Iron, Cobalt, and Nickel Complexes having Anomalous Magnetic Moments

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The measurement of magnetic susceptibility constitutes one of the most important experimental routes by which the chemist can easily and quickly acquire information on the structure and bonding in transition-metal complexes. There are available many books and reviews which deal in detail with theory, measurement and interpretation of normal magnetic behaviour.[1–5] We here review representative examples of those classes of compound which exhibit so-called *anomalous* magnetic moments and examine the mechanisms producing these non-standard values. Reference will be made only to systems which do not require consideration of interactions between two or more metal ions; *i.e.*, they are at least approximately magnetically dilute. Attention will be directed mainly to complexes of nickel(II) which provide the largest number of known examples of anomalous magnetic behaviour, but reference will also be made to the increasing number of cobalt(II), iron(II), and iron(III) complexes showing unusual magnetic behaviour.

First it is necessary to define what we mean by 'anomalous' in referring to magnetic moments. For the present we take it to mean any magnetic moment for a metal ion in a discrete molecular species having a value which falls outside the range of values predicted from considerations of the spin and orbital angular momenta in ligand fields of given strength and symmetry. For the metal complexes to be considered, the most common stereochemistries are octahedral, tetrahedral, square planar, and distorted forms derived from these. Let us briefly illustrate what we mean by 'anomalous' by reference to what is 'normal' for regular complexes of the metals to be considered (Table 1).

For nickel(II) in a regular octahedral complex consideration of spin–orbit coupling and contributions from the $^3A_{2g}$ and next higher $^3T_{2g}$ state (Figure 1) gives the maximum value somewhat above the spin-only moment of 2·83; the value[6] is about 3·3 B.M. for a Δ value of *ca.* 8000 cm.$^{-1}$ and $\lambda = 75\%$ of the free

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[1] P. W. Selwood, 'Magnetochemistry', 2nd edn., Interscience, New York, 1956.
[2] R. S. Nyholm, *J. Inorg. Nuclear Chem.*, 1958, **8**, 401.
[3] B. N. Figgis and J. Lewis, 'Modern Co-ordination Chemistry', ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960.
[4] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.
[5] B. N. Figgis, 'Introduction to Ligand Fields', Interscience, New York, 1966.
[6] A.B.P. Lever, *Inorg. Chem.*, 1965, **4**, 763.

Table 1 *Expected ranges of 'normal' and 'anomalous' room-temperature moments (B.M.) for complexes of the nickel*(II), *cobalt*(II), *iron*(II), *and iron*(III)

Ion[a]	*6-Co-ordinate pseudo-octahedral*	*5-Co-ordinate*[b]	*4-Co-ordinate pseudo-tetrahedral*	*4-Co-ordinate planar*	*Range for anomalous moments*[c]
Ni^{II} h.s.	3·0—3·3	3·0—3·45	3·45—4·0	—	$\sim$0—2·8
Ni^{II} l.s.	—	$\sim$0	—	0	
Co^{II} h.s.	4·7—5·2	4·2—4·6	4·2—4·8	—	$\sim$2·9—4·2
Co^{II} l.s.	1·8—2·0	1·7—2·1	—	2·1—2·9	
Fe^{II} h.s.	5·1—5·7	5·1—5·5	5·0—5·2	5·4	$\sim$0—5·1[d]
Fe^{II} l.s.	$\sim$0	2·9—3·1	—	—	
Fe^{III} h.s.	$\sim$5·9	—	—	—	$\sim$2·3—5·9
Fe^{III} l.s.	$\sim$2·3	—	—	—	

[a] h.s. is high-spin and l.s. is low-spin. [b] These are the ranges for both trigonal bipyramidal and square pyramidal geometries. [c] The moment of no species should fall within these ranges without being defined as anomalous. However, a low-spin Co^{II} complex, known to have O_h or pseudo-octahedral symmetry, with a moment as high as 2·9 B.M. would also be considered anomalous, etc. [d] This range excludes the low-spin 5-co-ordinate values as this geometry does not occur in any examples discussed.

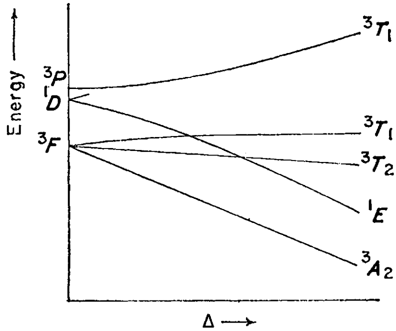

Figure 1 *Qualitative energy level diagram for d^8 systems showing triplet states and low-lying singlet states*

ion value. This also includes a small temperature-independent contribution. Ordinarily, μ_{eff} is in the range 3·0—3·3 B.M., although apparent values in excess of this have been noted.[7] Somewhat similar considerations apply to iron(II), iron(III), and cobalt(II); however, in some instances orbital angular momenta for the ground states of these ions in strict O_h symmetry are not quenched and the expression for μ_{eff} is more complicated. For these cases there also exists the

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[7] B. N. Figgis, *Nature*, 1958, **182,** 1568.

possibility of 'high spin' (h.s.) and 'low spin' (l.s.) complexes with variations in the ligand field strength (Figures 2, 3, and 4).

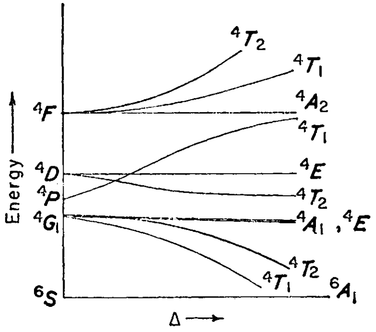

Figure 2 *Qualitative energy level diagram for* d^5 *systems such as iron*(III)

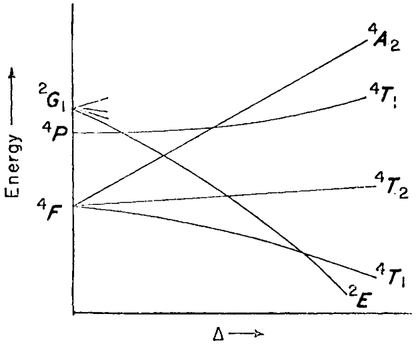

Figure 3 *Qualitative energy level diagram for* d^7 *systems like cobalt*(II)

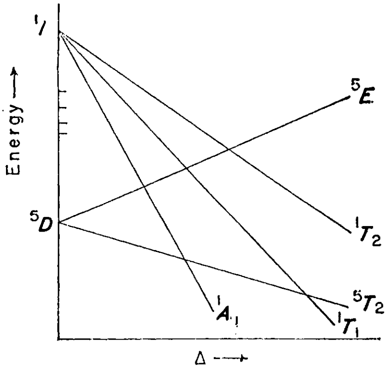

Figure 4 *Qualitative energy level diagram for* d^6 *systems like iron*(II)

For the high-spin cases of Co^{II}, Fe^{II}, and Fe^{III} there is a rather complicated dependence on λ and on kT.[5,7] Calculations give room-temperature values for the high-spin moments of 4·7 and 5·1 B.M. for Co^{II}. For this ion, as for all those where the ground-state configuration is T_{1g} resulting from a free ion F ground state, two cases must be considered in calculations; that where the ligand field is small compared with the interelectronic interactions and that where the field is large compared with interelectronic interactions. Values found experimentally fall in the range 4·7—5·2 B.M. depending on the ligand field strength and the amount of distortion from O_h symmetry. For iron(II) the free ion term is a ^5D state and the absence of adjacent higher terms of the same multiplicity simplifies calculations. The ground state in O_h symmetry is $^5T_{2g}$ and μ_{eff} is expected to have a value of 5·6 B.M. at room temperature. Experimentally, moments of 5·1—5·7 B.M. are observed. Iron(III) in weak ligand fields has a $^6A_1$ ground state coming from a free ion ^6S state and moments of the order of 5·9 B.M. are generally found.

The added possibility of spin pairing must be considered to determine the ranges in which moments are expected to fall. Iron(II) is simple since with strong ligand fields a singlet state falls lowest and the complexes are diamagnetic. This occurs only for very strong fields, such as those due to CN^-, CNR, and *o*-phenanthroline. For Co^{II}, when the ligand field is strong enough (and this is relatively rare) the ground state is an E state with one unpaired electron. Since the orbital angular momentum is essentially quenched, moments approaching the spin-only value of 1·73 B.M. are expected and values of 1·8—2·0 B.M. are observed. This may be only fortuitous, however, since the actual electronic structure can only be represented in terms of covalency theories (M.O. theory) and because a large amount of mixing between ligand and metal orbitals impairs the predictions of simple ligand field theory. Iron(III) has a low-spin $^2T_{2g}$ ground state with a normal moment of about 2·3 B.M. which corresponds to one unpaired electron. Since the ground state retains some orbital angular momentum, moments may range in value from $[4S(S+1)]^{\frac{1}{2}}$ to $[4S(S+1)+L(L+1)]^{\frac{1}{2}}$, the exact value depending on the temperature of measurement and the magnitude of the spin–orbit coupling.

Mention should be made of the only known example of what appears to be a diamagnetic pseudo-octahedral Ni^{II} complex. Tris-(*o*-phenylenebisdimethylarsine)nickel(II) ion, first reported[8] by Nyholm in 1950, has been prepared in greater yields and its possible structure discussed in light of its diamagnetism.[9] The nickel atom has μ_{eff} 0·6 B.M., presumably owing to TIP (temperature-independent paramagnetism). Nuclear magnetic resonance (n.m.r.) results indicate that the structure must involve D_3 symmetry with a pseudo-octahedral array of donors about the nickel atom. A qualitative molecular orbital scheme has been offered[9] to account for the observed diamagnetism. The principal feature of the model involves treatment of the orbitals of the nickel atoms as a set of functions quantised about the C_3 axis in D_3 symmetry. In such a treatment

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[8] R. S. Nyholm, *J. Chem. Soc.*, 1950, 2061.

[9] B. Bosnich, R. Bramley, R. S. Nyholm, and M. L. Tobe, *J. Amer. Chem. Soc.*, 1966, **88**, 3926.

the π and σ bonding distinction between specific orbitals is lost and mixing of all orbitals of like symmetry can occur. A qualitative M.O. scheme is presented in Figure 5. This scheme accommodates the last two electrons in a single orbital sufficiently separated from the next level so as to maintain spin pairing. As Nyholm and his co-workers point out it is not sufficient in this case to work with donor-group microsymmetry in explaining spectral and magnetic properties. In most instances involving bidentate chelates the chelate rings act as a minor perturbation on strictly octahedral functions whereas in Ni[diars]$_3^{2+}$ this is apparently not true.

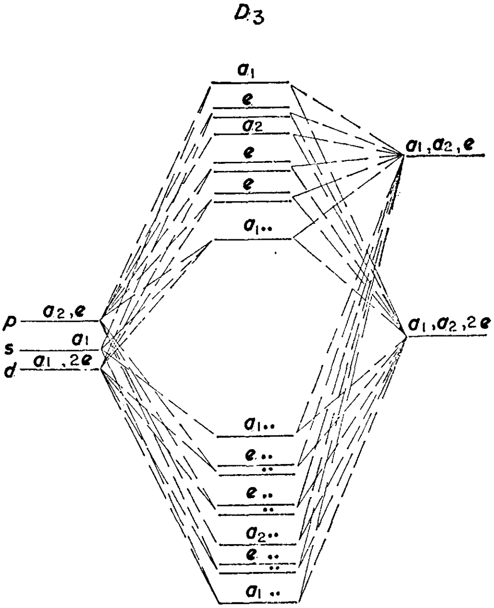

Figure 5 *A qualitative molecular orbital scheme for* Ni(diars)$_3^{2+}$ *showing the correlation between the nickel and arsenic atom orbitals in* D_3 *symmetry.*

For Ni$^{\text{II}}$ in tetrahedral fields the ground state is an orbitally degenerate *T* state and relatively large contributions to observed moments from orbital angular momentum are expected and observed. For regular tetrahedral complexes μ_{eff} should occur within the interval 3·5—4·0 B.M. However, in pseudo-tetrahedral complexes containing different ligands well separated in the spectrochemical series, there may be a loss of ground-state degeneracy giving a lower orbital contribution and hence lower moments. Tetrahedral Co$^{\text{II}}$ complexes usually exhibit moments closer to the spin-only values and these are of the order 4·2—4·8 B.M. Tetrahedral iron(II) and iron(III) complexes are somewhat rare and are not important to this Review.

Five-co-ordinate complexes of nickel(II) and cobalt(II) are fairly numerous and are now structurally well characterised. In addition a smaller number of iron(II) complexes are found to be five-co-ordinate. Although extensive spectral work has been done, no detailed magnetic study has appeared. For this reason the exact behaviour of such complexes cannot be predicted but approximate ranges for the experimental moments appear to be defined. Five-co-ordinate nickel(II) may be either high-spin with two unpaired electrons and moments in the range 3·0—3·4 or low-spin with no unpaired electrons and moments close to zero. These values apply to geometries approximating both trigonal bipyramidal and square pyramidal forms. Cobalt(II) complexes which are five-co-ordinate may also exhibit high-spin moments of 4·2—4·6 ($S = \frac{3}{2}$) or low-spin moments of 1·7—2·1 ($S = \frac{1}{2}$). Again the differences in geometry are not always obvious. Five-co-ordinate complexes of iron(II) are not included among the examples discussed in this Review but the high-spin range of moments appears to be 5·1—5·5 B.M. and the low-spin 2·9—3·1 B.M. These correspond to 4 and 2 unpaired electrons, respectively.

Square planar Ni^{II} complexes have no unpaired electron and exhibit essentially zero moments or small contributions due to temperature-independent paramagnetism. Square planar Co^{II} species are, however, paramagnetic and are reported to exhibit moments in the range 2·1—2·9 B.M., having slightly larger orbital contributions than low-spin octahedral complexes.[10] Theoretically, high-spin square planar Co^{II} species are possible, but none have yet been authenticated, although there have been reports[11,12] of such compounds which were later shown in actuality to be low-spin species[13a] (presumably contamination yielded erroneously high values), or to involve higher co-ordination numbers.[13b]

The ranges of occurrence of magnetic moments, for the normal complexes that provide the standard against which anomalous behaviour is measured, are summarised in Table 1. The ranges within which anomalous moments will fall for each metal are also shown.

It is useful to recall the elementary fact that a condition for our defined normal paramagnetic behaviour (except for the specified cases involving T ground states) is found in the temperature-dependence of the magnetic susceptibility of the metal ion, χ_a. The susceptibility should be linearly related to the reciprocal of the absolute temperature (T), conforming to the Curie–Weiss law, *i.e.*,

$$\mu_{eff} = 2{\cdot}83\sqrt{[\chi_a(T + \theta)]}$$

where the Weiss constant θ can be determined as a finite intercept in a plot of $1/\chi_a$ against T. As will be seen below, a departure of the measured magnetic susceptibilities from this simple dependence on temperature can frequently provide valuable clues concerning the origin of anomalous magnetic behaviour.

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[10] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1959, 338.

