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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

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ABSTRACT

DFT implemented by ADF2010.02 was applied to calculate and correlate 14 ESR, NQR, reflectance and magnetic parameters of the first transition metal ion complexes. Commands like Single Point, LDA, Default, Spin Orbit, Unrestricted, None and Collinear were applied to the software using DZ or TPZ *Basis sets*. 36 complexes such as $[\text{TiX}_4]$ (X=F, Cl, Br, I), $[\text{TiX}_4]^{2-}$ (X=F, Cl, I), $[\text{TiX}_6]^{3-4-}$ (X=F, Cl, Br, I), $[\text{Ti}(\text{OH}_2)_4]^{2+,3+}$, $[\text{VF}_4]^{0,1-}$ (X=F, Cl, Br, I), $[\text{VX}_6]^4$ (X = F, Cl, Br, I), $[\text{V}(\text{H}_2\text{O})_6]^{+2}$, $[\text{CrX}_6]^{3-}$ (X = F, Cl, Br, I, CN) and $[\text{Cr}(\text{NH}_3)]^{3+}$ having both the regular (T_d, O_h) and the distorted stereochemistries ($C_1, D_{4h}, D_{6h}, D_{12}$ and S_4) were selected to carry out all the computations in the gas phase. In $[\text{TiX}_6]^{4-}$ (X=Br, I), LDA was replaced by GGABP. Spin Polarization was kept equal to the number of unpaired electrons present in the metal ions respectively. All the complexes possessed a Nysom symmetry and definite Pre-optimization. The software gave ESR ($g_{11}, g_{22}, g_{33}, g_{\text{iso}}, a_{11}, a_{22}, a_{33}, A_{\text{ten}}$), NQR [$\eta, q_{11}, q_{22}, q_{33}, \text{NQCC}$] and optimization parameters [bonding energy, total energy having contributions from LDA and GGA components]. Two more ESR parameters [$H^{\wedge}, \Delta E_{\text{hf}}$] were calculated from these parameters. Also, two Reflectance parameters [$\lambda_{\text{complex}}, \% \text{ covalent character}$] were obtained from the g_{iso} parameter. Again, five magnetic parameters [$\mu_{\text{soc}}, \mu_t, \mu_{\text{net}}, t_{2g}$ electron delocalization and its constant k] were derived from ESR and Reflectance parameters. Lastly, the Laplace equation was verified from the NQR parameters (q_{11}, q_{22}, q_{33}). The values of the ESR parameter like t_{2g} electron delocalization constant (k) agreed well with the Reflectance parameter namely Nephelauxetic ratio (β_{35}) because both determine the % covalent character in the complexes. The values of all the parameters calculated by the selective use of 18 relations would change with the change in oxidation states of the metal ions but were always in agreement with their reported values.

Keywords: DFT, Nephelauxetic ratio, Pre-optimization.

INTRODUCTION

Effective Spin Hamiltonian (H^{\wedge}) is a mathematical expression that determines the energy of an ESR transition in a paramagnetic complex. It depends upon the ESR [anisotropic and isotropic splitting factors ($g_{11}, g_{22}, g_{33}, g_{\text{iso}}$), hyperfine coupling constants ($a_{11}, a_{22}, a_{33}, A_{\text{ten}}$)] and NQR [electric field gradient or *efg* (q_{11}, q_{22}, q_{33}), Nuclear Quadrupole Constant (Q)]*

parameters, (S), (β_e), (β_n), (I), (g_n) and nature of the surrounding nuclei possessing quadrupole moments ($I \geq 1$).

The following points necessitated the present study to be taken up with the help of software:

There had hardly been any attempt made to theoretically calculate and correlate ESR, NQR, Reflectance and Magnetic parameters of transition metal ion complexes.

I. Theoretical calculation of (H^{\wedge}) of the complexes was never reported before as a class.

II. With ESR transitions falling in low energy microwave region (X band: 9000-10000 MHz), the experiments required cumbersome cryoscopy conditions.

With certain commands, the ADF 2010.02 software gave the five ESR and NQR parameters. They were together used to calculate two other ESR parameters [effective spin Hamiltonian (H^{\wedge}) and hyperfine coupling energy (ΔE_{hf}). The g_{iso} parameter was further correlated to two Reflectance parameters [spin orbit coupling constant ($\lambda_{complex}$), % covalent character]. Again, ESR and Reflectance parameters were together used to calculate and correlate five magnetic parameters [magnetic moments like total (μ_t), net (μ_{net}) and that containing contributions from spin and orbital (μ_{soc} or μ_{ADF}), t_{2g} electron delocalization and its constant (k)].

This communication is an extension of our previous work⁽¹⁾. Here, we have calculated and correlated parameters of 36 Ti(II,III),V(II,III,IV) and Cr(III) complexes such as $[TiX_4]^{1-}$ (X=F, Cl, Br, I), $[TiX_4]^{2-}$ (X=F, Cl, I), $[TiX_6]^{3-,4-}$ (X=F, Cl, Br I), $[Ti(OH_2)_4]^{2+,3+}$, $[VF_4]^{0, 1-}$ (X=F, Cl, Br I), $[VX_6]^{4-}$ (X=F, Cl, Br I), $[V(H_2O)_6]^{2+}$, $[CrX_6]^{3-}$ (X=F, Cl, Br, I, CN) and $[Cr(NH_3)]^{3+}$ having both regular (T_d, O_h) and distorted stereochemistries ($C_1, D_{4h}, D_{6h}, D_{12}, S_4$). We applied DFT⁽²⁻³⁾ implemented in ADF 2010.02 software to obtain 5 parameters (g, a, q, NQCC, η) which were further used to calculate 9 more parameters [$H^{\wedge}, \Delta E_{hf}, \lambda_{complex}$, % covalent character, $\mu_t, \mu_{net}, \mu_{soc}, t_{2g}$ electron delocalization and its constant (k)].

(1) Calculation of ESR Parameters⁽⁴⁻¹²⁾

Effective Spin Hamiltonian (H^{\wedge}) and Hyperfine Coupling Energy (ΔE_{hf})

Four contributing factors to H^{\wedge} are: g, a, Q and interaction of nuclear magnetic moment with external magnetic field (I). Relations [1-3] having contributions from these four factors were used to

calculate H^{\wedge} . The Hyperfine Coupling Energy (ΔE_{hf}) was calculated by relations [4]. Relation [1] was used for systems with different values of g and a. [2] Was applied to axially symmetric systems. [3] Was applied if the systems had the same values of both a and g or g only. The first and the last terms in these relations were in ergs and the other two were in MHz (6.627×10^{-21} erg = one MHz; $\beta_e = 1.3994$ MHz/Gauss; $\beta_n = \beta_e / 1836$. g_n has a specific value for each metal). ΔE_{hf} and Q are in MHz).

(2) Calculation of NQR parameters⁽¹³⁻¹⁴⁾

Asymmetry Coefficient (η) and Laplace Equation are calculated by relations [5-6]. Relations [1-6] are given under Table: 1. 5 A.

Relations used for calculating Reflectance and Magnetic parameters⁽¹⁵⁻²⁰⁾

Parameters like $\mu_{soc}, \mu_t, \mu_{net}, t_{2g}$ electron delocalization (all in B.M), its constant k and $\lambda_{complex}$ (both in cm^{-1}) were calculated by relations [7-18] given below the Table: 1. 6 B. μ_{soc} was the magnetic moment from the spin orbit coupling and (μ_t) represented the total magnetic moment. χ_{tip} and μ_{tip} were the Zeeman Second Order molar magnetic susceptibility and Zeeman Second Order magnetic moment. $\chi_{Mol.s.o.}$, always represents the molar magnetic susceptibility from $\mu_{s.o}$ ($1250.0 \times 10^{-6}, 3333.3 \times 10^{-6}$ and 6250.0×10^{-6} c g s / mol with 1, 2 and 3 unpaired electrons respectively). χ_t was the total molar magnetic susceptibility and k was t_{2g} electron delocalization constant. n = 8 or 4 for A or E ground terms respectively. $\lambda_{Metal\ ion}$ and $\lambda_{complex}$ were the spin-orbit coupling constant of metal ions in different oxidation states when *free* and when they form complexes [$\lambda_{Ti(II,III)} = 61.5, 155.0$; $\lambda_{V(II,III,IV)} = 56.7, 105.0, 250.0$ and $\lambda_{Cr(III)} = 92.0$]. $\lambda_{complex}$ and $\lambda_{Metal\ ion}$ possessed different values. The g_t and g_{eff} were the total and effective values of g respectively. The former made use of the results obtained from the software while the latter used the reflectance parameters from the

literature. The constant $A=1.5$ for Ti (II, III) in the relation [18].

METHODOLOGY

After optimization of the complexes on ADF 2010.02, the software was run with Single Point, LDA*, Default, Spin Orbit, Unrestricted, None and Collinear commands by using DZ* or TPZ* Basis sets for all the Ti (II, III), V (II, III, IV) and Cr (III) complexes except $[\text{TiX}_6]^{4+}$ (X= Br, I) where LDA was replaced by GGABP*. All the complexes had Nysom* symmetry.

