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NMR, ESR, NQR and IR Studies of Paramagnetic Macrocyclic Complexes of 1st Transition Series Metal Ions Exhibiting MLCT Phenomenon: A DFT Application. Part: III. Tris (2, 2′-bipyridine) Complexes

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Abstract: *DFT implemented in ADF.2012.01 was applied to study the structures of three macrocyclic paramagnetic hexa coordinate complexes: $[L_3M]^{2+}$ {M=V(II), Ni(II)}, and $[L_3Cr]^{3+}$ (L=2,2′-bipyridine) by four spectral techniques. After their pre-optimization, the software was run by using Single Point, LDA, Default, Relativity, Spin Orbit, ZORA, Unrestricted, None, Collinear, Nosym using TZP or TZ2P Basis sets in ESR/EPR/EFG/ZFS Program to obtain ESR parameters: g_{11}, g_{22}, g_{33}, g_{iso}, a_{11}, a_{22}, a_{33}, A_{ten}. More ESR parameters (g_n. A_{ten}, ZFS) and NQR parameters {η, q_{11}, q_{22}, q_{33}, NQCC} were obtained by replacing Spin Orbit by scalar command in a new ADF Input. The software was, then, run using the "NMR Program" with Single Point, Default, None, Collinear, Nosym using the same Basis sets leaving unrestricted command blank to obtain Shielding Constants (σM, σ^{13}C, σ^{17}O), Chemical Shifts (δM, δ^{13}C, δ^{17}O), two diamagnetic, four paramagnetic and four spin orbit contributing terms in σ values of the constituents. The software was also run to obtain IR frequencies of normal modes of the (3n-6) fundamental vibration bands of the complexes. Five parameters: σ, δ, g.A_{ten}, η, NQCC of ^{14}N; four parameters: σ, δ, g.A_{ten}, η of ^{13}C and three parameters: σ, δ, g.A_{ten}, of ^{1}H corroborated to infer that the 30 Carbons were of 5 different types, the 24 Hydrogens were of 4 different types but the 6 Nitrogens were of the same type spatially in the three studied complexes. This study was important because we could confirm MLCT phenomenon by NMR; calculated four more NMR, ESR and NQR parameters: H^, $\Delta E_{hf,}$ Asymmetric coefficient (η), Laplace equation; classified the 177 bands into their vibration symmetries and IR activities and calculated some thermal parameters of the complexes.*

Keywords: *Chemical Shift, Total NMR Shielding Tensor***,** *Nuclear Quadrupole Coupling Constant, Effective Spin Hamiltonian, Asymmetric Coefficient*

I. Introduction

Density Functional Theory (DFT) had been extensively applied to study the 2, 2′- bipyridine (*Bipy)* complexes of 1st transition series metal ions with the general formula $[Bipy_3M]^{n+}$ of the 1st transition metal ions such as Ti(III,IV) (*1, 2*) , V(III,IV)(*1, 2*), Cr(III)(*1, 3, 4*), Mn(II)(*1, 5*)**,** Fe(II)(*1, 6-8*), Co(II)(*1, 9, 10*)**,** Ni(II)(*1*)**,** and Cu(II)(*1*) where different researchers had studied their structures, electromagnetic properties, vibrational and optical properties along with Spin- State Cross-Over phenomenon and Jahn-Teller effect using different set of commands. The perusal of the reported work led us to conclude that DFT had hardly been used in the calculation of NMR, ESR and NQR parameters in *tris* complexes of 1st transition series metal ions**.** The NMR technique was never used to ascertain the presence of Metal to Ligand Charge Transfer (MLCT) phenomenon in such complexes.

This tempted us to take up a few biologically important, analytically suitable and optically active macrocyclic paramagnetic complexes: $[L_3M]^{2+}${M=V(II), Ni(II)}, and $[L_3Cr]^{3+}$ where L=2,2′-bipyridine, which were known to exhibit MLCT phenomenon(*11-13*). Accurate computations of their NMR, ESR and NQR(*14-17*) parameters had become possible by DFT only recently(*18-20*).