[11] H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Amer. Chem., Soc.*, 1962, **84**, 3596.

[12] F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, 1960, **82**, 2979.

[13] (*a*) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, 1963, **85**, 3049; (*b*) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1965, **4**, 1145.

It must be noted, however, that anomalous magnetic moments may arise in the solid state where non-equivalent lattice sites are occupied by the metal atoms, and that the Curie–Weiss law will still be obeyed in such cases. This too can provide valuable information about the source of the anomaly.

Anomalous magnetic moments for Ni^{II} compounds have been recognised since 1942 when French, Magee, and Sheffield[14] observed that bis(formylcamphorethylenediamine)nickel(II), diamagnetic in the solid state, shows a moment of 1·9 B.M. in methanol solution. For iron(III), such phenomena have been known since 1931 when Cambi and his co-workers first published work on the iron(III)-*NN*-dialkyldithiocarbamates,[15–18] which show room-temperature moments between 2·3 and 5·9 B.M. The early investigators attributed the values to *a thermal equilibrium between two magnetically isomeric forms.* That the phenomenon is by no means rare is demonstrated by the large number of publications on the subject in recent years. A variety of models is required to account for the many examples of anomalous behaviour. These may be conveniently considered under the following categories: (1) Equilibrium between two spin states; (2) magnetically non-equivalent sites in the unit cell; (3) solute–solvent interaction; (4) solute–solute interaction; (5) configurational equilibrium.

1 Equilibrium between Two Spin States

A. Nickel(II).—In D_{4h} symmetry nickel may undergo a singlet–triplet spin state isomerism. This model has been invoked several times to explain unusual magnetic behaviour, but it has been convincingly demonstrated only recently. The theoretical basis for the understanding of this type of behaviour was laid by Maki[19] for a weak ligand field and by Liehr and Ballhausen[20] for a strong ligand field.

The application of a ligand field causes splitting of the five degenerate *d* levels of a transition-metal ion into two or more separate sets of levels, depending on the symmetry of the field. For fields of O_h symmetry, two such levels, e_g and t_{2g}, are produced. These exist as an upper doublet (*e.g.*, the $d_{x^2-y^2}$ and d_{z^2} orbitals) and a lower triplet (t_{2g}, the d_{xy}, d_{xz}, and d_{yz} orbitals) as shown in Figure 6. For weak ligand fields the spin multiplicity will be the maximum obtainable for any given number of *d* electrons, in accordance with Hund's rule. For strong fields, on the other hand, for which the energy separation Δ_0 of the e_g and t_{2g} sets of orbitals exceeds the electron-pairing energy (P.E.) the more stable configuration for d^4, d^5, d^6, and d^7 systems will be one in which the t_{2g} level is completely filled before any occupation of the higher-energy e_g level occurs. Thus, $Fe(NH_3)_6^{2+}$ exhibits a magnetic moment of 5·45 B.M. (high-spin)

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[14] H. S. French, M. Z. Magee, and E. Sheffield, *J. Amer. Chem. Soc.*, 1942, **64**, 1924.

[15] L. Cambi and L. Szego, *Ber.*, 1931, **64**, 2591.

[16] L. Cambi, L. Szego, and A. Cagnasso, *Atti Accad. naz. Lincei*, 1932, **15**, 266.

[17] L. Cambi and L. Szego, *Ber.* 1933, **66**, 656.

[18] L. Cambi and L. Malatesta, *Ber.*, 1937, **70**, 2067.

[19] (*a*) G. Maki, *J. Chem. Phys.*, 1958, **28**, 651; (*b*) G. Maki, *ibid*, 1958, **29**, 162 and 1129.

[20] A. D. Liehr and C. J. Ballhausen, *J. Amer. Chem. Soc.*, 1959, **81**, 538.

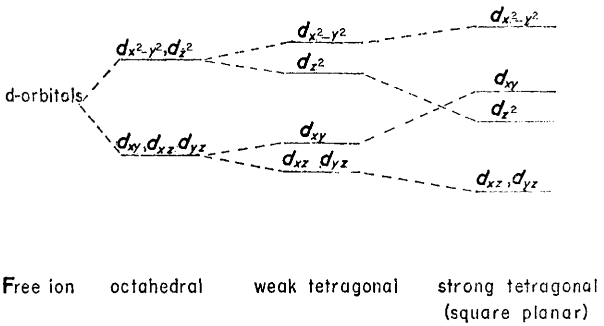
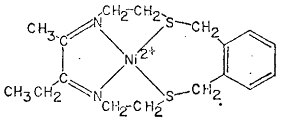


Figure 6 *Splitting of orbitals in octahedral, tetragonal, and square planar ligand fields*

indicating the presence of four unpaired electrons, whereas $Fe(CN)_6^{4-}$ is diamagnetic (low-spin). For Ni^{II} complexes of O_h symmetry there is clearly only one way in which the eight *d* electrons can be arranged for states of lowest energy. All regular octahedral complexes of Ni^{II} must therefore show a paramagnetism corresponding to the presence of two unpaired spins. This situation is alternatively represented by the energy level diagram in Figure 1 where it can be seen that the triplet $^3A_2$ state (paramagnetic) must always lie below the singlet ^1E state (the latter state would impose diamagnetism) for all values of Δ_0. The situation changes, however, whenever an axial distortion is applied to the originally regular octahedral field. Such distortion lowers the symmetry from O_h to D_{4h} and is accompanied by a further loss of degeneracy of the *d* orbitals When this tetragonal distortion is large the energy separation between the $d_{x^2-y^2}$ and d_{z^2} orbitals (Δ_1) or between d_{x2-y2} and d_{xy} orbitals (Δ_2) may exceed the electron-pairing energy. In this case there will be a change in magnetic moment from *ca.* 3·0 B.M. to zero. Conceptually, tetragonal distortion can be envisaged as arising by moving the two ligands on the *z* axis to greater distances from the metal ion. In fact this occurs only for certain electronic configurations and is an example of Jahn–Teller distortion. Alternatively, and more subject to control, the presence at these axial positions of different ligands which exercise a different perturbation on the *d* orbitals from those in the *xy* plane will generate the effect. In high-spin Ni^{II} complexes only the latter type of tetragonal distortion is found, as in mixed complexes of the type Nia_4b_2. Figure 6 represents the changes in orbital energy levels as the symmetry is progressively lowered from that of a regular octahedron to a strong tetragonal structure. It is clear that tetragonal distortion leads, in the limit, to square planarity and a co-ordination number of four. Proceeding in the reverse direction, for a square planar complex, Nia_4, which interacts along the *z* axis with two ligands b, there will be a reduction in the energy separation (Δ_1 or Δ_2) of the two highest-energy orbitals. For weak interactions, such as would be caused by ligands low in the spectrochemical series, *e.g.*, I^-, Δ_2 may still exceed the pairing energy. On the other hand, if the separation of the ligands a and b in the spectrochemical series is relatively small, then Δ_2 (or Δ_1) may be less than the pairing energy and a change in spin multiplicity will occur. Even in this simple model it is necessary to remain aware of the dependence of the pairing energy on the nature of the donor atoms, for at a fixed Δ value, reduction in magnitude of the pairing energy may produce the low-spin state.

There are many examples of series of tetragonal Ni^{II} complexes wherein a relatively small change in the nature of the axial ligands brings about the predicted magnetic cross-over. For example, Goodgame and Venanzi[21] found that for a series of *NN′*-diethylethylenediamine complexes of the type $Ni(diamine)_2X_2$ (X is a univalent anion) the complexes fall in two categories, diamagnetic and paramagnetic ($\mu = 3{\cdot}1$—$3{\cdot}3$ B.M.) and the cross-over in ground states occurs between X = Br (diamagnetic) and X = Cl ($\mu = 3{\cdot}29$ B.M.).

The sharpness of the change-over is demonstrated by the fact that chloride and bromide occupy adjacent positions in the spectrochemical series. Similar results have been observed for complexes of the planar quadri-dentate ligand (I).[22] Here also the magnetic moment varies with the nature of the axially coordinated univalent groups. Thus, the perchlorate and iodide are diamagnetic while the (anhydrous) bromide (in $CHCl_3$ solution), chloride, azide, and thiocyanate are paramagnetic ($\mu = 3{\cdot}1$—$3{\cdot}2$ B.M.). Some unusual features of the dibromo-complex will be discussed in Section (2). An equally sharp change is seen for complexes of 1,4,8,11-tetra-azacyclotetradecane (cyclam) (II)[23] where the chloride and bromide complexes are paramagnetic and the iodide is diamagnetic. Quinoxaline (III) complexes of Ni^{II} halides provide a third example of a rather different kind.[24] The complex with nickel iodide has the stoicheiometry NiQ_2I_2 (Q is quinoxaline); it is diamagnetic. The chloride and bromide, of stoicheiometry $NiQCl_2$ and $NiQBr_2$, are paramagnetic tetragonal polymers involving bridging halide and quinoxaline groups. In all of these systems the room-temperature magnetic behaviour is consistent with expectation for either



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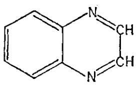
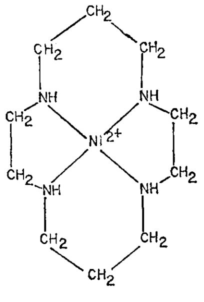


(III)



(II)

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[21] D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 1963, 616, 5909.

[22] G. R. Brubaker and D. H. Busch, *Inorg. Chem.*, 1966, **5**, 2114.

[23] B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, 1965, **4**, 1109.

[24] A. B. P. Lever, *J. Inorg. Nuclear Chem.*, 1965, **27**, 149.

the triplet or singlet ground state; *i.e.*, no anomalous behaviour was observed.

Certain systems are explicable on the basis of equilibria between coexisting singlet and triplet states whose energy states differ by amounts comparable with thermal energies. For such an equilibrium between spin isomers the distribution between the two states can be described by Maxwell–Boltzmann statistics, if it is assumed that there is no change in structure *other than the alteration in spin state.* It has been shown[25] that the magnetic susceptibility is given by:

$$\chi_a = \frac{2g^2N\beta^2}{3kT}\left[1 + \tfrac{1}{3}\exp\frac{\Delta E}{kT}\right]^{-1} + Na$$

where g is the Lande' splitting factor, N is Avogadro's number, β is the Bohr magneton, k is the Boltzmann constant, T is the absolute temperature, ΔE is the energy separation between the singlet and triplet states, and $N\alpha$ is the temperature-independent paramagnetism (TIP). The factor $\frac{1}{3}$ arises because a small increase in entropy ($R\ln 3$) is associated with the increase in spin multiplicity. Other sources of entropy change are ignored and this amounts to the assumption of a vertical transition between states as represented in a single Orgel diagram. It follows from this equation that the magnetic susceptibility will increase with temperature except where $\Delta << kT$, *i.e.*, when the singlet and triplet states are essentially degenerate. This is, of course, the opposite direction of change for χ_A from that predicted by the Curie–Weiss law.

The first convincing example of spin-state isomerism in a crystalline compound was reported in 1964 by Holt, Bouchard, and Carlin.[26] Dichlorotetrakis-(*NN'*-diethylthiourea)nickel(II) is spin-paired at temperatures lower than *ca.* 194°K, but attains partial paramagnetism reversibly, as the temperature is raised. The corresponding bromide and iodide are diamagnetic at room temperature, but the bromide becomes slightly paramagnetic at 373°K. The relative abundances of the triplet states among the three halides is that predicted by the Maki[19] and Ballhausen and Liehr[20] treatment of Ni^{II} in D_{4h} symmetry, since the separation between the singlet and triplet states is least for the chloride which lies closest in ligand field strength to the substituted thiourea. The authors calculated $\Delta H = 4$ kcal. mole^{-1} and $\Delta S = 10$ e.u. for the chloride. It may be noted that the gain in entropy is substantially larger than the value of 2·15 e.u. (R ln 3) predicted for a vertical transition (change in spin multiplicity alone). This suggests, not unreasonably, that the magnetic cross-over is accompanied by other, perhaps minor, structure changes, *i.e.*, the transition is not strictly vertical. This is common, in fact, to all reported examples of this phenomenon. Among the obvious changes that almost certainly must accompany the spin-state alteration is the decrease in in-plane metal–donor distance when the triplet changes into the singlet.

Other Ni^{II} compounds showing spin-state isomerism in the solid state are found among complexes with planar quadridentate macrocyclic ligands. A

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[25] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 1956, 3837.

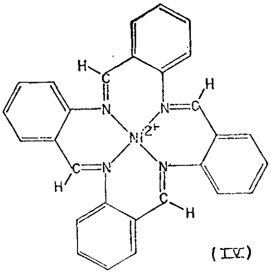
[26] S. L. Holt, R. J. Bouchard, and R. L. Carlin, *J. Amer. Chem. Soc.*, 1964, **86**, 519.

series of six-co-ordinate tetragonal complexes, Ni(TAAB)X_2 {TAAB is tetrabenzo[*b*, *f*, *j*, *n*]1, 5, 9, 13-tetra-azacyclohexadecane (IV)} have been examined where X is a singly charged anion.[27] Table 2 summarises the data obtained for these systems. The chloro- and bromo-complexes exhibit anomalous room-temperature moments, and susceptibility studies as a function of temperature give the non-Curie–Weiss plots shown in Figure 7. Rather than assuming the susceptibility equation for a vertical transition, Busch and his co-workers obtained equilibrium constants from

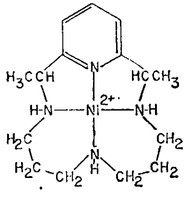
Table 2 *Magnetic data for* $Ni(TAAB)^{2+}$ *complexes*

Complex	μ_{eff}[a] (*B.M.*)
$Ni(TAAB)(ClO_4)_2$	Diamagnetic[b]
$Ni(TAAB)(BF_4)_2$	Diamagnetic[b]
$Ni(TAAB)(BPh_4)_2$	Diamagnetic[b]
$Ni(TAAB)(NCS)_2$	3·2
$Ni(TAAB)(NO_3)_2$	3·2
$Ni(TAAB)I_2$	3·2
$Ni(TAAB)Cl_2,H_2O$	1·7
$Ni(TAAB)Br_2,H_2O$	1·5

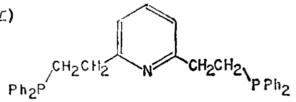
[a] Room temperature values. [b] There is a small residual paramagnetism.



(IV)



(V)



(VI)

$$K_{eq} = \frac{N_{\text{high spin}}}{N_{\text{low spin}}}$$

and the variation of log K_{eq} with the reciprocal of temperature; Figure 8 was used to derive enthalpy and entropy changes for the equilibrium. ΔH Values of 800 and 700 cal. mole^{-1} and ΔS values of +0·57 and −0·45 e.u. for the chloride and bromide were obtained. If the transition were vertical (and the simple equation properly applied) the ΔS value obtained would have agreed

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[27] (*a*) G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, 1964, **86**, 4830; (*b*) D. H. Busch, *Adv. Chem. Ser.*, 1967, **62**, 616; (*c*) E. B. Fleischer, personal communication.

