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CALCULATING ESR PARAMETERS (H^& $\Delta E_{h\ f}$) OF 4d AND 5d TRANSITION METAL ION COMPLEXES: A DFT STUDY.

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ABSTRACT

Density functional theory implemented in ADF 2009.01 was used to calculate the values of two ESR parameters namely effective spin Hamiltonian [H^] and hyperfine coupling energy (ΔE_{hf}) along with the values of four factors (g, a, Q, and I) which contribute to the total value of the Hamiltonian for 45 complexes of six congeners of 2nd and 3rd transition series metal ions such as Zr (III) , Hf (III) ; Nb (IV), Ta(IV) ; Mo(III), W(III) ; Tc (II), Re(II) ; Ru (III), Os(III) ; Rh (IV), Ir (IV). Four relations which hold good both in regular (O_h) as well as distorted stereochemistries (D_{6h}, D_{3d}, D_{12}, C_{2v}, C_1, C_2) of these complexes were applied. The basis sets used were DZ or TPZ. The complexes were optimized to obtain 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} and NQCC] which were then used to calculate [H^] and [$\Delta E_{h\ f}$].

INTRODUCTION

Effective spin Hamiltonian (H^) is a mathematical expression that determines energy of an ESR transition in a paramagnetic complex. The Hamiltonian depends upon a number of ESR parameters [anisotropic and isotropic splitting factors (g_{11}, g_{22}, g_{33}, g_{iso}), hyperfine coupling constants (a_{11}, a_{22}, a_{33}, A_{ten})], NQR parameters [electric field gradient or *efg* (q_{11},q_{22},q_{33}), Nuclear Quadrupole Constant (Q)][1], total electronic spin (S), Bohr Magneton of both the electron (β_e) and of the nucleus (β_n), nuclear spin quantum number (I), g_n (nuclear magnetic ratio) along with nature of the surrounding nuclei if they possess quadrupole moments ($I \geq 1$).

When certain commands were given to the ADF 2009.01, we obtained two ESR parameters (isotropic and anisotropic g, a) and three NQR [asymmetric coefficient (η), anisotropic electric field gradient or *efg* (q), nuclear quadrupole coupling constant or NQCC (Q)] parameters and optimization parameters of complexes. The three (g, a, Q) of these five parameters were used to calculate another two ESR parameters [effective spin Hamiltonian (H^) and hyperfine coupling energy (ΔE h f)] of complexes.

The need for taking up this study arose because not much work was reported [(1-29)] on ESR studies of 4d and 5d metal ion complexes. In fact, theoretical calculation of Effective Spin Hamiltonian (H^) on such a vast number of complexes was never reported before because:

(i) High values of spin orbit coupling constants ($\lambda_{\text{metal ion}}$) of these metal ions would not allow

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[1] Q or e Q is the nuclear quadrupole moment. q Or e q is the electric field gradient. The product of the quantities ($e\,Q \times e\,q = e^2Qq$) is nuclear quadrupole coupling constant (Q).

exact determination of the ESR parameters experimentally.

(ii) Cryoscopy conditions generally needed in low energy microwave region (X band: 9000-10000 MHz) were difficult to obtain and cumbersome to maintain.

The *relevance* and the *objective* of present work lied in the fact that simply by applying DFT (30-31) to ADF 2009.01; we were able to do away with all these limitations.

Four relations were selectively used to calculate H^ and ΔE $_{h\ f}$ parameters of 45 complexes such as $[ZrX_6]^{3-}$ (X=Cl , Br), $[HfX_6]^{3-}$ (X=F ,Cl, Br), $[Hf\ (NH_3)_6]^{3+}$, $[Nb\ (NH_3)_6]^{4+}$, $[NbX_6]^{2-}$ (X=F ,Cl, NCS), $[TaX_6]^{2-}$ (X= Cl, Br), $[MoX_6]^{3-}$ (X=F, Cl ,Br, NCS), $[Mo(OH_2)_6]^{3+}$,$[Mo(NH_3)_6]^{3+}$ $[WX_6]^{3-}$(X=F,Cl ,Br), $[W(OH_2)_6]^{3+}$, $[W(NH_3)_6]^{3+}$, $[TcX_6]^{4-}$(X= Cl ,Br, NCS) , $[Tc\ (NH_3)_6]^{2+}$, $[ReX_6]^{4-}$ (X= Cl ,Br), $[Re(NH_3)_6]^{2+}$, $[RuX_6]^{3-}$ (X=F, Cl ,Br), $[OsX_6]^{3-}$ (X=F, Cl ,Br), $[Os(NH_3)_6]^{3+}$, $[RhX_6]^{2-}$ (X=F, Cl ,Br), $[Rh(NH_3)_6]^{4+}$, $[IrX_6]^{2-}$ (X=F, Cl ,Br), $[Ir\ (NH_3)_6]^{4+}$.

Calculation of ESR parameters (32-52)

(a) Effective Spin Hamiltonian (H^):

Four factors which contribute to H^ are: g, a, Q and the interaction of nuclear magnetic moment with external magnetic field **(I)**.The following three relations were used to calculate H^(MHz).

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

$$H^{\wedge} = \beta_e\ [g_{ll}\ .Hz.\ S_z + g_{\perp}\ (Hx.\ S_x + Hy.\ S_y)] + [\ a_{ll}.\ Sz\ .Iz + a_{\perp}(S_x.I_x + S_y.I_y)] + Q[I_z-1/3.\ I(I+1)] - [g_{n}.\beta_n.H_0.I] \qquad \text{-----------------------} [2]$$

$$H^{\wedge} = \beta_e\,[g_{iso}.H_0.S] + [A_{ten}.S.1] + Q.I^2 - [g_{n}.\beta_n\ .Ho.\ I] \qquad \text{----------------------} [3]$$

[1]Was used for systems with different ***g*** *and* ***a*** *values.[2]Was applied in axially symmetric systems and [3] would hold good for systems with same or nearly same* ***g*** *value or both* ***g*** *and* ***a*** *values. The first and the last terms in [1-3] were in ergs and the other two in MHz. (6.627 X 10^{-21} erg =one MHz); β_e=1.3994 MHz; $\beta_{H*} = \beta_{e/}1836$. g_n had a definite value for each metal.*

(b) Hyperfine Coupling Energy

$$(\Delta E_{h\,f}) = A_{ten}/2 \qquad \text{-----------------------} [4]$$

Both $\Delta E_{h\,f}$ and A_{ten} were expressed in MHz .

