Predicting ESR Peaks in Titanium (III), Vanadium (IV) and Copper (II) Complexes of Halo Ligands by NMR, ESR and NQR Techniques: A DFT Study

HARMINDER SINGH[1], A. K. BHARDWAJ[2], M. L. SEHGAL[3], MEHJBEEN JAVED[4] and IRSHAD AHMAD[5]*

[1]Lovely Professional University, Phagwara - 144402, India.
[2]Department of Chemistry, D.A.V. College, Jalandhar - 144008, India.
[3]Former Head, Department of Chemistry, D.A.V. College, Jalandhar - 144008, India.
[4]Department of Zoology, Faculty of Life Sciences, A. M.U, Aligarh - 202002, India.
[5]Department of Biochemistry, Faculty of Life Sciences, A. M.U, Aligarh - 202002, India.
*Corresponding author E-mail: irshadahmad.bio@gmail.com

ABSTRACT

15 halo ($I \geq 1/2$) complexes of Ti (III), V (IV) and Cu (II) each possessing one unpaired electron were studied using DFT implemented in ADF.2010.02. A_{ten}, NQCC and η parameters of metal ions and ligands were obtained from ESR/EPR program while their σ and δ parameters were given by NMR/EPR program after optimization of complexes. Ligands having same values of these 5 parameters were spatially equivalent and, thus, would undergo same hyperfine interaction. Experimental determination of ESR lines in Cu (II) complexes became erroneous because the presence of both the large Jahn-Teller effect and the high value of its spin-orbit coupling constant ($\lambda_{Cu(II)}$ = -830 cm^{-1}) affect the A_{ten} parameter adversely. Cryoscopic conditions, generally required, in ESR experiments of Ti (III) and V (IV) complexes were difficult to obtain and cumbersome to maintain.

Key Words: Jahn-Teller; Chemical Shift; Shielding Constant

INTRODUCTION

We applied ADF 2010.02[1-10] to fifteen Ti (III), V (IV) and Cu (II) complexes with halo ligands. Each one of these three metal ions possessed only one unpaired electron. Cryoscopic conditions needed during ESR transitions of Ti (III) and V (IV) complexes[11-15] falling in low energy microwave region were difficult to obtain and cumbersome to maintain.No doubt, ESR spectra of Cu(II) complexes could be obtained at room temperature but the presence of the large Jahn-Teller effect and the high $\lambda_{Cu(II)}$ [-830 cm^{-1}] values would, again, cause errors[16-24] in their

experimentally determined the A_{ten} parameters. All these difficulties were overcome by the ADF software.

DFT enabled us to deeply understand the relation between magnetic parameters and electronic and geometrical structures of molecules. As ESR was related to the electronic structure and geometry of systems, DFT provided an alternative to the traditional Hartree - Fock (HF) and post-HF approaches to the calculation of ESR parameters. This had brought DFT on the forefront in calculating ESR parameters during the last decade.

The software gave one ESR [Hyperfine Coupling Constant (A $_{ten}$)], two NQR [Nuclear Quadrupole Coupling Constant**(Q)** , Asymmetric Coefficient (h)] and two NMR parameters [Shielding Constant (σ),Chemical Shift (δ)] of metal ions and Coordinating Atoms (CA).With the help of the 5 parameters: A $_{ten}$, NQCC,η, σ, δ ,we could predict the number of ESR peaks in halo complexes of these three univalent metal ions.

A very brief back ground of the development of DFT as applied to NMR of complexes of transition metal ions was given as follows:

While the discussion on NMR of transition metal complexes encircled around ligand field theory[25], in the late 70s, some review articles were collected[26] on small molecules. De Brouchere (1978) published a 100 page review containing 289 references[27]. But till then no calculations on nuclear shielding and spin- spin coupling parameters were carried out. **HF** approach given by Nakatsuzi[28] did present a paper on the calculation of the above named parameters of the complexes. But it was found lacking in high oxidation states of d^{10} systems[29].In 80s, NMR shielding codes based on **HFS** or X α method were developed which was latter known as DFT [29-31]. In 1993, Kohn-Sham DFT[32,33] employed IGLO method[32,33] to calculate nuclear shielding. LORG approach[34] as improved upon by GIAO DFT[35-37] and CSGT methods[37] was employed. The spin-spin coupling constants (j) of the metal complexes were first of all calculated by Malkin et al[38].In 1996, Dickson and Zieglar[39] calculated FC term[40] by finite-perturbation approach. Later on,

SD term[41,42] was also included in spin- spin coupling values.

