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ELECTRON SPIN RESONANCE, NUCLEAR QUADRUPOLE RESONANCE, REFLECTANCE AND MAGNETIC PARAMETERS OF COBALT (II) AND NICKEL (II) COMPLEXES USING DENSITY FUNCTIONAL THEORY

Harminder Singh[1], A.K. Bhardwaj[2], M.L. Sehgal[2], Susheel K. Mittal[3]

[1]Lovely Professional University, Phagwara, India
[2]Department of Chemistry, D.A.V. College, Jalandhar, India
[3]School of Chemistry and Biochemistry, Thapar University, Patiala, India

E-mail of Corresponding Author: smittal@thapar.edu

ABSTRACT

Density Functional Theory was used to calculate and correlate 14 ESR, NQR, Reflectance and Magnetic parameters of 20 Co^{+2} and Ni^{+2} complexes such as $[CoX_4]^{2-}$ (X = F, Cl , Br ,I), $[Co(OH_2)_4]^{2+}$, $[Co(NCO)_4]^{2-}$, $[CoX_6]^{4-}$ (X = F, Cl), $[NiX_4]^{2-}$ (X = Cl ,Br, I, NCO), $[NiX_6]^{4-}$ (X=F, Cl ,Br, I) $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(CH_3NH_2)_6]^{2+}$, $[Ni(NH_3)_4(NCS)_2]$. All computations were carried out in the gas phase using ADF2010.02 by applying Single Point, LDA, Default , Spin Orbit, Unrestricted, None, Collinear commands using DZ or TPZ basis sets. The complexes were optimized to obtain two ESR (g_{11}, g_{22}, g_{33}, g_{iso}, a_{11}, a_{22}, a_{33}, A_{ten}) and three NQR parameters [η, q_{11}, q_{22}, q_{33}, NQCC]. Two Reflectance parameters [$\lambda_{complex}$, % covalent character] were calculated from g_{iso}. In addition, five magnetic [μ_{soc}, μ_t, μ_{net}, t_{2g} electron delocalization and its constant k] and two more ESR [H^, ΔE_{hf}] parameters were calculated by combining the ESR and Reflectance data. We verified the Laplace equation using the NQR data. The delocalization parameter (k) and the reflectance parameter called Nephelauxetic ratio (β_{35}) were found to have almost the same values as both determine the covalence in complexes. The calculated values of parameters were found in agreement with their reported values.

Keywords: DFT, ESR, NQR, Reflectance, Magnetism, Nephelauxetic ratio, delocalization parameter

INTRODUCTION

Effective Spin Hamiltonian (H^) is a mathematical expression that determines energy of an ESR transitions when an ESR active metal ion is surrounded by ligands in a definite geometry. It 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 Coupling Constant(Q)][*], total electronic spin (S), Bohr Magneton of both the electron (β_e) and the nucleus (β_n), nuclear spin quantum number (I), g_n (nuclear magnetic ratio) and nature of surrounding nuclei having quadrupole moments(I≥1).

No doubt, ESR studies on some biologically important(1-2) Co^{+2} and catalytically(3) suitable Ni^{+2} complexes has already been reported, yet a correlation of their ESR, NQR, Reflectance and Magnetic parameters with the help of a software is rarely found in the literature.

With certain commands, the software gave five ESR and NQR parameters. They were together used to calculate two more ESR parameters [effective spin Hamiltonian (H^) and hyperfine coupling energy (ΔE_{hf})]. The g_{iso} parameter was

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[*] Q or e Q *is the nuclear quadrupole moment*. q Or e q *is the electric field gradient* and product of these quantities (e Q× e q= e^2Qq) *is nuclear quadrupole coupling constant* (Q).

further correlated to two Reflectance parameters [spin orbit coupling constant ($\lambda_{complex}$), % covalent character]. The ESR and the Reflectance parameters were together used to calculate and correlate five magnetic parameters [magnetic moments namely total (μ_t), net (μ_{net}) and that containing contributions from spin and orbital (μ_{soc} or μ_{ADF}), t_{2g} electron delocalization and its constant (k)]. The software also gave dipole moments and symmetry symbols of complexes. We could also verify Laplace equation for the complexes.

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

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

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

14 ESR, NQR, Reflectance and Magnetic parameters were correlated in **20** Co^{2+} and Ni^{2+} complexes of coordination numbers 4 and 6 by using ADF (Amsterdam Density Functional) 2010.02 software by applying of D.F.T. (Density Functional Theory) (7-9). The **5** parameters given by the software (g, a, q, NQCC,η) were used to calculate **9** other parameters [H^, ΔE_{hf}, $\lambda_{complex}$, % covalent character, μ_t , $\mu_{net,}$ μ_{soc} , t_{2g} electron delocalization and its constant (k)]. 23 relations were selectively used to calculate these parameters of complexes like $[CoX_4]^{2-}$ (X = F, Cl, Br, I), $[Co(OH_2)_4]^{2+}$, $[Co(NCO)_4]^{2-}$, $[CoX_6]^{4-}$ (X = F, Cl), $[NiX_4]^{2-}$ (X = Cl , Br, I, NCO), $[NiX_6]^{4-}$ (X = F, Cl, Br, I) $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(CH_3NH_2)_6]^{2+}$, $[Ni(NH_3)_4(NCS)_2]$.

These complexes possessed both regular ($T_{d,}$ Oh) as well as distorted stereochemistries ($C_{1,}C_2$, $D_{\infty h}$,$D_{4h,}$ D_{6h} ,D_{2d}).

(1) Calculation of ESR parameters (10-25)

(a) Effective Spin Hamiltonian (H^): Four factors which contributed to H^ (MHz) were: g, a, Q and interaction of nuclear magnetic moment with external magnetic field (I). Three relations were used to calculate H^ having contributions from these four factors:

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† ESR of only a few Ni (2) octahedral complexes (4- 6) are studied at room temperatures.

$H^\wedge = \beta e\,[g_{11}.Hx.S\_x + g_{22}.Hy.S\_y + g_{33}.Hz.S\_z] + [a_{11}.S\_x.\ I\_x + a_{22}.S\_y.I\_y + a_{33}.S\_z.I\_z] + Q\,[I\_z\text{-}1/3\ I\ (I+1)]$
$- [g_{\ n}.\beta_n.H_0.I]$ --------------------[1]

$H^\wedge = \beta_e\,[g_{ll}\ .Hz.\ S\_z + g_{\perp}\ (Hx.\ S\_x + Hy.Sy)] + [a_{ll}.\ Sz\ .Iz + a_{\perp}(S\_x.I\_x + S\_y.I\_y)] + Q\ [I\_z\ \ -1/3\ I(I+1)]$
$- [g_{\ n}.\beta_n.H_0\ .I]$ ----------------------------[2]

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

[1] Was used for systems with different values of **g** and **a**. [2] Was used for axially symmetric systems while [3] was used when **g** and/or **a** parameters had the same or nearly the same values. The first and the last terms in these relations were in ergs and the other two were in MHz (6.627 X 10^{-21} erg = one MHz; $\beta_{e=}1.3994$ MHz/Gauss; $\beta_{\ n} = \beta_{e/}1836$. g_n had a specific value for each metal).

