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Predicting ESR Peaks in the 4*d* and 5*d* 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 (σ) and chemical shifts (δ) 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, δ,h, σ) 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[1-5] like Zr (III)[6-8] ,Hf (III)[7-9] ; Nb (IV)[10-12], Ta (IV)[9] ; Tc (II)[9, 13, 14], Re (II)[15-17]; Ru (III)[18-24] , Os (III)[18-20,24]; Rh (IV)[25-27], Ir (IV)[26,27] 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 ion complexes, we tried DFT implemented in ADF 2010.01 to 34 complexes such as $[ZrX_6]^{3-}$(X= F, Cl , Br), $[HfX_6]^{3-}$ (X=F, Cl, Br), $[Hf(NH_3)_6]^{3+}$, $[NbX_6]^{2-}$ (X=F, Cl, I, NCS), $[Nb(NH_3)_6]^{4+}$, $[TaX_6]^{2-}$(X=Cl, Br), $[TcBr_6]^{4-}$, $[Tc(NH_3)_6]^{2+}$, $[ReX_6]^{4-}$(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), $[Ir(NH_3)_6]^{4+}$ belonging to 10 metal ions of the 2nd and 3rd transition series. All these six coordinate complexes containing either weak halo or comparatively stronger (ammine and thiocyanato -N) ligands belonged to five congeners of the 2nd and 3rd transition series. They, invariably, possessed one unpaired electron because their large Crystal Field Stabilization Energies (CFSE) would cause pairing of electrons even with the week ligands.

Need of the Study

There were two main reasons which tempted us to take up the present study:

(i) Only a limited research work had been done in the experimental determination of number of ESR peaks in 4d and 5d metal ion complexes because their authentic 10 Dq values were difficult to determine experimentally due to their high values of spin orbit coupling constants ($\lambda_M^{\ n+}$) which, in turn, would adversely affect ESR parameters (especially A_{ten}).

(ii) ESR transitions energies falling in microwave region, generally, needed cryogenic conditions which were difficult to obtain and cumbersome to maintain.

Methodology

ADF (Amsterdam Density Functional) software was installed on Windows XP platform as “ADF jobs”. A new directory was created using “File menu” of ADF jobs. After optimization of the complexes, different commands were filled into the software to obtain ESR, NQR[28-30] and NMR[31-33] parameters which were discussed in detail in our previous publications[28-33].

With these to the specific set of commands, the ADF software would give one ESR {Hyperfine Coupling Constants (A_{ten})}, two NQR {Nuclear Quadrupole Coupling Constant (NQCC), Asymmetric Coefficient (η)}[28-30] and two NMR parameters {Shielding Constant (σ) , Chemical Shift (δ) }[31-33]. These five parameters (A_{ten}, NQCC, η, σ, δ) 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_M, I_{CA}, g_M and g_{CA} as well as μ_M and μ_{CA} (in terms of β_n) and ratios of m_M and m_{CA} to predict the possibility of hyperfine interaction between metal ions and ligands.

Table: 2 contained A_{ten}, σ, δ values of metal ions and A_{ten}, NQCC, η, σ, δ 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_{ten}, NQCC, η, σ, δ) of metal ions and coordinating atoms (CA) of ligands were obtained from the software by giving it 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 ((μ_M) in terms of β_n

After knowing the values of nuclear spin quantum numbers and g factors of metals (I_M, g_M) and of coordinating atoms (CA) of ligands (I_{CA} , g_{CA}) from the literature, we could calculate nuclear magnetic moments of both the metal (μ_M) and coordinating atoms (μ_{CA}) of ligands in terms of β_n by the following relation:

$\mu_M = g_M [I_M (I_M+1)]^{1/2}$
$\mu_{CA} = g_{CA} [I_{CA} (I_{CA}+1)]^{1/2}$ ...(a*)

Knowing whether hyperfine interaction was possible or not

From $[\mu_M/\mu_{CA}]$ ratio called μ_n ratio, we could draw the following conclusions:

