Mean Magnetic Susceptibility and its Solvent Dependence for Several Substituted Ferrocenes, Ruthenocene and Di(η^6-benzene)chromium

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The mean magnetic susceptibility of several ferrocene derivatives, ruthenocene and di(η^6-benzene)-chromium as solutes in a number of solvents was determined *via* an NMR technique. The solvent dependence of this property was investigated and the variation in the magnetic susceptibility of the ferrocenyl group, due to substituent effects was analysed.

An experimental technique developed for the evaluation of the solution-state mean magnetic susceptibility of compounds has now been applied to the determination of this interesting and fundamental property for a series of organometallic molecules. This is a further aspect of the systematic investigations carried out by our research group into the electric and magnetic properties of the metallocene class of molecules.[1-6] The experimental determination of the susceptibility stems from the chemical-shift dependence upon the bulk magnetic susceptibility of the sample. This in turn is affected by the geometry of the NMR sample tube and its orientation to the applied magnetic field.

The molecules examined are ferrocene [Fe(η-C_5H_5)$_2$], decamethylferrocene [Fe(η-C_5Me_5)$_2$], 1,2,3,4,5-pentamethylferrocene [Fe(η-C_5H_5)(η-C_5Me_5)], 1,2,3,4,5-pentachloroferrocene [Fe(η-C_5H_5)(η-C_5Cl_5)], 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene [Fe(η-$C_4PH_2Me_2$)$_2$], ruthenocene [Ru(η-C_5H_5)$_2$] and di(η^6-benzene)chromium [Cr(η^6-C_6H_6)$_2$].

The response of any molecule to an applied magnetic field invariably contains a diamagnetic component,[7] despite any possibly dominating paramagnetic contribution arising from the presence of a permanent magnetic moment. Since the magnetizability is the magnetic analogue of the electric polarizability, which has been previously examined,[1,8] it was of interest to see whether the additivity present in the mean electric polarizability[1] is reproduced in the magnetizability. Due to the unusual diamagnetic susceptibility displayed by aromatic compounds the relation between susceptibility and aromaticity has been previously investigated, initially by the work of Pauling[9] and London[10] on delocalized π electrons, then more recently by studies on the resonance energy.[11-13] The latter energy dependence arises because the susceptibility is the second derivative of the energy with respect to the magnetic field and since this energy relates to the π electrons the susceptibility so determined also originates from these π electrons.

The susceptibility itself has no relation to aromaticity rather it is the exaltation of the susceptibility, defined as the difference between the susceptibility of a compound and that calculated for an olefinic structure according to Pascal's additivity principle,[14] which is important. However the diamagnetic susceptibility exaltation is not a good measure of aromaticity for heterocyclic rings[15] and probably not for organometallic compounds, due in part to the absence of any tabulated data relating to a suitable correction factor for the metal–ring bond.

Flygare and co-workers[16,17] have investigated the use of the magnetic anisotropy as a measure of aromaticity, with the result that the paramagnetic component of the anisotropy does show a correlation with aromaticity. To isolate the paramagnetic contribution to the magnetic anisotropy either the molecular quadrupole moment is required,[8] or the diamagnetic contribution to the anisotropy must be estimated, *e.g.* by the method of atom dipoles,[17,18] and then subtracted from the measured magnetic anisotropy. The latter method is not applicable for the same reason that the susceptibility exaltation is not a valid approach, *i.e.* the parametrization of the metal–ring bond is unknown. The use of the quadrupole moment, in conjunction with the measured magnetic anisotropy, is strictly applicable only to ferrocene and ruthenocene, and due to the different characteristics of the metals in these molecules, little can be said about their relative aromaticity.