- Divide by molecular mass for calculation of **(I)**

METHODOLOGY

After optimization of the complexes by ADF 2009.01, the software was run by applying Single Point, LDA*, Default, Spin Orbit, Unrestricted, None and Collinear commands by using DZ* or TPZ* Basis sets in all the 45 complexes except for $[Os\ (NH_3)_6]^{3+}$ and $[Rh(NH_3)_6]^{4+}$ where LDA was replaced by GGABP*. Each complex with NYSOM* symmetry generated an OUTPUT file of its own. It contained values of ESR (g_{11}, g_{22}, g_{33} and g_{iso}; a_{11}, a_{22}, a_{33} and A $_{t\ e\ n}$), NQR (η, q_{11}, q_{22}, q_{33}, NQCC) and optimization [geometry, dipole moment, bonding energy, total energy (X c) parameters having contributions from LDA and GGA*components; each being further made up

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* **Acronyms** are: **LDA** (Local Density Approximation); **DZ (**Double Zeta) **TPZ (**Triple Zeta) **GGA BP** (Generalized Gradient Approximation Becke Perdew); **Nysom** (Normalized)

of Exchange and Correlation parts].The bonding energy was computed as an energy difference between the molecule and fragments. As the fragments were single atoms, they were usually computed as Spherically Symmetric and Spin-Restricted. So this usually did not represent the true atomic ground state (53-54).

RESULTS

Tables: 1.1-1.12 and1.1-1 A-1.12A gave values of optimization parameters of 12 metals of the 2nd and 3rd transition series and their 45 complexes respectively. Tables: 1.1B - 1.12B contained ESR and NQR parameters like $\mathbf{g}_{\perp}$, $\mathbf{g}_{||}$, $\mathbf{g}_{iso}$; $\mathbf{a}_{\perp}$, $\mathbf{a}_{11}$, $\mathbf{A}_{ten}$ and **Q** along with contributions from their respective factors. It also contained contribution from the fourth factor called interaction of nuclear magnetic moment with external magnetic field factor **(I)** in **H^.** These tables also gave $\mathbf{\Delta E_{h f}}$ values of the complexes as calculated by [4].

[I] Calculation of H^ for Zr (III) and Hf (III) Complexes

(a) $[ZrX_6]^{3-}$ (X = F, Cl) in Table: 1.1B were of axial symmetry with (a) two of the three **g** called $\mathbf{g}_{\perp}$ being the same and the third of higher value was called $\mathbf{g}_{||}$. (b) Two of the three **a** called $\mathbf{a}_{\perp}$ were of same value and the third of higher value was called $\mathbf{a}_{11}$. (c) Two values of **q** out of the three were the same (d) η=0. Relation [2] was applied to calculate their H^.

(Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=2.5 and g_n= -0.5214480).

(b) The Hf (III) complexes were categorized as follows (Table: 1.2 B):

(i) $[Hf X_6]^{3-}$ (X=F, Br) had an axial symmetry with (a) two of the three **g** called $\mathbf{g}_{\perp}$ being the same and the third with higher value was called $\mathbf{g}_{||}$. (b) Two of the three **a** called $\mathbf{a}_{\perp}$ being the same and the third with higher value was called $\mathbf{a}_{11}$. (c) Two of the three **q** values were the same. (d) η=0. Relation [2] was applied to calculate their H^.

(ii) In $[Hf Cl_6]^{3-}$, all **g** and **a** parameters possessed same values respectively.

Relation [3] was applied to calculate its H^.

(iii) As **g** and **a** values respectively differ in $[Hf (NH_3)_6]^{3+}$, the relation [1] was used to calculate its H^. (Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=3.5 and g_n= 0.2267143).

Individual contributions from the four factors in the total value of H^ for these six complexes were given in small brackets of horizontal row shown at the bottom (→) of Tables: 1.1B, 1.2B).

(c) $\Delta E_{h f}$ values of these Zr (III) and Hf (III) complexes were calculated by [4] (Tables: 1.1 B, 1.2 B).

Table: 1.1. Energies (kJmole^{-1}) of Zr

Sum of the orbital energies	= -197941.631
Total energy	= -347017.623
Kinetic energy	= 358774.656
Nuclear attraction energy	= -838025.633
Electron repulsion energy	= 143024.955
Exchange energy	= -10791.601

Table: 1.1A .Optimization Parameters of Zr (III) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy: X c LDA(Exchange; Correlation)
$[ZF_6]^{3-}$	D_{6h}	≅ 0.0	-3414.22	-441104.44 (-421336.89; -19767.55)
$[ZBr_6]^{3-}$	D_{6h}	≅ 0.0	-3761.98	-1691021.63 (1631273.45; -59748.19)

Table: 1. 1B. Calculation of Contributions from g, A, Q & I Factors in (H^)

Complex	g values / [g_{iso}] (**g** contribution)	a values/**[A $_{ten}$]*** (**a** contribution)	Q [η] (**Q** contribution)	--- **(I)**
$[ZrF_6]^{3-}$ D_{6h} (2) →	ll 2.001331 ⊥ 1.967097 ⊥ 1.967089 [1.978506] ($1.400H_{ll}+2.753H_{\perp}$)	1l 1482.194 ⊥ 1427.985 ⊥ 1427.983 [1446.060] (5422.273)	-127.753(0.000) (53.23)	--- (-0.00099 $4H_0$)
$[ZrBr_6]^{3-}$ D_{6h} (2) →	ll 1.967507 ⊥ 1.875079 ⊥ 1.875038 [1.905875] ($1.38H_{ll}+2.624H\perp$)	ll -8.701 ⊥ -17.344 ⊥-17.401 [-14.482] (-54.308)	-25.798(0.000) (10.749)	--- (do)

