1. Guoy method : This method was developed by Guoy, a French Scientist in 1889. It is very simple method for the measurement of magnetic susceptibilities of various types of compounds.

Principle : On placing a compound in a magnetic field, its mass gets changed. Two conditions arises :

(1) Paramagnetic compound is attracted towards the magnetic field due to alignment of the tiny magnets.

(2) Diamagnetic compound is repelled by the magnetic field.

The magnitude of force acting on the compound can be measured which is related to magnetic susceptibility. A small volume of compound dv will experience a force dF which is given by

$$dF = H \,.\, K \,.\, dv \,.\, dH/dx \qquad \ldots (9.159)$$

where H = strength of magnetic field

K = volume susceptibility

$\frac{dH}{dx}$ = gradient of magnetic field.

Substituting $A.dx$ in place of dv, above equation takes the form

$$dF = H \,.\, K \,.\, A \,.\, dx \frac{dH}{dx} \qquad \ldots (9.160)$$

$= H \,.\, K \,.\, A \,.\, dH$ (A – cross sectional area dx – small height of sample compound)

$\ldots (9.161)$

Since the compound moves in a nonhomogeneous magnetic field (maximum at the centre and minimum outside the magnetic field) the total force experienced by the compound when it moves from outside the magnetic field ($H = 0 = H_0$) to the centre H of the field (H) can be obtained by integrating the equation between H and H_0.

$$F = \int dF = \int_{H_0}^{H} H \,.\, K \,.\, A \, dH \qquad \ldots (9.162)$$

$$F = A \,.\, K \,.\, \frac{1}{2}(H^2 - H_0^2) \qquad \ldots (9.163)$$

$$F = A \,.\, \chi_g \,.\, \rho \frac{1}{2} (H^2 - H_0^2) \qquad \ldots (9.164)$$

$$F = A \,.\, \chi_g \,.\, \frac{m}{v} \,.\, \frac{1}{2} (H^2 - H_0^2) \qquad \ldots (9.165)$$

$$F = \chi_g \,.\, \frac{m}{l} \,.\, \frac{1}{2} (H^2 - H_0^2) \qquad \ldots (9.166)$$

where m = mass of the sample

and l = length of the sample

$$F = \chi_g \,.\, \frac{m}{2l} \,.\, H^2 \ (H_0 \text{ negligible}) \qquad \ldots (9.167)$$

Buoyancy correction can be included, equation (9.167) takes the form

$$F = (\chi_g - \overset{\circ}{\chi}_g) H^2 \frac{m}{2l} \quad \ldots (9.168)$$

where $\overset{\circ}{\chi}_g$ = susceptibility of air

$$\therefore \quad \chi_g = \frac{2l \cdot F}{mH^2} \quad \ldots (9.169)$$

The force experienced by the compound is measured in terms of the masses *i.e.*, change in the weight of sample compound

$$\chi_g = \frac{2l \times \Delta\omega \times 981}{\text{mass of sample} \times H^2} \quad \ldots (9.170)$$

$\Delta\omega$ = change in mass can be known.

Thus, by observing F, the magnetic susceptibility can be calculated. In practice method is made simple instead of evaluating the cross-section of the sample tube and the magnetic field directly, the value of $\Delta\omega$ of standard sample whose magnetic susceptibility is known at the same value of H is measured.

Procedure : In this method, Guoy magnetic balance is used. At the one end of the microbalance a silver wire is joined through which tube of the sample is hanged. The sample tube is a cylindrical glass tube with flat bottom. The sample compound in the powder or in solution is filled in sample tube upto the mark. The sample tube is suspended from one arm of sensitive microbalance such that its lower part is in a strong magnetic field while the upper portion experiences zero magnetic field. The whole setup is kept inside a drought free enclosure. Usually, an electromagnet giving a constant magnetic field 5,000-10,000 gauss is satisfactory.

The sample tube is first weighed without magnetic field and then with the magnetic field on, thus the difference in weight of sample tube is calculated. The sample tube is then filled upto the mark with a standard compound (which is paramagnetic or a diamagnetic) whose susceptibility is known accurately. Then it is weighed without and with the magnetic field on and the difference in weight of the standard is recorded.

The sample tube is then cleaned. The weight of the empty tube and the difference in weight under the influence of the same magnetic field are measured. The sample tube is filled upto the mark with the sample compound and then it is weighed without and with the magnetic field on.