(a) A comparable μ_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 μ_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: $m_e = g_e [s (s+1)]^{1/2}$

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:

$$(2\,\mathbf{n}\,I_{CA}+1) \qquad ...(c)$$

(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:

$$(2\,\mathbf{n_1}\,I_{CA}+1)(2\mathbf{n_2}\,I_{CA}+1)(2\,n_3\,I_{CA}+1) \qquad ...(d)$$

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

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

(IV) If metal ion possessed higher A_{ten} 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_{ten} 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_{ten} 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 $[ZrX_6]^{3-}$ (X=F, Cl, Br) were discussed in two parts:

(a) $[ZrX_6]^{3-}$ (X=F, Br)

They showed the following features:

(1) The six F or Br possessed same values of A_{ten}, NQCC, η, σ, δ respectively so that all the ligands were spatially equivalent.

(2) A_{ten} value of Zr (III) was more than F but lesser than Br.

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

Their ESR spectra gave only a large *sextet* [(b)] from Z r (III) [2*5/2+1].

(b) $[ZrCl_6]^{3-}$

It showed the following features:

(1) As the six Cl had the same A_{ten}, NQCC, η, σ, δ values respectively, they should be spatially equivalent.

(2) Unpaired electron was delocalized both on Zr (III)

and Cl as their μ_n ratio was comparable[3]. A_{ten} 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 into19 lines[(c)] 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

Complexes like $[HfX_6]^{3-}$ (X=F, Cl, Br) and $[Hf (NH_3)_6]^{3+}$ were studied as follows:

(a) $[HfX_6]^{3-}$ (X=F, Br)

They showed the following common features:

(1) The six F or Br were spatially equivalent as they showed the same A_{ten}, NQCC, η, σ, δ values respectively.

(2) As their μ_n ratios were small, the unpaired electron would remain localized only on Hf (III) with no hyperfine interaction.

(3) A_{ten} value of Hf (III) was more than those of the F and the Br.

Their ESR spectra should give only an *octet* [(b)] from Hf (III) [2*7/2+1].

(b) $[HfCl_6]^{3-}$ and $[Hf (NH_3)_6]^{3+}$

Both showed the following features:

(1) The six Cl or NH_3 ligands were spatially equivalent with same A_{ten}, NQCC, η, σ, δ values respectively.

(2) Unpaired electron was delocalized both on Hf (III) and Cl or NH_3 as their μ_n ratios were comparable.

(3) A_{ten} 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)] or13 lines[(c)] by the hyperfine interaction of Hf (III) and the six equivalents Cl [2*6*3/2+1] or six N of six NH_3 ligands [2*6*1+1] respectively.

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

The study included 5 complexes such as: $[NbX_6]^{2-}$ (X=F, Cl, I, N CS) and $[Nb (NH_3)_6]^{4+}$. Their ESR discussion was divided into four parts:

(a) $[NbF_6]^{2-}$

It showed the following features:

(1) With the same A_{ten}, NQCC, η, σ, δ values respectively, all the ligands were equivalent.

(2) With comparable μ_n ratio, the unpaired electron was delocalized both on Nb (IV) and the F.

(3) A_{ten} of Nb (IV) was more than those of the F ligands.

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

(b) $[NbCl_6]^{2-}$ and $[Nb (NH_3)_6]^{4+}$

Both showed the following features:

(1) Six Cl or NH_3 had same values of A_{ten}, NQCC, η, σ, δ respectively. So, all the ligands were spatially equivalent respectively.

(2) Unpaired electron was localized on Nb (IV) but not on ligands.

(3) A_{ten} 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 μ_n ratios were large.

(c) $[Nb I_6]^{2-}$

It showed the following features:

(1) There were three sets of A_{ten}, NQCC, η, σ, δ 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 μ_n ratio of Nb and I was comparable respectively.

(3) A_{ten} 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 $[2*2*5/2+1]^3$ from hyperfine interaction between Nb (IV) and the six iodo ligands. In fact, its ESR spectrum would exhibit a *continuum*.

