^{1}H NMR & ^{13}C NMR Spectra of Some Nitrogen and Sulphur containing ligands and their complexes

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Abstract : ^{1}H NMR spectra of a number of Nitrogen and Sulphur containing ligands and their complexes with some transition and non transition metals have been recorded. The ligands used in the work are thiourea, thiosemicarbazide, ammonium dithiocarbamate and 1-substituted-tetrazoline-5-thione and metal ions used in this work are in Zn(II) , Cd(II), Hg(II), Co(II), Ni(II), Mn(II), As(III), Bi(III) and V(v) .

*Keywords***: Spectra, Ligands, Complexes.**

I. INTRODUCTION

The structure of the complexes were established by micro analysis, cryoscopy, conductometric measurement and infrared spectroscopy in the range of 4000-200cm-1 , electronic spectroscopy in the range of 200nm to 1000nm.In the case of Ni(II) and Co(II)- complexes, crystal field parameters have been calculated and the structure of the complexes conclusively established. Magnetic moment measurements were also made for Co(II), Ni(II) and Mn(II)- complexes [1].

NMR spectrometer as a tool of choice in characterizing molecules, from the structures of natural products and synthetic organic compounds to biomolecules and organometallic complexes. NMR spectroscopy takes advantage of the interaction between nuclei that are acting as tiny magnets and an external magnetic field and this provides a powerful means of probing the chemical bonding and environment of the nucleus. These phenomena are key to the applicability of ^{1}H and ^{13}C NMR to natural products [2.3].

^{1}H NMR Spectra

Hydrogen is present in almost every organic molecule, and its major isotope, ^{1}H, has an abundance of 98.985%. The ^{1}H nucleus reports a frequency specific to its immediate vicinity in an NMR spectrum. This frequency is extremely sensitive to the electronic environment thus giving each ^{1}H nucleus in an organic compound a type of identification number, called the NMR chemical shift. Magnetic nuclei, such as ^{1}H, also interact with each other. In solution or liquid-state NMR spectroscopy, these interactions, called couplings, are observed as "splitting" of lines in an NMR spectrum. The magnitude of these couplings not only depends on the number and type of bonds separating the interacting pair of ^{1}H nuclei but also on the spatial orientation between the nuclei. Both NMR chemical shifts and coupling constants provide immense information regarding structure and environment. Hence, NMR spectroscopy has become a powerful tool for the determination of organic structure [4-9].

These NMR interactions (chemical shifts and coupling constants), although very sensitive, are quite weak such that improvements in their detection have been one of the primary goals of developments in NMR instrumentation. Such limitations are no longer severe. The use of pulses and data processing by Fourier transformation, first introduced by Ernst and Anderson [10-15] and the availability of high-field superconducting magnets have allowed for efficient signal averaging such that nowadays, with an 11 T magnet (500 MHz), a ^{1}H NMR spectrum can be obtained even from very dilute solutions (micromolar concentration).

Pulse Fourier transform NMR spectroscopy, as in other spectroscopic methods, involves transitions between energy levels. However, unlike other spectroscopic methods, the transition probability in an NMR excitation is the same regardless of chemical environment. NMR spectroscopy does not need to consider oscillator strengths or extinction coefficients, which are important for infrared and UV-visible spectroscopy, respectively. The intensity of an NMR signal is determined solely by the excitation pulse, strength of the external magnetic field, and temperature. The magnetic field strength and temperature determine the Boltzmann population difference between the two energy levels while the excitation pulse dictates the extent of the transition. Since only one pulse is often used to excite all of the ^{1}H nuclei in a sample, the extent of transitions is the same for all. Furthermore, the NMR chemical shift, which reflects the differences in resonance frequencies of inequivalent ^{1}H nuclei, is very small: the differences are in parts per million (ppm). Hence, the Boltzmann distribution for the two spin states is essentially the same for every ^{1}H in a molecule. Indeed, as early as 1963, the area under each peak in a ^{1}H NMR spectrum has been shown to correspond proportionally to the number of hydrogen atoms sharing the same environment in a given compound [16-20]. This quantitative aspect applies not only to pure substances but also to mixtures. In fact, during the same year, a successful quantitative analysis by ^{1}H NMR spectroscopy of a mixture of aspirin, phenacetin, and caffeine was demonstrated.

