NMR, ESR, NQR and IR Studies of Paramagnetic Macrocyclic Complexes of first Transition Series Metal Ions Exhibiting MLCT Phenomenon (A DFT Application) Part: II. Bis (1, 10-Phenanthroline) Complexes

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ABSTRACT

D F T implemented in ADF.2012.01 was used to study the structures of 8 macrocyclic paramagnetic four coordinate D_{2d} complexes:$[Phen_2M]^{2+}${M= Mn (II), Fe(II), Co(II),Ni(II),Cu(II)};$[Phen_2M]^{3+}${M=Ti(III) V(III),Cr(III)}(Phen=1,10-phenanthroline) by applying four spectral techniques. After *pre-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 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 {$\eta, q_{11}, q_{22}, q_{33}$, NQCC} were obtained on replacing *Spin Orbit* by *scalar* command in a new ADF Input. The "NMR Program" with *Single Point, LDA, Default, None, Collinear, Nosym* using *DZ* or *TPZ Basis sets* leaving *Unrestricted* command blank gave the Shielding Constants ($\sigma M, \sigma\,^{13}C, \sigma\,^{17}O$), Chemical Shifts ($\delta M, \delta^{13}C, \delta^{17}O$),2 diamagnetic ,4 paramagnetic and 4 spin orbit contributing terms in the σ values of the constituents. The software was, then, run with *Frequencies* to obtain IR frequencies of normal modes of each of 129 fundamental vibration bands of the complexes. Importance of the study would lie in the fact that: (i) 5 parameter: $\sigma, \delta, \eta, g_n. A_{ten}$, NQCC of ^{14}N; 4 parameters: $\sigma, \delta, g_n. A_{ten}, \eta$ of ^{13}C and 3 parameters: $\sigma, \delta, g. A_{ten}$ of ^1H corroborated to infer that in all these complexes, the 24 C were of 6 types; the16 H of 4 types and all the 4 N were spatially of the same type(ii) it confirmed MLCT phenomenon by NMR(iii) calculated another parameter of each of NMR (H^) and ESR {ΔE_{hf}} and two of NQR {η,Laplace equation} (iv) classified129 bands into vibration symmetries and IR activities and (iv) gave thermal parameters of the complexes.

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

INTRODUCTION

Aromatic heterocyclic compounds such as 1, 10-phenanthroline (Phen) and 2, 2-bipyridine (Bipy) form an important class of compounds in which the Π and n electrons can form charge-transfer complexes[1, 2] where the electronic charge of their complexes having filled Π- molecular orbitals of energy comparable to the metal orbitals get transferred into the empty molecular orbitals with energy nearly equal to the ligand orbitals. They absorb in the visible region to exhibit intense color which is termed as Metal to Ligand Charge Transfer (MLCT) phenomenon. Unlike 2,2'-bipyridine, the 1,10-phenanthroline does not have the same conformational flexibility and it would bind metal ions more strongly[3,4]. This enantioselective interaction of 1, 10-phenanthroline complexes of iron (II), Co (III), Zn (II) is used as a structural probe and mediators of DNA cleavage reactions[5-7]. Homoleptic *bis*(1,10-phenanthroline) transition metal ions complexes $[Phen_2M]^{2+, 3+}$ were studied comparatively to a lesser extent both experimentally and by Density Functional Theory(DFT). Single crystal structures of bis [chloro bis(1,10-phenanthroline-N,N') (thiourea -S) nickel(II)] chloride nitrate was studied by L. Suescun and his coworkers[8]. Structure and magnetic properties of di-μ-hydroxo-bis [bis(1,10-phenanthroline) chromium(III)] iodide tetrahydrate were studied by Raymond Scaringe and Phritu Singh[9]. O. Yesilel, H. Olmez studied spectrothermal properties of 1, 10-phenanthroline complexes along with X-rays single crystal structure and photo luminance properties of Co (II), NI (II), Cu (II) and Cd (II) orotates with UV-Vis; and FTIR[10]. V. Chis et al[11] studied Spin-state cross-over in Fe $(Phen_2(NCS)_2$ by DFT. Ozel Aysen E. and coworkers[12] studied vibration spectra of copper(II)2,2'-bipyridine and 1,10-phenanthroline complexes by applying DFT[12]. DFT IR, UV and Mossbauer of 2, 2'-bipyridine and 1, 10-phenanthroline complexes of iron (II) was studied by Morigakii, Milton K. et al[13] with the help of DFT.H.Z. Chiniforoshan et al[14] studied the structures of complexes of Co (III) and Zn (II) with 2,2'-bipyridine and 1,10-phenanthroline by applying DFT. Sumit Sanotra et al applied DFT to study X-ray crystal structure and photo luminance properties of [Cd $(NO_3)_2$ (phen)$_2$][15]. Euan *K. Bre* chin and coworkers[16] studied UV,ESR and magnetic properties of Cr(III), Fe(II).N.S. Panina and coworkers[17] studied stabilities

of high and low spin isomers and X-ray structures of Ni(II) complexes. Zn Bz Li and Xiao yuan studied Raman spectra of bis- and tris (1, 10-phenanthroline) manganese (II) complexes[18].