The following 15 complexes such as $[TiX_4]^{1-}$ (X=F, Cl, Br, I), $[TiX_6]^{3-}$ (X=F, Cl, Br), $[VF_4]^0$ (X=F, Cl, Br, I), $[CuX_2]^{2-}$ (X=F, Cl , Br, I) were studied.

With the help of the five parameters A $_{ten}$, NQCC, η, σ, δ one ESR [Hyperfine Coupling Constant (A $_{ten}$)], two NQR [Nuclear Quadrupole Coupling Constant(Q) , Asymmetric Coefficient (h)] and two NMR parameters[Shielding Constant (ó) ,Chemical Shift (ä)] of metal ions and Coordinating Atoms (CA), we were able to predict the number of ESR peaks in the halo complexes of these three univalent metal ions [Ti (III), V (IV),Cu (II))].

Basis for prediction of the number of ESR peaks

As already stated, a total of 5 parameters of ESR (A $_{ten}$), NQR (NQCC,η) and NMR (σ, δ) of the metal ion and the coordinating atoms of ligands as obtained from the software were needed. The metal ion should have only one specific value for each one of these parameters, but these parameters might differ in values for coordinating atoms (CA) of the ligands. If the coordinating atoms had the same or nearly the same values of these five parameters, it would indicate that all the ligands were spatially equivalent. They might, further, undergo hyperfine interaction with the metal ion. Both the hyperfine interaction and relative magnitude of the parameters for metal and CA will form the basis to determine the number of ESR peaks.

Prediction of Hyperfine Interaction between Metals and Ligands in Ti (III) and V (IV) Complexes

After knowing the values of nuclear quantum number and g factor of the nucleus of metal (I_M, g_M) and of the coordinating atoms (CA) of ligands (I_{CA} , g_{CA}) from the literature, we would calculate the nuclear magnetic moments in terms of b_n both for the metal (m_M) and the coordinating atoms (m_{CA}) of ligands as follows:

$$m_M = g_M [I_M (I_M+1)]^{1/2} \qquad \rvert$$
$$\text{And} \qquad\qquad\qquad\qquad \rvert \qquad\qquad ...(1)$$
$$m_{CA} = g_{CA} [I_{CA} (I_{CA}+1)]^{1/2} \quad \rvert$$

Then [m $_M$/m $_{CA}$] ratio called **m$_n$** ratio was calculated to draw the following inferences:

(a)   If this ratio was comparable and isotopes with

non zero I possessed appreciable % natural abundance, the unpaired electron would be delocalized both on the metal ion and the ligands. So the hyperfine interaction between metal and ligands should be possible.

The peaks should arise both from the metal ion and the ligands.

(b)   Small or large ratios implied that m_{CA} of ligands and the metal (m_M) differ largely. No hyperfine interaction between metal ion and ligands should be possible. The electron would be localized only on metal ion irrespective of the values of I and % abundance of metal ions and CA.

The peaks should arise only from the metal ion.

Prediction of Hyperfine Interaction between Metals and Ligands in Cu (II) Complexes

The presence of a large Jahn-Teller effect, generally, allowed the hyperfine interaction and the peaks should arise both from the Cu (II) and the coordinating atoms of the ligands irrespective of their [m_{Cu}/m_{CA}] ratios.