$\Delta E_{hf} \approx 0.5\ A_{ten}$

Table: 1.2. Energies (kJmole^{-1}) of Hf

Sum of the orbital energies = -894267.484
Total energy = -1456491.418
Kinetic energy = 1629769.308
Nuclear attraction energy = -3628668.687
Electron repulsion energy = 572131.931
Exchange energy = -29723.970

Table: 1.2 A. Optimization Parameters of Hf (III) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy:X c LDA(Exchange; Correlation)
$[HfF_6]^{3-}$	D_{6h}	≅ 0.0	-48304.19	-943484.89 (-913888.11; -29596.78)
$[HfCl_6]^{3-}$	O_h	3.8	-48035.78	-1213450.90 (-1172999.12; -40451.78)
$[HfBr_6]^{3-}$	O_h	≅ 0.0	-49460.95	-2193402.23 (-2123824.82; -69577.42)
$[Hf(NH_3)_6]^{3+}$	D_6	≅ 0.0	-52045.43	-899668.85 (-871139.00; -28529.85)

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

Complex	g values / [g_{iso}] (**g** contribution)	a values/[$\mathbf{A}_{ten}$]* (**a** contribution)	**Q** (η) (**Q** contribution)	--- **(I)**
$[Hf\ F_6]^{3-}$ D_{6h} (2)→	ll 1.998439 ⊥ 1.906947 ⊥ 1.906947 [1.935841] ($1.398H_{ll}+2.669H_{\perp}$)	ll 4552.955 ⊥ 4425.702 ⊥ 4425.702 [4468.120] ((23457.63)	5690.54(0.000) (-9958.445)	--- (0.00061 H_0)
$[Hf\ Cl_6]^{3-}$ O_h (3)→	[1.638886] (1.147 H_0)	[-1004.72] (-1758.260)	-1331.25(0.000) (-16307.813)	--- (do)
$[Hf\ Br_6]^{3-}$ O_h (3) →	[1.687085] (1.180 H_0)	[-884.28] (-1547.494)	-1235.518(0.00) (-15135.096)	--- (do)
$[Hf(NH_3)_6]^{3+}$ D_6 (2) →	ll 1.980544 ⊥ 1.919257 ⊥ 1.919230 [1.939677] ($1.385H_{ll}+2.681H_{\perp}$)	l1 7001.279 ⊥6758.151 ⊥6758.153 [6839.19] (35905.748)	-7078.38(0.035) (12387.165)	--- (do)

$*\Delta E_{hf} \approx 0.5\ A_{ten}$

[1I] Calculation of H^ for Nb (IV) and Ta (IV) complexes:

(a) The complexes of Nb (IV) were categorized as follows (Table: 1.3 B):

(i) $[NbX_6]^{2-}$ (X = F, Cl) and $[Nb(NH_3)_6]^{4+}$ were of axial symmetry with (a) two of the three **g** being the same called $\mathbf{g}_{\perp}$ and the third with higher value was called $\mathbf{g}_{||}$. (b)Two of three **a** called $\mathbf{a}_{\perp}$ being the same and the third of higher value was called $\mathbf{a}_{11}$. (c) Two of the three **q** values were of the same magnitude. (d) **η**= 0. Relation [2] was applied to calculate their H^.

(ii) $[Nb\ (NCS)_6]^{2-}$ had different values of both **g** and **a** respectively. Relation [1] was applied to calculate its H^. (Put S_x=S_y=S_z=1/2; I_x=I_y=I_z= 4.5 and g_n= 1.3712222).

(b) The Ta (IV) complexes were categorized as follows (Table: 1.4 B):

(i) $[Ta\ Cl_6]^{2-}$ had an axial symmetry with (a) two of the three **g** called $\mathbf{g}_{\perp}$ being of same value and the third of higher value was called $\mathbf{g}_{||}$. (b) Two of the three **a** called $\mathbf{a}_{\perp}$ being of the same value and the third of higher value was called $\mathbf{a}_{11}$. (c) Two of the three **q** were of same value. (d) **η**=0. Relation [2] was used to calculate H^.

(ii) $[Ta\ Br_6]^{2-}$ possessed almost same values of **g** and **a**. Relation [3] was applied to calculate its H^. (Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=3.5 and g_n= 0.6772857).

Individual contributions from four factors in the total value of H^ for these six complexes were given in small brackets of horizontal row shown at the bottom (→) of Tables: 1.3 B, 1. 4B).

(c) $\Delta E_{h\ f}$ for these Nb (IV) and Ta(IV) complexes was calculated by [4] (Tables: 1.3 B, 1.4 B).

Table: 1.3. Energies (kJmole^{-1}) of Nb

Sum of the orbital energies = -220524.584
Total energy = -368353.927
Kinetic energy = 381463.682
Nuclear attraction energy = -890145.400
Electron repulsion energy = 151580.134
Exchange energy = -11252.343

Table: 1.3A. Optimization Parameters of Nb (IV) Complexes

Complex	Point Group	Dipole moment	Total bonding energy	Total Energy:X c LDA(Exchange; Correlation)
$[NbF_6]^{2-}$	D_{3d}	≅ 0.0	-4368.10	-453354.94 (-433286.88; -20068.06)
$[NbCl_6]^{2-}$	D_{3h}	≅ 0.0	-3852.22	-723320.86 (-692397.80; -30923.06)
$[Nb(NCS)_6]^{2-}$	C_2	2.56	36992.39	-854927.44; (-812445.73; -42481.71)
$[Nb(NH_3)_6]^{4+}$	D_{12}	≅ 0.0	-8540.86	-409541.28 (-390539.96; -19001.32)

