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Abnormal Magnetic Moment and Zero Field Splitting of Some Nickel (II) Complexes

Rajeev Ranjan[1], Navneet Sinha[2], Sahdeo Kumar[3], Chandra Mauleshwar Chandra[4], and Shivadhar Sharma[5]

[1,2,3,4,5] University Department of Chemistry, Magadh University, Bodh Gaya-824234, Bihar, India.

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ABSTRACT

Some complexes of Ni(II) have been prepared with 2-thio-3-acetyl hydantoin (TAHN) and 2-formyl pyridine thiosemicarbazone (FPTS). On the basis of elemental analysis and molar conductivity, the complexes have been formulated as NiL_2X_2*, where L = TAHN or FPTS and X =* Cl^-*,* Br^-*,* NCS^-*,* ClO_4^-*. The infrared spectra of complexes and free ligand reveal that the ligand TAHN is co-ordinated through sulphur and acetyl oxygen, while FPTS ligand co-ordinates through heterocyclic nitrogen and sulphur to Ni(II) metal ion. The magnetic moment of these complexes are found to be 3.20-3.25 B.M. The values are greater than* μ_S *value (2.828 B.M) corresponding to two unpaired electrons of a* d^8*-system. The appearance of four absorption bands in their electronic spectra reveal, the tetragonal distortion in the octahedral symmetry of complexes. The zero field splitting parameter(D) and the other crystal field parameters like* $Dq_{(xy)}$*,* $Dq_{(z)}$*, Dt have been calculated. The results show that, the tetragonal distortion parameter (Dt) increases in the order of* $NCS^- < Cl^- < Br^-$ *while the zero field splitting parameter (D) also increases in the same order for both the planer ligands.*

Key words **:-** *Heterocyclic nitrogen, Axial crystal field(*Dq_z*), Tetragonal distortion parameters.*

INTRODUCTION

The ground term ^3F of a d^8-system undergoes splitting due to octahedral (Oh) crystal field perturbation with ^3A_2g as the ground state cubic field term[1]. As it is orbitally non-degenerate, no orbital contribution is expected to the magnetic moment of octahedral Ni(II) complexes and generally it comes to be nearly 2.828 B.M corresponding to two unpaired electrons.[2,3] However several six co-ordinate complexes of Ni(II) with magnetic moment higher than expected (2.8 B.M) have been reported.[4-9] Such abnormal magnetic moment may arise due to mixing of several terms because of the lowering of symmetry by Jahn-Teller distortion. The departure of symmetry from perfect octahedron is generally not observed in Ni(II) complexes because, octahedral d^8 is not electronically degenerate, but the presence of different ligands in co-ordination sphere may also cause deviation from octahedral symmetry. According to Ballhausen, the combined effects of a non cubic field and the spin orbit coupling in six co-ordinate Ni(II) complexes lead to zero field splitting of the ground state cubic field term[10]. In the cubic field the ground state ^3A_2g is a three fold degenerate spin level. Its next excited state is ^3T_2g which is triply degenerate which under the perturbation of a tetragonal field, splits into a two fold orbital degenerate level and a singly degenerate one. Now the spin orbit coupling energy may be regarded as a perturbation which couples the ground state together with the excited states. Subsequently, the spin multiplate of the ground state experiences the splitting of the excited states. In consequence to this the triplet spin levels of ^3A_2g undergo a small splitting, which is called zero field splitting. The description of this class of distortion is subsequently in advance of the experimental facts[11-12]. We report here in the abnormal magnetic moment values of Six co-ordinate Ni(II) complexes with 2-thio-3-acetyl hydantoin and 2-formyl pyridine thiosemicarbazone and their zero field splitting.

EXPERIMENTAL

All the reagents used were of Anal. Grade procured from B.D.H. The ligand, 2-thio-3-acetyl hydantoin was prepared by the reaction of acetyl glycine and potassium thiocyanate whereby hydantoin separated as oil which instantly got solidified on stirring. It was recrystallised in ethanol and dried in desiccator. The other ligand i.e. 2-formyl pyridine thio semicarbazone was prepared by the method reported earlier[13]. The yellowish white solid was recrystallised from methanol. These two ligands were used for complexation with Ni(II) salts by refluxing the metal salt with ligands taken in 1 : 2 molar ratio in ethanol. The elemental analysis was carried out using Perkin-Elmer 2400 C.H.N elemental analyzer. The IR spectra of the ligand and complexes were recorded on Perkin-Elmer FTIR spectrometer spectrum-two using KBr disc technique. The electronic spectra of the complexes were recorded on Perkin-Elmer UV/Vis spectrometer Lambda 25. The magnetic moment of complexes was determined on Gouy balance at room temperature using mercury tetrathiocyanatocobaltate(II) as calibrant. The molar conductivity of complexes was determined in DMF solution of 10^{-3} M concentration on Elico Direct Reading Conductivity-meter.