(d) $[Nb (NCS)_6]^{2-}$

It showed the following features:

(1) There were three sets of A_{ten}, NQCC, η, σ, δ 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 μ_n

Table 1: Prediction of Hyperfine Interaction between Metals and Ligands

(I_M) [I_{CA}]	(g_M) [g_{CA}]	(μ_M) [μ_{CA}]	Ratio(μ_n) [μ_M/μ_{CA}]	Whether hyperfine interaction between M^{+n} and CA is possible
Zr & F (2.5)[0.5]	(-0.521448) [5.257736]	(-1.5425) [4.5333]	[1:3]	No ; as electron is localized only on Zr (III)
[Zr & Cl (2.5)[1.5]	(-0.521448) [0.5479162]	(-1.5425) [1.06]	[3:2]	Yes ; as electron is delocalized both on Zr (III) and ligands
Zr & Br (2.5)[1.5]	(-0.521448) [1.4042667]	((-1.5425) [4.2058]	[4:11]	No ; as electron is localized only on Zr (III)
Hf & F (3.5)[0.5]	(0.2267143) [5.257736]	(0.8997) [4.5333]	[1:5]	No ; as electron is localized only on Hf(III)
Hf & Cl (3.5)[1.5]	(0.2267143) [0.5479162]	(0.8997) [1.06]	[4:5]	Yes ; as electron is delocalized both on Hf(III) and ligands
Hf & Br (3.5)[1.5]	(0.2267143) [1.4042667]	(0.8997) [4.2058]	[3:14]	No ; as electron is localized only on Hf(III)
Hf & N (3.5)[1.0]	(0.2267143) [0.4037610]	(0.8997) [0.57092]	[3:2]	Yes; as electron is delocalized both on ligands and Hf (III)
Nb & F (4.5)[0.5]	(1.3712222) [5.257736]	(5.8268) [4.5333]	[5:4]	Yes ; as electron is delocalized both on Nb (IV) and ligands
Nb & Cl (4.5)[1.5]	(1.3712222) [0.5479162]	(5.8268) [1.06]	[11:2]	No ; as electron is localized only on Nb (IV) and not on ligands
Nb & I (4.5)[2.5]	(1.3712222) [1.1250392]	(5.8268) [3.3279]	[7:4]	Yes ; as electron is delocalized both on Nb (IV) and ligands
Nb & N (4.5)[1.0]	(1.3712222) [0.4037610]	(5.8268) [0.57092]	[10:1]	No ; as electron is localized only on Nb(IV) and not on ligands
Ta & Cl (3.5)[1.5]	(0.6772857) [0.5479162]	(2.6879) [1.06]	[2:5]	No ; as electron is localized only on Ta(IV)
Ta & Br (3.5)[1.5]	(0.6772857) [1.4042667]	(2.6879) [4.2058]	[2:3]	Yes; as electron is delocalized both on Ta(IV) and ligands
Tc & Br (4.5)[1.5]	(1.2632667) [1.4042667]	(6.28467) [4.2058]	[3:2]	Yes; as electron is delocalized both on Tc (II) and ligands
Tc & N (4.5)[1.0]	(1.2632667) [0.4037610]	(6.28467) [0.57092]	[11:1]	No ; as electron is localized only on Tc (II)
[Re & Cl] (2.5)[1.5]	(1.287880) [0.5479162]	(3.8096) [1.06]	[7:2]	No ; as electron is localized only on Re(II)
Re & Br (2.5)[1.5]	(1.287880) [1.4042667]	(3.8096) [4.2058]	[7:8]	Yes ; as electron is delocalized on both Re(II) and ligands
Re & N (2.5)[1.0]	(1.287880) [0.4037610]	(3.8096) [0.57092]	[20:3]	No ; as electron is localized only on Re(II)
Ru & F (2.5)[0.5]	(-0.287520) [5.257736]	(-0.8505) [4.5333]	[3:16]	No ; as electron is localized only on Ru(III)
Ru & Cl (2.5)[1.5]	(-0.287520) [0.5479162]	(-0.8505) [1.06]	[4:5]	Yes; as electron is delocalized both on Ru(III) and ligands
Ru & Br (2.5)[1.5]	(-0.287520) [1.4042667]	(-0.8505) [4.2058]	[1:5]	No ; as electron is localized only on Ru(III)
Os & F (1.5)[0.5]	(0.4399553) [5.257736]	(0.852) [4.5333]	[1:5]	No; electron being localized only on Os(III)
[Os & Cl	(0.4399553)	(0.852)	[4:5]	Yes; as electron is delocalized both on Os(III)

