NMR, ESR, NQR and IR Studies of Paramagnetic Macrocyclic Complexes of Iˢᵗ Transition Series, Metal Ions Exhibiting MLCT Phenomenon: (A DFT Application. Part: 1 [Bis (2, 2′-bi-pyridine)] Complexes)

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ABSTRACT

DFT implemented in ADF. 2012.01 was applied to study the structures of 8 macrocyclic paramagnetic four coordinate complexes: $[Bipy_2M]^{2+}$ {M= Mn (II), Fe(II), Co(II), Ni(II), Cu (II)}, $[Bipy_2M]^{3+}$\{M=Ti(III),V(III)\} and $[Bipy_2V]^{4+}$(Bipy=2,2′-bipyridine) by using 4 spectral techniques. After optimization of complexes, the software was run by using Single Point, LDA or GGA, Default, Relativity, Spin Orbit, ZORA, Unrestricted, None, Collinear , Nosym using TZP or TP2Z 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}. ESR parameters (g_n. A_{ten}, ZFS) and NQR parameters {h, q_{11}, q_{22}, q_{33}, NQCC} were obtained by replacing Spin Orbit by scalar command in a new ADF Input. On running the "NMR Program" with Single Point, Default, None, Collinear, Nosym and using the same Basis sets leaving Unrestricted command blank gave the Shielding Constants (σM, σ ^{13}C, σ ^{17}O), Chemical Shifts (δ M, δ^{13}C, δ^{17}O), 2 diamagnetic, 4 paramagnetic and 4 spin orbit contributing terms in σ values of constituents. The software was run with Frequencies to obtain IR frequencies of normal modes of the (3n-6) fundamental vibration bands of complexes. This study was important because: (i) the 5 parameter: σ, δ, h, g_n. A_{ten}, NQCC of ^{14}N; 4 parameters: σ, δ, g_n. A_{ten} h of ^{13}C and 3 parameters: σ, δ, g. A_{ten} of ^{1}H corroborated to infer that in these complexes, the 20 C were of 5 types; the16 H of 4 types while the 4 N were spatially of the same type (ii) it confirmed MLCT phenomenon in the complexes by NMR(iii) we calculated another parameter of each of NMR (H^)and ESR {DE$_{hf}$ }and two of NQR {Asymmetric coefficient (h), Laplace equation} (iv)it classified 117 fundamental bands of each complex into vibration symmetries and IR activities(v) it gave thermal parameters of the complexes.

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

INTRODUCTION

The lowest energy conformation of uncoordinated 2, 2′- bi-pyridine (Bipy) both in the solid state and in the solution was coplanar with the two N atoms occupying the *trans* positions[1,2]. It was for the sake of simplicity that we represent it with its two N atoms occupying *cis* conformation

except in the acidic medium. Anion effects on structures of Cd (II) complexes containing (2, 2'-bpy) ligands were studied, and compared with the similar Zn (II) complexes[3, 6]. J.J.Toni *et al.,* studied the role of [Ni (bipy)Br$_2$] in the polymerization of ethane[4]. Balaiah *et al.,* studied IR, EPR and optical absorption of [Cu(bipy)$_2$(C lO$_4$)$_2$], [Cu(bipy)$_2$(NCS)$_2$] and [Cu(bipy)$_2$(NCS)]ClO$_4$][5]. Jaap Boersma studied ESR of mono alkyl zinc-bipy complexes[7]. H.Oluwatola Omoregie *et al.,*[8] and Ozel Aysen E. and coworkers[9] studied vibration spectra of copper(II)2,2'-bipyridine and 1,10-phenanthroline complexes and [Zn(bipy)X$_2$] (X=Cl, Br) respectively by applying DFT[9]. H. Z. Chiniforoshan and coworkers[10] studied the structures of complexes of Co (III) and Zn (II) with 2, 2'-bipyridine and 1,10-phenanthroline by applying DFT. Morigakii, Milton K. *et al.,*[11] applied DFT to study IR, UV and Mossbauer of 2, 2'-bipyridine and 1,10-phenanthroline complexes of iron (II).

Need for the study

(a) What prompted us to take up the study of the 8 macrocyclic complexes such as [MBipy$_2$]$^{2+}${M= M n (II), Fe(II),Co(II), Ni(II), Cu (II)}], [Bipy$_2$M]$^{3+}${Ti(III),V(III)} and [Bipy$_2$M]$^{4+}$ {V(IV)} (Bipy=2,2'-Bipyridine) was the fact that their MLCT character was never studied by NMR before by DFT because accurate computations of their NMR and ESR[12-17] parameters became possible only recently1[8-20].

(b) Only IR, Raman and Electronic spectra had been used to study ML CT phenomenon. But, these complexes had a peculiar nature where two opposing factors would operate. The coordination of N to a transition metal ion should cause a lowering of $v_{(CN)}$ while the transfer of electronic charge from the molecular orbitals having predominantly metal character to those having the ligand character(MLCT) should increase $v_{(CN)}$. Moreover, $v_{(CN)}$ was not metal sensitive. So it was difficult to assign exact value to $v_{(CN)}$, since several free 2, 2'-bipyridine vibrations appeared in the same region[21, 22].

(c) U.V. technique had a limitation as $\Pi \to \Pi^*$ transition of the ligand absorbed in the same region {37109 (s), 34800 (vs), 29200, 26558, 23748 (cm^{-1}) (w)}

where MLCT transitions were observed in some complexes.

(d) We wanted to confirm the stereochemistry and the relative arrangement of the 40 constituent species (N, C, H) around each metal ion in these complexes.

(e) Spin Hamiltonian (H^) values of these complexes were never calculated.

Methodology

Different sets of commands were given to the software to obtain a very large number of parameters of four different spectral techniques for these complexes.