[I]- Complexes of Ti (II & III)

Ti (II) is a non –Kramer ion. The degeneracy of its m_j states is always completely removed even by the crystal field to give only singlet m_j levels. [a] (i) With no spin –orbit coupling in tetrahedral Ti (II) complexes having 3A_2 ground term, we would expect longer relaxation times to observe their ESR spectra easily. Of course, the electron cloud of 3A_2 ground term of Ti (II) would intermix with its higher 3T_2 term of the same multiplicity to make 3A_2 to acquire some T character. A weak spin –orbit coupling would operate but with hardly any affect on the relaxation times.

(ii) Only a few examples of ESR spectra of octahedral complexes of Ti (II) having $^3T_{1g}$ ground state were reported due to the presence of extensive spin -orbit coupling.

[b] (i) Although, tetrahedral Ti (III) complexes with 2E ground term did not possess any spin-orbit coupling, yet the electron cloud of the 2E term would intermix with electron cloud of its higher 2T_2 term to make 2E term to acquire some T character. A weak spin –orbit coupling would operate but without affecting the relaxation times. So their ESR spectra were easy to observe.

(ii) Ti (III) octahedral complexes ⁽²¹⁾ with ground term $^2T_{2g}$, always experience a considerable spin orbit coupling which shortens their spin relaxation times. ESR experiments in such cases

were observed only at the liquid helium temperatures.

No doubt, some work had been reported on Reflectance and Magnetic data of Ti (II, III) complexes ⁽²²⁻²³⁾, yet more study is needed to correlate their ESR, NQR, Reflectance and Magnetic parameters.

RESULTS

Each Output file of a complex gave values of two ESR (g_{11} , g_{22} , g_{33} and g_{iso} , product of g_n and $a_{11}, a_{22}, a_{33}, A_{ten}$) and three NQR ($\eta, q_{11}, q_{22}, q_{33}$, NQCC) parameters along with its optimization parameters [point group, dipole moment, bonding energy and total energy (X c)]. X c was made up of LDA and GGA components, each one further contained Exchange and Correlation parts]. The bonding energy was computed as an energy difference between molecule and fragments. With the fragments being single atoms, they were usually computed as Spherically Symmetric and Spin-Restricted. So this might not represent the true atomic ground state ⁽²⁴⁻²⁵⁾.

Tables: 1.1 and 1.1A contained values of the optimization parameters of the Ti (II, III) complexes.

Tables: 1.2 -1.5 gave values of all the five ESR and NQR parameters and verification of Laplace equation for four and six coordinate Ti (II, III) complexes respectively. Table: 1.2A -1.5 A gave g_{iso} , A_{ten} and Q values along with contributions from their respective factors and also contribution from the fourth factor called interaction of nuclear magnetic moment with external magnetic field

factor (I) into H^\wedge . They also contained their $\Delta E_{n f}$ ($\approx 0.5 A_{ten}$) values. The magnetic parameters of 10 out of the 17 complexes were given in Tables: 1.6, 1.6 A and 1.6 B.

DISCUSSION

The discussion regarding Ti (II, III) complexes was divided into two parts:

[A] Calculation of ESR and NQR parameters:**(a) Effective Spin Hamiltonian (H^{\wedge}):**

Depending upon the symmetries and the values of parameters, the complexes were categorized as:

- i) $[\text{Ti X}_4]^{1-}$ (X=F, Cl, Br, I) possessed characteristics of D_{4h} axial symmetry with (a) Two of three g called g_{\perp} were of same value and third of higher value called g_{\parallel} . (b) Two of three a called a_{\perp} parameters were of same value and third of higher value called a_{\parallel} . (c) Two of the three q parameters had same value. (d) $\eta=0$. Relation [2] was applied to calculate their H^{\wedge} .
- ii) $[\text{Ti}(\text{OH}_2)_4]^{3+}$ possessed C_1 symmetry and different g and a values. Relation [1] was applied to calculate its H^{\wedge} .
- iii) $[\text{Ti I}_4]^{2-}$ had characteristics of axial symmetry. Relation [2] was used to calculate its H^{\wedge} .
- iv) $[\text{TiX}_4]^{2-}$ (X=F, Cl) and $[\text{Ti}(\text{OH}_2)_4]^{2+}$ were of T_d and S_4 symmetries respectively with same g and a values. Relation [3] was applied to calculate their H^{\wedge} .
- v) $[\text{TiX}_6]^{3-}$ (X= F, Cl, Br) possessed D_{6h} , O_h , D_{6h} symmetries respectively but showed characteristics of D_{4h} axial symmetry. Relation [2] was applied to calculate their H^{\wedge} .
- vi) $[\text{TiI}_6]^{3-}$ possessed O_h symmetry with same g and a values. So its H^{\wedge} was calculated by [3].
- vii) $[\text{TiX}_6]^{4-}$ (X= F, Cl, I) possessed O_h symmetry but showed characteristics of D_{4h} axial symmetry. Relation [2] was applied to calculate their H^{\wedge} .
- viii) $[\text{TiBr}_6]^{4-}$ had distorted O_h symmetry with different values of g and a . Relation [1] was applied to calculate its H^{\wedge} . (Put $S_x=S_y=S_z=1/2$ for Ti^{3+} and 1 for Ti^{2+} ; $L_x=L_y=L_z=2.5$ and $g_n = -0.315392$). Values written in small brackets in horizontal rows at end of each complex

(Tables: 1.2A-1.5A) gave contributions from four factors (\rightarrow), i.e. g , a , Q and (I) into H^{\wedge} .

- (b) Verification of Laplace equation and parameters such as η (Tables: 1.2-1.5) and ΔE_{hf} (Tables: 1.2 A-1.5 A) were calculated by relations 6, 5 and 4 respectively.

[B] Calculation of Reflectance and Magnetic parameters from ESR parameters:

It included calculation of μ_{ADF} , χ_{tip} , μ_{tip} , μ_t , μ_{net} , g_t , t_{2g} electron delocalization, its constant (k), $\lambda_{complex}$ and % covalent character⁽²⁶⁾. It may be noted that:

- (i) No authentic 10 D q data of $[\text{TiI}_4]^{1-}$, $[\text{TiI}_4]^{2-}$, $[\text{TiI}_6]^{2-}$, $[\text{TiI}_6]^{3-}$, $[\text{TiX}_4]^{2-}$ (X=F, Cl) were found in literature. So calculations of magnetic parameters of these 7 complexes were omitted.
- (ii) $[\text{Ti X}_6]^{3-}$ (X= F, Cl, Br) with one unpaired electron possessed small magnetic moments and negligible t_{2g} electron delocalization. So, their $\lambda_{complex} \cong \text{free } \lambda_{\text{Ti(III)}} = 155.0 \text{ cm}^{-1}$.
- (iii) $[\text{Ti X}_6]^{4-}$ (X= F, Cl, Br) also should have very small t_{2g} electron delocalization due to small $\lambda_{\text{Ti(II)}} [61.2 \text{ cm}^{-1}]$. So their $\lambda_{complex}$ and % covalent character were not calculated.
- (iv) μ_{ADF} of these complexes was somewhat less than the spin only values of Ti (II, III).
- (a) Table: 1.6 contained $[\text{Ti X}_4]^{1-}$ (X=F, Cl, Br) and $[\text{Ti}(\text{H}_2\text{O})_4]^{3+}$ with 2E ground term for Ti (III). All the magnetic parameters were calculated by applying already given relations.
- (b) Table: 1.6 A contained $[\text{TiX}_6]^{3-}$ (X= F, Cl, Br) with ${}^2T_{2g}$ ground term for Ti (III). All the parameters except t_{2g} electron delocalization and % covalent character were calculated.
- (c) Table: 1.6 B contained $[\text{TiX}_6]^{4-}$ (X= F, Cl, Br) with ${}^3T_{1g}$ ground term Ti (II). All the parameters except t_{2g} electron delocalization and % covalent character were calculated.

[III] Complexes of V (II, III, IV) and Cr (III)

Some work has already been reported on Reflectance and Magnetic properties⁽²⁸⁻²⁹⁾ of V (II, III, IV) complexes. But, quite a large number of papers are reported on Cr³⁺ complexes⁽³¹⁻³⁸⁾ Still a detailed study was needed to know as to how parameters of a metal change with change in its oxidation states. V (IV), V (II) and Cr (III) are Kramer ions and V (III) is a non –Kramer ion.

(a) Both V (II) and Cr (III) [O_h] have ⁴A_{2g} ground state. Therefore, they should show Zero Field Splitting (D) and Jahn -Teller effect. But in [VX₆]⁴⁺ (X=F, Cl, Br, I), [V (OH₂)₆]²⁺, [CrX₆]³⁻ (X= F, Cl, Br, I, CN), [Cr (NH₃)₃]³⁺, the ligands were so chosen that either octahedral or nearly octahedral symmetry was enforced. So Jahn - Teller effect was neglected. The software was so designed that did not account for Zero Field Splitting.

