Magnetochemistry.

THE NINTH LIVERSIDGE LECTURE DELIVERED ON APRIL 15TH, 1943.

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WHEN Council honoured me with an invitation to deliver the Ninth Liversidge Lecture I thought it would be wise to make myself acquainted with the terms of the bequest. I found it laid down that " the lectures shall not be such as are termed popular lectures dealing with generalities and giving mere reviews of their subjects nor such as are intended for the ordinary class or lecture room instruction of undergraduates." Instead they are to be " such as will primarily encourage research and stimulate the lecturer and the public to think and acquire new knowledge by research."

The short title, Magnetochemistry, which I have chosen for this lecture therefore requires a little amplification. I shall not attempt to review the whole field of chemical applications of magnetic measurements; instead I shall endeavour to outline the present position of knowledge on a few problems in which interesting advances have been made. In particular I shall try to stress some parts of the subject in which modern theory has reached a limit which it is difficult to pass but in which further experimental study of the magnetic properties of chemical substances promises to add considerably to our knowledge of the behaviour of electrons in atoms and molecules.

Nearly a century has elasped since Faraday demonstrated that most substances are affected to some extent by a magnetic field and created the nomenclature which is used to-day. The great majority of elements and compounds are feebly repelled from the poles of a magnet and are termed diamagnetic. Others are feebly attracted and are termed paramagnetic. The constant which is most conveniently used in chemical discussions is the mass susceptibility and is usually indicated by the symbol χ. For a typical diamagnetic, water, χ has the value $-0{\cdot}72 \times 10^{-6}$ c.g.s. units. Copper sulphate, a typical paramagnetic, has a susceptibility of $+6 \times 10^{-6}$ at room temperature. These figures are very much smaller than those found for the strongly magnetic metals; for instance, Swedish wrought iron in weak fields shows a mass susceptibility of more than 40 c.g.s. units. The force exerted by a magnetic field on diamagnetics and paramagnetics is consequently more than a million-fold weaker than that experienced by iron. It is therefore necessary to use specially delicate methods of measurement if the susceptibility is to be measured with any degree of precision. Care has also to be taken to protect the specimens from dust, which may cause serious errors by introducing minute particles of ferromagnetic bodies.

The methods of measurement commonly used fall into two classes. The first measures the force exerted by the field on a cylindrical specimen which is long enough to ensure that the field strength differs considerably at the two ends. Usually one end is placed in the homogeneous field between the poles of an electromagnet whilst the other end is in a field of negligible strength. This method is termed, not quite correctly, the homogeneous field method and is associated with the name of Gouy. The force can be measured by a sensitive balance or, if the specimen is liquid, by hydrostatic methods.

The Gouy method is limited in sensitivity unless a powerful electromagnet is used. For this reason Faraday and many later workers have measured the force on a small specimen in an inhomogeneous field. By inclining the pole pieces of a magnet and by other devices a field can be produced which has axial symmetry. The force on the specimen is then proportional to the product of the field strength and its gradient $H \, . \, \delta H/\delta x$; since $\delta H/\delta x$ can be made large, this method gives a high sensitivity. The force can be measured by the displacement of the specimen if this is kept small by suitable control devices. An elegant modification of this method has been used by Bhatnagar and Mathur in which a light aluminium beam carries the specimen at one end and a plate of glass at the other. This plate forms part of a Rayleigh interferometer; small displacements can then be measured accurately by the movement of interference fringes.

The value of $H \, . \, \delta H/\delta x$ varies rapidly with the position of the specimen with respect to the magnet and passes through a sharp maximum at the point selected for measurements. Great care has to be taken to ensure that the specimen is always placed in the correct position and that its displacement when the field is applied is very small. These difficulties can be overcome by an ingenious arrangement due to Fereday. By shaping the poles of the magnet properly and by adjusting their distance apart a region can be found in which the product of the field and its gradient is constant over a considerable volume, so that accurate positioning of the specimen is not essential. An instrument based on this principle was built by Dr. W. P. Grove at University College, London, in 1939 and gave very promising results over a wide range of temperatures.

