NMR, ESR, NQR and IR Studies of Paramagnetic Macrocyclic Complexes of 1st Transition Series Metal Ions Exhibiting MLCT Phenomenon: A DFT Application. Part: IV. Tris(1, 10-phenanthroline) Complexes

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Abstract: *Density Functional Theory (DFT) implemented in ADF 2012.01 was used to study the structures of three macro-cyclic paramagnetic hexa coordinated complexes: $[L_3M]^{2+}$ {M=V(II), Ni(II)}, and $[L_3Cr]^{3+}$ where L=1,10-phenanthroline having symmetry point group D_3 to calculate their spectrochemical parameters. The software was run by using Single Point, 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} after the pre- optimization of the complexes. 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. Thereafter, the software was run using the "NMR Program" with Single Point, Default, None, Collinear, Nosym using the same Basis sets but leaving Unrestricted command blank to obtain the Shielding Constants (σM, $\sigma^{13}C$, $\sigma^{17}O$), Chemical Shifts (δM, $\delta^{13}C$, $\delta^{17}O$), 2 diamagnetic, 4 paramagnetic and 4 spin orbit contributing terms in the σ values of constituents. IR frequencies of normal modes of the 195 fundamental vibration bands of these complexes were obtained by using the keyword Freequencies.5 parameters: σ, δ, g. A_{ten}, η, NQCC of ^{14}N; 4 parameters: σ, δ, g. A_{ten}, η of ^{13}C and 3 parameters: σ, δ, g. A_{ten}, of ^1H corroborated to infer that in these 1,10-phenanthroline complexes, the 36 C were of 6 types while the 24 H of 4 types but all the 6 N were spatially of the same type .The importance of this study would lie in the fact that it confirmed MLCT phenomenon by NMR; calculated four other NMR,ESR and NQR parameters: H^, ΔE_{hf} Asymmetric coefficient(η), Laplace equation; classified the 195 fundamental bands into vibration symmetries and IR activities along with some thermal parameters of the complexes.*

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

I. Introduction

        The development of simple to complex transition metal compounds in which the metal ion is bonded to a variety of ligands have attracted immense attentions over the past few decades oweing to their unique characterstics that arises because of their enriched physicochemical, optical and electromagnetic properties. We have well established synthetic methods available in literature to modulate these properties.(*1-4*) The several potential applications of transition metal complexes but not limited to be involved in catalysis(*5-7*), components for energy storage devices, optical materials (*8, 9*), Sensors(*10*), biologically active materials (*11, 12*) and so on. Phenanthroline (Phen) ligand reported to be a promising building block component in the design of metal organic frameworks because of its rich cooridation modes and high stability and wide variety of practical applications in analytical chemistry, Catalysis and biochemistry.(*1, 13*) The practical application of these complex compounds rely mainly on their high yield synthetic methods and unique characterstics. To develope such compounds in high yield it is important to predict their charcterstics even before synthesis, should therefore be of great value. Density Functional theory (DFT) can serve as a valuable tool to this path and have been extensively used to study transition metal-phenanthroline or substituted phenanthroline complexes to study their structures and other electromagnetic properties.(*14-21*) The present study is an extension of our previously reported work (*22*) where we had studied macro-cyclic, paramagnetic complexes such as: $[L_3M]^{2+}$ {M=V(II), Ni(II)}, and $[L_3Cr]^{3+}$(L=2,2′ -bipyridine) exhibiting Metal to Ligand Charge Transfer (MLCT) phenomenon with the help of NMR, ESR, NQR and IR spectral techniques. We would try a few analogous biologically

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important macro-cyclic paramagnetic complexes of the 1,10-phenanthroline ligand: $[L_3M]^{2+}$ {M=V(II), and Ni(II) }, and $[L_3Cr]^{3+}$ (L=1,10-phenanthroline) using DFT implemented in ADF: 2012:01. Numerous research has been done to investigate the structures, magnetic, electronic, vibrational and optical properties, Spin- State Cross-Over phenomenon and Jahn-Teller effect using different keywords in case of a few homoleptic and mixed tris(1,10-phenanthroline) complexes of 1st transition series metal ions by DFT. (*23-27*) To the best of our knowledge DFT had hardly been used in the calculation of NMR, ESR and NQR parameters in the tris(1,10-phenanthroline) complexes of 1st transition series metal ions**.** Moreover NMR was never used to ascertain the presence of Metal to Ligand Charge Transfer (MLCT) phenomenon (*28, 29*) as accurate computations of their NMR, ESR and NQR (*30-33*) parameters had become possible by DFT only recently. (*34-36*)

II. Need For The Study

It was difficult to assign the exact value to ν_{CN} because several uncoordinated 1,10-phenanthroline vibrations (*37*) would also fall in the ν_{CN} region of these complexes. So IR and Raman spectra which were commonly used to study CT phenomenon in other cases had a limitation here. Reflectance technique was, also, not helpful as $\pi \to \pi^*$ transition of this ligand (*38*) absorbed in the same region where MLCT were observed in some complexes.