RESULT AND DISCUSSION

The elemental analysis data and their molar conductivities values in DMF solution of 10^{-3} M concentration of ligand as well as their Ni(II) complexes have been given in table-1, on the basis of which the complexes were formulated as NiL_2X_2 where L is 2-thio-3-acetyl hydantoin or 2-formyl pyridine thiosemicarbazone and X is Cl^-, Br^-, NCS^-, ClO_4^-.

Table – 1 Found/(Calculated)

	Ligand/ complex	M	C	H	N	S	Cl/Br	λ ohm^{-1} cm^2 mol^{-1}	Experimental calculated μ(B.M)
	TAHN	—	38.12 (37.97)	3.78 (3.81)	17.68 (17.72)	20.20 (20.25)	—	—	—
	FPTS	—	47.00 (46.67)	4.00 (4.45)	30.0 (31.1)	17.64 (17.78)	—	—	—
1.	$Ni(TAHN)_2Br_2$	10.25 (10.97)	23.00 (22.44)	2.00 (2.24)	10.00 (10.47)	12.00 (11.96)	30.00 (29.92)	15	3.12/ (3.16)
2.	$Ni(TAHN)_2Cl_2$	13.00 (13.17)	27.50 (26.92)	3.00 (2.69)	13.00 (12.56)	14.03 (14.36)	16.00 (15.93)	14	3.23/ (3.15)
3.	$Ni(TAHN)_2(NCS)_2$	12.00 (11.96)	30.26 (29.35)	2.50 (2.69)	17.00 (17.12)	25.98 (26.08)	—	18	2.99/ (3.4)
4.	$Ni(TAHN)_2(ClO_4)_2$	11.25 (11.51)	24.21 (23.54)	2.00 (2.35)	10.20 (10.98)	12.62 (12.55)	14.00 (13.93)	142	Diamagnetic
5.	$Ni(FPTS)_2Br_2$	10.00 (10.14)	30.20 (29.00)	2.90 (2.76)	19.13 (19.35)	11.12 (11.00)	27.24 (27.65)	15	3.20 (3.199)
6.	$Ni(FPTS)_2Cl_2$	12.00 (11.98)	35.12 (34.30)	3.20 (3.27)	22.32 (22.87)	13.51 (13.07)	14.00 (14.49)	16	3.16 (3.156)
7.	$Ni(FPTS)_2(NCS)_2$	11.00 (10.97)	36.35 (35.90)	3.00 (2.99)	25.89 (26.18)	23.48 (23.94)	—	17	3.15 (3.16)
8.	$Ni(FPTS)_2(ClO_4)_2$	10.80 (10.60)	31.15 (30.30)	2.42 (2.90)	20.00 (20.20)	11.00 (11.56)	12.24 (12.82)	145	Diamagnetic