(b) Because of the presence of extensive spin orbit coupling in ³T_{2g} ground term, only a few examples of ESR spectra of V (III) [Oh] complexes had been reported.

In V (III) [Td] complexes with ³A₂ ground term and no spin –orbit coupling, longer relaxation times were expected. Hence their ESR spectra were easy to observe. Of course, an intermixing of electron cloud of its ground ³A₂ term with higher ³T₂ term of the same multiplicity should cause ³A₂ term to acquire some T character to allow weak spin orbit coupling. But this weak coupling would hardly affect the relaxation times.

(c) In V (IV) [O_h] complexes, the ground term ²T_{2g} should experience a considerable spin orbit coupling to make their ESR spectra difficult to observe. V (IV) [T_d] complexes having ²E ground term did not possess any spin-orbit coupling.

But an intermixing of its ²E ground term with higher ²T₂ would make it to acquire T character. As it did not affect relaxation times, their ESR spectra were easy to observe.

RESULTS

- (A) Tables: 2.1, 2.1 A and 3.1, 3.1 A contained some optimization parameters of vanadium, chromium metals as well as of the V (II, III, IV) and Cr (III) complexes.
- (B) Tables: 2. 2 -2.4 and 3.2 give values of all the five ESR and NQR parameters for V (II, III, IV) and Cr (III) complexes respectively.
- (C) Tables: 2. 2 A -2.4A and 3.2 A give g_{iso}, A_{ten} and Q values and contributions from their respective factors along with contribution from the fourth factor (I) into H[^] and ΔE_{h f} (≈ 0.5 A_{ten}) for V (II,III,IV) and Cr (III) complexes respectively
- (D) Tables: 2.5-2.5B and 3.3 contain magnetic parameters of 7 out of the 13 V (II, III, IV) and 5 of the 6 Cr (III) complexes as calculated from their ESR and Reflectance parameters.

DISCUSSION**Calculation of ESR and NQR parameters****[A]Effective Spin Hamiltonian (H[^])**

- (a) The V (II, III, I V) complexes showed a variety of geometries .They were categorized as:
- (i) [VX₄] (X=F, Cl, Br, I) had D_{4h} symmetry with (a) Two of the three **g** called **g_⊥** had the same value and the third of higher value called **g_{||}**. (b) Two of three **a** called **a_⊥** parameters were of same value and third of higher value called **a_{||}**. (c) Two of the three **q** values were same. (d) η=0. Relation [2] was applied to calculate their H[^].
- (ii) [VX₄]¹⁻ (X=F, Cl, Br) were of regular T_d symmetry with same values for **g** and **a**. Relation [3] was applied to calculate their H[^].
- (iii) [VI₄]¹⁻ had D_{4 h} symmetry. Relation [2] was applied to calculate its H[^].
- (iv) [VX₆]⁴⁺ (X= Cl, Br, I) and [VF₆]⁴⁺ were of O_h and D₁₂ symmetries respectively with same **g** and **a** values. Relation [3] was applied to calculate their H[^].

(v) $[V(H_2O)_6]^{2+}$ had, no doubt, C_1 symmetry but its g values were nearly the same.

So relation [3] was applied to calculate its H^A .

(b) The Six Cr (III) complexes showed either O_h or nearly O_h geometries and were categorized as:

(i) $[CrX_6]^{3-}$ (X= F, Cl, Br, I, CN) were of O_h symmetry with same g and a parameters. Relation [3] was applied to all to calculate their H^A .

(ii) $[Cr(NH_3)_6]^{3+}$ had axial symmetry with (a) Two of the three g values called g_{\perp} were same and the third of higher value called g_{\parallel} . (b) Two of three a called a_{\perp} parameters were of same value and third of higher value called a_{\parallel} . (c) Two of the three q values were of same value. (d) $\eta \cong 0$. Relation [2] was applied to calculate H^A . (Put $S_x=S_y=S_z=1/2, 1$ and $3/2$ for V(IV,III,II); $I_x=I_y=I_z=3.5$; $g_n= 1.4710588$ and $S_x=S_y=S_z=3/2$; $I_x=I_y=I_z=1.5$ for Cr(III); $g_n= -0.3163600$).

The contributions from four factors towards the total value of H^A for all the thirteen V (II, III, IV) and six Cr(III) complexes are given in small brackets of horizontal rows shown at the bottom of each complex (\rightarrow) in Tables:2.2A-2.4A and 3.2A respectively.

(c) Parameters such as (η), verification of **Laplace equation** (Tables: 2.1-2.3 and 3.2) and

($\Delta E_{h f}$) (Tables: 2.1A- 2.3A and 3.2A) were calculated by relations 5, 6 and 4 respectively.

[B]Calculation of Reflectance and Magnetic parameters from ESR parameters

(1) calculation of μ_{ADF} , χ_{tip} , μ_{tip} , μ_t , μ_{net} , g_t , t_{2g} electron delocalization and its constant (k), $\lambda_{complex}$ and % covalent character⁽²⁶⁾ of V (II,III,IV) complexes.

(a) As the authentic 10Dq values of $[VX_4]$ (X=F, Br, I), $[VX_4]^{1-}$ (X=Cl, I) and $[VI_6]^{4-}$ were not reported in literature, calculation of their magnetic parameters was omitted.

(b) Table: 2. 5 contained only one complex $[VCl_4]$ with V (IV) having 2E ground term. All the above named parameters were calculated by putting $\lambda_{V(IV)} = 250.0 \text{ cm}^{-1}$.

(c) Table: 2.5 A contained complexes $[VX_4]^{1-}$ (X=F, Br) with ground term 3A_2 for V (III). All the above named parameters were calculated by putting $\lambda_{V(III)} = 105.0 \text{ cm}^{-1}$.

(d) Table: 2.5 B had complexes such as $[VX_6]^{4-}$ (X=F, Cl, Br) and $[V(OH_2)_6]^{2+}$ with ground term $^4A_{2g}$ for V (II). $\lambda_{V(II)}$ being small (56.7 cm^{-1}), they would possess negligibly small values of t_{2g} electron delocalization. The parameter (k) was found to be reasonably in agreement with Nephelauxetic Ratio (β_{35}) for these complexes^(27, 31-32).

(2) Calculation of μ_{ADF} , χ_{tip} , μ_{tip} , μ_t , t_{2g} electron delocalization, μ_{net} for Cr(III) complexes (Table:3.3)

The constant (k) and $\lambda_{Complex}$ could not be calculated as 10 D q values of octahedral Cr (III) complexes were very high while $\lambda_{Cr(III)}$ [92.0 cm^{-1}] was small. So μ_{tip} and t_{2g} electron delocalization would be very small [$\cong 2-4 \%$ and $\cong 1-2 \%$ of μ_{ADF} respectively]. Lastly, in V (III), Cr (III) and V (IV) complexes, μ_{net} values are expected to be somewhat less than their respective spin only (μ_{so}) values both in T_d and O_h geometries. But very minor differences occur because as the charge increases (+3, +4), covalence increases (Fazans' rule) and crystal field approximations become poorer. Therefore, calculated parameters differ slightly from the experimental values. Also, assuming t_{2g} electron delocalization to be equal to the average negative of difference of g_t and g_{iso} may not be an ideal assumption.

Abbreviations and frequently used Acronyms in DFT are given below ⁽³⁹⁾

Q (Nuclear Quadrupole Constant)	Q or e Q is the nuclear quadrupole moment. q Or eq is the electric field gradient. The product of these quantities ($e Q \times q = e^2 Qq$) is nuclear quadrupole coupling constant (Q).
Tip (temperature independent paramagnetism)	Zeeman Second Order Magnetic Moment
LDA	Local Density Approximation
DZ	Double Zeta
TPZ	Triple Zeta
GGABP	Generalized Gradient Approximation Becke Perdew
Nysom	Normalized

Table: 1. 1. Energies (kJmole⁻¹) of Ti

Sum of orbital energies	=	- 49034.160
Total energy	=	- 82193.590
Kinetic energy	=	83068.461
Nuclear attraction energy	=	-195833.367
Electron repulsion energy	=	34453.298
Exchange energy	=	- 3879.077

