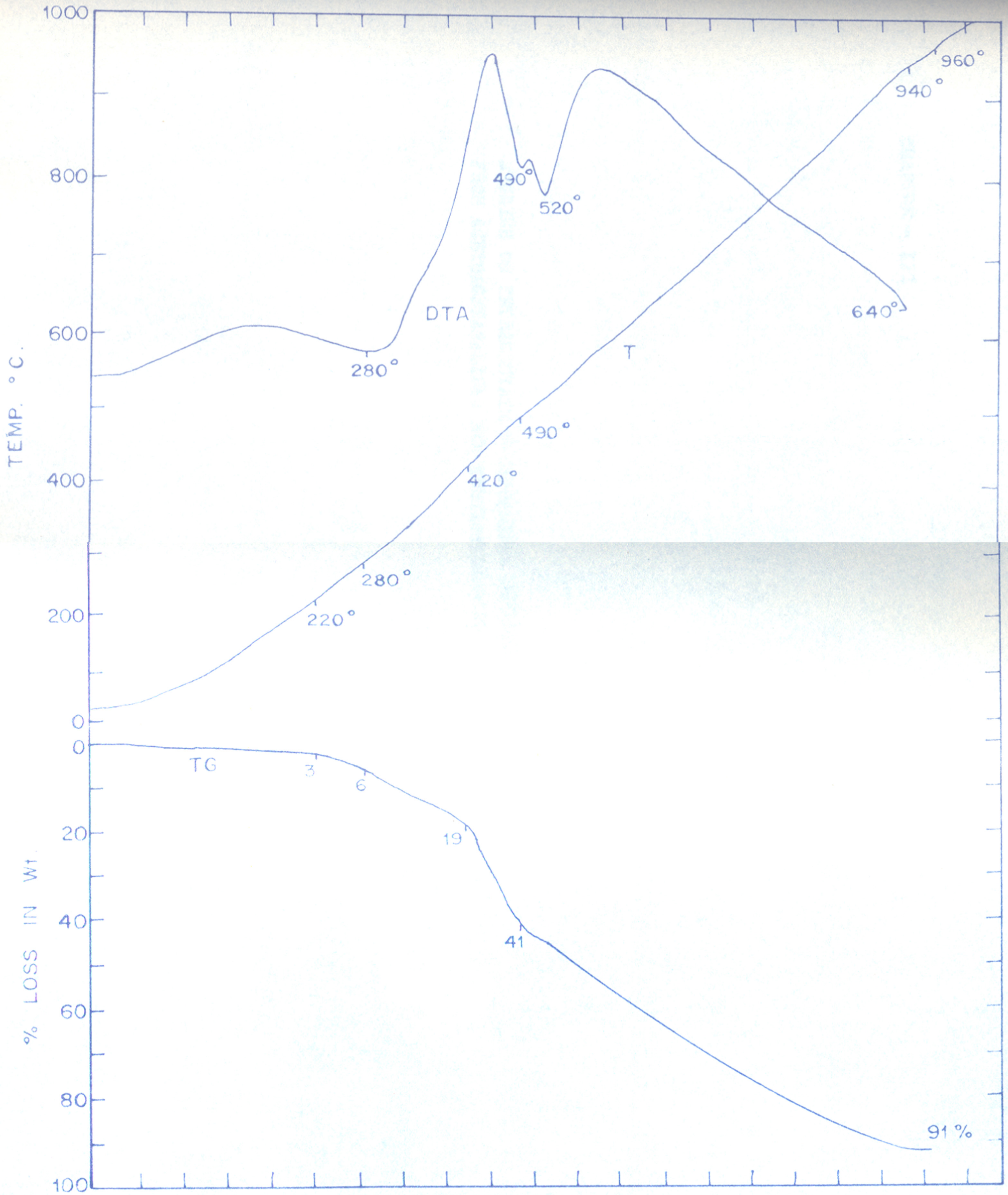


FIG. 14. TGA AND DTA CURVES FOR N,N'-ETHYLENE-BIS(SALICYLALDIMINATO)BERYLLIUM(II)

(AMOUNT TAKEN 200 mg., T DENOTES THE TEMPERATURE AS A FUNCTION OF THE TIME REPRESENTED BY ABSCISSA. DTA SENSITIVITY 1/10)

CHAPTER - III

STUDIES ON TETRADENTATE β-KETOAMINES DERIVED FROM ACETOACETANILIDES AND ETHYLENEDIAMINE

Abstract

Tetradentate β-ketoamines, namely, N,N'-ethylenebis(acetoacetanilide), N,N'-ethylenebis(2-chloroacetoacetanilide), N,N'-ethylenebis(3-chloroacetoacetanilide), N,N'-ethylenebis(2,4-dichloroacetoacetanilide), N,N'-ethylenebis(2,5-dichloroacetoacetanilide), N,N'-ethylenebis(2-methoxyacetoacetanilide), N,N'-ethylenebis(4-methoxyacetoacetanilide) and N,N'-ethylenebis(2,5-dimethoxyacetoacetanilide) have been synthesized for the first time. Infrared and pmr spectral studies of these compounds have been carried out in order to assign the bands due to amide NH and bonded NH groups.

Attempts to prepare the metal chelates by reported methods have failed. The major factors contributing to this may be the nonreactivity of the ligands due to the strong hydrogen bonding and the~~ir~~ hydrolytic instability of their metal chelates.

Introduction

β-ketoamines derived from acetylacetone, benzoylacetone, dibenzoylmethane are similar to salicylaldimines as these ligands contain O-N donor atoms and the presence of conjugated six membered chelate ring. These compounds are formed by the condensation of primary amines with β-diketones[3]. Dudek and coworkers[46,48,49] reported that these compounds solely exist in ketoamine form from their pmr spectra. The important features of these ligands is that they contain an intramolecularly hydrogen bonded ring. Bellamyand Beecher[129] showed that the strength of the hydrogen bond is measured by the downward shift of the C=O frequency. Subsequently, several structural studies of β-ketoamines have been made using dipole moment, infrared and ultraviolet[36-42,52-55] spectral techniques. Complexes of bidentate and tetradentate ligands with copper, nickel, cobalt, chromium, palladium, rhodium and iron have widely been studied, isolating the metal chelates from aqueous and non-aqueous medium[22,32,57-66]. Recently, a good number of reviews and papers[2,4,5,10,130-132] have appeared in the literature dealing with N,N'-ethylenebis(acetylacetone) or similar compounds and their metal chelates. However, no work has been reported on the β-ketoamines derived from the condensation of acetoacetanilide or its substituted derivatives with ethylenediamine. This Chapter deals with the preparation of eight such β-ketoamines, isolated for the first time, as well as their infrared and pmr spectral studies. All our attempts to isolate the metal chelates of these ligands were met with failures.

EXPERIMENTAL

Materials and Method

Acetoacetanilide (Sisco-Chem Product, Bombay) was purified by recrystallization. Ethylenediamine (Riedal) was distilled and stored in air-tight bottles. Chloro and methoxy substituted acetoacetanilides, used in the synthesis of β-ketoamines, were prepared by reported method[137].

Infrared spectra were recorded on a Perkin-Elmer Spectrophotometer Model 'Infracord' and Model 221 equipped with sodium chloride optics. The solution spectra in CCl_4 were recorded using 1 cm path length quartz cell. The pmr spectra were recorded on a Varian Associates Model A-60 and T-60, operating at 60 Mc/s with TMS as internal standard.

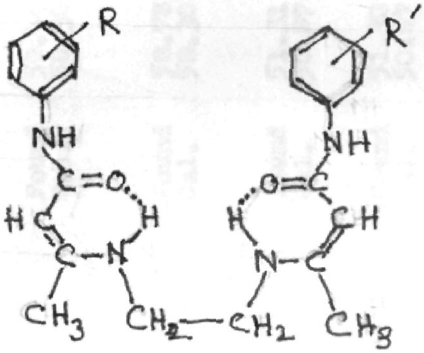
Preparation of β-ketoamines

Acetoacetanilide (35.4 g, 0.2 mole) was dissolved in 250 ml absolute alcohol taken in a 500 ml round bottom flask fitted with ground joint and a reflux condenser. The clear solution was heated to boiling on a water bath and then reacted with an alcoholic solution of ethylenediamine (6 g, 0.1 mole). A white precipitate was obtained within 5 minutes. The precipitate was refluxed further for 30 minutes, cooled, filtered on a glass sintered funnel, washed several times with 10-15 ml portions of cold alcohol and air dried.

All the substituted β-ketoamines were similarly prepared reacting substituted acetoacetanilides and ethylenediamine in 2:1 molar ratio. The yield ranged from 80-90%. The elemental analyses, m.p., ~~solubility~~ are given in Table 1. The following β-ketoamines were prepared (Fig.1).

Results and discussion

The possible structure of the compounds is given in Fig.1.



I R=R'=H.
II R=R'=2-chloro-.
III R=R'= 3-chloro-
IV R=R'=2,4-dichloro-
V R=R'=2,5-dichloro-
VI R=R'=2-methoxy-
VII R=R'=4-methoxy-
VIII R=R'=2,5-dimethoxy-

Fig. 1.

The infrared spectral data are presented in Table 2-4, figures 2-4. Table 2 and figures 3-4 show the stretching frequencies of the free amide NH and the intramolecularly hydrogen bonded NH recorded in carbon tetrachloride solution (0.01 mole approx.). These spectra show a strong, sharp band at ~ 3400 cm^{-1} attributed to the free amide NH stretching vibrations and the broad, medium intensity band, splitted in two compo~~unds~~nents, at 3200-3100 cm^{-1} is due to NH intramolecularly hydrogen bonded to the C=O group. The spectrum of N,N'-ethylenebis(acetylacetone) show two broad, medium intensity bands at 3220 cm^{-1} and 3170 cm^{-1} attributable

Table - 1

Elemental analyses of β-ketoamines

	Name	Formula/Mol.wt.		C%	H%	N%	m.p.
1.	N,N'-ethylenebis(acetylacetone)*	$C_{12}H_{20}N_2O_2$ (224)	Found Cal.	65.31 64.30	9.02 8.93	12.29 12.50	110-112°C
2.	N,N'-ethylenebis(acetoacetanilide)	$C_{22}H_{26}N_4O_2$ (378)	Found Cal.	68.46 71.42	7.06 6.88	13.14 14.81	209-10°C
3.	N,N'-ethylenebis(2-chloroaceto-acetanilide).	$C_{22}H_{24}N_4O_2Cl_2$ (447)	Found Cal.	59.46 59.30	6.02 5.41	12.39 12.59	148-150°C
4.	N,N'-ethylenebis(3-chloroaceto-acetanilide)	$C_{22}H_{24}N_4O_2Cl_2$ (447)	Found Cal.	58.78 59.30	5.41 5.41	12.25 12.59	190°C
5.	N,N'-ethylenebis(2,4-dichloro-acetoacetanilide)	$C_{22}H_{22}N_4O_2Cl_4$ (516)	Found Cal.	51.31 50.97	4.10 4.25	10.31 10.85	163-4°C
6.	N,N'-ethylenebis(2,5-dichloro-acetoacetanilide)	$C_{22}H_{22}N_4O_2Cl_4$ (516)	Found Cal.	51.30 50.97	4.36 4.25	10.96 10.85	163°C
7.	N,N'-ethylenebis(2-methoxy-acetoacetanilide)	$C_{24}H_{30}N_4O_4$ (438)	Found Cal.	65.49 65.75	6.49 6.85	12.45 12.21	176-8°C
8.	N,N'-ethylenebis(4-methoxy-acetoacetanilide	$C_{24}H_{30}N_4O_4$ (438)	Found Cal.	64.85 65.75	6.49 6.85	12.40 12.21	195°C
9.	N,N'-ethylenebis(2,5-dimethoxy acetoacetanilide)	$C_{26}H_{34}N_4O_6$ (498)	Found Cal.	62.43 62.66	7.29 6.82	10.84 11.25	180°C

* Reported J.Inorg.Nucle.Chem. 5,170 (1961)

Table - 2

Infrared absorption frequencies (cm^{-1}) of free NH and bonded N-H vibration

		N-H (free)	N-H (bonded)	N-D
1.	N,N'-ethylenebis(acetylacetone)	-	3220(m,b) 3170(m,b)	2440 2385
2.	N,N'-ethylenebis(acetoacetanilide)	3295(m,b)*	3220(w,b)* 3120(w,b)*	
3.	N,N'-ethylenebis(2-chloroaceto-acetanilide)	3418(vs)	3235(m,b) 3160(m,b)	
4.	N,N'-ethylenebis(3-chloroaceto-acetanilide)	3285(m,b)*	3210(w,b)* 3100(w,b)*	
5.	N,N'-ethylenebis(2,4-dichloro-acetoacetanilide)	3420(vs)	3240(m,b) 3160(m,b)	
6.	N,N'-ethylenebis(2,5-dichloro-acetoacetanilide)	3418(vs)	3240(m,b) 3160(m,b)	2530 (Free) 2375 (bonded)
7.	N,N'-ethylenebis(2-methoxyaceto-acetanilide)	3430(vs)	3235(m,b) 3155(m,b)	
8.	N,N'-ethylenebis(4-methoxyaceto-acetanilide)	3378(s)* 3333(s)*	3255(m,b)*	
9.	N,N'-ethylenebis(2,5-dimethoxy-acetoacetanilide)	3428(vs)	3235(m,b) 3100(s)	

---

* Values from the spectra recorded in HCB/Nujol mull.