II. Need For The Study

These complexes showed a peculiar nature where two opposing factors would operate. The coordination of N to a transition metal ion would cause lowering of ν_{CN} and the transfer of electronic charge from MOs having predominantly metal character to those having the ligand character should increase $\nu_{CN.}$ Moreover, ν_{CN} was not much metal sensitive. So It was difficult to assign exact value to ν_{CN} because several free 2, 2′-bipyridine vibrations would also fall in the ν_{CN} region {Hutchinson et al. tried metal isotope technique in

2,2′-bipyridine which showed bands at 37109 (s), 34800 (v s**),** 29200, 26558, 23748 cm^{-1} (w)}.Thus IR and Raman spectra which were commonly used to study MLCT phenomenon in other cases had a limitation in such complexes. Reflectance technique was, also, not helpful as $\pi \rightarrow \pi^*$ transition absorbed in the same region where MLCT were observed in some complexes. These limitations were overcome with the use of ADF software.

III. Methodology

We have already reported that the use of ADF software as a valuable tool to calculate NMR(*21-23*), IR(*24*), ESR(*25-27*) and NQR(*25-27*) parameters for various transition metal complexes.

IV. Results

Table: 1 showed the thermal parameters of the studied complexes. Table: 2 contained optimization parameters of the three complexes and [Mg_n], {M_I}, (M_S) values of metal ions. Table: 3 showed δ and σ values of M^{n+}, ^{14}N, ^{13}C, and ^{1}H of the three complexes. Table: 4 showed 10 Diamagnetic, Paramagnetic and Spin orbit contributing terms in σ values of constituents. Table: 5 showed ESR and NQR parameters of complexes. Table: 6 showed calculation of H^, ΔE_{hf} of the three complexes Table: 7 showed more ESR and NQR parameters for complexes. Table: 8 showed the IR Active bands in complexes. Table: 9 showed the $\sigma^{14}N$ values of the uncoordinated 2, 2′-bipyridine ligand and the complexes. Figure: 1 would represent ADF numbers of three *tris* (2,2′-bipyridine) complexes.

V. Discussion

Each tris(2,2′-bipyridine) complex contained a total of 61atoms which differed only in metal ion. The remaining 60 atoms consisted of 6 N's, 24 H's and 30 C's.

5.1. Relations used to calculate NMR parameters (*20*)

(a) σM^{n+}, $\sigma^{1}H$, $\sigma^{13}C$ and $\sigma^{14}N$ were equal to the sum of the values of 2 diamagnetic, 4 paramagnetic and 4 spin orbit terms.

(b) The δ and σ values of ^{1}H, ^{13}C, M and ^{14}N were related as follows:

$$\delta^{1}H = 31.7 - \sigma\ ^{1}H \qquad \text{----------(1)}$$

$$\delta^{13}C = 181.1 - \sigma\ ^{13}C \qquad \text{----------(2)}$$

$$\left.\begin{aligned} \sigma M &= -\delta M \\ \sigma^{14}N &= -\delta\ ^{14}N \end{aligned}\right\} \qquad \text{----------(3)}$$

5.2. Relations used to calculate ESR parameters

(a) *Effective Spin Hamiltonian (H^)*(*25-27*)

No doubt, three relations (*25-27*) were needed to calculate H^ but all the three complexes included in the present study were axially asymmetric having the same two **g** values represented as $\mathbf{g}_{\perp}$, while the third different **g** value was represented as $\mathbf{g}_{\eta}$.Correspondingly, two same **a** values ($\mathbf{a}_{\perp}$) while a different third **a** value was named as $\mathbf{a}_{\eta}$, only the following relation would suffice:

$$H\hat{} = \left\{\begin{aligned} &\beta_e [g_{\parallel} . H_{\parallel} . S + g_{\perp} (2H_{\perp} . S)] + [a_{\parallel} . S . I + a_{\perp} (2S . I)] \\ &+ Q [I - 1/3\ I (I+1)] + D [S_z^2 - S(S+1)/3] - [g_n . \beta_n . H_0 . I] \end{aligned}\right\} \qquad \text{-------(4)}$$

Five factors such as **g** factor, **a** factor, **Q** factor, Zero Field Splitting (ZFS) factor(*28, 29*) and interaction of nuclear magnetic moment with external magnetic field, i.e. I factor would contribute in the total value of Spin Hamiltonian (H^). S_z representing spin angular momentum was calculated as:

$$S_z = [S/S(S+1)]^{1/2} \qquad \text{---------- (5)}$$

(b) *Hyperfine Coupling Energy(28)*

$$\Delta E_{hf} = \tfrac{1}{2} [a_{11}^2 + a_{22}^2 + a_{33}^2]^{1/2} \qquad \text{---------- (6)}$$

$\Delta E_{hf} / A_{ten} \approx 0.86\text{-}0.90$; averaged to 0.88 was found in most of complexes.