Rules for calculating ESR Peaks in the metal ion Complexes

If I_M and I_{CA} were the nuclear spins of metal (M) and the CA respectively. Then:

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

(B)   Peaks arising from ligands could be predicted from their stereochemical arrangement if the hyperfine interaction was possible as follows:

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

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

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

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

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

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

(c)   In case, the A_{ten} of the metal ion was higher than that of CA, then first the lines obtained from metal ion should be calculated. Each one of this line *could*, further, split into a number of lines given by coordinating atoms if hyperfine interaction among the metal ion and the ligands was possible. Conversely, if coordinating atoms possessed higher A_{ten} value/s, then first the lines given by the ligands were calculated. Each line of ligands would, then, split by the metal ion.

(d)   There could happen an overlapping of ESR lines due to different reasons. So, experimentally observed number of lines might be less than theoretically predicted lines. Further, if the predicted number of lines were very large with small A_{ten} values of species, the lines would merge to give a *continuum*.

MATERIAL AND METHODS

Obtaining ESR and NQR parameters

After *optimization* of complexes, the software was run by *Single Point, LDA, Default, Spin Orbit, Unrestricted, Collinear* commands using *DZ* or *TPZ Basis sets* with *Nosym* symmetry in its "ESR/ EPR Program" to obtain ESR (A_{ten}) and NQR (NQCC,) parameters for the Cu(II) and the coordinating atoms (^{14}N, ^{35}Cl, ^{89} Br, ^{127} I) of the ligands [43-46].

Obtaining NMR Parameters

σ and δ values of Cu (II) and ^{14}N, ^{35}Cl, ^{89} Br, ^{127} I of ligands were obtained from "NMR/EPR Program" by the above commands except for replacing *Spin Orbit* by *None* [35, 9-10].

RESULTS

Table: 1A gave expanded forms of acronyms. Tables: 1B contained I_M, I_{CA}, g_M, g_{CA} , m_M and m_{CA} (in terms of b_n) and ratios (m_n) of m_M and m_{CA} to predict the possibility of hyperfine interaction between the metal ion and ligands.Tables:1C gave values of A_{ten}, NQCC, η, σ, δ parameters of CA of ligands, number of spatially different ligands along with A_{ten},σ, δ values of the metal ions along with the number of theoretically expected ESR peaks.

Table 1: Acronyms and their expanded forms

Acronyms	Expanded Forms	Acronyms	Expanded Forms
ZORA	Zeroth- Order Regular Approximation	CSGT	Continuous Set of Gauge Transformation
H F	Hartree- Fock	SD	Spin-dipole
HFS	Hartree-Fock-Dickson-Slater)	FC	Fermi-contact
IGLO	Independent or Individual Gauge of Localized Orbitals	LDA	Local Density Approximation
LORG	Localized Orbitals Resonance Gauge	DZ/TPZ	Double Zeta/Triple Zeta
GIAO	Gauge Including Atomic Orbitals	Nosym	Normalized or True