Need for the study

* A limited experimental research had been carried out in the calculation of NMR, ESR and NQR parameters of these 8 macro cyclic paramagnetic 1,10-phenanthroline complexes:$[Phen_2M]^{2+}$ {M=Mn (II),Fe(II) Co(II),Ni(II),Cu (II)}; $[Phen_2M]^{3+}$ {M=Ti(III),V(III),Cr(III)} as accurate computations of parameters of these techniques[19-23] had become possible by DFT[24,25] only recently .

* $v_{(CN)}$ would be lowered on coordination of N to a metal ion while the transfer of electronic charge from molecular orbitals mainly with metal character to those having the ligand character should increase $v_{(CN)}$. Since $v_{(CN)}$ was metal sensitive only to a limited extent, it would be difficult to assign exact value to $v_{(CN)}$ as many 1, 10-phenanthroline vibrations also appeared in the same region[26]. Also the $\Pi \rightarrow \Pi^*$ transition of the ligand and MLCT in some complexes [27] would absorb in the same region[19], the reflectance spectral technique might not help. Thus the NMR technique was tried which also enabled us to calculate the Spin Hamiltonian (H^) values of these complexes

Methodology

Use of ADF (Amsterdam Density Functional) software to calculate various NMR [(29-34)], IR [(28)], ESR [(35-39)] and NQR [(35-39)] parameters had, already, been reported.

RESULTS

Tables: 1-3 represented energies of metals, their g_n and I values, thermal and optimization parameters of complexes. Table 4 gave σ and δ values of ^{14}N, ^{13}C and ^1H of the free1, 10-phenanthroline. Table 5 contained σ and δ values of M^{+n}, ^{14}N, ^{13}C and ^1H of complexes. Table 6 contained contributions of 2 diamagnetic, 4 paramagnetic and 4 spin orbit terms (10 in all) in σ of M^{n+} ^{14}N, ^{13}C, ^1H of complexes .Table: 7 gave ESR and NQR parameter of the various types of H, C and N in complexes.

Table 8 gave some more ESR and NQR parameters of complexes. Table 9 contained contributions from five factors into H ^{Spin} and ΔE_{hf} values. Table 10 designated IR-active bands in the complexes. Table 11 gave $\sigma^{14}N$ values of the uncoordinated ligand and the complexes.

Figure 1 gave ADF numbers of the 8 bis (1, 10-phenanthroline) complexes

DISCUSSION

Each one of the eight 1, 10-phenanthroline complexes contained 45 atoms: 4 N,16 H, 24 C and a different transition metal ion.

Relations used to calculate NMR parameters[40]
- σ M $^{n+}$, σ^1H, $\sigma^{13}C$ and $\sigma^{14}N$ were equal to the sum of values of 2 diamagnetic, 4

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

M	Sum of orbital energies	Total 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. Optimization Parameters (kJmol^{-1}), [M g$_n$], {M$_l$ }and (M$_S$) of [Phen$_2$ M] $^{n+}$ Complexes

M $^{n+}$ (D$_{2d}$)	[M g$_n$] {M$_l$ } (M$_S$)	Total bonding energy**	Total Energy(X c) LDA(Exchange; Correlation) GGA(Exchange; Correlation) ^{a}	Nucleus
Ti(III) ^{a}	[-0.315392]{2.5} (0.5)	-25980.97	-511912.56 -442448.48, -34582.43 -52792.02, 17910.37	^{47}Ti
V(III)	[1.4710588]{3.5} (1.0)	-28816.33	-484494.18 -449671.64, -34822.54	^{51}V
Cr(III) ^{a}	[-0.316360]{1.5} (1.5)	-26138.48	-529520.63 -458827.75, -35164.23 -53626.90, 18098.25	^{56}Cr
Mn(II)	[1.387488]{2.5} (2.5)	-30145.34	-501580.82 -466197.13, -35383.70	^{55}Mn
Fe(II)	[0.181246]{0.5} (2.0)	-29988.39	-510676.41 -475004.40, -35672.01	^{57}Fe
Co(II)	[1.322000]{3.5} (1.5)	-29955.67	-520137.94 -484172.74, -35965.19	^{59}Co
Ni(II)	[-0.500133]{1.5} (1.0)	-29673.45	-530709.68 -494411.25, -36298.43	^{61}Ni
Cu(II)	[-1.4821933]{1.5} (0.5)	-29439.21	-540776.87 -504181.31, -36595.56	^{63}Cu

* Contains LDA and GGA;^{a} GGA contributes** Energy difference between molecule and fragments..

paramagnetic and 4 spin orbit terms of M^{n+}, ^1H, ^{13}C and ^{14}N respectively.