Table: 1.1 A Optimization Parameters of Ti (II, III) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total energy X c LDA(Exchange; Correlation)
[TiF ₄] ¹⁻	D _{4h}	2.6	-2983.59	-206509.90 (-195069.58; -11440.32)
[TiCl ₄] ¹⁻	D _{4h}	4.5	-2256.78	-386246.93 (-367579.39; -18667.54)
[TiBr ₄] ¹⁻	D _{4h}	≅0.0	-3150.53	-1039547.71 (-1001463.10; -38084.62)
[TiI ₄] ¹⁻	D _{4h}	4.4	-26333.36	-1956668.38 (-1898287.10; -58381.28)
[Ti(OH ₂) ₄] ³⁺	C ₁	7.1	-2692.08	-191684.71 (-180429.73; -11254.98)
[TiF ₄] ²⁻	T _d	4.5	-1294.98	-208003.82 (-196401.70; -11602.12)
[TiCl ₄] ²⁻	T _d	0.0	-2148.99	-386265.26 (-367594.52; -18670.74)
[TiI ₄] ²⁻	D _{4h}	5.8	-26348.19	-1955707.58 (-1897332.55; -58375.03)
[Ti(OH ₂) ₄] ²⁺	S ₄	≅0.0	-4434.52	-191684.50 (-180429.52; -11254.98)
[TiF ₆] ³⁻	D _{6h}	3.9	-2698.47	-257103.53 (-242283.12; -14820.40)
[TiCl ₆] ³⁻	O _h	---	-3844.81	-522193.82 (-496607.46; -25586.36)
[TiBr ₆] ³⁻	D _{6h}	3.5	-362.95	-1502665.06 (-1447466.92; -55198.14)
[TiI ₆] ³⁻	O _h	0.0	-39047.62	-2881334.54 (-2796114.23; -85220.30)
[TiF ₆] ⁴⁺	O _h	≅0.0	-3235.33	-253798.03 (-239060.58; -14737.45)

$[\text{TiCl}_6]^{4-}$	O_h	$\cong 0.0$	-3071.30	-522192.22 (-496607.02; -25585.19)
$[\text{TiBr}_6]^{4-}$ *	O_h	($\cong 0.0$)	-2594.20	-1576511.54 -1452747.96; -54791.33 (-90272.89; +21300.64)
$[\text{TiI}_6]^{4-}$ *	O_h	$\cong 0.0$	-37591.83	-3002005.83 -2798197.17; -85219.46 (-149482.45; +30893.25)

*GGA (Exchange; Correlation) Energies are $\neq 0$. They are zero for others.

Table: 1.2. ESR & NQR Parameters of Ti (III) Four Coordinate Complexes from SW

Complex	g values	$g_n \cdot a$ & (A_{ten})	q & (Laplace) ⁶	NQCC & (η) ⁵
$[\text{TiF}_4]^{1-}$ D_{4h}	ll 1.997564 ⊥ 1.908885 ⊥ 1.898030 g_{iso} 1.93844	ll -0.16095.10 ³ ⊥ -0.121302.10 ³ ⊥ -0.121303.10 ³ (-0.134521.10 ³)	-0.111074.10 ¹ -0.111061.10 ¹ 0.222134.10 ¹ ($\cong 0.0$)	0.44269.10 ² (0.02293)
$[\text{TiCl}_4]^{1-}$ D_{4h}	ll 1.992371 ⊥ 1.900325 ⊥ 1.908884 g_{iso} 1.93027	ll -0.110378.10 ³ ⊥ -0.703252.10 ³ ⊥ -0.704709.10 ² (-0.837246.10 ²)	-0.638978.10 ⁰ -0.598851.10 ⁰ 0.123783.10 ¹ ($\cong 0.0$)	0.24757.10 ² (0.03242)
$[\text{TiBr}_4]^{1-}$ D_{4h}	ll 1.975817 ⊥ 1.875497 ⊥ 1.875497 g_{iso} 1.908937	ll -0.977976.10 ² ⊥ -0.588703.10 ² ⊥ -0.588703.10 ² (-0.718461.10 ²)	-0.606593.10 ⁰ -0.579403.10 ⁰ 0.118600.10 ¹ ($\cong 0.0$)	0.216325.10 ² (0.00388)
$[\text{TiI}_4]^{1-}$ D_{4h}	ll 1.96668 ⊥ 1.833285 ⊥ 1.832548 g_{iso} 1.87736	ll -0.790829.10 ² ⊥ -0.407002.10 ² ⊥ -0.407010.10 ² (- 0.534997.10 ²)	-0.542913.10 ⁰ -0.538712.10 ⁰ 0.108163.10 ¹ ($\cong 0.0$)	0.28986.10 ² (0.00537)
$[\text{Ti}(\text{OH}_2)_4]^{3+}$ C_1	zz 1.957378 yy 1.859854 xx 1.716883 g_{iso} 1.84471	0.831398.10 ¹ 0.278261.10 ² 0.753121.10 ² (0.37015.10 ²)	-0.491148.10 ¹ 0.987638.10 ⁰ 0.392384.10 ¹ ($\cong 0.0$)	-0.9823.10 ² (0.59782)

Table: 1.2A. Calculation of Contributions from g, A, Q & I Factors in Total value of (H^\wedge)

Complex (Relation)	--- (g contribution)	A_{ten}^4 & (a contribution)	Q & (Q contribution)	--- I
$[\text{TiF}_4]^{1-}$ (²) →	(1.398H +2.671 H _⊥)	426.520 (1599.450)	44.269 (-18.445)	--- (-0.000 60H ₀)
$[\text{TiCl}_4]^{1-}$ (²) →	(1.390H +2.658 H _⊥)	265.462 (995.483)	24.767 (-10.315)	--- (do)
$[\text{TiBr}_4]^{1-}$ (²) →	(1.376 H +2.753H _⊥)	227.800 (854.25)	21.633 (-9.014)	--- (do)
$[\text{TiI}_4]^{1-}$ (²) →	(1.376H +2.566H _⊥)	169.629 (636.109)	28.986 (-12.078)	--- (do)
$[\text{Ti}(\text{OH}_2)_4]^{3+}$ (¹) →	(1.201H _x +1.301H _y +1.370H _z)	-117.362 (-440.108)	-98.230 (40.929)	--- (do)

Table: 1.3. ESR & NQR Parameters of Ti (II) Four Coordinate Complexes from SW

Complex	g values	g_n .a & (A_{ten})	q & (Lap lace) ⁶	NQCC & (η) ⁵
[TiF ₄] ²⁻ T _d	2.019323 1.999809 1.988208 g_{iso} 1.99911	-0.70724.10 ³ -0.723716.10 ³ -0.724717.10 ³ 0.718559.10 ³) (-	-0.331022.10 ¹ 0.160592.10 ¹ 0.170403.10 ¹ (\cong 0.0)	-0.662051. 10 ⁻² (0.02972)
[TiCl ₄] ²⁻ T _d	1.933862 1.933862 1.933862 g_{iso} 1.933862	0.228111.10 ² 0.228111. 10 ² 0.228111.10 ² (0.228111.10 ²)	-0.261922.10 ⁻³ 0.12911110 ⁻³ 0.132811.10 ⁻³ (\cong 0.0)	-0.52384.10 ⁻² (0.01413)
[TiI ₄] ²⁻ D _{4h}	2.090058 ⊥ 1.443463 ⊥ 1.443418 g_{iso} 1.65898	-0.378956.10 ³ ⊥ -0.377418.10 ³ ⊥ -0.377412.10 ³ (-0.377928.10 ³)	-0.602618.10 ⁰ -0.602582.10 ⁰ 0.120520.10 ¹ (\cong 0.0)	0.24104.10 ² (0.00003)
[Ti(OH ₂) ₄] ²⁺ S ₄	1.956628 1.956628 1.956628 g_{iso} 1.956628	0.245791.10 ² 0.239013.10 ² 0.239014.10 ² (0.241277.10 ²)	-0.102046.10 ⁰ -0.101901.10 ⁰ 0.203947.10 ⁰ (\cong 0.0)	0.407894.10 ¹ (0.00071)

Table:1.3A.Calculation of Contributions from g, A,Q & I Factors in Total value of (H[^])

Complex (Relation)	--- (g contribution)	A _{ten} ⁴ & (a contribution)	Q & (Q contribution)	--- I
[TiF ₄] ²⁻ (³) →	---- (2.797H ₀)	2278.304 (5695.76)	-66.205 (-413.785)	--- (-0.00060H ₀)
[TiCl ₄] ²⁻ (³) →	---- (2.706H ₀)	-72.326 (-180.815)	-0.00524 (-0.033)	--- (do)
[TiI ₄] ²⁻ (²) →	---- (2.925H +4.040H _⊥)	1198.280 (8987.168)	24.104 (-10.043)	--- (do)
[Ti(OH ₂) ₄] ²⁺ (³) →	---- (2.738H ₀)	-76.501 (-191.253)	4.079 (25.494)	--- (do)