Obtaining IR parameters

ADF 2012.01 was installed on Windows XP platform as ADF jobs. It was run by replacing Single Point with Geometry Optimization, *LDA or* GGA, Default, Large commands by using TZP or TZ2P *basis sets* to save the *optimized* complex by "Run" under File menu to click "Read New Coordinates". Geometry Optimization was replaced by *Frequencies, Spin Orbit* and Unrestricted commands*.* As the software did not allow Raman calculations of complexes with unpaired electrons, the software gave only frequencies of the normal modes, dipole strengths and absorption intensities of IR- active bands and classified the (3n-6) fundamental vibration bands in a number of Vibration Symmetry classes for the 8 complexes.

Obtaining NMR Parameters[23-28]

After *optimization*, the "NMR Program" for a paramagnetic complex was run by Single Point, LDA or GGA, Default, Unrestricted, Spin orbit, *Collinear, Nosym* with TZP or TZ2P basis sets. σ M^{n+}, σ^{14}N, σ^{13}C and σ^{1}H were obtained by clicking on the numbers of metal ions, the N, the C and the H of the complex and printing them along with "*Isotropic Shielding Constants*" and "*Full Shielding Constants*". NMR spectra gave Chemical Shifts (δ M^{n+}, δ^{14}N, δ^{13}C, δ^{1}H).

The σ values of all the species contained diamagnetic, paramagnetic and spin orbital contributions. Diamagnetic contribution was made up of two terms: diamagnetic core tensor{a} and diamagnetic valence tensor{b} while the

paramagnetic part contained four terms paramagnetic (b^) tensor {c}, paramagnetic (u^) tensor {d}, paramagnetic(s^) tensor{e} and paramagnetic gauge tensor{f}.These 6 terms always contributed to the total value of ó in a diamagnetic complex[12].In a paramagnetic complex, an additional contribution to σ values of all the constituents would arise from the spin orbital contribution which also contained the four paramagnetic terms with the same names but possessed different values. In a way, the σ was made up from six terms in a diamagnetic complex while it consisted of ten terms in a paramagnetic complex.

Obtaining ESR and NQR parameters[29-33]
They were obtained in three steps:

After optimization of complexes, ADF was run by using Single Point, LDA or GGA, Default, Spin Orbit, ZORA , Unrestricted, None, Collinear, Nosym using TPZ or TZ2P Basis sets in ESR/EPR/ EFG/ZFS Program for paramagnetic complexes to obtain ESR parameters: g_{11}, g_{22}, g_{33}, g_{iso}; a_{11}, a_{22}, a_{33}, A_{ten} .

More ESR parameters {product of g_n. A_{ten}, Zero Field Splitting Energy (ZFS)} and NQR parameters {η, q_{11}, q_{22}, q_{33}, NQCC} for species like M^{n+},^{13}C, ^{14}N and ^{1}H of the complexes were obtained by giving all the above commands except for replacing Spin Orbit by scalar command in a new ADF Input.

Two ESR (g_{11}, g_{22}, g_{33}, g_{iso} ; a_{11}, a_{22}, a_{33}, A_{ten}) and three NQR parameters (h; q_{11}, q_{22}, q_{33}; NQCC) enabled us to calculate values of an important ESR parameter called Effective Spin Hamiltonian (H^) and its five contributing factors whose sum would determine the energy of an ESR transition in each complex.

RESULTS

Tables. 1-3 contained bonding energies of metals, their I or M_I and g_n(M g_n)values and thermal and optimization parameters of 8 complexes[34, 35]. Table. 4 gave σ and δ values of ^{14}N, ^{13}C and ^{1}H of the uncoordinated ligand. Table. 5 contained σ and δ values of M^{+n}, ^{14}N, ^{13}C and ^{1}H of complexes. Table. 6 contained contributions of 2 diamagnetic, 4 paramagnetic and 4 spin orbit terms (10 in all) in σ values of M^{n+}, ^{14}N, ^{13}C, ^{1}H of complexes. Table. 7 gave ESR and NQR parameter of 4 types of H, 5 types of C and one type of N in 8 complexes. Table. 8 gave more ESR and NQR parameters of complexes Table. 9 contained contributions from five factors into H^ and DE_{hf}. Table. 10 designated IR active bands in complexes. Table. 11 gave σ ^{14}N values of the free 2, $2^{/}$-bipyridine and the complexes.

Figure.1 of the bis (2, $2^{/}$-bipyridine) complexes would give ADF numbers which were mentioned in the tables in parentheses where ever required.

Table. 1: Energies (kJmol^{-1}) of First Transition Metals

Metal	Sum of energies	Total orbital energy	Kinetic energy	Nuclear attraction energy	Electron repulsion energy	Exchange energy
Ti	- 49034.160	- 82193.590	83068.461	-195833.367	34453.298	- 3879.077
V	- 54453.277	- 91394.073	92457.572	- 218055.74	3 8338.78	- 4184.954
Cr	- 60139.891	- 101188.38	102462.98	- 241698.34	42549.246	- 4503.221
Mn	-18580.3096	-31364.4439	31791.632	-75034.4123	13237.036	-1358.702
Fe	-20333.522	-344593.341	349652.94	-82578.841	14339.914	-1455.918
Co	-78854.221	- 134234.27	136350.81	- 346177.79	57226.702	- 5539.960
Ni	-85650.855	-146522.795	148997.80	-352449.098	62843.648	-8809.705
Cu	- 9309.418	- 159479.16	162355.29	-384859.801	69353.856	- 6328.501