Table: 1(b) Prediction of Hyperfine Interaction between Metals and Ligands

M&X (I_M)& [I_{CA}]	(g_M) [g_{CA}]	(m_M) [m_{CA}]	Ratio [m_M/m_{CA}]	Whether hyperfine interaction between M^{+n} and CA possible
Ti& F (2.5)&[0.5]	(-0.311539) [5.257736]	(-0.9215) [4.5333]	[1:5]	No; as the electron is localized only on Ti(III)
Ti& Cl (2.5)&[1.5]	(-0.311539) [0.5479162]	(-0.9215) [1.06]	[9:10]	Yes; as the electron is delocalized both on Ti (III) and ligands.
Ti& Br (2.5)& [1.5]	(-0.311539) [1.4042667]	(-0.9215) [4.2058]	[2:9]	No; as the electron is localized only on Ti(III)
Ti& I (2.5)&[2.5]	(-0.311539) [1.1250392]	(-0.9215) [3.3279]	[2:7]	—do—
V & F (3.5)& [0.5]	(1.4710588) [5.257736]	(5.8381) [4.5333]	[5:4]	Yes; as the electron is delocalized on both V (IV) and ligands.
[V& Cl (3.5)& [1.5]	(1.4710588) [0.5479162]	(5.8381) [1.06]	[11:2]	No; as the electron is localized only on V (IV) and not on ligands.
V & Br (3.5)& [1.5]	(1.4710588) [1.4042667]	(5.8381) [4.2058]	[4:3]	Yes; as the electron is delocalized on both V (IV) and ligands.
V & I (35)& [2.5]	(1.4710588) [1.1250392]	(5.8381) [3.3279]	[7:4]	—do—
Cu & F (1.5)& [0.5]	(1.482193) [5.257736]	(-2.8703) [4.5333]	[1:2]	Yes ; as the electron is delocalized both on Cu(II) and ligands
Cu & Cl (1.5) &[1.5]	(1.482193) [0.5479162]	(-2.8703) [1.06]	[3:8]	—do—
Cu & Br (1.5)&[1.5]	(1.482193) [1.4042667]	(-2.8703) [4.2058]	[2:3]	—do—
Cu & I (1.5)&[2.5]	(1.482193) [1.1250392]	(-2.8703) [3.3279]	[6:7]	—do—

DISCUSSION

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

Table: 1B predicted of Hyperfine Interaction between Ti (III) and the halo ligands. Table: 1C contained A $_{ten}$, σ ,δ values of the parameters of Ti(III) and the A $_{ten}$, NQCC, η , σ , δ parameters of halo ligands for [TiX4]$^{1-}$ (X= F, Cl, Br, I) along with the predicted number of ESR peaks.

Their ESR discussion was divided into two parts:

Prediction of ESR peaks in [Ti X$_4$]$^{1-}$ (X =F, Br, I)

They showed the following common

Table 1(c): Prediction of Number of ESR peaks in Metal Ion Complexes

Complex	3 Parameters of M^{+n}			5 Parameters of CA					Spatial nature of ligands	No. of ESR peaks
	A$_{ten}$	σ	δ	A$_{ten}$	NQCC	η	σ	δ		
[TiF$_4$]$^{1-}$ D$_{4h}$	431.79	-4886.0	4886.0	3.69	*	*	-21.7	21.7	All equivalent	A large sextet only[b]
[TiCl$_4$]$^{1-}$ D$_{4h}$	268.74	-5614.1	5614.1	≈3.34	≈16.20	0.96	296.9	-296.9	-do-	A large sextet[b]; each line splits into tridacane[c]
[TiBr$_4$]$^{1-}$ D$_{4h}$	227.80	-205.0	205.0	≈4.20	≈131.33	0.92	1297.0	-1297.0	-do-	A large sextet[b]only
[TiI$_4$]$^{1-}$ D$_{4h}$	171.73	-7160.0	7160.0	-12.09	≈-447.0	0.99	2665.5	-2665.5	-do-	-do-
[TiF$_6$]$^{3-}$ D$_{6h}$	463.18	-1641.0	1641.0	≈5.97	*	*	-300.1	300.1	-do-	-do-
[TiCl$_6$]$^{3-}$ O$_h$	6.66	1132.7	-1132.7	-0.11 (3 lig) 6.15 (3 lig)	-22.32 (3 lig) -20.47 (3 lig)	0.057 (3 lig) 0.152 (3 lig)	901.0 (3 lig) 1063.3 (3 lig)	-901.0 (3 lig) -1063.3 (3 lig)	Two types ; each having three ligands	A large sextet[b]; each line splits into 100 lines[d]
[TiBr$_6$]$^{3-}$ D$_{6h}$	-266.25	-4395.9	4395.9	41.41	≈186.1	0.014	1846.5	-1846.5	All equivalent	A large sextet[b]only
[VF$_4$]D$_{4h}$	515.95	-7820.4	7820.4	≈10.36	*	*	- 252.6	252.6	-do-	A large octet[b]; each line splitting into a quintet[c]
[VCl$_4$]D$_{4h}$	339.39	-6554.0	6554.0	5.12	-22.55	0.12	- 372.0	372.0	-do-	A large octet[b]only
[VBr$_4$]D$_{4h}$	1446.47	-1560.9	1560.9	- 4.13	≈270.46	0.42	189.7	-189.7	-do-	An large octet[b], each line splits into tridecane[c]
[VI$_4$]D$_{4h}$	1128.65	-2164.4	2164.4	-23.73	-701.86	0.997	1602.7	-1602.7	-do-	A large octet[b]; each line splits into 21 lines[c]
[CuF$_4$]$^{2-}$ D$_{4h}$	72.02	-9585.9	9585.9	-14.45	*	*	396.1	-396.1	-do-	A large quartet [b]; each line splits into quintet[c]
[CuCl$_4$]$^{2-}$ D$_{4h}$	50.62	-619.1	619.1	41.69	- 31.9	0.396	915.4	-915.4	-do-	A large quartet[b]; each line splits into tridecane[c]
[CuBr$_4$]$^{2-}$ D$_{4h}$	81.28	-105.9	105.9	89.69	251.5	0.38	2449.0	-2449.0	-do-	A largetridecane[c]; each line splits into a quartet[b]
[CuI$_4$]$^{2-}$ D$_{4h}$	111.36	685.2	-685.2	222.4	-53.1	0.395	3996.5	-3996.5	-do-	21lines[c]; each line splits into a quartet[b]