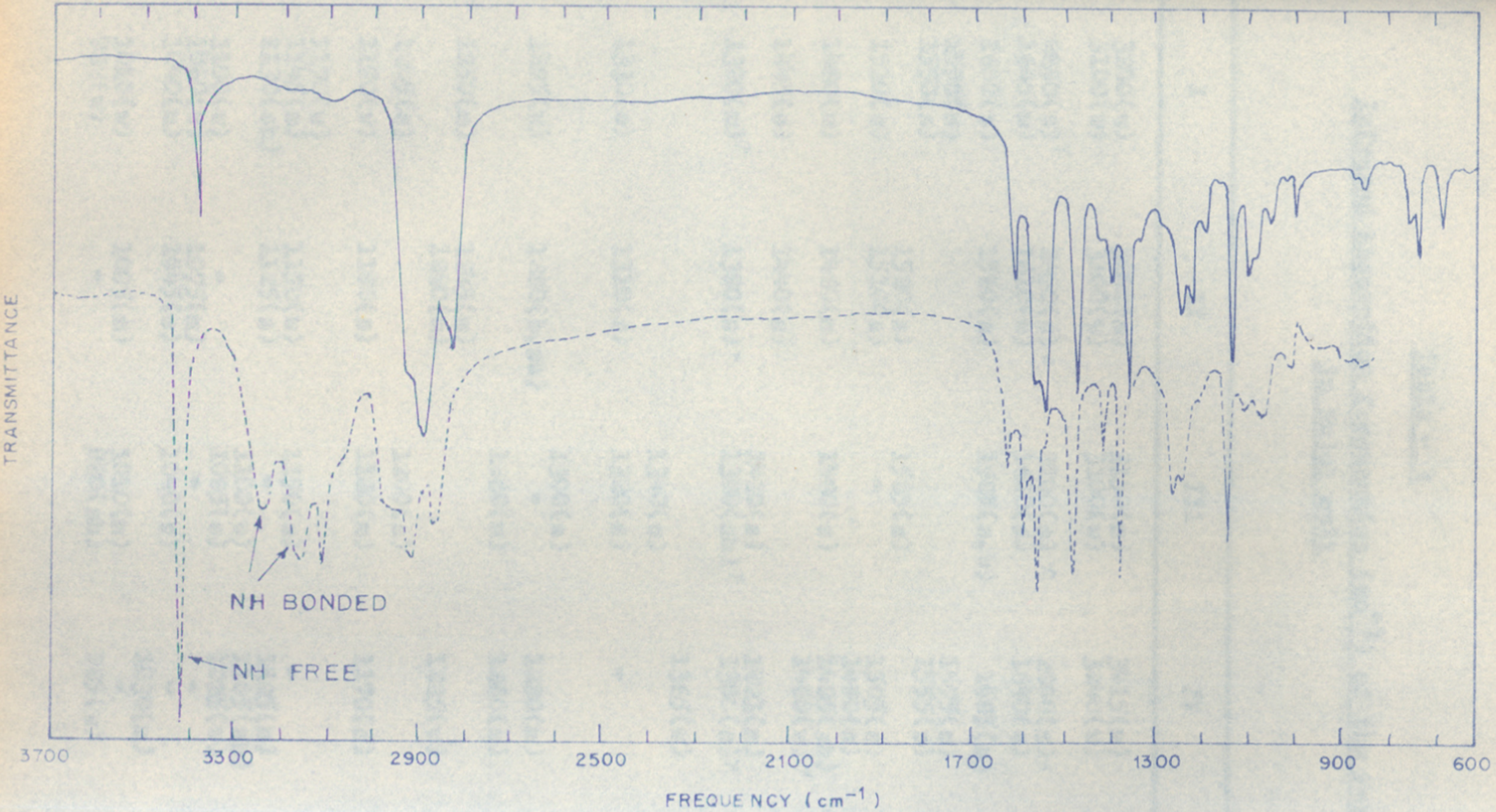


FIG. 2. INFRARED SPECTRA OF :

—— N, N'-ETHYLENEBIS(2,5-DICHLOROACETOACETANILIDE)
IN NUJOL MULL
------ IN CCl_4 SOLUTION (approx. 0·01 M)

Table - 3

Infrared absorption frequencies (cm^{-1}) of the β-ketoamines in Nujol mull

I	II	III	IV	V	Possible assignment
3200(w)	3200(m)	3150(m)	3415(m)	3424(m)	NH free str.vib.
3100(w)	3100(w)	3100(w)	3240(w)	3250(w,b)	NH bonde
2850(s) x	2850(s) x	2800(s) x	2900(s) x	2900(s) x	
1645(m)	1610(m)	1620(s)	1640(s)	1640(s)	Amide I C=C+C=O
1600(s)	1590(s)	1585(s,b)	1595(s)	1585(s,b)	Amide II
~~1550(s)~~			1575(s)		
1550(s)			1555(s)	1550(s)	
	1520(s)	1525(s)			
1510(s)	1510(s)	-	1505(s)	1500(sh)	
			1490(s)	1490(s,b)	
1480(m)	1480(m)	1480(s)	1485(sh)	-	
			1460(w) x	1455(w)	
1445(s)	1440(s)				CH$_3$ deg.
		1420(s)	1421(m)	-	def.
1390(m) x	1390(s) x	1380(sh) x	1390(s) x		CH$_2$wag.
				1375(s)*	Amide III
			1365(w)		
		1340(s)			
1330(s)	1310(s)	1320(s)	-	1310(s)	
				1290(s)	
		1300(s)			
1275(w)	1280(b,sh)	-	1280(m)	1280(s)	
		1260(m)	1260(m)		
1250(m)	1245(m)				
	1220(m)		1225(w)	1230(w)	
1205(s)		1200(s)		1210(m)	
1190(w)	1190(s)	1180(m)	1170(s)	1170(s)	CH in plane bending
1170(w)					
1145(m)	1150(w)	1150(s)	-	1150(s)	
1130(sh)	1125(s)	-	1125(m)	-	
		1100(w)	1105(sh)		
1100(w)	-	1095(s)	1085(w)	1095(s)	CH$_3$ rock
1060(w)	1075(m)	-	-	1060(w)	
1040(m)	1045(s)	1040(s)	-	-	
			1030(m)	1030(w)	
1010(w)	1005(m)	1010(m)	-	-	
988(w)	-	980(sh)	985(w)	980(w)	

Table - 3 (contd.)

I	II	III	IV	V	Possible assignment
975(w)	-	975(m)	-	-	
-	950(m)	-	-	-	
910(w)	-	920(m)	910(w)		
	890(m,b)	895(w)	885(m,b)		
	870(w)			865(s)	
				830(s)	
		800(s)			
		790(s)	795(s)		
785(s)	780(s)	780(s)	782(s)		
765(s)	760(s)		760(s)	760(s)	CH out of plane def.
	725(m)			730(m)	
	705(m,b)	710(s,b)	719(m)		
		685(w,b)		690(m)	

* Nujol peak

Table - 4

Infrared absorption frequencies (cm^{-1}) of the β-ketoamines in Nujol mull

VI	VII	VIII	Possible assignment
3450		3450(w)	
3300(w)			NH free and bonded
3200(m)	3200(m)		
	3150(w)	3150(m)	
		3050(w)	
2850(s)^{x}	2850(s)^{x}	2850(s)^{x}	
1640(s)	1640(s)	1640(s)	Amide I
1600(s)	1600(s)	1600(s)	C=C + C=O + CN
	1550(sh)	1545(s)	
1520(s)	1525(s)	1520(sh)	
1490(s)		1480(s)	
	1475(s)		
1460(s)^{x}		1455(s)^{x}	
1440(s)			
	1425(s)	1420(s)	CH_3 deg.def.
	1405(m)		
	1380(s)^{x}	1390(s)^{x}	CH_2-wag.
1340(s)	1340(sh)	1330(m)	Amide II
	1310(m)		
1300(s)	1300(sh)		
		1285(s)	
		1265(s)	
1255(s)	1250(m,b)	1250(s)	Amide III
1230(m)	1235(m,b)		
		1210(s)	
1190(s)			
1180(s)	1183(s,b)	1180(s)	CH in plane bending
1150(s)		1140(s,b)	
1135(s)	1135(s,b)		
1125(sh)			
1090(w)		1095(w)	
1060(s)		1055(s,b)	CH_3 rock
1040(s)	1030(s,b)	1030(m)	
1005(m)		1005(w)	
		985(m,b)	
970(m)	970(w,b)	965(w)	
942			
		905(w)	
885(w)	875(w)	875(s)	
855(w)	850(m)		
	845(m)		
835(w)	835(m)		
820(w)	820(w)	820(m,b)	
	810(w)		
795(w)		795(m,b)	
783(s)	780(m)	785(m,b)	CH out of plane
768(S)	774(W)		
755(S)	755(W)		
	735	728	
705		705	

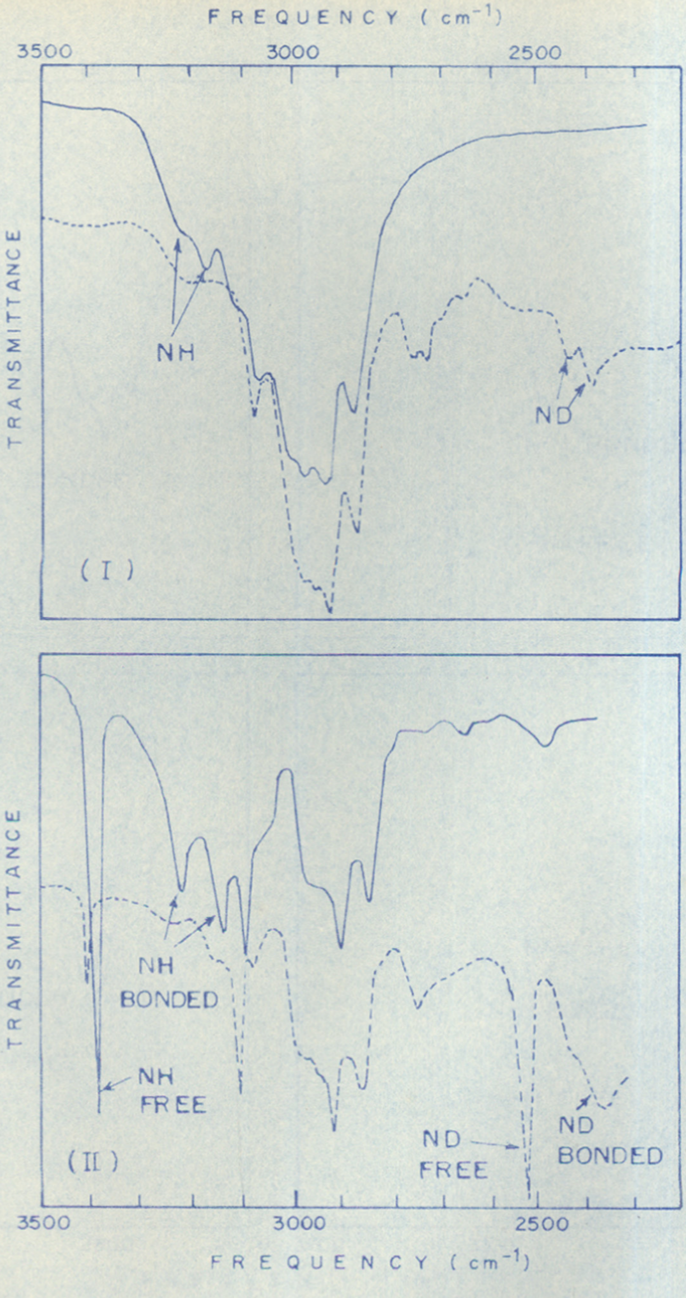


FIG. 3. INFRARED SPECTRA OF

(I)
——— N, N'-ETHYLENEBIS(ACETYLACETONE)
----- N, N'-ETHYLENEBIS(ACETYLACETONE) AFTER DEUTERATION

(II)
——— N, N'-ETHYLENEBIS (2,5-DICHLOROACETOACETANILIDE)
----- N, N'-ETHYLENEBIS(2,5-DICHLOROACETOACETANILIDE) AFTER DEUTERATION
IN CCl_4 SOLUTION