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

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

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

$$\sigma M = -\delta M\ |$$
$$\qquad\qquad\qquad | \qquad ...(3)$$
$$\sigma^{17}O = -\delta\ ^{14}N\ |$$

Relations used to Calculate ESR parameters[35-37]
Effective Spin Hamiltonian (H^)[35-37]

No doubt, three relations[35-39] were needed to calculate H^ but all the 8 complexes included in the present study were axially asymmetric having the same two g values (g⊥) while the third g of different value and was represented as $g_{||}$. Correspondingly, two same a values (a⊥) while the third a of different value was named as $a_{||}$, only the following relation would suffice:

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

Five factors: g factor, a factor, Q factor, Zero Field Splitting (ZFS) factor[41,42] 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:

Table 3: Thermal Parameters of [Phen$_2$ M]$^{n+}$ Complexes

[M]$^{n+}$	Zero Point Volume Energy (e V)	Entropy (cal mol^{-1}K^{-1})				Internal Energy (Kcal mol^{-1})				Constant Capacity (Kcal mol^{-1}K^{-1})			
		Trans.	Rot.	Vib.	Total	Trans.	Rot.	Vib.	Total	Trans.	Rot.	Vib.	Total
Ti(III)	9.2711	43.91	33.1	54.3	131.26	0.889	0.889	223.3	225.1	2.981	2.981	73.88	79.84
V(III)	9.246	43.93	-do-	49.0	126.00	-do-	-do-	222.3	224.1	-do-	-do-	74.43	80.39
Cr(III)	9.2647	43.94	-do-	51.2	128.21	-do-	-do-	222.9	224.7	-do-	-do-	74.03	80.0
Mn(II)	9.256	43.96	-do-	56.4	133.38	-do-	-do-	223.5	225.2	-do-	-do-	77.97	83.93
Fe(II)	9.277	43.97	-do-	70.4	147.44	-do-	-do-	225.4	227.2	-do-	-do-	83.66	89.62
Co(II)	9.244	43.99	-do-	63.3	140.34	-do-	-do-	223.8	225.6	-do-	-do-	80.3	86.3
Ni(II)	9.222	43.98	-do-	60.7	137.74	-do-	-do-	223.0	224.7	-do-	-do-	78.68	84.64
Cu(II)	9.294	44.02	-do-	64.1	141.21	-do-	-do-	225.2	227.0	-do-	-do-	81.34	87.30

Table: 4. σ N, σ H, δ N and δ H(ppm) of 1, 10 – Phenanthroline ^{a}

Ligand [C$_{2v}$]	δ N $^b_{(3)}$	σ N	δ C$^c_{(2)}$	σ C	δ H $^d_{(1)}$	σ H
1, 10-phenanthroline	(6,16) 138.4	N(6,16) -138.4	(1,11)133.38 (2,12)107.25 (3,13)114,51 (4,14)104.94 (5,15) 144.56 (7,17)114.14	(1,11)47.72 (2,12)73.85 (3,13)66.59 (4,14)76.16 (5,15) 36.54 (7,17)66.96	(8,18,21,22)7.65 (9,19) 7.23 (10,20) 9.60	(8,18,21,22)24.06 (9,19) 24.4(10,20) 22.1

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

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

Hyperfine Coupling Energy[41]

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

H^ values were calculated both in terms of MHz as well as in joules mol[1].

Their inter conversions were given as:

- One MHz = $6.627*10^{-21}$ erg = $3.9903124*10^{-7}$ kJ mol^{-1}
- 1cm^{-1} = 0.0119626kJ mol^{-1} = 29979.2458 MHz
- 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[43-45]. So g value of the complex (g_M^{n+}) and its frequency (v_M^{n+}) were related as follows:

$v_m^{n+} = 8388.255 * g_M^{n+}/2.00232$ ...(7)

The details of the various terms involved were discussed elsewhere[28].

Relations used to Calculate NQR Parameters[46, 47] Asymmetry Coefficient (h)[46, 47]

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

(η) lies in between 0-1.For axial symmetry, η=0. It was possible only when:

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

Laplace Equation[46, 47]

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

Calculation of four NMR and NQR parameters

Four more ESR and NQR parameters: H^, ΔE_{hf}, η , and Laplace equation which were calculated in addition to 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) parameters obtained from the software for 7 complexes excluding [Phen$_2$Fe]$^{2+}$where ADF software did not work.