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

Complex	g values / [g_{iso}] (**g** contribution)	a values/**[A $_{ten}$]*** (**a** contribution)	Q (η) (**Q** contribution)	--- **(I)**
$[NbF_6]^{2-}$ D_{3d} (2)→	ll 1.997058 ⊥ 1.910581 ⊥ 1.910545 [1.939395] ($1.397H_{ll}+2.674H_{\perp}$)	ll 1687.779 ⊥1514.006 ⊥1513.832 [1571.872] (10610.136)	- 248.99(0.023) (933.713)	--- (0.00470 $32H_0$)
$[NbCl_6]^{2-}$ D_{3h} (2) →	ll 1.994610 ⊥ 1.952732 ⊥ 1.952710 [1.966684] ($1.396H_{ll}+2.733H_{\perp}$)	ll 110.823 ⊥ -152.487 ⊥ -151.959 [-64.541] (-435.652)	201.541 (0.017) (-755.779)	--- (do)
Nb $(NCS)_6]^{2-}$ C_2 (1) →	zz 2.021949 yy 2.012788 xx 1.962290 [1.99901] ($1.373H_x+1.416H_y$ $+1.415\ H_z$)	zz -411.361 yy -402.903 xx -182.463 [-332.242] (-2242.635)	-38.546 (0.825) (144.548)	--- (do)
$[Nb(NH_3)_6]^{4+}$ D_{12} (2) →	l1 1.981543 ⊥ 1.848149 ⊥ 1.845451 [1.891714] ($1.387H_{ll}+2.584H_{\perp}$)	ll 560.082 ⊥ 262.279 ⊥ 261.709 [361.357] (2439.160)	334.684 (0.013) (-1255.065)	--- (do)

***$\Delta E_{hf} \approx 0.5\ A_{ten}$**

Table: 1.4. Energies (kJmole^{-1}) of Ta

Sum of the orbital energies = -926215.546
Total energy = -1507460.507
Kinetic energy = 1692808.00
Nuclear attraction energy = -3761202.892
Electron repulsion energy = 591400.512
Exchange energy = -39466.957

Table: 1.4 A. Optimization Parameters of Ta (IV) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy :X c LDA(Exchange; Correlation)
$[TaCl_6]^{2-}$	D_{3h}	≅ 0.0	-52811.48	--1233202.82 (-1192430.57;-40772.25)
$[TaBr_6]^{2-}$	O_h	≅ 0.0	-54446.40	-2213154.01 (-2143256.15; -69897.86)

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

Complex	g values / [g_{iso}] (**g** contribution)	a values/**[A $_{ten}$]*** (**a** contribution)	Q (η) (**Q** contribution)	--- **(I)**
$[TaCl_6]^{2-}$ D_{3h} (2) →	ll 1.949731 ⊥ 1.864718 ⊥ 1.863443 [1.682027] (1.364 H_{ll}+2.609$H_{\perp}$)	ll 1648.699 ⊥ 1108.296 ⊥ 1106.086 [1287.694] (6760.394)	- 4510.8 (0.000) (7893.90)	--- (0.0018 07H_0)
$[Ta\ Br_6]^{2-}$ O_h (3)→	[1.69233] (1.184 H_0)	[-1031.594] (-1805.290)	-1304.9 (0.000) (-15985.025)	--- (do)

***ΔE $_{hf}$ ≈ 0.5 A$_{ten}$**

[1II] Calculation of H^ for Mo (III) and **W (III) complexes:**

(a) All the six Mo (III) complexes (Table: 1.5 B) such as $[MoX_6]^{3-}$ (X=F, Cl, Br, CNS) as well as $[Mo\ (OH_2)_6]^{3+}$and $[Mo\ (NH_3)_6]^{3+}$ had nearly the same values of **a** and **g** parameters. Relation [3] was applied to calculate their H^. (Put S_x=S_y=S_z=3/2; I_x=I_y=I_z=2.5 and g $_n$= -0.3656800).

(b) All the five W (III) complexes (Table: 1.6 B) like $[W\ X_6]^{3-}$ (X=F, Cl, Br) as well as $[W\ (OH_2)_6]^{3+}$ and $[W\ (NH_3)_6]^{3+}$ possessed nearly the same values of **g** and **a** parameters**.** Relation [3] was applied to calculate H^ for all these complexes. (Put S_x=S_y=S_z=3/2; I_x=I_y=I_z=0.5 and g $_n$= 0.2355696).

Values of individual contributions from the four factors in the total value of (H^) for these eleven complexes were given in small brackets of a horizontal row shown at the bottom of each complex (→) of Tables: 1. 5 B and 1.6B.

With I=0.5, there is no NQCC for W (III) complexes. Therefore, only three factors would contribute in the total value of H^ in its complexes.

(c) ΔE $_{hf}$ for these Mo (III) and W (III) complexes was calculated by [4] (Tables: 1.5 B, 1.6 B).

Table: 1.5. Energies (kJmole^{-1}) of Mo

Sum of the orbital energies = -234162.483
Total energy = -390455.742
Kinetic energy = 405041.503
Nuclear attraction energy = -943980.382
Electron repulsion energy = 160198.325
Exchange energy = -11715.198

Table: 1.5A. Optimization Parameters of Mo (III) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy:X c LDA(Exchange; Correlation)
$[MoF_6]^{3-}$	O_h	≅ 0.0	-3908.97	-465710.47 (-445350.56; -20359.91)
$[MoCl_6]^{3-}$	O_h	≅ 0.0	-3381.79	-735677.36 (-704462.36; -31214.99)
$[MoBr_6]^{3-}$	O_h	≅ 0.0	-4874.10	-1715628.34 (-1655287.70; -60340.64)
$[Mo(NCS)_6]^{3-}$	O_h	≅ 0.0	-14164.86	-867278.62 (-824505.12; -42773.49)
$[Mo(OH_2)_6]^{3+}$	C_1	4.32	-6867.18	-443834.69 (-423738.42; -20096.28)
$[Mo(NH_3)_6]^{3+}$	C_{3i}	≅ 0.0	-10727.45	-421899.98 (-402606.51; -19293.48)