However it is possible to investigate the 'correction factor' for the metal–carbon bonds when a predictive model is used to generate the measured susceptibility. The two modelling schemes chosen are the atom-increment system of Pascal[14] and Pacault,[19] and the atom- and bonding-increment system of Haberditzl.[20,21]

Attempts to use a system devised by Gray and Cruickshank[22] based on representing all molecules by an ionic structure produced inconsistent results for the metal–ring bond corrections if the methylated ferrocenes were included. However their method closely approximated the cyclohexane solution susceptibilities of ferrocene, ruthenocene and di(η^6-benzene)-chromium when the following conditions applied: (*i*) the 'bond depression' for the aromatic carbon linkages was determined from a point-charge analysis of the quadrupole moment of gaseous benzene;[23] (*ii*) the metal–ring bond depressions were taken as the negative of the correction factor derived from a Pascal–Pacault type analysis; (*iii*) corrections were applied for steric interactions between methyl protons;[24] and (*iv*) the diamagnetic susceptibility of the metal was based on the metal atom charge,[1] and estimated from the corresponding corrections for neutral atoms and charged ions, as presented by Malli and Fraga.[25] For the present analysis, the susceptibility determined for the compounds as solutes in cyclohexane solution is assumed to represent the true molecular value.

Experimental

Substituted ferrocenes[3] and ruthenocene[8] were prepared as reported previously while di(η^6-benzene)chromium[1] involved a modification of a literature method. Di(η^6-benzene)chromium, an extremely water- and air-sensitive compound, was recrystallized from dry cyclohexane under nitrogen, and then sublimed immediately before measurement. Substituted ferrocenes and ruthenocene were purified by vacuum sublimation and/or recrystallization. Solutions were prepared and manipulated under nitrogen. The solvents employed were [$^2H_{12}$]cyclohexane, [$^2H_6$]benzene, [$^2H_8$]dioxane, [^2H]chloroform, carbon tetrachloride and acetonitrile.

The experimental technique used to determine the magnetic susceptibility derives from the NMR frequency of a given nucleus being dependent on the macroscopic sample, due to the contribution of the bulk susceptibility.[26] This is best understood by looking at the magnetization volume current density, j_{mag} [equation (1)], which describes the average currents inside

$$j_{mag} = \nabla \times M \quad (1)$$

magnetized materials, where ∇ is the differential operator and M the magnetization vector. This equation defines the magnetization in terms of the atomic currents that give rise to the large-scale currents, j_{mag}. The latter is related to the source of the magnetic field. For liquids and solutions the magnetization, M is given by equation (2) where χ_v is the volume susceptibility and

$$M = \chi_v \frac{B_{loc}}{\mu_0} \quad (2)$$

B_{loc} is the local field arising from the applied field B, and the induced field B_M, due to the current density j_{mag} [equation (3)].

$$B_{loc} = B + B_M \quad (3)$$

By choosing a suitably shaped sample,[27] in this instance a rectangular glass cell, the value of B_M can be determined from the product of the applied field and a demagnetization factor, $N(\theta)$, dependent on the orientation, θ, of the cell. Calibration was performed by determining the observed shift in frequency for the cell being oriented parallel and perpendicular to the external magnetic field, against standards of known magnetic volume susceptibilities. A linear relationship, equation (4), is

$$D(\chi_v) = A + B(\chi_v) \quad (4)$$

obtained where the constants A and B depend on the geometry of the rectangular cell. The demagnetization factor has disappeared because the magnetic-field difference between the two orientations is proportional to the volume susceptibility of the sample. Alternative means of determining the magnetic susceptibility exist using NMR techniques,[28] but the general applicability of this method to solution work dictated its selection.

Originally this method was applied to pure liquids,[27] with densities determined from tabulated values over a temperature range. It was necessary to modify the procedure to apply it to dilute solution-state susceptibilities. A much larger cell was required for the dilute (<4%) metallocene solutions and an accurate means of determining the solution densities of the samples at the operating temperature of the spectrometer (35.7 °C). The first of these difficulties was overcome by melting a standard 5 mm NMR tube onto a 2.50 × 1.75 mm stainless-steel former, which was subsequently removed upon cooling. The rectangular envelope thus formed was attached to a small diameter glass rod of appropriate length to enable the sample to be placed within the field, while the opposite end of the rod was attached to a calibrated barrel. This barrel served to seal the spectrometer, preventing thermal fluctuations, and enabled the rod to be readily rotated.

