

Synthesis and Studies on electronic spectra of Ni (II) Complexes with 3-hydroxy-2-Naphthalidene semicarbazone

Dr. Rajnikant

J.A.C.M. Inter College, Motihari

Abstract: The metal complexes have been Synthesised by allowing Ni-salts to catalyze the Condensation of 3-hydroxy-2-naphthaldehyde with semicarbazide hydrochloride in methanol. Electronic spectral analyses give valuable information about the geometry of complexes and hence its application is essentially needed The electronic absorption spectra of the Ni (II) complexes have been recorded in the range 200 nm to 845 nm. In this range only ligand absorption arising C = O group could be observed but except in few cases, no d-d band could be located due to high ligand absorption and expected low intensity of six coordinated Nickel (II) complexes. The complex in the present case exhibits two bands in the region 14000-19000 cm^{-1} and a third band near 24000 cm^{-1} . This spectral feature supports nearly octahedral environment of the donor atoms around the central metal ion.

Index Terms: 3- hydroxy-2-naphthaldehyde, Nickel salts, octahedral, semicarbazide hydrochloride, squareplanar, tetrahedral.

I. INTRODUCTION

The metal complexes have been Synthesized by allowing metal salts to Condense 3-hydroxy-2-Naphthaldehyde with semicarbazide hydrochloride in methanolic solution.

II. RESEARCH METHODOLOGY

Metal salts, aldehyde and semicarbazide hydrochloride + NiX_2 have been taken in the molar ratio 1 : 2 : 2. Alcoholic solutions have been used. Products separated out are filtered, washed with alcohol, dried and recrystallized. Analytical data and colours have been presented in Table.

III. RESULTS AND DISCUSSION

Table

Analytical data, color and decomposition temperature of ligand and metal complexes

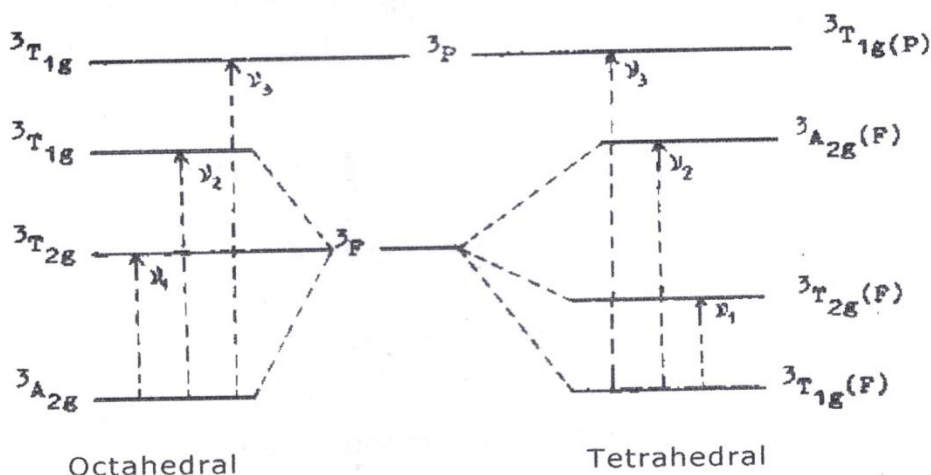
Electronic spectral analyses of complexes give valuable information about the geometry of complexes and hence its application is essentially needed. The electronic transitions occur, when electron within the molecules or ions move from one energy level to another. Therefore, absorption spectra reveal (a) which are the energy levels that are populated (the ground state) and which are the nearly empty energy levels into which electrons may be excited and (b) what are the Probabilities for the various possible absorptions to occur.

The absorption bands from the splitting of the d- orbitals^{1,2} are important since they supply bulk of valuable information for theory formulation, testing of oxidation states and geometry of complex molecules.

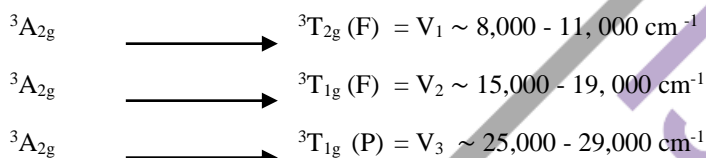
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Ni (II) COMPLEXES:

Nickel (II) (d^8) has 3F ground state term and 3p the next higher state term. The splitting of these states in weak crystal field is shown by the following diagram³



In octahedral, field the following three spin allowed transition are expected³.