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

Complex ($4d^3$)	[g_{iso}] (**g** contribution)	**[A $_{ten}$]*** (**a** contribution)	Q (η) (**Q** contribution)	--- **(I)**
$[MoF_6]^{3-}$ O_h (3)→	[1.958172] (4.110H_0)	[-234.754] (-880.328)	- 0.00879 (0.035) (-0.054953)	--- (-0.0006 968H_0)
$[MoCl_6]^{3-}$ O_h (3)→	[1.984449] (4.166 H_0)	[-186.562] (-699.608)	- 0.00669 (0.035) (-0.0418)	--- (do)
$[MoBr_6]^{3-}$ O_h (3)→	[2.014495] (4.229 H_0)	[-160.375] (-601.406)	- 0.007195(0.019) (-0.044968)	--- (do)
$Mo(NCS)_6]^{3-}$ O_h (3)→	[1.977407] (4.151H_0)	[-153.418] (-575.418)	- 0.0089 (0.027) (-055625)	--- (do)
$[Mo(OH_2)_6]^{3+}$ C_1 (3)→	[1.976455] (4.149 H0)	[-205.089] (-769.084)	-0.954543 (0.506) (-5.965893)	--- (do)
$[Mo(NH_3)_6]^{3+}$ C_{3i} (3)→	[1.990714] (4.178H0)	[-177.267] (-664.751)	0.72235 (0.016) (4.514688)	--- (do)

$*\Delta E_{hf} \approx 0.5\ A_{ten}$

Table: 1.6. Energies (kJmole^{-1}) of W

Sum of the orbital energies = -958924.160
Total energy = -1559565.445
Kinetic energy = 1757712.950
Nuclear attraction energy = -3897107.487
Electron repulsion energy = 611047.391
Exchange energy = -31218.299

Table: 1. 6A. Optimization Parameters of W (III) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy :X c LDA(Exchange; Correlation)
$[WF_6]^{3-}$	O_h	≅ 0.0	-57415.49	-983187.91 (952948.41; -30239.51)
$[WCl_6]^{3-}$	O_h	≅ 0.0	-56925.77	-1253156.05 (-1212061.43; -41094.63)
$[WBr_6]^{3-}$	O_h	≅ 0.0	-58417.00	-2233106.71 (-2162886.44; -70220.27)
$[W(OH_2)_6]^{3+}$	C_1	4.06	-60416.03	-961312.39 (-931336.49; -29975.90)
$[W(NH_3)_6]^{3+}$	C_1	0.02	-64302.58	-939377.26 (-910204.24; -29173.02)

Table: 1. 6B. Calculation of Contributions from g, A, Q & I Factors in (H^)

Complex ($5d^3$)	[g_{iso}] (**g** contribution)	**[A $_{ten}$]*** (**a** contribution)	Q (η)** (**Q** contribution)	--- **(I)**
$[WF_6]^{3-}$ O_h (3)→	[1.80193] (3.783H_0)	[-16.410] (-12.308)	-- (---)	--- (0.0000898 H_0)
$[WCl_6]^{3-}$ O_h (3)→	[1.868252] (3.922 H_0)	[- 153.522] (-115.142)	--- (---)	--- (do)
$[WBr_6]^{3-}$ O_h (3)→	[1.893263] (3.974 H_0)	[-128.087] (-96.065)	-- (---)	--- (do)
$[W(OH_2)_6]^{3+}$ C_1 (3) →	[1.859795] (3.903 H_0)	[-113.25] (-84.938)	-- (---)	--- (do)
$[W(NH_3)_6]^{3+}$ C_1 (3)→	[1.925022] (4.041H0)	[-141.875] (-106.406)	-- (---)	--- (do)

***ΔE $_{hf}$ ≈ 0.5 A$_{ten}$**

** With I=1/2, W (III) complexes do not possess NQCC and η. So **Q** does not contribute.

[IV] Calculation of H^ for Tc (II) and Re (II) complexes

(a) The Tc (II) complexes were categorized as follows (Table: 1. 7 B):

(i) $[TcX_6]^{4-}$ (X=Cl, Br) were of axial symmetry with (a) two of the three **g** called **g**$_\perp$ to be of the same value and the third having higher value was called **g**$_{||}$. (b) Two of the three **a** called **a**$_\perp$ being the same and the third of higher value was called **a**$_{11}$. (c) Two of the three **q** values were same.(d) **η**=0. Relation [2] was applied to calculate their H^.

(ii) $[Tc\ (NCS)_6]^{4-}$possessed quite different values of **g** and **a**. Relation [1] was applied to calculate its H^.

(iii) $[Tc\ (NH_3)_6]^{2+}$ looked like having axial symmetry as it obeyed three of the four conditions of axial symmetry like (a) two of the three **g** called **$g_\perp$** were of the same value and the third having higher value was called **$g_{\|}$**. (b) Two of the three **a** called **$a_\perp$** being of same value and the third with higher value was called **a_{11}**. (c) Two of the three **q** values were the same. But it does not obey the fourth condition because here $\eta \neq 0$.

So Relation [1] rather than [2] is applied to calculate their H^. (Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=4.5 and g_n= 1.2632667).

(b) The Re (II) complexes were categorized as follows (Table: 1.8 B):

(i) $[Re\ X_6]^{4-}$ (X= Cl, Br) had nearly the same values of **g** and **a** respectively.

Relation [3] was applied to calculate H^.

(ii) $[Re\ (NH_3)_6]^{2+}$ had quite different values of **g** and **a** parameters respectively.

Relation [1] was applied to calculate its H^.

(Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=2.5 and g_n= 1.287880)

Values of individual contributions from the four factors in the total value of H^ for the seven complexes were given in small brackets of a horizontal row shown at the bottom of each complex (→) in Tables: 1. 7 B and 1. 8B.

(c) ΔE_{hf} for these Tc(II) and Re(II) complexes was calculated by [4] (Tables:1.7 B, 1.7 B).

Tables: 1.7. Energies ($kJmole^{-1}$) of Tc

Sum of the orbital energies = -248217.224
Total energy = -413330.603
Kinetic energy = 429520.152
Nuclear attraction energy = -999838.176
Electron repulsion energy = 169176.367
Exchange energy = -12188.956

Tables: 1.7 A. Optimization Parameters of Tc (II) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy: X c LDA(Exchange; Correlation)
$[TcCl_6]^{4-}$	D_{6h}	≅ 0.0	-924.72	-747903.14 (-716414.73; -31488.41)
$[TcBr_6]^{4-}$	D_{6h}	≅ 0.0	-2517.74	-1727854.10 (-1667240.04; -60614.06)
$[Tc\ (NCS)_6]^{4-}$	C_2	3.16	39373.95	-879499.38 (-836453.19; -43046.19)
$[Tc\ (NH_3)_6]^{2+}$	D_6	≅ 0.0	-9442.19	-434121.29 (-414554.78; -19566.51)

Tables: 1.7 B. Calculation of Contributions from g, A, Q & I Factors in (H^)

Complex	g values / [g_{iso}] (**g** contribution)	a values/**[A $_{ten}$]*** (**a** contribution)	Q (η) (**Q** contribution)	--- **(I)**
$[TcCl_6]^{4-}$ D_{6h} (2)→	11 1.946701 ⊥2.150365 ⊥ 2.150460 [2.080509] ($1.362H_{ll}+3.009H_{\perp}$)	ll 15.429 ⊥-19.205 ⊥ -19.205 [-7.660] (-51.705)	110.57 (0.038) (-414.638)	--- (0.0043 33H_0)
$[TcBr_6]^{4-}$ D_{6h} (2)→	ll 2.009877 ⊥ 2.008253 ⊥1.942244 [1.986792] ($1.406H_{ll}+2.764H_{\perp}$)	ll -2.128 ⊥ -21.852 ⊥ -22.793 [-15.591] (-105.239)	124.18 (0.000) (-465.675)	--- (do)
$[Tc(NCS)_6]^{4-}$ C_2 (1) →	zz 1.940612 yy 1.930780 xx 1.929841 [1.933744] ($1.350H_x+1.351H_y$ $+1.358H_z$)	zz -163.279 yy -118.128 xx -145.567 [-142.325] (-960.694)	20.122 (0.291) (-75.476)	--- (do)
$[Tc(NH_3)_6]^{2+}$ D_6 (1) →	zz 5.103714 yy 1.904594 zx 1.898915 [2.968741] ($1.329H_x+1.333H_y$ $+3.571\ H_z$)	zz 957.834 yy - 19.540 xx - 20.332 [305.987] (2065.412)	22.659 (0.105) (-84.971)	--- (do)

***ΔE $_{hf}$ ≈ 0.5 A $_{ten}$**

Tables: 1.8. Energies (kJmole^{-1}) of Re

Sum of the orbital energies = -992453.637
Total energy = -1612818.552
Kinetic energy = 1824530.108
Nuclear attraction energy = -4036394.783
Electron repulsion energy = 631024.326
Exchange energy = -31978.204

Tables: 1.8 A. Optimization Parameters of Re (II) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy: X c LDA(Exchange; Correlation)
$[ReCl_6]^{4-}$	O_h	≅ 0.0	-60993.79	-1273383.09 (-1231963.38; -41419.71)
$[ReBr_6]^{4-}$	O_h	≅ 0.0	-62629.22	-2253333.71 (-2182788.36; -70545.35)
$[Re(NH_3)_6]^{2+}$	D_6	≅ 0.0	-70669.18	-959604.68 (-930106.53; -29498.15)

Tables: 1.8 B. Calculation of Contributions from g, A, Q & I Factors in (H^)

Complex	g values / [g_{iso}] (**g** contribution)	a values/**[A $_{ten}$]*** (**a** contribution)	Q (η) (**Q** contribution)	--- **(I)**
$[ReCl_6]^{4-}$ O_h (3) →	[2.346133] (1.642 H_0)	[535.840] (669.800)	313.030(0.000) (1956.437)	--- (0.00245H_0)
$[ReBr_6]^{4-}$ O_h (3) →	[2.39061] (1.673H_0)	[531.765] (664.706)	299.987 (0.000) (1874.919)	--- (do)
$[Re(NH_3)_6]^{2+}$ D_6 (2)→	11 4.159017 ⊥ 0.586016 ⊥ 0.562867 [1.76930] (2.91H_{11}+0.804$H_\perp$)	11 1032.922 ⊥187.452 ⊥ 183.324 [467.900] (1754.625)	-1217.20(0.095) (507.167)	--- (do)

***ΔE $_{hf}$ ≈ 0.5 A$_{ten}$**

[V] Calculation of H^ for Ru (III) and Os (III) complexes

(a) $[RuX_6]^{3-}$ (X=F, Cl, Br) possessed same values of **g** and **a** respectively (Table: 1. 9 B). Relation [3] was applied to calculate their H^. [Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=2.5 and g $_n$= -0.287520].

(b) The Os (III) complexes were categorized as follows (Table: 1.10 B):
(i) $[Os\ X_6]^{3-}$ (X=F, Cl, Br) had nearly the same values of **g** and **a** parameters respectively. Relation [3] was applied to calculate their H^.
(ii) $[Os\ (NH_3)_6]^{3+}$ looked like having axial symmetry as it obeyed three of the four conditions of axial symmetry such as (a) two of the three **g** called **g**$_\perp$ were of the same value and the third having higher value was called **g**$_\parallel$. (b) Two of the three **a** called **a**$_\perp$ were of the same value and the third of higher value was called **a$_{11.}$** (c) Two of the three **q** values were of same magnitude. But it does not obey the fourth condition because here η≠ 0. Relation [1] rather than [2] was applied to calculate their H^. (Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=1.5 and g_n= 0.4399553).
Values of individual contributions from four factors in the total value of H^ in MHz for these 7 complexes were given in small brackets of a horizontal row shown at the bottom of each complex (→) in Tables: 1.9 B and 1.10 B.