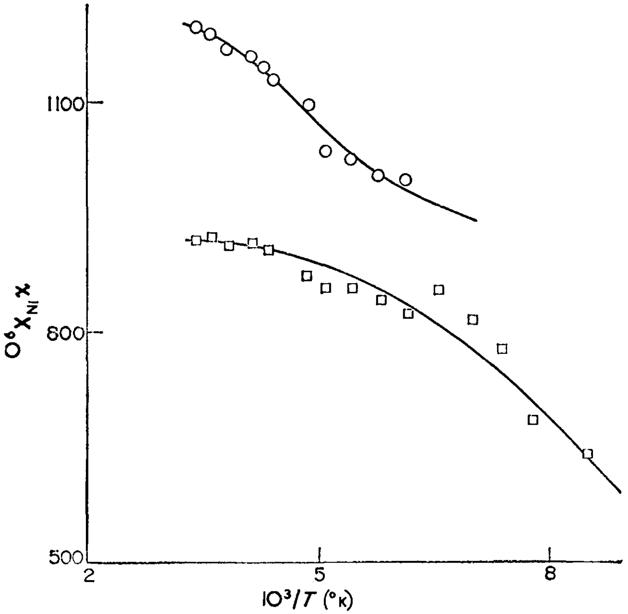

Figure 7 *Temperature-dependence of the magnetic susceptibility of* ○ Ni(TAAB)Cl_2,H_2O *and* □ Ni(TAAB)Br_2,H_2O

with the theoretical value of 2·15 e.u. It is noteworthy that for both TAAB complexes ΔS is closer to the predicted value of 2·15 e.u. than that observed for the first example cited.[26] This might well be associated with, for example, smaller structural changes on passing from the singlet to the triplet state in the case of complexes of the cyclic ligands than in those of the unidentate substituted thiourea. *X*-Ray crystallographic data do indeed indicate an increase in metal–donor bond distance for Ni(TAAB)$^{2+}$ complexes on going from singlet to triplet form.[27c] The nickel–nitrogen distance in Ni(TAAB)$(BF_4)_2$ is 1·90 Å while that for [Ni(TAAB)(H_2O)]I is 2·09 Å.

The role of lattice water in these systems has been discussed.[27b] This constitutes the first case where specific chemical interactions were blamed for this kind of spin-state change. Noting that the chloride and bromide form surprisingly stable hydrates, they assumed that this hydrate water takes part in the equilibrium. The residual charge on the anion should be greatest for the singlet state since the metal–halide bond is weaker in that case. Consequently it was suggested that the water may hydrogen bond strongly to the singlet chloride, but not to the triplet chloride, thereby contributing specifically to the energy balance of the poised system. Karn[28] has shown that an equilibrium between singlet and triplet spin states exists for the NiI_2 complex of a macrocyclic ligand (V). This complex has a room-temperature moment of 2·79 B.M. A temperature-dependent

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[28] J. Karn, Ph.D. Thesis, Ohio State University, 1966.

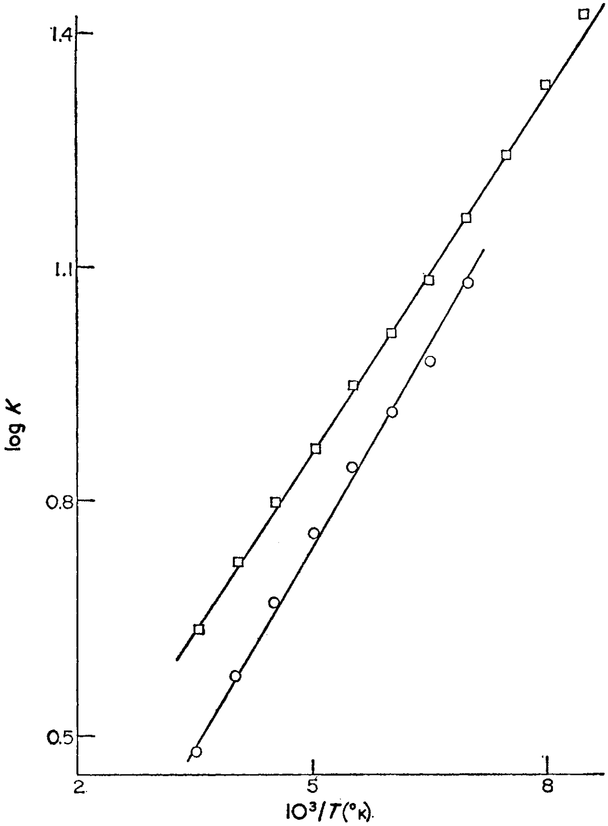

Figure 8 *Variation of* log K_{eq} *with* $1/T$ *for* ○ Ni(TAAB)Cl_2,H_2O *and* □ Ni(TAAB)Br_2,H_2O

susceptibility study from 100° to 340°K indicated Curie–Weiss dependence at low temperatures but increasing deviation from linearity at higher temperatures. This was attributed to a spin-state equilibrium between a triplet ground state and a *low-lying* singlet excited state. This is the first example for which the triplet lies lowest. Analytical treatment of the data yielded values of 1140 cal./mole and -0·68 e.u. for ΔH and ΔS, respectively. This complex represents one of the most extreme cases of tetragonal distortion documented with the apparent ligand field splitting parameter of the axial iodides (Dq^z = 216 cm.$^{-1}$) being only about one-fifth that of the in-plane ligands (Dq_{xy} = 1124 cm.$^{-1}$).

Additional examples of such equilibrium behaviour have been reported recently for other Ni^{II} complexes. $Ni(VPP)_2(NO_3)_2$ [VPP is $P(Ph)_2CH{=}CHP(PH)_2$] has been shown[29] to have non-Curie–Wiess behaviour in the temperature range 300—421°K with magnetic moments ranging from 1·67—3·14 B.M. This

[29] H. N. Ramaswamy, H. B. Jonassen, and A. M. Aguiar, *Inorg. Chim. Acta*, 1967, **1**, 141.

complex acts as a 2:1 electrolyte in nitromethane solution and gives spectra typical of square planar nickel. The magnetic behaviour was explained on the assumption that the nitrate produces an axial perturbation in the solid state. A perchlorate salt of the same complex cation is reported to have a room-temperature moment of 1·50 B.M. but to show Curie–Wiess behaviour over an unspecified temperature range. Room-temperature magnetic measurements on a sample of the perchlorate complex prepared in these laboratories give a molar susceptibility of -491×10^{-6} e.s.u. which yields a value of 0·52 B.M. after correction for the diamagnetism ($+611{\cdot}9 \times 10^{-6}$ e.s.u.). An interesting series of Ni^{II} complexes with benzimidazole has recently been reported.[30] Several of these compounds show unusual magnetic behaviour and one of them, having the stoicheiometry NiL_4Cl_2,S_2 (L is benzimidazole and S is acetone of solvation), is reported to show spin-state equilibrium behaviour.

Although a large number of 5-co-ordinate nickel(II) complexes of both high- and low-spin type have been characterised, only one compound has been found to exist with high- and low-spin forms in equilibrium. Nelson and Kelly have recently found[31] that the 5-co-ordinate complex $Ni(PNP)Cl_2$, where PNP is the terdendate ligand (VI) has a moment of 3·14 B.M. at 294°K which falls reversibly to 1·30 B.M. at 99°K. No change in the 299°K *X*-ray diffraction pattern, except that caused by anisotropic thermal expansion coefficients, was observed on cooling to 77°K. Application of the theory for a Maxwell–Boltzmann distribution between singlet and triplet states yielded a temperature-dependent energy separation, from which it appears that the ground state is a singlet below about 250°K and a triplet above this temperature. Additional examples of such phenomena may appear when extensive magnetic studies are performed on 5-co-ordinate systems.

While these appear to be the only examples of an equilibrium between Ni^{II} complexes of the same symmetry in singlet and triplet states in the crystalline phase, the phenomenon may well be more common in solution where solvent molecules provide the axial perturbation, as was suggested by Maki.[19] In this case it is difficult to distinguish between a spin-state equilibrium and one involving some combination of 4-co-ordinate, 5-co-ordinate (monosolvated) and/or 6-co-ordinate (disolvated) nickel(II) species.

B. Cobalt(II).—As previously described, the normal magnetic moments of 6-co-ordinate Co^{II} complexes should fall near the extremes of the range from *ca.* 1·8 B.M. to *ca.* 5·2 B.M. One survey of Co^{II} chemistry[32] notes that there are moments falling throughout this entire range. The energy-level diagram in Figure 3 shows that at some value of Dq the ^2E state crosses the $^4T_1$ state and in this region a thermal distribution between spin states could exist. This statement is oversimplified in view of spin–orbit interaction and the non-crossing rule.

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[30] D. M. L. Goodgame, M. Goodgame, and M. J. Meeks, *J. Chem. Soc.* (*A*), 1967, (*a*) 1125, (*b*) 1676.

[31] S. M. Nelson and W. S. J. Kelly, *Chem. Comm.*, 1968, 436.

[32] D. H. Busch, 'Cobalt', ed. R. S. Young, ch. 6, ACS Monograph series, Reinhold, New York, 1960.

This matter is discussed further in following examples. In 1961 Stoufer, Busch, and Hadley showed [33a] that a previously postulated[33b] equilibrium between a doublet and quartet state does indeed exist for the complex, bis-(2,6-pyridindialdihydrazone)cobalt(II) iodide ($[Co(PdAdH)_2]I_2$) which has a moment of 3·04 B.M.[34] at 300°K.

A study of the temperature-dependence of the magnetic susceptibility by these workers showed that the moment for the complex varies from 1·9 B.M. at 80°K to 3·7 B.M. at 337°K. A simple thermodynamic treatment ignoring spin–orbit coupling gave ΔH and ΔS values of $-2{\cdot}14$ kcal./mole and $-0{\cdot}44$ e.u., respectively for the equilibrium:

$$\text{spin-free} \rightleftharpoons \text{spin-paired}$$

However, the magnitude of λ should require its use in interpretation of the data.[8]

Other examples were not authenticated until 1966 when Stoufer *et al.*[35] reported temperature-dependence studies on the magnetic properties of six Co^{II} complexes (including additional work on the compound previously studied[33a]) which exhibit anomalous magnetic behaviour. Table 3 gives observed values for μ_{eff} at 100° and 300°K for the six complexes. These compounds, all containing ligands with unsaturated nitrogen donors, give non-linear Curie–Weiss plots (see Figure 9) and can best be explained qualitatively at present by considering the anomalous moments to arise from a Boltzmann distribution between the $^4T_1$ and ^2E states in the vicinity of the cross-over point. For the terpyridyl complexes a marked dependence of the observed susceptibility on the counter-anion has been noted.[35–37] Additional studies on this phenomenon have been reported by Judge and Baker.[38] Results obtained by these workers are shown in

Table 3 *Magnetic data for some magnetically anomalous cobalt*(II) *complexes*

*Complex**	*Magnetic moment (B.M.)* 100°K	300°K
$[Co(BMI)_3]I_2,H_2O$	1·91	2·91
$[Co(PMI)_3](BF_4)_2$	2·16	4·31
$[Co(terpy)_2]Br_2,H_2O$[36]	~1·9	~2·7
$[Co(PdAdH)_2]I_2$	2·22	2·85
$[Co(PBI)_2]I_2$	2·38	3·72
$[Co(DTPH)](ClO_4)_2$	2·36	1·90

* BMI, Biacetylbis (methylimine); PMI, pyridine-2-aldehyde methylimine; terpy, 2,2′,2″-terpyridyl; PdAdH, pyridine-2,6-dialdehyde dihydrazone; PBI, pyridine-2,6-dialdehyde bis(benzylimine); DTPH, 1,12-bis-(2-pyridyl)-1,2,11,12-tetra-aza-5,8-dithia-$\Delta^{2,10}$-dodecadiene.

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[33] (*a*) R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Amer. Chem. Soc.*, 1961, **83**, 3732; (*b*) R. C. Stoufer, Thesis, Ohio State University, Colombus, Ohio, 1958; P. E. Figgins and D. H. Busch, *J. Amer. Chem. Soc.*, 1960, **82**, 820.

[34] R. C. Stoufer and D. H. Busch, *J. Amer. Chem. Soc.*, 1956, **78**, 6016.

[35] R. C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, 1966, **5**, 1167.

[36] Data from R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 1962, 341.

[37] J. G. Schmidt, W. S. Brey, jun., and R. C. Stoufer, *Inorg. Chem.*, 1967, **6**, 268.

[38] J. S. Judge and W. A. Baker, jun., *Inorg. Chim. Acta*, 1962, **1**, 68.

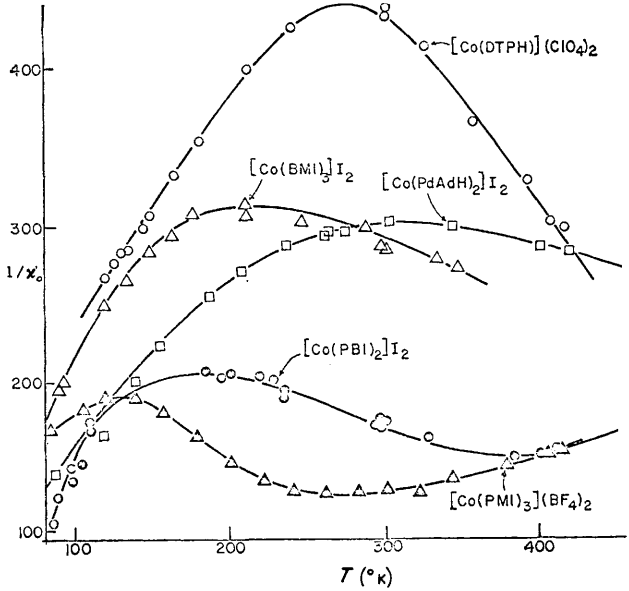

Figure 9 *Temperature-dependence of the magnetic susceptibility of some cobalt*(II) *complexes*

Table 4. There is a pronounced dependence of magnetic moment on the associated anion and the degree of hydration. This is attributed to low-symmetry fields resulting from crystal-packing effects.

Enthalpy calculations[35] on linear portions of the susceptibility curves (Figure 9) indicate that the $^2E(^2G)$ state is the one of lower energy suggesting that the ligand field is not strong enough to cause complete spin pairing. Further studies[37] by the electron paramagnetic resonance technique support the enthalpy data for a lower-lying ^2E state at low temperatures and a decreasing population of this state at higher temperatures. It was found, however, that at still higher temperatures the ^4T state becomes lowest, for the susceptibility continues to increase beyond the value expected for full degeneracy between the doublet and quartet states. More subtle effects, such as mixing of the ^2E state with the ^4T state under the influence of spin–orbit coupling in the vicinity of the cross-over point, have been treated by Stoufer and his co-workers.[39] Using the equation for the susceptibility:

$$\chi = \frac{N\Sigma^1[W_1^2/kT - 2W_2]\exp - (W_0/kT)}{\Sigma\exp - (W_0/kT)}$$

and deriving experimental curves for the dependence of χ on T, they obtained quite good agreement with the experiment. Here W is a function of two variables; ξ, the one electron spin–orbit coupling constant, and δ, the separation between

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[39] D. L. Williams, D. A. Smith, and R. C. Stoufer, *Inorg. Chem.*, 1967, **6**, 590.