Table. 2: Thermal Parameters of [Bipy₂ M] ⁿ⁺

[M]ⁿ⁺	Zero Point Energy	Thermal Parameters											
		Entropy (cal mol⁻¹ K⁻¹)				Internal Energy (Kcal mol⁻¹)				Constant Volume Capacity (Kcal mol⁻¹K⁻¹)			
		Tran.	Rot.	Vib.	Total	Trans.	Rot.	Vib.	Total	Trans	Rot.	Vib.	Total
Ti(III)	8.782	43.54	32.6	56.6	132.88	0.889	0.889	211.9	213.7	2.981	2.981	67.9	73.92
V(III)	8.791	43.56	32.5	54.7	130.74	-do-	-do-	212.0	213.7	-do-	-do-	67.6	73.60
V(IV)	8.850	43.56	32.5	46.9	122.99	-do-	-do-	212.6	214.4	-do-	-do-	66.2	72.12
Mn(II)	8.359	43.59	32.4	50.1	126.14	-do-	-do-	201.7	203.5	-do-	-do-	68.7	74.68
Fe(II)	9.000	43.60	32.5	63.8	139.89	-do-	-do-	217.8	219.6	-do-	-do-	72.5	78.48
Co(II)	8.440	43.63	32.4	66.6	142.61	-do-	-do-	202.3	204.1	-do-	-do-	77.4	83.31
Ni(II)	8.342	43.62	32.4	52.2	128.2	-do-	-do-	201.4	203.3	-do-	-do-	69.1	75.04
Cu(II)	8.911	43.66	32.4	50.6	126.71	-do-	-do-	213.9	215.7	-do-	-do-	66.2	72.12

Table. 3: Optimization Parameters (kJmol⁻¹), [M gₙ], { Mᵢ } and (Mₛ) of [Bi py₂ M] ⁿ⁺

Complex →	[Bi py₂ Ti]³⁺	[Bi py₂ V]³⁺	[Bi py₂ V]⁴⁺	[Bi py₂ Mn]²⁺	[Bi py₂ Fe]²⁺	[Bi py₂ Co]²⁺	[Bi py₂ Ni]²⁺	[Bi py₂ Cu]²⁺
Nucleus →	⁴⁷Ti	⁵¹V	⁵¹V	⁵⁵Mn	⁵⁷Fe	⁵⁹Co	⁶¹Ni	⁶³Cu
Mgₙ ↑	-0.315392	1.4710588	1.4710588	1.387488	0.181246	1.32200	-0.5000133	1.4821933
Mᵢ ↑	2.5	3.5	3.5	2.5	0.5	3.5	1.5	1.5
Mₛ ↑	0.5	1.0	0.5	2.5	2.0	1.5	1.0	0.5
*Bonding Energy	-22380.35	-22473.29	-20719.30	-23830.57	-23725.90	-23666.79	-23405.36	-23179.62

*Bonding energy is computed as an energy difference between molecule and fragments.

DISCUSSION

Discussion for the eight complexes, each containing 41 atoms: 4 N, 16, 20 C and different metal ion was subdivided into different headings as follows

Relations used to calculate NMR parameters[12]

For paramagnetic complexes, the NMR parameters were related as follows:

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 of M^{n+}, ^1H , ^{13}C and ^{14}N respectively.

The relations between (s) and (d) of ^1H and ^{13}C were given as follows:

$$\delta^1 H = 31.7 - \sigma\, ^1H \qquad ...(1)$$

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

δM^{n+} and $\delta^{14} N$ were numerically equal to σM^{n+} and $\sigma\, ^{14}N$ with reverse signs:

$$\sigma M^{n+} = - \delta M^{n+} \qquad ...(3)$$
$$\sigma^{17} O = - \delta\, ^{14}N7$$

Relations used to Calculate ESR parameters[29-31]

Following relations were used to calculate two ESR parameters for complexes:

Effective Spin Hamiltonian (H^)[29-31]

The g-tensor contributes in one of the most important ESR parameter called Effective Spin Hamiltonian ($) which is a mathematical expression that determines the energy of an ESR transition of an ESR active metal ion surrounded by ligands in a definite geometry. Its value depends upon a number of ESR parameters like anisotropic and isotropic values of Gyromagnetic splitting factors (g_{11}, g_{22}, g_{33} and g_{iso}), hyperfine coupling constants (a_{11}, a_{22}, a_{33} and A_{ten}) and NQR parameters like electric field gradient [efg] (q_{11}, q_{22}, q_{33}) and Nuclear Quadrupole Constant (Q). In addition, it depends upon total electronic spin value (S), nuclear spin quantum number (**I**) of nucleus of metal ion, Gyromagnetic nuclear magnetic ratio value (g_n cf. g_e for electron), Bohr Magneton of the electron (b_e) and Nuclear Magneton (b_n). Apart from these parameters, it depends upon nature of the surrounding nuclei if they possess quadrupole moments (I^31). I and g_n values of metals were reported in Table: 4.

It contained contribution from five factors namely g factor, a factor, Q factor, Zero Field Splitting (ZFS) factor and interaction of nuclear magnetic moment with external magnetic field, the I factor. No doubt, three relations[29-31] were needed to calculate H^ but all the complexes included in the present study were axially asymmetric having two same g values (named $g_{\parallel}$) while the third g of different value was represented as $g_{\wedge}$ Correspondingly, two same "a" values (named $a_{\wedge}$)

Table. 4: σ and δ values [ppm] of M +n, N, C & H of 2, 2′-Bipyridine [a]