III. Methodology

We have already reported the use of ADF software implemented in DFT has a potential to be used as a valuable tool to calculate various spectroscopic parameters of NMR (*39-41*)**,** IR(*42*), ESR and NQR (*43-45*) to predict the structure and properties of first transition series metal ion complexes.

IV. Results

Table: 1 Showed the thermal parameters of complexes. Table: 2 Showed the Optimization parameters of the 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 ^1H of the three complexes. Table: 4 showed 10 Diamagnetic, Paramagnetic and Spin orbit contributing terms in σ values of constituents. Table: 5 Showed the ESR and NQR parameters of the three complexes. Table: 6 Showed calculation of H^, ΔE_{hf} of the paramagnetic complexes. Table: 7 Showed more ESR and NQR parameters of complexes.Table:8 Showed the IR active bands of complexes. Table: 9 Showed the $\sigma^{14}N$ values of the uncoordinated tris(1,10-phenanthroline) ligand and the complexes. Figure: 1 Represented ADF numbers as mentioned in tables in parentheses where ever required for the tris(1,10-phenanthroline) complexes.

V. Discussion

Each of the three tris(1,10-phenanthroline) metal complex possessed a total of 67 constituent atoms which differ only in the nature of metal ion present in them. The remaining 66 atoms are being: 6 Nitrogen atoms, 24 Hydrogen atoms and 36 Carbon atoms. The detailed discussion of various calculated parameters and the mathematical equations used to calculate them (see supporting materials at the end) of all three studied complexes are discussed below.

5.1. Relations used to calculate NMR , ESR and NQR parameters

We would obtain as many as thirteen different ESR(*43-45*), NQR(*46, 47*) and NMR(*36*) parameters such as: ESR (g_n, A_{ten}), NQR (NQCC, η) and NMR {$\sigma^{13}C$, $\delta^{13}C$, $\sigma^{14}N$, $\delta^{14}N$, σ^1H, δ^1H, σM, δM and 10 terms (2 diamagnetic and 4 paramagnetic and 4 spin orbit) each for M, ^{14}N, ^{13}C, and ^1H} having different units. We have reported earlier the various mathematical equations (see supporting materials at the end) that showed the relationship between the above mentioned parameters and also with the two other ESR parameters (H^, ΔE_{hf}) (*22, 42, 48*). They , all , helped us to ascertain the stereochemistry of these complexes.

5.2. Calculation of four ESR and NQR parameters:

Other 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) parameters given by the software for the two complexes $[Phen_3V]^{2+}$ and $[Phen_3Cr]^{3+}$. However, for the third complex $[Phen_3Ni]^{2+}$ the ADF software did not work. These complexes possessed axial symmetry with (a) Two of three **g** called $\mathbf{g_\perp}$ were of the same value and third of higher value was called $g_\parallel$ (b) Two **a** called $\mathbf{a_\perp}$ were of same value and the third of higher value was called $\mathbf{a_{11}}$. (c) Two of the three **q** parameters were of the same value. (d) η=0, equation (4) (see supporting materials at the end) was applicable 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 (7,8,10) respectively (see supporting materials at the end) in Tables: 6,7. The parameters like NQCC, **a**, **q** were expressed in MHz while the g parameter was unit less.

5.3. Confirmation of Spatial Equivalence of NMR parameters of N, C, H
The same stereochemistry of the three complexes having D_3 point group was ascertained as follows by two ways:

5.3.1. From the equivalence of NMR parameters of complexes
Spatially equivalent species having same values of δ, σ and each one of 10 contributing terms in the total value of σ of constituents respectively (*22, 42, 48*) led us to infer that the three tris(1,10–phenanthroline) complexes: $[L_3M]^{2+}$ {M=V(II), Ni(II) and $[L_3Cr]^{3+}$, where L= tris(1,10–phenanthroline) contained 4 types of stereo chemically different H; each type possessing 6 equivalent protons which showed four different series of values of σ^1H, δ^1H and the 10 contributing terms respectively. They also contained six types of spatially different C atoms; each type having six equivalents C; giving six different series of values of $\sigma^{13}C$ and $\delta^{13}C$ and the 10 contributing terms respectively. All the six ^{14}N nuclei were equivalent with the same values of $\sigma^{14}N$ and $\delta^{14}N$ and the 10 contributing terms respectively (Tables:3 and 4).

5.3.2. From the equivalence in five NMR, ESR and NQR parameters
5 parameters of used spectroscopic techniques [ESR (A_{ten}), NQR (NQCC, η) {Tables:5 and 6} and NMR (σ, δ) {Tables:3,4}] were used to ascertain the similar stereochemistry of the complexes by the fact that stereo chemically equivalent species would possess same values of these parameters. 5 parameters: σ, δ, g. $A_{ten,}$ η, NQCC of ^{14}N; 4 parameters: σ, δ, g. $A_{ten,}$ η of ^{13}C and 3 parameters: σ, δ, g. $A_{ten,}$ of ^1H corroborated to infer that in all these complexes, 36 C were of 6 types. The 24 H were of 4 types and all the 6 N were spatially of the same type.