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

features:
[i] The four halo ligands possessed same values of **A $_{ten}$, NQCC , η , σ , δ** parameters respectively to show that all the ligands were spatially equivalent.
[ii] A $_{ten}$ of Ti (III) was higher than those of the ligands.
[iii] The unpaired electron was localized only on Ti (III) because the small m_{Ti} / m_{CA} ratio would not allow any hyperfine interaction.

Their ESR spectra would show only a large *sextet* from Ti (III) [2.5/2+1].

Prediction of ESR peaks in [TiCl$_4$]$^{1-}$

It showed the following features:
[i] Four chloro ligands possessed same values of **A $_{ten}$, NQCC, η, σ, δ** parameters respectively.So all the ligands were spatially equivalent.[ii] A$_{ten}$ of Ti (III) was higher than all the chloro ligands. [iii] Ti (III) and ligands had comparable m_{Ti} / m_{Cl} ratio to allow unpaired electron to be delocalized. So the hyperfine interaction was possible among them.

Its ESR spectrum would give a large *sextet* from Ti (III) [2.5/2+1].Its each line would, further, split up into a *tridecane* from 4 equivalent Cl [2.4.3/2+1] due to hyperfine interaction.

Prediction of ESR peaks in six- coordinate complexes [Ti X$_6$]$^{3-}$ (X =F, Cl, Br)

Again, two cases would arise:

Prediction of ESR peaks in [Ti X$_6$]$^{3-}$ (X=F, Br)

They showed the following common features:
[i] Six halo ligands possessed nearly the same values of their **A $_{ten}$, NQCC, η , σ, δ** parameters respectively to indicate that they were spatially equivalent. [ii] A $_{ten}$ of Ti (III) was higher than those of the ligands. [iii]With small m_{Ti} / m_{CA} ratios, the unpaired electron was localized only on Ti (III).

Their spectra would give only a large *sextet* from Ti (III) [2.5/2+1] with no hyperfine interaction.

Prediction of ESR peaks in [TiCl$_6$]$^{3-}$

It showed the following features:
[i] It gave two sets of values of **A$_{ten,}$ NQCC, h, ó, ä** parameters to indicate two types of chloro ligands; each type containing three ligands. [ii] A $_{ten}$

of Ti (III) was higher than those of the ligands. [iii]The unpaired electron was delocalized both on Ti (III) and the ligands due to their comparable $m_{Ti/}$ m $_{Cl}$ ratio.

Its spectrum would give a *sextet* from Ti (III) [2.5/2+1]. Each line of this sextet would, further, split into 100 lines[d] from two types of spatially different Cl [2.3.3/2+1]^2 due to hyperfine interaction. In fact, a *continuum* should be observed.