All the 7complexes possessed axial symmetry with (a) Two of three g called g$\perp$ were of

Table: 5. σ and δ values (ppm) of M^{+n} , N, C, H in [Phen$_2$M]$^{n+}$ With M^{n+} Complexes^a

M^{n+}	δ M^{+n} [3] σ M^{+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	δ C[2] σ C
	1	7,17, 29 39	9, 19, 31, 41	10,20, 32,42	11,21, 33,43	22,23 44 ,45	4, 14, 26, 36	5,15, 27,37	6,16 28 ,38	8,18 30 ,40	3, 13, 25, 35	2,12 24,34
Ti	2119.95	-316.5	-57.62	-47.07	-43.9	-48.17	-230.3	-158.00	-9.11	-236.62	-241.10	-235.5
(III)	-2119.95	316.50	89.32	78.77	75.56	79.87	411.35	339.14	190.21	417.72	423.20	416.56
V	8217.00	-296.3	-57.17	-47.21	-47.2	-47.12	-226.7	-159.40	-20.26	-232.96	236.18	-199.50
(III)	-8217.00	296.30	88.87	78.91	78.93	78.82	407.75	340.51	201.36	414.06	417.28	380.62
Cr	3690.89	-310.2	-57.98	-46.54	-42.7	-48.49	-228.4	-159.40	-24.41	-234.00	-239.40	-211.70
(III)	-3690.89	310.20	89.68	78.24	73.40	80.19	409.46	340.46	205.51	415.13	420.54	392.80
Mn	345.51	-178.4	-58.27	-46.72	-42.2	-48.48	-227.3	-153.00	-5.01	-235.90	-240.30	-207.7
(II)	-345.51	178.39	89.97	78.42	73.86	80.18	408.4	334.13	186.11	417.01	421.43	388.79
Fe	6885.75	-140.7	-58.21	-46.65	-41.7	-48.51	-227.7	-154.20	-4.62	-236.44	-240.30	-210.20
(II)	-6885.75	140.68	89.91	78.35	73.4	80.21	408.81	335.27	185.72	417.54	421.37	391.25
Co	14190.2	-84.80	-57.68	-46.23	-42.9	-47,8	-227.7	-151.10	-7.27	-235.40	-238.40	-203.6
(II)	-14190.2	84.80	89.38	77.93	74.61	79.50	408.80	332.18	188.37	416.50	419.52	384.70
Ni	11912.7	1.15	-58.07	-44.71	-37.1	-48.3	-228.3	-145.20	2.13	-235.17	-238.90	-212.10
(II)	-11912.7	-1.15	89.77	76.41	68.82	79.99	409.33	326.61	178.97	416.27	419.97	393.23
Cu	3546.36	163.10	-57.38	-41.98	-35.3	-47.18	-221.8	-136.20	10.97	-223.50	-139.70	-220.10
(II)	-3546.36	-163.1	89.08	73.68	67.0	78.88	402.89	317.90	170.73	404.60	419.43	401.84

a. ADF Numbers in parentheses [Fig .1] ; Apply Relation[1, 2, 3]

Table: 6. Diamagnetic, Paramagnetic & Spin orbit contributions in σ (ppm) of [Phen₂M] ⁿ⁺ Complexes [a]