(b) Hyperfine Coupling Energy

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

(2) Calculation of NQR parameters (26-30)

(a) Asymmetry Coefficient (η): The q_{11}, $q_{22,}$ q_{33} obtained from the software were changed to $q_{\ zz}$, $q_{\ yy}$ and $q_{\ zz}$ when expressed in decreasing order of their absolute values (modulus):

$|\mathbf{q}_{\ zz}| \geq |\mathbf{q}_{\ yy}|\ \geq |\mathbf{q}_{\ xx}|$ **.** Then:

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

(η) lies in between 0 to1.For axial symmetry, η=0.It was possible only when:

$q_{\ xx} = q_{\ yy} \neq q_{\ zz}$ ------------------------------------- [6]

(b) Laplace Equation: $q_{\ xx} + q_{\ y\,y} + q_{\ zz} = 0$. ------------------------------------- [7]

(3) Relations used for calculating Reflectance and Magnetic parameters (31-41)

(a) Calculation of μ_{soc}, μ_t, $\mu_{n\,e\,t}$, t_{2g} electron delocalization (B.M), its constant k and $\lambda_{\ \mathbf{complex}}$ for Co^{2+} (T_d) and Ni^{2+} (O_h) complexes having **A** ground terms :

$(\mu_{\ soc})$ or $(\mu_{\ ADF}) = [\ g_{\ iso}{}^2\ s\ (s+1)\ ]^{1/2}$ ----------------------------- ---- [8]

$\chi_{\ tip} = 8N\ \beta^2/10Dq$ ---------------------------------- [9]

$\mu_{\ tip} = \ \chi_{tip}\ X\ \mu_{s\ .o}\ /\chi(_{Mol\ .s.\ o})$ --------------------------------- [10]

$\mu_{\ t} = \ (\mu_{ADF}) + \mu_{\ t\ .i\ .p}$ --------------------------------- [11]

$\chi_t = \mu_t^{\ 2}\ \chi_{Mol\ .s\ .o}\ \ /\ \mu_{\ s.\ o.}{}^{2}$ ------------------------------------ [12]

and $\chi_t = {}^{\chi}{}_{Mol\ .s\ .o.}\ [1 - 8\ k^2\ \lambda_{\ metal\ ion}\ \ /10Dq] + 8\ k^2\ N\ \beta^2/10\ D\ q)$ ------------------ -------------- [13]

$\lambda_{complex} = k\ X\ \lambda_{\ metal\ \ ion}$ ------------------------------------ [14]

% covalent character (c.c.) = (1 –k) X100 ------------------------------------ [15]

Here, μ_{soc} was the magnetic moment given by spin orbit coupling. The (μ_t) was total magnetic moment while χ_{tip}[‡] and μ_{tip} were Zeeman Second Order molar magnetic susceptibility and Zeeman Second Order magnetic moment respectively. χ_t was the total molar magnetic susceptibility and (k) was t_{2g} electron delocalization constant. Molar magnetic susceptibilities ($\chi_{Mol\ s.o)}$ of Ni^{2+} and Co^{2+} with 2 and 3 unpaired electrons respectively were 3333.33 X10^{-6} and 6250.0X10^{-6} cgs/mol.

$\lambda_{metal\ ion}$ and $\lambda_{\ complex}$ were the spin-orbit coupling constants of the *free* metal ion and of the same metal ion *present in the complex* respectively. Free $\lambda_{Co}{}^{2+}$ and free $\lambda_{\ Ni}{}^{\ 2+}$ had values -172.0 and -316.0 cm^{-1} respectively. Total value of g called g_t and similar term g_{eff} were calculated by [16

[‡] t i p (temperature independent paramagnetism)

&17]. The former made use of the software while the latter used the reflectance parameters.

$\mu_t = [g_t^2 \, s(s+1)]^{1/2}$ ------------------------------------ [16]

$g_{eff} = 2(1 - 4\,\lambda_{complex} /10Dq)$ ------------------------------------ [17]

Still another parameter called t_{2g} electron delocalization was calculated by the average negative of the difference between g_t or g_{eff} and g_{iso}. Then:

t_{2g} electron delocalization = $-0.5(g_t - g_{iso})$ ---------------------------------- [18]

or t_{2g} electron delocalization = $-0.5(g_{eff} - g_{iso})$ ---------------------------------- - [18a]

μ_{net}, which is less than μ_t and is calculated as:

$\mu_{net} = \mu_t$ -| Reduction of magnetic moment from t_2g electron delocalization| -------------------------[11a]

Reduction of magnetic moment = $[(t_2g \text{ electron delocalization})^2 \, s(s+1)]^{1/2}$ ------------------------ [11b]

(b) Calculation of μ_{soc}, μ_t, μ_{net}, t_{2g} electron delocalization (B.M), its constant k and $\lambda_{complex}$ for

Co^{2+} (O_h) and Ni^{2+} (T_d) complexes having T ground terms:

(1) For calculation of μ_{ADF}, relation [8] was used.

(2) Relations [9 &10] were omitted.

(3) Total value of magnetic moment (μ_t) was calculated by the following relation[11 c]

$\boldsymbol{\mu_t = 2A|\lambda| /10Dq + \mu_{ADF}}$ ----------------------**[11c]**

A=1.5 for Ni^{2+} (T_d) and 1.4 for Co^{2+} (O_h) complexes.

(4) μ_{net} was calculated by [11a].

(5) g_t was calculated by [16] .

(6) t_{2g} electron delocalization was calculated by [18] or [18a].

(7) Delocalization constant (k) was calculated by the following relation [13a].

$\mathbf{k = 1 - (g_t - g_{iso})}$ --------------------------**[13a]**

(8) $\lambda_{complex}$ and the % covalent character were calculated by [14 & 15] respectively.

METHODOLOGY

After optimization of the complexes(42-43) by ADF 2010.02, the SW 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 Co^{2+} complexes and octahedral Ni^{2+} complexes. In Ni^{+2} tetrahedral complexes, LDA was replaced by GGABP*. All the complexes have Nysom* symmetry.

Complexes of Cobalt (II)

Co^{2+}, with three unpaired electrons and a quartet ground state, should show both the Zero Field Splitting (D) and Jahn-Teller effect. But in the four coordinate complexes like $[CoX_4]2^{\pm}$ (X= H_2O, F, Cl, Br, I, CNS), an almost tetrahedral symmetry was enforced. Also, the two high spin six coordinate complexes $[CoX_6]^{4-}$ (X= Cl, F) possessed an axial and nearly an axial symmetry respectively. Moreover, this software did not take an account of Zero Field Splitting. So, both these effects were neglected.

Only a few relevant papers on Reflectance and Magnetic (44-57) and ESR studies (58-62) of Co^{2+} complexes were reported. Theoretically calculated parameters obtained from the results of the software agreed well with their experimental values (53-54).