Table 4 *Magnetic moments of* Co(terpy)$_2^{2+}$ *with various anions as a function of temperature*[a]

Compound	*Effective magnetic moments*[b]										
Temp(°K)	15	20	30	60	100	150	200	250	300	350	400
Co(terpy)$_2^{2+}$ (soln.)	—	—	—	—	—	—	—	—	3·3	—	—
Co(terpy)$_2$Cl$_2$, 3·5 H$_2$O	3·75	3·78	3·81	3·83	3·84	3·87	3·94	4·04	4·17	4·31	—
Co(terpy)$_2$Cl$_2$	4·17	4·20	4·30	4·37	4·46	4·57	4·61	4·62	4·65	4·70	4·73
Co(terpy)$_2$Br$_2$, 3H$_2$O	—	—	—	—	—	2·26	2·41	2·66	2·94	3·24	—
Co(terpy)$_2$I$_2$, H$_2$O	1·89	1·91	1·94	1·96	2·03	2·23	2·63	3·05	3·40	—	—
Co(terpy)$_2$I$_2$	2·14	2·14	2·15	2·16	2·31	2·84	3·38	3·74	3·97	4·11	—
Co(terpy)$_2$F$_2$, 3·5 H$_2$O	—	1·94	1·94	—	—	—	—	—	2·15	—	—
Co(terpy)$_2$F$_2$, 4·5 H$_2$O	—	—	—	—	—	3·56	3·71	3·86	4·00	—	—
Co(terpy)$_2$(ClO$_4$)$_2$	2·07	2·07	2·07	2·08	2·25	2·89	3·62	4·17	4·49	4·66	—
Co(terpy)$_2$(SCN)$_2$, H$_2$O	2·57	2·58	2·61	2·72	2·82	3·13	3·43	3·75	4·01	4·25	—
Co(terpy)$_2$(NO$_3$)$_2$	1·87	1·87	1·87	1·87	1·88	1·89	2·04	2·42	2·96	3·52	4·00
[Co(terpy)$_2$][Co(CN)$_4$]	—	2·12	2·27	2·43	2·58	2·73	2·90	3·06	3·21	3·53	3·58

[a] From Ref. 38. [b] Corrected for TIP and ligand diamagnetism.

the original ^2E and ^4T states. In addition δ depends explicitly on T, being of the form $\delta = \delta_0 + aT + bT^2 + cT^3$. Although agreement appears, on the surface, quite good this could be coincidental because, as Judge and Baker point out,[38] any treatment probably should include low-symmetry ligand field effects. Calculations similar to those of Williams *et al.*[39] have been reported by Barraclough.[40] These are the only examples among Co^{II} compounds which have been relatively well characterised with respect to this type of anomalous magnetic behaviour.

C. Iron.—An extensive series of compounds having the general formula Fe $phen_2X_2$ has been reported, where X covers a large part of the spectrochemical series. When X is Cl, Br, I, N_3, OCN, HCO_2, and CH_3CO_2, high-spin compounds are formed[41–43] while CN, NCO, and NO_2 give low-spin diamagnetic compounds.[44–46] The high-spin derivatives have reported room-temperature moments in the range of 5·1—5·3 B.M. which is lower than that predicted for spin-free, d^6, octahedral systems considering spin–orbit coupling.[7,47] This lowering of the moment is attributed, in part, to the non-cubic field arising from the difference in ligand field strength of *o*-phen (*o*-phenanthroline) and the anion X.

Temperature-dependence studies have been completed on a series of such compounds where X is I, N_3, SCN, and SeCN.[48] The magnetic behaviour for the Cl, Br, I, and N_3 at least approximate to what is expected for octahedral complexes although the moments are never as high as 5·6 B.M. and there is a slight decrease at lower temperatures rather than the increase expected due to spin–orbit coupling.[8] The SCN and SeCN complexes, on the other hand, show moments of *ca.* 5·0 B.M. at room temperature and drop sharply to *ca.* 1·5 B.M. at 110°K and 150°K, respectively. Similar behaviour was also noted for $Fe(bipy)_2(NCS)_2$. From a consideration of infrared data these workers formulated a dimeric structure with bridging thiocynates and considered the anomalous magnetic behaviour to result from co-operative interactions between the two metal atoms. It was recognised that the behaviour is somewhat different from that previously reported for dimeric systems.[49] It might be noted that there have been more recent reports on such co-operative interactions,[50] though, again, these are explicitly omitted from this Review.

Other investigators concerned with the $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2(NCSe)_2$ systems[51] have suggested that the anomalous behaviour is better

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[40] C. G. Barraclough, *Trans. Faraday Soc.*, 1966, **62**, 1033.

[41] F. Basolo and F. P. Dwyer, *J. Amer. Chem. Soc.*, 1954, **76**, 1454.

[42] K. Madeja and E. König, *J. Inorg. Nuclear Chem.*, 1963, **25**, 377.

[43] W. A. Baker, jun., and H. M. Bobonich, *Inorg. Chem.*, 1963, **2**, 1071.

[44] A. A. Shilt, *J. Amer. Chem. Soc.*, 1960, **82**, 3000.

[45] W. Beck and E. Schuierer, *Chem. Ber.*, 1962, **95**, 3048.

[46] K. Madeja, *Chem. Zvesti*, 1965, **19**, 186.

[47] J. S. Griffith, *Trans. Faraday Soc.*, 1958, **54**. 1109.

[48] W. A. Baker, jun., and H. M. Bobonich, *Inorg. Chem.*, 1964, **3**, 1184.

[49] A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 1961, 396.

[50] J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. (A)*, 1967, 1014; A. V. Khedekar, J. Lewis, F. E. Mabbs, and H. Weigold, *ibid*, p. 1561.

[51] E. König and K. Madeja, *Inorg. Chem.*, 1967, **6**, 48.

represented as an equilibrium between $^5T_2$ and $^1A_1$ ground states. High-spin forms would be obtained when the ligand field strength (Δ) is less than the pairing energy (P.E.) for the iron(II) d^6 ions. When $\Delta >$ P.E. compounds of the low-spin form result. If Δ and P.E. are of approximately the same magnitude then such an equilibrium could result between t_{2g}^6 (spin-paired) and $t_{2g}^4e_g^2$ (spin-free). It is well known[52] that Δ for spin-paired forms is greater than that for spin-free forms, and as Ewald *et al.*[53] have shown for such equi-energetic configurations Δ (high spin) $<$ P.E. $<$ Δ (low spin).

The temperature-dependence of the susceptibility for Fe(phen)$_2$(NCS)$_2$ and Fe(phen)$_2$(NCSe)$_2$ determined by König and Madeja is shown in Figure 10.

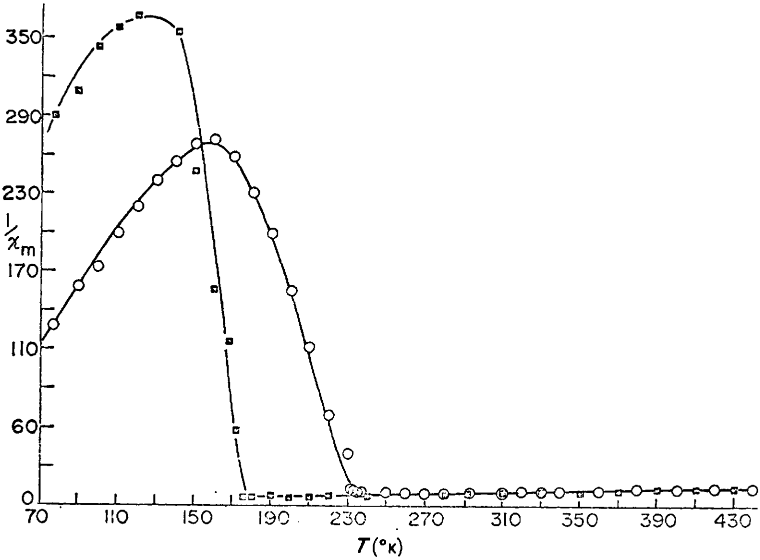

Figure 10 *Temperature-dependence of the magnetic susceptibility for* ☐ Fe(phen)$_2$(NCS)$_2$ *and* ○ Fe(phen)$_2$(NCSe)$_2$

The general behaviour is similar to that reported previously[48] and it was noted that individual preparations gave somewhat different values in certain temperature ranges, but the shapes of the curves are the same. Such transitions do take place reversibly with temperature. When data were incomplete it was thought that acceptable agreement between measured and calculated values of μ_{eff} would be found,[54] but the data from the complete study could not be fitted well to the traditional Van Vleck equation.[55]

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[52] C. K. Jørgenson, 'Absorption Spectra and Chemical Bonding in Complexes', Pergamon Press, Oxford, 1962, p. 128.

[53] A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.*, 1964, *A*, **280**, 235.

[54] E. König and K. Madeja, *Chem. Comm.*, 1966, 61.

[55] J. H. Van Vleck, 'The Theory of Electric and Magnetic Susceptibilities', Oxford Univ. Press, 1932.

Further work, including attempts to apply the treatment of Ewald *et al.*,[53] account being taken of the variation of the metal–ligand bond distance with population of a particular ground state, did not improve the fit. Careful investigations of the electronic, Mössbauer, and i.r. spectra indicated a change in molecular structure between 300° and 77°K and one may assume that this must occur at the point where there is a sharp reduction in magnetic moment. These systems may qualitatively exhibit a $^1A_1$–$^5T_2$ equilibrium which is associated with a modification in molecular structure, such that the usual theoretical equations do not specifically apply. One possibility could be a crystalline phase change between two solid solutions (low-spin dissolved in high-spin $\rightleftharpoons$ high-spin dissolved in low-spin) at the point where there is an abrupt change in susceptibility. However, *X*-ray powder data appear to contradict this.

Recent magnetic studies on $Fe(dipy)_2(NCS)_2$[56] have revealed a behaviour quite similar to that for $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2(NCSe)_2$ as noted previously.[48] $Fe(dipy)_2(NCS)_2$ has been found[56] to exist in three polymorphic forms exhibiting related but distinctly different magnetic behaviour. One of these is found to have a slight field-dependent susceptibility. In all cases at some critical temperature there is a more or less sudden decrease in susceptibility and concomitant change in ground state for the complex. This change is found to be essentially complete for one of the polymorphs but some molecules remain in the quintet state in each of the other two forms. Again such a sharp change in ground state is not characteristic of a *bona fide* equilibrium between two spin states, but rather must indicate a significant variation in structural parameters. Nonetheless, again no crystalline phase change is indicated.

Depending upon the substituents on the rings, some iron(II) poly-(1-pyrazolyl) borates (VII) have also been found to undergo a $^1A_1$–$^5T_2$ spin-state equilibrium.[57a] Where R = H and X and Y are CH_3 the complex is fully paramagnetic while when R = Ph and X = Y = H the compound is diamagnetic. However, when R = X = Y = H or when R = X = H and Y is isopropyl, intermediate room-temperature moments (*ca.* 2·7 B.M.) are found. An extensive study of the temperature-dependence of the susceptibility in chloroform by the n.m.r. technique[57b] indicated that the intermediate moments might arise from an equilibrium between $^1A_1$ and $^5A_1$ states (the $^5A_1$ in the D_{3d} point-group is derived, by descent in symmetry, from the $^5T_1$ state in O_h symmetry). The structure of the complex precludes a conformational equilibrium such as has been observed for some systems (see p. 491). The positions of the resonances in the n.m.r. spectrum for the complex undergoing the spin equilibrium were intermediate between those of the diamagnetic and paramagnetic compounds and exhibit a non-Curie–Weiss dependence on temperature. A range in moments from 1·5 B.M. at 250°K to *ca.* 3·5 B.M. at 340°K was observed. ΔH and ΔS values of 3·85 kcal./mole and 11·4 e.u. were derived by analysis of the results. Since the entropy in going from a $^1A_1$ to $^5A_1$ spin state is again in excess of that expected for the change

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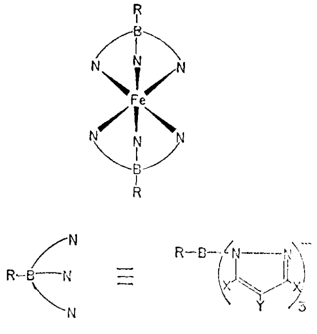
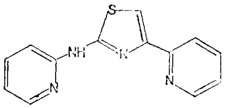
[56] E. König, K. Madeja, and K. J. Watson, *J. Amer. Chem. Soc.*, 1968, **90**, 1146.

[57] (*a*) J. P. Jesson, S. Trofimenko, and D. R. Eaton *J. Amer. Chem. Soc.*, 1967, **89**, 3158; (*b*) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, 1963, **85**, 397.



(VII)



(VIII)

in spin degeneracy alone there must be a large contribution due to ligand field alterations, bond-distance changes, and/or solvation effects. The same general phenomenon is evident in the solid state but the equilibrium is shifted to favour the diamagnetic form. It is noteworthy that this system has allowed the first direct observation by Mössbauer spectroscopy of the cross-over between spin-states[58] giving distinct spectra for the quintet state at higher temperatures and for the singlet state at lower temperatures.

Recently the unusual magnetic properties of some iron(II) complexes of 2-(2-pyridylamino)-4-(2-pyridyl) thiazole (papth) VIII) have been investigated.[59] Bis-complexes of this ligand have been found to be spin-free for Co^{II} and Ni^{II}; however, for Fe^{II} there is a strong dependence on the anion and in some cases the degree of hydration. Table 5 gives some room-temperature magnetic data, including θ values for the normal compounds.

A number of interesting features were noted in this system. In addition to a large variation in magnetic behaviour with associated anion and degree of hydration the anhydrous nitrate requires about 3 hr. to attain an equilibrium or constant moment at low temperatures. Also there appear to be spin isomers of the [Fe(papth)$_2$]Cl$_2$, these being yellow (normal high-spin behaviour) and red-brown (predominantly spin-paired). In all cases, a sample which has a high moment at room temperature appears yellow and as the temperature is decreased it becomes red-brown. No difference in the reflectance spectrum is evident, however, between yellow and red-brown samples so these workers attribute the vastly different appearance to differences in band intensities.

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[58] J. P. Jesson and J. F. Weihner, *J. Chem. Phys.*, 1967, **46**, 1995.
[59] R. N. Sylva and H. A. Goodwin, *Austral. J. Chem.*, 1967, **20**, 479.

