Predicting ESR Peaks in the 4d and 5d Transition Metal Ion Complexes by NMR, ESR and NQR Parameters: A DFT Study

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ABSTRACT

Computational chemistry was used to predict the number of ESR peaks in the 2nd and 3rd transition metal ion complexes by applying DFT implemented in ADF 2012.01. Only a limited experimental ESR research had been carried out in this field because high values of spin orbit coupling constants of these metal ions which provide an important energy transfer mechanism would adversely affect the values of ESR and NMR parameters (especially \( A_{ten} \)) of their complexes. Therefore, theoretical predictions were useful. ESR (\( A_{ten} \)) and NQR (\( NQCC, h \)) parameters of transition metal ions and the coordinating atoms of ligands were obtained from the ESR/EPR program while their shielding constants (\( s \)) and chemical shifts (\( d \)) were obtained from the NMR/EPR program after optimization of the complexes. Ligands whose coordinating atoms (CA) possessed the same values of the five parameters (\( A_{ten}, NQCC, \delta, h, s \)) were expected to be spatially equivalent and would undergo the same hyperfine interaction with the central metal ion. 34 complexes of 10 metal ions consisting of five congeners: Zr (III), Hf (III); Nb (IV), Ta (IV), Tc (II), Re (II); Ru (III), Os (III), Rh (IV), Ir (IV) were selected to predict the number of ESR peaks.

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

INTRODUCTION

Only a limited research work had been done in the experimental determination of number of ESR peaks in complexes of 4d and 5d metal ions like Zr (III), Hf (III); Nb (IV), Ta (IV), Tc (II), Re (II); Ru (III), Os (III), Rh (IV), Ir (IV) which formed five congeners of 2nd and 3rd transition series.

As DFT had, hardly, been applied to determine number of ESR peaks in these metal ions...
ion complexes, we tried DFT implemented in ADF 2010.01 to 34 complexes such as $[\text{ZrX}_6]^{\text{3-}} (X=F, \text{Cl, Br}), [\text{HfX}_6]^{\text{3-}} (X=F, \text{Cl, Br}), [\text{TaX}_6]^{\text{3+}} (X=\text{Cl, Br}), [\text{TcBr}}_6]^{\text{3+}}$, $[\text{ReX}_6]^{\text{3+}}$, $[\text{IrX}_6]^{\text{3+}} (X=F, \text{Cl, Br}), [\text{OsNH}_{3}]^{\text{2+}}$, $[\text{TcNH}_{3}]^{\text{2+}}$, $[\text{ReNH}_{3}]^{\text{2+}}$, $[\text{RuNH}_{3}]^{\text{2+}} (X=F, \text{Cl, Br})$. These five parameters ($A_{\text{an}}$, NQCC, $\eta$, $\sigma$, $\delta$) together were, then, used to predict the number of ESR peaks in the 2nd and 3rd transition series metal ion complexes.

RESULTS

Results for 34 complexes of 10 metal ions were tabulated in Tables: 1-2.

Table: 1 contained values of $I_{\text{M}}, I_{\text{CA}}, g_{\text{M}}$ and $g_{\text{CA}}$ as well as $\mu_{\text{M}}$ and $\mu_{\text{CA}}$ (in terms of $\beta_{\text{M}}$) and ratios of $m_{\text{M}}$ and $m_{\text{CA}}$ to predict the possibility of hyperfine interaction between metal ions and ligands.

Table: 2 contained $A_{\text{an}}, \eta, \sigma, \delta$ values of metal ions and $A_{\text{an}}, \text{NQCC}, \eta, \sigma, \delta$ and CA of ligands, number of spatially different ligands along with the theoretically predicted number of ESR peaks in these complexes.

DISCUSSION

It was taken up under the following headings:

Basis for prediction of number of ESR peaks

Five parameters ($A_{\text{an}}, \text{NQCC}, \eta, \sigma, \delta$) of metal ions and coordinating atoms (CA) of ligands were obtained from the software by giving certain commands. A metal ion possessed only one value of each one of these 5 parameters while the values of the parameters might differ in case of the coordinating atoms (CA) of ligands. When, the ligands possessed the same or nearly the same values of these 5 parameters, it indicated that all the ligands were spatially equivalent. The relative magnitudes of the values of the parameters of metal ion and CA would also be taken into account while predicting ESR peaks of the complexes.