RESULTS

Each OUTPUT file of a complex gave values of two ESR (g_{11}, g_{22}, g_{33} and g_{iso}, product of g_n and a_{11},a_{22},a_{33},A_{ten})and three NQR(η, q_{11},q_{22},q_{33},NQCC) parameters along with its optimization parameters [geometry, dipole moment, bonding energy and total energy(Xc)].

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

Xc was made up from *LDA* and *GGA* components; each being further made up of Exchange and Correlation parts]. The bonding energy was computed as an energy difference between molecule and fragments. When the fragments were single atoms, they were usually computed as Spherically Symmetric and Spin-Restricted. This, usually, did not represent the true atomic ground state (42-43).

Tables: 1. 1 and1.1 A give the optimization parameters of cobalt metal and all the Co^{2+} complexes. Tables: 1.2 -1.3 give values of all the five ESR and NQR parameters, verification of Laplace equation and (η) for four and six coordinate Co^{2+} complexes respectively. Table: 1 .2 A and 1.3A give g_{iso}, A_{ten} and Q values along with contributions from their respective factors. They also give contribution from the fourth factor called interaction of nuclear magnetic moment with external magnetic field factor **(I)** into H^ along with ΔE_{hf} ($\approx 0.5\ A_{ten}$) values for both the four and six coordinate Co^{2+} complexes respectively. Tables: 1.4, 1.4 A and 1.5 contain magnetic parameters of four and six coordinate Co^{2+} complexes as calculated by applying the results from ESR and Reflectance techniques.

DISCUSSION

The necessity, the originality, the relevance, the objective of present work and how it moved the body of scientific knowledge forward had already been explained in our previous communication. We could successfully calculate/correlate 14 parameters of the four techniques in 36 $Ti^{2+,3+}$, $V^{+2,3+,4+}$ and Cr^{3+} complexes(63).

The discussion was divided into two parts:

[l] Calculation of ESR and NQR parameters

(a) Effective Spin Hamiltonian (H^)

(i) The four complexes $[CoX_4]^{2-}$(X=F, Cl, Br, I) were of T_d symmetry while both $[Co\ (OH_2)_4]^{2+}$ and $[Co(NCO)_4]^{2-}$ complexes possessed C_1 symmetry. But in both these types of complexes, the software gave nearly the same values of **g.** Also, none of them would obey the conditions of axial symmetry. So, for all these six complexes, the H^ was calculated by [3].

(ii) $[CoF_6]^{4-}$ and $[CoCl_6]^{4-}$ with point groups $D_{\infty h}$ and D_{6h} respectively had axial symmetry with (a) Two of the three **g** called $\mathbf{g}_{\perp}$ had the same values and third of higher value was called $g_{\parallel}$ (b) Two **a** parameters called $\mathbf{a}_{\perp}$ were of the same value and third of higher value was named $\mathbf{a}_{11}$. (c) Two of the three **q** parameters were of the same value (d) η=0.

Relation [2] was used to calculate H^.[S_x=S_y=S_z=3/2; I_x=I_y=I_z=3.5 and g_n= 1.3220000]. Individual contributions from four factors in the total value of H^ for the eight Co^{2+} complexes are given in small brackets of horizontal row shown at the bottom (→) in Tables: 1.2A and 1.3A.

(b) Relation [7] was used for the verification of Laplace Equation (Table: 1.2-1.3) while parameters such as η and ΔE_{hf} (Tables: 1.2 A-1. 3A) were calculated by [5, 4] respectively.

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

(a) μ_{ADF} and μ_t parameters: The discussion was divided into two parts:

(i) Four Coordinate Complexes: Table:1.4 gave values of magnetic moments due to spin orbit coupling (μ_{ADF}) as calculated from g_{iso} values by applying [8].This moment arose from an intermixing of ground $^4A_2$ term of Co^{2+} with its immediately higher in energy $^4T_2$ term which made $^4A_2$ to acquire some T character. Contribution of magnetic moment from Second Order Zeeman Effect ($\mu_{t.i.p}$) was calculated by [9 &10]. The former gave $\chi_{t.i\ p.}$ while the latter gave $\mu_{t\ i\ p.}$ Finally, the sum of μ_{ADF} and μ_{tip} resulted in μ_t which was calculated by [11].

(ii) Six Coordinate Complexes: Table:1.5 contained μ_t values of two high spin six coordinate Co^{2+} complexes as calculated by a different relation [11c] because the ground term in octahedral Co^{+2} complexes was $^4T_{1g}$ while its tetrahedral complexes had $^4A_2$ ground state.

(b) Calculations of t_{2g} electron delocalization, its constant (k), $\lambda_{complex}$, % covalent character, μ_{net} and g_t

(i) Four Coordinate Complexes: [Table: 1.4A] First we calculated total molar magnetic susceptibility (χ_t) by applying [12].Then (k) was calculated by [13].The term 8 N $\beta^{2/}$10Dq, called the Second Order molar magnetic susceptibility, i.e. $\chi_{t.i.p}$ had already been calculated by [9] (Table: 1.4). Knowing (k), we could calculate $\lambda_{complex}$ by [14]. It gave the weight by which $\lambda_{Co}{}^{2+}$ (-172.0 cm^{-1}) was reduced to give $\lambda_{complex}$ on the formation of Co^{2+} complexes. This decrease was due to delocalization of electron cloud which had brought about covalence in metal-ligand bonds (64). The % covalent character was calculated by [15].The g_t values of complexes were calculated by [16] .They were found in agreement with g_{eff}. The g_{eff} values, in turn, were calculated from 10Dq values of complexes given by reflectance spectra by [17]. Similarly, t_{2g} electron delocalization was calculated either indirectly from g_t values [18] or from g_{eff} [18a] . The values obtained from both these methods would almost agree. Lastly, μ_{net} was calculated by [11a]. It was noticed that (k) did not agree well with Nephelauxetic Ratio (β_{35}) in tetrahedral Co^{2+} complexes. On the contrary, the $\lambda_{complex}$ as calculated by [14] as well as its value obtained from reflectance spectral method agreed well with each other (53-54). This difference in (k) and (β_{35}) values was due to the fact that in tetrahedral Co^{2+} complexes, the lowest energy band (ν_1) , being so low in energy would not fall in u v.-vis. region (≅300-1000 nm). In such cases, (β_{35}) was calculated from the ratio of ν_2 and ν_3 bands. Both these bands had vibration character i.e. were quite broad and errors occurred in locating the exact positions of their λ_{max} values.

(ii) **Six Coordinate Complexes:** With negligible t_{2g} electron delocalization, parameters like g_t, $\lambda_{complex}$, (k) and the % covalent character could not be calculated.