(1.5)[1.5]	[0.5479162]	[1.06]		and ligands
Os & Br	(0.4399553)	(0.852)	[1:5]	No; as electron is localized only on Os(III)
(1.5)[1.5]	[1.4042667]	[4.2058]		
Os & N	(0.4399553)	(0.852)	[3:2]	Yes; as electron is delocalized both on Os(III)
(1.5)[1.0]	[0.4037610]	[0.570692]		and ligands
Rh & F	(-0.176800)	(-0.1531)	[1:30]	No; as electron is localized only on Rh(IV)
(0.5)[0.5]	[5.257736]	[4.5333]		
Rh & Cl	(-0.176800)	(-0.1531)	[1:7]	-do-
(0.5)[1.5]	[0.5479162]	[1.06]		
Rh & Br	(-0.176800)	(-0.1531)	[1:27]	-do-
(0.5)[1.5]	[1.4042667]	[4.2058]		
Rh & N	(-0.176800)	(-0.1531)	[2:7]	-do-
(0.5)[1.0]	[0.4037610]	[0.570692]		
Ir & F	(0.1091333)	(0.2113)	[1:22]	No ; as electron is localized only on Ir (IV)
(1.5)[0.5]	[5.257736]	[4.5333]		
Ir & Cl	(0.1091333)	(0.2113)	[1:5]	-do-
(1.5)[1.5]	[0.5479162]	[1.06]		
Ir & Br	(0.1091333)	(0.2113)	[1:20]	-do-
(1.5)[1.5]	[1.4042667]	[4.2058]		
Ir & N	(0.1091333)	(0.2113)	[3:8]	-do-
(1.5)[1.0]	[0.4037610]	[0.57092]		

ratio of Nb and N of NCS^{1-} was small.

(3) A_{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_{ten}, NQCC, η, σ, δ values respectively.

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

(3) A_{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_{ten}, NQCC, η, σ, δ values respectively.

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

(3) A_{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_{ten}, NQCC,h, ó, ä values respectively, the six bromo ligands were equivalent.

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

(3) A_{ten} of Tc (II) was more than the Br ligands.

