

NUCLEAR MAGNETIC RESONANCE CONTACT SHIFTS AND DELOCALIZATION MECHANISMS IN Ni(II)—DIOXO COMPLEXES

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The temperature dependence of the proton NMR-spectra of bis(1,3-diphenyl-1,3-propanedionato)Ni(II) and of bis(1,3-di-*p*-tolyl-1,3-propanedionato)Ni(II) has been determined.

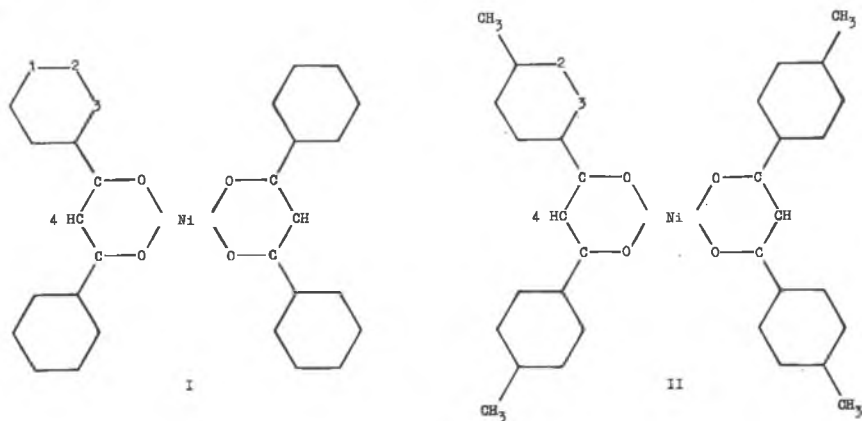
We have interpreted the results using a model with two unpaired electrons per molecule. We conclude that the contact shifts of the various proton resonance signals result from delocalized unpaired electrons in the σ as well as the π system of the ligands.

Introduction

In a previous article, one of us¹ described the formation of two different dimers of 1,3-diphenylpropanedione (DBM) upon reduction with an alkali metal. The information on the structure of these dimers was obtained from electron spin resonance experiments. The unpaired electrons in the molecules under study, required for electron spin resonance, were produced by addition of one extra electron to DBM^- . Adding an electron to the already negative DBM^- ion is possible because of the low reduction potential of DBM^- .

Since then we have become interested in the NMR spectrum of this ligand, complexed with Ni(II) (see structure formula I) and in the NMR spectrum of the Ni complex of 1,3-di-*p*-tolyl-1,3-propanedionate (PMDBM), the *para*-methyl substituted analogue of DBM (see II) (the structural formulae are not meant to represent a stereochemical configuration). From the NMR spectra information will be obtained on the spin delocalization of the unpaired electrons from the metal to the ligand or *vice versa*.

¹ F. W. Pijpers, H. van Willigen and J. J. Gerding, Rec. Trav. Chim. **86**, 511 (1967).



The proton NMR spectrum of an organic ligand complexed with a paramagnetic transition metal consists normally of broad absorption peaks due to the coupling of the proton nuclei and the spins of the unpaired electrons^{2, 3}. This coupling causes a shift of the resonance signals with respect to the positions found with uncomplexed ligands or with ligands complexed with diamagnetic metals. These shifts depend on temperature and are under certain conditions given by:

$$(\Delta H)_n = - (A_H)_n H_0 \frac{(g\beta)^2 s(s+1)}{\gamma_n \hbar} \frac{1}{3kT} \quad [1]$$

In this formula $(A_H)_n$ equals the coupling constant between nucleus n and the unpaired electrons; it represents the magnetic field, expressed in gauss, caused by the unpaired electrons at the position of the hydrogen nucleus n ^{4, 5, 6, 7} and reflects the distribution of these electrons over the molecule. The other symbols have their usual meaning.

Normally an isotropic hyperfine coupling constant $(A_H)_n$ arises from a Fermi contact interaction and from a pseudo contact interaction^{5, 6},

² D. R. Eaton, A. D. Josey, W. D. Phillips and A. E. Benson, *Discussions Faraday Soc.* **34**, 77 (1962).

³ D. R. Eaton, and W. D. Phillips: 'Advances in magnetic resonance' **1**, 103 (1965). Acad. Press New York (edited by John S. Waugh).

⁴ H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.* **28**, 107 (1958).

⁵ H. M. McConnell and R. E. Robertson, *ibid.* **29**, 1361 (1958).

⁶ J. P. Jesson, *ibid.* **47**, 579 (1967).

⁷ A. Carrington and A. D. McLachlan: 'Introduction to magnetic resonance' Harper and Row publishers, Inc. New York, 80 (1967).

the latter being a combination of electron spin – orbit interaction, electron orbit – nuclear spin dipolar coupling and electron spin – nuclear spin dipolar coupling.