The interpretation of magnetic data has been greatly clarified and extended by the development of modern quantum theory. The magnetic properties of atoms and molecules can now be described in terms of the number and distribution of the extra-nuclear electrons. (The spin of the nucleus makes a very small contribution which is negligible except at very low temperatures.) Diamagnetism is associated with the precession of the orbital motion of the electrons, as was shown as early as 1905 by Langevin on classical theory. Paramagnetism is due to the magnetic moment which each electron possesses in virtue of its orbital motion and its spin. These moments have to be compounded in accordance with the rules of quantum theory and cancel out for all completed sub-groups of the atom, so that it is only necessary to consider the contribution of a small number of electrons in an incomplete sub-group. It is for this reason that notable paramagnetism is found mainly in " odd " molecules which contain an odd number of electrons and in compounds of elements of the transition series in which the atoms contain incomplete sub-groups. It has been shown by van Vleck, who has contributed largely to the fundamental theory, that in molecules another small paramagnetic contribution due to resonance between the ground state and higher states has also to be considered. The susceptibility per gram-molecule, χ_M, can thus be represented as the sum of three terms

$$\chi_M = \chi_d + \chi_\mu + \chi_R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The first is the diamagnetic contribution, the second the paramagnetic contribution due to the magnetic moment of the atom or molecule, and the third is the small resonance term. For most molecules which contain an even number of electrons the second term vanishes and the third term is smaller than the first so that the substance is found to be diamagnetic. Occasionally, as in potassium permanganate, the third term is greater than the first and a small paramagnetism is found which does not vary with temperature.

This qualitative agreement is satisfactory, but difficulties begin to arise when quantitative comparisons are made between theory and experiment. For atoms with a centro-symmetric field, *e.g.*, the inert gases and ions with an inert-gas structure, the second and third terms vanish so that only the first term remains and this should be given by

$$\chi_d = -\frac{\boldsymbol{N}\boldsymbol{e}^2}{6\boldsymbol{m}\boldsymbol{c}^2} \cdot \sum_n \bar{r}^2 = -2{\cdot}84 \times 10^{-10} \sum_n \bar{r}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $\boldsymbol{e}$ and $\boldsymbol{m}$ are the charge and mass of the electron, $\boldsymbol{N}$ is Avogadro's number and r the distance from the nucleus. Pauling and van Vleck have deduced an expression for $\bar{r}^2$ in terms of the principal and serial quantum numbers, n and l. This is

$$\bar{r}^2 = \frac{a_0{}^2 n^2}{(Z - S)^2} \left\{ \frac{5}{2} n^2 - \frac{3l(l + 1) - 1}{2} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $a_0 = 0{\cdot}528 \times 10^{-8}$ cm. and is the radius of the electron orbit in the ground state of the hydrogen atom; Z is the charge on the nucleus and S is a screening constant. It is this last quantity which is most difficult to estimate and which may be responsible for the poor agreement between observed and calculated values for krypton and xenon shown below.

Diamagnetism of the Inert Gases.

	He.	Ne.	A.	Kr.	Xe.
$-10^6\chi_M$, obs.	1·88—1·95	6·65—6·75	18·1—19·7	28·0—29·2	42·4—44·1
Calc. : Pauling	1·54	5·7	21·5	42	66
,, : Slater	1·68	5·7	18·9	31·7	48·0

Similar methods of calculation can be applied to ions with an inert-gas structure and again the agreement between observed and calculated figures cannot be considered good. This subject was reviewed in the *Annual Reports* for 1941 so that it need not be discussed in detail here.