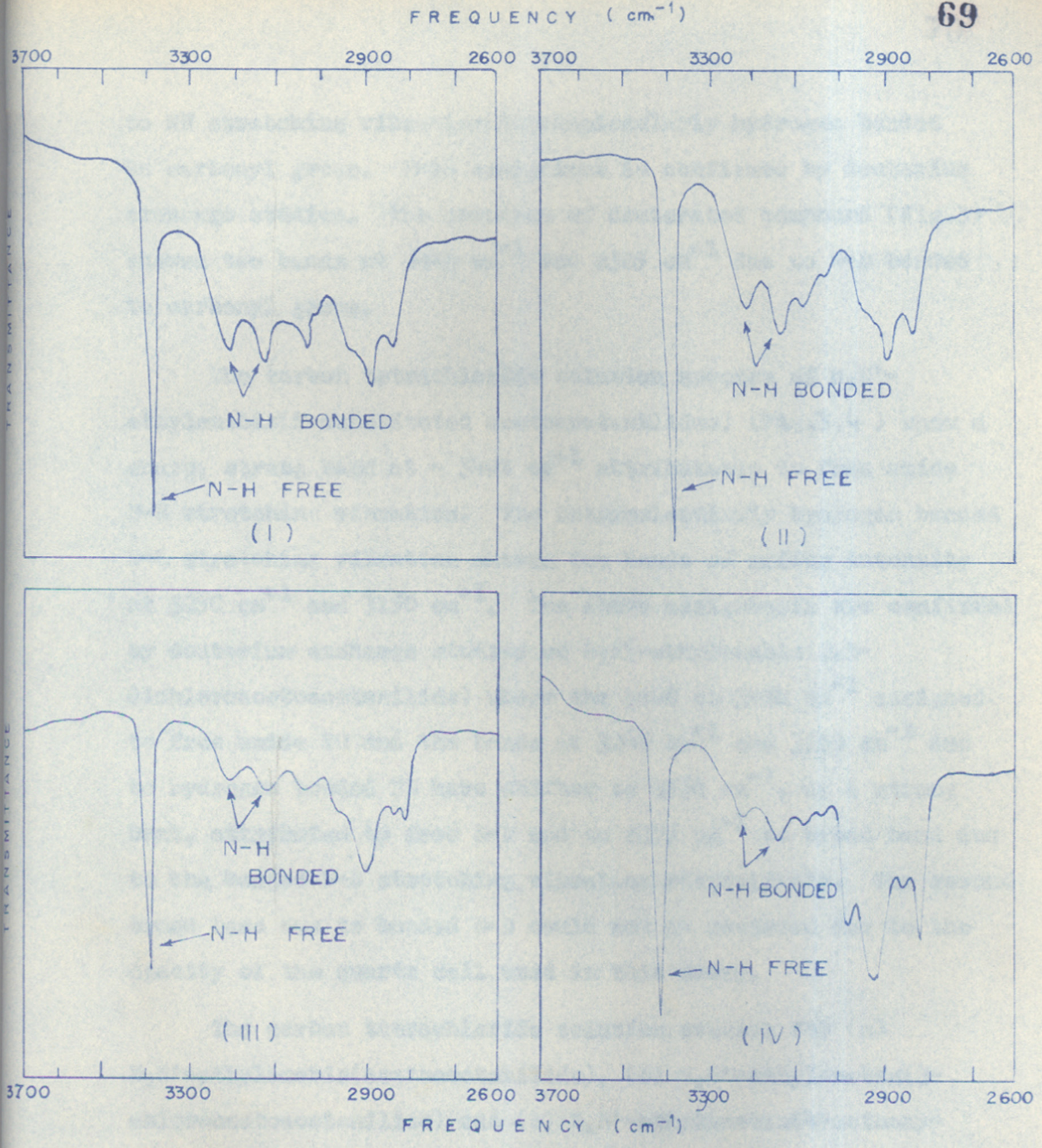


FIG. 4. INFRARED SPECTRA OF:

(I) N,N'-ETHYLENEBIS(2-CHLOROACETOACETANILIDE)
(II) N,N'-ETHYLENEBIS(2,4-DICHLOROACETOACETANILIDE)
(III) N,N'-ETHYLENEBIS(2-METHOXYACETOACETANILIDE)
(IV) N,N'-ETHYLENEBIS(2,5-DIMETHOXYACETOACETANILIDE)

IN CCl_4 SOLUTION (1 cm QUARTZ CELL)
]

to NH stretching vibrations intramolecularly hydrogen bonded to carbonyl group. This assignment is confirmed by deuterium exchange studies. The spectrum of deuterated compound (Fig.3) showed two bands at 2440 cm^{-1} and 2385 cm^{-1} due to N-D bonded to carbonyl group.

The carbon tetrachloride solution spectra of N,N'-ethylenebis(N-substituted acetoacetanilides) (Fig.3,4) show a sharp, strong band at ~ 3400 cm^{-1} attributable to free amide N-H stretching vibration. The intramolecularly hydrogen bonded N-H stretching vibration showed two bands of medium intensity at 3250 cm^{-1} and 3150 cm^{-1}. The above assignments are confirmed by deuterium exchange studies on N,N'-ethylenebis(2,5-dichloroacetoacetanilide) where the band at 3420 cm^{-1} assigned to free amide NH and the bands at 3245 cm^{-1} and 3160 cm^{-1} due to hydrogen bonded NH have shifted to 2530 cm^{-1}, as a strong band, attributed to free N-D and to 2375 cm^{-1} as broad band due to the bonded N-D stretching vibrations respectively. The second broad band due to bonded N-D could not be recorded due to the opacity of the quartz cell used in this study.

The carbon tetrachloride solution studies for (a) N,N'-ethylenebis(acetoacetanilide), (b) N,N'-ethylenebis(3-chloroacetoacetanilide) and (c) N,N'-ethylenebis(4-methoxyacetoacetanilide) could not be carried out due to their insolubility. The assignment for N-H stretching vibrations is, therefore, made from their HCB/Nujol mull spectra (Fig.5).

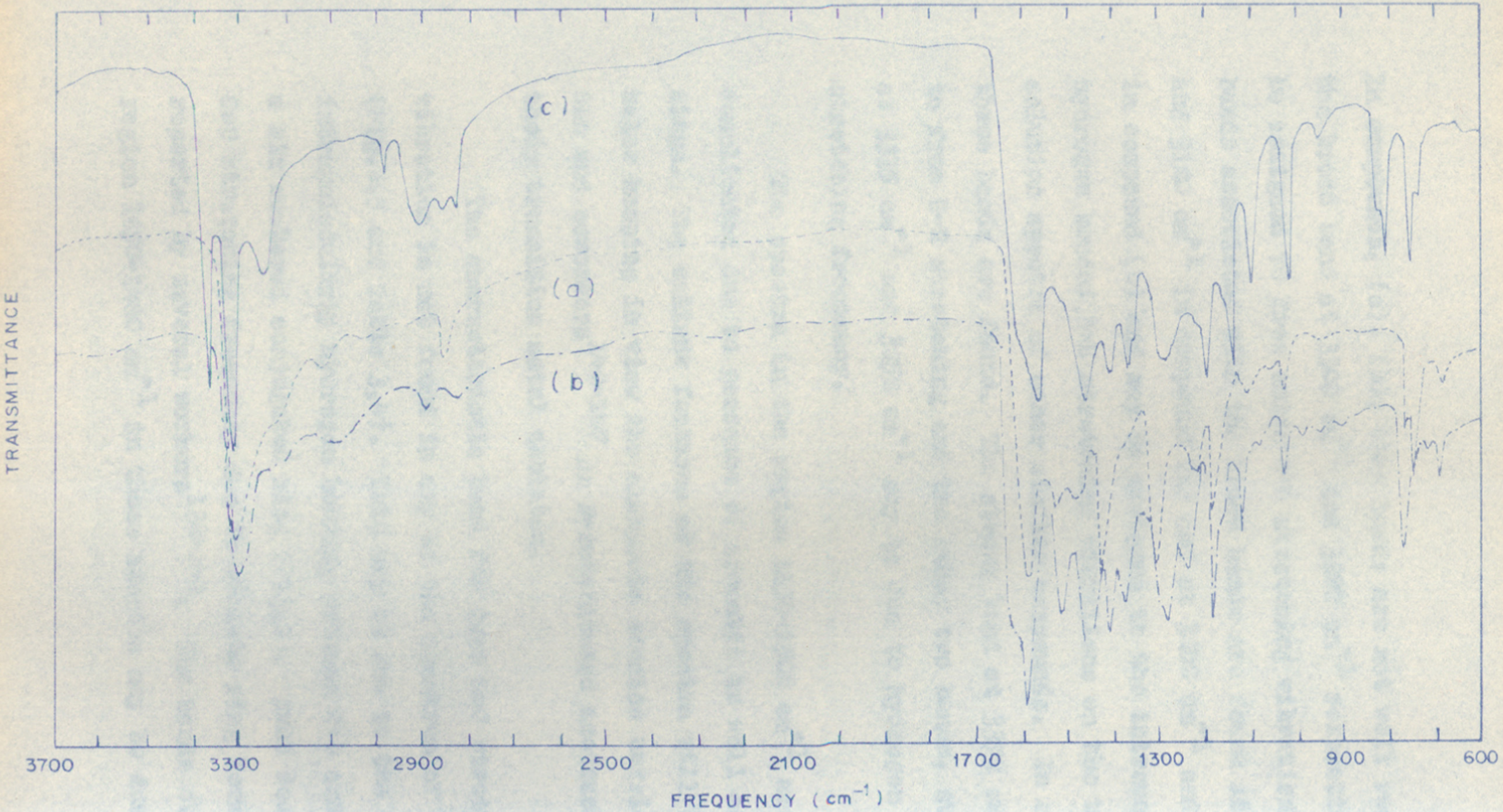


FIG. 5. INFRARED SPECTRA OF :

(a) ------ N,N'-ETHYLENEBIS(ACETOACETANILIDE)

(b) -·-·- N,N'-ETHYLENEBIS(3-CHLOROACETOACETANILIDE)

(c) ——— N,N'-ETHYLENEBIS(4-METHOXYACETOACETANILIDE)

IN HCB / NUJOL MULL

In compounds, (a), (b), (the bands are not well resolved), the broad band at 3300 cm^{-1} and 3290 cm^{-1} respectively may be assigned to free amide N-H stretching vibrations. The weak bands associated with the broad bands are found at 3220 cm^{-1} and 3120 cm^{-1} in compound (a) and at 3200 cm^{-1} and 3100 cm^{-1} in compound (b) and may be assigned to the intramolecularly hydrogen bonded N-H stretching vibrations on the basis of CCl_4 solution spectra of other similar compounds. In compound (c), three bands are found. The strong band at 3378 cm^{-1} may be due to free N-H stretching and the other two bands, strong and broad, at 3335 cm^{-1} and 3258 cm^{-1} may be due to hydrogen bonded N-H stretching frequency.