Relation to Calculate of nuclear magnetic moment ($\mu_{\text{M}}$) in terms of $\beta_{\text{M}}$

After knowing the values of nuclear spin quantum numbers and g factors of metals ($I_{\text{M}}, g_{\text{M}}$) and of coordinating atoms (CA) of ligands ($I_{\text{CA}} , g_{\text{CA}}$) from the literature, we could calculate nuclear magnetic moments of both the metal ($\mu_{\text{M}}$) and coordinating atoms ($\mu_{\text{CA}}$) of ligands in terms of $\beta_{\text{M}}$ by the following relation:
Knowing whether hyperfine interaction was possible or not

From $\mu = g \sqrt{I(I+1)}$ ratio called $\mu_n$ ratio, we could draw the following conclusions:

(a) A comparable $\mu_n$ ratio for isotopes with I > 0 having appreciable % natural abundance would mean that the unpaired electron was delocalized both on the metal and the ligands. So the hyperfine interaction between the metal ion and the ligands was most probable. The peaks would arise both from the ligands and the metal ion.

(b) Very small or very large ratios implied that $\mu_n$ of ligands and metal differ largely. In such a case, no hyperfine interaction between the metal and the ligands was possible. Electron would remain localized on the metal irrespective of the values of I and the % abundance. The peaks would arise only from the metal ion.

*Analogous to an electronic spin: $m_s = g_s \sqrt{s(s+1)}$

Predicting the number of ESR peaks

(I) Assuming $I_M$ and $I_{CA}$ the nuclear spins of the metal and [CA] respectively:

Number of ESR peaks given by a metal ion was $2I_M + 1$ ...(b)

(II) Number of ESR peaks arising from ligands was predicted from their spatial arrangement as follows:

(i) When all the $n$ ligands were spatially equivalent, then each ESR line of metal ion would be split up into the lines:

$$(2n I_{CA} + 1)$$ ...(c)

(ii) If $n_1$ ligands were spatially of one type; $n_2$ are of the other type and so on, then the total number of lines into which one line of the metal ion would be split:

$$(2n_1 I_{CA} + 1)(2n_2 I_{CA} + 1)(2n_3 I_{CA} + 1)$$ ...(d)

(iii) If all the ligands were nonequivalent, one line of metal ion would split into:

$$(2 I_{CA} + 1)^n$$ ...(e)

(IV) If metal ion possessed higher $A_{\text{ion}}$ than the coordination atoms (CA) of ligands, we should first calculate number of lines obtained from metal ion. Each line of the metal ion might further, split into more number of lines depending upon whether the ligands could undergo hyperfine with the metal ion or not. Conversely, if the coordinating atoms of ligands had higher $A_{\text{ion}}$ values, then first calculate number of lines from ligands. Each line of ligands should, then, split by metal ion if the hyperfine interaction was possible.

(V) There might occur overlapping of ESR lines from different factors. So experimentally observed number of lines might be less than the theoretically predicted lines. Also, when the predicted number of lines was large and $A_{\text{ion}}$ value/s of species undergoing hyperfine interaction was/were very small, the lines would merge to give a continuum.

The ESR peaks of the following 34 complexes were theoretically predicted.

The metal wise discussion was subdivided into ten headings (5.2-5.11).

Prediction of number of ESR peaks in Zr (III) Complexes

ESR spectra of $[\text{ZrX}_6]^3-$ ($X=\text{F, Cl, Br}$) were discussed in two parts:

(a) $[\text{ZrX}_6]^3-$ ($X=\text{F, Br}$)

They showed the following features:

(1) The six F or Br possessed same values of $A_{\text{ion}}$, NQCC, $\eta$, $\sigma$, $\delta$ respectively so that all the ligands were spatially equivalent.

(2) $A_{\text{ion}}$ value of Zr (III) was more than F but lesser than Br.

(3) With small $\mu_n$ ratios, the unpaired electron was localized only on Zr(III).

Their ESR spectra gave only a large sextet from $\text{Zr} \ (\text{III}) [2^*5/2+1]$.