For molecules the resonance term cannot be neglected. The only molecule for which even approximate numerical values can be calculated from the basic theory is that of hydrogen. Here $10^6\chi_d$ is $-4{\cdot}7$ and $10^6\chi_R$ is $+0{\cdot}5$, giving a predicted molar susceptibility of $-4{\cdot}2$ in fair agreement with the observed value of $-4{\cdot}0$. The notable feature of this calculation is the relative magnitude of the resonance term which may be associated with bond formation.

For more complex molecules it is not possible to make calculations based on fundamental theory and one has to fall back on semi-empirical methods. In a series of investigations between 1908 and 1913 Pascal measured the susceptibilities of a large number of organic compounds and showed that they could be expressed as an additive function of contributions from each atom in the molecule together with some correction terms for special structures. There have been a number of later attempts to improve and extend Pascal's method of analysis. One interesting line of attack has been opened by Gray and Cruikshank which involves an interpretation of bonding contributions in terms of screening constants, bond moments, and internuclear distances. Unfortunately, these quantities are themselves not known with any degree of precision.

The principal difficulty in the way of a more detailed analysis of the relation between diamagnetism and chemical constitution is the lack of agreement between the values found experimentally by different workers for the susceptibility of a given compound. Data for the two well-known substances, benzene and acetone, are collected in the following table.

Much greater discrepancies are found for substances which have not been studied so extensively; *e.g.*, for chlorobenzene Kido finds 68·9 against Bhatnagar's value of 72·45; for *o*- and *p*-nitrotoluene Kido's results are also some 3% lower than those obtained in Bhatnagar's laboratory.

The most self-consistent data at present available are those of Bhatnagar and his collaborators. It is clearly desirable to obtain values for a number of types of organic compound accurate to, say, one part in 500 and to have some of them checked by using different methods of measurement.

Another field in which more experimental work is needed is the variation of diamagnetism with temperature. Theoretically neither χ_d nor χ_R should be temperature-dependent in the neighbourhood of 300° K., since molecular motions should not appreciably affect the movements of the electrons. Water undoubtedly shows a temperature coefficient but this may be ascribed to changes in its degree of association. Some of the Indian workers

Susceptibility of Benzene and Acetone.

Date.	Observer.	$-10^6\chi_M$.	Date.	Observer.	$-10^6\chi_M$.
		Benzene.			
1908—1913	Pascal (corrected)	55·1	1933	Boecker	54·49
1914	Ishiwara	55·58	1934	Bhatnagar, Neogi, & Khanna	55·58
1931	Rao	54·79	1934	Bhatnagar, Mitru, & Tuli	55·64
1932	Kido	54·71	1934	Cabrera & Fahlenbrach	53·13
1933	Azim, Bhatnagar, & Mathur	55·58	1936	Trew & Spencer	55·43
1933	Rao	55·03	1936	Seely	55·45
		Acetone.			
1908—1913	Pascal (corrected)	33·7	1932	Cabrera & Madinaveitia	34·23
1931	Rao	34·53	1933	Trew & Watkins	34·52
1931	,,	34·66	1933	Rao	34·37
1931	Buchner	34·83	1935	Salceanu & Gheorgi	34·65
1932	Kido	34·43	1936	Bhatnagar, Neogi, & Mathur	33·85
1932	Fahlenbrach	33·96			

have also reported measurable changes in the diamagnetism of alkyl iodides with temperature; if this is confirmed, it will have interesting theoretical consequences.

For paramagnetic substances the predominant term in equation (1) is the second term, which may be written

$$\chi_\mu = N\mu^2\beta^2/3kT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here β is a convenient unit, the Bohr magneton, in which to measure the magnetic moment, μ, and has the value $0{\cdot}9174 \times 10^{-20}$ erg, gauss^{-1}. For a free atom or ion the third term in equation (1) vanishes, so that the effective moment per gram-molecule can be calculated from the susceptibility by the relation

$$\mu_{\text{eff.}} = N\sqrt{\frac{3k}{N\beta^2}} \cdot \sqrt{(\chi_M - \chi_d)T} = 2{\cdot}84\sqrt{(\chi_M - \chi_d)T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If equation (5) holds, the susceptibility varies inversely as the absolute temperature (Curie's law) and $\mu_{\text{eff.}}$ is independent of temperature. Equation (5) can also be applied to molecules, since in many cases the resonance term is small: in special cases a more detailed analysis is necessary. Thus, van Vleck has shown the variation of $\mu_{\text{eff.}}$ for the two paramagnetic diatomic gases, oxygen and nitric oxide, can be predicted in accurate agreement with the observed values over a wide range of temperatures.