The second problem was surmounted by setting the temperature of a Paar densitometer to 35.7 °C and determining the cell constant for the apparatus under these conditions. This cell constant was used in subsequent determinations of the incremental densities of the solutions, after the separation, ΔD, between the ^{1}H NMR peaks had been determined for the two cell orientations. The final requirement was calibration with solvents of known volume susceptibilities, which allowed the determination of the constants relating the observed peak separation to the diamagnetic volume susceptibility of the sample, as given by equation (5). A linear analysis yielded

$$\chi_v = A + B\Delta D \quad (5)$$

$$\chi_M = \frac{\chi_v M}{4\pi\rho_{12}}, \quad \chi = \frac{\chi_M}{N_A} \quad (6)$$

$$\rho_{12} = \rho_1 + \Delta\rho \quad (7)$$

$A = -(3.143 \pm 0.115) \times 10^{-3}$ J kg T^{-2} m^{-3} and $B = -(0.0702 \pm 0.0018) \times 10^{-3}$ J kg s T^{-2} m^{-3} for a plot of $10^6(\chi_v M/4\pi\rho_{12})$(J T^{-2} mol^{-1}) *vs.* ΔD (Hz), with a correlation coefficient of 0.998. In order to derive a molar susceptibility, χ_M, or a molecular magnetizability, χ, then the relationships (6) apply, where M is the molecular weight of the solute, N_A is the Avogadro constant and ρ_{12} [equation (7)] is the density of the solution.

Here ρ_1 is the tabulated density of cyclohexane at 35.7 °C and $\Delta\rho$ is the incremental density obtained from the densitometer. The spectrometer used was a Hitachi-Elmer R24B (60 MHz) run in the unlocked mode. Results are collected in Table 1, where the error in χ_v depends on the deviations of the slope and intercept of equation (5), along with the precision of ΔD. The error in χ_M further included the uncertainty in the density $\Delta\rho$, the latter set at a nominal value of ±0.002, this being the maximum variation obtained when different solvents were used to derive the cell constant of the densitometer at 35.7 °C.

Results and Discussion

The susceptibility determinations were carried out using a number of solvents, with the results displaying a substantial variation. It is noteworthy that the [$^2H_{12}$]cyclohexane solution of ferrocene reproduced the crystal determination of Fox and co-workers[29] almost exactly (-125×10^{-5} J T^{-2} mol^{-1}), and well within the experimental uncertainty of this NMR technique (2–5%), thereby reinforcing the initial choice[1-4,8] of the cyclohexane solution data as the most appropriate to represent the free molecule values. The inertness (in the NMR sense[30]) of this solvent is in agreement with the minimal solubility of the metallocenes in cyclohexane, while the solvents displaying the largest variations, *i.e.* carbon tetrachloride and [^{2}H]chloroform, also cause most of these molecules eventually to decompose. Indeed it was impossible to measure the magnetic susceptibility of decamethylferrocene as a solute in carbon tetrachloride before the compound had decomposed.

It is apparent from Table 1 that the additivity between the three molecules decamethylferrocene, pentamethylferrocene and ferrocene is found in the magnetic susceptibility. This is analogous to what was found for the electric polarizability,[1] *i.e.* the value for the penta-substituted compound lies intermediate between that for decamethylferrocene and ferrocene itself. Of interest is the fact that the ruthenocene susceptibility is at variance with the crystal determination.[31] However this holds not only for the mean susceptibility, but as has been shown previously,[8] there is disagreement with the anisotropy in this property. It has been suggested[32] that the crystal measurements are in error for the orthorhombic space group of ruthenocene, possibly because of difficulties concerning the relationship between the crystalline and molecular axes, and hence the observed magnetizabilities. This problem does not attend the solution-state determination of the mean (*isotropic*) and anisotropic magnetizabilities.

If the [$^2H_{12}$]cyclohexane values of the magnetic susceptibility given in Table 1 are taken as being the values closest to the free molecular quantities, then the following general trends emerge. (*i*) The values for ferrocene and di(η^6-benzene)chromium are very similar, an observation in accord with their isoelectric structure; (*ii*) the ruthenocene susceptibility is substantially larger than that of ferrocene, in line with the richer electron density of the ruthenium metal atom compared to that of iron; and (*iii*) for the molecules tetramethylphosphaferrocene and

pentamethylferrocene the susceptibility is similar, in agreement with the similar degree of substitution while the pentachloroferrocene value is noticeably greater than that of either of these two members. This can be rationalized if the more electron-rich chlorine atoms are taken into consideration.