The formula used for the determination of magnetic susceptibility of compound

$$\chi_g = (\chi_g)_S \times \frac{W_S}{\Delta W_S} \times \frac{\Delta W_C}{W_C} \quad \ldots (9.171)$$

where $(\chi_g)_S$ = Susceptibility of standard compound

W_S = Weight of the standard compound

ΔW_S = Change in weight of standard in magnetic field

W_c = Weight of the sample compound

ΔW_c = Change in weight of the sample in magnetic field

The standard compound may be $Hg[Co(NCS)_4]$, $Ni[(en)_3]S_2O_3$ pure water, $CuSO_4.5H_2O$ used.

Table 9.14 : Magnetic susceptibility of some standard compounds

Standard	Temperature Coefficient (298 K)	Magnetic susceptibility
$Hg[Co(NCS)_4]$	-0.05×10^{-6} cgs unit/degree	16.44×10^{-6} cgs units
$Ni[(en)_3]S_2O_3$	-0.04×10^{-6}	$+11.03 \times 10^{-6}$ cgs units
H_2O (pure)	0.0012×10^{-6}	-0.72×10^{-6} cgs units
$CuSO_4 . 5H_2O$		$+5.92 \times 10^{-6}$ cgs units

Among all these standard compounds $Hg[Co(NCS)_4]$ is most commonly used as $CuSO_4 . 5H_2O$ does not pack well into the tube and water is not a good standard for the measurement of magnetic susceptibility of paramagnetic compounds.

The molar susceptibility can be found by multiplying χ_g with the molecular weight of the sample compound. The χ_m is corrected for the diamagnetism of the ligands, anions, metal atom, solvents of crystallisation and the temperature independent paramagnetism (TIP).

Thus, $$\chi_M^{Corr.} = \chi_m - (\chi_{dia} + TIP) \quad \ldots (9.172)$$

Using the Curie equation $(\mu_{eff} = 2.83(\chi_M^{Corr} \times T)^{1/2})$ BM magnetic moment of the sample compound can be obtained.

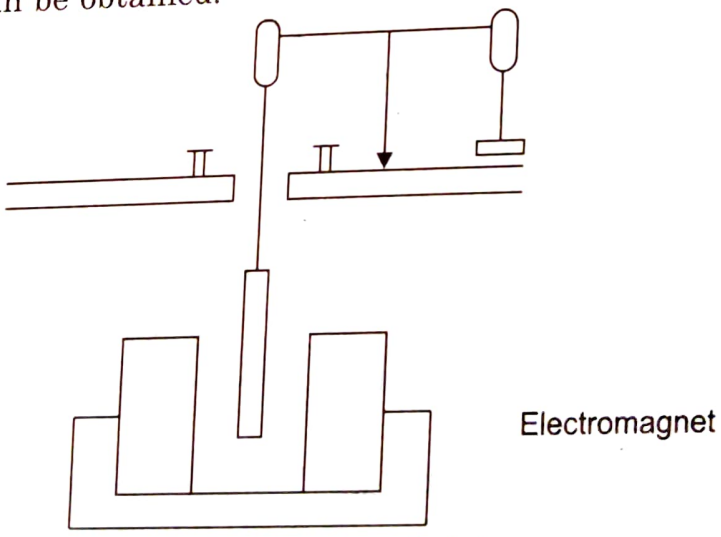

Fig. 2.15 : Guoy magnetic balance.

If the experimental temperature is different from 293 K (20°C), the χ_g of the standard $Hg[Co(NCS)_4]$ at the experimental temperature can be calculated using temperature coefficient (dx/dT) data and then this $(\chi_g)_S^T$ values is used to calculate the magnetic susceptibility of the sample compound.

The following data are given for the sample compound $[Co_{(Biguanide)}]Cl_2.2H_2O$ taking $Hg[Co(CNS)_4]$ as standard.

1. Temperature 293 K.
2. Weight of empty tube without magnetic field = 9.72303 gm.
3. Weight of empty tube with magnetic field = 9.72246 gm.
4. $\Delta x = (3 - 2) = (9.72246 - 9.72302)$ gm $= -0.00057$ gm.
5. Weight of tube and Hg $[Co(NCS)_4]$ without magnetic field = 10.73997 gm.
6. Weight of tube and Hg $[Co(NCS)_4]$ with magnetic field = 10.76296 gm.
7. Weight of standard, $W_s = (5 - 2) = 1.01694$ gm.
8. $\Delta_y = (6 - 5) = (10.76297 \text{ gm} - 10.73997)$ gm $= 0.2299$ gm
9. $\Delta W_s = \Delta_y - \Delta_x = (0.2299 + 0.00056)$ gm $= 0.02355$ gm
10. Weight of empty tube without magnetic field $= 9.72298$ gm
11. Weight of empty tube with magnetic field $= 9.72298$ gm
12. $\Delta_m = (11 - 10) = (9.77245 - 9.72298)$ gm $= -0.00053$ gm
13. Weight of tube and compound without magnetic field = 10.05913 g
14. Weight of the tube and compound with magnetic field = 10.060139
15. Weight of compound = $W_c = (13 - 10) = 0.33615$ g
16. $\Delta_n = (14 - 13) = (10.06013 - 10.05913) = 0.001009.$
17. $\Delta W_c = (\Delta_n - \Delta_m) = (0.00100 + 0.00053)$ g