The value of $\mu_{\text{eff.}}$ will not of course be a whole number of Bohr magnetons because of the restrictions which the quantum theory sets on the coupling of orbital and spin moments. For an isolated atom, theory shows that

$$\mu_{\text{eff.}} = g\sqrt{J(J+1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where g is Lande's splitting factor and J is the quantum number defining the total angular momentum of the atom. This formula gives good agreement with the data for most of the rare earths. Samarium and europium show some disagreement but a more detailed analysis by van Vleck has accounted fully on theoretical grounds for this divergence. The ions of the elements of the first transition series do not have moments predicted by formula (6); instead, they show approximate agreement with the simpler formula

$$\mu_{\text{eff.}} = \sqrt{4S(S+1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which only the spin of the electrons in the incomplete $3d$ group contributes to the magnetic moment.

Van Vleck has shown that this is due to the perturbing effect of adjacent atoms on the electrons of the $3d$ group. Measurements on these ions are always made in solution or in the solid state, so these perturbations must be considered. In effect these interatomic interactions so perturb the orbital motions of the $3d$ electrons that their resultant contribution to the magnetic moment becomes zero, or, as van Vleck describes it, the orbital moment is quenched, leaving the spin moment only to contribute to the magnetism. With the ions of the rare earths the incomplete $4f$ level is screened from disturbance by a complete shell of eight electrons in the $5sp$ sub-groups and hence quenching of the orbital components does not take place.

A closer scrutiny of the data for the first transition series shows that the " spin only " formula (7) is not too closely obeyed and that the cobaltous ion and to a smaller extent the ferrous and nickelous ions give higher values of $\mu_{\text{eff.}}$ than can be accounted for on this basis. The following table gives some typical results.

Deviations from " spin only " formula.

Ion.	Substance measured.	$\mu_{\text{eff.}}$, obs.	$\mu_{\text{eff.}}$, calc.	Ion.	Substance measured.	$\mu_{\text{eff.}}$, obs.	$\mu_{\text{eff.}}$, calc.
$Mn^{\cdot\cdot}$	$MnSO_4,4H_2O$	5·9	5·9	$Co^{\cdot\cdot}$	$CoSO_4,7H_2O$	5·0	3·9
$Fe^{\cdot\cdot}$	$FeSO_4,7H_2O$	5·2	4·9	$Ni^{\cdot\cdot}$	$NiSO_4,7H_2O$	3·3	2·8

The large deviation shown by cobaltous sulphate is very much greater than can be ascribed to experimental errors. The susceptibility is proportional to the square of the magnetic moment, so the susceptibility found experimentally is 60% greater than it should be if the spin of the $3d$ electrons were alone responsible.

A preliminary survey of simple and complex cobaltous compounds was made by Dr. E. P. D. Barkworth a few years ago (Ph.D. Thesis, London, 1938), and very considerable variations in $\mu_{\text{eff.}}$ were found which depended on the chemical character of the groups attached to the cobalt atom. Perhaps the most interesting case which was encountered was a pair of isomerides which differed considerably in their magnetic moment. When tetrapyridinocobaltous chloride (Co $\mathrm{py_4Cl_2}$) is heated to 120° it loses two molecules of pyridine to leave a blue powder of the composition Co $\mathrm{py_2Cl_2}$ which changes in a few hours into a violet substance of the same composition. The blue form can be regenerated by heating to 110° or by dissolving the violet form in chloroform and adding ligroin, whereupon the blue form is precipitated. The interesting fact which emerged from Barkworth's investigation is that these compounds of identical composition have notably different magnetic moments. The stable violet form gives $\mu_{\text{eff.}}$ 5·33, and the blue form $\mu_{\text{eff.}}$ 4·62. The corresponding bromide had so far only been obtained in the blue form. The diammino-complexes, $\mathrm{Co,2NH_3,Cl_2}$ and $\mathrm{Co,2NH_3,Br_2}$, are both known to exist in red and blue forms, but all have about the same effective moment of about 5·5. The corresponding di-iodides give a lower moment of 4·6 in both red and blue forms.