A more informative trend is uncovered if the variation in the correction factor, λ, for an additive scheme, as discussed earlier, is examined. Only the cyclohexane solutions are considered and the Pascal–Pacault[14,19] and the Haberditzl[20,21] atom- and bonding-increment system (ABIS) correction factors, λ(P–P) and λ(ABIS), are given in Table 2.

The conclusions that can be drawn from Table 2 must be very qualitative in nature, since the increment λ represents changes in the susceptibility of both the rings and metal, together. As the progressive substitution of methyl groups by ring protons occurs, to produce first pentamethylferrocene then ferrocene, followed by substitution with electron-withdrawing chlorine atoms to form pentachloroferrocene, one observes that the correction factor becomes increasingly more diamagnetic, *i.e.* either an underlying paramagnetic contribution to λ is being reduced or a genuine increase in the diamagnetism of the molecule is being observed. Some feel for the differing effects that the ring and metal susceptibilities have upon determining the value of λ can be gleaned by looking at the λ(ABIS) of pentachloroferrocene and ruthenocene. Despite having indistinguishable values of λ(P–P), the values of λ(ABIS) are clearly different. The value for tetramethyldiphosphaferrocene lies between the ferrocene and pentachloroferrocene values indicating that, despite the presence of four methyl groups, the effect of the phosphorus atoms in the ligand rings is to localize the electron distribution, analogous to the effect of the chlorine atoms. The way in which this may occur is for the substituents partially to disrupt the delocalized electron pathway through the rings. Hence if this notion can be viewed as a criterion for aromaticity, then the tetramethyldiphosphaferrocene molecule would be less aromatic than the equivalent tetramethylferrocene.

Table 1 Experimental values of the mean volume (χ_v) and molar susceptibilities (χ_M) of metallocene solutions

Compound	Solvent	$10^{-3}\ \rho_{12}$[a]/ kg m^{-3}	ΔD/Hz	$-10^6\ \chi_v$/ J T^{-2} m^{-3}	$-10^5\ \chi_M$/ J T^{-2} mol^{-1}	Δ[b](%)
[Fe(η-C_5Me_5)$_2$]	C_6D_{12}	0.890 44	61.0 ± 1.0	7.52 ± 0.17	220 ± 5	—
	C_6D_6	0.874 97	64.5 ± 1.0	7.78 ± 0.18	232 ± 5	5
	$C_4D_8O_2$	1.020 97	60.3 ± 3.0	7.48 ± 0.27	191 ± 7	−13
	$CDCl_3$	1.424 05	84.0 ± 1.0	9.18 ± 0.20	168 ± 4	−24
[Fe(η-C_5H_5)(η-C_5Me_5)]	C_6D_{12}	0.908 73	62.8 ± 2.0	7.65 ± 0.22	172 ± 5	—
	C_6D_6	0.885 84	67.0 ± 5.0	7.96 ± 0.40	184 ± 9	7
	$C_4D_8O_2$	1.118 22	65.8 ± 2.0	7.87 ± 0.22	144 ± 4	−17
	$CDCl_3$	1.452 05	85.8 ± 2.0	9.30 ± 0.24	131.0 ± 3.4	−24
	CCl_4	1.556 06	76.4 ± 3.0	8.63 ± 0.28	113.3 ± 3.7	−34
[Fe(η-C_5H_5)$_2$]	C_6D_{12}	0.896 58	62.0 ± 1.00	7.60 ± 0.17	126.0 ± 2.9	—
	C_6D_6	0.891 91	64.5 ± 1.0	7.78 ± 0.18	129.6 ± 3.0	3
	$C_4D_8O_2$	1.020 97	65.0 ± 1.0	7.81 ± 0.18	113.7 ± 2.6	−10
	$CDCl_3$	1.453 13	84.4 ± 2.0	9.23 ± 0.24	94.3 ± 2.4	−25
	CCl_4	1.562 59	76.8 ± 4.0	8.66 ± 0.34	82.3 ± 3.2	−35
	MeCN	0.777 89	50.8 ± 1.0	6.79 ± 0.16	129.8 ± 3.1	3
[Fe(η-C_5H_5)(η-C_5Cl_5)]	C_6D_{12}	0.913 54	62.3 ± 2.0	7.62 ± 0.21	239 ± 7	—
	C_6D_6	0.898 96	66.7 ± 2.0	7.93 ± 0.22	253 ± 7	6
	$C_4D_8O_2$	1.138 06	65.2 ± 3.0	7.82 ± 0.27	197 ± 7	−18
	$CDCl_3$	1.482 51	86.7 ± 2.0	9.37 ± 0.24	181 ± 5	−24
	CCl_4	1.571 10	78.8 ± 5.0	8.80 ± 0.40	160 ± 7	−33
[Fe(η-$C_4PH_2Me_2$)$_2$]	C_6D_{12}	0.947 703	67.2 ± 6	7.97 ± 0.46	186 ± 10	—
[Ru(η-C_5H_5)$_2$]	C_6D_{12}	0.775 08	61.0 ± 1.0	7.52 ± 0.17	179.6 ± 4.2	—
	C_6D_6	0.884 20	65.3 ± 1.0	7.83 ± 0.18	163.7 ± 3.7	−9
	$C_4D_8O_2$	1.131 80	64.8 ± 1.0	7.79 ± 0.18	127.2 ± 2.9	−29
	$CDCl_3$	1.481 19	86.7 ± 2.0	9.37 ± 0.24	116.7 ± 3.0	−35
	CCl_4	1.570 44	77.0 ± 2.0	8.67 ± 0.23	101.9 ± 2.7	−43
[Cr(η^6-C_6H_6)$_2$]	C_6D_{12}	0.880 31	60.5 ± 1.0	7.49 ± 0.17	141.6 ± 3.3	—