Table 5 *Magnetic data for compounds of the type* [Fe(papth)$_2$]X$_2$,*n*H$_2$O

Anion	*No. of water molecules*	μ_{eff} (298°K)	θ (°K)
$C_2O_4^{2-}$	1	5·28	−16
$2I^-$	1	~5·0	−20
$2ClO_4^-$	1	~5·1	−38
$2Cl^-$ (yellow)	0	~5·4	−5
SO_4^{2-}	3·5	~5·0	−11
SO_4^{2-}	5	~3·4	
$2Cl^-$	2	~1·9	
$2Cl^-$ (red-brown)	0	~1·8	
$PtCl_6^{2-}$	2	~3·1	
$2SCN^{2-}$	1	4·48	
$2NO_3^-$	1	~2·4	
$2Br^-$	2	1·3	
$2NO_3^-$	0	5·18	

Quantitative treatment of these systems *via* a Boltzmann distribution over spin-states is not adequate but an empirical treatment in which relative concentrations of the two spin forms were considered was used to obtain ΔH values for the various compounds studied. With the exception of [Fe(papth)$_2$]Br$_2$,2H$_2$O the plots of log K against T are not straight lines over the whole temperature range, but may show continuous curvature or have segments which approximate to straight lines of different slopes. Such deviations indicate something besides a vertical spin-state equilibrium and may be attributed in part to a modification of the crystal lattice. Such an interpretation indicates that the time-dependence found for the anhydrous nitrate is the consequence of a slow phase change at low temperatures. This suggests that the two anhydrous forms of the chloride are, in fact, lattice isomers first (allotropes) and spin isomers as a consequence of the structure modification. There are additional possibilities of solid solutions and perhaps some less obvious intermolecular interactions. Determinations of the susceptibilities at different field strengths might be helpful for further elucidation of the anomalies.

Tris-(2-aminomethylpyridine)iron(II) is reported to undergo a spin-equilibrium[60] with the associated anion (Cl$^-$, Br$^-$, I$^-$) determining the specific behaviour observed. Moments show behaviour similar to those for Fe(phen)$_2$(NCS)$_2$[48,51] in dropping to a constant value at some intermediate temperature and remaining there to 20°K. No success was achieved in fitting the data to an equilibrium between $^1A_1$ and $^5T_2$ states. The existence of two spin states is supported by Mössbauer data for the Cl and I salts. Dilution experiments of the Cl$^-$ salt with the corresponding zinc complex supports the conclusion that intermolecular factors do not determine the magnetic behaviour.

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[60] G. A. Renovitch and W. A. Baker, jun., *J. Amer. Chem. Soc.*, 1967 **89**, 6377.

At present, these constitute the documented cases of spin-state equilibria among iron(II) complexes. There is an interesting compound, phthalocyanine iron(II), which has been the topic of continued discussion since Klemm's first work showed a moment about midway between high-spin ($S = 2$) and low-spin ($S = 0$). The possibility of a spin-state equilibrium has been considered.[61] Because of this possibility a more complete temperature study was performed on this compound along with other phthalocyanines.[62a] This work agreed well with that of Klemm (room-temperature moment = 3·85 B.M.) and covered a greater temperature range (100—340°K). Approximate Curie–Weiss dependence was found with some slight curvature at low temperatures. This observation fails to support a spin-state equilibrium and the small Weiss constant of 9°K casts doubt on the possibility of antiferromagnetism. Lever[62a] considered the moment to arise from the $S = 1$ spin configuration which is probably $b_{2g}^2 \cdot e_g^3 \cdot a_{1g}$ giving a ^3E_g term (for $S = 2$ the configuration would be $b_{2g}^2 \cdot e_g^2 \cdot a_{1g} \cdot b_{1g}$). No electron spin resonance signal has been observed for the complex.[63]

A triplet ground state ($S = 1$) has also been claimed recently for iron(II) in a six-co-ordinate environment. König and Madeja[62b] report moments of 3·98 B.M. and 3·80 B.M., respectively, at 292°K for $Fe(phen)_2ox,5H_2O$ and $Fe(phen)_2 mal,7H_2O$ (ox = oxalate and mal = malonate). Curie–Weiss behaviour, with small θ, is observed for both compounds and the moments are unchanged on dissolution in methanol. ^{57}Fe Mössbauer and i.r. spectra are not consistent with the occurrence either of $^5T_2$ or of $^1A_1$ states but show a greater similarity to those expected for the latter.

No doubt there will be other cases of spin-equilibrium for iron(II) complexes when more extensive studies have been carried out. Workers should beware of the pitfalls of ferromagnetism and antiferromagnetism which can exist particularly with iron(II). Also 'magnetic purity' is a matter of considerable concern for analytically acceptable samples can sometimes yield reproducible values whose magnitudes depend on the purification procedure.

D. Iron(III).—The prime examples of spin-state equilibria involving iron(III) occur with the *NN*-dialkyldithiocarbamates. These compounds, first investigated by Cambi and his co-workers in the late 1930's,[15–18] have been extensively studied more recently.[53,64,65] The later workers have presented detailed studies of the magnetic behaviour of 18 iron(III)-dialkyldithiocarbamates over the temperature range 80—400°K. There exist three types of behaviour depending on

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[61] L. Orgel, Proc. 10th Solvay Conference, Brussels, 1956, ed. R. Stoops, Brussels, 1956.

[62] (*a*) A. B. P. Lever, *J. Chem. Soc.*, 1965, 1821; (*b*) E. König and K. Madeja, *J. Amer. Chem. Soc.*, 1966, **88**, 4528.

[63] D. J. E. Ingram and J. E. Bennett, *J. Chem. Phys.*, 1954, **22**, 1136, *Discuss. Faraday Soc.*, 1955, **19**, 140.

[64] A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Austral. J. Chem.*, 1964, **17**, 294.

[65] R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and A. H. White, *J. Chem. Phys.*, 1966, **45**, 2688.

the alkyl substituent. Room-temperature moments range from high-spin ($\mu_{\text{eff}} = 5{\cdot}83$, R = pyrrolidyl) to a minimum value of $\mu_{\text{eff}} = 3{\cdot}02$ (R = isobutyl). Almost any intermediate value can be achieved by proper choice of alkyl group or combination thereof. It is well established that the compounds show the same general behaviour in solution and that they are monomeric, non-conducting molecular species. Pressure-dependent magnetic studies show a tendency toward the spin-paired state with increased pressure. This is as expected, for it is established that Δ(spin-paired) should be greater than Δ(spin-free),[53] and this can best arise by a decrease in the metal–donor bond distance, giving, in turn, a smaller molal volume. It should be noted, however, that the change in molal volume with spin state is very small at constant pressure.

These workers have produced one of the most complete studies so far on spin equilibria, treating the data by application of Van Vleck's equation:

$$\mu^2 = \frac{\frac{3}{4}g^2 + 105\exp[-(1 + E/\delta)] + 8x^{-1}[1 - \exp(-\frac{3}{2}x)]}{1 + 2\exp(-\frac{3}{2}x) + 3\exp[-(1 + E/\delta)]\,x}$$

where $x = \delta/kT$, E is the separation between zero-point levels of the two states undergoing the equilibrium and g is a parameter to account for interactions of the $^2T_2$ state with higher terms. The variation of magnetic susceptibility with temperature is explained qualitatively quite well by this equation, which predicts, with proper choice of constants, a maximum and minimum similar to that observed in the experimental temperature studies. However, no exact fit could be obtained. Three reasons were suggested to help explain this inadequacy: (1) Failure of parameter g to account for interactions with higher states; (2) reduction of effective symmetry from O_h; and (3) differences in vibrational frequencies of the $^6A_1$ and $^2T_2$ states. Of these three ideas only the third was thought to be profitable for further treatment. These workers were able to assign metal–donor stretching modes for the $^2T_2$ and $^6A_1$ states and by choosing probable values for the S—Fe—S bending modes they were able to modify the above equation to account for free-energy changes and thus alter the population levels at the measurement temperature. After such a modification a satisfying agreement could be obtained. The treatment still does not give exact molecular parameters. This would require precise values for the populations of the energy levels.

An n.m.r. study of this equilibrium in solution was recently reported and supports the previous conclusions.[65] Some interesting comments on the mean pairing energy for iron(III), long a topic of discussion, were presented by these workers.[53]

Ho and Livingstone[66] have recently reported magnetic behaviour best explained by a thermal equilibrium between t_{2g}^5 and $t_{2g}^3e_g^2$ spin states for iron(III) complexes of monothio-β-diketones. For complexes of the type $\text{Fe[R}^1\text{C(S)}\text{-}\text{CH}{\cdot}\text{C(O)R}^2]_3$ the magnetic behaviour is dependent on the nature of the R

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[66] R. K. Y. Ho and S. E. Livingstone, *Chem. Comm.*, 1968, 217.

groups and electron-withdrawing substituents appear to increase the population of the spin-paired configuration.

One of the most interesting cases of spin equilibrium occurs among the ferrihaemoprotein hydroxides. Pauling and his co-workers measured the magnetic moment of ferrihaemoglobin hydroxide in 1937 and obtained a value of 4·7 B.M.[67] This differs considerably from that of the F^- (5·92 B.M.) and from those of the CN^- and SH^-, 2·5 and 2·26 B.M., derivatives respectively. Since that time there has been a continuing discussion of the electronic structures of such complexes. The first workers postulated a configuration with 3 unpaired electrons corresponding to an intermediate spin state between high-spin ($S = \frac{5}{2}$) and low-spin ($S = \frac{1}{2}$) configurations. Theoretical treatment of this electronic state shows it to be unstable in a strict octahedral donor environment.[68a] This does not mean that it is not likely in species of lower symmetry, but Griffith has concluded $S = \frac{3}{2}$ states are highly improbable for these compounds[68b] whereas high-spin and low-spin configurations are definitely established.

Spectra of a series of ferrihaemoproteins are, for the most part, identical for a particular axial ligand; however, the hydroxide shows band shifts throughout the same series.[69] These workers have used such spectral data in connection with magnetic data to support the postulated existence of an equilibrium between high- and low-spin forms. In fact, through sensitive experimental technique- they were able to measure and reduce spectral data into component contribus tions from high-spin and low-spin ferrimyglobin hydroxide. This treatment is supported by the results of indirect susceptibility determinations over a rather narrow temperature range (1°—30°c) which reveals a non-Curie–Weiss dependence, as expected for a thermal equilibrium between spin states. From μ_{eff} values of 5·92 and 2·24 for high-spin and low-spin forms, respectively, the percentages of the configurations for several haemoproteins were calculated to be as shown in Table 6.

Table 6

	High-spin (%)	Low-spin (%)
Myglobin	70	30
Haemoglobin	50	50
Peroxidase	7	93

Such equilibria have been postulated for other derivatives where the magnetic moment differs appreciably from ideal high- or low-spin values, but no other detailed study has been reported.[70]

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[67] C. D. Coryell, F. Stitt, and L. Pauling, *J. Amer. Chem. Soc.*, 1937, **59**, 633.

[68] (*a*) J. S. Griffith, *J. Inorg. Nuclear Chem.*, 1956, **2**, 1, and 229. (*b*) J. S. Griffith, *Proc. Roy. Soc.*, 1956, *A*, **235**, 23.

[69] P. George, J. Beetlestone, and J. S. Griffith, 'Haematin Enzymes', Pergamon Press, New York, 1961, p. 111.

[70] (*a*) W. Scheler, G. Schoffa, and F. Jung, *Biochem. Z.*, 1957, **329**, 232; (*b*) R. Havemann and W. Haberditzl, *Z. phys. Chem.*, 1958, **209**, 135.

This completes the discussion of spin-state equilibria wherein a single symmetry characterises both low- and high-spin forms. Many of these systems leave something to be desired in the quantitative interpretation but at present the equations generally employed are not adequate to describe the many perturbations a system undergoes in a transition from one spin state to another. The phenomenon remains a molecular dimorphism of the most interesting kind.

2 Magnetically Non-equivalent Sites in Unit Cell

The coexistence of metal ions with two different stereochemistries within the unit cell is well documented in a number of cases. This is well known only for Ni^{II} and, so far, involves two general situations. The first circumstance requires the metal ion to exhibit the same co-ordination number and the same set of attached ligands, but different stereochemistries. The second produces two different co-ordination numbers and hence different stereochemistries within the unit cell.

Kilbourn, Powell, and Darbyshire[71] have carried out an *X*-ray investigation of the green complex dibromobis(benzyldiphenylphosphine)nickel(II), which has a moment of 2·7 B.M. (a red, diamagnetic form is also known). They showed that there are three 4-co-ordinate nickel atoms in the unit cell, one $Ni[P(Ph{\cdot}CH_2{\cdot})Ph_2]_2Br_2$ is square planar and two $Ni[P(Ph{\cdot}CH_2{\cdot})Ph_2]_2Br_2$ units are tetrahedral. When allowance was made for only two of the three nickel atoms being high-spin the moment of the tetrahedral nickel atoms was calculated to be 3·3 B.M., in good agreement with the values generally observed for nickel in pseudo-tetrahedral environments. Powell suggested the term 'interallogon' for such compounds. An analogous explanation has been suggested to account for the low moment (2·78 at 20°C) of bis-(2-methyl-1,2-diaminopropane)nickel(II) nitrate perchlorate on the basis of an incomplete *X*-ray investigation and temperature-dependent magnetic studies.[72]

An example of the second type of isomerism has been observed in the yellow form of the Lifschiltz compound, bis-(*meso*-stilbenediamine)nickel(II) dichloroacetate $\frac{2}{3}C_2H_3OH,\frac{4}{3}H_2O$, which has been extensively studied by magnetic spectral and *X*-ray measurements.[73] Here the room-temperature moment is 2·58 B.M. and the unit cell contains both 6-co-ordinate and planar 4-co-ordinate nickel atoms in the ratio 2:1. In the distorted octahedra, the axial positions are occupied by water molecules. Recalculation of the magnetic data on this basis leads to a value of 3·16 B.M. for each paramagnetic ion, a value that is completely consistent with high-spin six-co-ordinate nickel(II).

Quinoxaline complexes of nickel(II) have been mentioned previously. Two forms of $Ni\,Q(Br)_2$ appear to exist.[24] It has been suggested from spectral evidence that the brown isomer (μ_{eff} = 3·51 B.M.) also contains two stereochemical components within the unit cell. In this case alternating tetrahedra and tetra-

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[71] B. T. Kilbourn, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 1963, 207.

[72] D. Hall and J. M. Waters, *Inorg. Chem.*, 1964, 3, 615.

[73] W. C. E. Higginson, S. C. Nyburg, and J. S. Wood, *Inorg. Chem.*, 1964, 3, 463; S. C. Nyburg and J. S. Wood, *ibid.*, 1964, 3, 468.

gonally distorted octahedra are suggested to coexist in a polymeric structure involving bridging bromides. Since the nickel atoms are high-spin in both environments a resultant moment in excess of 2·83 B.M. is to be expected.