The spectra in the region 1650-1500 cm^{-1} are much complicated due to presence of aromatic as well as conjugated rings. The salient features of the spectra will be discussed below keeping in view the elaborate studies carried out by Sen and coworkers[142-147] on N-substituted acetoacetanilides and their transition metal chelates.

The characteristic band for free C=O stretching vibration is not found in any of the spectrum of these compounds. (Fig.2,5 and Table 3,4). This may be due to the existence of an intramolecular~~ly~~ hydrogen bonding between C=O and N-H forming a six membered conjugated ring (Fig.1). Such decrease in the C=O stretching frequency due to chelate ring formation is reported by several workers[138-141]. The bands observed in the region 1650-1480 cm^{-1} in these spectra may be due to strong coupling between C=C, C=O and C=N and amide group bond stretchings[41,136]. The bands between 1480-1350 cm^{-1} are chiefly due to CH_3, CH_2 deformation modes[136]. The bands in the further lower region are due to presence of phenyl ring moment, C-H in plane and out of plane vibrations.

In order to get a clearer insight ~~of~~ into these ligands, the pmr spectral studies were carried out in $CDCl_3$ and DMSO and the data are presented in Table 5 (Fig.6-14).

The spectrum of N,N'-ethylenebis(acetylacetone) was recorded in carbon tetrachloride and compared with the spectra of N,N'-ethylenebis(N-substituted acetoacetanilides). In the spectrum of N,N'-ethylenebis(acetylacetone) two signals at ~ 1.93 δ are observed which are due to the two unequivalent CH_3 groups. The value is in good agreement with the reported value[2]. In the spectra of β-ketoamines derived from N-substituted acetoacetanilides the $-CH_3$ protons signal is found as a singlet in the region of 1.96 δ - 2.00 δ. The signal due to CH_2 protons, in the region 3.27 δ - 3.43 δ, appears as a triplet due to spin-spin coupling of the CH_2 protons with the proton on nitrogen atom[47,133-135]. On deuterium exchange the triplet collapses into a singlet confirming the assignment and suggesting a similar structure for β-ketoamines as assigned to N,N'-ethylenebis(acetylacetone)[47]. A sharp singlet is found in the spectra of all the β-ketoamines studied here, at 4.47 δ - 4.50 δ due to CH proton of the conjugated hydrogen bonded ring. In the case of N,N'-ethylenebis(acetoacetanilide) this signal is found at 4.61 δ (Fig.6). In the

Table - 5

The pmr spectral data (δ) of β-ketoamines in $CDCl_3$ solution

	Name	$-CH_3$	$-CH_2$	$-CH$	$-OCH_3$	N-H	O-H	Ring
1.	N,N'-ethylenebis(acetylacetone)	1.90 1.93	3.43	4.83	-	10.97	-	-
2.	N,N'-ethylenebis(acetoacetanilide)	1.96	3.27	4.61	-	9.13 9.30	-	6.9- 7.7
3.	N,N'-ethylenebis(2-chloroaceto-acetanilide)	2.00	3.37	4.47	-	9.33	-	6.7 -8.4
4.	N,N'-ethylenebis(2,4-dichloro-acetoacetanilide)	1.97	3.40	4.50	-	9.40	-	7.0-8.43
5.	N,N'-ethylenedibis(2,5-dichloroacetoacetanilide)	2.00	3.40	4.50	-	9.40	-	6.73-8.50
6.	N,N'-ethylenedibis(2-methoxy-acetoacetanilide)	1.97	3.40	4.47	3.87	9.43		6.80-8.43
7.	N,N'-ethylenedibis(2,5-dimethoxyacetoacetanilide)	1.97	3.43	4.50	3.80 3.83	9.37		6.37-8.1

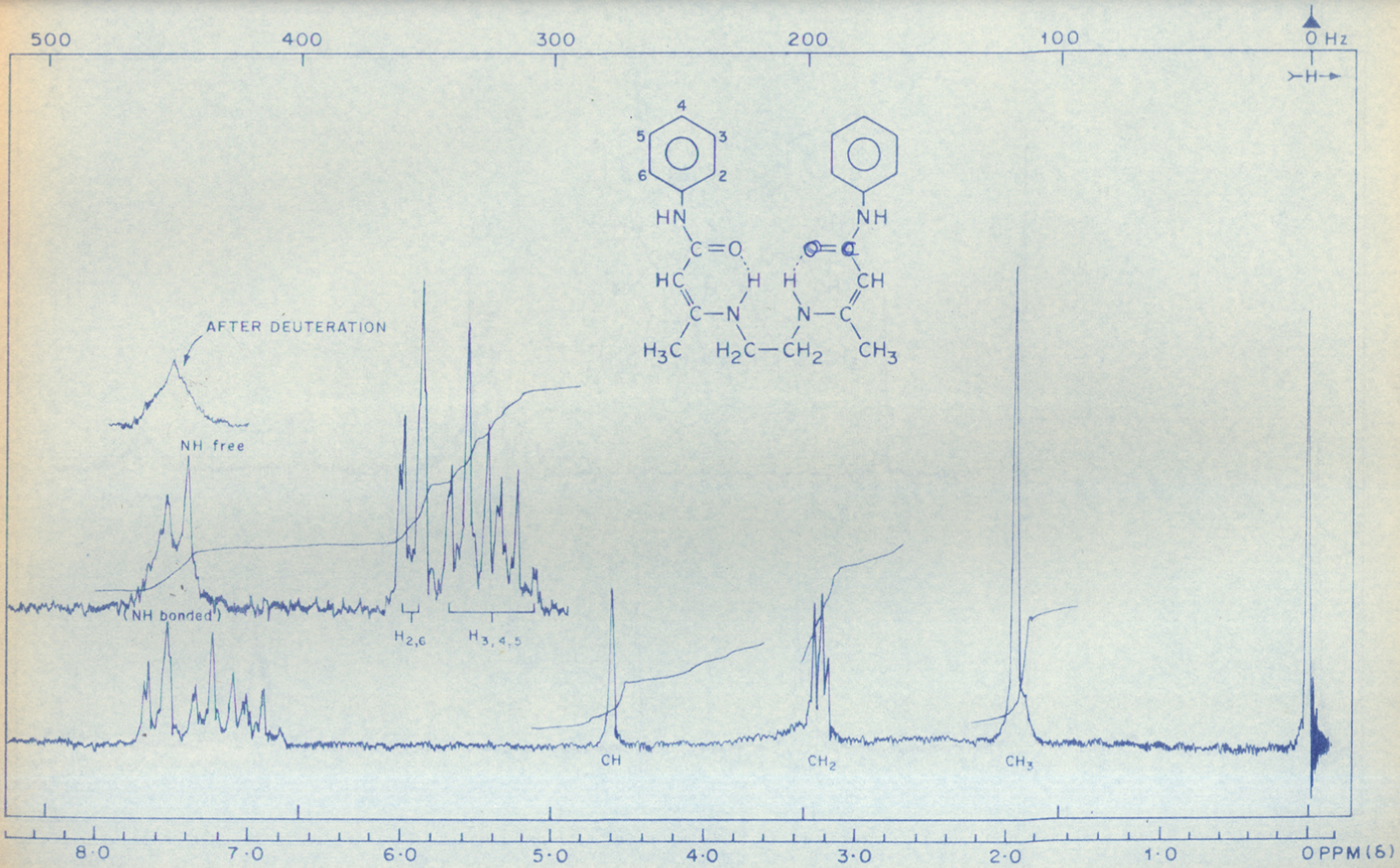


FIG. 6. PMR SPECTRUM OF N, N'-ETHYLENEBIS(ACETOACETANILIDE) IN DRY DMSO.

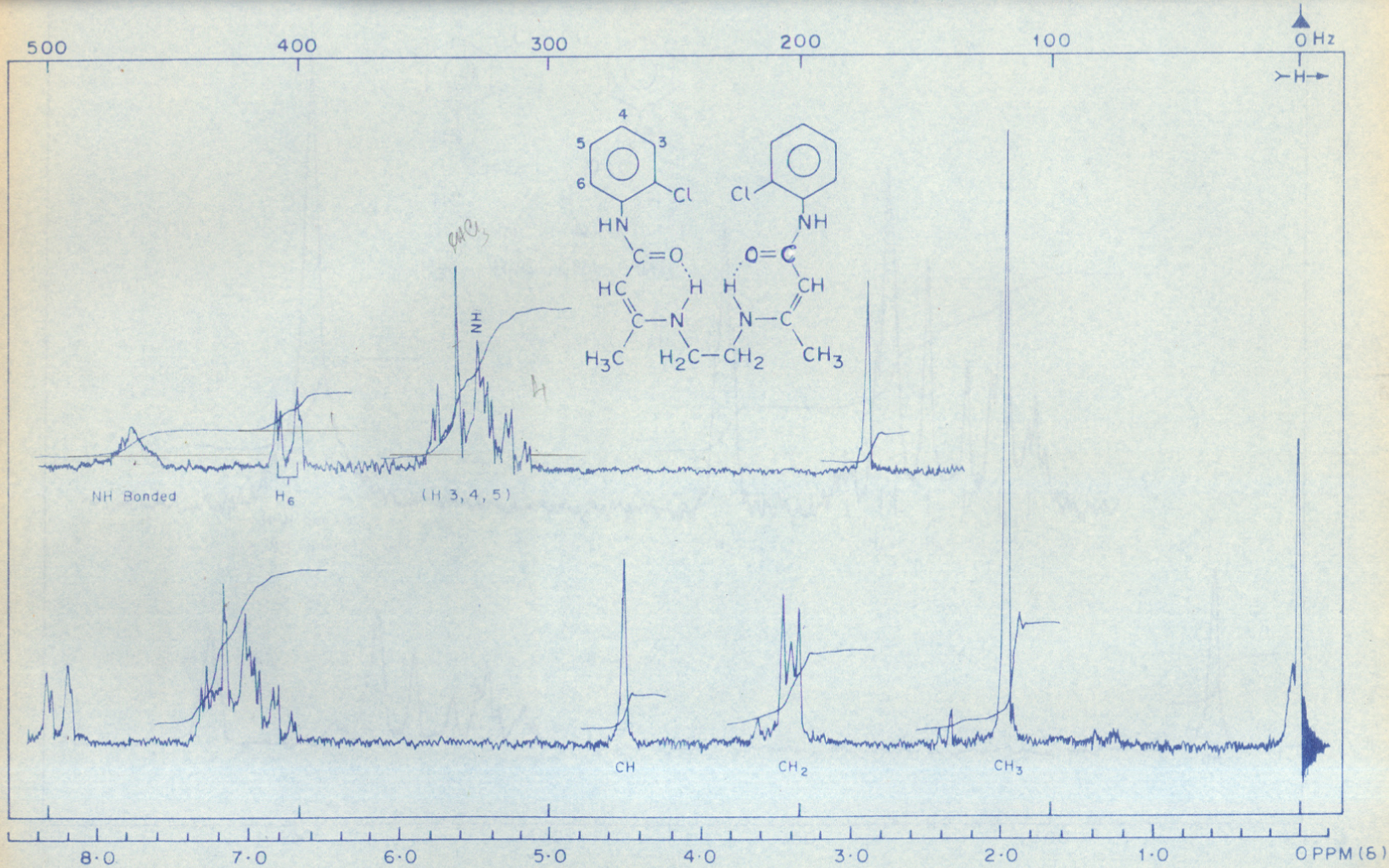


FIG. 7. PMR SPECTRUM OF N,N'-ETHYLENEBIS(2-CHLOROACETOACETANILIDE) IN $CDCl_3$.