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

Sum of orbital energies = -78854.221
Total energy = - 134234.270
Kinetic energy = 136350.812
Nuclear attraction energy = - 346177.790
Electron repulsion energy = 57226.702
Exchange energy = - 5539.960

For Co nucleus I =3.5 and g_n = 1.322000

Table: 1.1 A. Optimization Parameters of Co(II) Complexes

Complex	Geometry	Dipole moment	Bonding Energy (Decomposition)	Total Energy(X c) LDA(Exchange; Correlation)
$[CoF_4]^{2-}$	T_d	2.7	-2573.04	-250917.02 -238058.29; -12858.73
$[CoCl_4]^{2-}$	T_d	6.6	-2084.67	-430649.46 -410563.30; -20086.16
$[CoBr_4]^{2-}$	T_d	≈0.0	-3139.39	-1085306.75 -1045787.41; -39519.34
$[CoI_4]^{2-}$	T_d	4.8	-26294.47	-2001076.20 -1941276.42; -59799.77
$[Co(NCS)_4]^{2-}$	D_{2d}	≈0.0	-8559.48	-518460.69 -490659.48; -27801.20
$[Co(OH_2)_4]^{2+}$	C_1	4.1	-4399.88	-233654.72 -221393.81; -12260.92
$[CoF_6]^{4-}$	$D_{\propto h}$	0.0	737392.60	-301140.38 284914.72; -16225.66
$[CoCl_6]^{4-}$	D_{6h}	0.0	223.55	-571102.89 -544022.47; -27080.41

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

Complex	g values	$g_{n.}$ a & (A_{ten})	q & (Laplace)	NQCC & (η)
$[CoF_4]^{2-}$ T_d	2.160893 2.154175 2.152548 g_{iso}2.15587	$0.234196.10^2$ $0.117327.10^2$ $0.162654.10^1$ ($0.122596.10^2$)	$-0.364296.10^0$ $0.616109\ .10^{-1}$ $0.307685.10^0$ (0.00)	$-0.152584.10^2$ (0.6682)
$[CoCl_4]^{2-}$ T_d	2.162156 2.161934 2.145083 g_{iso}2.156391	$0.386583.10^2$ $0.381700.10^2$ $0.275109.10^2$ ($0.347798.10^2$	$-0.131999.10^0$ $-0.103871.10^0$ $0.235869.10^0$ (≅ 0.0)	$0.99065.10^1$ (0.11925)
$[CoBr_4]^{2-}$ T_d	2.175937 2.175937 2.175937 g_{iso}2.175937	$0.473101.10^2$ $0.473101.10^2$ $0.473099.10^2$ ($0.473100.10^2$)	$-0.389817.10^{-2}$ $0.194723.10^{-2}$ $.195093.10^{-2}$ (≅ 0.0)	$-0.163723.10^0$ (0.00095)
$[CoI_4]^{2-}$ T_d	2.217141 2.207908 2.172734 g_{iso}2.199261	$0.854897.10^2$ $0.729583.10^2$ $0.479297.10^2$ ($0.687925.10^2$)	$-0.\ 598451.10^0$ $0.864913\ .10^{-1}$ $0.511960.10^0$ (≅ 0.0)	$-0.251349.10^2$ (0.71095)
$[Co(NCS)_4]^{2-}$ D_{2d}	2.134501 2.134500 2.106184 g_{iso}2.125062	$0.313784.10^2$ $0.313785.10^2$ $0.121313.10^2$ ($0.249627.10^2$)	$-0.208031.10^{-1}$ $-0.931947.10^{-2}$ $0.301225.10^{-1}$ (0.00)	$0.126515.10^1$ (0.38123)
$[Co(OH_2)_4]^{2+}$ C_1	2.141408 2.109295 2.105068 g_{iso}2.11859	$0.267219.10^2$ $-0.175043.10^2$ $-0.334591.10^2$ ($-0.80805.10^1$)	$-0.584275.10^0$ $-\ 0.293892.10^0$ $0.878167.\ 10^0$ (0.00)	$0.390271.10^2$ (0.54997)

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

Complex	(**g** contribution)	***A_{ten}**&(**a** contribution)	**Q**& (**Q** contribution)	**I**
$[CoF_4]^{2-}$ →	(2.155872) (4.525 H_0)	9.274 (48.686)	-15.258 (-186.915)	---- (0.00353H_0)
$[CoCl_4]^{2-}$ →	(2.15639) (4.526 H_0)	26.308 (138.117)	9.907 (121.355)	--- (do)
$[CoBr_4]^{2-}$ →	(2.174937) (4.566H_0)	35.787 (187.882)	-0.164 (-2.009)	--- (do)
$[CoI_4]^{2-}$ →	(2.199261) (4.617Ho)	52.037 (273.194)	-25.135 (-307.903)	--- (do)
$[Co(NCS)_4]^{2-}$ →	(2.125062) (4.460H_0)	18.883 (99.136)	1.265 (15.496)	--- (do)
$[Co(OH_2)_4]^{2+}$ →	(2.11859) (4.447H_0)	-6.112 (-32.088)	39.027 (478.082)	--- (do)

*$\Delta E_{h\,f} \approx 0.5\ A_{ten}$

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

Complex	g values	$g_{n.}$ a &(A_{ten})	q & (Laplace)	NQCC & (η)
$[CoF_6]^{4-}$ $D_{\propto h}$	ll 2.486623 ⊥2.063879 ⊥2.062261 $g_{iso.}$ 2.20425	ll $0.155012.10^3$ ⊥$0.151297.10^3$ ⊥$0.147560.10^3$ ($0.152290.10^3$)	$-0.773482.10^1$ $0.377646.10^1$ $0.395836.10^1$ (0.00)	$-0.324862.10^3$ (0.00)
$[CoCl_6]^{4-}$ D_{6h}	ll 2.001142 ⊥2.107973 ⊥2.107973 g_{iso}.2.07236	ll$-0.227948\ .10^3$ ⊥ $0.441221.10^2$ ⊥$0.441215.10^2$ ($-0.465681.10^2$)	$-0.347481.10^1$ $0.173740.10^1$ $0.173741.10^1$ (0.00)	$-0.145922.10^3$ (0.02352)

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

Complex	(**g** contribution)	***A**$_{ten}$& (**a** contribution)	**Q**(**Q** contribution)	**I**
$[CoF_6]^{4-}$ →	---- $(5.22H_{ll} + 8.66H_{\perp})$	115.197 (1814.353)	-324.862 (568.509)	--- $(0.00353H_0)$
$[CoCl_6]^{4-}$ →	------ $(4.20H_{ll+}8.85H_{\perp})$	-35.225 (554.794)	-145.922 (255.364)	--- (do)

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

.