$$\chi_g = (\chi_g)_s \times \frac{W_s}{\Delta W_s} \times \frac{\Delta W_c}{W_c} \qquad \ldots (9.173)$$

$$= 16.44 \times 10^{-6} \times \frac{1.01694}{0.02335} \times \frac{0.00153}{0.33615}$$

$$= 3.2298 \times 10^{-6} \text{ cgs units}$$

$$\chi_M = \chi_g \times \text{molecular weight} \qquad \ldots (9.174)$$

$$= 3.2298 \times 10^{-6} \times 372.5$$

$$= 1203 \times 10^{-6} \text{ cgs units.}$$

Diamagnetic correction for $[Cu(\text{biguanide})]Cl_2 . 2H_2O$

$$= -207 \times 10^{-6} \text{ cgs units}$$

$$TIP = +50 \times 10^{-6} \text{ cgs units}$$

$$\chi_M^{corr} = 1203 \times 10^{-6} - (-207 \times 10^{-6}) - 50 \times 10^{-6} \text{ cgs units.}$$

$$= 1360 \times 10^{-6} \text{ cgs units.}$$

$$\mu_{eff} = 2.83 (1360 \times 10^{-6} \times 293)^{1/2} \; BM$$

$$= 1.79 \; BM.$$

2. Bhatnagar-Mathur method : In 1928, Bhatnagar and Mathur made some modification in the Guoy's method. This method can be used for the measurement of magnetic susceptibilities of liquid.

Principle : On placing the sample in magnetic field the weight gets changed and this difference in weight can be used to calculate the applied force on the sample compound.

6. Faraday Method

Principle : In this method, a very small volume of the sample is subjected to a region of fairly strong magnetic field so that the product $H.dH/d_x$ is constant over the volume of the sample.

where dH/dx is the gradient of the magnetic field.

No integration of the magnetic field is then necessary. The region of uniform $H\ .dH/d_x$ is determined by applying a small volume of a standard (of mass n) of known susceptibility at different points along the magnetic field. The value of $H\ .dH/d_x$ is determined from the following relations :

$$dF = m\ .\chi_g\ .H\ .\frac{dH}{d_x} \qquad \ldots(9.192)$$

$$\Rightarrow \qquad \frac{dF}{m\ .\chi_g} = H\ .\frac{dH}{dx} \qquad \ldots(9.193)$$

Procedure : The sensitive weighing techniques such as, quartz fibre torsion balances or ring balance are used in this experiment. The sample is usually packed in quartz ampoules (≈ 1 mm internal diameter) and suspended from the balance. The force on the sample is observed by the deflection of a small mirror or a quartz spring with the help of a cathetometer. The whole set up is kept in an enclosure which can be cleared with nitrogen or helium. With the help of the measurements with a standard first and then with the sample. The following equation holds :

$$\chi_s = \chi_c \cdot \frac{d_s}{d_c} \cdot \frac{m_c}{m_s} \qquad \ldots(9.194)$$

where χ_s = mass susceptibility of standard compound

χ_c = mass susceptibility of sample compound

m_c = mass of sample compound

m_s = mass of standard compound

d_c = deflection in the standard compound at the same $H.\frac{\partial_H}{d_x}$

d_s = deflections in the sample compound at the same $H.\frac{\partial_H}{d_x}$

Anomalous Magnetic Moments : The anomalous magnetic moments are the values of magnetic moments which come outside the range of values predicted from orbital and spin angular momentum contributions in crystal fields of given magnitude and symmetry for a metal ion in a molecular species.

In octahedral ligand field, ground state of Ni (II) is $^3A_{2g}$ which has no orbital contribution, but the excited state $^3T_{2g}$ of Ni(II) carry some orbital moment due to spin-orbit coupling. The value of magnetic moment depends on crystal field splitting energy Δ and spin-orbit coupling constant λ.

$$\mu = \mu_s \left(1 - \frac{\alpha\lambda}{\Delta}\right) \qquad \ldots(9.195)$$

donor ligands may give both high spin and low spin complexes. Table 9.16 lists ranges for the normal and anomalous moments for nickel (II), cobalt (II) ion (II) and iron (III).