Barkworth suggests that the pyridine complexes are not true isomerides but that the colour change is associated with the change in structure

$$\underbrace{\underset{\text{red}}{[\mathrm{Co\,py_4}]^{++}}\underset{\text{blue}}{[\mathrm{CoCl_4}]^{--}}}_{\text{violet}} \rightleftarrows 2\underset{\text{blue}}{[\mathrm{Co\,py_2Cl_2}]}$$

This conclusion is by no means certain but it receives some support from other lines of evidence. What does seem to be established, however, is that the coupling of the spin and orbital momenta of the 3*d* electrons in the cobaltous ion is very sensitive to perturbation by interatomic forces. A more detailed study of these cobaltous compounds is clearly needed; in particular, measurements of the effective moment over a large temperature range would give results of the greatest interest.

Most cobaltous compounds have moments which are larger than those predicted by the "spin only" formula; many other co-ordination compounds have long been known to have moments which are much lower than the predicted values. For instance, potassium ferrocyanide should have an effective moment of 5·2 and potassium nickelocyanide a moment of 2·8 if the 3*d* electrons are exerting their maximum spin; both substances are diamagnetic and have zero moment.

This behaviour has given rise to many theoretical interpretations of which the most interesting is that of Pauling (1931). This attempts to correlate the stereochemistry of the complex with the type of electronic bond and hence with the magnetism. Pauling's theory as applied to complexes derived from elements of the first transition series may be summarised as follows. (*a*) Four bonds with tetrahedral symmetry are produced by combining *s* and *p* eigenfunctions only or by combining *s*, *p*, and three *d* eigenfunctions. (*b*) Four bonds at 90° in a plane are produced by the combination of *s*, *p*, and one *d* eigenfunctions. (*c*) Six bonds directed towards the corners of an octahedron are formed by the combination of *s*, *p*, and two *d* eigenfunctions. (*d*) *d* eigenfunctions which are used in bond formation are not available for occupation by the incomplete 3*d* group of electrons.

It is this last condition which relates the magnetism of the complexes to their stereochemistry. For example, if the nickelous ion forms a planar complex by using one *d* eigenfunction the eight 3*d* electrons must occupy the remaining four *d* eigenfunctions. By Pauli's rule they must in consequence pair their spins and have zero moment. If the number of 3*d* electrons is small, then the use of *d* eigenfunctions may not cause a fall in magnetic moment. Thus in potassium chromicyanide, $\mathrm{K_3Cr(CN)_6}$, the use of two *d* eigenfunctions to form the octahedral complex still leaves three 3*d* eigenfunctions to accommodate the three 3*d* electrons of the chromic ion. They can therefore exert their maximum spin and the chromicyanide has the same moment as the simple chromic salts.

Pauling's theory has had a large measure of success. It predicts the planar character of diamagnetic nickel complexes which has been verified by *X*-ray analysis and by the isolation of *cis-trans*-isomerides. It also predicts correctly the magnetic moment of a large number of complex compounds of the transition elements. A closer scrutiny, however, reveals a number of difficulties.