Ligand [C_{2v}]	[b] δ N [3]	σ N	[c] δ C [2]	σ C	[d] δ H [1]	σ H
2, 2′-Bipyridine	(6) 124.7	(6) -124.7	(1) 164.723	(1) 16.38	(7) 6.90	(7) 24.84
	(16) 132.4	(16) -132.4	(2) 99.91	(2) 81.19	(8) 7.61	(8) 24.09
			(3) 127.35	(3) 53.75	(9) 6.87	(9) 24.83
			(4) 106.30	(4) 74.80	(10) 8.97	(10) 22.73
			(5)141.30	(5) 39.79	(17) 7.76	(17) 23.94
			(11) 155.74	(11) 25.36	(18) 7.37	(18) 24.33
			(12) 104.06	(12)77.04	(19) 6.87	(19) 24.84
			(13) 114.12	(13) 66.98	(20) 9.12	(20) 22.58
			(14) 105.67	(14)75.43	———	———
			(15) 142.37	(15) 38.73	———	———

a. ADF Numbers in parentheses; b. standard zero; c. standard 181.1; d. standard 31.7;Apply Relation [1,2,3]

Table. 5: σ and δ values [ppm] [a] of M [+n], N, C & H in [Bipy$_2$ M] [n+]

M [n+] [Fig:1]	δM [+n] [3] / σ M [+n]	δN [3] / σN	δ H[1] / σH	δ H[1] / σH	δ H[1] / σH	δ H[1] / σH	δ C[2] / σC	δ C[2] / σC	δ C[2] / σC	δ C[2] / σC	δ C[2] / σC
	1	7,17, 27, 37	8, 18, 28, 38	9, 19, 29, 39	10,20, 30,40	11,21 31 ,41	3, 13, 23, 33	4, 14, 24, 34	5,15, 25,35	6,16 26 ,36	2,12 22,32
Ti(III)	1953.3	-318.6	-54.2	-55.5	-42.6	-36	-251.5	-190.1	-155.6	-2.48	-180.2
	-1953.3	318.57	85.94	87.2	74.32	67.72	432.58	371.19	336.66	183.58	361.33
V(III)	6810.9	-341.8	-53.2	-55.3	-42.5	-38.9	-249.8	-187.8	-156.3	-15.5	-267.4
	-6810.9	341.8	84.89	86.95	74.24	70.63	430.9	368.95	337.44	196.58	348.46
V(IV)	5239.7	-285.3	-52.8	-56.5	-40.7	-37	-238.3	-183.7	-144.8	-5.09	-159.6
	-5239.7	285.33	84.53	88.19	72.35	68.73	419.41	364.78	325.91	186.19	340.65
Mn(II)	316.8	-184.4	-55.1	-55.9	-42.3	-33.8	-247.7	-187.6	-150.5	4.18	-148.3
	-316.8	184.36	86.82	87.55	73.96	65.51	428.75	368.72	331.56	176.92	329.41
Fe(II)	6510	-148	-55.1	-55.83	-42.2	-33.3	-248.2	-188.1	-152.1	2.89	-152.1
	-6510	148.05	86.79	87.53	73.91	64.99	429.28	369.23	333.25	178.21	333.18
Co(II)	13720.9	-93.9	-53.75	-55.46	-41.87	-34.6	-246.2	-188.5	-149.5	0.23	-146.3
	-13720.9	93.89	85.45	87.16	73.57	66.31	427.29	369.63	330.6	180.87	327.39
Ni(II)	11534.5	-11.9	-54.9	-55.8	-40.2	-28.4	-245.5	-188.8	-143.6	9.6	-151.9
	-11534.5	11.93	86.56	87.47	71.93	60.05	426.57	369.89	324.66	171.51	333
Cu(II)	3512.2	106.4	-52	-54.65	-37.4	-25.65	-244.1	-188.2	-136.1	10.33	-162
	-3512.2	-106.4	83.69	86.35	69.09	57.35	425.15	369.29	317.16	170.77	343.48

a. ADF Numbers in parentheses ; Apply Relations [1, 2, 3] ; Values of parameters in p pm

Table. 6: Sum of Diamagnetic, Paramagnetic & Spin orbit contributions [ppm] in Å of [Bipy$_2$M]$^{n+}$

M^{n+} [Fig:1]	^{a}ãM^{n+1}			^{a}σN of each of 4 N 7,17,27,37			σ^{1}H of 4 types of H^a 8,18,28,38;(9,19,29,39),[10,20,30,40];[11,21,31,41]			σ^{13}C of 5 types of C^a 3,13,23,33,(4,14,24,34),{5,15,25,35},[6,16,26,36] 2,12,22,32		
	Dia.	Para.	S.O.	Dia.	Para.	S.O.	Dia.	Para.	S.O.	Dia.	Para.	S.O.
Ti(III)	1598.8	-2492.98	-1059	325.03	-5.798	-0.667	35.553	50.501	-0.11	258.2	174.1	0.29
							28.134	59.154	-0.091	256.7	113.9	0.6
							28.138	46.928	-0.745	257.3	84.53	-5.21
							28.527	40.466	-1.269	257.9	-30.9	-43.4
										254.5	115.5	-8.65
V(III)	1703.9	-7852.27	-662.5	324.75	12.012	5.031	35.416	9.204	0.271	257.9	171.6	1.39
							28.074	58.886	-0.015	256.5	112.3	0.18
							28.128	46.844	-0.728	257.3	82.5	-2.34
							28.632	43.185	-1.189	257.8	-39.2	-22
										253.9	95.06	-0.49
V(IV)	1702.5	-6223.27	-719	325.56	-35.45	-4.788	34.835	48.249	1.443	257.9	164	-2.5
							27.195	60.441	0.556	256.4	107.6	0.76
							27.232	48.188	-3.073	257.2	88.2	-19.5
							28.179	40.207	0.345	258.1	-44.7	-27.2
										254.3	99.73	-13.3
Mn(II)	1927.9	-1924.17	-320.6	324.48	-12.78	-127.4	35.852	51.044	-0.072	257.7	172	-1.06
							28.824	58.537	0.19	256.2	115.6	-3.09
							28.949	46.297	-1.289	257.4	83.67	-9.59
							29.139	40.261	-3.892	256.9	-52.6	-27.3
										253	86.2	-9.76
Fe(II)	2039.1	-8131.7	-417.4	324.47	-33.07	-143.3	35.8	51.28	-0.31	257.7	172.9	-1.39
							28.79	58.57	0.16	256.1	115.3	-2.2
							28.96	46.19	-1.24	257.5	84.55	-8.83
							29.14	39.68	-3.83	256.9	-58.74	-19.9
										253	88.97	-8.73
Co(II)	2152.8	-16031.5	157.77	324.32	-41.2	-189.2	35.8	50.36	-0.71	257.7	171.5	-1.86