(c) H^ values were calculated both in terms of MHz as well as in joules mol^{-1}. Their inter conversions were given as:
(i) 1 MHz = 6.627×10^{-21} erg = 3.9903124×10^{-7} kJ mol^{-1}
(ii) $1cm^{-1}$= 0.0119626 kJ mol^{-1} = 29979.2458 MHz
(iii) For 8388.255 MHz in a 0.30T, the **g** value of the standard substance: 2, 2′-diphenyl-1-picrylhydrazyl (DPPH) was: g_{DPPH} = 2.00232 (*30-32*). So **g** value of the complex ($g_M{}^{n+}$) and its frequency ($\nu_M{}^{n+}$) were related as follows:

$$\nu_M{}^{n+} = (8388.255 \times g_M{}^{n+}) / 2.00232 \quad \text{----------(7)}$$

5.3. Relations used to Calculate NQR Parameters(*33, 34*)
(a) *Asymmetry Coefficient (η)*

$$\eta = (q_{xx} - q_{yy}) / q_{zz} \quad \text{----------(8)}$$

The value of η lies in between 0-1 for all types of symmetries. For axial symmetry of the complexes, η=0. It was possible only when:

$$q_{xx} = q_{yy} \neq q_{zz} \quad \text{----------(9)}$$

(b) *Laplace Equation*

$$q_{xx} + q_{yy} + q_{zz} = 0 \quad \text{----------(10)}$$

5.4. Calculation of four ESR and NQR parameters:

Four more ESR and NQR parameters such as H^, ΔE_{hf}, η, and Laplace equation were calculated from five ESR (g_{11}, g_{22}, g_{33}, g_{iso} ; a_{11}, a_{22}, a_{33}, A_{ten}) and NQR parameters (η; q_{11}, q_{22}, q_{33}; NQCC) which were given by the software. All these complexes possessed axial symmetry with (a) Two of three **g** parameters called $\mathbf{g}_\perp$ were of the same value and third of higher **g** value was called $\mathbf{g}_\eta$ (b) Two of the three **a** parameters called $\mathbf{a}_\perp$ were of same value and the third of higher **a** value was called $\mathbf{a}_\eta$. (c) Two of the three **q** parameters were of the same value. (d) η=0, equation 4, was applicable to all to calculate H^. Individual values of these four factors in the total value of H^ were given at bottom and were represented as (→). ΔE_{hf}, η, Laplace Equation were calculated by relations (7, 8, and 10) respectively in Tables: 5-7. Parameters NQCC, **a**, **q** were expressed in MHz while **g** was unit less.

5.5. Confirmation of Spatial Equivalence from NMR parameters of N, C, H

As many as 13 parameters of three techniques: ESR ($\mathbf{g_n}$, $\mathbf{A_{ten}}$), NQR (NQCC, η) and NMR {σ^{13}C, δ^{13}C, σ^{14}N, δ^{14}N, σ^{1}H, δ^{1}H, σM, δM and 10 terms (2 diamagnetic, 4 paramagnetic and 4 spin orbit) each for M, ^{14}N ^{13}C, ^{1}H} given by the software were used to ascertain the stereochemistry of the three paramagnetic complexes by the following two ways:

5.5.1. From Equivalence of NMR parameters of complexes

As already stated, the spatially equivalent species would possess the same values of δ, σ and each one of the ten contributing terms towards the total value of σ of constituents respectively. Following these arguments, the three tris(2,2′- bipyridine) complexes: $[L_3M]^{2+}$ where {M= V(II) and Ni(II)} and $[L_3Cr]^{3+}$ {L=2,2′-bipyridine} in each complex contained 4 types of stereo chemically different H; each type possessing 6 equivalent protons which showed four different series of values $\sigma^{\mathbf{1}}$H, $\delta^{\mathbf{1}}$H and the 10 contributing terms respectively. The complexes also contained 5 types of spatially different C atoms; each type having six equivalents C; giving six different series of values of $\sigma^{\mathbf{13}}$C and $\delta^{\mathbf{13}}$C and the 10 contributing terms respectively. All the six $^{\mathbf{14}}$N nuclei were also equivalent with the same values of $\sigma^{\mathbf{14}}$N and $\delta^{\mathbf{14}}$N and the 10 contributing terms respectively (Tables:3 and 4).