It has been suggested on the basis of magnetic susceptibility measurements that Ni(PEX)Br_2 (1) may belong to this class of compound,[22,27b,74] specifically to the second type. Anhydrous Ni(PEX)Br_2 has a moment of 1·57 B.M. at room temperature and the magnetic susceptibility obeys the Curie law with only a small Weiss constant. If one assumes three diamagnetic ions for each paramagnetic species a moment of 3·14 B.M. for the paramagnetic species is calculated. This is supported by the fact that addition of $\frac{1}{2}$ mole of lattice water causes the complex to become fully spin-paired. It was suggested that the transformation involves hydrogen bonding of the water to the bromide and effective removal of that ion from the co-ordination sphere of the nickel(II) ion. The magnetic behaviour with temperature for such compounds stands in strong contrast to that of materials of class 1 and to others to be considered. This emphasises the fact that the measurement of susceptibility over a wide range of temperature can be a very useful aid to an understanding of the origin of an anomaly, as indicated previously. Examples of such effects among derivatives of cobalt and iron appear not to have been observed.

3 Solute–Solvent Interactions

A large number of Ni^{II} complexes which are diamagnetic in the solid state become paramagnetic when dissolved, without gross decomposition, in a variety of solvents. In many cases the paramagnetism corresponds to a moment per nickel atom of less than 2·9 B.M. Similarly certain complexes of cobalt(II) appear to undergo changes from $S = \frac{1}{2}$ to $S = \frac{3}{2}$ upon dissolution. Such changes may come as a result of several possible types of interaction. The character of the solvent is a key factor in determining the type of interaction that occurs. In most common polar solvents, a strong ligating atom, such as nitrogen or oxygen, is present and this may exercise a moderate *d*-orbital perturbation with a resultant change in the co-ordination number and spin state of a particular species. Such cases are well documented experimentally and are explained theoretically for Ni^{II} by the treatments of Maki[19] and Liehr and Ballhausen.[20] Such arguments can logically be extended to cobalt(II) or even iron(II). Willis and Mellon[75a] noted that several diamagnetic bis(salicylaldimine)nickel(II) complexes are fully paramagnetic (μ = 3·0—3·2 B.M.) in pyridine solution, a phenomenon which they attributed to the formation of 6-co-ordinate pyridine adducts. Attempts to isolate the adducts in the solid state failed; however, Basolo and Matoush[75b] were subsequently able to obtain the dipyridine adducts in pure form. Other solid diamagnetic Ni^{II} complexes of similar type show[75c] partial paramagnetism in pyridine. In these cases it was assumed that the origin

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[74] G. R. Brubaker, Ph.D. Thesis, Ohio State University, 1965.

[75] (*a*) J. B. Willis and D. P. Mellon, *J. Amer. Chem. Soc.*, 1947, **69**, 1237; (*b*) F. Basolo and W. R. Matoush, *ibid.*, 1953, **75**, 5663; (*c*) H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 1955, 3431, 3435.

of the paramagnetism is the same and that it corresponds to the equilibrium:

$$\text{Solvent} + \text{Planar (diamagnetic)} \rightleftharpoons \text{pseudo-octahedral (paramagnetic)}$$

Similar behaviour has been observed in water, pyridine, and acetonitrile for the nickel complex of the macrocyclic ligand, CRH, shown in Structure (5).[27b,28] Detailed studies on the equilibrium

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

in water by spectroscopic and magnetic methods reveal ΔH and ΔS values of 4·5 kcal./mole and 16 e.u. respectively for a $3{\cdot}02 \times 10^{-2}$M solution of complex. These values are concentration-dependent because of changes in solvent activity. Solvent activity may be particularly important in determining the position of the equilibrium and therefore the apparent magnetic moments of such systems. Notable examples are those of $\mathrm{Ni(trien)^{2+}}$ [76] and bis-(*meso*-2,3-diaminobutane)-nickel(II)[77] while others have been discussed.[27b] Jørgensen found that addition of quantities of extraneous salts to aqueous solutions of $\mathrm{Ni(trien)(H_2O)_2^{2+}}$ caused a new band to appear in the visible spectrum with a decrease in intensity of those already present. This new band could be assigned to a transition of square planar nickel produced by loss of 2 water molecules from the complex nickel ion. Similar results are obtained with bis(*meso*-2,3-diaminobutane)-diaquonickel(II) where the relative amounts of spin-free and spin-paired forms as a function of added salt concentrations have been estimated spectroscopically.[77] This loss of water is apparently a result of the reduced activity of the solvent water.

Nelson and his co-workers have studied similar equilibria spectrophotometrically for some $\mathrm{Co^{II}}$ complexes ($\mathrm{CoL_2X_2}$, where L is pyridine, substituted pyridine, or isoquinoline) only in this case the equilibrium proceeds from a tetrahedral form to the octahedral structure.[78] The equilibrium involves two paramagnetic species with only slightly different magnetic moments; however, careful measurements should indicate a change in moment with an increase in the amount of octahedral complex.

Of greater interest and complexity are the anomalous moments frequently observed for solutions of nickel and cobalt complexes in so-called 'inert' solvents, such as $\mathrm{CHCl_3}$, $\mathrm{CCl_4}$, $\mathrm{CS_2}$, $\mathrm{C_6H_6}$, etc., and even in co-ordinating solvents when they do not act as donor species. The first work on such systems used nickel(II) compounds. The model initially suggested for this behaviour was that of a diamagnetic planar-paramagnetic tetrahedral rearrangement.[75,79,80]

This model is consistent with the temperature-dependence of the moment in

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[76] C. K. Jørgenson, *Acta Chem. Scand.*, 1957, **11**, 399.

[77] D. L. Leussing, J. Harris, and P. Wood, *J. Phys. Chem.*, 1962, **66**, 1544.

[78] H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 1963, 5449; 1964, 4832; S. M. Nelson and T. M. Shepherd, *ibid.*, 1965, 3284; J. de O. Cabral, H. C. A. King, S. M. Nelson, T. M. Shepherd, and E. Körös, *ibid.*, (*A*), 1966, 1348.

[79] S. Fujii and M. Surnitani, *Sci. Reports, Tokoku Univ., Ser. I*, 1953, **37**, 49.

[80] H. C. Clark and A. L. Odell, *J. Chem. Soc.*, 1956, 520.

solutions of bis-(*N*-methylsalicylaldimine)nickel(II).[77,79] Also, in the case of solutions of bis(formylcamphor)ethylenediaminenickel(II) in methylbenzenes, Basolo and Matoush[75b] found no direct correlation between the paramagnetism and the base strength of the solvent. From this they also inferred that the formation of tetrahedral species, rather than solvation, is responsible for the paramagnetism. In none of these systems, however, was the presence of tetrahedral species actually demonstrated. In fact, it was not until some years later that tetrahedral nickel(II) complexes were first conclusively characterised.[81–84]

Indeed, it was shown by Sacconi, Paoletti, and Del Re[85] that bis-(*N*-alkylsalicylaldimine)nickel(II) complexes possess zero dipole moment in benzene solution and that tetrahedral molecules could therefore not be present in significant concentrations. The same conclusion was subsequently reached by Holm[86] on electronic spectral grounds because solutions of this class of compound show none of the spectral characteristics of Ni^{II} in tetrahedral or pseudo-tetrahedral symmetry.[87] Sacconi and his co-workers[88,89] showed further that paramagnetism occurs in the molten state, as well as in solution, and they concluded that interaction with solvent is not a necessary condition for the development of paramagnetism. It soon became clear that no single model could account satisfactorily for all of the observed behaviours, even within the *N*-substituted salicylaldimine class of compound. However, as a result of concentrated efforts, particularly by Sacconi and Holm and their co-workers, it appears that the two models consistent with most of the experimental evidence are (i) molecular association (solute–solute interaction) and (ii) planar–tetrahedral equilibria. Similar behaviour in both categories has been found for cobalt(II) and this is discussed at an appropriate point. It should be noted that most of the work on Co^{II} has been guided by analogy with the Ni^{II} examples, many times using the same ligand systems.

4 Solute–Solute Interaction

A. Nickel(II).—An early indication that the anomalous moment of bis-(*N*-methylsalicyladimine)nickel(II) in solution might be due to molecular association was provided by the isolation of a buff-coloured, paramagnetic (μ = 3·2 B.M.), solid form of the complex by heating the diamagnetic green form to 150—200°.[90,91] In contrast to the diamagnetic isomers, the paramagnetic form was observed to have a very low solubility in organic solvents and a polymeric

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[81] L. M. Venanzi, 4th International Conference on Coordination Chemistry, Rome 1957; *J. Chem. Soc.*, 1958, 719.

[82] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.

[83] D. M. Gruen and R. L. McBeth, *J. Phys. Chem.*, 1959, **63**, 393.

[84] A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, 1959, **6**, 134.

[85] L. Sacconi, P. Paoletti, and G. Del Re, *J. Amer. Chem. Soc.*, 1957, **79**, 4062.

[86] R. H. Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 4683.

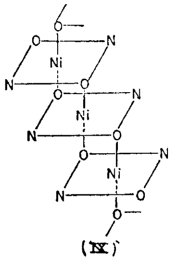
[87] F. A. Cotton, O. D. Faut, and D. M. L. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.

[88] L. Sacconi, R. Cini, and F. Maggio, *J. Amer. Chem. Soc.*, 1957, **79**, 3933.

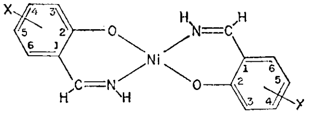
[89] L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Amer. Chem. Soc.*, 1960, **82**, 3487.

[90] C. H. Harris, S. L. Lenzer, and R. L. Martin, *Austral. J. Chem.*, 1958, **11**, 331.

[91] L. Sacconi, P. Paoletti, and R. Cini, *J. Inorg. Nuclear Chem.*, 1958, **8**, 492.



(IX)



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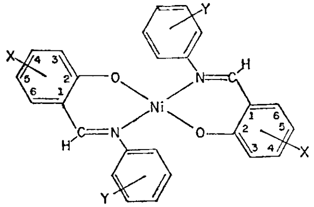

(XI)

structure was suggested.[90] This suggested that six-co-ordination is attained by the stacking of the planar units in a manner such that the oxygen atoms of adjacent molecules interact axially with the metal ions as shown in structure (IX). Further examples of salicylaldimine complexes that are paramagnetic in the solid state were later found by Holm and by Clark and O'Brien. It is convenient to consider the *N*-alkyl-substituted salicylaldimine complexes as a function of the nature of the substituent on nitrogen. An excellent review on Schiff base and β-ketoamine chemistry is now available.[92]

(i) N-n-*Alkylsalicylaldimine complexes.* The *N*-methyl compound has been studied to the greatest extent. It exhibits moments of *ca.* 1·9—2·3 B.M. at 20° depending on the solvent.[85] The moments of higher members of the n-alkyl series (ethyl to n-pentyl) are lower. In all cases the dipole moments in benzene or dioxan are practically zero, thus ruling out the earlier suggestion[75,77,79] of a planar–tetrahedral conformational equilibrium. A re-examination of the electronic spectra, made possible after publication of the spectra[82–84] of proven tetrahedral nickel complexes, conclusively confirms the absence of tetrahedral species in these solutions.[86,93–95] Thirdly, the alternative possibility of a thermally regulated population of singlet and triplet states seemed unsatisfactory in view of the observation by Holm[86] that in order to make the magnetic data fit the equation for the susceptibility in such systems the energy separation ΔE must itself be dependent on temperature to an unrealistic degree. Positive evidence

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[92] R. H. Holm, G. W. Everett, jun., and A. Chakravorty, *Progr. Inorg. Chem.*, 1967, **7**, 83.

[93] H. C. Clark and R. J. O'Brien, *Canad. J. Chem.*, 1961, **39**, 1030.

[94] R. H. Holm and T. M. McKinney, *J. Amer. Chem. Soc.*, 1960, **82**, 5506.

[95] J. Ferguson, *Spectrochim. Acta*, 1961, **17**, 316.

for solute association was provided by the observation of simultaneous increases with increasing concentration, in magnetic moment, n.m.r. contact shifts, and molecular weight for the *N*-methyl complex in chloroform and benzene as well as by spectral data.[86,95,96] Solute association in solutions of the higher *N*-n-alkyl-substituted analogues is apparently less,[97] these being mainly monomeric and diamagnetic at ordinary temperatures.

A test of the solute–solute interaction model for *N*-alkylsalicyl-aldimine complexes was provided by introducing steric barriers to solute association by means of suitable substituents (X) on the benzene ring. Holm[86] showed that the presence of a substituent in the 3-position eliminates the paramagnetism in the *N*-methyl series whereas substituents in the 5-position are less effective. The former position is, of course, expected to be sterically the more critical (see structure 10).

In recent solution studies on these n-alkyl-substituted complexes Ewald and Sinn[98] found that the pressure-dependence was as expected. The associated paramagnetic form prevails at higher pressures and the magnetic moment varies accordingly. Solid complexes subjected to high pressures (as a suspension in a non-solvent) also show a small increase in susceptibility, but this does not result in isolation of a solid exhibiting permanent polymerisation.

(ii) N-*Aryl-substituted salicylaldimine complexes.* Diverse behaviour has been found for *N*-aryl-substituted salicylaldimine complexes, the controlling factor being the nature and position of the substituents X and Y in the aryl rings[99] (structure 11). A certain regularity in behaviour exists. With few exceptions, complexes containing Y in the 2-position are diamagnetic both in the solid and in solution. They are also monomeric in solution. The diamagnetism is retained even at high temperatures. Models show that the presence of Y substituents in the 2-*N*-aryl position or of X substituents in the 3-position of the salicylaldimine ring demand that *N*-aryl ring be rotated out of the plane of the chelate rings thereby preventing the lateral association, in much the same way (though more effectively) as do the *N*-(straight-chain alkyl) substituents other than methyl. One exception is the complex in which Y = tolyl at position 2 and X = isopropyl at position 3. This complex is weakly paramagnetic. Compounds in which there are no substituents in the 2- and 3-positions of the *N*-aryl and salicylaldimine rings, respectively, all show solution paramagnetism to a greater or less degree and a satisfactory correlation between solution moment and degree of association, as judged by molecular-weight or spectral data, was found for most of these systems. Exceptions are the *N*-phenyl and *N*-*p*-fluorophenyl complexes which show a solution paramagnetism greater than can be accounted for solely on the assumption of solute association. An extension of Holm and Swaminathan's studies on the *N*-arylsalicylaldimine complexes was made by Sacconi and Ciampolini.[100] Magnetic and spectral measurements in xylene or

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[96] W. Ludwig, *Helv. Chim. Acta*, 1962, **45**, 665.

[97] H. C. Clark, K. Macvicar, and R. J. O'Brien, *Canad. J. Chem.*, 1962, **40**, 822.

[98] A. H. Ewald and E. Sinn, *Inorg. Chem.*, 1967, **6**, 40.

[99] R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1962, **1**, 599.