A number of explanations have been given to explain for the anomalous magnetic behaviour. These are :

1. Solute – solvent interaction
2. Solute – solute interaction
3. Configurational equilibrium
4. Equilibrium between two spin-states
5. Magnetically non-equivalent sites in the unit cell

1. Solute-solvent interaction : The anomalous magnetic moment values may develop when a species under consideration combines with a coordinating solvent. Thus, many squares planar diamagnetic nickel (II) complexes become partially paramagnetic due to an equilibrium of the type given below :

Solvent + square planar complex (diamagnetic) $\rightleftharpoons$ Pseudo-octahedral complex (paramagnetic)

$$2H_2O + ML_4 \rightleftharpoons [ML_4(H_2O)_2]$$

The following equilibrium of Ni (II) in water was studied

$$[Ni(CRH)]^{2+} + x\ H_2O \rightleftharpoons [Ni(CRH)(H_2O)_x]^{2+}$$

diamagnetic paramagnetic

$[Ni(CRH)]^{2+}$ is the macrocyclic complex obtained by the catalytic hydrogenation of $[Ni(CR)]^{2+}$ which was prepared by the condensation of 2, 6-diacetyl pyridine and 3, 3°-diamino-dipropylamine in the presence of nickel (II) ions. Thermodynamic parameters enthalpy change, ΔH and entropy change ΔS are concentration dependent because of the change in solvent activity which determines the position of the equilibrium and hence value of the magnetic moment in solution. The addition of quantities of extra salts to aqueous solution lowers the activity of the solvent water and thus influences the relative amounts of the spin free (high spin) and spin paired (low spin), two forms bis (meso-2, 3 diamino butane) diaquonickel (II) and bis (meso-2, 3-diamino butane) nickel (II), respectively.

Taking a value of Δ_0 = nearly 8000 cm^{-1}

and $\lambda = 315\ cm^{-1}$, μ comes out to be 3.3 BM.

In a tetrahedral ligand field ground state of Ni (II) is $^3T_1$ and the value of magnetic moment comes in the range ~ 3.5 – 4.0 BM.

The square planar complexes of Ni (II) are diamagnetic and hence, have zero magnetic moment values. Five coordinated high spin complexes of Ni (II) have magnetic moments value in the range 3.0 – 3.4 BM while the low spin complexes are diamagnetic. Thus, the range 0 – 2.8 BM is the range of anomalous magnetic moments for Ni (II). The high spin five coordinated complexes are usually formed by oxygen and nitrogen donor ligands of high electronegativity while the low spin complexes are obtained with phosphorus, arsenic as donor atoms. Sulphur, selenium, chlorine, bromine and iodine donor ligands may give both high spin and low spin complexes. Table 9.16 lists ranges for the normal and anomalous moments for nickel (II), cobalt (II) ion (II) and iron (III).

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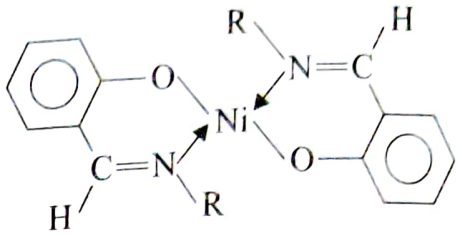
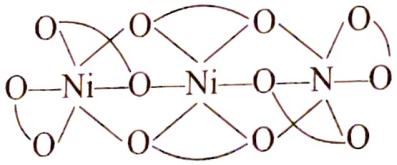
2. Solute-solute interaction : Solute-solute interaction results in an increase in the coordination number of the metal ion due to which the spin state of the ion are changed. Bis (N–methyl salicylaldiminato) nickel (II) is diamagnetic in the solid state but shows anomalous moment value of 1.9 – 2.3 BM in solution depending on the nature of the non coordinating solvent. Dipole moment in benzene or dioxan are practically zero, thus a planar-tetrahedral equilibrium is rejected. The positive evidence for solute association was given by simultaneous increase in magnetic moment and molecular weight with increase in concentration of the complex.