5.5.2. From Equivalence among five NMR, ESR and NQR parameters

A total of 5 parameters of three spectral techniques [ESR (A_{ten}), NQR (NQCC, η) {Table: 5} and NMR (σ, δ) {Table: 3}] were used to ascertain the similar stereochemistry of the three paramagnetic complexes following the rule that stereo chemically equivalent species would possess the same values of these parameters. The 5 parameters: σ, δ, g. $A_{ten,}$ η, and NQCC of ^{14}N; 4 parameters: σ, δ, g. A_{ten}, and η of ^{13}C and 3 parameters: σ, δ, and g. $\mathbf{A_{ten,}}$ of ^{1}H corroborated to infer that in these 2, 2′- bipyridine complexes, the 30 C atoms were of 5 types while the 24 H atoms of 4 types and all the 6 N atoms were spatially of the same type in all the three complexes.

5.6. Evidence of MLCT Phenomenon from NMR parameters of complexes

As already explained (*24*), σ value of any nucleus was directly related to its electron density, so any change in the σ value should serve as an indicator to the change in electron density on it. The $\sigma^{14}N$ (Table: 9), and $\sigma^{13}C$, $\sigma^{1}H$ (Table: 3) values in these complexes were higher but $\delta^{14}N$, $\delta^{13}C$, and $\delta^{1}H$ values were found to be lower than their corresponding values of uncoordinated ligand(*24*) to confirm the transfer of electronic charge from the metal atom to the ligand and, thus, would support the presence of MLCT phenomenon in these complexes.

5.7. IR Studies of the Complexes (*35*)

(1) ADF software gave values of frequencies, dipole strengths and intensities of IR normal modes of all the (3n-6) fundamental vibration bands of the complexes. Each one of the177 fundamental bands was given a vibration symmetry symbol. Further, each complex was given a Vibration Symmetry Class where the bands were classified according to their IR activities (Table: 8).

(2) 177 bands in the three paramagnetic complexes: $[Bipy_3M]^{2+}$ {M= V(II) and Ni(II)} and $[Bipy_3Cr]^{3+}$ were classified into A_1, A_2, and E symmetry symbols with 30, 29, 118 bands respectively. Thus, the Vibration Symmetry Class was represented as $[30A_1+29A_2+59\ E]$. 147 bands (A_2, E) were found to be IR-active while the remaining 30 bands of A_1 symmetry were IR- inactive (Table: 8).

VI. Conclusions

(i) NMR technique was able to authenticate the presence of MLCT phenomenon in these 3 complexes by the fact that the NMR parameters such as $\sigma^{14}N$, $\sigma^{13}C$, and $\sigma^{1}H$ were found to have higher and the $\delta^{14}N$, $\delta^{13}C$, and $\delta^{1}H$ showed lower values than those of their values in uncoordinated 2,2′-bipyridine ligand. This confirmed an increase in electron density on the bipyridine ligands and thus transfer of electron cloud from the metal into the ligand orbitals was justified.

(ii) The spectral techniques such as NMR, ESR and NQR corroborated to prove that these paramagnetic complexes possessed the same symmetry point group (D_3) as all the 60 constituting species were occupying the same relative positions around each one of the metal ion.

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Table: 1. Thermal Parameters of $[Bipy_3M]^{n+}$ Complexes

M^{n+}	Zero Point Energy (e V)	Thermal Parameters											
		Entropy (cal mole^{-1} K^{-1})				Internal Energy (Kcal mole^{-1})				Constant Volume Capacity (Kcal mole^{-1} K^{-1})			
		Trans.	Rot.	Vib.	Total	Trans.	Rot.	Vib.	Total	Trans.	Rot.	Vib.	Total
V(II)	12.567	44.63	32.7	74.9	152.26	0.889	0.889	302.5	304.3	2.981	2.981	102.6	108.5
Cr(III)	12.507	-do-	-do-	84.7	162.19	-do-	-do-	303.0	304.8	-do-	-do-	108. 2	114.2
Ni(II)	12.547	-do-	-do-	72.1	149.4	-do-	-do-	302.5	303.9	-do-	-do-	102.6	108.5

Table: 2. Optimization Parameters (kJmol^{-1}), [M g_n], {M_I}, (M_S) of $[Bipy_3M]^{n+}$ Complexes