The Fermi contact interaction arises from unpaired spin density in either the π or the σ frame work of the ligands or from a combination of these. The type of delocalization mechanism encountered depends on the symmetry of the molecular orbitals in which the unpaired electrons are found.

In the present work we have studied the temperature dependence of the proton NMR spectrum of Ni(II)(DBM)₂ and of Ni(II)(PMDBM)₂.

Experimental

A. Preparation:

The Ni(II) complexes of DBM and of PMDBM were prepared by slow addition of excess aqueous nickel acetate solution to a solution of the sodium salt of the ligand in ethanol. A green coloured precipitate of the Ni(II) complex is formed that can be recrystallized from ethanol.

Physical properties and analysis

	Compound I		Compound II	
Empirical/formula ***	C ₃₀ H ₂₆ O ₆ Ni		C ₃₄ H ₃₄ O ₆ Ni	
m.p. (°C)*	267.5-268.5		320-321	
	exp.	theor.	exp.	theor.
Ni (%w)	10.74	10.85	9.8	9.85
C (%w)	66.28	66.57	68.36	68.32
H (%w)	4.86	4.86	5.74	5.73
mag. mom. (B.M.)	3.2 ± 0.1 ^a		3.8 ± 0.6 ^{**b}	

* At ~ 100° the green crystals lose water and become yellow.

** The magnetic moments were measured with a Gouy balance at room temperature only. The measurements on the THF solutions are less accurate than those on the solid crystals because of the low solubility of the complex in THF.

*** Including two molecules of H₂O per Ni atom. Our attempt to complex 2-methyl-1,3-diphenyl-1,3-propanedione with Ni(II) for further comparisons failed.

^a Measured on crystals.

^b Measured on solutions in THF.

B. Nuclear magnetic resonance measurements:

The NMR spectra of the compounds in dilute solution of tetrahydrofuran (THF) were measured at various temperatures between 205°-330°K with a Varian HA 100 spectrometer.

In order to establish the contact shift, a suitable diamagnetic reference compound had to be chosen. We measured the spectra of Zn(II)(DBM)_2 and of Zn(II)(PMDBM)_2 and compared these with the corresponding spectra of Na(DBM) and Na(PMDBM) , respectively. It was noticed that minor differences were found of about 30-40 cps in peak positions of the corresponding Na- and Zn-complexes. These small differences can be neglected in comparison with the large effect of the contact shifts. The Zn-complexes were selected as diamagnetic reference because of the assumed analogy in structure between the Ni- and the Zn-complexes. Typical spectra are shown in Fig. 1.