Table: 1.4. ESR & NQR Parameters of Ti (III) Six Coordinate Complexes from SW

Complex	g values	g_n .a & (A_{ten})	q & (Laplace) ⁶	NQCC & (η) ⁵
[TiF ₆] ³⁻ D _{6h}	2.014857 ⊥ 1.963836 ⊥ 1.963752 g_{iso} 1.98082	-0.1597.10 ³ ⊥ -0.13681.10 ³ ⊥ -0.1368.10 ³ (-0.1443.10 ³)	-0.24502.10 ¹ -0.244433.10 ¹ 0.489334.10 ¹ (\cong 0.0)	0.97867.10 ² (0.00137)
[TiCl ₆] ³⁻ O _h	2.002185 ⊥ 2.001527 ⊥ 2.001527 g_{iso} 2.001747	-0.2405.10 ¹ ⊥ -0.1944.10 ¹ ⊥ - 0.19444.10 ¹ (- 0.20978.10 ¹)	-0.385682.10 ⁻¹ 0.192836.10 ⁻¹ 0.192846.10 ⁻¹ (\cong 0.0)	-0.771364.10 ⁰ (0.00003)
[TiBr ₆] ³⁻ D _{6h}	3.089795 ⊥ 0.606969 ⊥ 0.606624 g_{iso} 1.434463	-0.25115.10 ³ ⊥ 0.25023.10 ³ ⊥ 0.25026.10 ³ (-0.82947.10 ²)	-0.818723.10 ⁰ -0.802241.10 ⁰ 0.162115.10 ¹ (\cong 0.0)	0.32425.10 ² (0.01006)
[TiI ₆] ³⁻ O _h	2.003802 2.003802 2.003802 g_{iso} 2.00380	0.145600.10 ¹ 0.145600.10 ¹ 0.145600.10 ¹ (0.14560.10 ¹)	-0.614724.10 ⁻¹ -0.614659.10 ⁻¹ 0.122938.10 ⁰ (\cong 0.0)	0.245849.10 ¹ (0.00005)

Table:1.4A. Calculation of Contributions from g, A, Q & I Factors in Total value of (H[^])

Complex (Relation)	---- (g contribution)	A _{ten} ⁴ & (a contribution)	Q & (Q contribution)	--- I
[TiF ₆] ³⁻ (²) →	--- (1.410H +2.748H _⊥)	457.526 (1715.723)	97.867 (-40.820)	--- (-0.000 60H ₀)
[TiCl ₆] ³⁻ (²) →	--- (1.400H +2.800H _⊥)	6.651 (24.941)	-0.771 (0.321)	--- (do)
[TiBr ₆] ³⁻ (²) →	--- (2.162H + 0.850H _⊥)	262.996 (986.235)	32.425 (-13.510)	--- (do)
[TiI ₆] ³⁻ (³) →	--- (1.402H ₀)	-4.616 (-5.770)	2.458 (15.363)	--- (do)

Table: 1.5. ESR & NQR Parameters of Ti (II) Six Coordinate Complexes from SW

Complex	g values	g _n .a& (A _{ten})	q & (Laplace) ⁶	NQCC & (η) ⁵
[TiF ₆] ⁴⁻ O _h	2.00239 ⊥2.001921 ⊥2.00191 g _{iso} 2.002008	-0.280211.10 ¹ ⊥-0.265670.10 ¹ ⊥ -0.265340.10 ¹ (-0.270407.10 ¹)	-0.246026.10 ⁻¹ 0.119583.10 ⁻¹ 0.126444.10 ⁻¹ (≅0.0)	-0.492053.10 ⁰ (0.02789)
[TiCl ₆] ⁴⁻ O _h	2.002270 ⊥2.001855 ⊥2.001855 g _{iso} 2.0020	0.387646.10 ⁰ ⊥ 0.378560.10 ⁰ ⊥0.378614.10 ⁰ (0.381607.10 ⁰)	-0.192326.10 ⁻¹ -0.192308.10 ⁻¹ 0.384634.10 ⁻¹ (≅0.0)	0.769268.10 ⁰ (0.00005)
[TiBr ₆] ⁴⁻ O _h	zz 1.995673 yy1.922616xx 1.087422 g _{iso} 1.66857	zz 0.795253.10 ² yy 0.326404.10 ² xx 0.812108.10 ¹ (0.400956.10 ²)	-0.374942.10 ¹ 0.187471.10 ¹ 0.187471.10 ¹ (≅0.0)	-0.749885.10 ² (0.000)
[TiI ₆] ⁴⁻ O _h	2.038348 ⊥1.950155 ⊥1.950154 g _{iso} 1.979552	0.241091.10 ² ⊥ 0.176459.10 ² ⊥0.176460.10 ² (0.198003.10 ²)	-0.106307.10 ¹ -0.104657.10 ¹ 0.210964.10 ¹ (≅0.0)	0.421929.10 ² (0.00782)

Table:1.5 A. Calculation of Contributions from g, A, Q & I Factors in Total value of (H[^])

Complex (Relation)	---- (g contribution)	A _{ten} ⁴ & (a contribution)	Q & (Q contribution)	--- I
[TiF ₆] ⁴⁻ (²) →	--- (2.802H +5.603H _⊥)	8.574 (64.305)	- 0.492 (0.205)	--- (-0.001 68H ₀)
[TiCl ₆] ⁴⁻ (²) →	--- (2.802H +5.602H _⊥)	-1.210 (-9.075)	0.769 (-0.320)	--- (do)
[TiBr ₆] ⁴⁻ (¹) →	--- (1.52H _{xx} +2.69H _{yy} +2.79H _{zz})	-127.129 (-953.468)	-74.989 (-31.245)	--- (do)
[TiI ₆] ⁴⁻ (²) →	--- (2.852H +5.459H _⊥)	-62.780 (-470.850)	42.193 (-17.580)	--- (do)

$$H^{\wedge} = \beta e [g_{11}.H_x.S_x + g_{22}.H_y.S_y + g_{33}.H_z.S_z] + [a_{11}.S_x.I_x + a_{22}.S_y.I_y + a_{33}.S_z.I_z] + Q [I_z - 1/3 I(I+1)] - [g_n.\beta_n.H_0.I] \text{----- [1]}$$

$$H^{\wedge} = \beta_e [g_{11}.H_z.S_z + g_{\perp} (H_x.S_x + H_y.S_y)] + [a_{11}.S_z.I_z + a_{\perp}(S_x.I_x + S_y.I_y)] + Q [I_z - 1/3 I(I+1)] - [g_n.\beta_n.H_0.I] \text{-----[2]}$$

$$H^{\wedge} = \beta_e [g_{iso}.H_0.S] + [A_{ten}.S.I] + Q.I^2 - [g_n.\beta_n.H_0.I] \text{----- [3]}$$

$$\Delta E_{hf} = A_{ten}/2 \text{----- [4]}$$

$$\eta = q_{xx} - q_{yy} / q_{zz} \text{----- [5]}$$

$$q_{xx} + q_{yy} + q_{zz} = 0 \text{----- [6]}$$

Table: 1.6 Reflectance & Magnetic Parameters of Ti (III) Four Coordinate Complexes

Complex (² E)	g _{iso} {μ _{ADF} } [7]	10Dq* (cm ⁻¹)	χ _{tip} [8]** (μ _{tip})[9] μ _t [10]	g _t [16] (t _{2g})[17] μ _{net} [11,12]	k[13] (β _{3s})	λ _{complex} [14] % c. c [15]
[TiF ₄] ¹⁻	1.938444 {1.6787}	8120.0 ⁽²⁷⁾	128.438 (0.1780) 1.857	2.1442 (-0.1028) 1.768	0.79 (--)	122.5 21.0
[TiCl ₄] ¹⁻	1.930215 {1.6716}	7218.0 ⁽²⁷⁾	144.488 (0.2002) 1.872	2.1616 (-0.1157) 1.771	0.77 (--)	119.4 23.0
[TiBr ₄] ¹⁻	1.911538 {1.6554}	6857.0 ⁽²⁷⁾	152.095 (0.2107) 1.866	2.1548 (-0.1216) 1.755	0.76 (--)	117.8 24.0
[Ti(OH ₂) ₄] ³⁺	1.844705 {1.5976}	9022.0 ⁽²⁷⁾	115.597 (0.1602) 1.758	2.0297 (-0.0925) 1.678	0.82 (--)	127.1 18.0

*10Dq of T_d complexes ≈ 4/9 of O_h complexes ** Multiply by 10⁻⁶ c g s /mol

Table: 1.6 A. Reflectance & Magnetic Parameters of Ti (III) Six Coordinate Complexes

Complex (² T _{2g})	g _{iso}	μ _{ADF} [7]	10Dq(cm ⁻¹)	μ _t [18]	g _t [16] (t _{2g})[17]	μ _{net} [11,12]
[TiF ₆] ³⁻	1.980815	1.715	18270.0 ⁽²⁷⁾	1.741	2.01033 (-0.0148)	1.728
[TiCl ₆] ³⁻	1.997868	1.730	16240.0 ⁽²⁷⁾	1.758	2.030 (-0.021)	1.603
[TiBr ₆] ³⁻	1.911538	1.6554	15428.0 ⁽²⁷⁾	1.686	1.9468 (-0.001)	1.685

Table: 1.6 B. Reflectance & Magnetic Parameters of Ti (II) Six Coordinate Complexes