M^{n+} (D_3)	[M g_n], {M_I} (S)	Total bonding Energy**	Total Energy: X c* LDA (Exchange; Correlation)	Nucleus
V(II)	[1.4710588] {3.5},(1.5)	-38786.97	-596049.80 -552139.79 , -43910.01	^{51}V
Cr(III)	[-0.316360], {1.5},(1.5)	-37777.71	-604991.71 -37777.71 , -44219.72	^{56}Cr
Ni(II)	[-0.5000133] {1.5},(1.0)	-38401.78	-642275.78 -596888.30 , -45387.48	^{61}Ni

*****Made up of LDA and GGA with zero GGA**.**** Energy difference between molecule and fragments.

Table: 3. δ and σ values of M^{n+}, N, C, H in $[Bipy_3M]^{n+}$ Complexes[a]

M^{n+}	δM^{n+} [3] σM^{n+}	δ N [3] σ N	δ H [1] σ H	δ H [1] σ H	δ H [1] σ H	δ H [1] σ H	δ C [2] σ C	δ C [2] σ C	δ C [2] σ C	δ C [2] σ C	Δ C [2] σ C
[Fig .1]	1	7,17,27, 37,47,57	8, 18,28, 38,48,48	9, 19, 29, 39,49,59	10,20,30 40,50,60	11,21,31 41 ,51,61	3, 13, 23, 33,43,53	4, 14, 24, 34,44,54	5,15,25 35,45,55	6,16,26 36 ,46,56	2,12,22 32,42,52
V(II)	2168.43 -2168.43	-367.0 367.0	-48.38 80.08	-53.52 85.22	-48.33 80.03	-52.33 84.03	-128.8 309.90	-188.6 369.72	-191.6 372.69	-96.90 278.2	-78.88 259.98
Cr(III)	689.63 -689.63	-72.34 72.34	3.59 28.11	39.83 -8.83	20.13 11.57	-75.48 107.18	99.69 81.41	122.43 58.67	96.84 84.26	69.22 111.88	86.24 94.86
Ni(II)	7322.67 -7322.67	-394.75 394.75	-48.16 79.86	-53.6 85.27	-45.75 77.45	-72.5 104.48	-134.8 315.93	-188.1 369.15	-168.3 349.38	-143.8 324.9	-124.2 305.34

[a]ADF Numbers in parentheses; Apply Relations[1,2,3]

Table: 4. Sum of Diamagnetic, Paramagnetic & Spin orbit contributions in σ of $[Bipy_3M]^{n+}$ Complexes [a]

[a] M^{n+} [Fig.1]	σ M^{n+} 1			σ N of same type of 6 N 7,17, 27, 37,47,57			σ H of 4 types of H each with 6H 8, 18, 28, 38,48,48(9, 19, 29, 39,49,49)[10, 20, 30, 40,50,60] { 11, 21, 31, 41,51,61}			σ C of 5 types of C each with 6 C 3,13,23, 33,43, 53(4,14,24,34,44,54) [5,15,25,35,45,55]{6,16,26,36,46,56}{{2,12,22 32,42,52}}		
	Dia.	**Para.**	**S.O.**	**Dia.**	**Para.**	**S.O.**	**Dia.**	**Para.**	**S.O.**	**Dia.**	**Para.**	**S.O.**
V(II)	1708.3	-3822.29	-54.5	320.02	104.68	-57.71	27.226 28.605 29.875 32.565	55.695 56.961 49.262 80.128	-2.840 -0.349 0.890 -8.601	254.7 256.5 259.1 258.2	70.32 121.7 118.3 80.82	-15.1 -8.52 -4.78 -60.9
Cr(III)	1792.0	-2488.83	7.24	314.47	-224.4	-17.78	27.625 28.709 30.030 33.703	1.856 -37.54 -18.90 76.115	-1.376 0.003 0.441 -2.637	255.5 255.7 256.1 257.2 257.4	-170.0 -194.0 -170.1 -110.0 -134.7	-4.20 -3.02 -1.71 -35.3 -27.8
Ni(II)	2273.9	-9818.18	222.4	322.98	78.292	-6.526	27.200 28.594 29.945 32.814	55.563 56.802 49.227 80.298	-2.901 -0.130 -1.725 -8.634	254.8 256.4 259.3 259.0 253.1	65.57 120.9 117.4 75.22 73.71	-4.43 -8.18 -27.4 -9.37 -21.5

a.ADF Numbers. **Dia**.[Diamagnetic core & valence tensors] **Para.** [Paramagnetic b^, u^, s^ & gauge tensors] **S.O.** [four paramagnetic tensors with same names but different values]