5.4. Evidence of MLCT Phenomenon from NMR parameters of complexes
As the σ value of any nucleus(*22, 42, 48*) 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. The $\sigma^{14}N$ (Table: 9), $\sigma^{13}C$, σ^1H (Table:3) values in these complexes were higher but $\delta^{14}N$, $\delta^{13}C$, δ^1H values were found to be lower than their corresponding values of uncoordinated ligand(*22*) to confirm the transfer of electronic charge from the metal to the ligand. So NMR results supported the presence of MLCT phenomenon in these complexes.

5.5. IR Studies of the Complexes (*49*)
ADF software gave values of frequencies, dipole strengths and intensities of IR normal modes of the 195 fundamental vibration bands of these complexes. Each band was given a vibration symmetry symbol while each complex was represented by a Vibration Symmetry Class (*49*). The bands were classified according to their IR activities with symmetry symbols A_1, A_2, and E having 33, 32 and 130 bands (Table:8) respectively with a vibration symmetry class [$33A_1 + 32A_2 + 65E$]. Bands with A_2 and E symmetries were IR-active while the bands with A_1 symmetry were IR- inactive.

VI. Conclusions
With NMR parameters like $\sigma^{14}N$, $\sigma^{13}C$, σ^1H having higher and the $\delta^{14}N$, $\delta^{13}C$, δ^1H showing lower values than those of their values in the uncoordinated ligand, an increase in electron density on ligand was authenticated. This implied the transfer of electron charge from the metal into the ligand orbitals and thus justified the presence of MLCT phenomenon. NMR, ESR and NQR justified that these complexes possessed the same symmetry point group (D_3) where the 66 constituting species would occupy the same relative positions around the metal ion.

Table: 1. Thermal Parameters of $[Phen_3M]^{n+}$ Complexes

M^{n+}	Zero Point Energy (eV)	Thermal Parameters											
		Entropy (cal mol⁻¹ K⁻¹)				Internal Energy (Kcal mol⁻¹)				Constant Volume Capacity (Kcal mol⁻¹K⁻¹)			
		Trans.	Rot.	Vib.	Total	Trans.	Rot.	Vib.	Total	Trans.	Rot.	Vib.	Total
V(II)		45.02	33.8	68.3	147.08	0.889	0.889	277.2	279.0	2.981	2.981	96.9	102.9
Cr(III)	12.547	-do-	-do-	86.4	165.13	-do-	-do-	279.8	281.6	-do-	-do-	102.4	108.4
Ni(II)		-do-	-do-	85.0	163.85	-do-	-do-	278.7	280.5	-do-	-do-	103.5	109.5

Table: 2. Optimization Parameters (kJmol⁻¹), [Mg_n], {M_I} and (M_S) of $[Phen_3M]^{n+}$ Complexes

M^{n+} (D_3)	[M g_n], {M_I} (S)	**Total bonding energy	*Total Energy :Xc LDA(Exchange; Correlation)	Nucleus
V(II)	[1.4710588] (1.5)	-45688.81	-670489.56 -620721.59, -49767.9	^{51}V
Cr(III)	[-0.316360] (1.5)	-44826.18	-679431.25 -629353.61, -50077.64	^{56}Cr
Ni(II)	[-0.500013] (1.0)	-45232.03	-716715.35 -665469.98 , -51245.37	^{61}Ni

*X c is made up of LDA and GGA components. Here all have zero GGA. **Bonding energy is computed as an energy difference between molecule and fragments.

Table: 3 . σM^{n+}, σN, σH and δH in [Phen$_3$M]$^{n+}$ Complexes [a]

M^{n+} δM^{n+} σM^{n+}	δN[3] σN	δH[1] σH	δH[1] σH	δH[1] σH	δH[1] σH	δC[2] σC	δC[2] σC	δC[2] σC	δC[2] σC	δC[2] σC	δC[2] σC
[Fig .1] 1	7,17,29, 39,51,61	9,19,31, 41,53,63	10, 22,23, 44,45,66	11,21,33, 43, 55,65	20,32,42, 54,64,67	4,14,26, 54,64,67	5,15,25, 36,48,58	6,16,28, 38,50,60	8,18,30, 40,52,62	3,13,25, 35,47,57	2,12,24, 36,46,56
V^{2+} 2416.84 -2416.84	-413.0 413.0	-64.04 95.74	-54.8 86.5	-72.85 104.55	-58.78 90.48	-254.4 435.48	-192.6 373.66	-67.0 248.11	-236.97 418.07	-218.84 399.94	-206.94 388.04
Cr^{3+} 2900.40 -2900.40	-411.2 411.22	-64.09 95.79	-55.06 86.76	-70.64 102.34	-57.61 89.31	-252.4 433.54	-191.2 372.25	-73.24 254.34	-238.8 419.94	-219.8 400.88	-217.9 399.03
Ni^{2+} 9248.43 -9248.43	-373.96 373.96	-53.7 95.45	-54.7 85.40	-64.66 96.36	-54.46 86.16	-249.6 430.7	-151.7 332.78	-44.51 225.61	-232.6 413.9	-202.1 383.18	-199.4 380.50