Complex (³ T _{1g})	g _{iso}	μ _{ADF} [7]	10Dq(cm ⁻¹)	μ _t [18]	g _t [16] (t _{2g})[17]	μ _{net} [11,12]
[TiF ₆] ⁴⁻	1.995846	2.8225	12180.0 ⁽²⁷⁾	2.8376	2.0065 (-0.0053)	2.734
[TiCl ₆] ⁴⁻	2.022666	2.8605	10827.0 ⁽²⁷⁾	2.8775	2.0346 (-0.0059)	2.768
[TiBr ₆] ⁴⁻	1.99682	2.824	10285.0 ⁽²⁷⁾	2.8419	2.0095 (-0.0063)	2.730

$$(\mu_{\text{soc}}) \text{ or } (\mu_{\text{ADF}}) = [g_{\text{iso}}^2 s(s+1)]^{1/2} \quad [7] \quad \chi_{\text{tip}} = n N \beta^2 / 10Dq \quad [8]$$

$$\mu_{\text{tip}} = \chi_{\text{tip}} X \mu_{\text{s.o}} / \chi_{\text{(Mol.s.o)}} \quad [9] \quad \mu_t = (\mu_{\text{ADF}}) + \mu_{\text{t.i.p}} \quad [10]$$

$$\mu_{\text{net}} = \mu_t - |\text{Reduction of magnetic moment from } t_{2g} \text{ electron delocalization}| \quad [11]$$

$$\text{Reduction of magnetic moment} = [(t_{2g} \text{ electron delocalization})^2 s(s+1)]^{1/2} \quad [12]$$

$$k = 1 - (g_t - g_{\text{iso}}) \quad [13] \quad \lambda_{\text{complex}} = k X \lambda_{\text{(free metal ion)}} \quad [14]$$

$$\% \text{covalent character (c. c)} = (1 - k) X 100 \quad [15] \quad \mu_t = [g_t^2 s(s+1)]^{1/2} \quad [16]$$

$$t_{2g} \text{ electron delocalization} = -0.5(g_t - g_{\text{iso}}) \quad [17] \quad \mu_t = 2A|\lambda| / 10Dq + \mu_{\text{ADF}} \quad [18]$$

Table: 2.1. Energies (kJmole⁻¹) of Ti

Sum of orbital energies	= - 54453.277
Total energy	= - 91394.073
Kinetic energy	= 92457.572
Nuclear attraction energy	= - 218055.741
Electron repulsion energy	= 3 8338.781
Exchange energy	= - 4184.954

Table: 2. 1 A. Optimization Parameters of V (II, III, IV) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total energy X c LDA(Exchange; Correlation)
[VF ₄]	D _{4h}	≅ 0.0	-2526.09	-214400.40 (-202697.24; -11703.16)
[VCl ₄]	D _{4h}	≅ 0.0	-1889.37	-394382.02 (-375441.99; -18940.02)
[VBr ₄]	D _{4h}	≅ 0.0	-2325.36	-1044970.23 (-1006316.94; -38653.29)
[VI ₄]	D _{4h}	≅ 0.0	-26315.81	1964084.37 (-1905416.29; -58668.08)
[VF ₄] ¹⁻	T _d	≅ 0.0	-3015.59	-214401.32 (-202698.08; -11703.23)
[VCl ₄] ¹⁻	T _d	≅ 0.0	-2391.16	-394378.34 (-375438.42; -18939.92)
[VBr ₄] ¹⁻	T _d	4.155	-3296.54	-1047678.90 (-1009321.90; -38357.00)
[VI ₄] ¹⁻	D _{4h}	3.673	-26342.15	-1964718.19 (-1906075.58; -58642.61)
[VF ₆] ⁴⁻	D ₁₂	4.403	+1885.12	268156.61 (-252802.55; -15354.07)
[VCl ₆] ⁴⁻	O _h	≅ 0.0	-1218.95	-534836.47 (-508902.62; -25933.84)
[VBr ₆] ⁴⁻	O _h	3.82	+235.25	-1511040.84 (-1455549.65; -55491.19)
[VI ₆] ⁴⁻	O _h	≅ 0.0	-37823.53	-2890345.71 (-2804857.80; -85487.92)
[V(OH ₂) ₆] ²⁺	C ₁	3.24	-7940.62	-243235.52 (-228405.08; -14830.45)

Table: 2.2. ESR & NQR Parameters of V (IV) Four Coordinate Complexes from SW

Complex	g values	g_n, a & (A_{ten})	q (Laplace) ⁶	NQCC(η) ⁵
[VF ₄] D _{4h}	1.991749 1.876228 1.876228 g_{iso} 1.914735	0.802141.10 ³ 0.505241.10 ³ 0.505241.10 ³ (0.604208.10 ³)	0.936517.10 ⁻¹ 0.934116.10 ⁻¹ -0.18706.10 ⁰ (\cong 0)	- 0.785710 ¹ (0.00128)
[VCl ₄] D _{4h}	1.987658 1.894332 1.894333 g_{iso} 1.925441	0.577448.10 ³ 0.307442.10 ³ 0.307440 .10 ³ (0.397443.10 ³)	0.923783.10 ⁻¹ 0.923778.10 ⁻¹ -0.18475.10 ⁰ (\cong 0)	- 0.7760.10 ¹ (0.000)
[VBr ₄] D _{4h}	1.980544 1.907412 1.907404 g_{iso} 1.93178	0.176799.10 ⁴ 0.165633.10 ⁴ 0.165631.10 ⁴ (0.169355.10 ⁴)	0.508862.10 ⁻¹ 0.507788.10 ⁻¹ -0.10167.10 ⁰ (\cong 0)	0.427.10 ¹ (0.00106)
[VI ₄] D _{4h}	2.023153 1.812448 1.812403 g_{iso} 1.88266	0.138805.10 ⁴ 0.128855.10 ⁴ 0.128854.10 ⁴ (0.132171.10 ⁴)	0.36534. 10 ⁻¹ 0.364989.10 ⁻¹ -0.73033.10 ⁻¹ (\cong 0)	-0.3067.10 ¹ (0.00048)

Table: 2.2A. Calculation of Contributions from g, A, Q & I Factors in Total value of (H[^])

Complex (Relation)	g values (g contribution)	(A_{ten}) ⁴ (a contribution)	Q value (Q contribution)	--- (I)
[VF ₄] (²) →	1.991749 ⊥ 1.876228 ⊥ 1.876228 g_{iso} 1.914735 (1.394H +2.626H _⊥)	545.281 ⊥ 343.453 ⊥ 343.453 A_{ten} 410.730 (2156.332)	- 7.857 (13.750)	--- (0.0039 52H ₀)
[VCl ₄] (²) →	1.987658 ⊥ 1.894332 ⊥ 1.894333 g_{iso} 1.925441 (1.391H +2.651H _⊥)	392.539 ⊥ 208.993 ⊥ 208.993 A_{ten} 270.175 (1418.418)	- 7.760 (13.580)	--- (do)
[VBr ₄] (²) →	1.980544 ⊥ 1.907412 ⊥ 1.907404 g_{iso} 1.93178 (1.39H + 2.669H _⊥)	1201.849 ⊥ 1125.937 ⊥ 1125.937 A_{ten} 1151.246 (6044.042)	4.270 (- 7.472)	---- (do)
[VI ₄] (²) →	2.023153 ⊥ 1.812448 ⊥ 1.812403 g_{iso} 1.88266 (1.416H +2.54 H _⊥)	943.572 ⊥ 875.930 ⊥ 875.930 A_{ten} 898.475 (4716.994)	- 3.067 (5.368)	--- (do)

Table: 2.3 ESR & NQR Parameters of V(III) Four Coordinate Complexes from SW

Complex	g values	g_n , a & (A_{ten})	q (Lap lace) ⁶	NQCC (η) ⁵
[VF ₄] ¹⁻ T _d	1.937673 1.937673 1.937673 g _{iso} 1.937673	-0.124815.10 ³ -0.124815.10 ³ -0124815.103 (-0.124815.10 ³)	0.516526.10 ⁻² 0.414732.10 ⁻² -0.93126.10 ⁻² (≅0)	-0.3913.10 ⁰ (0.1091)
[VCl ₄] ¹⁻ T _d	1.947051 1.947051 1947051 g _{iso} 1.947051	-0.105031.10 ³ -0.105031.10 ³ -0.105031.10 ³ -0.105031.10 ³)	-0.48378.10 ⁻⁴ 0.23898.10 ⁻⁴ -0.23898.10 ⁻⁴ (≅0)	0.2032.10 ⁻² (0.01204)
[V Br ₄] ¹⁻ T _d	1.968615 1.968 615 1.968615 g _{iso} 1.968615	-0.898672.10 ² -0.898672.10 ² -0.898672.10 ² (-0.898672.10 ²)	0.876502.10 ⁻¹ 0.79608.10 ⁻¹ 0.1627259.10 ⁰ (≅0)	-0.2039.10 ² (0.0019)
[V I ₄] ¹⁻ D _{4h}	2.216395 ⊥1.164064 ⊥1.162987 g _{iso} 1.51448	0.112794.10 ³ ⊥-0.139215.10 ³ ⊥-0.141211.10 ³ (-0.55.877310 ²)	-0.70342.10 ⁰ -0.70127.10 ⁰ 0.140459.10 ¹ (≅0)	-0.1716.10 ² (0.00153)

Table:2.3 A. Calculation of Contributions from g,A,Q & I Factors in Total value of (H[^])