[100] L. Sacconi and M. Ciampolini, *J. Amer. Chem. Soc.*, 1963, **85**, 1750.

bibenzyl solution were made at temperatures up to 200°C. By comparison with the spectra of Ni^{II} chelates of known tetrahedral geometry, bands at 6700 and 11,100 $cm.^{-1}$ were attributed to the presence of tetrahedral species. These bands increased in intensity with rising temperature while other spectral bands assigned to the six-co-ordinate, associated molecules decreased. Further, in the lower temperature range μ_{eff} decreases with an increase in temperature in accord with expectation for the association model whereas at higher temperatures small increases in μ_{eff} become apparent. It was concluded, therefore, that three forms of the *N*-aryl complexes (Y = H, 3-Cl, 4-Cl, 3-methyl, 4-methyl, 3,4-benzo) can coexist in solution:

$$\underset{\text{(paramagnetic)}}{\text{Associated}} \rightleftharpoons \underset{\text{(diamagnetic)}}{\text{Planar}} \rightleftharpoons \underset{\text{(paramagnetic)}}{\text{Tetrahedral}}$$

At room temperature the proportion of molecules in the associated form is greater than 80%. With an increase in temperature the percentage of the tetrahedral form increases. Significantly, the same shift in equilibrium should be achieved, isothermally, by dilution.

An interesting application of n.m.r. spectroscopy to the problem of the *N*-3-tolylsalicylaldimine complexes in non-co-ordinating solvents has been noted by Phillips and his co-workers.[101] Following studies on nickel(II) chelates of the aminotroponeimineates (to be described) they attributed the large proton shifts to delocalisation of unpaired spin density on to the salicylaldimine ring, a result consistent with the presence of paramagnetic associated chelate molecules in solution.

A discussion of other nickel(II) complexes of salicylaldimine in which the *N*-substituent is an α-branched alkyl group is deferred to section (5).

(iii) *β-Diketone complexes.* Until relatively recently bis(acetylacetone)nickel(II), which has a normal magnetic moment of 3·07 B.M. at 20°C, was considered to be an example of a planar nickel compound with a triplet ground state (see ref. 19). The compound can be sublimed and it has been shown to be monomeric[102] and planar[103] in the vapour phase. However, in 1961 Bullen, Mason, and Pauling showed conclusively from *X*-ray investigations that the structure is trimeric in which each nickel atom is surrounded by a distorted octahedron of oxygen atoms; the central octahedron shares a triangular face with each of the two terminal octahedra (XII).[104,105] Fackler and Cotton[106] demonstrated, from electronic spectral studies, that the trimeric unit persists in solution but becomes reversibly dissociated into the red monomer at high temperatures. Molecular weight measurements in dichloromethane also indicated association.

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[101] E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *J. Amer. Chem. Soc.*, 1962, **84**, 3968.

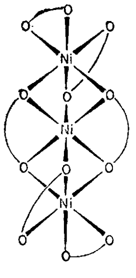
[102] F. Gach, *Monatsh.*, 1900, **21**, 98.

[103] S. Shibata, *Bull. Chem. Soc. Japan*, 1957, **30**, 753.

[104] G. J. Bullen, *Nature*, 1956, **177**, 537.

[105] G. J. Bullen, R. Mason, and P. Pauling, *Nature*, 1961, **189**, 291.

[106] F. A. Cotton and J. P. Fackler, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 2818.



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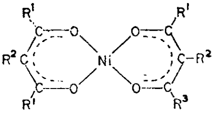

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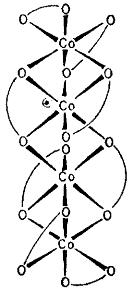

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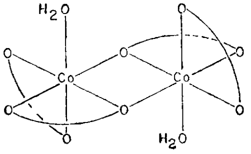

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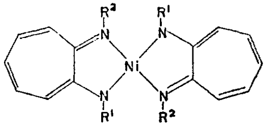

(XVI)

Replacement of the methyl groups R^1 of the acetylacetonate ion (XIII) by t-butyl hinders the close approach of the individual units to such a degree that the complex is diamagnetic and remains so in solution in non-co-ordinating solvents.[107] While the bulky t-butyl groups completely prevent an increase in co-ordination number by means of molecular association, six-co-ordination can still be achieved by the introduction of small ligands such as water, alcohols, or amines. Thus, such complexes are blue-green and paramagnetic.

When $R^1 = R^2 =$ isopropyl the steric restriction to molecular association is reduced to a degree intermediate between R = methyl and R = t-butyl. The solid is green and paramagnetic, but a significant proportion of monomeric species is observed at much lower temperatures than in the case of $R^1 =$ Me. Steric hindrance of a comparable degree is also present in the paramagnetic form of the chelate $R^1 =$ H, $R^2 =$ Ph since the phenyl group cannot assume coplanarity with the chelate ring.[108]

B. Cobalt(II).—Sacconi demonstrated that bis-(*N*-methylsalicylaldiminato) cobalt(II) achieves 5-co-ordination by association in the solid state.[109] As a result, this complex has a moment of 4·62 B.M. Dissolution in benzene gives a brown solution and spectral studies indicate the species is largely monomeric and tetrahedral at low concentrations. No moment is reported for the complex in solution.

Gach[102] also prepared the bisacetylacetonate complex of Co^{II}, but its solid-

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[107] J. P. Fackler and F. A. Cotton, *J. Amer. Chem. Soc.*, 1960, **82**, 5005.
[108] J. P. Fackler and F. A. Cotton, *J. Amer. Chem. Soc.*, 1961, **83**, 3775.
[109] P. L. Orioli, M. Di Vaira, and L. Sacconi, *Chem. Comm.*, 1965, 103.

state structure remained in question until recently. Cotton and Holm first postulated it to be a high-spin square planar Co^{II} complex,[12b] having a moment of 4·8—4·9 B.M. in the solid state and in solution. However, comparison of the spectrum with that of Co(dipivaloylmethane)$_2$, which is known to be pseudo-tetrahedral,[110] indicated that this compound is also tetrahedral in the monomeric state. In addition a strong deviation from Beer's law was observed in non-co-ordinating solvents and molecular-weight measurements showed a concentration-dependent association.

Co(acac)$_2$ can be isolated in several forms; Co(acac)$_2$,2H$_2$O, [Co(acac)$_2$,-H$_2$O]$_2$, [Co(acac)$_2$]$_{2-3}$,H$_2$O and [Co(acac)$_2$]$_4$. *X*-Ray studies on a twinned crystal show [Co(acac)]$_4$ to have a structure somewhat like that of the nickel complex.[13b] Cotton and Elder suggest considering the tetramer as two diastereomeric fragments joined along a common octahedral edge (XIV). *X*-Ray studies[111] of [Co(acac)$_2$,H$_2$O]$_2$ show it to be the centre portion of the tetrameric species with bridge bonds on the two faces occupied by water molecules (XV), so regardless of the stoicheiometry Co(acac)$_2$ achieves 6-co-ordination and high-spin character.

It is possible for association to lead to a low-spin form for Co^{II}. Recently studies on Co(PEt$_3$)$_2$(NCS)$_2$ have shown that the magnetic moment and electronic and i.r. spectra depend strongly on temperature and concentration in dichloromethane and dichloroethane solutions.[112,113] This has been interpreted in terms of a monomeric (high-spin) tetrahedral $\rightleftharpoons$ dimeric (low-spin) 5-co-ordinate equilibrium where the 5-co-ordinate dimer uses bridging thiocyanates. Further substantiation of such an equilibrium was obtained through the study of reactions of tertiary phosphines with Co(PR$_3$)$_2$X$_2$ complexes to obtain 5-co-ordinate species. The reaction of Co(PEt$_3$)$_2$(NCS)$_2$ with excess of PEt$_3$ causes a decrease in the observed moment from 3·4 to 2·05 B.M. Although no solid was isolated, cryoscopic measurement indicated Co(PEt$_3$)$_3$(NCS)$_2$ to be present.

5 Configurational Equilibrium

An equilibrium between diamagnetic planar molecules and paramagnetic tetrahedral molecules was the mechanism first postulated, and later disproved, to explain the intermediate magnetic moments of bis-(*N*-methylsalicylaldimine)-nickel(II) in non-co-ordinating solvents. The model was subsequently invoked to account for some of the properties of solutions of *N*-aryl-substituted salicylaldimines[100] (see section 4). It is important to recognise that planar and tetrahedral molecules have the same co-ordination number and that, whereas a planar configuration may be stabilised by crystal lattice forces, a lower-energy state in solution may sometimes be achieved simply by an intramolecular rearrangement. A difficulty to the conclusive recognition of the presence of planar–tetrahedral equilibria for solutions of solid diamagnetic complexes for

[110] F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1962, **84**, 872.
[111] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1966, **5**, 423.
[112] M. Nicolini, C. Pecile, and A. Turco, *J. Amer. Chem. Soc.*, 1965, **87**, 2379; *Co-ord. Chem. Rev.*, 1966, **1**, 133.
[113] T. Boschi, M. Nicolini, and A. Turco, *Co-ord. Chem. Rev.*, 1966, **1**, 269.

many years was the fact that the stereochemical species had not been characterised spectrally.[82–84,87] After about 1959 the isolation[114] in some cases of planar and tetrahedral isomeric forms, for example, bis(benzyldiphenylphosphine)-nickel(II) halides, provided a useful guide in recognizing planar–tetrahedral equilibria in benzene solutions of these and complexes of related type which exhibit moments between 0 and *ca.* 2·9 B.M.[114–116]

A particularly thorough study of solutions of nickel(II) chelates of the aminotroponeimineates has been carried out by Phillips and his co-workers.[117–120] For these, the magnetic susceptibility and the electronic and n.m.r. spectra were observed to be dependent on temperature, solvent, and the nature of the *N*-substituent (XVI). Very large proton contact shifts in deuteriochloroform were interpreted as being due to the presence of electron spin density on the seven-membered hydrocarbon rings; the magnitude of the shift depends on the proportion of tetrahedral molecules in solution. The contact shifts, which were measured relative to the free ligand or to the corresponding diamagnetic zinc chelate, permitted the evaluation of equilibrium constants for the planar–tetrahedral equilibrium. In all cases ΔG decreased with temperature (200—350°c) and the ΔH values, which varied from *ca.* 1 to 6 kcal. mole^{-1}, were calculated from the temperature-dependence. Derived entropy changes were positive, falling in the range 8—17 cal. deg.$^{-1}$ mole^{-1}. (It has been pointed out by Horrocks[121] that some of the thermodynamic values calculated for this system and for some others are based on an incorrect form of the equation for the isotropic shifts.)

The magnetic susceptibility data (for $CDCl_3$ solutions) were similarly treated in terms of a Maxwell–Boltzmann distribution of nickel ions between the two spin states. Thermodynamic functions were also evaluated from the intensities of electronic spectral bands at *ca.* 800 and 1200 mμ, attributed, respectively, to the diamagnetic and paramagnetic forms. The thermodynamic functions evaluated by the three different methods were in good agreement. That the paramagnetic species in solution are tetrahedral was established by evidence from several sources: (i) the complexes are monomeric in solution; (ii) satisfactory assignment of the near-infrared spectra of almost completely diamagnetic and almost completely paramagnetic systems to transitions predicted for planar and tetrahedral symmetries, respectively, could be made; (iii) the magnetic susceptibilities increase with an increase in temperature; and (iv) no correlation exists between the position of equilibrium and the expected co-ordinating power of the solvent.

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[114] M. C. Browning, J. P. Mellor, D. J. Morgan, S. A. J. Pratt, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 1962, 693.

[115] C. R. C. Coussmaker, M. H. Hutchinson, J. P. Mellor, L. E. Sutton, and L. M. Venanzi, *J. Chem. Soc.*, 1961, 2705.

[116] R. G. Hayter and F. S. Humiec, *J. Amer. Chem. Soc.*, 1962, **84**, 2004.

[117] W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, 1960, **33**, 607.

[118] R. E. Benson, D. R. Eaton, A. D. Josey, and W. D. Phillips, *J. Amer. Chem. Soc.*, 1961, **83**, 3714.

[119] D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, 1962, **37**, 347.

[120] D. R. Eaton, W. D. Phillips, and D. J. Caldwell. *J. Amer. Chem. Soc.*, 1963, **85**, 397.

[121] W. D. Horrocks, jun., *J. Amer. Chem. Soc.*, 1965, **87**, 3779.

Recent pressure-dependent spectral and magnetic studies[98] indicate the planar form to be favoured at high pressures suggesting a smaller partial molar volume than for the tetrahedral form. This is consistent with what has been found for the Fe^{III} dithiocarbamates,[76] where bond length increases have been found upon the unpairing of spins. Further, there was no indication of a transformation to a co-ordination number greater than 4 with increasing pressure.

The variation in behaviour with change in the nature of the group R can be fairly satisfactorily accounted for on steric grounds. Clearly, as the R groups become bulky, steric repulsions between them are expected to become important in a planar structure. Rotation of the planes of the chelate rings toward a tetrahedral configuration for the central nickel atom should relieve the steric strain. It is predicted, therefore, that the equilibrium should shift in favour of the tetrahedral form as the size of R is increased. This proved to be the case as shown in Table 7. The extensive diamagnetism of the *N*-aryl-substituted complexes was attributed to a rotation of the plane of the aryl ring out of the plane of the 7-membered ring.

Table 7 *Magnetic character of aminotroponeiminate complexes as a function of N-substituent*

N-substituent	*Magnetic character of chelate at* 23 °C *in* $CDCl_3$
$R^1 = R^2 = H$	Diamagnetic
$R^1 = H$, $R^2 =$ alkyl	Diamagnetic
$R^1 = R^2 = CH_3$	Slightly paramagnetic (< 1 %)
$R^1 = R^2 =$ aryl	25—75 % paramagnetic
$R^1 = R^2 =$ ethyl	Almost completely paramagnetic (> 99 %)

The discussion of the magnetic behaviour of *N*-alkylsalicylaldimine complexes having secondary and tertiary alkyl groups has been deferred to this point because of their different behaviour. In contrast to solutions of the *N*-methyl- and most *N*-aryl-salicylaldimine complexes of nickel(II), where the paramagnetism can be accounted for mainly in terms of molecular association, the paramagnetism of α-branched *N*-alkyl-substituted complexes appears to be due predominantly to the presence of tetrahedral species.[122] The effect of branching of the *N*-alkyl substituent is reflected in the solid state as well. Thus, the n-propyl compounds, for example, are planar even when substituents are present in the 3-position of the salicylaldimine ring. The t-butyl chelates on the other hand are all pseudo-tetrahedral. Both stereochemistries are found for the solid s-alkyl complexes, the choice of configuration in these cases depending on the nature and position of the ring substituent. In inert solvents at room temperature the n-propyl derivatives are predominantly planar, the t-butyl derivatives largely pseudo-tetrahedral, and the s-alkyl chelates coexist in comparable proportions of both forms. Assignment of stereochemistry in the solid state was made on the basis of magnetic moments and reflectance spectra and, in solution, on the bases of dipole-moment and molecular-weight evidence. Although there is evidence

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[122] L. Sacconi, M. Ciampolini, and N. Nardi, *J. Amer. Chem. Soc.*, 1964, **86**, 819.