^{13}C NMR spectroscopy

^{13}C also has a spin of ½ and is therefore likewise NMR active. However, because the ^{13}C isotope occurs at only 1.108%, it is difficult to observe. (The major carbon isotope, ^{12}C, is not NMR-active.) David Grant and coworkers published a series of papers on ^{13}C NMR spectroscopy that spanned two decades . In the first paper of this series, inherent difficulties in observing ^{13}C NMR spectra were addressed by proton decoupling and sample spinning. Since carbon atoms are frequently attached to hydrogen atoms in organic compounds, ^{13}C-^{1}H coupling is present and leads to splitting of ^{13}C resonances. Proton decoupling removes this interaction, consolidating multiple 13C peaks into a single taller peak. Moreover, additional enhancement of ^{13}C signals is observed when the 1H spin populations are perturbed, similar to the effect observed by Overhauser with electron spins. Taking advantage of both the nuclear Overhauser effect (NOE) and the increased signal due to the collapse of multiple peaks, measurement of ^{13}C NMR spectra became routine and easy to interpret. Being in the proximity of more than one pair of electrons, ^{13}C nuclei offer a much wider range of chemical shifts than ^{1}H (200 ppm for ^{13}C versus 10 ppm for ^{1}H). In addition, since the probability that a ^{13}C nucleus is attached to another ^{13}C nucleus is very small (about 0.0001), ^{13}C-^{13}C couplings are usually not observed thereby providing a much simpler ^{13}C NMR spectrum [21].

Using ^{13}C NMR spectroscopy as a powerful analytical tool can be easily appreciated by considering the three isomers of a simple hydrocarbon C_5H_{12} . n-Pentane ($CH_3CH_2CH_2CH_2CH_3$), produces three peaks with a 1:2:2 intensity ratio, 2-methylbutane ((CH_3)$_2$$CHCH_2CH_3$) displays four peaks with a 1:1:2:1 intensity ratio, and neopentane ((CH_3)$_4$C) gives two peaks of 4:1 intensity ratio. For the above reasons, a qualitative and quantitative analysis that is nondestructive and requires no separation is possible with ^{13}C NMR spectroscopy [18]. All that one needs is a library of ^{13}C NMR spectra of all possible components, a good spectral prediction software, and an efficient algorithm that can do the search and construct a simulated spectrum that matches the observed spectrum. All of these requirements are already available today. A similar treatment has been shown to be feasible in determining the acyl profile in various vegetable oils [22] and in characterizing the various sesquiterpenes in essential oils from juniper, rosemary, cedarwood, and ginger [23].

II. PROCEDURE
The following complexes have been prepared:
(1)[Zn(IPT5TH)$_4$]SO$_4$
(2) Cd(IPT5TH)$_2$Cl$_2$]
(3) [Hg(IPT5TH)$_2$Cl$_2$]2H$_2$0
(4) Co(IPClPT5TH)$_2$Cl$_2$]
(5) [Mn(IPT5TH)$_2$ Cl$_2$]
(6)[As(OTDTC)$_3$(H$_2$0)$_2$]
(7) Sb(DTDTCH)$_2$Cl$_3$]
(8) (Bi(OTDTC)$_2$Cl(H$_2$O)$_2$]
(9) H+[V(TU)$_6$].H$_2$0
(10) NH$_4$+[V(TU)$_6$]
(11) [Ni(1PT5T)$_2$(H$_2$O)$_2$].H$_2$0
Complexes of Zn(II) ,Cd(II) , Hg(II), As(III), Sb(III) and Bi(III) were found to be diamagnetic expected.

The ^{1}HNMR spectra of urea contains a strong signal at 7.4 ppm corresponding to 4H atoms Of the urea molecule. This Indicates that all the protons of the urea molecule are magnetically and chemically equivalent.