These bands are spin - forbidden transitions and so their molar extinction coefficients lie between 1 and 3. Ballhausen⁴ calculated the energies of different states and measured the spectra of a large number of octahedral complexes and has generalized the results by the following relations.

$$\nu_1 = 10Dq$$

$$\nu_2 = 9/5 (10Dq)$$

$$\nu_3 = 17,000 + 6/5 (10Dq)$$

His experimental values were very much in agreement with calculated one. From above equations the ratio of ν_2/ν_1 is found to be 1.8 which according to Ballhausen is one of the reliable criteria of octahedral nickel (II) complexes. Jorgensen³, however, experimentally found that the ratio of ν_2/ν_1 lies in the range 1.6 to 1.8.

In octahedral complexes, the value of ν_1 is directly taken to be equal to ν_1 transition. To obtain a satisfactory agreement between experimental value and theory for energy of ν_1 and ν_2 bands, it is necessary to assume that 3F

3P term distance in the complexes is reduced from its free ion value⁵ for nickel (II). This separation is $15B$ where B is the Racah inter electronic repulsion parameter. The reduction of the B value is always taken to be as an evidence for extent of covalence character in the complex. The reduction of spin orbit coupling constant, as calculated from the magnetic date $[\mu_{eff} = \mu_s \cdot o (1 - 4\pi/10Dq)]$ has been attributed to the same effect⁶. The value for the complex is also related to the Lande 'g' factor by the equation.

$$g = 2(1 - 4\pi/10Dq)$$

when all the three spin allowed bands ν_1 , ν_2 and ν_3 are observed in the spectra of the octahedral nickel (II) complexes. The value of B in the complex ion can be computed from the diagonal sum rule⁷.

$$15B = \nu_2 + \nu_3 - 3\nu_1$$

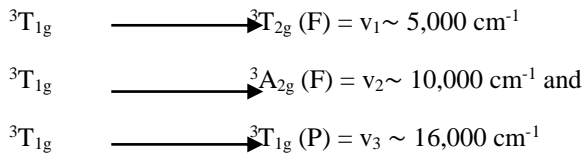
In case, when the ν_3 band is obscured by ligand transition or charge-transfer bands, the energy of Racah parameter B and ν_3 band are qualitatively evaluated from Tanabe and Sugano energy level diagram⁸.

Higginson et al.¹⁸ derived qualitative relation between energies of the different levels with those of energies of B parameters, either in strong or weak field approach the energies of the two components of ${}^3T_{1g}$ arising 3F and 3P terms are given by expression.

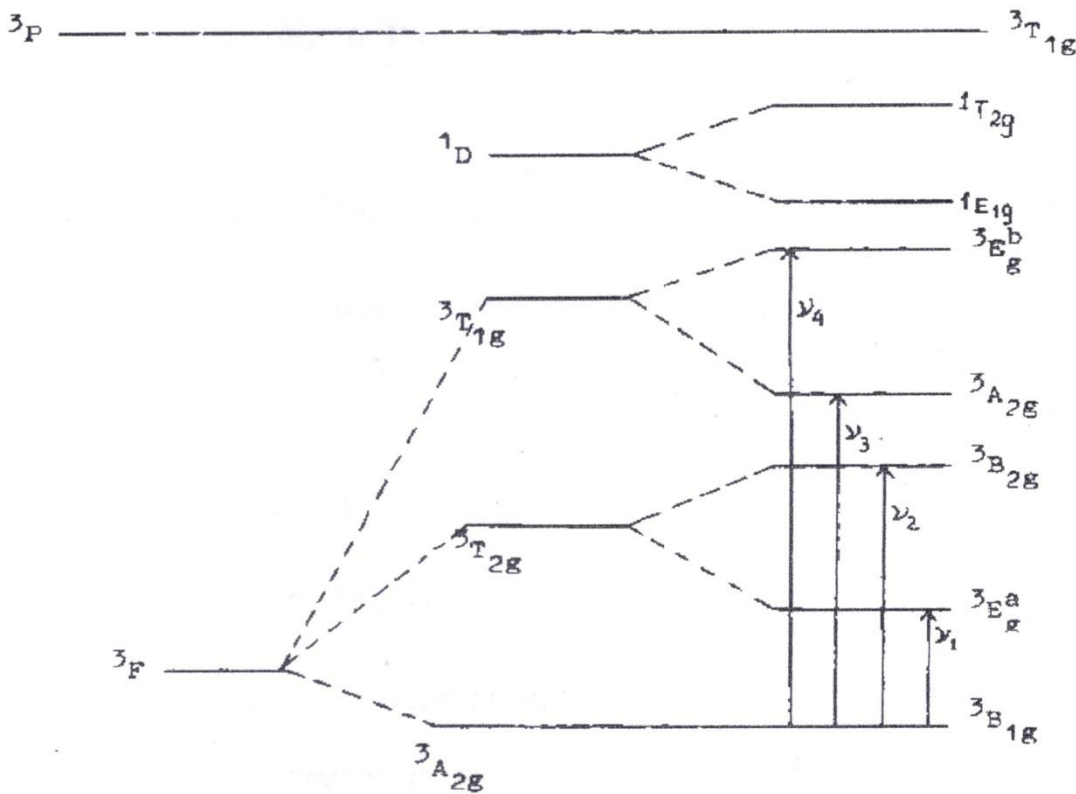
$${}^3t_{1g}(F,P) = (7.5B + 0.3) \pm [1/2(15B)^2 - 18B^2]^{1/2}$$