Table: 1.4. Reflectance & Magnetic Parameters of Co (II) Four Coordinate Complexes

Complex ($^4A_2$)	**$g_{iso.}$**	**μ_{ADF} [8]**	**10Dq(cm^{-1})**	**$\chi_{tip}10^{-6\ erg}$ [9] [μ_{tip}] [10]**	**μ_t[11]**
$[CoF_4]^{2-}$	2.15587	4.175	3600.0$^{(65)}$	579.466 [0.359]	4.534
$[CoCl_4]^{2-}$	2.15639	4.176	3125.0 $^{(53)}$	667.468 [0.414]	4.590
$[CoBr_4]^{2-}$	2. 1759	4.214	2800.0$^{(53)}$	744.942 [0.462]	4.676
$[Co\ I_4]^{2-}$	2.19926	4.259	2650.0 $^{(53)}$	787.109 [0.488]	4.747
$[Co(NCS)_4]^{2-}$	2.13197	4.129	4550.0 $^{(54)}$	458.426 [0.284]	4.413
$[Co(OH_2)_4]^{2+}$	2.11859	4.103	4445.0 $^{(65)}$	474.050 [0.297]	4.400

Table: 1.4 A. Calculations of Magnetic Parameters of Four Coordinate Co (II) Complexes

Complex ($^4A_2$)	**χ_t[12] cgs/mol**	**k[13] (β_{35})**	**$\lambda_{complex}$ [14] {Expt'l } (%c. c) [15]**	**g_t[16] g_{eff} [17]**	**$t_{2g\ electr\ delocal}$ [18] μ_{net} [11a]**
$[CoF_4]^{2-}$	8566.7	0.884 (---)	-151.80 {---} (11.6)	2.341 2.337	-0.0926 4.355
$[CoCl_4]^{2-}$	8777.0	0.858 (0.73)^{53}	-147.60 {145.0}$^{(53)}$ (14.2)	2.370 2.378	-0.1068 4.380
$[CoBr_4]^{2-}$	9111.8	0.864 (0.72)^{53}	-148.9 {152.0}$^{(53)}$ (13.4)	2.415 2.425	-0.120 4.444
$[Co\ I_4]^{2-}$	9789.0	0.881 (0.69)^{53}	-152.0 {155.0}$^{(53)}$ (11.9)	2.448 2.459	-0.1244 4.500
$[Co(NCS)_4]^{2-}$	8113.9	0.887 (0.71)^{54}	-152.8 {149.0}$^{(54)}$ (11.3)	2.279 2.269	-0.077 4.268
$[Co(OH_2)_4]^{2+}$	8041.0	0.858 (--)	-147.6 {---} (14.2)	2.269 2.266	-0.075 4.256

Table: 1.5. Reflectance & Magnetic Parameters of Co (II) Six Coordinate Complexes

Complex($^4T_{1g}$)	**$g_{iso.}$**	**μ_{ADF} [8]**	**10Dq(cm^{-1})**	**μ_t[11c]**
$[CoF_6]^{4-}$	2.20372	4.2685	8370.0 $^{(65)}$	4.326
$[CoCl_6]^{4-}$	2.07236	4.0131	7740.0 $^{(65)}$	4.075

Complexes of Nickel (II)

[A] Octahedral Complexes of Nickel (II)

Ni $^{2+}$ is a *non-Kramer* ion. With S=1, it had m $_j$ =0, ±1, ----- j ±1 states. Their degeneracy was completely removed even by the crystal field. So they gave only the singlet levels.

There were only a few cases where ESR spectra of Ni^{2+} octahedral complexes could be observed at room temperature(4-6) because its ground state m $_j$ =0 was separated from the first excited state (m $_j$ =1) by an energy more than the energy of microwave region. No doubt, the detailed studies were reported on Reflectance and Magnetic data of Ni^{2+} complexes (66-83), yet a further study was needed to know as to how the results thus obtained could be correlated with their ESR parameters.

RESULTS

Tables: 2.1 and 2.1A give optimization parameters of nickel metal and the Ni^{+2} complexes. Table: 2.2 gives values of the five ESR and NQR parameters, verification of Laplace equation and another parameter (η) for the six coordinate Ni^{2+} complexes. Table: 2 .2 A gives g $_{iso,}$ A$_{ten}$ and Q values and contributions from their respective factors. It also gives contribution from the fourth factor called interaction of nuclear magnetic moment with external magnetic field factor **(I)** into H^ as well as ΔE$_{hf}$ (≈0.5 A$_{ten}$) values.Tables:2.3-2.3A contain magnetic parameters of the six coordinate Ni^{2+} complexes as calculated by applying the results from ESR and reflectance techniques.

DISCUSSION

The discussion was divided into two parts:

[l] Calculation of ESR and NQR parameters

(a) Effective Spin Hamiltonian: All the eight Ni^{+2} complexes had nearly the same values of **g** parameters. Also, none of them obeyed all the conditions of axial symmetry. So relation [3] was applied to calculate H^ values for all.

[Put S_x=S_y=S_z=1; I_x=I_y=I_z=1.5 and g $_n$ = - 0.5000133].

The individual contributions from four factors in the total value of H^ were given in small brackets of horizontal row shown at the bottom (→) of each complex [Table: 2.2A].

(b) Relation [7] was used for the verification of Laplace Equation (Table: 2.2) and parameters such as η and Δ E$_{hf}$ (Tables: 2.2- 2. 2A) were calculated by [5, 4] respectively.

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

(a)Calculation of μ_{ADF} and μ_t: Table: 2.3 gave values of magnetic moments due to spin-orbit coupling (μ_{soc} or μ_{ADF}) as calculated from g$_{iso}$ by [8].These values were generally more than their respective $\mu_{so.}$ values. This was due to intermixing of ground $^3A_{2g}$ term of Ni^{2+} with its immediately higher in energy $^3T_{2g}$ term of same multiplicity. This made its $^3A_{2g}$ term to acquire some T character. The contribution from Second Order Zeeman Effect (μ_{tip}) was calculated by [9&10]. The former gave $\chi_{t.i.p.}$ and latter gave $\mu_{t\ i.p}$. Sum of μ_{ADF} and μ_{tip} was equal to the total magnetic moment (μ_t) [11]. As expected, the net magnetic moments (μ_{net}) of these complexes were somewhat more than their respective (μ_{so}) values.

(b)Calculation of t$_2$g electron delocalization constant (k), $\lambda_{complex}$ and % covalent character (Table: 2.3A): Total molar magnetic susceptibility (χ_t) and its constant (k) were calculated by [12, 13] respectively. The term 8 N β$^{2/}$10 Dq representing the Second Order molar magnetic susceptibility ($\chi_{t.\ i.\ p}$) had already been calculated [Table: 2.3]. $\lambda_{complex}$ was calculated by [14]. It gave the weight by which λ_{Ni} $^{2+}$ [-316.0 cm^{-1}] was reduced in Ni^{2+} complexes. This reduction was due to the delocalization of electron cloud which had brought about covalence (64) in metal-ligand bonds by intermixing of electron clouds of Ni^{2+} t_{2g} orbitals with ligand orbitals as both the metal ion and ligand orbitals were of suitable symmetry and comparable energies. The % covalent character was calculated by [15]. The calculated (k) values agreed well with Nephelauxetic Ratios (β_{35}) of Ni^{2+} complexes wherever reported in literature or were theoretically calculated from three reflectance spectral bands of the complexes (66, 83).