[a] All solutions were saturated, with an error of 0.002 (10^3 kg m^{-3}) assumed for the density (see text). [b] The quantity Δ is defined as the difference in χ_M between a particular solvent and cyclohexane. The error associated with Δ is of the order of 2–3%.

Table 2 Correction factors, λ, for additivity of the magnetic susceptibility and the variation, Δ, due to the solvent dependence of χ_M

Compound	$-10^5\lambda$(P–P)[a]/ J T^{-2} mol^{-1}	$-10^5\lambda$(ABIS)[b]/ J T^{-2} mol^{-1}	Δ[c](%) C_6D_6	$C_4D_8O_2$	$CDCl_3$	CCl_4	MeCN
[Fe(η-C_5Me_5)$_2$]	−10.7 ± 5.1[d]	24.3 ± 5.1	5	−13	−24	*e*	—
[Fe(η-C_5H_5)(η-C_5Me_5)]	3.0 ± 4.9[d]	37.1 ± 4.9	7	−17	−24	−34	—
[Fe(η-C_5H_5)$_2$]	18.2 ± 2.9	51.4 ± 2.9	3	−10	−25	−35	3
[Fe(η-C_5H_5)(η-C_5Cl_5)]	45.7 ± 6.8[f]	104.3 ± 6.8	6	−18	−24	−33	—
[Fe(η-$C_4PH_2Me_2$)$_2$]	27 ± 10	—	—	—	—	—	—
[Ru(η-C_5H_5)$_2$]	54.0 ± 4.2	82.2 ± 4.2	−9	−29	−35	−43	—
[Cr(η^6-C_6H_6)$_2$]	12.3 ± 3.3	53.4 ± 3.3	—	—	—	—	—

[a] Difference required to be added to the atom-increment model of Pascal and Pacault, in order to reproduce the experimental value. The model increments used were taken from refs. 7 and 18. [b] Difference required to be added to the ABIS model of Haberditzl.[20,21] [c] Defined as in Table 1. [d] The correction factor for steric interactions occurring within the methyl groups was derived from ref. 24. [e] Solution decomposed. [f] A correction factor for an aromatic C–Cl bond of 0.3 × 10^{-5} J T^{-2} mol^{-1} was applied. This was determined as the difference between the calculated and measured susceptibilities of chlorobenzene as given by Pacault.[33] It is noteworthy that the values for the calculated and measured susceptibilities of trichlorobenzene, given in Table 17 of this reference, appear to be interchanged and hence were not considered.