Ni(II)	2268	-14377.4	574.91	-30.64	324.43	-281.9	28.8	58.35	0.03	256.2	114.6	-1.15
							29	46.16	-1.56	257.6	82.98	-9.96
							29.1	41.68	-4.52	256.8	-59.4	-16.5
										252.8	79.91	-5.36
							35.79	52.06	-1.29	257.7	171	-2.11
							28.75	58.89	-0.16	256.1	115.5	-1.76
							28.96	45.75	-2.77	257.6	82.5	-15.4
							29.13	37.6	-6.68	256.9	-62.3	-23.1
										252.7	76.2	4.07
Cu(II)	2389	-7064.27	1163.1	-10.71	322.42	-418.1	35.8	51.34	-3.42	257.6	171	-3.44
							28.8	58.69	-1.1	256.3	115.7	-2.69
							28.9	46.04	-5.89	257.5	83	-23.4
							29.1	39.19	-10.9	257.1	-55.94	-30.4
										253.2	84.49	5.77

a. ADF Numbers. Dia: Diamagnetic {core & valence tensors} Para: Paramagnetic {b^, u^, s^ & gauge tensors} S.O: Spin Orbit {same names of four paramagnetic terms with different values; may shield or de shield, so can be (-) or (+)}.

while the third "a" of different value was called $a_{\parallel}$. Since, Z axis was generally assumed to be major axis, the magnetic field along the parallel Z- axis was called Hz or H_{11} and perpendicular applied field were represented as $H_\wedge$ or H_x and H_y. The common relation used for these paramagnetic complexes was given as follows with $S_x = S_y = S_z = S$ = total spin of the metal ion and $I_x = I_y = I_z = I$.

Zero field splitting (ZFS) included various interactions of the energy levels of an electron spin(S>1/2) even in the absence of an applied magnetic field. ZFS parameter [36] consisted of two terms D and E; the former representing axial and the latter called rhombic zero-field splitting parameters respectively. As all the 8 complexes included in this study possessed axial symmetry for which E»0, the ZFS was calculated only by the D parameter. Again, D (cm⁻¹) was positive for an *oblate* spin distribution- a flattening in one direction but was negative for *prolate*-an elongation spin distribution in one direction[37].

$$H^\wedge = \beta_e [g_{\parallel} .H_{\parallel}. S + g_\wedge (2H_\wedge. S)] + [a_{\parallel}. S .I + a_\wedge (2S.I)] + Q [I -1/3 I (I+1)] + D \{S_z^2 - S(S+1)/3\} - [g_n . \beta_n .H_0 .I] \quad ...(4)$$

S_z^2 representing square of spin angular momentum was calculated as:

$$S_z = S/S(S+1)^{0.5} \quad ...(5)$$

$H^\wedge$ values were calculated both in terms of MHz as well as in joules mol¹⁻.

The units used and their inter conversions were given as follows:

(i) β_e =1.3994 MHz gauss¹⁻ and $b_n = b_e /1836$.
(ii) 1cm⁻¹ = 0.0119626kJ mol⁻¹ = 29979.2458 MHz
(iii) For 8388.255 MHz frequency in a 0.30T, g value of the standard substance: 2, 2-diphenyl-1-picrylhydrazyl (DPPH) was g_{DPPH} =2.00232[36]. So g value of the complex (g_M^{n+}) and its frequency (μ_M^{n+}) were related as follows:

$$\mu_M^{n+} = 8388.255 * g_M^{n+} /2.00232 \quad ...(6)$$

Hyperfine Coupling Energy[36]

$$D E_{hf} = 1/2[a_{11}^2 + a_{22}^2 + a_{33}^2]^{1/2} \quad ...(7)$$

$\Delta E_{hf} / A_{ten}$H"0.86-0.90; averaged to 0.88 was calculated in complexes. But when three **"a"** differed largely or had different signs, ratios varied largely.

Relations used to calculate NQR Parameters[38, 39]

The following relations applied to calculate two NQR parameters:

Asymmetry Coefficient (h)[38, 39]

q_{11}, $q_{22,}$ q_{33} changed to q_{xx}, q_{yy} and q_{zz} if expressed in the decreasing order of their absolute values (modulus): $|q_{zz}| ³ |q_{yy}| ³ |q_{xx}|$ .Then:

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

(η) lies in between 0 to1.For axial symmetry, h=0. It was possible only when:

$$q_{xx} = q_{yy} ¹ q_{zz} \quad ...(9)$$

Laplace Equation[38, 39]

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

Calculation of four NMR and NQR parameters: H^, $DE_{h f}$, Asymmetric Coefficient (h) and Laplace equation

We calculated four more ESR and NQR parameters such as H^, $DE_{h f}$, h and Laplace equation in addition to 5 ESR (g_{11}, g_{22}, g_{33}, g_{iso}; a_{11}, a_{22}, a_{33}, A_{ten}) and NQR parameters (h; q_{11}, q_{22}, q_{33}; NQCC) parameters given by the software for the 7 complexes excluding[Bipy$_2$Fe] $^{2+}$where the ADF software did not work.