[a] ADF Numbers in parentheses; Apply Relations[1,2,3 (see supporting material)]

Table: 4. Sum of Diamagnetic, Paramagnetic, Spin orbit Terms in σM^{n+}, N, H, C of [Phen$_3$M]$^{n+}$ Complexes [a]

a M^{n+} [Fig .1]	σ M^{n+} 1			σ N of each of the 6 N 7,17,29, 39,51,61			σ H of 4 types of H* 9,19,31,41,53,63{10,22,23, 44,45,66}[11,21,33,43,45,65] {20,32,42,54,64,67}			σ C of 6 types of C* 4,14,26,36,48,58{5,15,25, 37,49,59}[6,16,28,38,50,60] {8,18,30,40,52,62}{{3,13,25, 35,47,57}}[[2,12,24,36,46,56]]		
	Dia.	Para.	S.O.	Dia.	Para.	S.O.	Dia.	Para.	S.O.	Dia.	Para.	S.O.
V(II)	1704.1	-4144.3	23.32	321.77	96.211	-4.988	28.605 28.650 28.184 28.90	67.61 58.467 74.513 61.837	-0.475 -0.605 1.802 0.093	255.5 256.4 256.0 259. 253.4 253.5	151.8 118.8 5.89 164.7 151.8 166.3	1.23 -1.55 -1.54 -13.8 -4.22 -33.8
Cr(III)	1808.8	-4742.4	-33.18	322.20	90.143	-1.129	28.018 28.123 28.701 28.343	67.96 58.94 72.740 61.110	0.186 -0.301 0.897 -0.143	255.6 256.4 256.5 256.9 253.6 253.9	177.1 115.8 3.283 165.2 148.5 162.1	0.84 0.06 -5.43 -0.09 -1.21 -14.9
Ni(II)	2268.4	-11900.6	383,8	324,4	58.949	-9.39.2	28.568 28.567 29.062 28.981	67.54 58.75 73.782 60.833	-0.647 -1.912 -6.524 -3.658	255.4 256.7 256.3 254.6 253.6 253.9	178.1 112.3 -4.221 164.3 150.8 148.7	-2.87 -36.1 -26.4 -5.1 -21.2 -22.1

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

Table: 5. ESR and NQR Parameters from Software for [Phen$_3$M]$^{n+}$ Complexes

* M^{n+}	g$_n$. A$_{ten}$ values of 4 types of H;each type having 6 H*	g$_n$. A$_{ten}$ values of 6 types of C; each type having 6 C	η values of 6 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)	-1.839, 0.016, -0.051, -2.058	6.089,-1.021,4.296, -2.350,6.082,0.239	0.220,0.524,0.071, 0.150,0.628,0.191	-4.070	-2.6993 (≈0.2623)
Cr(III)	-1.345, -0.153, -1.803, -0.002	2.918,-0.563,1.437, -1.153,2.497,0.055	0.919,0.803,0.980, 0.904,0.399,0.017	≈-5.397	≈3.186 (≈0.025)
Ni(II)	0.525, 0.050, 3.494, 1.295	-0.73,1.915,-0.698, 4.101,0.817,0.360	0.453,0.545,0.091, 0.143,0.777,0.224	≈25.170	≈ - 2.840 (≈0.052)

*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 M^{n+} in [Phen$_3$M]$^{n+}$ Complexes

* M^{n+}	g values	g$_n$.a&[A$_{ten}$]	q & (Laplace)[10]	NQCC& (η)[8]	ZFS[D,E]
V(II)	1.994805 1.995166 1.995167 g$_{iso}$1.9951	-0.622079.10^2 -0.764113.10^2 -0.764101.10^2 [-71.6743]	0.295637.10^{-1} -0.147382.10^{-1} -0.148255.10^{-1} (0.00)	1.24167 (0.003)	[-0.08927, -0.0001]
Cr(III)	1.993387 1.992852 1.992859 g$_{iso}$1.99303	0.203662.10^2 0.203542.10^2 0.187 012.10^2 [19.8072]	0.929232.10^0 -0.462359.10^0 -0.466874.10^0 (≈0.00)	5.5754 (0.005)	[-0.0183, 0.0001]

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: 7

Table :7. Calculation of H^, ΔE$_{hf}$ Parameters of [Phen$_3$M]$^{n+}$ Complexes