(b) $[\text{ZrCl}_6]^3-$

It showed the following features:

(1) As the six Cl had the same $A_{\text{ion}}$, NQCC, $\eta$, $\sigma$, $\delta$ values respectively, they should be spatially equivalent.

(2) Unpaired electron was delocalized both on Zr (III)
and Cl as their \( \mu_n \) ratio was comparable\(^3\). \( A_{\text{rad}} \) value of Zr (III) was more than those of the six Cl.

Its ESR spectrum would give a large sextet \(^{(b)}\) from Zr (III) \([2^*5/2+1]\) with each line further splitting into 19 lines\(^{(b)}\) by the hyperfine interaction of Zr (III) and six equivalents Cl \([2^*6^*3/2+1]\).

**Prediction of number of ESR peaks in Hf (III)**

Complexes like \([\text{HfX}_6]^{2-}\) (\( X = F, Cl, Br \)) and \([\text{Hf} (\text{NH}_3)_6]^{3+}\) were studied as follows:

(a) \([\text{HfX}_6]^{2-}\) (\( X = F, Br \))

They showed the following common features:
1. The six F or Br were spatially equivalent as they showed the same \( A_{\text{rad}}, \) NQCC, \( \eta, \sigma, \delta \) values respectively.
2. As their \( \mu_n \) ratios were small, the unpaired electron would remain localized only on Hf (III) with no hyperfine interaction.
3. \( A_{\text{rad}} \) value of Hf (III) was more than those of the F and the Br.

Their ESR spectra should give only an octet \(^{(a)}\) from Hf (III) \([2^*7/2+1]\).

(b) \([\text{HfCl}_6]^{2-}\) and \([\text{Hf} (\text{NH}_3)_6]^{3+}\)

Both showed the following features:
1. The six Cl or NH\(_3\) ligands were spatially equivalent with same \( A_{\text{rad}}, \) NQCC, \( \eta, \sigma, \delta \) values respectively.
2. Unpaired electron was delocalized both on Hf (III) and Cl or NH\(_3\) as their \( \mu_n \) ratios were comparable.
3. \( A_{\text{rad}} \) of Hf (III) was more than Cl or N of NH\(_3\).

Their spectra showed a large octet \(^{(b)}\) from Hf (III) \([2^*7/2+1]\) with each line further splitting into 19 \({}^{(c)}\) or 13 lines \({}^{(c)}\) by the hyperfine interaction of Hf (III) and the six equivalents Cl \([2^*6^*3/2+1]\) or six N of NH\(_3\) ligands \([2^*6^*1^*1+1]\) respectively.

**Prediction of number of ESR peaks in Nb (IV)**

The study included 5 complexes such as: \([\text{NbX}_6]^{2-}\) (\( X = F, Cl, I, N \text{ CS} \)) and \([\text{Nb} (\text{NH}_3)_6]^{4+}\). Their ESR discussion was divided into four parts:

(a) \([\text{NbF}_6]^{2-}\)

It showed the following features:
1. With the same \( A_{\text{rad}}, \) NQCC, \( \eta, \sigma, \delta \) values respectively, all the ligands were equivalent.
2. With comparable \( \mu_n \) ratio, the unpaired electron was delocalized both on Nb (IV) and the F.
3. \( A_{\text{rad}} \) of Nb (IV) was more than those of the F ligands.

Its spectrum gave a large decane \(^{(a)}\) from Nb (IV) \([2^*9/2+1]\) with each line splitting into a smaller septet \(^{(b)}\) by the hyperfine interaction of Nb (IV) and the six F \([2^*6^*1^*2+1]\).

(b) \([\text{NbCl}_6]^{2-}\) and \([\text{Nb} (\text{NH}_3)_6]^{4+}\)

Both showed the following features:
1. Six Cl or NH\(_3\) had same values of \( A_{\text{rad}}, \) NQCC, \( \eta, \sigma, \delta \) respectively. So, all the ligands were spatially equivalent respectively.
2. Unpaired electron was localized on Nb (IV) but not on ligands.
3. \( A_{\text{rad}} \) value of Nb (IV) was more than those of Cl or NH\(_3\).

ESR spectra would give only a large decane \(^{(b)}\) from Nb (IV) \([2^*9/2+1]\) with no hyperfine interaction between Nb (IV) and Cl or NH\(_3\) as their \( \mu_n \) ratios were large.