All the 7 complexes possessed axial symmetry with (a) Two of three g called g$_∧$ were of the same value and third of higher value was called g$_{||}$ (b) Two "a" called a$_∧$ were of same value and the third of higher value was called a$_{11}$. (c) Two of the three q parameters were of the same value. (d) h=0. Relation (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 ($\rightarrow$). The parameters: DE$_{hf}$,h and Laplace equation were calculated by relations (7, 8, 10) respectively (Tables. 7-9).While g was unit less, the NQCC, "a" and q were calculated in MHz.

Table. 7: ESR and NQR Parameters from Software for H, C and N in [Bipy$_2$ M] $^{n+}$

M $^{n+}$	g$_n$. A $_{ten}$ values of 4 types of H; each type having four H	g$_n$. A $_{ten}$ value of each N	g$_n$. A $_{ten}$ values of 5 types of C; each type having four C	h values of 5 types of C; each type having four C	NQCC and h values of each N
Ti(III)	0.412,0.589 1.077,-0.206	-7.8447	4.215,-0.061,0.039, 2.343, 20.017	0.156,0.675,0.156 0.300,0.673	-2.02332 -0.881
V(III)	-0.030,-0.831 0.401,-1.116	-6.77795	0.958, -0.799,0.392 0.124, 7.375	0.047,0.709 0.225 0.358,0.469	1.57497 -0.799
V(IV)	-0.975,0.783 4.354,-2.211	-10.2214	0.330, 0.509,1.854, -0.740, 16.212	0.091,0.786,0.274 0.419,0.365	1.29898 -0.597
Mn(II)	0.414,-0.717 0.370,0.432	2.02067	1.733, -0.412,0.531, 0.520, 3.638	0.18,0.635,0.156 0.206,0.508	-2.2247 -0.521
Co(II)	0.839, -0.509 0.682 ,1.968	9.3322	0.439,-0.017,0.461, 1.188, 1.46	0.202,0.649,0.155 0.213,0.559	-1.9375 -0.588
Ni(II)	1.068, -0.466 1.178, 4.478	H"26.570	-2.512, 0.056,0.300 2.510, 2.194	0.241,0.648,0.154 0.228,0.356	-2.605 (H"0.290)
Cu(II)	2.514, 0.256 3.562, 6.475	23.726	-4.155,0.824,0.005 3.502, 2.379	0.291,0.626,0.085 0.186,0.569	-1.9221 -0.718

Confirmation of Spatial Equivalence of N, C, H in complexes

It was confirmed by the following two ways:

From the equivalence of NMR parameters

In order to ascertain the stereochemistry of the complexes, the 4 coordinating N, the 20 C and the 16 H were classified according to their spatial displacements. The metal ion formed a class of its own. Spatially equivalent species would possess the same values of δ, σ and each one of the 10 diamagnetic and paramagnetic contributing terms in the complexes towards the total value of σ of constituents respectively. δM^{n+}, $\delta\ ^{14}N$, $\delta\ ^{13}C$, $\delta\ ^{1}H$, σM^{n+}, $\sigma\ ^{14}N$, $\sigma\ ^{13}C$, $\sigma\ ^{1}H$ of all the 41 species in each one of the 8 complexes having ten contributing terms in their σ values were reported (Tables. 5,6). All the four coordinating N atoms were spatially

Table. 8: ESR and NQR Parameters from Software *for M $^{+n}$ in [Bipy$_2$ M] $^{n+}$

M^{n+}	g values	g_n .a & [A_{ten}]	q &(Laplace Eqn)[10]	NQCC & (h)[8]	[ZFS[D,E]
Ti(III)	1.97977	$-0.936556.10^{2}$	$-0.851917.10^{1}$	-170.383	[0.000,
	1.9797	$-0.936553.10^{2}$	$0.425910.10^{1}$	($\approx$0.00)	0.000]
	1.99258	$-0.137265.10^{3}$	$0.426007.10^{1}$		
	g_{iso}1.994097	[-107.196]	($\approx$0.00)		
V(III)	1.918066	$0.139679.10^{3}$	$0.425185.10^{0}$	17.8578	[-10.1696,
	1.982626	$0.154964.10^{3}$	$-0.212592.10^{0}$	0	0.000]
	1.982627	$0.154965.10^{3}$	$-0.212592.10^{0}$		
	g_{iso}1.961116	[149.869]	($\approx$0.00)		
V(IV)	1.904474	$0.374081.10^{3}$	$0.597011.10^{0}$	27.075	[0.000
	1.974112	$0.374085.10^{3}$	$-0.298505.10^{0}$	0	0.000]
	1.974112	$0.518442.10^{3}$	$-0.298505.10^{0}$		
	g_{iso}1.9509	[422.202]	0		
Mn(II)	2.000893	$-0.202098.10^{2}$	$-0.370082.10^{1}$	-74.0165	[0.117967,
			$0.185041 .10^{1}$		
	2.001934		$0.185041.10^{1}$		
	2.001934 g_{iso}	$-0.206414.10^{0}$	0	0	0.000]
	2.001587	$-0.206341.10^{0}$			
		([-6.87419]			
Co(II)	2.067452	$-0.247636.10^{2}$	$-0.246526.10^{1}$	-103.54	[-22.18509,
	2.071201	$-0.225313.10^{2}$	$0.123263.10^{1}$	0	0.000]
	2.291344	$0.987883.10^{2}$	$0.123263.10^{1}$		
	g_{iso}2.143333	[17.1645]	0		
Ni(II)	2.006924	$0.174985.10^{1}$	$-0.520413.10^{1}$	62.4495	[34.69027,
	2.173656	$0.174982.10^{1}$	$-0.520413.10^{1}$	0	0.000]
	2.173656	-0.1380771	$0.10408.10^{2}$		
	g_{iso}2.118079	[-3.43601]	(H"0.00)		
Cu(II)	2.127228	$-0.193244.10^{3}$	$-0.320224.10^{1}$	-20.4503	——-
		641568.10^{1}	$-0.321343.10^{1}$		
	2.127229	$-0.193244.10^{3}$	($\approx$0.00)	0.00174	
	2.531218 g_{iso}	$0.106350.10^{4}$			
	2.261892	-225.668			