The ^{1}HNMR spectra of thiosemicarbazide contain three broad signals at **δ**=4.55 ppm (2H). **δ**= 7.5 ppm (2H) and **δ**=8.78 ppm (GH). Olivia & =8.78 ppm signal of imino proton (N-H).

 δ = 7.5 ppm signal is due to SCNH$_2$ **δ**= 4.45 ppm signal is due to -C- N-NH2,
protons.

The large broadness of the three signals in because of quadrupole broadening because these protons are linked to N-atom. ^{1}HNMR spectra of L-phenyltetrazoline-5-thione and ammonium 5th dithiocarbamate have also been recorded

The physio-chemical investigations of the ligand and complexes indicate that Zn(II). Cd (II) and Hg (II)-complexes are tetrahedral in which the ligand is linked to the metal ions through S-atom only. Mn (II), Co (lI) and Ni(II) - complexes are octahedral in which the ligands are linked to the metal ions both through N-atom as well as through S-atom. As (III), Sb (II) and (BD) (III) complexes no triangular bipyramidal in which ligand molecule are linked only through S-atom [24].

III. RESULTS AND DISCUSSION
The structure and configuration of the complexes are supported by their Electronic spectra as well as their ^{1}HNMR spectra and ^{13}C spectra.^{13}C NMR spectra of H^{+}[V(TU)6]$^{-}$H$_2$O and NH$_4$V(TU)$_6$] have been recorded and they contain only I-signal of ^{13}C which confirms the equivalence of 6 molecules of thiourea linked to V^{5+}-ions and confirms their Octahedral structure

IV. ACKNOWLEDGEMENT

V. REFERENCES
[1]   Mardelli,M.gasparri,G.F.Battistim,G.C. & Mesatti , A , Chem.Commun , 187(1965)
[2]   Mirzubaimov,B& Toktomamatov,A,Chem.Abstr,103(4),513,6170Ed(1935)

[3]   Samus,NM,Zh.Neorg.Khim,8,72(1963)

[4]   Campbell ,MJ & Grzeskowiak,R,J Chem.Soc,4,396(1967)

[5]   William Dj & Wynne ,KJ Inorg Chem ,17,1108(1978)

[6]   Haines , R.A & Sun KKW, Cenad.J.Chem,46,3241(1968)

[7]   Podchainova,VN Chechneva ,AN & Krylov ,EI,ZH . NeoirgKhim , 10,535(1965)

[8]   Wiles ,DM,Gingras,BA&Supruchuk,T,Cannad.J.Chem,45,1735(1967)

[9]   Kozokov& Vostovska,Chem Abstr,43,1057(1949)

[10] Goddard,DR & Nwankivo,SL .J.Ind.Chem.Soc,51,387(1974)

[11] Goldstein.M&Urworth,WD,Inorg Chim Acta ,4,342(1971)

[12] Pannu,BS & Chopra , SL.J.Ameer.Chem.Soc,51,387(1974)

[13] Lucheski,PJ & Classes ,WA,Chem.Soc,78,42(1976)

[14] Nakanishi,K,IRAbs Spect,Holden – Day Inc ,SanFransisco,207(1964)

[15] Bellamy.LJ,IR Spectra of Complex Molecules ,John Willey & Sons ,INC ,NY (1956)

[16] Khan.MM,J,Inorg Nucl Chem ,39,25(1977)

[17] Kokot.E.Mockler,GM &Sefron,GL,Anat.J.Chem,28,299(1975)

[18] Singh,B&Singh,RD.J.Inorg,Nuclchem,39,25(1977)

[19] Watt,CW &Mc Commick ,BJ.Spectra.Chim .Acta,21,753(1965)

[20] Lippinott , ER ,Pselloos,JA & Tobin,MC.J.Chem Phys,20,536(1952)

[21] Haim,A & Sutin ,N,J.Ameer,Chem.Soc,88,434(1966)

[22] Ardon,M. & Taube,H,Ibid ,89,3661(1967)

[23] Kanth,KM,Pandeya,KB & Nigam ,HL Ind.j.Chem,11,103`(1973)

[24]   Lacaster, EW & Gordy ,GJ .Chem.Phys,19,118(1951) Idwm,Ibid,20,744(1952).