The solvent effect on the susceptibility is of interest because it allows a quantitative assessment of the manner in which a solvent molecule is likely to interact with a specific solute. I therefore define a parameter Δ which gives the percentage variation of the susceptibility in a given solvent from that value derived when the solvent is cyclohexane. The sign of Δ is positive if an increase in the susceptibility is observed and negative if the solution value is less than that of a cyclohexane solution. These values are also in Table 2.

Due to the error (2–3%) associated with the Δ values, only variations exceeding this uncertainty will be meaningful. Examining the solvent benzene, a uniform increase of about 6% for the substituted ferrocenes is observed, which is twice that of ferrocene itself. Interestingly ruthenocene displays a reduction of some 9%. A rationalization of this trend is that the electron-rich rings of decamethylferrocene and the electron surplus present on the negative end of the dipole in the penta-substituted ferrocenes interact more readily with the π orbitals of the benzene ring than would the electron distribution in the parent ferrocene. The ruthenocene Δ value being in the opposite direction, *i.e.* a decrease, can possibly be explained in terms of the differing charge states of the two metals. It may be that the charge density of the ruthenium atom, and the associated metal–ring bond-orbital populations, results in a different mode of interaction with the solvent benzene ring than occurs for the case of the iron atom in ferrocene.

The solvent dioxane has a chair conformation as opposed to the planar benzene ring, which may allow a more stereospecific interaction. The trend observed is a decrease in the susceptibility with the largest variation being for ruthenocene, followed by pentachloroferrocene and pentamethylferrocene (these two being approximately equal), then decamethylferrocene, with ferrocene being the least interactive solute. Of the two possible mechanisms whereby a solvent molecule could interact with the metallocene structure,[34] the process involving attack of the solvent molecule on the metal is effectively precluded because any pentasubstituted molecules would sterically hinder approach to the metal, hence causing a reduction of any interaction. The alternative mechanism, involving a ring-directed interaction, is in agreement with the rationalization used for the solvent benzene. As in the case of benzene, the presence of excess electron density on the rings of substituted molecules would favour the interaction of the electron-depleted centre of the dioxane molecule. The larger Δ value of ruthenocene appears to be a generally observed phenomenon for all solvents and is probably more of an indication of the effect the differing metal atom is having, in that it provides a baseline from which to compare relative molecular changes, *e.g.* for different substituents.

The observed variations when chloroform and carbon tetrachloride are used are informative. Discussions with Buckingham[35] on the role of solvents in determining magnetizabilities indicate that the classical dipolar coupling between solute and solvent will have a much smaller effect for magnetizabilities than for polarizabilities. Thus the effect of intermolecular forces at long range will not be significant for magnetizabilities, *i.e.* intrinsic changes in the susceptibility by electron correlation and dipolar coupling. The remaining short-range effects include intrinsic changes due to short-range overlap forces, non-linear magnetization due to the presence of strong intermolecular magnetic fields, non-uniformity of the intermolecular magnetic field or distortion of the molecular structure. The case of the halogenated solvents illustrates the short-range effects well. For both chloroform and carbon tetrachloride, all solutes display a uniform variation. The chloroform Δ values average to 75% of the carbon tetrachloride value, within a 5% scatter. Considering that chloroform has *ca.* 75% of the chlorine content of carbon tetrachloride, then the role of the chlorine atoms appears to fit the short-range requirements admirably. In order to ensure that the dipolar nature of the solvent was not the cause of the variation, a sample of ferrocene in acetonitrile was also examined. This showed a barely significant increase.

A disturbing point relating to the abnormally large solvent effect of carbon tetrachloride is the uncertainty introduced into solution-state birefringence studies employing this non-dipolar solvent, which claim to derive effectively 'free' molecular values. This is particularly true for effects which depend on the anisotropy present in molecular properties such as electric polarizability or magnetizability.

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