(c) \([\text{NbI}_6]^{2-}\)

It showed the following features:
1. There were three sets of \( A_{\text{rad}}, \) NQCC, \( \eta, \sigma, \delta \) values respectively for the iodo ligands; each set having two values. So there were three types of stereo chemically different ligands respectively.
2. Unpaired electron was delocalized both on Nb (IV) and ligands as \( \mu_n \) ratio of Nb and I was comparable respectively.
3. \( A_{\text{rad}} \) value of Nb (IV) was more than those of the iodo ligands respectively.

Its spectrum showed a large decane \(^{(b)}\) from Nb (IV) \([2^*9/2+1]\) with each line splitting into 1331 lines \([2^*2^*5/2+1]\) from hyperfine interaction between Nb (IV) and the six iodo ligands. In fact, its ESR spectrum would exhibit a continuum.

(d) \([\text{Nb} (\text{NCS})_6]^{3+}\)

It showed the following features:
1. There were three sets of \( A_{\text{rad}}, \) NQCC, \( \eta, \sigma, \delta \) values respectively for the isothiocyanato ligands; each set having two values. So there were three types of stereo chemically different ligands.
2. Unpaired electron was localized on Nb (IV) as \( \mu_n \)
# Table 1: Prediction of Hyperfine Interaction between Metals and Ligands

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<th>$I_m$</th>
<th>$g_m$</th>
<th>$\mu_m$</th>
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<th>Ratio($\mu_m$)</th>
<th>Whether hyperfine interaction between $M^{n+}$ and CA is possible</th>
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<td>[4.5333]</td>
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ratio of Nb and N of NCS\(^{-}\) was small.

(3) \(A_{\text{ten}}\) value of Nb (IV) was more than N of ligands.

Its spectrum should give only a large decane\(^{(b)}\) from Nb (IV) \([2^*9/2+1]\) with no hyperfine interaction between Nb (IV) and the six isothiocyanato ligands.

**Prediction of number of ESR peaks in Ta (IV) Complexes**

Two complexes such as \([Ta \ X_{6}]^{2-}\) (X= Cl, Br) were studied

(a) \([Ta \ Cl_{6}]^{2-}\)

It showed the following features:

(1) Six chloro ligands were equivalent as they possessed the same \(A_{\text{ten}}\), NQCC, \(\eta\), \(\sigma\), \(\delta\) values respectively.

(2) As their \(\mu_r\) ratio was small, the unpaired electron remained localized only on Ta (IV) with no hyperfine interaction.

(3) \(A_{\text{ten}}\) of Ta (IV) was more than those of six equivalent chloro ligands.

So its ESR spectrum would give a large octet\(^{(b)}\) from Ta (IV) \([2^*7/2+1]\) only.

(b) \([TaBr_{6}]^{2-}\)

It showed the following features:

(1) Six bromo ligands were equivalent with same \(A_{\text{ten}}\), NQCC, \(\eta\), \(\sigma\), \(\delta\) values respectively.

(2) With comparable \(\mu_r\) ratio, the unpaired electron was delocalized both on ligands and Ta (IV).

(3) \(A_{\text{ten}}\) of Ta (IV) was more than the bromo ligands.

Thus its spectrum would give a large octet \(^{(b)}\) from Ta (IV) \([2^*7/2+1]\) whose each line split into 19 lines\(^{(c)}\) by the hyperfine interaction between Ta(IV) and six equivalents Br \([2^*6(3/2+1]\].

**Prediction of number of ESR peaks in Tc (II) Complexes**

The complexes like \([Tc \ Br_{6}]^{4-}\) and \([Tc \ (NH_{3})_{6}]^{2+}\) were studied.

(a) \([TcBr_{6}]^{4-}\)

It showed the following features:

(1) With same \(A_{\text{ten}}\), NQCC, \(h\), \(\delta\) values respectively, the six bromo ligands were equivalent.

(2) With comparable \(\mu_r\) ratio, unpaired electron was delocalized both on Tc (II) and Br ligands.