Complex (Relation)	g values (g contribution)	(A_{ten}) ⁴ & (a contribution)	Q & (Q contribution)	--- (I)
[VF ₄] ¹⁻ (³) →	g _{iso} 1.937673 (2.712H ₀)	A _{ten} -84.847 (-296.965)	-0.391 (-4.793)	--- (0.0039 52H ₀)
[VCl ₄] ¹⁻ (³) →	g _{iso} 1.947051 (2.725 H ₀)	A _{ten} -71.398 (-249.893)	0.002 (0.025)	--- (do)
[V Br ₄] ¹⁻ (³) →	g _{iso} 1.968615 (2.765H ₀)	A _{ten} -61.090 (-213.815)	-20.390 (-249.778)	--- (do)
[V I ₄] ¹⁻ (²) →	2.216395 ⊥1.164064 ⊥ 1.162987 g _{iso} 1.514479 (3.102H +3.256H _⊥)	76.675 ⊥-94.636 ⊥ -95.993 A _{ten} -37.984 (-398.832)	-17.160 (30.030)	--- (do)

Table: 2.4. ESR & NQR Parameters of V (II) Six Coordinate Complexes from SW

Complex	g values	g_n .a & (A_{ten})	q(Laplace) ⁶	NQCC(η) ⁵
[VF ₆] ⁴⁻ D ₁₂	1.999779 1.999779 1.999779 g _{iso} 1.999779	0.855453.10 ² 0.855453.10 ² 0.855453.10 ² (0.855453.10 ²)	0.432127.10 ⁻⁷ - 0.40104.10 ⁻⁸ -0.39159.10 ⁻⁷ (\cong 0.0)	0.18149.10 ⁻⁵ (0.81339)
[VCl ₆] ⁴⁻ O _h	1.989058 1.989058 1.989058 g _{iso} 1.989058	-0.107047.10 ³ -0.107047.10 ³ -0.107047.10 ³ (-0.10705.10 ³)	0.462664.1 ⁻⁵ 0.37518.10 ⁻⁵ - 838484.10 ⁻⁵ (\cong 0.0)	- 0.352.10 ⁻³ (0.10358)
[VBr ₆] ⁴⁻ O _h	2.00172 2.00171 2.00169 g _{iso} 2.0017	0.726556.10 ² 0.725152.10 ² 0.727888.10 ² (0.726597.10 ²)	0.13748.10 ⁻² 0.405451.10 ⁻³ 0.178031.10 ⁻² (\cong 0.0)	- 0.748.10 ⁻¹ (0.54451)
[VI ₆] ⁴⁻ O _h	2.03660 2.03660 2.03660 g _{iso} 2.03660	0.705609.10 ² 0.705609.10 ² 0.705609.10 ² (0.705609.10 ²)	0.25531 10 ⁻⁴ 0.24703.10 ⁻⁴ 0.50234.10 ⁻⁴ (\cong 0.0)	- 0.211.10 ⁻² (0.01647)
[V(OH ₂) ₆] ²⁺ C ₁	1.991328 1.984256 1.981686 g _{iso} 1.985757	- 0.133978.10 ³ - 0.853209.10 ² - 0.610587.10 ² (- 0.93454.10 ²)	-0.95989.10 ⁻¹ -0.33684.10 ⁻¹ 0.129673.10 ⁰ (\cong 0.0)	-0.5446.10 ¹ (0.48048)

Table:2.4 A.Calculation of Contributions from g,A,Q & I Factors in Total value of (H[^])

Complex (Relation)	g _{iso} (g contribution)	(A _{ten}) ⁴ & (a contribution)	Q & (Q contribution)	--- (I)
[VF ₆] ⁴⁻ (³) →	g _{iso} 1.999779 (4.198H ₀)	58.152 (305.298)	0.000002 (0.00002)	--- (0.0039 52H ₀)
[VCl ₆] ⁴⁻ (³) →	g _{iso} 1.989058 (4.175H ₀)	72.771 (-382.047)	-0.00035 (-0.0043)	--- (do)
[VBr ₆] ⁴⁻ (³) →	g _{iso} 2.00170 (4.202 H ₀)	49.393 (259.313)	- 0.0747728 (-0.91597)	--- (do)
[VI ₆] ⁴⁻ (³) →	g _{iso} 2.03660 (4.275 H ₀)	47.966 (251.822)	- 0.00211 (-0.0258)	--- (do)
[V(OH ₂) ₆] ²⁺ (³) →	g _{iso} 1.985757 (4.168H ₀)	-63.528 (-333.522)	-5.446 (-66.714)	--- (do)

Table: 2.5. Reflectance & Magnetic Parameters of V (IV) Four Coordinate Complexes

Complex (² E)	g _{iso} . { μ_{ADF} }[7]	10Dq(Vapor) (cm ⁻¹)	χ_{tip} [8]* { μ_{tip} }[9] μ_{l} [10]	k[13] { β_{35} } {t _{2g} }[16,17]	$\lambda_{complex}$ [14] {%c.c.}[15] μ_{net} [11,12]
[VCl ₄]	1.972695 {1.7084}	9000.0 ⁽³⁰⁾	115.880 {0.1605} 1.869	0.814 {--} {- 0.093}	203.6 (18.6) 1.684

Table: 2.5 A. Reflectance & Magnetic Parameters of V (III) Four Coordinate Complexes

Complex (3A_2)	g_{iso} , μ_{ADF} [7]	10Dq (cm^{-1})	χ_{tip} [8]* { μ_{tip} }[9] μ_t [10]	k[13] { β_{35} } t_{2g} [16,17]	$\lambda_{complex}$ [14] {% c. c}[15] μ_{net} [11,12]
[VF ₄] ¹⁻	1.937857 2.7405	7440.0 ⁽²⁷⁾	280.354 {0.2379} 2.9784	0.832 {--} 0.084	87.3 {16.8} 2.810
[VBr ₄] ¹⁻	1.941277 2.7454	6283.0 ⁽²⁷⁾	331.981 {0.2817} 3.027	0.80 {--} 0.1	84.0 {20.0} 2.827

Table: 2.5 B. Reflectance & Magnetic Parameters of V (II) Six Coordinate Complexes

Complex ($^4A_{2g}$)	g_{iso} , μ_{ADF} [7]	10Dq (cm^{-1})	χ_{tip} [8]* { μ_{tip} }[9] μ_t [10]	k[13] { β_{35} } t_{2g} [16,17]	$\lambda_{complex}$ [14] {% c. c} [15] μ_{net} [11,12]
[VF ₆] ⁴⁺	1.99699 3.867	11070.0 ⁽²⁷⁾	188.422 {0.1168} 3.984	0.94 {0.93} ⁽²⁷⁾ -0.03	53.3 {6.0} 3.92
[VCl ₆] ⁴⁻	1.99616 3.866	9840.0 ⁽²⁷⁾	211.975 {0.1314} 4.000	0.92 {0.98} ⁽³¹⁾ -0.04	52.2 {8.0} 3.92
[VBr ₆] ⁴⁻	2.0017 3.876	9348.0 ⁽²⁷⁾	223.975 {0.1388} 4.014	0.928 {0.82} ⁽²⁷⁾ -0.034	52.6 {6.8} 3.95
[V(OH ₂) ₆] ²⁺	1.98576 3.845	12300.0 ⁽²⁷⁾	169.58 {0.1051} 3.951	0.94 {0.91} ⁽³²⁾ -0.03	53.3 {3.0} 3.89

* Multiply by 10⁻⁶ c g s /mol**Table: 3.1. Energies (kJmole⁻¹) of Cr**

Sum of orbital energies	= - 60139.891
Total energy	= - 101188.375
Kinetic energy	= 102462.976
Nuclear attraction energy	= - 241698.341
Electron repulsion energy	= 42549.246
Exchange energy	= - 4503.221

Table: 3. 1A.Optimization Parameters of Cr (III) Complexes

Complex	Point Group	Dipole moment	Total Bonding Energy	Total Energy X c LDA(Exchange; Correlation)
[CrF ₆] ³⁻	O _h	≅ 0.0	-3013.07	-273856.57 (-258468.98; -15387.60)
[CrCl ₆] ³⁻	O _h	≅ 0.0	-3181.89	-544300.45 (-517838.21; -26462.24)
[CrBr ₆] ³⁻	O _h	≅ 0.0	-3855.70	-1523773.67 (-1468405.41; -55368.25)
[CrI ₆] ³⁻	O _h	≅ 0.0	-40000.53	-2899914.99 (-2814033.33; -85881.67)
[Cr(CN) ₆] ³⁻	O _h	≅ 0.0	-11038.10	-293748.25 (-275405.30; -18342.95)
[Cr(NH ₃) ₆] ³⁺	D ₆	≅ 0.0	-9456.09	-230044.50 (-215723.50; -14321.00)