for some association in solutions of the s-alkyl derivatives, it has been shown that at, or above, 37°C they are essentially monomeric under the same conditions of solvent, concentration, and temperature where they were found to be appreciably paramagnetic.[123] An indication of configuration is shown by the dipole moments in Table 8. With the exception of the t-butyl chelate, an increase in temperature leads to a shift in the position of the planar–tetrahedral equilibrium toward the tetrahedral form as evidenced by (*a*) an increase in solution magnetic moments and (*b*) an increase in intensity of the band near 6200 cm.$^{-1}$ attributable to the pseudo-tetrahedral species (a decrease was observed in the case of the t-butyl compound).[122] Sacconi *et al.*[122] calculated the percentages of the tetrahedral form for the n-propyl and isopropyl series from the electronic polarization, susceptibility, and electronic spectral data and good agreement of the derived thermodynamic functions by the three methods was obtained. The data in Table 9 show that for the straight-chain series the planar form is more stable than the tetrahedral form by about 2·8 kcal. mole^{-1}. The relatively large enthalpy difference, 4·6—5·2 kcal. mole^{-1}, means that at room temperature the concentration of tetrahedral molecules is negligible and not more than 10% at 170°C. The data also show that for the isopropyl series the tetrahedral form is, comparatively, strongly favoured over the planar. Steric

Table 8 *Dipole moments for some (N-alkylsalicylaldimine)nickel*(II) *chelates in benzene at* 25°C

R	μ (*D*)
Pr^n	0·00
Bu^n	0·00
Pr^i	2·51
Bu^s	2·34
Bu^t	4·74

Table 9 *Thermodynamic quantities associated with the planar–tetrahedral equilibrium for N-alkylsalicylaldiminenickel*(II) *complexes, as a function of the ring substituent*

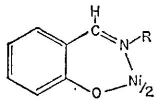
R	*X*	ΔG (kcal. mole^{-1})	ΔH (kcal. mole^{-1})	ΔS (cal. mole^{-1} deg.)
Pr^n	H	2·9	4·6	4
Pr^n	5-Me	2·8	4·6	4
Pr^n	5-Cl	2·7	5·2	6
Pr^i	H	−0·52	3·2	10
Pr^i	3-Cl	0·35	3·0	7
Pr^i	5-Me	0·20	2·5	6
Pr^i	5-Cl	0·16	2·0	4

[123] R. H. Holm and K. Swaminathan, *Inorg. Chem.*, 1963, **2**, 181.

considerations seem to control the behaviour of the s- and t-alkyl derivatives. Intramolecular repulsion between the large t-butyl groups attached to the *N*-position and the chelate rings prevents a planar arrangement. Such repulsion is smaller in the s-alkyl compounds and still smaller in the n-alkyl chelates, so that in the latter case only the planar configuration is present except at rather high temperatures. Thus, the percentage of tetrahedral form increases in the order R = n-alkyl < s-alkyl < t-alkyl.

In general, substitution in the phenyl ring is less critical than is the nature of the *N*-R substituent (Table 9) except perhaps in the case of benzo-substitution. Benzo-substitution in 5,6-positions enhances the stability of the diamagnetic planar isomer, whereas the benzo-group in the 3,4-ring position has the opposite effect.[122] In the latter case severe steric interaction between the benzo-group and the *N*-substituent is predicted. While steric effects are generally dominant in deciding the position of the planar–tetrahedral equilibrium, electronic factors also must play a significant role in some cases. For example, for the chelates in which R = isopropyl and X = 3-Cl and 3-Br the planar form is more stable than expected on the basis of steric considerations alone.[122]

An extension of the investigation of *N*-s-alkylsalicylaldiminenickel(II) systems by n.m.r. spectroscopy has been carried out by Holm, Chakravorty, and Dudek.[124] Their results provide general support for the interpretation of the properties of this class of salicylaldimine chelate in terms of planar–tetrahedral equilibria. As with the aminotroponeimineates discussed previously, large isotropic proton hyperfine contact shifts (to both high- and low-field) relative to the resonance position of the free ligands were observed. For the protons at the 3- and 5-ring-carbon atoms the shifts are positive while those for the protons at the 4- and 6-positions are negative. The derived spin-density distribution indicates resonance among the valence-bond structures (17—21). These are the same



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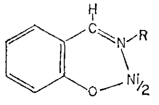

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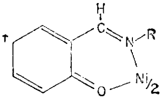

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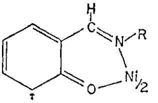

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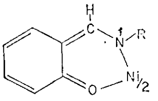

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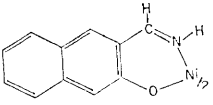

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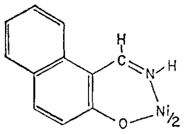

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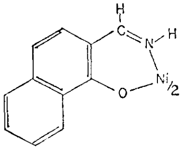

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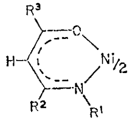

(XXV)

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[124] R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, 1964, **86**, 379.

valence-bond structures predicted for a transfer of spin density on to the ring by d_π–p_π bonding in the tetrahedral complex.

Holm and Chakravorty have also studied a series of bis-(*o*-hydroxynaphthaldimine)nickel(II) complexes.[125] These have the general form shown in (XXII—XXIV). Table 10 lists their magnetic behaviour as a function of ring substituent and R group, both in the solid and in solution. The anomalous moments in solution have been found to arise from a planar–tetrahedral equilibrium. Spin-density calculations were performed and thermodynamic data were obtained by use of n.m.r. contact shift methods.

Table 10 *Magnetic properties of bis-*(o-*hydroxynaphthaldimine*)*nickel*(II) *complexes*

Naphthaldimine	*R*	*Solid*	*Solution*[a]
22	Pr^i	Diamag.	0·86 (30°)
22	Bu^t	Paramag.[b]	3·23 (25°)
23	Pr^i	Paramag.	2·78 (20°)—2·83 (50°)
23	Et_2CH	Paramag.	2·93 (20°)—2·96 (50°)
24	Pr^i	Diamag.	
24	Et_2CH	Diamag.	1·80 (50°)
24	Bu^t	Paramag.	3·23 (25°)

[a] Solvent is chloroform. [b] Paramagnetic species have moments of 3·30 ± 0·03 B.M. at 25°.

The n.m.r. technique, which appears to be a powerful one for the evaluation of the thermodynamic functions for diamagnetic–paramagnetic equilibria, has recently been extended by Everett and Holm[126] to bis-(β-ketoamino)nickel(II) complexes. These complexes, depending on the R substituents (XXV) display greatly varied behaviour. Two groups of complexes having $R^2 = R^3 = CH_3$ and $R^2 = CH_3$; $R^3 = C_6H_5$ were studied and in each series a planar–tetrahedral equilibrium was found. For both series when R^1 is s-alkyl the complexes are essentially tetrahedral at room temperature, but when R^1 is aryl for $R^2 = R^3 = CH_3$ or R^1 is n-alkyl and $R^2 = CH_3$, $R^3 = C_6H_5$, then the complexes are largely planar. A small amount of association was found when R^1 is aryl.

More recently a planar–tetrahedral equilibrium has also been demonstrated for analogous bis-(β-ketoamino)cobalt(II) complexes.[127] The types of compound studied and their solid and solution configurations are listed in Table 11. The formation of the tetrahedral cobalt species is endothermic as for the nickel compounds. A comparison of the data for the nickel and cobalt systems[127] indicates that any substituents which promote tetrahedral behaviour for Ni^{II} cause Co^{II} to be fully tetrahedral and substituents on Co^{II} inducing planar behaviour cause Ni^{II} to be fully planar. Following this idea Holm and his co-workers prepared

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[125] A. Chakravorty and R. H. Holm, *Inorg. Chem.*, 1964, **3**, 1010.

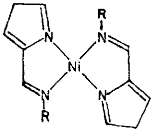
[126] G. W. Everett and R. H. Holm, *Proc. Chem. Soc.*, 1964, 238; *J. Amer. Chem. Soc.*, 1965, **87**, 2117.

[127] G. W. Everett, jun., and R. H. Holm, *J. Amer. Chem. Soc.*, 1966, **88**, 2442.

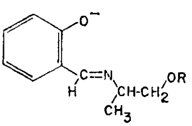
Table 11 *Configurations of bis-(β-ketoamino)cobalt*(II) *complexes in solid state and in Solution*

R^1	R^2	R^3	*Configuration*	
			Solid	*Solution*
Me, Pr^n, Ph	Me	Me, Ph	Tetrahedral	Tetrahedral
H	Me	Me	Planar	Tetrahedral and planar
H	Me	Ph	Planar	Tetrahedral and planar
H^a	H	Me	Planar	Tetrahedral and planar

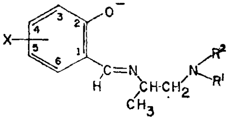
The methine proton is replaced by a methyl group in this complex.



(XXVI)



(XXVII)



(XXVIII)

bis(pyrrole-2-aldimino)-complexes of nickel(II) and cobalt(II).[128] These have the structure (XXVI) which is quite similar to the β-keto-amine complexes.

The only Co^{II} complex which could be prepared, that with R = t-butyl, was tetrahedral. The solution properties of the Ni^{II} series show a similar dependence on R to that of the salicylaldimine complexes in that no tetrahedral form is present if R = n-alkyl, and no planar for R = t-butyl. Likewise when R is s-alkyl both configurations are found in solution at room temperature. It might be noted that when R = CH_3 there appears to be some association but no paramagnetic species is found. The s-alkyl complexes have a moment per nickel atom less than 2 B.M. and all spectra show tetrahedral components. Molecular-weight measurements do not indicate association and spectral studies indicate an endothermic equilibrium of planar ($S = 0$) and tetrahedral ($S = 1$) forms. This equilibrium was demonstrated for R = isopropyl, s-butyl, 1-ethylpropyl, cyclohexyl, and 1,2-dimethylpropyl as R groups. At lower temperatures, n.m.r. signals are broadened and ΔF plots are non-linear for these derivatives in a direction which indicates a less paramagnetic species than the planar–tetrahedral equilibrium should give at the same temperature.

In addition, for R = $-CH(CH_3)\cdot CH_2OCH_3$ markedly different spectral and proton resonance patterns are observed and it has been suggested that there may be planar–tetrahedral–octahedral equilibria involved. This has been observed for Ni^{II} systems containing the ligand (XXVII) where R is CH_3- or -H.[129] Here ring-closure can occur with the two oxygen atoms completing an octahedral co-ordination sphere. In these cases the equilibria involved are between *monomeric* octahedral, planar, and tetrahedral species and the magnetic moment varies accordingly.

Monomeric octahedral–square planar equilibria also occur in solutions with

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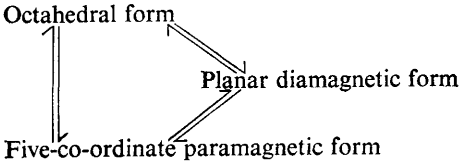
[128] R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, 1966, **5**, 625.

[129] A. Chakravorty, J. P. Fennessey, and R. H. Holm, *Inorg. Chem.*, 1965, **4**, 26.

non-co-ordinating solvents of complexes of the related ligand series (XXVIII).[130] This occurs only when $R^1 = H$ and $R^2 = C_6H_5$-, α-naphthyl, or substituted phenyl. The nature of the X substituent determines the solid-state behaviour. In solution an increase in temperature shifts the equilibrium towards the 4-co-ordinate form giving a smaller moment. A measure of steric hindrance to ring-closure seems to be responsible for the coexistence of the two conformations in solution of this series of complexes. When the R^1 and R^2 substituents are made less bulky, as when $R^1 = H$, R^2 = n-alkyl or benzyl, the complexes are monomeric octahedral both in solid state and in solution. On the other hand, when $R^1 = H$ and R^2 = *o*-tolyl or α-naphthyl the complexes are all square planar and diamagnetic in the solid state. Further increase in steric hindrance, as in R^1 = phenyl and R^2 = methyl or phenyl prevents the terminal (β) nitrogen atom from co-ordinating at all; *i.e.*, the Schiff base acts as a bidentate ligand and the complexes are completely square-planar and diamagnetic in both the solid state and in solution. Sacconi and his co-workers[131] subsequently found that when $R^1 = R^2$ = ethyl and the ring substituents are 3-Cl, 5-Cl, or 3,4-benzo that the solid complexes are paramagnetic (μ = *ca.* 3·3 B.M.) and 5-co-ordinate. While diamagnetic 5-co-ordinate nickel(II) complexes are now well known these are the first examples of this co-ordination number in the high-spin state. A distorted square pyramidal structure for the 5-chloro-derivative is indicated by *X*-ray studies.[132] The nickel atom lies a little above the mean basal plane. Moments in benzene intermediate between 0 and *ca.* 3·3 B.M. were observed and electronic absorption spectra suggested the following equilibria:[130]



where one or both of the β-nitrogen atoms is detached to give a 5- or 4-co-ordinate species and the stereochemical form is determined by the free energy of the system at a particular temperature and in a particular solvent. Interestingly, the diethyl derivative can be studied in the molten state where a similar dependence of the magnetic moment on temperature is found as in solution. The presence of greater amounts of planar form at higher temperatures indicates the endothermic nature of the change from pseudo-octahedral to the planar form. A ΔH value of 3·4 kcal. mole^{-1} was calculated.

More recently, Sacconi and his co-workers have studied both types of equilibrium for the Schiff bases formed from salicylaldehydes and *NN*-substituted ethylenediamines by the n.m.r. technique.[133] They were able to assign spin

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[130] L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, 1965, **4**, 818.

[131] L. Sacconi, P. Nannelli, N. Nardi, and M. Campigli, *Inorg. Chem.*, 1965, **4**, 943.

[132] L. Sacconi, P. L. Orioli, M. Di Vaira, *J. Amer. Chem. Soc.*, 1965, **87**, 2059.

[133] J. D. Thwaites and L. Sacconi, *Inorg. Chem.*, 1966, **5**, 1029; J. D. Thwaites, I. Bertini, and L. Sacconi, *Inorg. Chem.*, 1966, **5**, 1036.

densities to positions on the phenylene ring and to determine ΔG values for the equilibrium reactions.

Most of the preceding discussion has dealt with systems containing quite similar ligand systems with nitrogen and/or oxygen donors. Recently it was reported that a planar–tetrahedral equilibrium was found for a 4-co-ordinate system having phosphorus and halogen donors.[134] When $Ni[(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2]X_2$ (X is Br, Cl, or I and the ligand denoted dpp) is dissolved in methylene dichloride, nitrobenzene, or chloroform, spectral studies indicated a band in the region 12,500—10,000 cm.$^{-1}$, attributable to tetrahedral species, none of which is present in the solid state. Gouy measurements for $Ni(dpp)Br_2$ in nitrobenzene (22°) and $Ni(dpp)I_2$ in nitrobenzene (23°) and chloroform (24°) gave moments of 2·12, 2·62, and 2·73 B.M., respectively. The equilibrium was studied by the temperature-dependence of isotropic shifts in the n.m.r. in nitrobenzene and chloroform. Entropy and enthalpy contributions favour the tetrahedral form of the iodide more than the bromide. Since $Ni[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]X_2$ complexes are completely planar in solution it was suggested that steric factors control the equilibrium to a large extent.

We thank the U.S. Public Health Service for support.

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[134] G. R. Van Hecke and W. D. Horrocks, jun., *Inorg. Chem.*, 1966, **5**, 1968.