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

Table: 1B predicted of Hyperfine Interaction between V (IV) and the halo ligands. Table: 1C contained A $_{ten}$, ó , ä values of the parameters of V(IV) and the A $_{ten}$, NQCC, h , ó , ä parameters of halo ligands for [VX4] (X= F, Cl, Br, I) along with the predicted number of ESR peaks Their ESR discussion was divided into two parts:

Prediction of ESR peaks in [V X$_4$] (X= F, Br, I)

They showed the following common features:
[i] The four halo ligands possessed same values of their **A $_{ten}$, NQCC, η , σ, δ** parameters respectively; meaning thereby that all the ligands were spatially equivalent. [ii] A $_{ten}$ of V (IV) was more than those of the ligands. [iii] With comparable m_V / m_{CA} ratios, the unpaired electron would be delocalized both on the V (IV) and the ligands.

Their ESR spectra would first give a large octet from V (IV) [2.1.7/2+1]. Each line of this octet would, further, split up into a *quintet* or *13 lines* or *21 lines* from four equivalent F [(2.4.1/2+1)] or Br [(2.4.3/2+1)] or I [2.4.5/2+1)] respectively due to hyperfine interaction.

Prediction of ESR peaks in [V Cl$_4$]

It showed the following features:
[i] Four chloro ligands possessed same values of their **A $_{ten}$, NQCC, η, σ, δ** parameters respectively; meaning there by that the ligands were spatially equivalent.[ii]A $_{ten}$ of V (IV) was more than those of the ligands.[iii] The unpaired electron was localized only on V (IV) and not on ligands as their m_V / m_{Cl} ratio was large.

So its ESR spectrum would give only a

large octet from V (IV) [2.1.7/2+1] with no hyperfine interaction among the chloro ligands and V (IV).

Prediction of number of ESR peaks in Cu (II) Complexes

Table: 1B predicted of Hyperfine Interaction between Cu (II) and the halo ligands. Table: 1C contained A_{ten}, σ, δ values of parameters of Cu(II) and A_{ten}, NQCC, δ, ó , ä parameters of halo ligands for [CuX4]$^{2-}$ (X= F, Cl, Br, I) along with the predicted number of ESR peaks. Their ESR discussion was divided into two parts:

Prediction of ESR peaks in [Cu X$_4$]$^{2-}$ X= (F, Cl)

It showed the following common features:

Both the ligands possessed same values of their **A_{ten} ,NQCC, η, σ, δ** parameters respectively; meaning there by that they were spatially equivalent.[ii] A_{ten} of Cu (II) was more than ligands.[iii]Unpaired electron was delocalized both on Cu (II) and ligands.

ESR spectra should give a large *quartet* from Cu (II) [2.3/2+1] whose each line would, further, split up into a smaller *quintet* or a *tridecane* from four equivalent F [(2.4.1/2+1)] or Cl [2.4.3/2+1] respectively due to hyperfine interaction between Cu(II) and F or Cl.

Prediction of ESR peaks in [Cu X$_4$]$^{2-}$ (X= Br, I)

They showed following common features:

Both the ligands possessed same values of A_{ten}, NQCC , η, σ, δ parameters respectively; meaning there by that all were spatially equivalent. [ii] A_{ten} of Br and I were more than that of Cu (II). [iii] The unpaired electron was delocalized both on Cu (II) and four equivalent ligands.

Their ESR spectra would first give a large *tridecane* from the four equivalent Br [2.4.3/2+1] or *21 lines* from four equivalents I [2.4.5/2+1].Then its each line would, further, split into a smaller quartet from Cu (II) [2.1.3/2+1] due to hyperfine interaction between Cu (II) and Br or I.

CONCLUSION

The originality, the relevance, the objective of this work and how it moved the body of scientific knowledge forward would lay in the fact that we were able to theoretically predict the number of ESR peaks in Ti (III),V(IV) and Cu(II) complexes having mono-dentate ligands.

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