(c)Calculation of total value of g called g_t, t_{2g} electron delocalization and μ_{net} (Table: 2.3 A): Total value of g called g_t was calculated by [16] while the total magnetic moment (μ_t) was calculated by [11] .Theoretical g_t values were well in agreement with g_{eff} values as calculated by [17] from 10Dq values obtained from reflectance data. Same was the case of t_{2g} electron delocalization values. Whether they were calculated from g_t by [18] or were calculated from g_{eff} by [18a], their values were found to be in agreement. The μ_{net} was calculated by [11a].

Tables: 2.1.Energies (kJ mole^{-1}) of Ni

Sum of orbital energies = -85650.855
Total energy = -146522.795
Kinetic energy = 148997.799
Nuclear attraction energy = -352449.098
Electron repulsion energy = 62843.648
Exchange energy = -8809.705

For Ni nucleus I =1.5 and g_n = -0.500133

Table: 2.1A. Optimization Parameters of Ni (II) Six and Four Coordinate Complexes

Complex	Geometry	Dipole moment	Bonding Energy (Decomposition)	Total Energy(X c) LDA(Exchange; Correlation) *GGA (Exchange; Correlation)
$[NiF_6]^{4-}$	O_h	2.0	-699.73	-311829.82 -295271.10; -16558.72
$[NiCl_6]^{4-}$	O_h	≈0.0	-772.69	-581795.15 -554381.47; -27413.69
$[NiBr_6]^{4-}$	O_h	≈0.0	-2388.79	-1561745.48 -1505206.19; -56539.28
$[NiI_6]^{4-}$	O_h	6.4	-37428.45	2937304.80 -2850337.03; -86967.77
$[Ni(OH_2)_6]^{2+}$	C_2	0.2	-7653.81	-290192.62 -273882.70; -16309.92
$[Ni(NH_3)_6]^{2+}$	D_{6h}	3.3	-10642.07	-268017.73 -252525.60; -15492.13
$[Ni(CH_3NH_2)_6]^{2+}$	C_1	4.1	-19357.37	-349745.50 -327152.00; -22593.50
$[Ni(NH_3)_4(NCS)_2]$	C_1	3.6	-11907.34	-416671.52 -393337.87; -23333.64
$[NiCl_4]^{2-}$	T_d	≈0.0	-1640.45	-466091.81 -421452.42; -20425.59 -32966.80; 8753.00
$[NiBr_4]^{2-}$	T_d	0.2	-2616.69	-1145260.17 -1055442.60; -39840.49 -65427.18; 15450.11
$[NiI_4]^{2-}$	T_d	0.01	-25873.52	-2095578.08 -1952410.36; -60125.99 -104890.56; 21848.83
$[Ni(NCO)_4]^{2-}$	D_{2d}	≈0.0	-8417.00	-379370.66 -335934.08; -20905.54 -32485.35; 9954.31

*GGA (Exchange; Correlation) Energies=0.00 in the six coordinate Ni^{2+} complexes

Table: 2.2. ESR & NQR Parameters of Ni (2) Six Coordinate Complexes from SW

Complex	**g values**	**$g_{n.}$ a & (A_{ten})**	**q & (Laplace)**	**NQCC & (η)**
[NiF$_6$]$^{4-}$ O$_h$	2.121005 2.119440 2.118655 g_{iso}2.11970	$0.195006.10^{1}$ $0.770718.10^{0}$ $-0.339882.10^{0}$ ($0.793631.10^{0}$)	$-0\ .22256.10^{0}$ $0{\cdot}29675.10^{-1}$ $0.192889\ .10^{1}$ (≅ 0.0)	$-0.1335.10^{1}$ (0.733)
[NiCl$_6$]$^{4-}$ O$_h$	2.097238 2.097238 2.097238 g_{iso}2.097238	$-0.336828.10^{1}$ $-0.336829.10^{1}$ $-0.336828.10^{1}$ (- $0.336828.10^{1}$)	$-0.146305.10^{-2}$ $0.727382.10^{-3}$ $0.735673.10^{-3}$ (≅ 0.0)	-0.8778310^{-2} (0.00567)
[NiBr$_6$]$^{4-}$ O$_h$	2.091462 2.091462 2.09146 g_{iso}.2.09146	$0.235379.10^{1}$ $0.235379.10^{1}$ $0.235380.10^{1}$ ($0.235380.10^{1}$)	$-0.420010.10^{-2}$ $0.209288.10^{-2}$ $0.210722.10^{-2}$ (0.0)	$-0.252006.10^{-1}$ (0.00342)
[NiI$_6$]$^{4-}$ O$_h$	2.081882 2.079307 2.074749 g_{iso}2.078646	$0.155908.10^{2}$ $0.120592.10^{2}$ $0.163998.10^{2}$ ($0.146833.10^{2}$)	$-0\ .387073.10^{0}$ $-0.313423.10^{0}$ 0.7004910^{0} (0.0)	$0.41559.10^{2}$ (0.105)
[Ni(OH$_2$)$_6$]$^{2+}$ C$_2$	2.086347 2.085234 2.07790 g_{iso}2.083166	$0.102101.10^{2}$ $0.115758.10^{2}$ $0.373190.10^{1}$ ($0.850591.10^{1}$)	$-0.577827.10^{0}$ $-0.336062.10^{0}$ $0.913889.10^{0}$ (≅ 0.0)	$0.548333.10^{1}$ (0.26455)
[Ni(NH$_3$)$_6$]$^{2+}$ D$_{6h}$	2.054413 2.054023 2.052899 g_{iso}2.05378	$0.171309.10^{2}$ $0.166744.10^{2}$ $0.139415.10^{2}$ ($0.159156.10^{2}$)	$-0.226989.10^{0}$ $-0.671116.10^{-1}$ $0.294100.10^{0}$ (≅ 0.0)	$0.176460.10^{1}$ (0.54361)
[Ni(CH$_3$NH$_2$)$_6$]$^{2+}$ C$_1$	2.075579 2.057511 2.016589 g_{iso}2.049893	$0.933663.10^{1}$ $0.995775.10^{2}$ $-0.526478.10^{2}$ ($0.187554.10^{2}$	$-0.151384\ .10^{2}$ $-0.102075\ .10^{1}$ $0.161592.10^{2}$ (≅ 0.0)	$0.97161.10^{2}$ (0.87499)
[Ni(NH$_3$)$_4$(NCS)$_2$] C$_1$	2.071381 2.057440 2.046342 g_{iso}2.058388	$0.252515.10^{2}$ $-0.631391.10^{1}$ $0.64054.10^{1}$ (0.84476810^{1})	$-0.159011\ .10^{1}$ $0.42220.\ 10^{-1}$ $0.154789.10^{1}$ (≅ 0.0)	$-0.952734.10^{1}$ (0.947)