For instance a number of four-covalent complexes are known which have been snown to have a planar configuration by *X*-ray analysis but are difficult to reconcile with Pauling's theory. The cupric compounds of β-diketones fall into this group; the bivalent copper ion has 9 electrons in the 3*d* level and hence there is no vacant *d* level; yet these compounds undoubtedly have a planar configuration and also have a magnetic moment which indicates one unpaired spin. A still more difficult case is that of the beryllium compound of phthalocyanine; the beryllium atom presumably forms its bonds with 2*s* and 2*p* electrons and there is no *d* level available to take part in Pauling's planar arrangement of bonds.

Other difficulties are encountered with octahedral complexes. Many such compounds are known in which the central atom is not one of the transition elements, so the 3*d* group has not begun to be built up in the parent ion. It is possible that 3*d* levels might still be used in forming the complex but this seems doubtful from considerations of energy. Furthermore, within the transition elements the predicted fall in magnetic moment does not always take place. These points may be illustrated by the trisacetylacetonates of aluminium, iron, and cobalt.

$\mathrm{Al(acac)_3}$.	$\mathrm{Fe(acac)_3}$.	$\mathrm{Co(acac)_3}$.
$\mu_{\text{eff.}} = 0$	$\mu_{\text{eff.}} = 5{\cdot}9$	$\mu_{\text{eff.}} = 0$

The aluminium compound is derived from a non-transition element and must therefore have zero moment. The ferric compound should, on Pauling's theory, have a moment of 1·83 due to one unbalanced spin; instead it has a moment which indicates five unbalanced spins, so none of the 3*d* levels is used in forming the octahedral complex. The cobaltic compound has zero spin, in agreement with the theory.

It has been suggested that compounds which do not show the expected fall in magnetism contain ionic and not covalent linkages. It is difficult to accept this view, since it implies that the ferric compound contains a type of bond which differs from that found in the aluminium and cobalt derivatives. The ferric compound can be volatilised, is soluble in non-polar solvents, and has all the properties usually associated with covalent binding.

Another example may be cited for which the attribution of ionic linkages leads to great difficulties. Bivalent iron and nickel form trisdipyridyl derivatives of the formula $[M(dipy)_3]Br_2,6H_2O$, both of which have been resolved. The iron compound has zero moment, in agreement with the Pauling theory, whereas the nickel compound has a moment of 3·0, indicating two unpaired spins. None of its 3*d* levels can therefore be used to form the octahedral arrangement of links. If the ionic explanation is to be used here, it involves the assumption that the trisdipyridyl nickel *ion* is bound together with ionic links which do not ionise in solution, whilst the closely related trisdipyridyl ferrous ion is bound by covalent linkages.

A more general theory of the magnetic behaviour of complex compounds has been developed by van Vleck (1935). He comes to the conclusion that the fall in magnetic moment can be associated with strong perturbations of the incomplete group of electrons by the close approach of other atoms. If these interatomic reactions are sufficiently powerful, they can not only quench the orbital contribution to the magnetic moment but can also bring about pairing of spins. His general argument is along the following lines. The most stable state of a free atom, *i.e.*, the one with lowest energy, is that of maximum spin. When computations are made of the energy associated with the interatomic reactions either by the Heitler–London theory or by other methods it is found that the energy associated with the atomic interactions is least when the spin is least. There are thus two opposing tendencies in a complex molecule or ion. If the interactions between the central atom and its neighbours are not too great, the tendency towards maximum spin predominates; if the interactions with the neighbouring atoms are greater, the tendency to pair spins predominates. Thus a fall in magnetic moment when a complex is formed indicates a deeper interaction or, in chemical terms, a more intimate bonding.

From this standpoint the study of the magnetism of co-ordination compounds has a renewed interest for chemistry. Already a number of observations have been made which show that even small changes in the chemical character of the outer groups can alter the coupling of electron spins in the central atom. For example, Cambi (1935) found that the nickel compound of succinimide, $Ni(su)_2,2H_2O$, has an effective moment of about 3, indicating two unpaired spins. This moment is retained if two molecules of pyridine are added to the complex, but if methylamine, ethylamine, or piperazine replaces the pyridine the moment falls to zero. Here co-ordination with primary and secondary bases appears to be more effective than co-ordination with a tertiary base. The double salt $K_2[Ni(su)_4],4H_2O$ is also found to have zero moment.