(3) \(A_{\text{ten}}\) of Tc (II) was more than the Br ligands.
Table 2: Prediction of Number of ESR peaks in Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>3 Parameters of M (D)</th>
<th>5 Parameters of CA</th>
<th>Spatial nature of ligands</th>
<th>No. of ESR peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A_m</td>
<td>σ</td>
<td>δ</td>
<td>A_m</td>
</tr>
<tr>
<td>[ZrF_6]^3- (D_6h)</td>
<td>1446.0</td>
<td>793.7</td>
<td>-793.7</td>
<td>11.62</td>
</tr>
<tr>
<td>[ZrCl_6]^3- (D_6h)</td>
<td>143.7</td>
<td>-22045.3</td>
<td>22045.3</td>
<td>8.58</td>
</tr>
<tr>
<td>[ZrBr_6]^3- (D_6h)</td>
<td>-14.47</td>
<td>-7719.2</td>
<td>7719.2</td>
<td>-18.74</td>
</tr>
<tr>
<td>[HfF_6]^3- (D_6h)</td>
<td>4468.1</td>
<td>3449.5</td>
<td>-3449.5</td>
<td>11.75</td>
</tr>
<tr>
<td>[HfCl_6]^3- (O_h)</td>
<td>-1004.7</td>
<td>2609.8</td>
<td>-2609.8</td>
<td>-229.3</td>
</tr>
<tr>
<td>[HfBr_6]^3- (O_h)</td>
<td>-884.3</td>
<td>2347.5</td>
<td>-2347.5</td>
<td>-35.81</td>
</tr>
<tr>
<td>[Hf(NH_3)_6]^3+ (D_12)</td>
<td>-6839.0</td>
<td>-3148.2</td>
<td>3148.2</td>
<td>12.81</td>
</tr>
<tr>
<td>[NbF_6]^2- (D_3d)</td>
<td>1570.5</td>
<td>-1940.4</td>
<td>1940.4</td>
<td>5.79</td>
</tr>
<tr>
<td>[NbCl_6]^2- (O_h)</td>
<td>-64.54</td>
<td>-1818.3</td>
<td>1818.3</td>
<td>-1.00</td>
</tr>
<tr>
<td>[NbI_6]^2- (C_2v)</td>
<td>-147.35</td>
<td>-3592.5</td>
<td>3592.5</td>
<td>-15.97, -853.3</td>
</tr>
<tr>
<td>[Zr (NCS)_6]^2- (C_2v)</td>
<td>-332.2</td>
<td>3202.0</td>
<td>-3202.0</td>
<td>14.93, 6.43, 0.052, 9.3, -9.3,</td>
</tr>
</tbody>
</table>