M ⁿ⁺	σ M ⁺ⁿ			σ N of each of the 4N 7,17, 29,39			σ H of 4 types of H 9, 19, 31, 41,(10, 20 ,32, 42), {11,21,33,43},[22,23, ,44,,45]			σ C of 6 types of C 4, 14, 26, 36,(5, 15 ,27, 37), {6,16,28,38},[8, 18,30,40] ((3,13,25,35)),{{2,12, 24,34}}		
	Dia.	Para.	S.O.	Dia.	Para.	S.O.	Dia.	Para.	S.O.	Dia.	Para.	S.O.
Ti (III)	1599.5	-2510.16	-1209.3	323.18	-6.390	-0.330	28.163	61.255	-0.097	256.2	154.5	0.65
							28.268	51.158	-0.657	257.2	86.22	-4.25
							28.593	48.098	-1.128	57.5	-27.45	-39.8
							28.452	51.338	0.076	255.2	161.9	0.54
										255.2	167.5	0.38
										255.4	167.7	-6.56
V (III)	1706.0	-9199.86	-723.1	322.88	-3.785	-22.80	28.087	60.781	0.003	256.0	151.4	0.36
							28.257	51.259	-0.608	257.2	85.53	-2.21
							28.624	51.385	-1.079	257.3	-33.20	-22.8
							28.376	50.424	0.020	255.0	159.2	-0.08
										255.1	163.2	-1.05
										254.8	145.3	-19.6
Cr (III)	1812.2	-4962.47	-540.6	322.83	2.296	-14.93	28.067	61.561	0.048	255.8	153.8	-0.11
							28.259	50.633	-0.655	257.1	84.2	-0.86
							28.658	45.956	-1.212	257.3	-38.27	-13.5
							28.310	51.779	0.101	254.9	160.3	-0.05
										255.0	165.3	0.23
										254.4	147.9	-9.57
Mn (II)	1927.8	-1905.32	-368.0	322.72	-14.21	28.770	28.770	60.914	0.289	255.6	156.2	-3.36
							29.041	50.622	-1.246	257.3	85.24	-8.43
							29.172	48.012	-3.327	256.6	-43.0	-27.5
										254.8	161.8	0.41
										254.8	167.6	-0.98
										253.8	141.2	-6.22
Fe (II)	2039.0	-8441.23	-483.5	322.78	-36.23	-145.9	28.742	60.926	0.246	255.5	155.6	-2.28
							29.045	50.543	-1.242	257.4	85.97	-8.09
							29.165	47.553	-3.323	256.5	-49.92	-20.9
							28.863	51.339	0.007	254.8	162.6	0.23
										254.9	167.8	-1.28
										253.8	143.0	-5.54
Co	2152.6	-16502.9	160.06	322.68	-44.73	-193.2	28.74	60.56	0.082	255.5	154.6	-1.35
							29.04	50.45	-1.564	257.4	83.92	-9.19
							29.16	49.41	-3.965	256.5	-50.16	-17.9
							28.85	50.89	-0.24	254.7	161.8	-0.03
										254.9	166.4	-1-69

										255.5	154.6	-1.35
Ni(II)	2267.8	-14775.7	595.86	322.81	-32.20	-291.7	28.724	61.158	-0.111	255.4	156.1	-2.26
							29.039	50.127	-2.752	257.4	83.51	-14.3
							29.141	45.543	-5.861	256.5	-51.90	-25.7
							28.835	51.807	-0.654	254.7	161.9	-0.33
										254.9	166.9	-1.88
										253.6	134.5	5.10
Cu(II)	2389.8	-7080.12	1144.7	320.89	-16.32	-467.6	28.728	60.92	-0.572	255.6	156.2	-8.87-
							29.047	50.273	-5.637	257.4	84.03	23.6
							29.130	47.036	-9.177	256.6	-46.74	-39.2
							28.815	51.535	-1.473	254.8	160.3	-10.6
										254.7	167.2	-2.53
										254.1	141.0	6.79

a. ADF Numbers. Dia: Diamagnetic [core & valence tensors]; Para: Paramagnetic [b^, u^, s^ & gauge tensors]; SO: Spin Orbit [4 paramagnetic terms with same names but different values; may shield or deshield so can be (-) or (+)]

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

M $^{n+}$	g$_n$. A $_{ten}$ values of 4 types of H; each type having 4H	g$_n$. A $_{ten}$ value of each one of 4 N	g$_n$. A $_{ten}$ values of 6 types of C; each type having 4 C	η values of 6 types of C each type having 4 C	NQCC and η values of each N
Ti(III)	0.776, 0.898, -0.087 -0.092	-7.654	3.109, -0.070, 0.05, 1.994,18.360, 0.197	0.222,0.251,0.137, 0.411,0.680,0.336	-1.786 (0.969)
V(III)	0.244, 0.572, 0.465,0.118	-6.862	6.118, 0.057, 0.863, 0.573, 8.492, 0.317	0.394,0.267.0.141, 0.443,0.617,0.339	1.621 (0.558)
Cr(III)	0.115, -0.324, -0.70, 0.825	-4.715	3.261, 0.059, 0.08, 3.429, 0.207, 0.795	0.345,0.250,0.139, 0.465,0.606,0.332	1.511 (0.464)
Mn(II)	-1.233, 0.629, -0.333, 0.88	2.184	1.125, -0.357, 0.436, 0.313, 3.512, 0.122	0.104,0.150,0.080, 0.256,0.597,0.229	-2.112 (0.635)
Fe(II)	-0.962, 0.677, 0.247, 0.152	5.221	0.831, -0.106, 0.314, 0.553, 2.012, 0.118	0.038,0.154,0.077, 0.247,0.683,0.230	-2.073 (0.597)
Co(II)	-0.895, 0.928, 0.913, 0.299	9.623	0.857, 0.188, 0.292, 0.95, 1.622, 0.158	0.092,0.160,0.078, 0.262,0.665,0.231	-1.893 (0.698)
Ni(II)	-1.191, 1.907, 2.324, 0.466	16.892	-2.322, 0.146, 0.321, 1.922, 2.661, 0.015	0.056,0.155,0.077, 0.276,0.661,0.230	-1.807 (0.710)
Cu(II)	-1.686, 3.080, 2.934, -0.62	19.753	-2.992, 0.349, 0.372, 2.06, 5.007, -0.866	0.032,0.144,0.076, 0.261,0.679,0.211	-1.959 (0.581)

the same value and third of higher value was called g$_{||}$ (b) Two "a" called a⊥ were of the 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) η=0. Relation (4) was applicable to all to calculate H^. Individual values of these five 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, 8,10) respectively in Tables:7-9.NQCC, a, q were expressed in MHz while g was unit less.