Table 2: Prediction of Number of ESR peaks in Complexes

Complex (Point group)	3 Parameters of M^{n+} A_{ten}	σ	δ	5 Parameters of CA A_{ten}	NQCC	η	σ	δ	Spatial nature of ligands	No. of ESR peaks
$[ZrF_6]^{3-}$ (D_{6h})	1446.0	793.7	-793.7	11.62	*	*	-51.8	51.8	All equivalents	A large sextet[b]
$[ZrCl_6]^{3-}$ (D_{3d})	143.7	-22045.3	22045.3	8.58	-16.87	0.26	-237.5	237.5	-do-	A large sextet[b]; each line of which further splits into 19 lines[c]
$[ZrBr_6]^{3-}$ (D_{6h})	-14.47	-7719.2	7719.2	-18.74	114.0	0.49	1597.5	-1597.5	-do-	A large sextet[b]
$[HfF_6]^{3-}$ (D_{6h})	4468.1	3449.5	-3449.5	11.75	*	*	490.0	-490.0	-do-	A large octet[b]
$[Hf\,Cl_6]^{3-}$ (O_h)	-1004.7	2609.8	-2609.8	-229.3	≈ -15.87	—-	844.5	-844.5	-do-	An octet; each line of which further splits into 19 lines[c]
$[HfBr_6]^{3-}$(O_h)	-884.3	2347.5	-2347.5	-35.81	≈ 129.75	0.22	2405.1	-2405.1	-do-	-do-
$Hf(NH_3)_6]^{3+}$ (D_{12})	-6839.0	-3148.2	3148.2	12.81	≈ 2.39	0.37	109.7	-109.7	-do-	A large octet[b]; each line of which further splits in13lines[c]
$[NbF_6]^{2-}$ (D_{3d})	1570.5	-1940.4	1940.4	5.79	*	*	-268.3	268.3	-do-	A large decane[b]; each line of which further splits into a septet[c]
$[NbCl_6]^{2-}$ (D_{3h})	-64.54	-1818.3	1818.3	-1.00	-26.09	0.82	424.2	-424.2	-do-	A large decane[b]
$[NbI6]^{2-}$ (C_{2v})	-147.35	-3592.5	3592.5	-15.97,	-853.3,	0.062,	1848.7,	-1848.7,	Three types	A large decane[b] each line of which
				-15.97,	-853.3,	0.062,	1848.7,	-1848.7,	of ligands;	further splits into 1331 lines from 3 types
				-	-944.0,	0.944,	3188.0,	-3188.0,	each	of stereochemically different I ligands.
				34.5,	-	0.944,	3188.0,	-3188.0,	containing	In fact a *continuum* is expected.
				-34.5,	944.0,	0.966,	2727.3,	-2727.3,	two ligands	
				-	-740.0,	0.966	2727.3	-2727.3		
				24.2,	-					
				-24.2	740.0					
Nb $(NCS)_6]^{2-}$ (C_2)	-332.2	3202.0	-3202.0	14.93,	6.43,	0.052,	9.3,	-9.3,	-do-	A large decane[b]
					6.43,	0.052,	9.3,	-9.3,		
				14.93,	6.20,	0.127,	18.7,	-18.7,		
					6.20,	0.127,	18.7,	-18.7,		
				-2.35,	6.15,	0.145,	43.8,	-43.8,		
					6.15	0.145	43.8	-43.8		