^{(a)} Each line of which further splits into 19 lines.
^{(b)} Each line of which further splits into 19 lines.
^{(c)} Each line of which further splits into 19 lines.
\[
\begin{array}{cccccccc}
\text{Compound} & \text{D} & \text{E} & \text{F} & \text{G} & \text{H} & \text{I} & \text{J} & \text{K} \\
\text{Nb(NH}_3\text{)}_6^{4+} & 361.4 & -4335.8 & 4335.8 & -5.80 & -1.84 & 0.18 & 194.4 & -194.4 & \text{All equivalents} & \text{—do—} \\
\text{TaCl}_6^{2-} & 1287.7 & -1059.5 & 1059.5 & \approx 16.23 & \approx -30.5 & \text{—do—} & 466.9 & -466.9 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{Nb(NH}_3\text{)}_6^{4+} & -1031.6 & 139.9 & -139.9 & \approx 47.59 & \approx 138.6 & \text{—do—} & 1815.5 & -1815.5 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{Tc(NH}_3\text{)}_6^{2+} & 350.7 & -3058.4 & 3058.4 & \approx -8.3 & -2.263 & 0.43 & 252.1 & -252.1 & \text{A large decanet}^{(a)} & \text{—do—} \\
\text{TaBr}_6^{2-} & 535.84 & -5950.6 & 5950.6 & 7.14 & -21.53 & 0.04 & 1152.5 & -1152.5 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{OsF}_6^{3-} & 668.95 & -8827.7 & 8827.7 & 18.19 & * & * & 600.4 & -600.4 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{ReF}_6^{3-} & -80.93 & -2443.6 & 2443.6 & \approx 0.85 & -34.92 & 0.06 & 792.3 & -792.3 & \text{A large quartet}^{(a)} & \text{—do—} \\
\text{Re(NH}_3\text{)}_6^{2+} & 467.90 & -4566.7 & 4566.7 & -2.5 & -2.54 & 0.54 & 260.8 & -260.8 & \text{A large decanet}^{(a)} & \text{—do—} \\
\text{ReCl}_6^{2-} & 600.68 & -8735.5 & 8735.5 & 21.52 & * & * & 601.8 & -601.8 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{OsCl}_6^{3-} & 549.02 & -5199.8 & 5199.8 & 19.71 & -32.36 & \approx 0.0 & 990.8 & -990.8 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{OsBr}_6^{3-} & 513.39 & -5029.6 & 5029.6 & 32.58 & \approx 256.7 & \approx 0.0 & 2558.4 & -2558.4 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{ReBr}_6^{2-} & 668.95 & -8827.7 & 8827.7 & 18.19 & * & * & 600.4 & -600.4 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{OsBr}_6^{2-} & -80.93 & -2443.6 & 2443.6 & \approx 0.85 & -34.92 & 0.06 & 792.3 & -792.3 & \text{A large quartet}^{(a)} & \text{—do—} \\
\text{RuF}_6^{2-} & 467.90 & -4566.7 & 4566.7 & -2.5 & -2.54 & 0.54 & 260.8 & -260.8 & \text{A large decanet}^{(a)} & \text{—do—} \\
\text{RuCl}_6^{2-} & 600.68 & -8735.5 & 8735.5 & 21.52 & * & * & 601.8 & -601.8 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{RuBr}_6^{2-} & 549.02 & -5199.8 & 5199.8 & 19.71 & -32.36 & \approx 0.0 & 990.8 & -990.8 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{OsF}_6^{3-} & 513.39 & -5029.6 & 5029.6 & 32.58 & \approx 256.7 & \approx 0.0 & 2558.4 & -2558.4 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{OsCl}_6^{3-} & 668.95 & -8827.7 & 8827.7 & 18.19 & * & * & 600.4 & -600.4 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{OsBr}_6^{3-} & -80.93 & -2443.6 & 2443.6 & \approx 0.85 & -34.92 & 0.06 & 792.3 & -792.3 & \text{A large quartet}^{(a)} & \text{—do—} \\
\text{RhF}_6^{2-} & 467.90 & -4566.7 & 4566.7 & -2.5 & -2.54 & 0.54 & 260.8 & -260.8 & \text{A large decanet}^{(a)} & \text{—do—} \\
\text{RhCl}_6^{2-} & 600.68 & -8735.5 & 8735.5 & 21.52 & * & * & 601.8 & -601.8 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{RhBr}_6^{2-} & 549.02 & -5199.8 & 5199.8 & 19.71 & -32.36 & \approx 0.0 & 990.8 & -990.8 & \text{A large octet}^{(a)} & \text{—do—} \\
\text{Os(NH}_3\text{)}_6^{3+} & 781.87 & -3589.7 & 3589.7 & 27.09 & 258.94 & \approx 0.0 & 264.9 & -264.9 & \text{A large quartet}^{(a)} & \text{—do—} \\
\text{Rh(NH}_3\text{)}_6^{3+} & 702.15 & -166170.4 & 166170.4 & 14.1 & \approx 1.19 & \text{Four} & 1701.5 & -1701.5 & \text{All} & \text{—do—} \\
\end{array}
\]
Its spectrum showed a large decane\(^{(b)}\) from Tc (II) \([2^{*}9/2+1]\). Each line of this decane would, further, split into smaller 19 lines\(^{(a)}\) due to hyperfine interaction between Tc (II) and six stereo chemically equivalent bromo ligands \([2^{*}6*3/2+1]\).

(b)\([\text{Tc (NH}_3)_3]^{2+}\)

It showed the following features:
1. With the same \(A_{\text{iso}}, \text{NQCC}, \eta, \sigma, \delta\) values respectively, six NH\(_3\) ligands were equivalent.
2. As their \(\mu_n\) ratio was large, the unpaired electron was localized on Tc (II) only.
3. \(A_{\text{iso}}\) value of Tc (II) was less than those of N of NH\(_3\) ligands.