(c) ΔE $_{h\ f}$ for the Ru (III) and Os (III) complexes was calculated by [4] (Tables: 1.9 B,1.10 B).

Tables: 1.9. Energies (kJmole^{-1}) of Ru

Sum of the orbital energies = -262694.771
Total energy = -436990.048
Kinetic energy = 454919.503
Nuclear attraction energy = -1057755.694
Electron repulsion energy = 178519.845
Exchange energy = -12673.712

Tables: 1.9 A. Optimization Parameters of Ru (III) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy : X c LDA(Exchange; Correlation)
$[RuF_6]^{3-}$	O_h	≅ 0.0	-3850.67	-491226.84 (-470269.69; -20957.15)
$[RuCl_6]^{3-}$	O_h	3.8	-3480.20	-761194.08 (-729381.83; -31812.25)
$[RuBr_6]^{3-}$	O_h	≅ 0.0	-4986.66	-1741145.05 (-1680207.15; -60937.90)

Tables: 1.9 B. Calculation of Contributions from g, A, Q & I Factors in (H^)

Complex	$[g_{iso}]$ (**g** contribution)	**[A $_{ten}$]*** (**a** contribution)	Q (η) (**Q** contribution)	--- **(I)**
$[RuF_6]^{3-}$ O_h (3) →	[2.818343] (1.972H_0)	[600.682] (750.853)	99.310 (0.000) (620.688)	--- (-0.000548H_0)
$[RuCl_6]^{3-}$ O_h (3)→	[2.853948] (1.997H_0)	[549.020] (686.275)	85.869 (0.000) (536.681)	--- (do)
$[RuBr_6]^{3-}$ O_h (3)→	[2.742377] (1.919 H_0)	[513.095] (641.369)	71.409 (0.000) (446.306)	--- (do)

$^*\Delta E_{hf} \approx 0.5 A_{ten}$

Tables: 1.10. Energies ($kJmole^{-1}$) of Os

Sum of the orbital energies = -1026749.174
Total energy = -1667237.716
Kinetic energy = 1893323.949
Nuclear attraction energy = -4179218.245
Electron repulsion energy = 651404.529
Exchange energy = -32747.940

Tables: 1.10 A. Optimization Parameters of Os (III) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy : X c LDA(Exchange; Correlation) *GGA[Exchange; Correlation]
$[OsF_6]^{3-}$	O_h	≅ 0.0	-67946.11	-1023848.81 (-992956.76; -30892.06)
$[OsCl_6]^{3-}$	D_{6h}	≅ 0.0	-66154.24	-1293817.36 (-1252070.08; -41747.27)
$[OsBr_6]^{3-}$	O_h	≅ 0.0	-69118.31	-2273767.29 (-2202894.46; -70872.83)
$[Os(NH_3)_6]^{3+}$	D_{12}	≅ 0.0	-75579.75	-1028260.38 (-956526.51; -30308.62) [-53454.55; 12029.31]

*GGA (Exchange; Correlation) Energies=0 for all except for $[Os(NH_3)_6]^{3+}$

Tables: 1.10 B. Calculation of Contributions from g, A, Q & I Factors in (H^)

Complex	g values / [g_{iso}] (**g** contribution)	a values/[**A** $_{ten}$]* (**a** contribution)	Q (η) (**Q** contribution)	--- **(I)**
$[OsF_6]^{3-}$ O_h (3)→	[2.110344] ($1.477H_0$)	[668.950] (501.713)	-12.186 (0.000) (-27.419)	--- (0.0005 03H_0)
$[OsCl_6]^{3-}$ D_{6h} (3)→	[2.008006] (1.405 H_0)	[-80.930] (-60.698)	-511.51 (0.000) (-1150.898)	--- (do)
$[OsBr_6]^{3-}$ O_h (3) →	[2.170049] (1.518 H_0)	[637.382] (478.037)	91.790 (0.000) (206.528)	--- (do)
$[Os(NH_3)_6]^{3+}$ D_{12} (1) →	zz 4.625234 yy0.900445 xx0.853802 [2.126494] ($0.597H_x$+$0.630H_y$ +$3.236H_z$)	zz 1738.769 yy 394.253 xx 392.480 [841.834] (1894.127)	-973.74 (0.298) (-243.435)	--- (do)

$*\Delta E_{hf} \approx 0.5\ A_{ten}$

[V1] Calculation of H^ for Rh (IV) and Ir (IV) complexes

(a) The Rh (IV) complexes were categorized as follows (Table: 1.11 B):

(i) $[RhX_6]^{2-}$ (X=F, Cl, Br) had nearly the same values of **g** and **a** parameters respectively. Relation [3] was applied to calculate their H^.

(ii) The complex $[Rh\ (NH_3)_6]^{4+}$ possessed different values of **g** and **a** parameters respectively. Relation [1] was applied to calculate H^. (Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=0.5 and g_n= -0.176800).

(b) The Ir (IV) complexes were categorized as follows (Table: 1.12 B):

(i) $[Ir\ X_6]^{2-}$(X=F, Cl, Br) had nearly the same values of **g** and **a** parameters respectively. Relation [3] was applied to calculate their H^.