M^{n+} [Relations]	g &g$_{iso}$ (g contribution) MHz	[A$_{ten}$]&{ΔE$_{hf}$/A$_{ten}$ {a-contribution} MHz	NQCC {Q-contribution} MHz	{I-contribution} MHz*	[D,E]{ZFS Cont. in cm^{-1} (4,5) {MHz}[7]**	H^***(MHz)[7] (J mol^{-1})
V(II) (4)→ {H^} (6)	g$_{∥}$ 1.994805 g$_⊥$ 1.995166 g$_⊥$ 1.995167 g$_{iso}$ 1.995046 (4.187H$_{∥}$+8.376H$_⊥$) {34989.807+70006.679}	A$_{∥}$ -42.288 A$_⊥$ -51.943 A$_⊥$ -51.940 [-48.723](0.88) (-767.387) {-767.387}	1.24167 (-2.173) {-2.173}	---- (0.003952H$_0$) {33.150}	[1.24167,0.0001] (0.7450) {22334.598}	(126528.37) {50.503}
Cr(III) (4)→ {H^} (6)	g$_{∥}$ 1.993387 g$_⊥$ 1.992852 g$_⊥$ 1.992859 g$_{iso}$1.99303 (4.184H$_{∥}$+8.366H$_⊥$) {34939.882+69844.453}	A$_{∥}$ -59.114 A$_⊥$ -64.377 A$_⊥$ -64.955 [-63.610](0.88) (-422.615.) {-422.615}	5.57539 (1.394) {1.394}	---- (-0.00036 H$_0$) {-3.02}	[5.5754,0.0005] (3.34524) {100287.772}	(204653.91) {81.686}

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

Table: 8. Designations of IR Active Bands in [Phen$_3$M]$^{n+}$ 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$_1$(33) ,A$_2$(32) ,E(65)	A$_2$(32),E(65)	A$_1$(33)	{33 A$_1$ +32 A$_2$ +65E}

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

Table: 9. σN values of 1, 10-Phenanthroline and [Phen$_3$M]$^{n+}$ Complexes

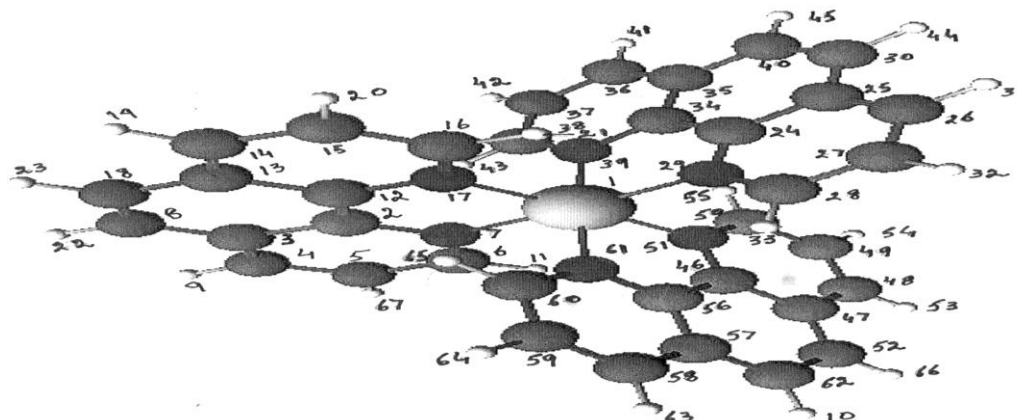| σ values	Phen	Ti(II)	Cr(III)	Ni(II)
σN	-138.4	413.0	411.22	373.96

Fig.1 [Phen$_3$M]$^{n+}$ Complexes {M= V (II), Ni (II), Cr (III) at number:1}

Refrences

[1]   Tai, X. S., Li, Y. F., and Zhao, W. H. (2014) Synthesis and crystal structure of tris(1,10-phenanthroline)-nickel(II) diperchlorate, J. Chem. Phar. Res. 6, 869-873.

[2]   Ma, S., Fillinger, J. A., Ambrogio, M. W., Zuo, J.-L., and Zhou, H.-C. (2007) Synthesis and characterizations of a magnesium metal–organic framework with a distorted (10, 3)-a-net topology, Inorg. Chem. Commun. 10, 220-222.

[3]   Tai, X. S., Li, Y. F., and Zhao, W. H. (2014) Synthesis and crystal structure of Mg (II) complex with 3-amino-2-pyrazinecarboxylic acid ligand J. Chem. Phar. Res. 6, 516-520.

[4]   Liu, C.-M., Zhang, D.-Q., Qin, A.-J., Ye, C., Hu, H.-M., and Zhu, D.-B. (2002) A Novel Nickel(II) Complex Adopting a cis-Configuration: Solvothermal Synthesis and Crystal Structure of [NiL$_2$(H$_2$O)$_4$] (L = 1,4-Dihydropyrazine-2,3-dione-5,6-dicarboxylate), Eur. J. Inorg. Chem. 2002, 1595-1598.

[5]   Soriego, R., Farias, L., and Moya, S. A. (1997) Complexes with heterocyclic nitrogen ligands—IV: complexes of ruthenium(II) and applications in catalysis, Polyhedron 16, 3847-3850.

[6]   Samnani, P. B., Bhattacharya, P. K., Ganeshpure, P. A., Koshy, V. J., and Satish, S. (1996) Mixed ligand complexes of chromium(III) and iron(III): synthesis and evaluation as catalysts for oxidation of olefins, J. Mol. Catal. A: Chem. 110, 89-94.