Its ESR spectrum would give only a large decane\(^{(b)}\) from Tc (II) \([2^{*}9/2+1]\) with no hyperfine splitting between Tc (II) and NH\(_3\) ligands as their \(m_n\) ratio was large.

**Prediction of number of ESR peaks in Re (II) Complexes**

It included three complexes such as: \([\text{Re } X_6]^{4-}\) and \([\text{Re } (\text{NH}_3)_6]^{2+}\).

(a) \([\text{Re } Cl_6]^{4-}\) and \([\text{Re } (\text{NH}_3)_6]^{2+}\)

Both showed the following features:
1. With the same \(A_{\text{iso}}, \text{NQCC}, \eta, \sigma, \delta\) values respectively, the six Cl and the NH\(_3\) ligands were equivalent.
2. Unpaired electron was localized only on Re (II) as there was no hyperfine interaction between Re (II) and ligands due to large \(\mu_n\) ratios respectively.
3. \(A_{\text{iso}}\) of Re (II) was more than those of Cl or N of NH\(_3\).

Their ESR spectra showed only a large sextet\(^{(b)}\) from Re (II) \([2^{*}5/2+1]\).

(b) \([\text{Re } Br_6]^{4+}\)

It showed the following features:
1. With the same \(A_{\text{iso}}, \text{NQCC}, \eta, \sigma, \delta\) values respectively, the six bromo ligands were equivalent.
2. Unpaired electron was delocalized both on Re (II) and stereo chemically equivalent bromo ligands as their \(\mu_n\) ratio was comparable.
3. \(A_{\text{iso}}\) of Re (II) was more than those of bromo ligands.
Its ESR spectrum would show a large sextet \( \text{(b)} \) from Re (II) \([2^*5/2+1]\). Each line of this sextet, further, split up into a smaller 19 line \( \text{(c)} \) pattern due to hyperfine interaction between Re (II) and six equivalents Br \([2^*6^*3/2+1]\).

**Prediction of number of ESR peaks in Ru (III) Complexes**

Three complexes such as \([\text{RuX}_6]^3-\) \((X= \text{F, Cl, Br})\) were included.

(a) \([\text{RuF}_6]^3-\) \((X=\text{F, Br})\)

They showed the following features:

1. With the same \( A_{\text{ten}}, \text{NQCC}, \eta, \sigma, \delta \) values respectively, all the ligands were equivalent.
2. The unpaired electron was present only on Ru (III) because with small \( \mu_n \) ratios, there was no hyperfine interaction between Ru (III) and F or Br.
3. \( A_{\text{ten}} \) of Ru (III) was more than the F or the Br.

Their ESR spectra gave only large sextet \( \text{(b)} \) from Ru (III) \([2^*5/2+1]\).

(b) \([\text{RuCl}_6]^3-\)

It showed the following features:

1. With same \( A_{\text{ten}}, \text{NQCC}, \eta, \sigma, \delta \) values respectively, the six Cl were equivalent.
2. The unpaired electron was delocalized on both Os (III) and the six equivalents Cl.
3. The \( A_{\text{ten}} \) value of Os (III) was more than those of the six Cl.

Its ESR spectrum showed a large quartet \( \text{(b)} \) from Os (III) \([2^*3^*2^*1+1]\) as there was no hyperfine interaction between Os (III) and the F or the Br due to small \( \mu_n \) ratio.

(c) \([\text{Os} (\text{NH}_3)_6]^3+\)

It showed the following features:

1. There were three sets of \( A_{\text{ten}}, \text{NQCC}, \eta, \sigma, \delta \) values respectively for the six N of the six NH\(_3\); each set having two values. So there were present three types of stereochemically different ligands respectively.
2. The unpaired electron was delocalized both on Os and N as \( \mu_n \) ratio of Os and N was comparable.
3. \( A_{\text{ten}} \) value of Os (III) was more than those of the ligands.

Its spectrum would give a large quartet \( \text{(b)} \) from Os (III) \([2^*3^*2^*1+1]\) whose each line would, further, split into 125 \( \text{(d)} \) lines \([2^*2^*1^*1+1]^3 \) from 3 types of stereochemically different NH\(_3\) by the hyperfine interaction between Os(III) and the ligands. In fact, its ESR spectrum would exhibit a continuum.