Table: 5. ESR and NQR Parameters from Software for $[Bipy_3M]^{n+}$ Complexes

* M^{n+}	g_n. A_{ten} values of 4 types of H; each type having 6H	g_n. A_{ten} values of 5 types of C; each type having 6 C	η values of 5 types of C; each type having 6 C	g_n. A_{ten} value of each N	NQCC and η values of each N
V(II)	0.762,-1.526, 0.089,-1.247	5.674 .-0.607 ,2.123, -1.907, 8.085	0.756,0.519,0.768, 0.751,0.691	≈ - 2.800	-2.82037 (≈0.347)
Cr(III)	0.577,-1.089, 0.151,-1.538	7.374,0.094,-0.194, -1.278,3.600	0.756,0.499,0.972, 0.247,0.269	≈ - 4.858	≈3.091 (≈0.250)
Ni(II)	1.068, -0.466, 1.178, 4.478	-0.053,-0.27,-0.628, 3.065,-1.020	0.43.0.523,0.806, 0.781,0.738	≈26.570	2.605 (≈0.290)

*With I=1/2 for ^{1}H and ^{13}C; their NQCC =0.0. All η values =0.0 for 24 ^{1}H.

Table: 6. More ESR and NQR Parameters from Software* for $[Bipy_3M]^{n+}$ Complexes

M^{n+}	g values	g_n .a & $[A_{ten}]$	q & (Laplace)[10]	NQCC& (η)[8]	ZFS[D,E]
V(II)	1.988580 1.994506 1.994515 g_{iso}1.992534	$-0.837060.10^{2}$ $-0.604135.10^{2}$ $-0.60412.10^{2}$ [-68.177]	$0.237189.10^{-1}$ $-0.117634.10^{-1}$ $-0.11955.10^{-1}$ (0.00)	0.9962 (0.008)	[-0.276393, --0.0001]
Cr(III)	1.992292 1.994868 1.995130 g_{iso}1.994097	$-0.138874.10^{2}$ $-0.167867.10^{2}$ $-0.167909.10^{2}$ [-15.822]	$0.0923568.10^{-1}$ $0 .085610,10^{-1}$ $-0.177967.10^{0}$ (0.00)	-1.0678 (0.038)	[-0.010013, -0.0001]
Ni(II)	2.049276 2.049332 2.050934 g_{iso} 2.049848	$0.356037.10^{2}$ $0.355180.10^{2}$ $0.281004.10^{2}$ [33.0737]	$-0.98012.10^{0}$ $-0.95349.10^{0}$ $0.19336.10^{1}$ (≈0.00)	11.602 (0.0138)	[-0.545, -0.0002]

NQCC **a**, **q**, are expressed in **MHz** and **g** is unit less.

Table: 7. Calculation of H^, ΔE_{hf} Parameters of $[Bipy_3M]^{n+}$ Complexes

M^{n+} [Relation]	g & g_{iso} {g- contribution} MHz	$[A_{ten}]$&$(\Delta E_{hf}/A_{ten})$ {a- contribution} MHz	NQCC {Q-contribution} MHz	{I-contribution} MHz*	[D,E](ZFSconst.cm^{-1}) (4,5) {MHz}**}	H^ MHz*** {J mol^{1-}}
V(II) (4)→ {H^} (6)	g_{ll} 1.988580 $g_{\perp}$ 1.994506 $g_{\perp}$1.994515 g_{iso}1.992534 $(4.174H_{ll}+8.373H_{\perp})$ {34772.319+69960.945}	A_{ll} -56.902 $A_{\perp}$ -41.068 $A_{\perp}$ -41.067 [-46.346](0.88) (-729.951) {-729.951}	0.9962 (-1.743) {-1.743}	----- (0.003952H_0) {33.150}	[-0.276393,--0.000] (-0.166616) {4981.2915}	 (108949.71) {43.487}
Cr(III) (4)→ {H^} (6)	g_{ll} 1.992292 $g_{\perp}$ 1.994868 $g_{\perp}$ 1.995130 g_{iso}1.994097 $(4.182H_{ll}+8.373H_{\perp})$ {34903.997+69964.067}	A_{ll} 43.897 $A_{\perp}$ 53.062 $A_{\perp}$ 53.075 [50.013] (0.88) (337.585) {337.585}	-1.0678 (0.267) {0.267}	------ (-0.00036H0) {-3.02}	[-0.010013,-0.0001] (-0.0060078) {180.1093}	 (105389.05) {42.065}
Ni(II) (4)→ {H^} (6)	g_{ll} 2.050934 $g_{\perp}$ 2.049332 $g_{\perp}$ 2.049276 g_{iso} 2.049848 $(2.870H_{ll}+5.736H_{\perp})$ {24658.788+49243.943}	A_{ll} -56.186 $A_{\perp}$-71.188 0 $A_{\perp}$ -71.205 [- 66.130] (0.88) (-297.585) {-297.585}	11.602 (2.901) {2.901}	----- (-0.00057H_0) {-4.781}	[-0.545, -0.0001] (-0.2725) {8169.344}	 (81782.17) {32.643}