Introduction of steric barrier via substitution in the 3-position of the benzene ring removed paramagnetism while the substituents in the 5-position were less effective. Clearly, the substituents in the 3-position did not allow the phenolic oxygen to get attached axially to a second nickel (II), thus preventing the change of the spin state. Bis (acetyl acetonato) nickel (II) is indeed trimeric (linear) each nickel (II) being six coordinated with a magnetic moment value 3.23 BM per nickel (II). The octahedral structure is attained through some of the oxygen atoms working as a bridge between nickel atoms. The trimeric unit stable in solution as evidenced from molecular weight and spectral measurements but becomes reversibly dissociated into the red monomer at nearly 200°C. The anomalous magnetic moment arises due to the following equilibrium :



Planae monomer $\rightleftharpoons$ octahedral trimer

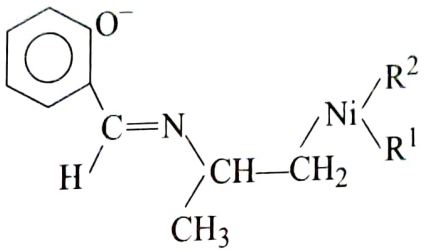
Solvents like pyridine destroy the trimeric structure and give solvents coordinated six coordinated monomer. Substitution of the methyl group of acetyl acetone by the very bulky-$C(CH_3)_3$ group restricts polymerisation and produces only the diamagnetic, planar monomer. The substitutent groups which are intermediate between $—CH_3$ and $—C(CH_3)_3$ provide monomer-trimer equilibrium in non-coordinated solvents giving anomalous magnetic moments.

3. Configurational equilibrium : The anomalous magnetic moment value of bis (N-sec-alkyl salicyl aldiminato) nickel (II) in inert solvent at room temperature indicate the presence of both the planar diamagnetic form and the tetrahedral paramagnetic form in comparable amounts. The assignment of the coordination geometry in the solid state was made on the basis of magnetic moment value and in solution on the basis of dipole moment value and molecular weight determination. Although, there is proof for some association in solution, it has been shown that above 37°C, they are essentially monomeric under the same conditions of solvent, concentration and temperature where they were found to be appreciably paramagnetic.

Planar-tetrahedral equilibrium has also been found for bis (o-hydroxynaphthal diminato) nickel (II) complexes. For example, when the aldehyde is

o-hydroxynaphthaldehyde and the amine is $Et_2CH - NH_3$ the nickel (II) Schiff base complex is diamagnetic in the solid state but develops a moment value of 1.80 BM at 50°C in chloroform solution. A planar-tetrahedral equilibrium has also been found for bis (β-ketoimine) cobalt (II) complexes.

Monomeric octahedral-square planar equilibrium has been found for nickel (II) complexes containing the ligand given below in non-coordinating solvents. The equilibrium appears only when $R' = H$ and $R^2 = C_6H_5$, α-naphthyl or substituted phenyl. The nature of the substituent determines the solid state behaviour. In solution, an increase in temperature shifts the equilibrium towards the 4-coordinated form giving a smaller overall moment.



4. Equilibrium between two spin states : For the d^4, d^5, d^6 and d^7 ion high spin $\rightleftharpoons$ low spin state equilibrium may arise in the octahedral geometry if the crystal field strength is in the region of the critical 10 Dq or cross over. But in the case of d^8 ion [Ni (II)], no crystal field in octahedral geometry is there to have a low-spin state since the $^3A_{2g}$ ground state and the ^1E_g excited states almost run parallel. Ground state of a weakly tetragonal, nickel (II) complex is diamagnetic if $\Delta_1 > P$, $(eg)^4 (b_{2g})^2 (a_{1g})^2$ or paramagnetic $\Delta_1 < P$, $(eg)^4 (b_{2g})^2 (a_{1g})^1 (b_{1g})^1$. Again two magnetic forms may be written for strongly tetragonal nickel (II) complex : diamagnetic, $\Delta_2 > P (eg)^4 (a_{1g})^2 (b_{2g})^2$ or paramagnetic, $\Delta_2 > P$ $(eg)^4 (a_{1g})^2 (b_{1g})^1 (b_{2g})^1$, thus tetragonal distortion of an octahedral geometry may lead to a change in the spin state of nickel (II). This effect will be generated if we have a mixed ligand complex $[Ni(a)_4 (b)_2]$ where ligand b occupies axial position. If a and b have similar crystal field strength, it is probable that Δ_1 and Δ_2 will be small and the value of magnetic moment will be close to 3.0 BM. On the contrary, if b ligands has a very low position compared to ligand a in the spectrochemical series, Δ_1 or Δ_2 may exceed P and a diamagnetic complex may be obtained. If Δ_1 or Δ_2 is close to P, we will have spin state equilibrium in tetragonal nickel (II) complexes.