**Prediction of number of ESR peaks in Os (III) Complexes**

It included four complexes such as \([\text{OsX}_6]^3+\) \((X= \text{F, Cl, Br})\) and \([\text{Os} (\text{NH}_3)_6]^3+\).

(a) \([\text{OsF}_6]^3+\) \((X=\text{F, Br})\)

Both the complexes showed the following common features:

1. With same \( A_{\text{ten}}, \text{NQCC}, \eta, \sigma, \delta \) values, all the ligands were equivalent.

(b) \([\text{OsCl}_6]^3+\)

It showed the following features:

1. With comparable \( \mu_n \) ratio, the unpaired electron was delocalized on both Os (III) and the six equivalents Cl.
2. The \( A_{\text{ten}} \) value of Os (III) was more than those of the six Cl.

Its ESR spectrum showed a large quartet \( \text{(b)} \) from Os (III) \([2^*3^*2^*1+1]\). Each line of this quartet further split up into 19 lines \( \text{(c)} \) from six spatially equivalents Cl \([2^*6^*3^*2^*1+1]\) due to hyperfine interaction as their \( \mu_n \) ratio was comparable.

(c) \([\text{Os} (\text{NH}_3)_6]^3+\)

It showed the following features:

1. Unpaired electron was localized on Os (III).
2. \( A_{\text{ten}} \) of Os (III) was more than the F or the Br.

Their ESR spectra gave a large quartet \( \text{(b)} \) from Os (III) \([2^*3^*2^*1+1]\) as there was no hyperfine interaction between Os (III) and the F or the Br due to small \( \mu_n \) ratio.

**Prediction of number of ESR peaks in Rh (IV) Complexes**

It included four complexes: \([\text{RhX}_6]^3+\) \((X= \text{F, Cl, Br})\) and \([\text{Rh} (\text{NH}_3)_6]^3+\) which showed the following
features:
(1) With the same $A_{an}$, NQCC, $\eta$, $\sigma$, $\delta$ values respectively, the ligands like F, Cl, Br, NH$_3$ were equivalent.
(2) The unpaired electron was present only on Rh (IV).
(3) $A_{an}$ of Rh (IV) was more than the F, Cl or Br or N of NH$_3$.

Their ESR spectra should give only a large doublet $^{[b]}$ from Rh (IV) $[2^1/2 + 1]$ with no hyperfine interaction between Rh (IV) and any one of the four different types of ligands due to small $\mu_n$ ratios between Rh (IV) and the ligands respectively.

**Prediction of number of ESR peaks in Ir (IV) Complexes**

It included four complexes: [IrX$_6$]$^{2-}$ (X= F, Cl, Br) and [Ir(NH$_3$)$_6$]$^{4+}$ which showed the following features:
(1) With the same $A_{an}$, NQCC, $\eta$, $\sigma$, $\delta$ values respectively, the ligands like F, Cl, Br, NH$_3$ were equivalent.
(2) The unpaired electron was present only on Ir (IV)
(3) $A_{an}$ of Ir (IV) was more than the F, Cl or Br or N of NH$_3$.

Their ESR spectra would give only a large quartet $^{[b]}$ from Ir (IV) $[2^3/2 + 1]$ because no hyperfine interaction between Ir (IV) and any one of four different types of ligands due to small $\mu_n$ ratios between Ir(IV) and ligands respectively.

**CONCLUSION**

Simply by knowing $I$ and $g_n$ of metals and coordinating atoms (CA) of the ligands from the literature; calculating their nuclear magnetic moments and thus their relative $\mu_n$ ratios, we could predict the number or ESR lines in a vast number of complexes of 10 metal ions of 2$^{nd}$ and 3$^{rd}$ transition series which, hitherto, seemed tenacious experimentally.. In addition, there lies a future use of this study in predicting the number of ESR peaks in complexes containing a very large variety of spatially different NMR and ESR active both quadrupolar and nonquadrupolar coordinating nuclei because the software allows us to select or ignore the interacting nuclei at our choice. This clearly makes the DFT a very powerful diagnostic tool at the hands of the theoretical Chemists to deduce the future applications of transition metal complexes.

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**REFERENCES**

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