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

Complex	**g** $_{iso}$ (**g** contribution)	***A** $_{ten}$ (**a** contribution)	**Q** (**Q** contribution)	**---** (**I**)
[NiF$_6$]$^{4-}$ →	2.1197 (2.9663 H$_0$)	-1.587 (-2.381)	-1.335 (-3.004)	--- (-0.00057H$_0$)
[NiCl$_6$]$^{4-}$ →	2.097238 (2.935 H$_0$)	6.735 (10.104)	-0.009 (-0.020)	--- (do)
NiBr$_6$]$^{4-}$ →	2.091462 (2.927H$_0$)	-4.707 (-7.060)	(-0.025) (-0.056)	--- (do)
[Ni I$_6$]$^{4-}$ →	2.078646 (2.9089Ho)	-29.366 (-44.049)	41.559 (93.508)	--- (do)
[Ni(OH$_2$)$_6$]$^{2+}$ →	2.083166 (2.915 H$_0$)	-17.011 (-25.517)	5.483 (12.337)	--- (do)
[Ni(NH$_3$)$_6$]$^{2+}$ →	2.053778 (2.874H$_0$)	-31.830 (-47.745)	1.765 (3.971)	--- (do)
[Ni(CH$_3$NH$_2$)$_6$]$^{2+}$ →	2.049893 (2.8687 H$_0$)	-37.501 (-56.251)	97.161 (218.612)	--- (do)
]Ni(NH$_3$)$_4$(NCS)$_2$] →	2.05839 (2.8806 H$_0$)	-16.895 (-25.342)	-9.527 (-21.437)	--- (do)

$*\Delta E_{h\,f} \approx 0.5\ A_{ten}$

Tables: 2.3. Reflectance & Magnetic Parameters of Ni (2) Six Coordinate Complexes

Complex ($^3A_{2g}$)	$g_{iso.}$	μ_{ADF} **[8]**	**10Dq(cm^{-1})**	$\chi_{tip}10^{-6cgs}$ **[9]** [μ_{tip} **[10]**	μ_t**[11]**
$[NiF_6]^{4-}$	2.1197	2.998	11000.0 $^{(65)}$	189.62 [0.1609]	3.159
$[NiCl_6]^{4-}$	2.0973	2.966	9000.0 $^{(65)}$	231.176 [0.1966]	3.163
$[NiBr_6]^{4-}$	2.091	2.959	10000.0$^{(65)}$	208.584 [0.177]	3.136
$[Ni\ I_6]^{4-}$	2.0787	2.938	8500.0 $^{(65)}$	245.392 [0.2082]	3.147
$[Ni(OH_2)_6]^{2+}$	2.083	2.946	8500.0 $^{(66)}$	245.392 [0.2082]	3.154
$[Ni(NH_3)_6]^{2+}$	2.0538	2.905	10800.0 $^{(66)}$	194.00 [0.1646]	3.070
$[Ni(CH_3NH_2)_6]^{2+}$	2.0499	2.900	10000.0$^{(66)}$	208.584 [0.1769]	3.077
$[Ni(NH_3)_4(NCS)_2]$	2.0584	2.911	10750.0$^{(66)}$	194.03 [0.1646]	3.076

Table 2.3A. Other Magnetic Parameters of Six Coordinate Ni(II) Complexes

Complex ($^3A_{2g}$)	χ_t**[12]** 10^{-6} **cgs**	**k[13]** (β_{35})	$\lambda_{complex}$**14]** **(%c. c)[15]**	g_t**[16]** [g_{eff}]**[17]**	$t_{2\ g\ electr\ delocal}$ **[18]** {μ_{net}}**[11a]**
$[NiF_6]^{4-}$	4159.2	0.93 (--)	-293.0 (7.0)	2.234 [2.213]	-0.057 {3.08}
$[NiC_{l6}]^{4-}$	4169.8	0.81 (----)	-255.2 (19.0)	2.237 [2.227]	-0.07 {3.07}
$[NiBr_6]^{4-}$	4098.9	0.85 (--)	-268.6 (15.0)	2.218 [2.214]	-0.064 {3.05}
$[NiI_6]^{4-}$	4127.7	0.80 (---)	-252.0 (20.0)	2.226 [2.237]	-0.074 {3.04 }
$[Ni(OH_2)_6]^{2+}$	4148.8	0.80 (0.89)$^{(66)}$	-252.0 (20.0)	2.231 [2.237]	-0.074 {3.05}
$[Ni(NH_3)_6]^{2+}$	3928.2	0.78 (0.84)$^{(66)}$	-246.5 (22.0)	2.171 [2.182]	-0.059 {2.99}
$[Ni(CH_3NH_2)_6]^{2+}$	3946.7	0.78 (0.87) $^{(66)}$	-246.5 (22.0)	2.175 [2.197]	-0.063 {2.99}
$[Ni(NH_3)_4(NCS)_2]$	3943.6	0.81 (0.83) $^{(66)}$	-256.0 (19.0)	2.175 [2.191]	-0.058 {2.99}

[B] Tetrahedral Complexes of Ni (II)

The presence of an extensive spin–orbit coupling in $^3T_1$ ground state of Ni^{2+} made *spin relaxation times* very small. So it became quite difficult to observe ESR spectra of four coordinate Ni^{2+} complexes $^{(83-89)}$. Of course, like octahedral Ni^{2+}complexes, numerous papers were reported on Reflectance spectral and Magnetic properties of Ni^{2+} tetrahedral complexes.

RESULTS

Table: 2.4 gives values of all the five ESR and NQR parameters, verification of Laplace equation and the parameter (η) for four coordinate Ni^{2+} complexes. Table: 2 .4 A gives g_{iso} , A_{ten} and Q values along with contributions from their respective factors .It also gives contribution from the fourth factor called interaction of nuclear magnetic moment with external magnetic field factor **(I)** into H^ as well as $\Delta E_{h\,f}$ ($\approx 0.5\ A_{ten}$) values for the four coordinate Ni^{2+} complexes. Tables: 2.5 and 2.5A contain magnetic parameters of four coordinate Ni^{2+} complexes as calculated by applying the ESR and Reflectance spectral results.

DISCUSSION

[l] Calculation of ESR and NQR parameters

(a) Effective Spin Hamiltonian H^

The complexes like $[NiX_4]^{-2}$(X= Cl, Br, I) belonged of T_d point group while the complex (X=NCO) had a D_{2d} symmetry. All these complexes had different values of parameters like **g** and **a**. So Relation [1] was applied to calculate their H^ (Table: 2.4 A).

(**b)** Relation [7] was used for the verification of Laplace Equation (Table: 2.4) and parameters such as η and $\Delta\ E_{hf}$ (Tables: 2.4- 2. 4A) were calculated by [5, 4] respectively.

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

(a) Calculation of μ_{ADF} and μ_t (Table: 2.5): μ_{ADF} was calculated from g_{iso} by [8] while μ_t was calculated by [11a] while the relation [11] was used to calculate the same parameter in Ni^{2+} octahedral complexes. It was due to the reason that Ni^{2+} had $^3T_1$ ground state in its tetrahedral complexes while it had $^3A_{2g}$ state in the octahedral complexes.Net magnetic moments (μ_{net}) of these tetrahedral complexes, as expected, were found to be some what more than the six coordinate complexes because of spin–orbit coupling.