The molar conductivity values of complexes fall in between 14-18 ohm^{-1} cm^2 mol^{-1} except two complexes i.e. complex no. (4) and (8) which exhibit comductivity value 142 and 145 $ohm^{-1}cm^2mol^{-1}$ respectively. It is indicative of the fact that these two complexes are 1 : 2 electrolyte while the rest complexes are non electrolyte in nature.[14-15] Out of cumbersome spectra of ligands and complexes, the important bands of interest are interpreted here. The free ligand, 2-thio-3-acetyl hydantoin absorbs strongly at 3270 cm^{-1} due to ν_{N-H} stretching vibration. In complexes it does not show considerable change in its absorption frequency, which confirms the non co-ordination through 'N' of the N–H group to the metal ion.[16–17] The absorption due to $\nu_{C-\overset{\overset{C}{|}}{N}-C}$ moiety of the free ligand occurs at 1180 cm^{-1} which remains almost intact in the IR spectra of complexes indicating the non-involvement of other endocyclic 'N' in co-ordination. In the region of 1600–1750 cm^{-1} the free ligand exhibit two absorption band i.e. one very strong at 1740 cm^{-1} and other strong at 1690 cm^{-1}. The $>C=O$ group of acetyl group must absorb at higher frequency in respect of the other $>C{=}O$ group of the ligand due to +I effect of $-CH_3$ group to $>C{=}O$ of acetyl group.[18-20] The other band at 1690 cm^{-1} may be due to vibrational frequency of $>C{=}O$ group attached to hydantoin ring. The band at 1690 remains unchanged in complexes while the band at 1740 cm^{-1} gets red shifted in the IR-spectra of complexes indicating co-ordination through acetyl oxygen to Ni(II). The other major change is observed in the absorption frequency of $V_{>C=S}$ which shifts from 1450 cm^{-1} in free ligand to nearly 1400 cm^{-1} in IR spectra of complexes, which is indicative of co-ordination through thionyl sulphur.[21-23] Thus the first ligand i.e. 2-thio-3-acetyl hydantoin behaves as neutral bidentante, co-ordinating through acetyl carbonyl oxygen and thione sulphur forming six membered chelate ring. The other ligand 2-formyl pyridine thiosemicarbazone absorbs strongly at 3440 cm^{-1}, 3270 cm^{-1} and 3163 cm^{-1} due to $\nu_{\mathrm{asym\,NH_2}}$, $\nu_{\mathrm{sym\,NH_2}}$ and $\nu_{(\mathrm{NH+NH_2})}$ respectively.[24-27] In the spectra of complexes there is no considerable change in these absorption frequencies of free ligand. It shows that neither $-NH$ nor $-NH_2$ takes part in the co-ordination to the metal ion. The absorption band at 825 cm^{-1} due to $V_{>C=S}$ stretching vibration of the free ligand is found to have undergone red shift and appears at 740–770 cm^{-1} in the spectra of complexes. At the same time the combination band appearing at 1470 and 1300 cm^{-1} in free ligand due to $V_{>C=S} + \nu_{\mathrm{CN}} + \nu_{\mathrm{NH_2}}$ are found to have moved to slightly higher frequencies in all the four complexes. These facts predict the involvement of sulphur of the ligand in co-ordination to the Ni(II) ion. The pyridine ring vibrations occurring at 990, 600 and 400 cm^{-1} in the free ligand undergo significant positive shift which indicate conclusively the co-ordination of ligand takes place via pyridine ring nitrogen.[28-29] The aforesaid facts, thus reveal that the ligand, 2-formyl pyridine thiosemicarbazone acts as a neutral bidentate ligand co-ordinating through sulphur and heterocyclic nitrogen. The co-ordination through oxygen and sulphur in the complexes of first ligand and through nitrogen and sulphur in that of the second ligand is further confirmed by the appearance of some new bands in the spectra of complexes. The bands appearing at 500-525 cm^{-1} are assigned to $□_{\mathrm{Ni-O}}$ and bands at 450–455 cm^{-1} are assigned to $□_{\mathrm{Ni-N}}$ absorption frequency while the bands appearing at 350–370 cm^{-1} are assigned to $□_{\mathrm{Ni-S}}$ absorption frequency.[30-33] In the complexes number (1) (2) (5) and (6), two new bands of weak intensity appear at 275 cm^{-1} and 300 cm^{-1} which confirm the co-ordination through Br^- and Cl^- respectively in these complexes. In complexes no. (3) and (7) the new bands appearing at 2083 cm^{-1} and 800 cm^{-1} shows the presence of NCS within their co-ordination sphere.[34] The complexes no. (4) and (8) display a strong band at 1100 cm^{-1} which is indicative of the ionic nature of the ClO_4^- ion in the complex. Vibrational band at 900 cm^{-1}, indicative of co-ordinated ClO_4^- is not observed in the IR spectra of the complexes which supports our assertion that the perchlorate ion is present as free ion.[35-36]

MAGNETIC MOMENT AND ELECTRONIC SPECTRA

The magnetic moment values of complexes are found 2.99 to 3.23 B.M. at room temperature while the complexes no. (4) and (8) are found diamagnetic. The □ values are higher or abnormal in respect to $□_s$ value corresponding to two unpaired electrons in octahedral Ni(II) complexes. The higher values of $□_{\mathrm{effective}}$ of each complexes predict them to be a tetrahedral geometry where there is appreciable orbital contribution from $^3T_{1g}$ ground state of ^3F term of d^8-system. But on the basis of elemental analysis, IR-spectra and molar conductivity values, the complexes are found six co-ordinate for which the ground state ^3F of d^8-system is $^3A_{2g}$, which is orbitally non degenerate. Hence it neither contributes to the magnetic moment to octahedral Ni(II) complexes nor does it splits by field of lower symmetry. However it has $^3T_{2g}$ as its next excited state which is orbitally triply degenerate. Under such circumstances, Ballhausen[10] suggested that the strong spin orbit coupling promotes the spin orbit components of the triply degenerate excited state interact with the spin component of the ground state. This results in the splitting of the triplet spin state of $^3A_{2g}$ and triplet orbital degeneracy of $^3T_{2g}$. The extent of splitting of the triplet spin state of $^3A_{2g}$ is called zero field splitting represented by 'D' while the extent of splitting of $^3T_{2g}$ is the measure of tetragonal distortion represented by K_1. The two splitting factors are correlated by $D = 9.K_1.□^2/□^2$, where □ = 10 Dq and □ is spin orbit coupling constant, which is 315 cm^{-1} with negative sign[37]. Due to spin orbit coupling the $□_{\mathrm{effective}}$ is given by, $□_0(1-□\ □\ □/□)$ where □ = 4 for high spin Ni(II) complexes, □ = 10 Dq and $□_0 = □_{\mathrm{spin}}$ only. This explains as to why the $□_{\mathrm{effective}}$ values of Ni(II) complexes no. (1), (2), (3), (5),