				- 2.35,					
				- 6.74,					
				- 6.74					
$Nb(NH_3)_6]^{4+}$ (D_{12})	361.4	-4335.8	4335.8	- 5.80	-1.84	0.18	194.4	-194.4	All equivalents	—do—
$[TaCl_6]^{2-}$ (D_{3h})	1287.7	-1059.5	1059.5	≈16.23	≈ -30.5	—-	466.9	-466.9	-do-	A large octet [b]
$[TaBr_6]^{2-}$ (O_h)	-1031.6	139.9	-139.9	- 47.59	≈ 138.6	—-	1815.5	-1815.5	-do-	A large octet[a] ; each line of which further splits into 19 lines[c]
$[TcBr_6]^{4-}$ (D_{6h})	-15.59	-1240.6	1240.6	≈ 5.8	≈ 204.7	0.083	≈ 2628.0	-2628.0	-do-	A large decane[b] ; each line of which further splits in19 lines[c]
$[Tc(NH_3)_6]^{2}$ (D_6)	305.7	-3058.4	3058.4	≈ -8.3	-2.263	0.43	252.1	-252.1	-do-	A large decane[b]
$[ReCl_6]^{4-}$ (O_h)	535.84	-5950.6	5950.6	7.14	-21.53	0.04	1152.5	-1152.5	-do-	A large sextet[b]
$[ReBr_6]^{4-}$ (O_h)	531.74	-6658.6	6658.6	11.95	170.0	≈0.0	2997.3	-2997.3	-do-	A large sextet[b]; each line of which splits into 19 lines[c]
$Re(NH_3)_6]^{2+}$ (D_6)	467.90	-4566.7	4566.7	-2.5	-2.54	0.54	260.8	-260.8	-do-	A large sextet [b]
$[RuF_6]^{3-}$ (O_h)	600.68	-8735.5	8735.5	21.52	*	*	601.8	-601.8	-do-	-do-
$[RuCl_6]^{2-}$ (O_h)	549.02	-5199.8	5199.8	19.71	-32.36	≈ 0.0	990.8	-990.8	-do-	A large sextet[b] ; each line of which splits into19 lines[c]
$[RuBr_6]^{2-}$ (O_h)	5 13.39	-5029.6	5029.6	32.58	≈ 256.7	≈ 0.0	2558.4	-2558.4	-do-	A large sextet [b]
$[OsF_6]^{3-}$ (O_h)	668.95	-8827.7	8827.7	18.19	*	*	600.4	-600.4	-do-	A large quartet[b]
$[OsCl_6]^{3-}$ (D_{6h})	-80.93	-2443.6	2443.6	≈ 0.85	-34.92	0.06	792.3	-792.3	-do-	A large quartet[b] ; each line further splits into19 lines[c]
$[Os Br_6]^{3-}$ (O_h)	637.72	-4059.6	4059.6	27.09	258.94	≈ 0.0	2649.4	-2649.4	-do-	A large quartet[b]
$[Os(NH_3)_6]^{3+}$(D_{12})	781.87	-35899.7	35899.7	-2.61,	-2.77,	0.346,	226.0,	-226.0,	Three types	A large quartet; each line splits into 125 [d]
				-4.0,	-2.72,	0.384,	239.2,	-239.2,	of ligands ;	lines by hyper fine interaction of Os^{+3} and
				-	-	0.345,	246.7,	-246.7,	two belong	N having comparable m_n ratio; a *continuum*
				2.56,	2.78,	0.346,	226.0,	-226.0,	to each type	is expected.
				-4.0,	-2.77,	0.384,	239. 2,	-239.2,		
				-2.61,	-2.72,	- 2.78	0.345	246.7	-246.7	
				-2.56						
$[RhF_6]^{2-}$ (O_h)	532.79	-7418.6	7418.6	29.99	*	*	380.5	-380.5	All equivalents	A largedoublet[b]
$[RhCl_6]^{2-}$ (O_h)	892.32	-3939.2	3939.2	197.15	-46.67	≈ 0.0	335.2	-335.2	-do-	-do-
$[RhBr_6]^{2-}$ (O_h)	426.45	-6658.6	6658.6	52.03	342.63	0.05	2997.3	-2997.3	-do-	-do-
$[Rh(NH_3)_6]^{4+}$ (D_6)	702.15	-166170.4	166170.4	14.1,	≈1.19	Four	1701.5,	-1701.5,	All	-do-
				14.9,		≈ 0.72	1926.3,	-1926.3,	non	

				4.4,		and	1686.0,	-1686.0,	equivalents	
				15.1,		two	1285.0,	-1285.0,		
				6.5,		≈ 0.73	1840.7,	-1840.7,		
				9.9			1254.9	-1254.9		
$[IrF_6]^{2-}$ (O_h)	711.34	-7657.8	7657.8	25.43	*	*	437.8	-437.8	All equivalents	A large quartet(b)
$[IrCl_6]^{2-}$ (O_h)	892.32	-3939.2	3939.2	28.25	-47.20	≈ 0.0	512.0	-512.0	-do-	-do-
$[IrBr_6]^{2-}$ (O_h)	603.73	-97.8	97.8	48.82	367.23	≈ 0.0	2990.9	-2990.9	-do-	-do-
$[Ir(NH_3)_6]^{4+}$ (D_{12})	980.68	-12930.0	12930.0	≈1.38	0.80	≈ 0.2	256.2	-256.2	-do-	-do-

*With I=1/2, F possesses neither h nor NQCC

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(c) due to hyperfine interaction between Tc (II) and six stereo chemically equivalent bromo ligands [2*6*3/2+1].

(b) $[Tc (NH_3)_6]^{2+}$

It showed the following features:

(1) With the same A_{ten}, NQCC, η, σ, δ values respectively, six NH_3 ligands were equivalent.

(2) As their μ_n ratio was large, the unpaired electron was localized on Tc (II) only.