NQCC a, q, are expressed in MHz and g is unit less. *To be used in the calculation of H^ and DE_{hf} in Table: 9

Table. 9: Calculation of H^ and ?Eh f Parameters of [Bipy2 M] n+

M^{n+} (Relations)	g values & g$_{iso}$ {g- contribution} (MHz)	[A$_{ten}$]&(D E$_{hf}$/A$_{ten}$) {a-contribution} (MHz)	NQCC {Q-contribution} (MHz)	{I- contribution}* (MHz)	[D,E] {ZFScm^{-1}} (4,5) (MHz)**	H^(MHz)*** {J mol^{-1}}
Ti(III)	II 1.99258 ^ 1.979770 ^1.979770 g$_{iso}$ 1.994097	A$_{\parallel}$ 435.220 A$_{\wedge}$ 293.950 A$_{\wedge}$ 293.949 [341.040] (0.88)	-170.383	——	[0.000, 0.000]	
(4)® {H^}(6)	(1.494H$_{\parallel}$+2.770H$_{\wedge}$) {247.217+2274.000}	-1278.938 {1278.939}	-70.993 {70.933}	(-0.0006H$_0$) {-5.033}	0 {0.000}	-36800.14 {14.689}
V(III)	II 1.918066 ^1.982626 ^1.982627 g$_{iso}$ 1.961116	A$_{\parallel}$ 94.951 A$_{\wedge}$105.342 A$_{\wedge}$ 105.342 [101.879](0.87)	17.8578	——	[-10.1696, 0.000]	
(4)® {H^}(6)	(2.684H$_{\parallel}$+5.549H$_{\wedge}$) {21566.725+46088.639}	-1069.73 {1069.939}	(-31.251) {-31.251}	(0.003952H$_0$) {33.150}	(-13.5595) {406502.258}	475229.79 {189.632}
V(IV)	II 1.904474 ^ 1.974112 ^ 1.974112 g$_{iso}$ 1.950899	A$_{\parallel}$ 352.427 A$_{\wedge}$254.516 A$_{\wedge}$ 254.517 [287.006](0.88)	27.075	--	[0.000.0.000]	
(4)® {H^}(6)	(1.333H$_{\parallel}$+2.763H$_{\wedge}$) {10635.143+22850.242}	-1506.782 {1506.782{	(-47.381) {-47.850}	(0.003952H$_0$) {33.150}	0 {0.000}	-34977.47 {13.957}
Mn(II)	II 2.000893 ^2.001934 ^2.001934 g$_{iso}$ 2.001587	A$_{\parallel}$ -14.566 A$_{\wedge}$-0.149 A$_{\wedge}$ -0.147 [- 4.954] (1.47)	-74.0165	——	[0.117967,0.000]	
(4)® {H^} (6)	(7.000H$_{\parallel}$+14.02H$_{\wedge}$) {58675.938+117580.66}	(-92.888) {-92.688}	-30.84 {30.840}	(0.001889H$_0$) {15.845}	-0.6881 {20629.943}	-196840.54 {78.546}
Co(II)	II 2.291344 ^ 2.067452 ^2.071201	A$_{\parallel}$ 74.726 A$_{\wedge}$18.732 A$_{\wedge}$ -17.053	-103.541	——	[-22.18509,0.000]	

(4)® {H^} (6) Ni(II)	g_{iso} 2.143333 (4.810$H_{\parallel}$+8.687$H_{\wedge}$) {46171.450+75375.003} ∥ 2.006924 ^2.173656 ^2.173656	[12.984] (3.04) -204.498 {204.498} $A_{\parallel}$ 27.615 $A_{\wedge}$ -3.500 $A_{\wedge}$ -3.499	-181.197 {181.197} 62.4495	(0.00353H_o) {29.611} ———	(-55.463) {1662730.666} [34.69027,0.000]	-1784692.4 {712.148}
(4)® {H^} (6) Cu(II)	g_{iso} 2.118079 (2.808$H_{\parallel}$+6.084$_{\wedge}$) {23608.379+55401.708} ∥ 2.531218 ^2.127228 ^2.127229	[6.872] (2.04) -30.924 {30.924} $A_{\parallel}$ 717.450 $A_{\wedge}$ 130.377 $A_{\wedge}$ 130.377	-15.612 {15.612} -20.45	(-0.00057H_o) {-4.781} ———	-46.2537 {1386650.842} [0.000, 0.000]	-1465702.3 {584.861}
(4)® {H^} (6) {14.689}	g_{iso} 2.261892 (1.771$H_{\parallel}$+2.977$_{\wedge}$) {10603.950+26529.632}	[-152.25] (2.43) (-342.569)	(-5.113) {-342.569}	(-0.001695H_o) {-14.218} {-5.113}	0	-36800.12 { 0.000}

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

equivalent with one value of each of σ ¹⁴N, δ ¹⁴N and 10 contributing terms. Again, all these complexes contained four types of stereo chemically different H; each type possessing four equivalent protons as they showed four different series of values σ ¹H, δ ¹H and the 10 contributing terms respectively. Lastly, the complexes also contained five types of spatially different C atoms; each type having four equivalents C as they gave five different series of values of σ ¹³C and δ ¹³C and 10 contributing terms respectively.