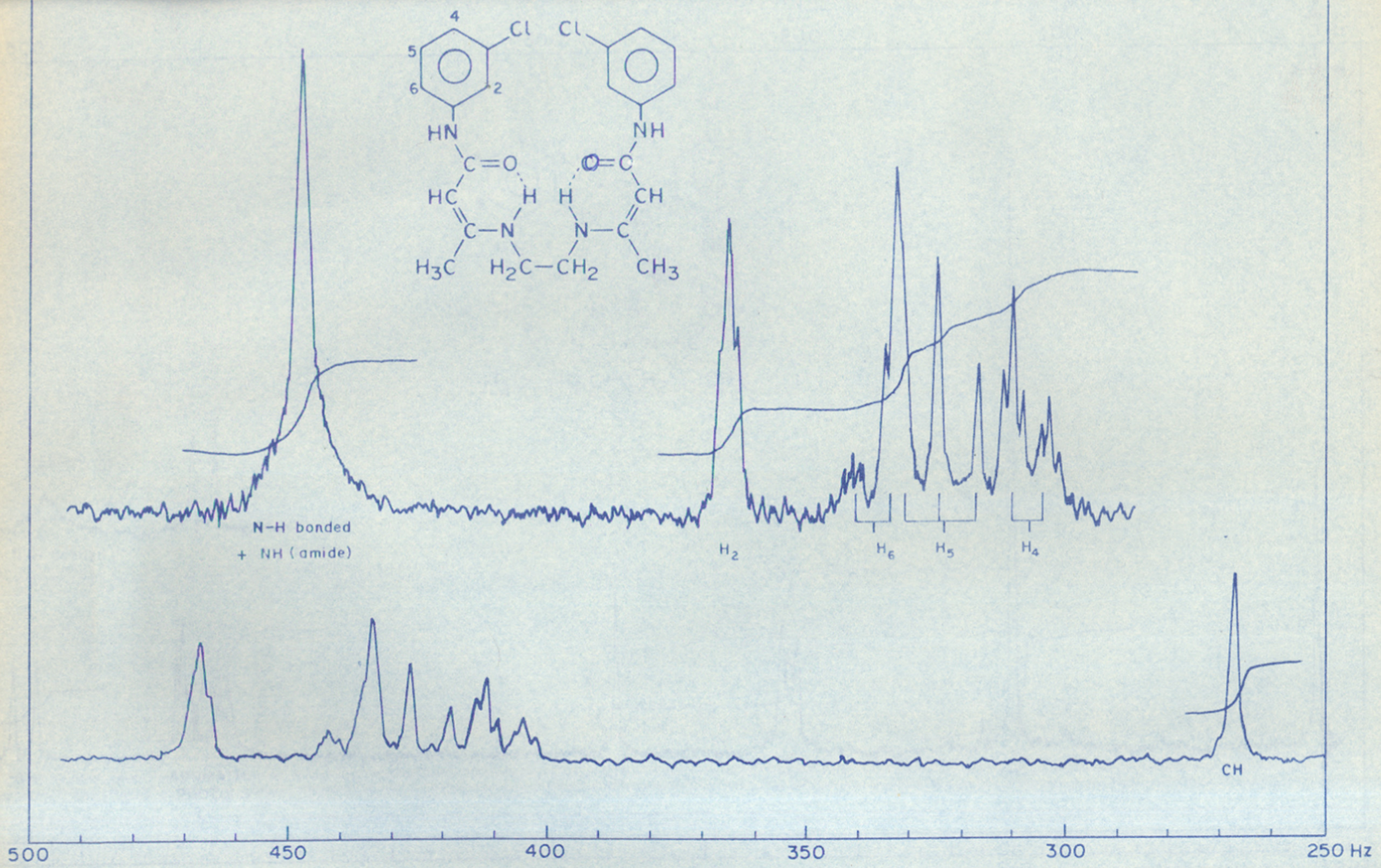


FIG. 8. PMR SPECTRUM OF N,N'-ETHYLENEBIS(3-CHLOROACETOACETANILIDE) IN DRY DMSO.

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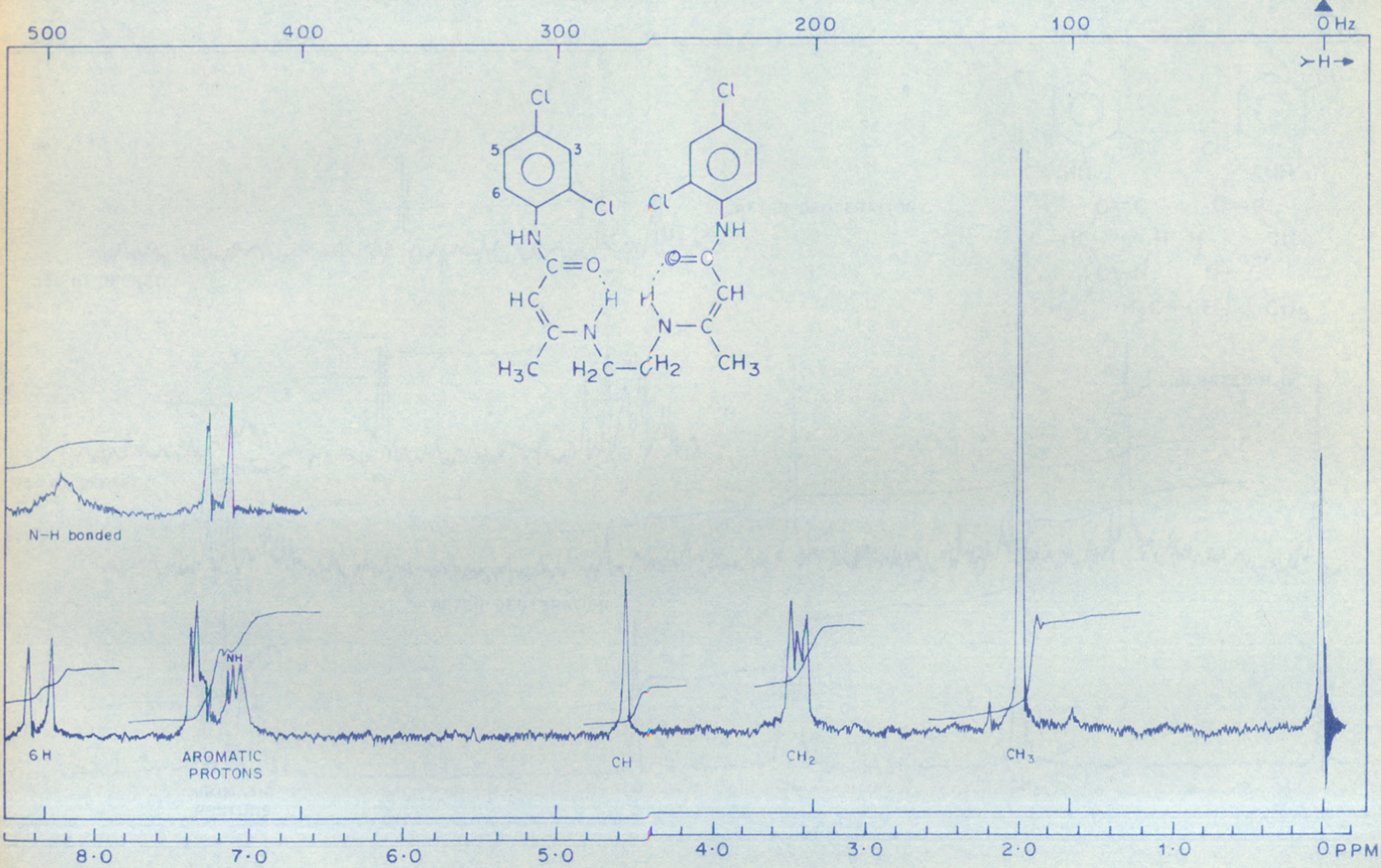


FIG. 9. PMR SPECTRUM OF N,N'-ETHYLENEBIS(2,4-DICHLOROACETOACETANILIDE) IN $CDCl_3$

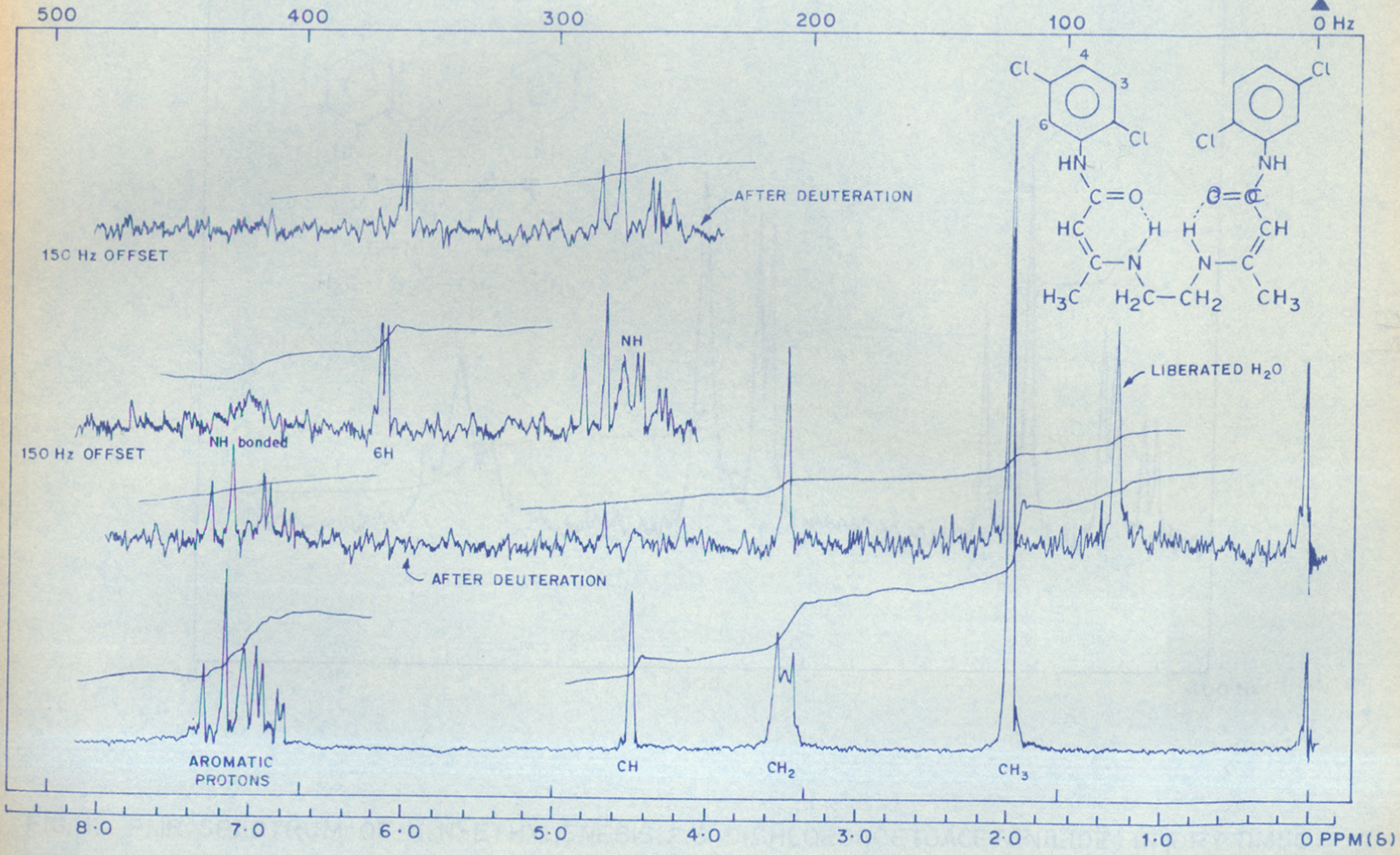


FIG. 10. PMR SPECTRUM OF N, N'-ETHYLENEBIS (2,5-DICHLOROACETOACETANILIDE) IN CCl_4.