[2(b)] Calculation of t_{2g} electron delocalization, its delocalization constant (k), $\lambda_{complex}$ and % covalent character (Table:2.5 A):Total value of g called g_t was calculated from the total magnetic moment by [16] .The average of the difference between g_t and g_{iso} with a negative sign gave t_{2g} electron delocalization parameter [18a]. It was, then, related to another parameter called t_{2g} electron delocalization constant (k) by [13a]. Again, the relations [18a] and [13a] used here were different from those of [18] and [13] relations as the two latter relations were used to calculate the same parameters respectively in octahedral Ni^{2+}complexes.This, again, was because of the difference in ground states of Ni^{2+} in its octahedral and tetrahedral geometries. The values of (k) as calculated by [13a] and the experimentally determined Nephelauxetic Ratios (β_{35}) of tetrahedral Ni^{2+} complexes (54a, 84) were given in Table ; 2.5 A** for a comparison. Lastly, the constant (k) was related to the covalent character in these complexes by [15].This covalence was brought about by intermixing of electron clouds of Ni^{2+} "**e"** orbitals with the ligand orbitals.

** If we look into the Table: 2.5 A, we find that the theoretical (k) values differ slightly from the experimental (β_{35}) values. It is, again, due to the fact that like Co^{2+} tetrahedral complexes, the lowest energy band (ν_1) in the tetrahedral Ni^{2+} complexes is also low lying in energy. So it does not fall in u v. - vis. region. The (β_{35}) parameter in such cases is calculated from the ratio of ν_2 and ν_3 bands. As both these bands have vibration character ,i.e. are quite broad and errors occur, invariably, in locating the exact positions of their λ_{max} values.

Tables: 2.4. ESR & NQR Parameters of Ni (2) Four Coordinate Complexes from SW

Complex	g values	$g_{n.}$ a & (A_{ten})	q &(Laplace)	NQCC& (η)
$[NiCl_4]^{2-}$ T_d	g_{zz} 2.518256 g_{yy} 2.14318 g_{xx} 2.13926 g_{iso}2.26690	$-0.217770.10^3$ $-0.566463.10^2$ $-0.115896.10^2$ ($-0.95335.10^2$)	$-0.869917.10^1$ $0.434935.10^1$ $0.434983.10^1$ (≅0.0)	$-0.521950.10^2$ (0.00006)
$[Ni\ Br_4\ ]^{2-}$ T_d	g_{zz} 2.147922 g_{zz} 2.097710 g_{xx} 1.879465 g_{iso}2.041699	$-0.101428.10^2$ $-0.286688.10^2$ $0.207999.10^3$ ($0.563956.10^2$)	$-0.866423.10^1$ $-0.501016.10^0$ $0.916525.10^1$ (≅0.0)	$0.549915.10^2$ (0.89067)
$[Ni\ I_4]^{2-}$ T_d	g_{zz} 2.114253 g_{yy} 2.109345 g_{xx} 2.036781 g_{iso}2.086793	$0.390727.10^2$ $-0.328458.10^1$ $0.242600.10^2$ ($0.200160.10^2$	$-0.448391.10^1$ $-0.166590.10^1$ $0.614982.10^1$ (≅ 0.0)	$0.368989.10^2$ (0.45823)
$[Ni(\ NCO)_4]^{2-}$ D_{2d}	g_{zz} 2.324534 g_{yy} 2.17492 g_{xx} 2.01550 g_{iso} 2.17165	$-0.103374.10^3$ $-0.231936.10^2$ $-0.212169.10^2$ ($-0.492614.10^2$)	$-0.766666.10^1$ - $0.465420.10^1$ $0.123209.10^2$ (≅ 0.0)	$0.739252.10^2$ (0.24450)

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

Complex	---- (**g** contribution)	**A_{ten*}** (**a** contribution)	**Q** (**Q** contribution)	---- (**I**)
$[NiCl_4]^{2-}$ →	--- (2.99 H_x +3.00H_y+3.52Hz)	190.665 (857.786)	-52.195 (-13.049)	--- (-0.00057H_0)
$[Ni\ Br_4\ ]^{2-}$ →	--- (2.63 H_x+2.936H_y+3.06Hz)	-112.788 (507.546)	54.992 (13.748)	--- (do)
$[Ni\ I_4]^{2-}$ →	---- (2.78 H_x+2.95H_y+2.959Hz)	-40.031 (180.140)	36.899 (9.225)	--- (do)
$[Ni(NCO)_4]^{2-}$ →	---- (2.82 H_x+3.04Hy+3.25Hz)	98.520 (443.340)	73.925 (18.481)	--- (do)

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

Tables: 2.5. Reflectance & Magnetic Parameters of Ni (II) Four Coordinate Complexes

Complex($^3T_1$)	**$g_{iso.}$**	**μ_{ADF} [8]**	**10Dq (cm^{-1})**	**μ_t [11c]**
$[NiCl_4]^{2-}$	2.2669	3.206	4090.0 (54a)	3.438
$[NiBr_4]^{2-}$	2.0417	2.888	3790.0(54a)	3.139
$[Ni\ I_4]^{2-}$	2.0868	2.951	3820.0 (54a)	3.118
$[Ni(NCO)_4]^{2-}$	2.1717	3.070	5060.0(84)	3.257

Tables: 2.5A. Calculation of Contributions from g, A, Q & I Factors in Total value of (H^)

Complex	**g_t[16]** **{g $_{iso}$}**	**t_{2g} el. del.[18a]** **{μ_{net} }[11a]**	**k[13a]** **{Exp'l β_{35}}**	**$\lambda_{complex}$[14]** **{% c.c. }[15]**
$[NiCl_4]^{2-}$	2.431 {2.2669}	-0.082 {3.356}	0.836 {0.76}(54a)	264.14 {16.4}
$[NiBr_4]^{2-}$	2.2196 {2.0417}	-0.089 {2.961}	0.82 {0.70}(54a)	259.12 {18.0}
$[Ni\ I_4]^{2-}$	2.2047 {2.0868}	-0.088 {3.000}	0.88 {0.73}(54a)	278.08 {18.0}
$[Ni(NCO)_4]^{2-}$	2.3033 {2.1717}	-0.066 {3.164}	0.86 {0.80}(84)	271.76 {12.3}

CONCLUSIONS

With certain commands, the ADF software gave five ESR and NQR parameters. These parameters were used to calculate nine other ESR, NQR, Reflectance and Magnetic parameters by the selective use of 23 relations. So these14 parameters of the four techniques were correlated in the 20 Co^{+2} and Ni^{+2} complexes without the help of any diagnostic instruments. Theoretically calculated values of these parameters were found to be fairly in agreement with their experimental values reported in the literature. The authors had already proved this fact in 36 $Ti^{2+,3+}$, $V^{2+,3+,4+}$ and Cr^{3+} complexes in the previous communication and hope to prove the same in forty five more complexes of 2nd and 3rd transition series metal ions in the forthcoming communication.

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