(3) A_{ten} 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: $[Re X_6]^{4-}$ (X=Cl, Br) and $[Re (NH_3)_6]^{2+}$.

(a) $[Re Cl_6]^{4-}$ and $[Re (NH_3)_6]^{2+}$

Both showed the following features:

(1) With the same A_{ten}, NQCC, η, σ, δ 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 μ_n ratios respectively.

(3) A_{ten} 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) $[Re Br_6]^{4-}$

It showed the following features:

(1) With the same A_{ten}, NQCC, η, σ, δ 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 μ_n ratio was comparable.

(3) A_{ten} of Re (II) was more than those of bromo ligands.

Its ESR spectrum would show a large *sextet* [(b)] from Re (II) [2*5/2+1]. Each line of this *sextet,* further, split up into a smaller 19 line[(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 $[RuX_6]^{3-}$ (X= F, Cl, Br) were included.

(a) $[RuF_6]^{3-}$(X=F, Br)

They showed the following features:

(1) With the same A_{ten}, NQCC, η, σ, δ values respectively, all the ligands were equivalent.

(2) The unpaired electron was present only on Ru (III) because with small μ_n ratios, there was no hyperfine interaction between Ru (III) and F or Br.

(3) A_{ten} of Ru (III) was more than the F or the Br.

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

(b) $[RuCl_6]^{3-}$

It showed the following features:

(1) With the same A_{ten}, NQCC, η, σ, δ values respectively, the six Cl were equivalent.

(2) With comparable μ_n ratio, the unpaired electron was delocalized both on Ru (III) and six Cl.

(3) A_{ten} of Ru (III) was more than those of the ligands.

Its ESR spectrum showed a large *sextet* [(b)] from Ru (III) [2*5/2+1] with each line of which would, further, split into smaller 19 lines [(c)] by the hyperfine interaction of six Cl [2*6*3/2+1] and Ru (III).

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

It included four complexes such as $[Os X_6]^{3-}$ (X= F, Cl, Br) and $[Os (NH_3)_6]^{3+}$

(a) $[OsX_6]^{3-}$ (X=F, Br)

Both the complexes showed the following common features:

(1) With same A_{ten}, NQCC, η, σ, δ values, all the ligands were equivalent.

(2) Unpaired electron was localized on Os (III).

(3) A_{ten} of Os (III) was more than the F or the Br.

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

(b) $[OsCl_6]^{3-}$

It showed the following features:

(1) With same A_{ten}, NQCC, η, σ, δ 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_{ten} value of Os (III) was more than those of the six Cl.

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

(c) $[Os (NH_3)_6]^{3+}$

It showed the following features:

(1) There were three sets of A_{ten}, NQCC, η, σ, δ values respectively for the six N of the six NH_3 ; each set having two values. So there were present three types of stereo chemically different ligands respectively.

(2) Unpaired electron was delocalized both on Os (III) and the six NH_3 as μ_n ratio of Os and N was comparable.

(3) A_{ten} value of Os (III) was more than those of the ligands.

Its spectrum would give a large *quartet* [(b)] from Os (III) [2*3/2+1] whose each line would, further, split into 125[(d)] lines$[2*2*1+1]^3$ 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 Rh (IV) Complexes

It included four complexes: $[RhX_6]^{2-}$ (X= F, Cl, Br) and $[Rh (NH_3)_6]^{4+}$ which showed the following features:

(1) With the same A_{ten}, NQCC, η, σ, δ values respectively, the ligands like F, Cl, Br, NH_3 were equivalent.

(2) The unpaired electron was present only on Rh (IV).

(3) A_{ten} 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 μ_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_{ten}, NQCC, η, σ, δ values respectively, the ligands like F, Cl, Br, NH_3 were equivalent.

(2) The unpaired electron was present only on Ir (IV) (3) A_{ten} 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 μ_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 μ_n ratios, we could predict the number or ESR lines in a vast number of complexes of 10 metal ions of 2nd and 3rd 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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