Here the energy of the ground state term being -1.2. Thus, knowing and B values, the energy of v_2 and v_3 bands can be calculated and compared with experimental one.

In tetrahedral symmetry $^3T_{1g}$ state term originating from 3F level becomes ground state. Thus, in tetrahedral field three spin allowed bands corresponding to transitions are observed.



The most striking difference between the spectra of tetrahedral and octahedral complexes is intensity of the bands at maxima. For tetrahedral complexes, the λ_{max} are in the range of 100 whereas those of octahedral complexes are due to lack of centre of symmetry where Laporte rule is somewhat broken down. In tetrahedral field the crystal field stabilization energy is only $8 Dq$, whereas, for octahedral complexes the crystal field stabilization energy is $12 Dq$. Therefore, tetrahedral field is less preferred than the octahedral one. Thus, many apparently tetrahedral complexes have really octahedral geometry. In most of the complexes the planar arrangement of ligands around nickel (II) ions are not usually achieved due to symmetry and size of the ligands, consequently distortion takes place leading to a D_{4h} symmetry. In the most of the mixed ligand octahedral complexes, the symmetry of the field is lower due to mixing of different ligands of different electro negativity, Polariability, size and nature. Hence, in a large number of cases it becomes difficult to analyze the spectra of the complexes confidently. In case of distorted octahedral complexes (D_{4d} symmetry), through the intensity of the absorption at maxima is not large, however, Splitting of the bands are encountered due to distortion of the field.



Free ion splitting in o_h , D_{4h} symmetry

Brubaker and Busch⁵ studied the spectral behavior of complexes with D_{4h} symmetry and calculated the energies of the different terms. They found that the order of energy for the transitions between various energy levels derived from 3F terms is as shown below:

Thus, in D_{4h} symmetry the following transitions are expected.

$$\begin{array}{ll}
 v_1 = {}^3E_g^a & \longrightarrow {}^3B_{1g} = 10Dq - 35/4 Dt. \\
 v_2 = {}^3B_{2g} & \longrightarrow {}^3B_{1g} = 10Dq. \\
 v_3 = {}^3A_{2g} & \longrightarrow {}^3B_{1g} = 18Dq - 4Ds - 5 Dt. \\
 v_4 = {}^3E_g^b & \longrightarrow {}^3B_{1g} = 18Dq - 2Ds - 25/4Dt. \\
 v_5 = {}^3T_{1g}(P) & \longrightarrow {}^3B_{1g} = 15B + 12Dq.
 \end{array}$$

The amount of splitting in the first band (${}^3A_{2g} \leftarrow {}^3T_{2g}$ of oh Symmetry) may be taken to be the measure of the degree of distortion ($35/4Dt.$) The degree of tetragonal distortion determines which of the states (${}^3E_g^a$ of ${}^3B_{2g}$) derived from ${}^3T_{2g}$ (OH symmetry) lies lowest. If the field due to axial ligands is weaker than that of those present in the xy plane, ${}^3E_g^a$ lies lowest and vice-versa. In both the cases the transition ${}^3B_{2g} \leftarrow {}^3B_{1g}$ determines the ligand field Para-meter and transition ${}^3E_g^a \leftarrow {}^3B_{1g}$ measures the tetragonal character of the complex.

For square planar diamagnetic complexes (d^8 system) three spin allowed transition arising from.

$$\begin{array}{l}
 d_{xy} \leftarrow d_{x^2-y^2}, \\
 d_z^2 \leftarrow d_{x^2-y^2}, \\
 \text{and } d_{xz}, d_{yz} \leftarrow d_{x^2-y^2}
 \end{array}$$

are expected. The spectra of planar complexes are interesting since the relative energies of the d-orbitals in square planar complexes are not known with certainty. The ordering of the energy of levels $x^2 - y^2$, xy , z^2 and xz , yz depends upon the nature of the - orbital's furnished by the ligand.

IV. ACKNOWLEDGEMENT

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