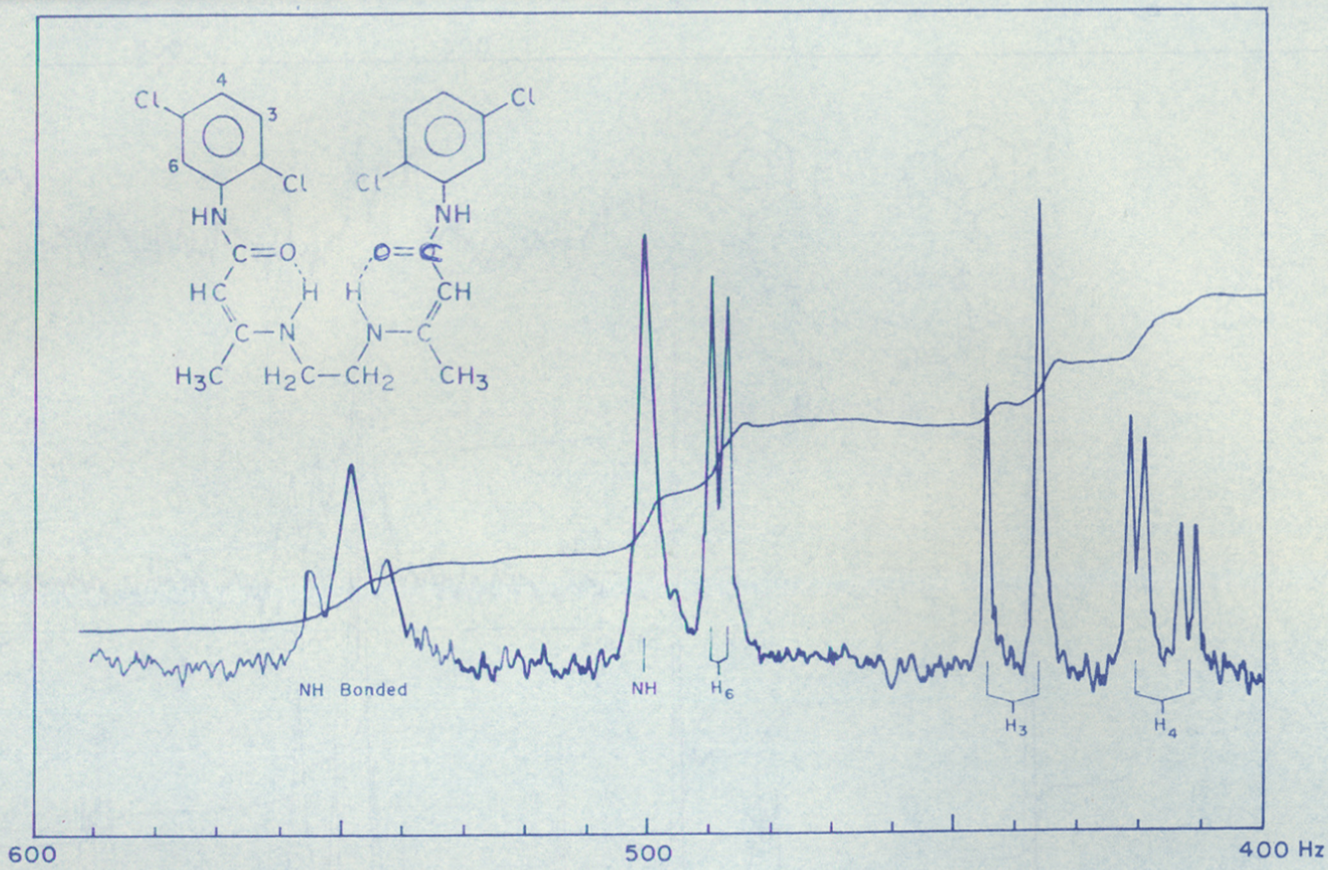


FIG. 11. PMR SPECTRUM OF N,N'-ETHYLENEBIS(2,5-DICHLOROACETOACETANILIDE) IN DRY DMSO.

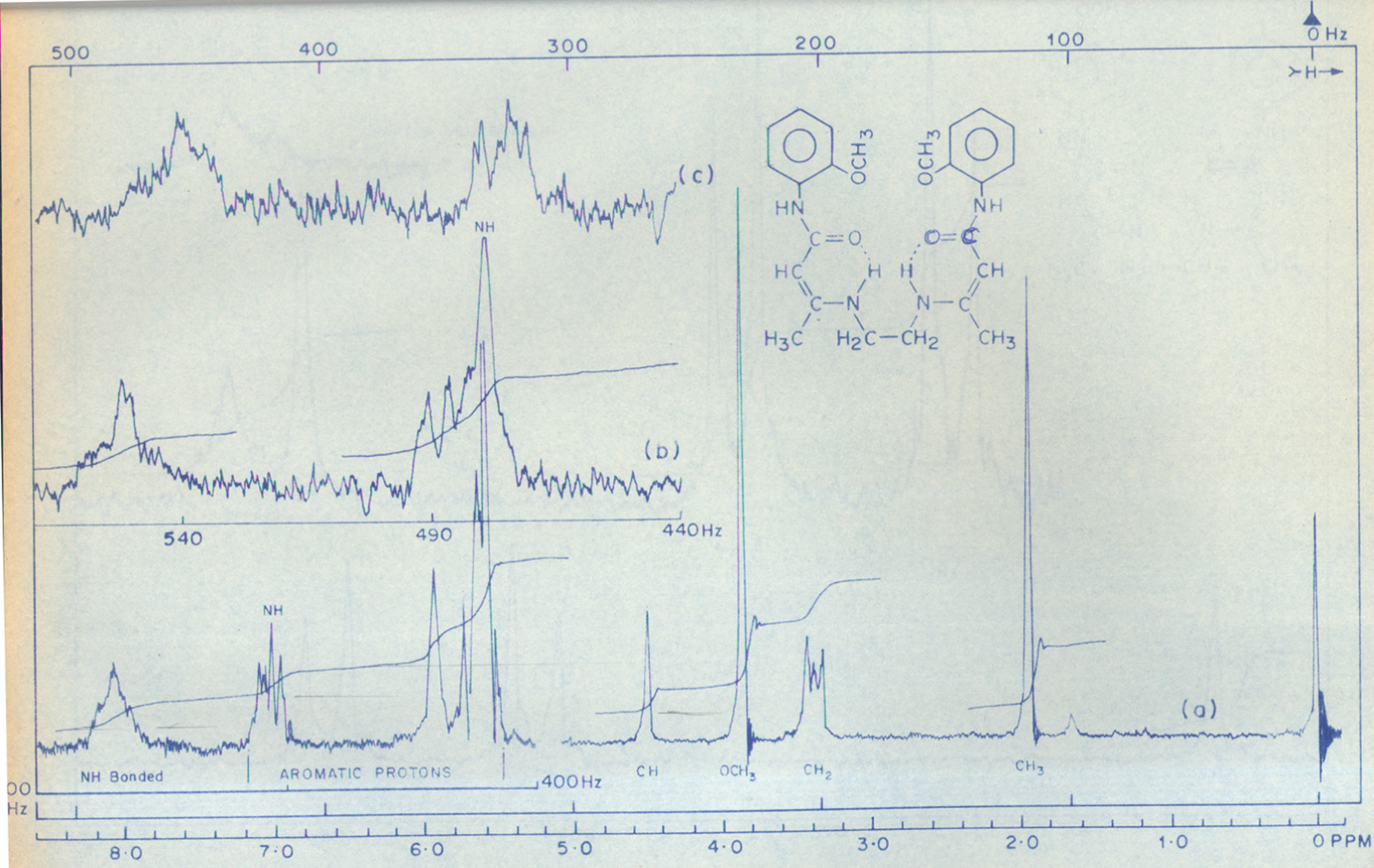


FIG. 12. PMR SPECTRA OF N,N'-ETHYLENEBIS(2-METHOXYACETOACETANILIDE)
(a) IN $CDCl_3$, (b) IN DRY DMSO, (c) AFTER DEUTERATION IN DMSO.