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

It was confirmed by following two ways:

From the equivalence of NMR parameters

For ascertaining the stereochemistry of the complexes, the 4 coordinating N, the 24 C and the 16 H were classified according to their spatial displacements. The metal ion formed a class of its own. The spatially equivalent species possessed same values of δ, σ along with each one of the ten contributing terms towards the total value of σ of the constituents. δ M^{n+}, δ ^{14}N, δ ^{13}C , δ ^{1}H, σ M^{n+}, σ ^{14}N, σ ^{13}C, σ ^{1}H and 10 contributing terms of all the 45 species in each one of the 8 complexes were reported(Tables 5,6). All the four coordinating ^{1}N in each complex were spatially equivalent with the same value each for σ^{14}N, δ^{14}N and the 10 contributing

terms respectively. Each complex having 16 ^{1}H contained four types of stereo chemically different ^{1}H; each type possessing four equivalent protons as they showed four different series of values σ^{1}H, δ^{1}H and 10 contributing terms respectively. The 24 ^{13}C of each complex contained 6 types of spatially different ^{13}C; each type having four equivalents ^{13}C as they gave six different series of values of σ^{13}C and δ^{13}C and contributing 10 terms respectively.

From equivalence among five NMR, ESR, NQR parameters

A total of five parameters of three techniques [ESR (A$_{ten}$), NQR (NQCC,η) and NMR (σ, δ)] were

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

Complex	g values	g n .a& [A ten]*	q & (Laplace)^{10}	NQCC& (η)^{8}	ZFS[D,E]
Ti(III)	1.979469	-0.153030.10^3	-0.871306.10^1	-174.261	[0.000,
	1.979473	-0.109561.10^3	0.435652.10^1	(0.000)	0.000]
	1.998857	-0.109567.10^3	0.435654.10^1		
	g$_{iso}$1.985933	[-124.053]	(0.000)		
V(III)	1.918096	0.139679.10^3	0.444424.10^0	18.666	[-4.10898,
	1.982626	0.154964.10^3	-0.222210.10^0	(0.0001)	-0.00000]
	1.982627	0.154965.10^3	-0.222214.10^0		
	g$_{iso}$ 1.961116	[149.869]	(0.000)		
Cr(III)	1.983371	0.124604.10^1	0.230748.10^1	13.845	[2.703741,
	1.983371	0.127569.10^2	-0.115370.10^1	(0.000)	0.000001]
	2.001192	-0.127570.10^2	-0.115378.10^1		
	g$_{iso}$ 1.989312	[-8.0893]	(0.000)		
Mn(II)	2.000961	-0.301476.10^2	-0.383780.10^1	-76.756	[-0.00684,
	2.002174	0.117779.10^2	0.191890.10^1	(0.000)	0.000000]
	2.002174	-0.117776.10^2	0.191890.10^1		
	g$_{iso}$ 2.00177	[-17.9011]	(0.000)		
Co(II)	2.056954	-0.384734.10^2	-0.252450.10^1	-106.029	[-6.08746,
	2.056955	0.384718.10^2	0.126225.10^1	(0.000)	0.0000]
	2.135381	-0.187778.10^2	0.126225. 10^1		
	g$_{iso}$ 2.083097	[-31.9076]	(0.000)		
Ni(II)	2.007395	0.152867.10^2	-0.551246.10^1	66.1494	[24.31671,
	2.147515	0.152867.10^2	0.551245.10^1	(0.000)	0.00000]
	2.147515	-0.155095.10^2	0.110249.10^2		
	g$_{iso}$ 2.10081	[5.02128]	(0.000)		
Cu(II)	2.008951	-0.350692.10^3	641568.10^1	38.494	
	2.071098	0.271541.10^2	0.320224.10^1	(0.000))	—-
	2.075582	0.273496.10^2	-0.321343.10^1		
	g$_{iso}$2.051877	[-98.7293]	(0.00174))		

NQCC a, q, are expressed in MHz and g is unit less. *To be used in the calculation of H^ and ΔE$_{hf}$ in Table: 8.