Dichlorotetrakis (N, N'-diethyl thiourea) nickel (II) complex is low spin below temperature 194K but with the rise of temperature, if gets partial paramagnetism reversibly. It is believed that nickel (II) has a weak tetragonal field and that the magnetic property is instructed only by the thermal population of the two spin states. The equilibrium constant K for the reaction can be calculated from mole fraction $N_{l.s.}$ and $N_{h.s.}$

singlet (low spin) $\rightleftharpoons$ triplet (high spin)

K = [triplet]/[singlet]

The magnetic moment value of the fully paramagnetic dichloro tetrakis (N, N'-diethyl thiourea) nickel (II) has been taken to be 3.2 BM and that of the low spin form as 0.0 BM.

Observed $\chi_M = N_{hs} \cdot \chi_M(l.s.) + N_{h.s} \cdot \chi_M(h.s.)$ ...(2.196)

$N_{l.s.}$ = mole fraction of low spin state

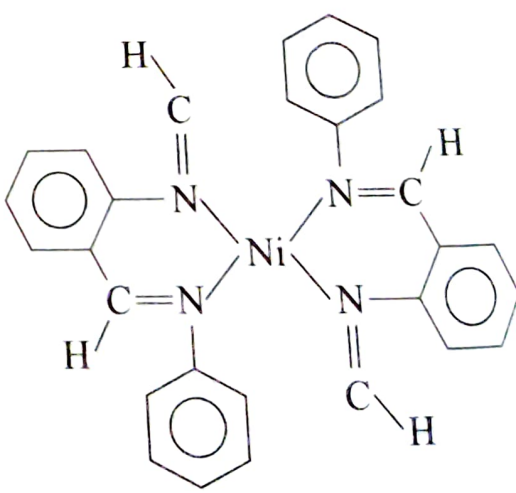
$N_{h.s.}$ = mole fraction of high spin state

Some results at different temperatures are given below :

$T°$ (K)	μ	$N_{l.s.}$	$N_{h.s.}$	K
< 194	0.0	1.00	0.00	–
280	1.10	0.88	0.12	0.17
300	1.33	0.82	0.18	0.21
320	1.57	0.76	0.24	0.33
360	2.05	0.58	0.42	0.72

Thermodynamic parameters like ΔH, ΔF, ΔS were calculated from a graph of log K vs $1/T$. The shortest Ni-Ni distance in dichloro tetra thiourea nickel (II) complex is over 8Å and the same case with rejected tetra kis (N, N'-diethyl thiourea) nickel (II) complex also. Thus, direct metal-metal bonding is discarded and no path for super exchange via small bridging atoms is seen.

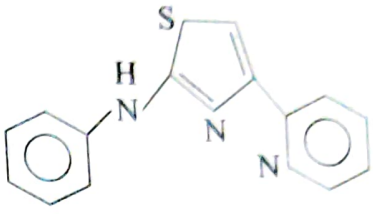
The nickel (II) complexes of the planar quadridentate macrocyclic ligand tetraanhydroamino benzaldehyde TAAB which is obtained by self-condensation of o-aminobenzaldehyde in presence of suitable nickel (II) salts in alcoholic medium. The anhydrous perchlorate, tetrafluoro borate and the tetraphenylborate salts of $[Ni(TAAB)]^{2+}$ are diamagnetic but the anhydrous thiocyanate, nitrate and iodide salts are paramagnetic and the magnetic moments value are found to be – 3.2 BM. The chloride and bromide salts of $[Ni(TAAB)]^{2+}$ show anomalous moment values of 1.7 BM and 1.5 BM at room temperature. The spin state equilibria were studied and K values were evaluated. The halide ions show an anomalous order of crystal field strengths I > Cl > Br. The residual charge on the anion is likely to be highest for the singlet state because of the weakness of the nickel-halide bond. Therefore the water molecule may strongly hydrogen bond to the singlet chloride but not to the triplet chloride. Thus, the contribution of the hydrate water to the energy balance of the system is important.



For an octahedral ligand field, the possibility of spin state equilibrium exists for the following configurations

$$d^4 - {}^5E_g - {}^3T_{1g} \quad (Cr^{2+}, Mn^{3+})$$
$$d^5 - {}^6A_g - {}^2T_{1g} \quad (Mn^{2+}, Fe^{3+})$$
$$d^4 - {}^5E_g - {}^1A_{1g} \quad (Fe^{2+}, Co^{3+})$$
$$d^7 - {}^4T_g - {}^2E_g \quad (Co^{2+})$$