Table: 3.2 ESR & NQR Parameters of Cr (III) Six Coordinate Complexes from SW

Complex	g values	g _n , a & (A _{ten})	q (Lap lace) ⁶	NQCC (η) ⁵
[CrF ₆] ³⁻ O _h	1.983129 1.98312 9 1.98312 9 g _{iso} 1.983129	0.258967.10 ² 0.258967.10 ² 0.258967.10 ² (0.258967.10 ²)	0.131364.10 ⁻³ 0.129679.10 ⁻³ -0.261043.10 ⁻³ (≅0)	0.113345.10 ⁻² (0.00645)
[CrCl ₆] ³⁻ O _h	1.992475 1.992451 1.994029 g _{iso} 1.992457	-243180.10 ² -242934.10 ² -243033.10 ² (-24306.10 ²)	0.18890.10 ¹ -0.9401700.10 ⁰ -0.948912.10 ⁰ (≈0.00)	0.113345.10 ² (0.00463)
[CrBr ₆] ³⁻ O _h	2.022007 2.022007 2.022007 g _{iso} 2.022007	0.165256.10 ² 0.165256.10 ² 0.165256.10 ² (0.165256.10 ²)	0.508862.10 ⁻¹ 0.507788.10 ⁻¹ - 0.10167.10 ⁰ (≅0)	-0.481051.10 ⁻² (0.00618)
[CrI ₆] ³⁻ O _h	2.054592 2.054592 2.054592 g _{iso} 2.054592	-0.410216.10 ² -0.410216.10 ² -0.410216.10 ² (-0.41022.10 ²)	0.199917.10 ¹ 0.19968410 ¹ -0.39960.10 ¹ (≅0)	-0.493282.10 ² (0.00362)
[Cr(CN) ₆] ³⁻ O _h	1.997817 1.997817 1.997817 g _{iso} 1.997817	0.183288.10 ² 0.183288.10 ² 0.183288.10 ² (0.183288.10 ²)	0.933959.10 ⁻⁴ 0.9014950 ⁻⁴ -0.18354.10 ⁻³ (≅0)	-0.110127.10 ⁻² (0.01769)
[Cr(NH ₃) ₆] ³⁺ D ₆	1.996891 ⊥ 1.994468 ⊥ 1.994468 g _{iso} 1.995274	0.165897.10 ² ⊥ 0.788442.10 ¹ ⊥ 0.787900.10 ¹ (0.107844.10 ²)	0.223814.10 ¹ 0.11051610 ¹ -0.113298.10 ¹ (≅0)	0.134289.10 ² (0.01243)

Table: 3.3. Reflectance & Magnetic Parameters of Six Coordinate Cr (III) Complexes

Complex*	g_{iso} $\mu_{ADF}[7]$	$10Dq(cm^{-1})$ $\chi_{tip}[8]**$	$\{\mu_{tip}[9]\}$ $\mu_t [10]$	$t_{2g}[16,17]$ $\{\mu_{net}\}[11,12]$
$[CrF_6]^{3-}$	1.983129 3.840	14900.0 ⁽³²⁾ 139.989	{0.0867} 3.927	-0.023 {3.88}
$[CrCl_6]^{3-}$	1.992457 3.858	13180 ⁽³³⁾ 158.360	{0.0981} 3.956	-0.025 {3.91}
$[CrBr_6]^{3-}$	2.022007 3.916	13224.0 ⁽²⁷⁾ 157.833	{0.0978} 4.014	0.026 {3.96}
$[Cr(CN)_6]^{3-}$	1.997817 3.868	26700.0 ⁽³²⁾ 78.121	{0.0484} 3.916	-0.013 {3.89}
$[Cr(NH_3)_6]^{3+}$	1.995274 3.864	21550.0 ⁽³²⁾ 96.790	{0.060} 3.924	-0.017 {3.89}

*No authentic 10Dq value for $[CrI_6]^{3-}$ is reported. ** Multiply by 10^{-6} c g s /mol

CONCLUSIONS

With certain commands, the ADF software gave five ESR and NQR parameters. These parameters were used to calculate nine other ESR, NQR, Reflectance and Magnetic parameters by the selective use of 18 relations. So these 14 parameters of the four techniques were correlated in 36 Ti (II, III), V (II, III, IV) and Cr (III) complexes. Theoretically calculated values of these parameters were found to be fairly in agreement with their experimental values reported in the literature. The authors had already proved this fact in 20 Co (II) and Ni (II) complexes⁽¹⁾ in the previous communication and hope to prove the same in forty five more complexes of 2nd and 3rd transition series metal ions in the forthcoming communication.

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REFERENCES

1. Harminder Singh, Bhardwaj, A.K., Sehgal, M.L. and Susheel K. Mittal, IJCRR., 4[22](2012)12-28.
2. Atanasov, M., Daul, C. A. and Penka Fowe, E., Monatshefte für Chemie., 136 (2005)925-63.
3. Atanasov, M. and Daul, C.A., Chimia., 59(2005)504-10.
4. Pedersen, E. and Toftlund, H., Inorg. Chem., 13(1974)1603.
5. Urbach, F., J. Amer. Chem. Soc., 98 (1976) 5144.
6. Mcgarvey, B.R., Can. J. Chem., 53 (1975) 2498.
7. Malatesta V. and Mcgarvey B.R., Can. J. Chem., 53(1975)3791.
8. Reuvani, A., Malatesta V. and Mcgarvey, B. R., Can J. Chem., 55 (1977)70.
9. Hastey E., Colburn T.J. and Hendrickon, D.N., Inorg. Chem., 12(1973)2414.
10. Van Lanthe. E, vander Aroird and Wormer, P.E.S., J. Chem. Phys., 107(1997)2488-98.
11. Van Lanthe. E, vander Aroird and Wormer, P.E.S., J. Chem. Phys., 108(1998)783-96.
12. Van Lanthe. E. and Baerends, J., J. Chem. Phys., 108 (2000) 8279- 92.
13. Wulfsberg Gary, P., "Nuclear Quadrupole Resonance (NQR) Spectroscopy," Online (2011)

14. Sathyanarayana D.N., "Introduction to Magnetic Resonance Spectroscopy ESR, NMR, NQR" (2009) Amazon.com .
15. Orgel. L. E., "Transition Metal Chemistry," (1966) ; Methuen, London.
16. Tanabe, Y. and Sugano, S., J. Phys. Soc. Japan, 39(1954)753, 766.
17. Figgis B.N., "Introduction to Ligand Fields, p.265 -66 ; 276-77(1966) " Inter science , N.Y.
18. Ballhausen, C.J., "Introduction to Ligand Field Theory,"(1962) ;McGraw-Hill, N.Y.
19. Cotton F.A. et al., J. Am. Chem. Soc., 83(1961) 4161 and references therein.
20. Leslie K.A., Drago, R.S., Stucky, G.D., Kitko, D. J. and Breesee, J.A., Inorg. Chem., 18(1979) 1885.
21. Schoenherr, T., Atanasov, M. and Schmidtke, H., Inorg. Chim. Acta., 141(1988)27-32.
22. Gruen, D.M. and Mcbeth, R.L, Nature, 194(1962)468.
23. Fowles, G.W.A., Hoodless, R.A. and Walton, R.A., J. Inorg & Nuc. Chem., 27(1965) 391.
24. Baerends, E. J., Branchadel, V. and Sodup, Chem. Phys. Lett., 265(1997) 481.
25. Lipkowitz, K. B. and Boyd, D. B., "Kohn-Sham Density Functional Theory: Predicting and Understanding Chemistry" in Rev. Comput. Chem., p.1-86, Vol.15 (2000) Wiley-VCH, N.Y.
26. Atanasov, M., Daul, C.A. and Rauzy, C., Chem.Phys.Lett., 367(2003)737-46.
27. Jorgensen C. K., "Absorption Spectra and Chemical Bonding in Complexes,"(1962) Pergamon Press, N .Y.
28. Kilty P.A. and Nicholls, D., J. Chem. Soc., (1965) 4915.
29. Bedon, H.D., Horner, S.M. and Tyree, S.Y., J; Inorg . Chem., 4 (1965)743.
30. Blankenship, F. A. and Linn Belford, R., J. Chem. Phys., 36 (1962) 633.
31. Gruen D. M. and Mcbeth R. , Proc.7th I.C.C.C., Stockholm, p.23.
32. Jorgensen, C. K., Advn. Chem. Phys., 5(1963)33.
33. Hatfield W. E., Fay R.C., Pfluger C.E. and Piper T. S., J. Am .Chem.Soc., 85 (1963)265.
34. Wood D.L., Ferguson, J., Knox ,K. and Dillon Jr. J.F., J.Chem.Soc., 85(1963) 265.
35. Meak D.W., Drago, R. S. and Piper, T.S., Inorg.Chem ., 1(1962)285.
36. Adamson A. and Dunn ,T. M., J .Mol. Spectroscopy., 18 (1965) 83.
37. Wentworth, R.A.D. and Piper, T.S., Inorg. Chem., 4 (1965) 709.
38. Bull W.E. and Ziegler, R.G., Inorg. Chem., 5(1966) 689.
39. Koch, W., Hotthausen, M., "A Chemist's Guide to Density Functional Theory," Wiley-VCH Weinheim, 2001.