Table: 9. Calculation of H^ and ΔEh f Parameters of [Phen2 M] n+ Complexes

M^n+ Relation	g& giso {g-contribution} MHz	[Aten]& (ΔEh f /A ten) {a-contribution} MHz	NQCC{Q-contribution} MHz	{I-contribution} MHz*	[D,E](ZFS; cm- 1)(4,5) {MHz}**}[7]	H^ (MHz)*** {J mol1-}
Ti(III) (4){H^} (6)	‖ 1.998857 ⊥1.979469 ⊥1.979473 giso1.985933 (1.399H‖+2.77 H⊥) {11714.87+} 22970.344	A ‖ 487.480 A ⊥347.380 A⊥347.381 [393.330](0.88) {1474.988} (1474.988)	-174.261 (72.609) {72.609}	----- (-0.00060H0) {-5.033 }	[0.000,] 0.000 (0.000) {0.000}	 (36237.88) {14.464}
V(III) (6) (4){H^}	1.918096 ⊥1.982627 giso 1.961116 (2.684H‖+5.55 H⊥) {21567.062+ 46096.94}	A ‖ 94.951 A⊥105.342 [101.878](0.88) (1069.719) {1069.719}	18.666 (-32.666) {-32.666}	----- (0.003952H0) {33.150}	[-4.10898, -0.0000] (-5.4786) {164245. 495}	A 105.342 (232979.70) {92.966}
Cr(III) (4) {H^}) (6	‖ 2.000961 1.983371 ⊥1.983371 giso 1.989312 (4.20H‖+8.327 H⊥) {35210.824+ 69187.98}	A ‖ 3.939 A⊥ - 40.324 A⊥ - 40.324 [25.570] (0.81) (-172.598) {-172.598}	13.845 ------ (3.461) {3.462}	 (-0.00036 H0) {-3.020}	[2.703741,] 0.000 (6.7594) {202640.29}	 (306866.69) {122.449}
Mn(III) (4) {H^} (6)	‖ 2.000961 ⊥2.002174 ⊥2.002174 giso 2.00177 (7.00H‖+14.01⊥) {58677.93+ 117510.884}	A ‖ - 21.728 A⊥ -8.489 A⊥ -8.489 [-12.902] (0.96) (-241.913) {-241.913}	-76.756 (31.982) {31.982}	------ ((0.001889H0) {15.454}	[-0.00684, 0.000] (-0.05984) {1794.198}	 (177788.54) {70.943}
Co(III) (4) {H^} (6)	‖ 2.135381 ⊥2.056954 ⊥2.056955 giso 2.083097 (5.482H‖+8.636H⊥) {49040.235+ 74417.584}	A ‖ -14.204 A⊥-29.100 A⊥-29.102 [-24.135] (0.90) (-380.126) {-380.126}	-106.029 (185.551) {188.551}	------ (0.00353H0) {29.611}	[-6.08746, 0.000] (-15.2187) {456243. 649}	 (579539.50) {231.254}
Ni(III) (4) {H^} (6)	‖ 2.007395 ⊥2.147515 ⊥2.147515 giso 2.10081 (2.809H‖+6.01H⊥) {23622.329+ 54069.060}	A ‖ 49.025 A⊥-48.321 A⊥-48.321 [-15.872] (2.65) (-71.424) {-71.424}	66.1494 (16.537) {16.537}	------- (-0.00057H0) {-4.781}	[24.31671, 0.000] (32.422) {971995.502}	 (1049627.2) {418.834}
Cu(III) (4) {H^} (6)	‖ 2.008951 ⊥2.071098 ⊥2.075582 giso 2.051877 (1.406H‖+2.90H⊥) {11832.944+ 25215.991}	A ‖ 236.613 A⊥ -18.321 A⊥-18.452 [66.610] (1.79) (149.873) {149.873}	38.494 (9.624) {9.624}	------ (- 0.001695H0) {-14.218}	[0.000, 0.000] (0.000) {0.000}	 (37222.65) {14.857}