From equivalence of NMR, ESR and NQR parameters of complexes

A total of five parameters of three spectral techniques [ESR (A_{ten}), NQR (NQCC,h) (Table. 7) and NMR (σ, δ) (Table. 5) were used to ascertain the similar stereochemistry of 7 paramagnetic complexes. Again, stereo chemically equivalent species possessed same values of these parameters of the three techniques. The 4 N atoms possessed the same values of above named five parameters. The four parameters: g_n. A_{ten},h, σ, δ of the 20 C were divided into 5 types; each having 4 equivalents C. Three parameters (g_n. A_{ten}, σ, δ) of the 16 H were of 4 types; each type having 4 equivalents H (Table. 7). Thus the three techniques corroborated with one another to confirm that each one of these complexes possessed the same type of 4 N; five types of 20 C and four types of 16H. It may, well, be noted that due to paucity of space, two NMR parameters (σ, δ) of constituents were contained in Table. 5. The remaining three {one of EPR (A_{ten}) and two of NQR (NQCC,h)} were shown in Table: 7 for the constituents. With I=1/2 for ¹H and ¹³C; their NQCC =0.0.This left 4 parameters each for ¹H and ¹³C. Since, h=0 for all 16 ¹H, so it left only 3 parameters for ¹H.

Evidence of MLCT Phenomenon from NMR parameters of complexes

The MLCT bands would result from the shift of charge density from the molecular orbitals mainly metal in character to those with predominantly of ligand character and there by, would increase the electron density on ligand. As σ of any nucleus was directly related to its electron density, any change in its σ value should serve as an indicator to the change in electron density on it. In all these complexes, the σ ¹⁴N (Table. 11), σ ¹³C,

σ ^1H (Table. 5) values were higher than their corresponding σ values in the free ligand (Table. 4) respectively which confirmed the transfer of electronic charge from the metal to (Bipy) ligand to lend support to the presence of MLCT phenomenon in these complexes by NMR.
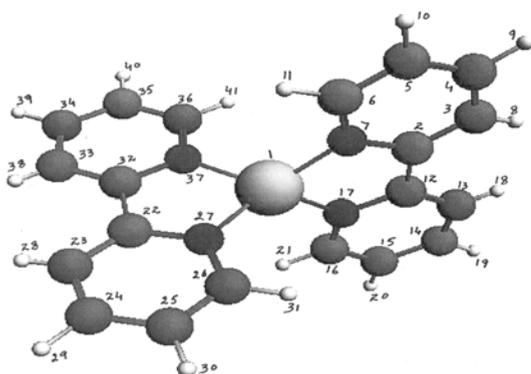
Fig. 1. [Bipy$_2$M]$^{n+}${M= Ti (III), V(III), Mn (II), Fe(II) Co(II),Ni(II),Cu(II) at No:1}

IR Parameters of complexes

The software gave values of frequencies, dipole strengths and absorption intensities of normal modes of the (3n-6) fundamental vibration bands in the complexes. They were studied with their Vibration Symmetry Classes to give a definite vibration symmetry symbol to each one of their (3n-6) bands.

Also, the bands were classified according to their IR- activities as follows[40]:

(i)   117 fundamental vibration bands in each one of four complexes: [Bipy$_2$M]$^{3+}$ (M=Ti, V)and [Bipy$_2$M]$^{2+}$(M=Mn , Ni) were classified into A,B$_1$,B$_2$,B$_3$ symmetry symbols having 30, 29, 29 and 29 bands respectively with Vibration Symmetry Class [30A+29B$_1$+29B$_2$ +29B$_3$](Table:10; A and B were singly degenerate).

(ii)   In the remaining 4 complexes [Bipy$_2$M]$^{4+}$(M= V) and [Bipy$_2$M] $^{2+}$(M= Fe ,Co, Cu), the 117 fundamental vibration bands had symmetry symbols A$_1$, A$_2$,B$_1$, B$_2$, E having 20,9,10,20 and 58 bands respectively with Vibration Symmetry Class: [20A$_1$+9A$_2$+10B$_1$+20 B$_2$+29 E](Table:10; E was doubly degenerate).

Table. 10: Designations of IR Active Bands in [Bipy2M] n+

Complex with M +n	Vibration Symmetries of bands*	IR active bands	IR inactive bands	Vibration Symmetry Class
Ti(III), V(III), M n, (II) ,Ni(II)	A(30), B$_1$(29), B$_2$(29), B$_3$ (29)	B$_1$(29), B$_2$(29), B$_3$ (29)	A(30)	[30A+29B$_1$+29B$_2$ +29B$_3$]
V(IV),Fe(II), Co(II), Cu(II)	A$_1$(20), A$_2$(9), B$_1$(10), B$_2$(20), E(29)	B$_2$(20) , E(29)	A$_1$(20). A$_2$ (9), $_1$(10)	[20A$_1$+9A$_2$ +10B$_1$ + 20 B$_2$+29 E]

*Numbers in parentheses indicate the number of bands of a specific symmetry

Table. 11: σN values [ppm] of 2, 2$^/$-Bipyridine ligand and its [Bipy$_2$M] $^{n+}$ complexes

σ values	Bipy	Ti(III)	V(III)	V(IV)	Mn (II)	Fe(II)	Co(II)	Ni(II)	Cu(II)
σN	(6) -124.7, (16) -132.4	18.57	341.80	285.33	184.36	148.05	93.89	11.93	-106.4

CONCLUSION

NMR technique supported the presence of MLCT phenomenon in the 8 complexes by showing much higher σ ^{14}N, σ ^{13}C, σ ^1H values of the constituent species relative to those of uncoordinated ligand to confirm an increase in the electron density on the coordinated 2, 2$^/$-bipyridine

implying there was a transfer of electron cloud from molecular orbitals lying mainly on metal into the molecular orbitals having energies comparable to ligand orbitals and thus the presence of MLCT. Cumulatively, the spectral techniques proved that all these complexes possessed the same stereochemistry with all the 40 atoms occupying the same relative positions around each one of the 8 metal ions respectively.

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