(ii) $[Ir\ (NH_3)_6]^{4+}$ was of axial symmetry with (a) two of the three **g** called $\mathbf{g}_\perp$ were the same and the third with higher value was called $\mathbf{g}_\parallel$. (b)Two of the three **a** parameters called $\mathbf{a}_\perp$ being of the same value and the third of higher value was called $\mathbf{a}_{11.}$ (c) Two of the three **q** values were of the same value (d) **η** ≅ 0. Relation [2] was applied to calculate their H^. (Put S_x=S_y=S_z=1/2; I_x=I_y=I_z=1.5 and g_n= 0.1091333).

Values of individual contributions from four factors in the total value of H^ in MHz for these 8 complexes were given in small brackets of a horizontal row given at the bottom of each complex (→) in Tables: 1.11 B and 1.12 B.

With I=0.5, there is no NQCC for Rh (IV) complexes. Therefore, only three factors would contribute in the total value of H^ in its complexes.

(c) ΔE_{hf} for these Rh(IV) and Ir(IV) complexes was calculated by [4] (Tables:1.11 B,1.12 B).

Tables: 1.11. Energies (kJmole^{-1}) of Rh

Sum of the orbital energies = -277600.622
Total energy = -461445.676
Kinetic energy = 1893323.949
Nuclear attraction energy = -481259.711
Electron repulsion energy = 188234.896
Exchange energy = -13169.545

Tables: 1.11 A. Optimization Parameters of Rh (IV) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy :X c LDA(Exchange; Correlation)
$[RhF_6]^{2-}$	O_h	≅ 0.0	-4613.31	-504390.16 (-483128.51; -21261.66)
$[RhCl_6]^{2-}$	O_h	≅ 0.0	-4008.09	-774357.62 (-742240.85; -32116.78)
$[RhBr_6]^{2-}$	O_h	≅ 0.0	-5531.05	-1754338.01 (-1693090.56; -61247.45)
$[Rh(NH_3)_6]^{4+}$	D_6	≅ 0.0	-6799.75	-484539.94 (-441158.01; 8925.88) [-32083.34; -20224.47]

Tables: 1.11 B. Calculation of Contributions from g, A, Q & I Factors in (H^)

Complex ($4d^{5}$)	g values / [g_{iso}] (**g** contribution)	a values/**[A $_{ten}$]*** (**a** contribution)	Q (η)** (**Q** contribution)	-- (**I**)
$[RhF_6]^{2-}$ O_h (3) →	[2.327833] ($1.629H_0$)	[532.790] (133.198)	-- (---)	--- (-0.0000 $674H_0$)
$[RhCl_6]^{2-}$ O_h (3) →	[2.233967] ($1.563H_0$)	[433.993] (108.498)	-- (---)	--- (do)
$RhBr_6]^{2-}$ O_h (3)→	[2.1426] ($1.500\ H_0$)	[426.450] (106.613)	-- (---)	--- (do)
$[Rh\ (NH_3)_6]^{4+}$ D_{12} (1) →	zz 3.603577 yy 1.762655 xx1.548919 [2.30505] ($1.084H_x$+$1.233H_y$ +2.521Hz)	zz 893.326 yy 202.919 xx 52.820 [383.022] (287.267)	-- (---)	--- (do)

***ΔE $_{hf}$ ≈ 0.5 A$_{ten}$**

** With I=1/2, Rh (IV) complexes do not possess NQCC and η. So **Q** contribution is zero.

Tables: 1.12. Energies (kJmole^{-1}) of Ir

Sum of the orbital energies = -1061815.440
Total energy = -1722839.330
Kinetic energy = 1964156.569
Nuclear attraction energy = -4325667.832
Electron repulsion energy = 672199.867
Exchange energy = -33527.933

Tables: 1.12 A. Optimization Parameters of Ir (IV) Complexes

Complex	Point group	Dipole moment	Total bonding energy	Total Energy : X c LDA(Exchange; Correlation)
$[IrF_6]^{2-}$	O_h	≅ 0.0	-74565.96	-1044541.55 (-1013320.57; -31220.97)
$[IrCl_6]^{2-}$	O_h	≅ 0.0	-73959.80	-1314509.65 (-1272433.54; -42076.11)
$[IrBr_6]^{2-}$	O_h	≅ 0.0	-75407.81	-2294460.05 (-2223258.31; -71201.74)
$[Ir(NH_3)_6]^{4+}$	D_{12}	≅ 0.0	-78865.09	-1000815.05 (-970654.01; -30161.04)

Tables: 1.12 B. Calculation of Contributions from g, A, Q & I Factors in (H^)

Complex ($5d^5$)	g values / [g_{iso}] (**g** contribution)	a values/**[A $_{ten}$]*** (**a** contribution)	Q (η) (**Q** contribution)	--- **(I)**
$[IrF_6]^{2-}$ O_h (3)→	[1.960903] (1.372H_0)	[711.343] (533.507)	-70.890 (0.002) (-159.493)	--- (0.0001 248H_0)
$[IrCl_6]^{2-}$ O_h (3) →	[1.938232] (1.356H_0)	[630.605] (472.954)	51.220 (0.004) (115.245)	--- (do)
$[IrBr_6]^{2-}$ O_h (3) →	[1.92585] (1.348H_0)	[603.730] (452.798)	43.560 (0.000) (98.0)	--- (do)
$[Ir\ (NH_3)_6]^{4+}$ D_{12} (2) →	1l 3.686342 ⊥ 1.005770 ⊥ 1.000407 [2.259355] (2.579H_{ll}+1.404$H_\perp$)	ll 1473.724 ⊥735.630 ⊥732.682 [980.680] (2206.527)	-688.45 (0.093) (-172.113)	--- (do)

***ΔE $_{hf}$ ≈ 0.5 A_{ten}**

CONCLUSIONS

Effective Spin Hamiltonian (H^) and Hyperfine Coupling Energy (ΔE$_{hf}$) of a number of complexes of the 2nd and 3rd transition metal ions in their most common oxidation states have been successfully calculated. The values of all the four important factors which contribute to the total energy of ESR transitions of complexes were calculated accurately. The data generated is quite useful to the body of scientific knowledge.

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