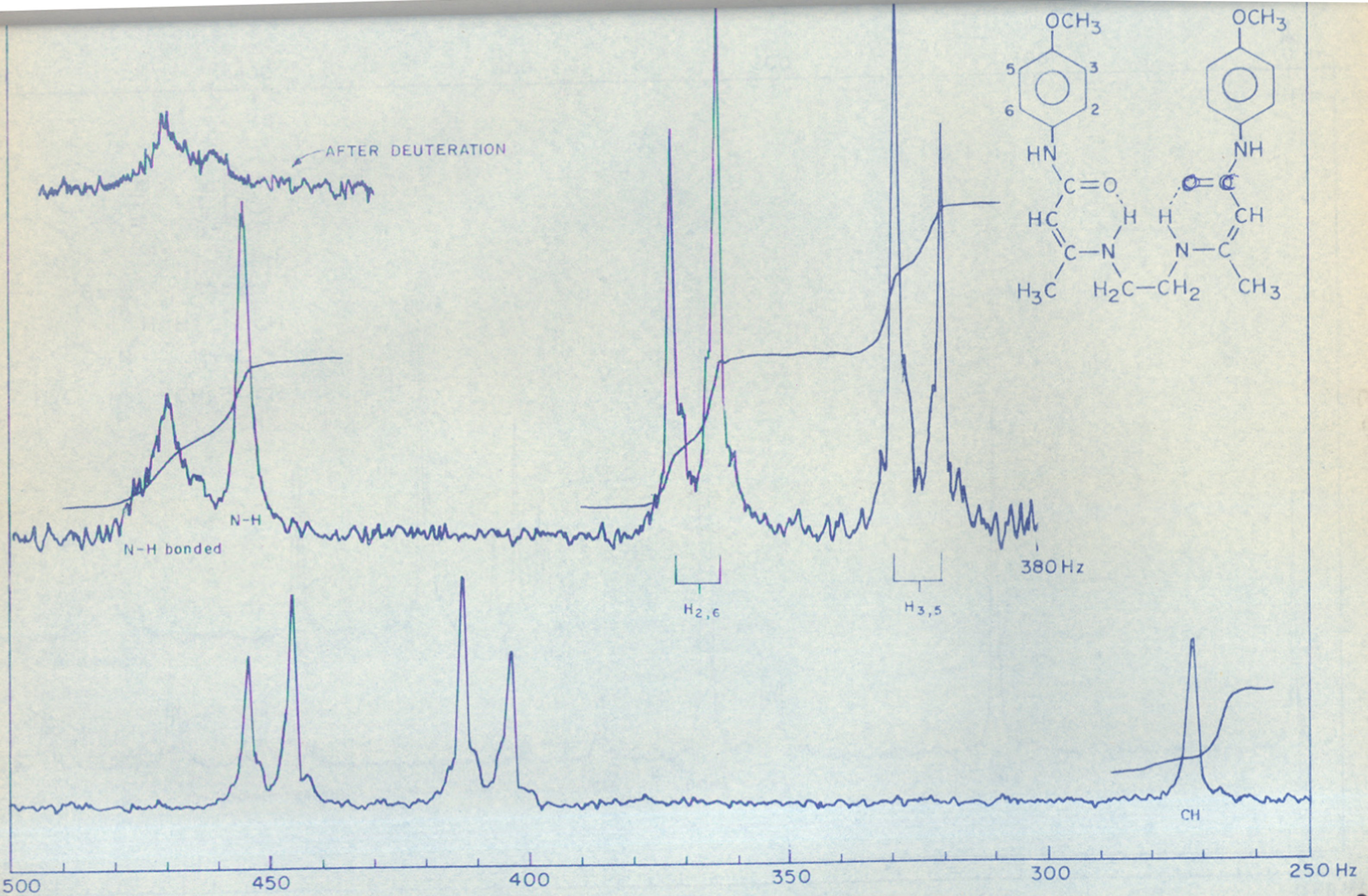


FIG.13. PMR SPECTRUM OF N,N'-ETHYLENEBIS(4-METHOXYACETOACETANILIDE) IN DRY DMSO

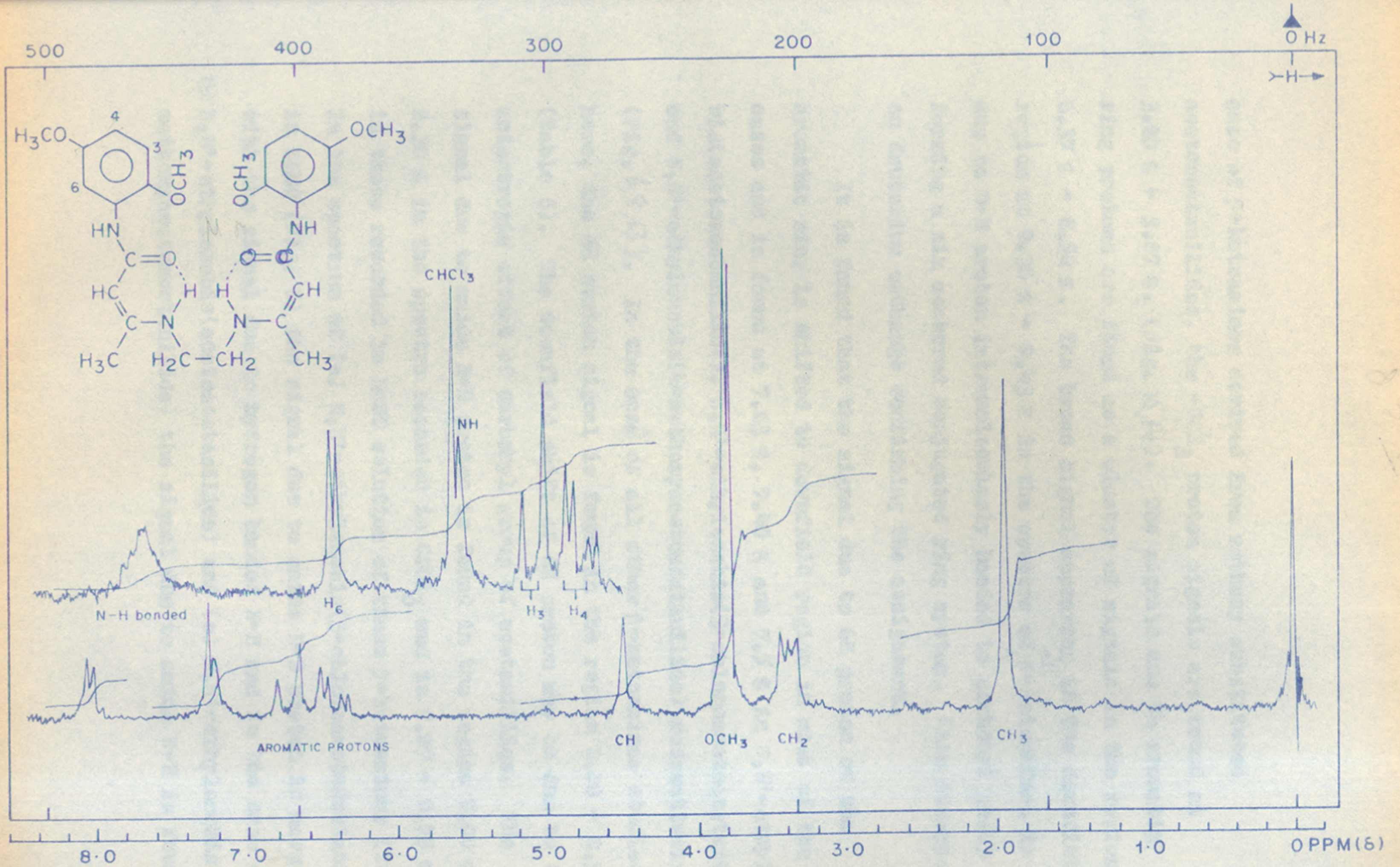


FIG. 14. PMR SPECTRUM OF N, N'-ETHYLENEBIS(2,5-DIMETHOXYACETOACETANILIDE) IN CDCl$_3$.

case of β-ketoamines derived from methoxy substituted acetoacetanilides, the $-OCH_3$ proton signals are found at 3.80 δ - 3.87 δ. (Fig. 12,14). The signals due to aromatic ring protons are found as a cluster of signals in the region 6.37 δ - 8.50 δ. The broad signal appearing in the downfield region at 9.30 δ - 9.43 δ in the spectra of all β-ketoamines is due to N-H proton intramolecularly bonded to carbonyl group forming a six membered conjugated ring system. This disappears on deuterium exchange confirming the assignment.

It is found that the signal due to 6H proton of the aromatic ring is shifted to downfield region in most of the cases and is found at 7.63 δ, 7.40 δ and 7.5 δ in N,N'-ethylenebis(acetoacetanilide), N,N'-ethylenebis(3-chloroacetoacetanilide) and N,N'-ethylenebis(4-methoxyacetoacetanilide) respectively (Fig. 6,8,13). In the case of all other β-ketoamines studied here, the 6H proton signal is found in the region 8.00 - 8.50 δ (Table 6). The downfield shift of 6H proton may be due to the anisotropic effect of carbonyl group of acetanilides. The signal due to amide N-H proton is found in the region 7.00 δ - 8.30 δ in the spectra recorded in $CDCl_3$ and in 7.97 - 9.75 δ in those recorded in DMSO solution of these β-ketoamines (Table 6). In the spectrum of (a) N,N'-ethylenebis(3-chloroacetoacetanilide) in DMSO (Fig. 8) the signal due to amide N-H proton is merged with the signal due to hydrogen bonded N-H and in the case of (b) N,N'-ethylenebis(acetoacetanilide) and (c) N,N'-ethylenebis(4-methoxyacetoacetanilide) the signal due to amide N-H is found

Table - 6

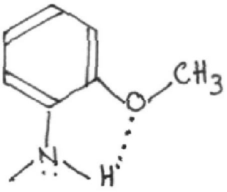
Chemical shift of 6H, amide N-H ~~and hydrogen bonded N-H~~ protons ppm(δ)

		6H	Amide N-H proton CDCl$_3$	 DMSO
1.	N,N'-ethylenebis(acetoacetanilide)	7.63*	-	9.10
2.	N,N'-ethylenebis(2-chloroacetoacetanilide)	8.33	7.00	-
3.	N,N'-ethylenebis(3-chloroacetoacetanilide)	7.40*	-	9.15
4.	N,N'-ethylenebis(2,4-dichloroacetoacetanilide)	8.33	7.03	-
5.	N,N'-ethylenebis(2,5-dichloroacetoacetanilide)	8.50	7.05	8.50
6.	N,N8-ethylenebis(2-methoxyacetoacetanilide)	8.33	7.18 8.30	7.97
7.	N,N'-ethylenebis(4-methoxyacetoacetanilide)	7.50	-	8.93
8.	N,N'-ethylenebis(2,5-dimethoxyacetoacetanilide)	8.03	7.21	-

* Value from DMSO solution spectra.

near the bonded N-H proton signal at 9.1 δ and 8.93 δ respectively. These assignments were confirmed by D_2O exchange (Fig. 6,13). In case of (a) the deuterium exchange study could not be carried out as the ligand separated out on addition of D_2O. The spectrum of N,N'-ethylenebis(2,5-dichloroacetoacetanilide) in dry DMSO shows the amide N-H proton signal at 8.50 δ. In this case the signal due to intramolecularly bonded N-H proton appears as a triplet due to coupling with $-CH_2$ proton (Fig.11).

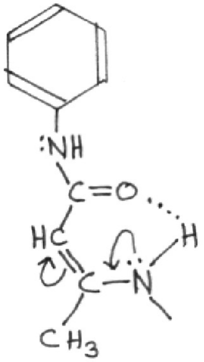
In order to confirm these assignments, deuterium exchange studies on N,N'-ethylenebis(2,5-dichloroacetoacetanilide), the most soluble compound in carbon tetrachloride, (Fig 10) and N,N'-ethylenebis(2-methoxyacetoacetanilide) in DMSO (Fig.12) were carried out. In the spectrum of N,N'-ethylenebis(2,5-dichloroacetoacetanilide), a signal at 7.03 δ disappears and this signal is assigned to amide N-H proton. In the case of N,N'-ethylenebis(2-methoxyacetoacetanilide) (Fig. 9) a signal at 8.23 δ disappears and therefore similarly is assigned to amide N-H proton. The shift of N-H proton to downfield in the latter case may be due to hydrogen bonding between amide N-H and $-OCH_3$ group attached at ortho position forming a five membered chelate ring. This signal appears in the same position even in DMSO spectrum.



Further, it is observed that the intramolecularly bonded N-H proton is not easily deuterated indicating that the hydrogen atom is very strongly held between the carbonyl oxygen and amine nitrogen atom. Warming of the sample solution with D_2O or keeping it overnight showed partial disappearance of this signal.

Another characteristic change occured in the spectrum of N,N'-ethylenebis(2,5-dichloroacetoacetanilide) after deuteration (Fig. 10) is the disappearance of 4.45 δ signal attributed to CH proton of the hydrogen bonded conjugated six membered ring. The appearance of CH proton signal at ~ 4.5 δ in the upfield region rather than in the expected region (4.9 δ - 5.3 δ) is due to an enamine structure.

Our attempts to prepare metal chelates of these ligands by adopting aqueous and non-aqueous methods[4] failed. This is to a large extent due to the hydrolytic instability of the metal-chelates towards moisture or any nucleophile present in the reaction. Furthermore, it is found that the reactivity



of the substituted β-diketones decreases as $-CH_3$ groups are replaced by aromatic rings in the order acetylacetone > benzoylacetone > dibenzoylmethane. It is known that the acetoacetanilides are much less reactive due to presence of anilide groups than the above compounds. It is not surprising, therefore, to find that the β-ketoamines derived from them also show the same trend in their reactivity.

Another significant factor which contributes to the unreactive nature of these β-ketoamines is the presence of a very strong intramolecularly bonded hydrogen atom. The replacement of such a hydrogen with a metal ion seems to be difficult. D_2O exchange studies showed that the bonded hydrogen is not readily exchanged and this supports the above assumption.

REFERENCES

References

1. L.Sacconi, Coord.Chem.Rev., 1, 126(1966).

2. S.Yamada, Coord.Chem.Rev., 1, 415(1966).

3. N.H. Cromwell, Chem.Rev., 38,83 (1946).

4. R.H. Holm, G.W. Everett, Jr. and A.Chakravorty, Prog. in Inorg.Chem., 7, 83(1966).

5. M. Calligaries, G.Nardin and L.Randaccio, Coord.Chem.Rev.,7, 385 (1971).

6. M.D.Hobday and T.D. Smith, Coord.Chem.Rev., 9, 311(1972-73).

7. H.S. Maslen and T.M. Waters, Coord.Chem.Rev., 17, 137(1975).

8. R.H. Holm and M.J.O'Connor, Prog. in Inorg.Chem., 14,253(1971).

9. B.O. West, New Pathways in Inorganic Chemistry, Cambridge University Press, 303,(1968).

10. G.McLendon and A.E. Martell, Coord.Chem.Rev., 19, 1 (1976).

11. A.E. Martell and M.Calvin, Chemistry of the Metal Chelated Compounds, Prentice-Hall,Inc., N.J.(USA), (1956) 3rd Ed.

12. H.Schiff, Ann., Suppl., 3, 343 (1864).

13. C.Ettling, Ann., 35,241 (1840).

14. H.Schiff, Ann., 150, 193 (1869).

15. M. Delepine, Bull.Soc.,Chim.France, 21, 943 (1899).

16. J.V. Dubsky and A. Sokol, Coll.Czech.Chem.Comm., 3,548 (1931).

17. P.Pfeiffer, E.Buchholz and O.Bauer, J.Prakt.Chem., 129,163,(1931).

18. P.Pfeiffer, E.Breith, E.Lubbe and T.Tsumaki, Ann., 503, 84 (1933).

19. P.Pfeiffer and H.Pfitzinger, J.Prakt.Chem., 145,243(1936).

20. P.Pfeiffer, T.Hesse, H.Pfitzinger, W.Scholl and H.Thielert, J.Prakt.Chem., 149,217(1937).

21. P.Pfeiffer and H.Thielert, Chem.Ber., 71B, 119(1938).

22. P.Pfeiffer, W.Christeleit, T.Hesse, H.Pfitzinger and H.Thielert, J.Prakt.Chem., 150, 261(1938).

23. P.Pfeiffer, H.Thielert and H.Glaser, J.Prakt.Chem., 152, 145(1939).

24. P.Pfeiffer and H.Glaser, J.Prakt.Chem., 153,265(1939).

25. P.Pfeiffer and H.Krebs, J.Prakt.Chem., 155, 77(1940).

26. P.Pfeiffer and S. Saure, Chem.Ber., 74B, 935(1941).

27. P.Pfeiffer, Angew.Chem., 53, 93 (1940).

28. P.Pfeiffer, W.Offermann and H.Werner, J.Prakt.Chem., 159, 313(1942).

29. H.Thielert and P.Pfeiffer, Chem.Ber., 71,1399(1938).

30. ~~A.~~G.O. Dudek and E.P. Dudek, Chem.Comm. 464 (1965).