* Multiply by 8388.255; ** Modulus**; ***** Sum of values in II-V columns

Table: 8. Designations of IR Active Bands in Paramagnetic $[Bipy_3M]^{n+}$ Complexes

M^{n+}	Number of bands and their Vibration Symmetries*	IR active bands	IR inactive bands	Vibration Symmetry Class
V(II), Cr(III), Ni(II)	A_1 (30),A_2 (29),E (59)	A_2 (29),E (59)	A_1(30)	$\{30A_1+29A_2 + 59 E\}$

*Numbers in parentheses indicate the number of bands of a specific symmetry [Fig. 1]

Table: 9. σN values of 2, 2/ -Bipyridine and $[Bipy_3M]^{n+}$ complexes

σ values	Bipy	Ti(II)	Cr(III)	Ni(II)
σN	(6) -124.7, (16) -132.4	367.0	72.34	394.75

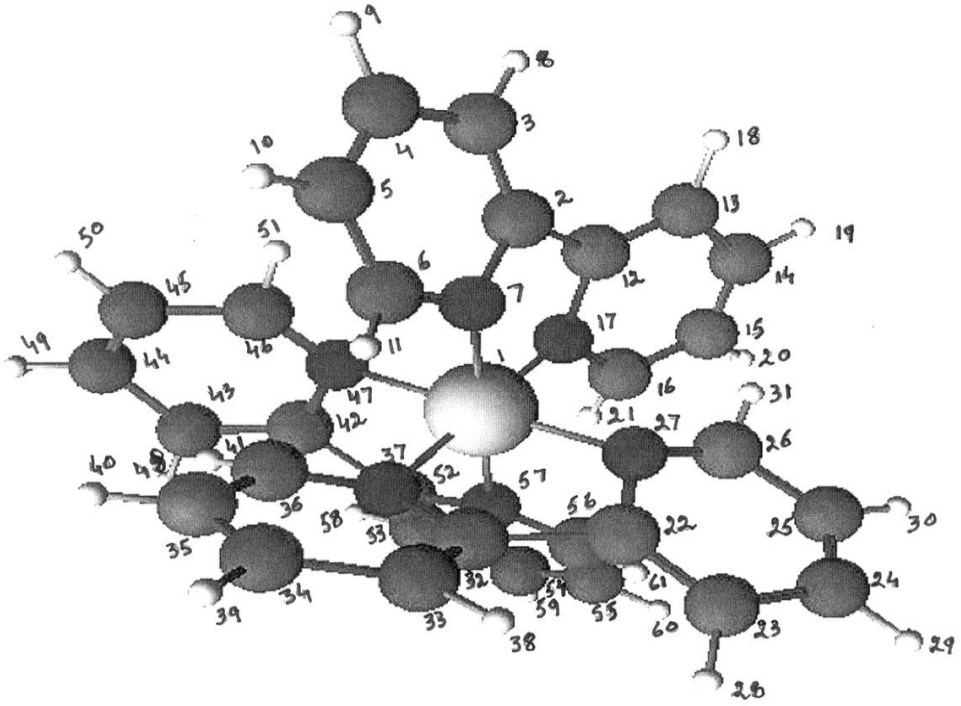

Fig.1. $[Bipy_3M]^{n+}$ Complexes {M= V (II), Cr(III), Ni(II) at number :1}