[7]   Gupta, K. C., and Sutar, A. K. (2008) Catalytic activities of Schiff base transition metal complexes, Coord. Chem. Rev. 252, 1420-1450.

[8]   Xu, H.-H., Tao, X., Li, Y.-Q., Shen, Y.-Z., and Wei, Y.-H. (2012) Synthesis and characterization of a series of transition metal polypyridyl complexes and the pH-induced luminescence switch of Zn(II) and Ru(II) complexes, Polyhedron 33, 347-352.

[9]   Chen, Y., Guan, R., Zhang, C., Huang, J., Ji, L., and Chao, H. (2016) Two-photon luminescent metal complexes for bioimaging and cancer phototherapy, Coord. Chem. Rev. 310, 16-40.

[10]   Harvey, E. C., Feringa, B. L., Vos, J. G., Browne, W. R., and Pryce, M. T. (2015) Transition metal functionalized photo- and redox-switchable diarylethene based molecular switches, Coord. Chem. Rev. 282–283, 77-86.

[11]   Sankaraperumal, A., Karthikeyan, J., Shetty, A. N., and Lakshmisundaram, R. (2013) Nickel(II) complex of p-[N,N-bis(2-chloroethyl)amino]benzaldehyde-4-methyl thiosemicarbazone: Synthesis, structural characterization and biological application, Polyhedron 50, 264-269.

[12]   Mathan Kumar, S., Dhahagani, K., Rajesh, J., Nehru, K., Annaraj, J., Chakkaravarthi, G., and Rajagopal, G. (2013) Synthesis, characterization, structural analysis and DNA binding studies of nickel(II)–triphenylphosphine complex of ONS donor ligand – Multisubstituted thiosemicarbazone as highly selective sensor for fluoride ion, Polyhedron 59, 58-68.

[13]   Ferreira, H., Conradie, M. M., von Eschwege, K. G., and Conradie, J. (2017) Electrochemical and DFT study of the reduction of substituted phenanthrolines, Polyhedron 122, 147-154.

[14]   Panina, N. S., Demidov, V. N., and Simanova, S. A. (2008) A DFT study of transition metal complexes with 1,10-phenanthroline, C-C-dimeric 2,2′-bi-1,10-phenanthroline, and its tetraaza chromophore anion, Russ. J. Gen. Chem. 78, 919-924.

[15]   Reiher, M., Brehm, G., and Schneider, S. (2004) Assignment of Vibrational Spectra of 1,10-Phenanthroline by Comparison with Frequencies and Raman Intensities from Density Functional Calculations, J. Phys. Chem. A 108, 734-742.

[16]   Ronayne, K. L., Paulsen, H., Hofer, A., Dennis, A. C., Wolny, J. A., Chumakov, A. I., Schunemann, V., Winkler, H., Spiering, H., Bousseksou, A., Gutlich, P., Trautwein, A. X., and McGarvey, J. J. (2006) Vibrational spectrum of the spin crossover complex [Fe(phen)$_2$(NCS)$_2$] studied by IR and Raman spectroscopy, nuclear inelastic scattering and DFT calculations, Phys. Chem. Chem. Phys. 8, 4685-4693.

[17]   Bucko, T., Hafner, J., Lebegue, S., and Angyan, J. G. (2012) Spin crossover transition of Fe(phen)$_2$(NCS)$_2$: periodic dispersion-corrected density-functional study, Phys. Chem. Chem. Phys. 14, 5389-5396.

[18]   Koenig, E., and Madeja, K. (1967) 5T2-1A1 Equilibriums in some iron(II)-bis(1,10-phenanthroline) complexes, Inorg. Chem. 6, 48-55.

[19]   Bousseksou, A., McGarvey, J. J., Varret, F., Real, J. A., Tuchagues, J.-P., Dennis, A. C., and Boillot, M. L. (2000) Raman spectroscopy of the high- and low-spin states of the spin crossover complex Fe(phen)$_2$(NCS)$_2$: an initial approach to estimation of vibrational contributions to the associated entropy change, Chem. Phys. Lett. 318, 409-416.

[20]   Sorai, M., and Seki, S. (1974) Phonon coupled cooperative low-spin 1A1 high-spin 5T2 transition in [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$] crystals, J. Phys. Chem. Solids 35, 555-570.

[21]   Paulsen, H. (2016) Periodic Density Functional Calculations in Order to Assess the Cooperativity of the Spin Transition in Fe(phen)$_2$(NCS)$_2$, Magnetochemistry 2, 14.

[22]   Sehgal, M. L., Aggarwal, A., and Singh, S. (2017) 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, IOSR- J. Appl. Chem, 10(6), Ver II, 78-84.

[23]   Anichina, J., Zhao, X., and Bohme, D. K. (2006) Metal- and Ligation-Dependent Fragmentation of [M(1,10-Phenanthroline)$_{1,2,3}$]$^{2+}$ Cations with M = Mn, Fe, Co, Ni, Cu, and Zn: Comparison between the Gas Phase and Solution, J. Phys. Chem. A 110, 10763-10769.