31. J.J. Charette, Spectrochim.Acta, 19A, 1275(1963).

32. A. Combes, Compt.Rend., 108, 1252(1899).

33. G.T. Morgan and J.D. Main-Smith, J.Chem.Soc.,127,2030 (1925).

34. G.T. Morgan and J.D. Main-Smith, J.Chem.Soc., 912(1926).

35. G.O. Dudek and R.H. Holm, J.Am.Chem.Soc., 83,2099(1961).

36. H.F. Holtzclaw, Jr., J.P. Collman and R.M. Alire, J.Am.Chem.Soc., 80, 1100(1958).

37. J. Dabrowski and U.Dabrowska, Roczniki Chem., 32, 821(1958).

38. N.H. Cromwell, F.A. Miller, A.R. Johnson, R.L. Frank, and D.J. Wallace, J.Am.Chem.Soc., 71, 3337(1949).

39. J.Weinstein and G.M. Wyman, J.Org.Chem., 23,1618 (1958).

40. B.Witkop, J.Am.Chem.Soc., 78, 2873 (1956).

41. K. Ueno and A.E. Martell, J.Phys.Chem., 59, 998(1955).

42. M. Honda and G.Schwarzenbach, Helv.Chim.Acta, 40,27 (1957).

43. D.F. Martin, G.A. Janusonis and B.B. Martin, J.Am.Chem.Soc., 83, 73 (1961).

44. D.F. Martin and F.F. Cantwell, J.Inorg.Nucl.Chem., 26,2219(1964).

45. P.Teyssie and J.J.Cha~~r~~rette, Spectrochim.Acta, 19, 1407(1963) and references therein.

46. G.O. Dudek and R.H. Holm., J.Am.Chem.Soc., 84,2691(1962).

47. G.O. Dudek and R.H. Holm, J.Am.Chem.Soc., 83, 3914 (1961).

48. G.O. Dudek and G.P. Volpp, J.Am.Chem.Soc., 85, 2697 (1963).

49. G.O. Dudek and E.P. Dudek, J.Am.Chem.Soc., 86, 4283(1964).

50. C. Beyer, Ber., 20, 1767 (1887).

51. L.Claisen, Ber., 59, 144 (1926).

52. P.J. McCarthy and A.E. Martell, J.Am.Chem.Soc., 78, 264(1956).

53. K.Ueno and A.E. Martell, J.Phys.Chem., 61, 257 (1957).

54. R.J. HoVey and A.E. Martell, J.Am.Chem.Soc., 82, 364 (1960).

55. R.J. Hovey and A.E. Martell, J.Am.Chem.Soc., 82, 2697 (1960).

56. G.E. Gurr, Inorg.Chem., 3, 614 (1964).

57. G.W. Everett, Jr. and R.H. Holm, J.Am.Chem.Soc., 87, 2117 (19650;
Proc.Chem.Soc., 238 (1964).

58. F. Lions and K.V. Martin, J.Am.Chem.Soc., 80, 3858 (1958).

59. R.H. Holm, J.Am.Chem.Soc., 82, 5632 (1960).

60. R.D. Archer, Inorg.Chem., 2, 292 (1963).

61. T.M. Hseu, D.F. Martin and T. Moeller, Inorg.Chem., 2, 587(1963).

62. E. Uhlemann, J.Prakt.Chem., 21, 277 (1963).

63. A. Combes and C.Combes, Bull.Soc.Chim., France [3], 7, 778(1892).

64. A.S. Kudryavtsev and I.A. Savich, Vestn.Mosk.Univ., Ser II,
Khim., 17(3), 55(1962); 18(4), 61 (1963).

65. P.J. McCarthy, R.J. Hovey, K.Ueno and A.E. Martell,
J.Am.Chem.Soc., 77, 5820 (1955).

66. A.E. Martell, R.L. Belford and M.Calvin, J.Inorg.Nucl.Chem.,
5, 170 (1958).

67. M.J. O'Connor and B.O. West, Ph.D. Thesis - M.J. O'Connor,
Monash University (1966).

68. J.P. Collman and E.T. Kittleman, Inorg.Chem., 1, 499 (1962).

69. A.W. Struss and D.F. Martin, J.Inorg.Nucl.Chem., 25, 1409(1963).

70. E.J. Olszewski and D.F. Martin, J.Inorg.Nucl.Chem., 27, 345(1965).

71. E.J. Olszewski and D.F. Martin, J.Inorg.Nucl.Chem., 26, 1577(1964).

93. J.Csaszar and J.Balog, Acta Chim.Acad.Sci.Hung, 87, 321 (1975).

94. R.K. Kohli and P.K. Bhattacharya, Indian J.Chem., 15A, 566 (1977).

95. A.Syamal, Coord.Chem;Rev., 17, 309 (1975).

96. K.K. Chatterjee and B.E. Douglas, Spectrochim. Acta, 21, 1625 (1965).

97. J.Charette, G.Fatthansl, P.H. Teyssie, Spectrochim.Acta, 20, 597 (1964).

98. J.E. Kovacic, Spectrochim.Acta, 23A, 183 (1967).

99. E.P. Dudek and G.O. Dudek, Inorg.Nucl.Chem.Lett., 3,241 (1967).

100. G.O. Dudek and E.P. Dudek, J.Am.Chem.Soc., 88, 2407 (1966).

101. V.Bekarek, Coll.Czech.Chem.Comm., 33, 994 (1968).

102. G.C. Percy and D.A. Thornton, J.Inorg.Nucl.Chem., 34, 3357 (1972).

103. E.C. Alyea and A.Malek, Can.J.Chem., 53, 939 (1975).

104. N.M.D. Brown and D.G. Nonhebel, Tetrahedron, 24, 2655 (1968).

105. N.S. Biradar and V.H. Kulkarni, Z.Anorg.Alleg.Chem., 387, 275 (1972).

106. N.S. Biradar, M.D. Patil and T.R. Goudar, J.Inorg.Nucl.Chem., 37, 1437 (1975).

107. A.K. Mujamdar and B.C. Bhattacharya, J.Inorg.Nucl.Chem., 28,1215 (1966); 30,1116 (1968); J.Indian Chem.Soc.,53, 1208 (1976).

108. H.Mahanta and K.C. Dash, J.Inorg.Nucl.Chem., 39, 1345 (1977).

109. S.K. Agarwal, and J.P. Tandan, Monatshefte fur Chemie, 107, 777 (1976).

110. S.K. Agrawal and J.P. Tandon, Monatshefte fur Chemie, 108, 175 (1977).

111. G.E. Bately and D.P. Graddon, Aust.J.Chem., 20, 877,885 (1967).

112. A.I. Vogel, "A Text Book of Quantitative Inorganic Analysis" Longman's Green and Co.Ltd., London, p.517 (1963).

113. A.W. Baker and A.T. Shulgin, J.Am.Chem.Soc., 81, 1523 (1959).

114. C.N.R. Rao, "Chemical Application of Infrared Spectroscopy" Academic Press, New York (1967).

115. C.S. Marvel, S.A. Aspey and E.A. Dudley, J.Am.Chem:Soc., 78,4905 (1956).

116. K.Tabei and E.Saitoy, Bull.Chem.Soc., Japan, 42,1440,2693 (1969).

117. High Resolution NMR spectra catalog, compiled by N.S. Bhacca, D.P. Hollis, L.F. Johnson and E.A. Pier, Instmument Division, Varian Associates (1963).

118. D.J. Ellas and R.G. Gillis, Aust. J.Chem., 19, 251 (1966).

119. I.W. Fraser, J.L. Garnett and I.K. Gregor, Org.Mass Spectrom., 10, 1047 (1975).

120. M.N. Sastry and T.P. Prasad, Talanta, 14, 481 (1967).

121. A.M. Hundekar, P.Umapathy and D.N. Sen - in press

122. G. Urbain and H.Lacombe, Compt.Rend., 133, 874 (1917).

123. C.M. Harris and E.Sinn, J.Inorg.Nucl.Chem., 30,2723 (1968).

124. J.Balog and J.Csaszar, Acta Chim.Acad.Sci.Hung., 88, 53 (1976).

125. K. Ueno and A.E. Martell, J.Phys.Chem.,60, 1270 (1956).

126. M.Oki and H.Iwamura, J.Am.Chem.Soc., 89, 576 (1967).

127. P.J. Krueger, Can.J.Chem., 42, 201 (1964); 41, 363 (1963).

128. K.K. Ramaswamy, C.I. Jose and D.N. Sen, Indian J.Chem., 5, 156 (1967).

129. L.J. Bellamy and L.Beecher, J.Chem.Soc., 4487 (1954).

130. E.V. Dose, K.M.M. Murphy and L.J. Wilson, Inorg.Chem., 15, 2622 (1976).

131. R.H. Balundgi and A.Chakravorty, J.Inorg.Nucl.Chem., 35, 2078 (1973).

132. K. Dey and S.K. Sen, J.Indian Chem.Soc., 54, 447 (1977).

133. R.J. Abraham and H.J. Bernstein, Can.J.Chem., 37,1056 (1957).

134. V.J. Kowaleski and D.G. dekowasleski, J.Chem.Phys., 32, 1272 (1960).

135. H.S. Gutowsky and C.H. Holm, J.Chem.Phys., 25, 1228 (1956).

136. A. Bigotto, V.Galasso and G.DeAlti, Spectrochim.Acta, 28A, 1581 (1972).

137. BIOS, Final Report No.986, Part I, p.22.

138. J.Lecomte, Discussion Faraday Soc., 9, 125 (1950).

139. R. West and R.Riley, J.Inorg.Nucl.Chem., 5, 295 (1958).

140. K.E. Lawson, Spectrochim.Acta, 17, 248 (1961).

141. K. Nakamoto, P.J. McCarthy and A.E. Martell, J.Am.Chem.Soc., 83, 1272 (1961).

142 . D.N. Sen and P. Umapathy, Indian J.Chem., 4, 454,455 (1966).

143. D.N. Sen and P. Umapathy, Indian J.Chem., 6, 516 (1968).

144. D.N. Sen and N. Thankarajan, Indian J.Chem., 6, 278 (1968).

145. P. Umapathy, C.I. Jose,and D.N. Sen, J.Indian Chem.Soc., 48, 1131 (1971).

146. A.P. Budhkar, P. Umapathy and D.N. Sen, Indian J.Chem., 9, 376 (1971).

147. J.N. Patil and D.N. Sen, Indian J.Chem., 13, 291 (1975).

148. T.J. Lane CSC and A.J. Kandathil, J.Am.Chem.Soc., 83, 3782 (1961).

149. E.W. Gooden, Aust.J.Chem., 18, 637 (1965).

150. A. Arch and R.C. Young, 'Inorganic Synthesis', McGrow Hill, Vol. 2, 17 (1946).

151. G.T. Morgan and H.W. Moss, J.Chem.Soc., 105, 189 (1914).
M.M. Jones, J.Am.Chem.Soc., 81, 3188 (1959).

152. T. Moeller, 'Inorganic Syntheses', McGraw Hill, Vol.3, 4 (1950).

153. V. Amirthalingam, V.M. Padmanabhan and J.Shankar, Acta Cryst., 13, 201 (1960).

154. (Miss) H.V. Berde, V.N. Gogte, C.I. Jose and B.D. Tilak, Indian J.Chem., 8, 493 (1970).