(6) and (7) are higher than spin only value.[38] The complexes no. (4) and (8) display three absorption bands in their electronic spectra which is indicative of square planer symmetry around Ni(II) in these two complexes. In their true C_{2V} symmetry, these bands may be assigned to the following spin allowed transitions $\square_1({}^1B_{1g} \leftarrow {}^1A_{1g})$, $\square_2({}^1A_{2g} \leftarrow {}^1A_{1g})$ and$\square$ $\square_3({}^1B_{2g} \leftarrow {}^1A_{1g})$[39-40]. The square planer geometry of these complexes is also supported by their diamagnetic character. The rest complexes display four bands in their electronic spectra which are indicative of axially distorted octahedral symmetry around Ni(II) in these complexes. Under D_{4h} symmetry these bands may be assigned to the following transitions.[37, 41]

$\square_1 = {}^3E_g{}^a \leftarrow {}^3B_{1g}$ 10 Dq – 35/4 Dt
$\square_2 = {}^3B_{2g} \leftarrow {}^3B_{1g}$ 10 Dq
$\square_3 = {}^3A_{2g} \leftarrow {}^3B_{1g}$ 10 Dq – 4 Ds – 5Dt
$\square_4 = {}^3E_g{}^b \leftarrow {}^3B_{1g}$ 10 Dq – 2Ds – 25/4 Dt

The values of electronic bands have been displayed in table (2).

Table – 2

Values of electronic spectral bands (in cm^{-1}).

	Complexes	$\square_1$	$\square_2$	$\square_3$	$\square_4$
(1)	$Ni(TAHN)_2Br_2$	8900	10700	18250	24000
(2)	$Ni(TAHN)_2Cl_2$	9200	10790	18300	24100
(3)	$Ni(TAHN)_2(NCS)_2$	9700	10880	18400	24900
(4)	$Ni(TAHN)_2(ClO_4)_2$	16050	20100	25000	—
(5)	$Ni(FPTS)_2Br_2$	9010	10800	18300	24200
(6)	$Ni(FPTS)_2Cl_2$	9300	10850	18600	24000
(7)	$Ni(FPTS)_2(NCS)_2$	9810	10920	18400	24800
(8)	$Ni(FPTS)_2(ClO_4)_2$	16200	20300	24900	—

$\square_1$ is the measure of the tetragonal character in complexes, $\square_2$ i.e. ${}^3B_{2g} \leftarrow {}^3B_{1g}$ however, is free from the influence of 'Ds' and 'Dt' and virtually it is the measure of the plane ligand field splitting parameter $Dq_{(x,y)}$. The axial distorition 'Dt' is calculated by Wentworth and Piper formula[42] i.e. $Dt = \frac{4}{7} Dq_{(xy)} - Dq_{(z)}$ or by 35/4 Dt = $\square_2 – \square_1$. $Dq_{(z)}$ is derived from the expression $Dq_{(z)} = (2\square\ \square_1 – \square_2)/10$. The zero field splitting parameter has been calculated using the expression.[43]

$$D = \frac{9.K_1}{\alpha^2}\left\{\frac{\mu_{eff.}}{\mu_0} - 1\right\}^2$$

The value of these parameters have been given in table-3.

Table – 3

Complexes	**$Dq_{(xy)}(cm^{-1})$**	**$Dq_{(z)}(cm^{-1})$**	**$Dt(cm^{-1})$**	**$K_1(cm^{-1})$**	**$D(cm^{-1})$**
$[Ni(TAHN)_2Br_2]$	1070	710	205.71	1800	13.16
$[Ni(TAHN)_2Cl_2]$	1079	761	181.71	1590	10.82
$[Ni(TAHN)_2(NCS)_2]$	1088	852	134.85	1180	8.03
$[Ni(FPTS)_2Br_2]$	1080	722	204.57	1790	12.18
$[Ni(FPTS)_2Cl_2]$	1085	775	177.14	1550	11.68
$[Ni(FPTS)_2(NCS)_2]$	1092	870	126.85	1110	8.11

CONCLUSION

The study reveals that the axial crystal field splitting parameter $Dq_{(z)}$ increases from Br^- to NCS^- in both the series of complexes i.e. $NCS^- > Cl^- > Br^-$. Tetragonal distortion parameter (Dt) however increases in the reverse order in both the series of complexes i.e. $NCS^- < Cl^- < Br^-$. The parameter 'K_1' related to the splitting of first excited term i.e.${}^3T_{2g}$ and zero field splitting parameter 'D' also increase in the same order.

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