Around the cross over region, the energies of the two spin states differ by thermal energy $-kT$. So that their relative populations change with temperature. The d^5 and d^6 ions have their spin-obit coupling integrals between the two terms of differing spin multiplicities as zero because of the participation of an A_{1g} term so that there is no notable spin-orbit interaction between the two spin states. The overall magnetic susceptibility is then taken as population weighed average of the magnetic susceptibilities of the two terms :



$$\chi_m = \frac{(2S_1 + 1)\chi_{m_1} + (2S_2 + 1)\chi_{m_2} e^{(-\Delta/kT)}}{(2S_1 + 1)(2S_2 + 1)e^{(-\Delta/kT)}} \quad \ldots(9.197)$$

S_1 = spin quantum number of first spin state

S_2 = spin quantum number of second spin state

χ_{m_1} = molar susceptibility of first state

χ_{m_2} = molar susceptibility of second state

Δ = energy difference between the two spin states $(E_{h.s.} - E_{l.s.})$

For the d^4 and d^7 configurations spin-orbit coupling integrals between the two spin states are non-zero. Consequently, the susceptibility equation becomes extremely complex. In these cases, the concept of spin-multiplicity becomes ill-defined.

The spin-state equilibrium was observed in $[Fe(papth)_2]X_2$ where papth = 2 (2-pyridyl amino)-4 (2-pyridyl thiazole) chloride and few other salts were obtained in two coloured forms. The yellow-coloured complex showed normal high spin behaviour with magnetic moments value nearly 5.0 BM, while the red-brown form were prediminantly low spin with magnetic moments value nearly 1.3 – 1.4 BM. For d^6 iron (II) $S_1 = 0$, $S_2 = 2$, $\chi_{m_1} = 0$ so that the susceptibility equation given above reduces to :

$$\Delta = KT \log\left[5\left(\frac{\chi_{m_1}}{\chi_{m_2}} - 1\right)\right] \quad \ldots(9.198)$$

Assuming that Δ is independent of temperature and the temperature dependence of χ_{m_2} can be well estimated, the above equation will provide the value of Δ. The Δ values of any particular compound at different temperatures varied as much as 400%.

low spin $\rightleftharpoons$ high spin K = [high spin]/[low spin]

The plots of $\log K$ versus T are not straight line over the temperature range studied with the exception of bromide salt. Such deviations indicated the importance of modification of crystal lattice besides a vertical spin state equilibrium.

The spin-state equilibrium is also found in the complex bis (2, 6-pyridine dialdehydrazone) cobalt (II) iodide. At temperature 80K, this complex has a magnetic moment value of 1.9 BM which changes to 3.7 BM at 337 K. An empirical approach for the high spin $\rightleftharpoons$ low spin equilibrium was used. The high spin magnetic moment value of 5.2 BM and a low spin moment of 1.9 BM were used for the evaluation of the equilibrium constant K = [high spin]/[low spin]

A linear relation was observed between equilibrium constant $\log K$ and inverse temperature.

The magnetic properties of iron (III) complexes of ligand monothio β-diketones are best illustrated by a thermal equilibrium between $t_{2g}{}^5$ (low spin) and $t_{2g}{}^3 eg^2$ (high spin) states. It was further found that the magnetic behaviour was dependent on the nature of substituent R groups of the complex Fe [R′C(S) - CH . C(O)R′′]$_3$. The electron withdrawing groups favour the low-spin form. The spectral data along with the magnetic data have verified the existence of an equilibrium between the high spin and low spin forms in ferrihaemo proteins. The percentage of the configurations for several haemoproteins were calculated taking 5.92 BM and 2.24 BM as the magnetic values of high-spin and low-spin isomers.

	High spin (%)	**Low spin (%)**
Myoglobin	70	30
Haemoglobin	50	50
Peroxidase	07	93

Spin-state equilibrium has not been established for a d^4 system.

5. Magnetically non-equivalent sites in unit cell : The green coloured complex dibromo bis (benzyl diphenyl phosphine) nickel (II) [Ni(P(Ph . CH_2)Ph_2] Br_2) show anomalous magnetic moment value of 2.7 BM. An X-ray diffraction study of this complex shows that there are three nickel (II) complexes in the unit cell : 1. one square planar 2. two tetrahedral. The additivity of the squares of the magnetic moments and taking into account the respective mole fractions :

$$(2.7)^2 = 0.33 \times 0^2 + 2 \times 0.33 \times \mu^2 \ Ni^{2+} \ (Td)$$

The magnetic moment value of tetrahedral nickel (II) comes out as 3.3 BM. Such spin isomers, which differ only in bond angles are termed as intrallogons–("allos" meaning different and gonia meaning angle.)