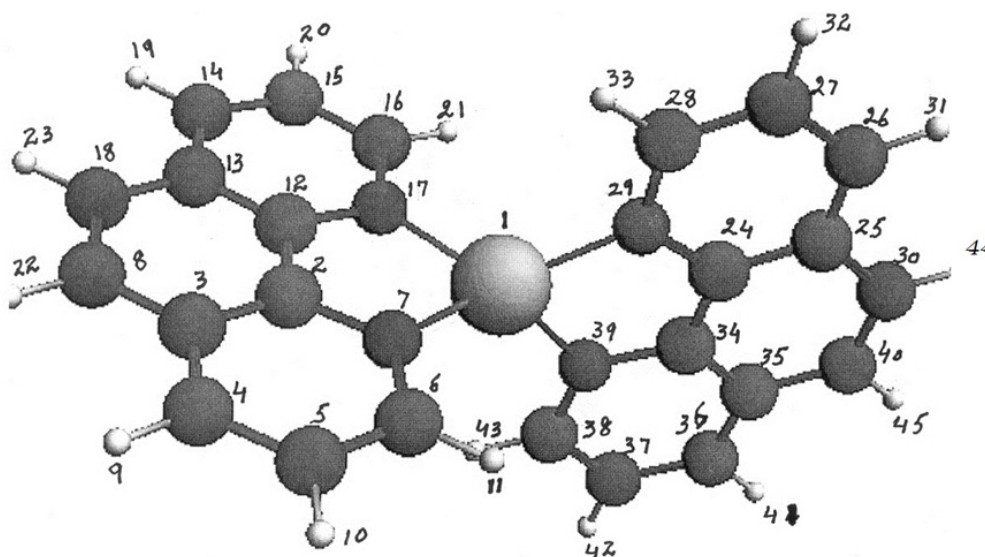*Multiply by 8388.255;**Modulus; ***Sum of values in II-V columns

Table: 10. Designations of IR Active Bands in [Phen2 M] n+ Complexes

Complex with M +n	Vibration Symmetry of bands*	IR active bands	Vibration Symmetry Class
Ti(III),V(III),Cr(III), Mn(II), Fe(II), Co(II),Ni(II),Cu(II)	A(129)	A(129)	[129A]

*Numbers in parentheses indicate bands of a specific symmetry

Table: 11. σ N values of 1, 10-Phenanthroline and its complexes with metal ions

σ values	Phen	Ti(III)	V(III)	Cr(III)	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)
σN	-138.4	316.50	296.30	310.20	178.39	140.68	84.80	-1.15	-163.1

Fig.1: [Phen₂M]ⁿ⁺{M=Ti (III),V(III), Cr(III) ,Mn (II),Fe(II), Co(II),Ni(II),Cu(II) at:1}

used to ascertain similar stereochemistry of 8 paramagnetic complexes. Four stereo chemically equivalent N possessed the same values of above named five parameters. The four parameters: g_n. A_{ten},η, σ, δ of 24 ^{13}C were categorized into 6 types(NQCC=0 for all); each having 4 equivalents C. Three parameters (g_n. A_{ten}, σ, δ) of the 16 H were of 4 types (NQCC and η =0 for all); each type having 4 equivalents ^{1}H. So the three techniques corroborated to confirm that each one of these complexes possess one type of 4 N; six types of 24 C and four types of 16 H. Further, the two NMR parameters (σ, δ) of constituents were shown in Table: 5 and the remaining three [one of EPR (A_{ten}) and two of NQR (NQCC,η) were shown in (Table: 7). Again, with I=1/2 for ^{1}H and ^{13}C; their NQCC =0.0.This

left 4 parameters each for^{1}H and ^{13}C. All the η values were zero for all the 16 ^{1}H.So three parameters were reported for ^{1}H.

Evidence of MLCT Phenomenon from NMR parameters of complexes

MLCT phenomenon would increase an electron density on the ligand by shifting electronic charge from the filled molecular orbitals of complex lying mainly on metal to its vacant molecular orbitals with energies comparable to the ligand. As σ of a nucleus was directly related to its electron density, any change in its value should serve as an indicator to the change in electron density on it. In 7 of the 8 complexes {except in [Phen₂Cu] $^{2+}$}, total shielding tensors of the σ^{14}N, σ^{13}C, σ^1H (Tables:11,5) were

observed to be higher and the $\delta^{14}N$, $\delta^{14}C$, $\delta^{1}H$ were found to be lower than their values in the uncoordinated ligand (Table:4).It confirmed the transfer of electronic charge from metal to the ligand and thereby the MLCT.

IR Parameters of complexes

The software gave values of frequencies, dipole strengths and absorption intensities of IR-active normal modes of all the 129 fundamental vibration bands of the complexes; each having A (singly degenerate) symmetry according to their IR-activities[48] with a Vibration Symmetry Class {129A} (Table: 10).

CONCLUSIONS

- With higher $\sigma^{14}N$, $\sigma^{13}C$, $\sigma^{1}H$ and lower $\delta^{14}N$, $\delta^{14}C$, $\delta^{1}H$ values of constituents in these complexes relative to uncoordinated ligand would confirm an increase in the electron density on the ligand in the complexes to lend support to the transfer of electron cloud from the metal into the ligand orbitals as per MLCT definition.

- NMR, ESR and NQR results corroborated with one another to prove that all these 8 complexes possessed the same stereochemistry as all the 44 atoms were occupying the same relative positions around each one of metal ion.

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