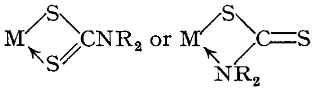
Cambi and Cagnassi have also studied a number of chelate compounds of ferrous iron. When these groups are attached at both ends by nitrogen atoms in the compounds with dipyridyl, *o*-phenanthroline, and dimethylglyoxime the magnetic moment is reduced practically to zero. If the chelate group is attached at one end through nitrogen and at the other end through oxygen, as in the compounds derived from *iso*nitroso-ketones, then a partial reduction in magnetic moment to between 1·8 and 3·6 is found.

The effect of a fixed grouping on a related series of ions is also interesting: the compounds obtained by coupling *o*-phenanthroline with bivalent manganese, iron, cobalt, and nickel have the following compositions and moments :

$Mn(phen)_2Cl_2$.	$Fe(phen)_2Br_2$.		
5·7	0		
	$Fe(phen)_3Br_2$.	$Co(phen)_3Br_2$.	$Ni(phen)_3Br_2$.
	1·1	5·1	3·0
(5·9)	(5·2)	(5·0)	(3·3)

The figures in parentheses in the bottom row are the moments of the simple hydrated metal ions. It will be seen that it is only the ferrous ion which shows any fall in magnetic moment.

Another series of interest is furnished by the substituted dithiocarbamates, which are co-ordinated either by two sulphur atoms or by sulphur and nitrogen :



A number of these have been examined by Cambi and his school, with the results shown below :

Parent ion.	Compound.	μ, obs.	μ, calc. (spin only).	Compound.	μ, obs.	μ, calc. (spin only).
Mn^{III}	$Mn(S_2CNR_2)_3$	4·8—5·0	4·9			
Fe^{III}	$Fe(S_2CNHR)_3$	5·3—6·0	5·9	$Fe(S_2CNR_2)_3$	2·5—5·4	5·9
Co^{III}	$Co(S_2CNHR)_3$	0·3	4·9	$Co(S_2CNR_2)_3$	0·4	4·9
Ni^{II}	$Ni(S_2CNHR)_2$	0·3	2·8	$Ni(S_2CNR_2)_2$	0·2—0·7	2·8

Here the tervalent manganese complex shows no reduction in magnetic moment. The iron complexes are of special interest, since they show little reduction with monosubstituted but a considerable reduction with some disubstituted dithiocarbamates. The tervalent cobalt compounds and the bivalent nickel compounds give the full reduction predicted by the Pauling theory. The ferric compounds seem to be a borderline case and would repay detailed examination over a range of temperatures and substituents.

These examples will suffice to show that the nature of the central atom and the nature of the atoms and groups attached to it both play a part in determining the magnetic moment of the complex. Further systematic study of the magnetism of co-ordination compounds is certain to lead to interesting results which will deepen and extend our knowledge of valency forces. In particular, it may be noted that most of the observations so far made have been at room temperature. A re-examination of a number of compounds of special interest over a wide range of temperature will not only confirm the values found for the magnetic moments but may lead to the discovery of systems which are so delicately balanced that change of temperature may bring about coupling or uncoupling of electronic spins.

The few topics which I have discussed form only a small part of the subject; there are many other magnetic investigations which have interesting applications to chemical problems but which lack of time forbids me even to mention. I have deliberately restricted myself to a discussion of some parts of the subject in which gaps in knowledge suggest immediate lines of attack both experimental and theoretical. This has been done in the hope that some of our younger colleagues may be tempted to undertake work in this new branch of physical chemistry. If this hope should be realised then this Ninth Liversidge Lecture will in some measure have fulfilled the wishes expressed by its founder.