[24]   England, J., Bill, E., Weyhermüller, T., Neese, F., Atanasov, M., and Wieghardt, K. (2015) Molecular and Electronic Structures of Homoleptic Six-Coordinate Cobalt(I) Complexes of 2,2′:6′,2″-Terpyridine, 2,2′-Bipyridine, and 1,10-Phenanthroline. An Experimental and Computational Study, Inorg. Chem. 54, 12002-12018.

[25]   Le Guennic, B., Hieringer, W., Görling, A., and Autschbach, J. (2005) Density Functional Calculation of the Electronic Circular Dichroism Spectra of the Transition Metal Complexes [M(phen)$_3$]$^{2+}$ (M = Fe, Ru, Os), J. Phys. Chem. A 109, 4836-4846.

[26]   Zhang, W., Zhao, F., Liu, T., Yuan, M., Wang, Z.-M., and Gao, S. (2007) Spin Crossover in a Series of Iron(II) Complexes of 2-(2-Alkyl-2H-tetrazol-5-yl)-1,10-phenanthroline: Effects of Alkyl Side Chain, Solvent, and Anion, Inorg. Chem. 46, 2541-2555.

[27]   Vander Griend, D. A., Bediako, D. K., DeVries, M. J., DeJong, N. A., and Heeringa, L. P. (2008) Detailed Spectroscopic, Thermodynamic, and Kinetic Characterization of Nickel(II) Complexes with 2,2'-Bipyridine and 1,10-Phenanthroline Attained via Equilibrium-Restricted Factor Analysis, Inorg. Chem. 47, 656-662.

[28]   Záliš, S., Consani, C., Nahhas, A. E., Cannizzo, A., Chergui, M., Hartl, F., and Vlček Jr, A. (2011) Origin of electronic absorption spectra of MLCT-excited and one-electron reduced 2,2′-bipyridine and 1,10-phenanthroline complexes, Inorg. Chim. Acta 374, 578-585.

[29]   Rzokee, A. A., and Ahmad, A. (2014) Spectroscopic Studies of Charge-Transfer Complexes of 1,10-Phenanthrolein Monohydrate With Some p acceptor, Int. J. Basic App. Chem. Sci. 4, 37-50.

[30]   Kaupp, M., Malkin, V. G., and Malkina, O. L. (1998) NMR of transition metal compounds" in "Encyclopedia of Computational Chemistry, John Wiley & Sons, Chichester.

[31]   Buhl, M. (2004) NMR of transition metal compounds" in, "Calculation of NMR and EPR parameters-Theory and applications, Wiley-VCH, Weinheim.

[32]   Autschbach, J., and Zieglar, T. (2002) Relativistic computations of NMR shielding and spin- spin coupling constants, In Encyclopedia of Nuclear Magnetic Resonance, pp 306-323, John Wiley & Sons, Chichester.

[33]   Bühl, M. (2002) Structure, Dynamics, and Magnetic Shieldings of Permanganate Ion in Aqueous Solution. A Density Functional Study, J. Phys. Chem. A 106, 10505-10509.

[34]   Buhl, M., and Mauschick, F. T. (2002) Thermal and solvent effects on ^{57}Fe NMR chemical shifts, Phys. Chem. Chem. Phys. 4, 5508-5514.

[35]   Bühl, M., Mauschick, F. T., Terstegen, F., and Wrackmeyer, B. (2002) Remarkably Large Geometry Dependence of ^{57}Fe NMR Chemical Shifts, Angew. Chem. Int. Ed. 41, 2312-2315.

[36]   Autschbach, J. (2004) The Calculation of NMR Parameters in Transition Metal Complexes, In Principles and Applications of Density Functional Theory in Inorganic Chemistry I (Kaltsoyanis, N., and McGrady, J. E., Eds.), pp 1-43, Springer Berlin Heidelberg, Berlin, Heidelberg.

[37]   Brahma, S., Sachin, H. P., Shivashankar, S. A., Narasimhamurthy, T., and Rathore, R. S. (2008) Adducts of bis(acetylacetonato)zinc(II) with 1,10-phenanthroline and 2,2'-bipyridine, Acta Cryst. C64, m140-m143.

[38]   Schilt, A. A., and Taylor, R. C. (1959) Infra-red spectra of 1:10-phenanthroline metal complexes in the rock salt region below 2000 cm^{-1}, J. Inorg. Nuc. Chem. 9, 211-221.

[39]   Wolff, S. K., and Ziegler, T. (1998) Calculation of DFT-GIAO NMR shifts with the inclusion of spin-orbit coupling, J. Chem. Phys. 109, 895-905.

[40]   Singh, H., Bhardwaj, A. K., Sehgal, M. L., and Ahmad, I. (2015) Predicting ESR Peaks in Copper (II) Chelates Having Quadrupolar Coordinating Sites by NMR, ESR and NQR Techniques: A DFT Study, Orient. J. Chem. 31, 671-679.