Yellow form of the Lifschitz compound, bis (meso-stilbenedi-amine) nickel (II) dichloro acetate $2/3\ C_2H_5OH\ .\ 4/3\ H_2O$ has a magnetic moment value 2.58 BM and the unit cell of this complex consists of two six coordinate nickel (II) and one planar four coordinate nickel (II). Calculations using the room temperature magnetic moment data provide a value of 3.16 BM for the pseudo octahedral nickel (II).

Table 9.16 : Normal and Anomalous Magnetic moments Ni (II), Co (II), Fe (II) and Fe (III).

Ion	Octahedral	5 coordinate	Tetra hedral	Square planar	Range for anomalous magnetic moment
Nickel (II) high spin	3.0–3.3	3.0–3.45	3.45–4.0	–	~ 0–2.8
Nickel (II) low spin	–	~ 0	–	0	
Cobalt (II) high spin	4.7–5.2	4.2–4.6	4.2–4.8	–	~ 2.9–4.2
Cobalt (II) low spin	1.8–2.0	1.7–2.1	–	2.1–2.9	
Iron (II) high spin	5.1–5.7	5.1–5.5	5.0–5.2	5.4	~ 0–5.1
Iron (II) low spin	~ 0	2.9–3.1	–	–	
Iron (III) high spin	~ 5.9	–	–	–	~ 2.3–5.9
Iron (III) low spin	~ 2.3	–	–	–	

Table 9.17 : Magnetic moment of complexes with *A* and *E* ground terms : $\mu_{eff} = (1 - \alpha\ \lambda/10\ Dq)\ \mu$ spin only

d-electrons	Geometry	Examples	Ground Term	Sign of λ	α	μ_{eff} (expected)	μ_{eff} (exp.)	μ spin only (300K)
1.	Tet	VCl_4	^2E	+	2	$< \mu_{s.o.}$	1.72	1.73
2.	Tet	–	$^3A_2$	+	4	$< \mu_{s.o.}$	–	2.83

3.	Oct	Chrome alum	$^4A_{2g}$	+	4	$< \mu_{s.o.}$	3.84	3.87
4.	Oct	$[Cr(H_2O)_6]SO_4$	^5E_g	+	2	$< \mu_{s.o.}$	4.82	4.90
5.	Oct	Ferric alum	$^6A_{1g}$		0	$= \mu_{s.o.}$	5.89	5.92
	Tet	$(Et_4N)[FeCl_4]$	$^6A_1$		0	$= \mu_{s.o.}$	5.88	5.92
6.	Tet	$(Et_4N)_2[FeCl_4]$	^5E	–	2	$> \mu_{s.o.}$	5.40	4.90
7.	Tet	$Cs_2[CoCl_4]$	$^4A_2$	–	4	$> \mu_{s.o.}$	4.71	3.87
8.	Oct	$[Ni(H_2O)_6]SO_4$	$^3A_{2g}$	–	4	$> \mu_{s.o.}$	3.23	2.83
9.	Oct	$[Ag(dipy)_3](ClO_4)_2$	^2E_g	–	2	$> \mu_{s.o.}$	1.90	1.73
	Oct	$[Cu(H_2O)_6]SO_4.K_2SO_4$	^2E_g	–	2	$> \mu_{s.o.}$	1.91	1.73

Tet-Tetrahedral, Oc -Octahedral

Table 9.18 : Magnetic moments of transition metal ions with *T* ground terms

Configuration	Ground term	Weak field μ_e^2
d^1 Oct d^9 Tet	$+\zeta$ $-\zeta$ $\Big\}$ $^2T_2$	$8+(3x-8)\dfrac{e^{(-3x/2)}}{x[2+e^{-3x/2}]}$
d^2 Oct d^8 Tet	$+\zeta/2$ $-\zeta/2$ $\Big\}$ $^3T_1$	$\dfrac{3[0.625x+0.6+(0.125x+4.09)e^{(-3x)}-10.89e^{\left(\frac{9x}{2}\right)}}{x[5+3e^{(-3x)}+e^{(-9x/2)}]}$
d^6 Oct d^4 Tet	$+\zeta/4$ $-\zeta/4$ $\Big\}$ $^5T_1$	$\dfrac{3[28x+9.33+(22.5x+4.17)e^{-3x}+(24.5x-13.5)e^{-5x}]}{x[7+5e^{(-3x)}+3e^{(-5x)}]}$
d^7 Oct d^3 Tet	$-\zeta/3$ $+\zeta/3$ $\Big\}$ $^4T_1$	$\dfrac{3[3.15x+3.92+(2.84x+2.13)e^{-15x/4}+(4.7x-6.05)e^{(-6x)}]}{x[3+2e^{(-15x/4)}+e^{(-6x)}]}$
		strong field μe^2