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STUDY ON MAGNETIC SUSCEPTIBILITY AND ELECTRONIC SPECTRA OF NI(II) COMPLEXES

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ABSTRACT:

The recent development of self assembled supramolecular chemistry can rationally design and synthesize metal-organic coordination polymers depending on the ligand geometry and coordination propensity of the metal ion. Organic ligand formed by reaction between the amino acids and aldehydes are good candidates to construct metal clusters more and more geometrically intriguing. Supramolecular structures derived from such ligands, for example, helices5, capsules6 and polymer clusters with different number of metal ions7, 8 have successfully obtained. Semicarbazone and thiosemicarbazone ligands are commonly used as ligands in coordination chemistry and are biologically active compounds. Their complexation with different metals enhances the biocidal activity of these molecules. These metal based complexes have attracted considerable interest in chemical and biological studies due to their potentially beneficial biological activity which may be attributed to formation of them chelates with metal ions.

MECCHANISM AND RESULTS:

Magnetic Susceptibility and electronic spectra of Ni(II) complexes

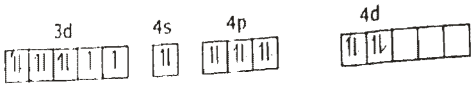
Magnetic Susceptibility of Ni(II) complexes

Ni(II) has 3d8 system. It can form :-

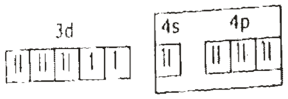
Octahedral having sp3d2 hybridisation.

Tetrahedral having sp3 hybridisation.

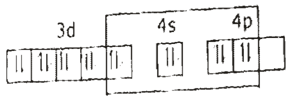
Square planar having dsp2 configuration.



sp^{3}d^2 outer orbital octahedral



sp^3 hybridisation



dsp2 hybridisation

All the electrons in 3d orbitals of Ni(II) ion are paired up and the square planar complexes are diamagnetic.

The spin only value indicates the magnetic moment of 2.84 B.M. for two unpaired electrons. The structure of the complexes may be either tetrahedral or outer orbital octahedral and are paramagnetic. If the complexes are diamagnetic, the configuration of the complex would be either square planar or trigonal bipyramidal. In most of the cases, the magnetic moment values fails to explain the exact geometry of the complexes although it can help in distinguishing between tetrahedral and octahedral configuration. In Ni(II) octahedral field the triplet t2g lies lower in energy compared to doublet eg and ground state may be written for Ni(II) as (t2g) 6 (eg) 2. All the t2g levels are filled and all eg levels are singly occupied. Hence it is non degenerate and not liable to John-Tellor-distortion.34 The electrons of eg levels are spin parallel and since there is no resultant orbital, the degeneracy of the d-orbitals is lifted and the magnetic moment value should be close to 2.8 B.M. (spin only value). However, the first excited triplet level (3-1,0 has essentially the configuration (t29) (eg)2. dyz orbitals retain rotational properties with respect to Z axis. This level therefore, has orbital angular momentum and the spin orbital coupling of Ni(II) is large enough to allow the mixing of this level with the lowest level to produce the true ground state. Hence the net angular moment is not completely 'quenched' by the ligand field and magnetic moment values are within the range of 2.83 B.M. - 3.4 B.M. which are independent of temperature indicating that Ni(II) complex, are octahedral.

The Stark pattern in tetrahedral complex is inverted and d-orbitals are split into a lower doublet (eg) dx2, y2 and dz2 and upper triplet (t29) dxy, dxz, dyz. There is three fold degeneracy which leads to two important consequences :-

In '2, level there are odd electrons partially distributed between dxz and dyz orbitals which still retain their degeneracy and their rotational properties with respect to Z axis.

The orbital angular moment is accordingly not quenched by ligand field and thus moment normally found for tetrahedral Ni(II) complexes are in the range of 3.5 B.M. - 4.2 B.M. and are temperature dependent.

C.K.J. Jorgensen35 reported the magnetic moment values of several octahedral complexes of Ni(II). These values are within the range of 3.13 B.M. - 3.28 B.M.

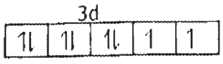
In the present investigation the magnetic moment value of Ni(II) complexes has been found in the range 3.05 to 3.18 B.M. at 25°C. These values are in accordance with octahedra129.30'36 complexes. The magnetic moment value of Ni(II) has been tabulated in Table 1

Table – 1 Magnetic moment value of the Ni(II) complexes of the type [Ni(MPQS)2X2] and [Ni(MPQT)2X2]

Compounds	Ileff B.M.	Temperature
[Ni(MPQS)2C12]	3.05	295°K
[Ni(MPQT)2Cl2]	3.16	295°K
[Ni(MPQS)2Br2]	3.07	295°K
[Ni(MPQT)2Br2]	3.11	295°K
[Ni(MPQS)2I2]	3.12	295°K
[Ni(MPQT)2I2]	3.08	295°K
[Ni(MPQS)2(NO3)2]	3.09	295°K
[Ni(MPQT)2(NO3)2]	3.13	295°K
[Ni(MPQS)2(CI04)2]	3.10	295°K
[Ni(MPQT)2(C104)21	3.06	295°K