[41]   Singh, H., Bhardwaj, A. K., Sehgal, M. L., Javed, M., and Ahmad, I. (2015) Predicting ESR Peaks in Titanium (III), Vanadium (IV) and Copper (II) Complexes of Halo Ligands by NMR, ESR and NQR Techniques: A DFT Study, Orient. J. Chem. 31, 1461-1468.

[42]   Sehgal, M. L., and Ahmad, I. (2017 (accepted)) NMR, ESR,NQR and IR studies of paramagnetic macro cyclic complexes of 1st transition series metal ions exhibiting MLCT phenomenon: A Density Functional Theory application:Part:1 Bis (2, 2'- bipyridine) complexes, Orient. J. Chem.

[43]   Singh, H., Bhardwaj, A. K., Sehgal, M. L., and Mittal, S. K. (2012) Electron Spin Resonance, Nuclear Quadrupole Resonance, Reflectance and Magnetic Parameters of Cobalt(II) and Nickel(II) Complexes Using Density Functional Theory, Int. J. Curr. Res. Rev. 4, 12-28.

[44]   Harminder, S., Bhardwaj, A. K., Sehgal, M. L., and Mittal, S. K. (2013) Correlation of electron spin resonance, nuclear quadrupole resonance, reflectance and magnetic parameters of Ti (II, III),V (II, III, IV) and Cr (III) complexes: A DFT study, Int. J. Curr. Res. Rev. 5, 13-31.

[45]   Harminder, S., Bhardwaj, A. K., Sehgal, M. L., and Mittal, S. K. (2013) Calculating ESR parameters (H^ & DE$_{hf}$) of 4d and 5d transition metal complexes: A DFT Study, Int. J. Curr. Res. Rev. 5, 71-88.

[46]   Edmonds, D. T. (1974) Advances in Quadrupole Resonance, Vol. 1, Heyden & Sons, London.

[47]   Smith, A. S. (1977) Advances in Nuclear Quadrupole Resonance, Vol. Vol 2. (1975), Vol 3. (1977), Heyden and Sons, London.

[48]   Sehgal, M. L., and Ahmad, I. (2017) NMR, ESR,NQR and IR studies of paramagnetic macro cyclic complexes of 1st transition series metal ions exhibiting MLCT phenomenon: A Density Functional Theory application:Part:1 Bis (1,10- phenanthroline) complexes, Orient. J. Chem., 33(4), 1714-1725.

[49]   Nakamoto, K. (1986) Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Ed. ed., John Wiley & Sons Inc.

Supporting Materials

Relations to calculate various spectroscopic constants using DFT implemented in ADF 2012.01. software.

Relations used to calculate NMR parameters

(a) Sum of values of 2 diamagnetic, 4 paramagnetic and 4 spin orbit terms gave σM^{n+}, σ^1H, $\sigma^{13}C$ and $\sigma^{14}N$ respectively.

(b) δ and σ of ^1H and ^{13}C were related as follows:

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

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

(c) δM and $\delta^{14}N$ were numerically equal but having reverse signs of σM and $\sigma^{14}N$:

$$\left.\begin{array}{l} \sigma M = -\delta M \\[2mm] \sigma^{14}N = -\delta^{14}N \end{array}\right\} \text{ ----------------------------(3)}$$

Relations used to calculate ESR parameters

(a) Effective Spin Hamiltonian (H^)

The 3 complexes were axially asymmetric with same two **g** values (**g$_\perp$**) and third **g** being different (**g$_{II}$**),Two same **a** values (**a$_\perp$**) and third **a** of different value was called **a$_{II}$**,.So following relation would be sufficient to calculate H^:

$$H^\wedge = \left\{\begin{array}{l} \beta_e\,[g_{II}\,.H_{II}.\,S + g_\perp\,(2H_\perp.S)] + [a_{II}\,.\,S\,.I + a_\perp\,(2S.I)] \\[2mm] + Q\,[I -1/3\,I\,(I+1)] + D\,[S_z^2 - S(S+1)/3] - [g_n.\beta_n.H_0\,.I] \end{array}\right\} \text{ ----- (4)}$$

Five factors: g factor, a factor, Q factor, Zero Field Splitting (ZFS) factor and interaction of nuclear magnetic moment with external magnetic field, i.e. I factor would contribute in total value of Spin Hamiltonian (H^).

(b) S$_z$ representing spin angular momentum was calculated as:

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

(c) Hyperfine Coupling Energy

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

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

(d) H^ values were calculated both in terms of MHz as well as in joules mol^{-1}.

The units like MHz, erg, kJ mol^{-1} and cm^{-1} were interrelated as follows:

(i) One MHz=6.627*10^{-21} erg = 3.9903124*10^{-7} kJ mol^{-1}

(ii) 1cm^{-1} = 0.0119626kJ mol^{-1} = 29979.2458 MHz

(e) 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[37-39]. So g value of complex (g$_M^{n+}$) and its frequency (ν_M^{n+}) were related as follows:

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

Relations used to Calculate NQR Parameters

(f) Asymmetry Coefficient (η)

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

No doubt, (η) would lie in between 0-1 but for complexes with axial symmetry, should always be η=0. This was possible only when:

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

(g) Laplace Equation

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