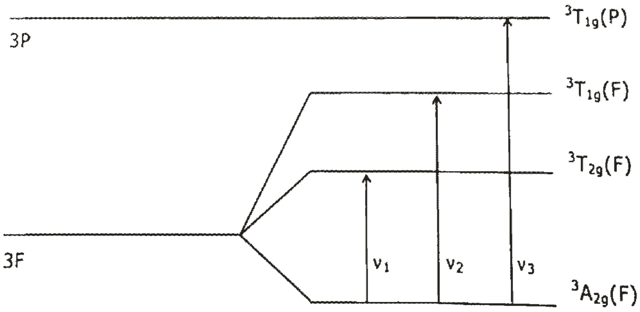
Electronic Spectra of Ni(II) Complexes:

In order to decide whether the complexes of Ni(II) are tetrahedral or octahedral, it will be assumed that weak crystal field is a good approximation for such complexes containing a metal ion in +2 oxidation state e.g.:- Ni(II) has 3d8 configuration. Its ground term can be written as :-

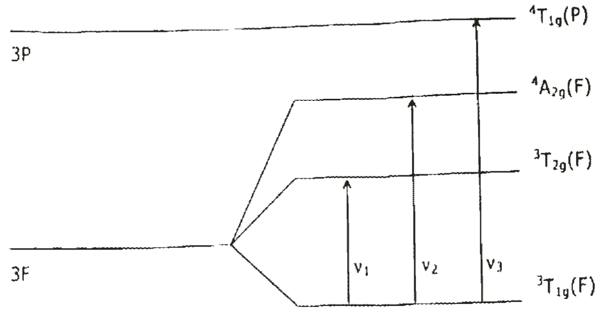


1111111111111111
S = + 1/2 - 1/2 + 1/2 - 1/2 + 1/2 - 1/2 + 1/2 + 1/2 = 1
2S + 1 = 2 X 1 + 1 = 3
L = 3
Ground Term = 3F

The next higher state having the same spin multiplicity as 3P. The splitting of these in weak octahedron' and Tetrahedron' field occurs as shown below :



Energy level diagram for octahedral Ni (II) ion



Energy level diagram for tetrahedral Ni(II) ion

In octahedral field three bands corresponding to the following transitions should be expected :-

(i) 3T2g(F)3A2g(F) 10,000 cm-1
(ii) 31-1g(F) c— 3A2g(F) 16,000 cm-1
(iii)3T1g(P)3A2g(F) 26,000 cm-1

These are Laporte forbidden transitions37 and the extinction coefficients are within 1-20.

In case of tetrahedral field around Ni(II) ion, the splitting is as shown in the figure (above).

Tetrahedral complexes of Ni(II) have also three bands corresponding to the transitions :-

(i) 3T2g(F) 3T1g(F) 5,000 cm-1
(ii) 3T2g(F) 3T1g(F) 10,000 cm-1
(iii) 3T„(P) 3T1g(F) 16,000 cm'

Therefore, one of the criterion22"24 to distinguish between tetrahedral and octahedral symmetries is the appearance of a band in infrared region in the latter case due to the transition.

3T29(F) 4-- 3A29(F)

The next criteria for distinguishing rather more confidently between tetrahedral and octahedral geometrics is the values of the extinction co-efficients of the bands at the maxima. The extinction coefficient in tetrahedral complex is about 500 which is much greater as compared to octahedral one (— 10). The reason is that there is lack of centre of symmetry in the tetrahedral field whereby Laporte rule is somewhat broken down. It is therefore difficult to analyse the spectra of tetrahedral complexes due to spin orbital coupling effect.

During the present investigation all the Ni(II) complexes show three bands in the regions 12000 - 12860 cm-1, 19780-20280 cm"' and 25430-26310 cm-1 which may be assigned to 3A2g(F) 3T2g(F), 3A2g(F) 3Tig(F) and 3A2g(F) 3Tig(P) transitions respectively, which indicate octahedra131,32,39 geometry of the Ni(II) complexes. The geometry of Ni(II) complexes are further confirmed28,29'36 by the gel, value in the range 3.05-3.18 B.M. The electronic spectra of all the complexes are recorded in Table 3

Electronic Spectra of Ni(II) complexes of the type [Ni(MPQS)2X2] and [Ni(MPQT)2X2]

Complexes	Bond position with assignment		
	3T29(F)(3A29(	3TIO(F) 4- 3A20(F)	31-10(P)4-- 3A29(F)
[NI(MPQS)202]	12140	19830	26200
[Ni(MPQT)2C12]	12060	19900	26310
[Ni(MPQS)2Br2]	12000	19990	26080
[Ni(MPQT)28r2]	12340	19700	26110
[Ni(MPQS)2I2]	12380	10100	25430
[Ni(MPQT)212]	12100	20200	25300
[Ni(MPQS)2(NO3)2]	12800	20200	26140
[Ni(MPQT)2(NO3)2]	12200	20140	26060
[Ni(MPQS)2(C104)z]	12740	20110	25600
[Ni(MPQT)2(C104)2]	12860	20260	25480

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