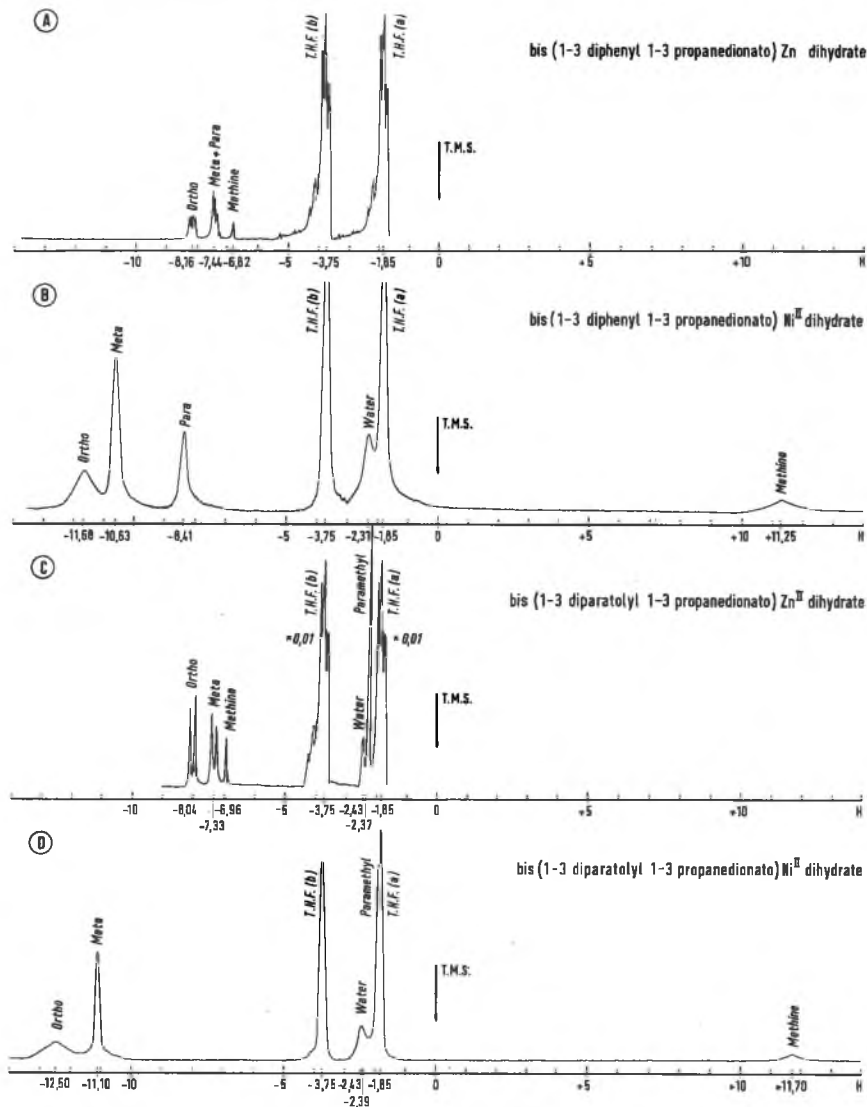


Fig. 1. 100 Mc proton NMR spectra of paramagnetic Ni complexes (curves B and D) dissolved in perdeuterated THF (with some isotopic impurities) and of diamagnetic Zn complexes (curves A and C) in non-deuterated THF. Abcissa in p.p.m.

The high field THF signal at $\delta = 1.85^8$ was used as an internal proton standard. A variable frequency audio-oscillator in combination with a Hewlett Packard frequency counter was used to calibrate the spectra.

From Fig. 1 it is seen that the resonance signal of the water protons is found in between the two signals of the THF protons, irrespective of whether the diamagnetic or the paramagnetic solutions are considered. In a mixture of THF with a few percent of H_2O , the protons are found at the same location. From this observation we conclude that in solution the water is no longer coordinated to the paramagnetic Ni(II) ion.

This raises the question of whether THF is coordinated as a substitute for water. The possible coordination of THF instead of water should result in a shift of both THF signals with respect to noncoordinated THF and a change of the distance between the two THF signals. Fig. 1 reveals none of these effects.

The contact shift $(\Delta H)_T$ at various temperatures was obtained from the relationship:

$$(\Delta H)_T = (H_e)_T - (H_d)_T \quad [2]$$

in which H_e equals the experimental chemical shift in herz, with respect to tetramethylsilane (TMS), of a proton group of the paramagnetic compound and H_d the chemical shift – at the same temperature T of the corresponding proton group – in the diamagnetic reference compound.

In order to find the chemical shifts of the corresponding proton group in the diamagnetic and the paramagnetic compounds at the same temperatures, the measured signal positions were plotted as a function of the temperature. From these plots the chemical shift at the desired temperature was obtained by linear interpolation.

Theory

The dependence of the contact shift of nucleus n on temperature is given in equation [1]. The application of this formula to the molecules studied here requires a value of s, the electron spin.

The spin only value is 1 (see the magnetic susceptibility measurements). It results from two unpaired electrons per complexed nickel ion. Substitution of the experimental contact shifts at various temperatures in this equation yields the value of the coupling constant $(A_H)_n$ at the various positions n. In view of a recent criticism of *Kurland* and *McGarvey*⁹ of the applicability of equation [1], we might wonder whether $(\Delta H/H_e)$ is a linear function of $1/T$, as required or not.

From the plots of the experimental data in Figs. 2-5 it is seen that the linear relationship is well followed. Therefore it can be concluded that the deviation from equation [1] for a thermal population of excited states, as given by *Kurland* and *McGarvey*, is small in the cases under study here. A relationship exists between the isotropic hyperfine coupling constant of a proton nucleus at position n, $(A_H)_n$, and unpaired spin density at the adjacent carbon nucleus ρ_c , which depends on the mechanism yielding the delocalization of the unpaired electrons from the metal ion into the ligands². This delocalization depends on the symmetry of the MO-s involved, which

⁸ Varian Catalog, vol. 1, 77, compiled by N.S. Bhacca et al.

⁹ R. J. Kurland and B. R. McGarvey, Journ. Magn. Res. 2, 286 (1970).

in turn depend on the symmetry of the complex. This symmetry is not known. The solid crystals of the complexes contain two water molecules and two ligand molecules per Ni-ion. The Ni in these crystals may be in a six-coordinated structure. Upon dissolving the complex in THF, this coordination probably changes.

Complete removal of the water molecules without changing the geometrical structure of the remaining ligand-metal combination should result in a planar molecule which would be expected to be diamagnetic in accordance with the literature on planar Ni(II)-complexes^{10, 11, 12}.

A configurational rearrangement into a molecule with a tetrahedrally surrounded Ni(II)-ion results in a partially occupied degenerate MO, which accounts for the observed paramagnetism.

We conclude therefore that at least some molecules must be in a tetrahedral configuration, probably during part of the time, as suggested by Eaton et al.² for similar complexes.

The g-value of a tetrahedral Ni complex being isotropic, the pseudo contact distribution to the chemical shift is expected to be small¹³.

According to Prins¹⁴ three different delocalization mechanisms may be distinguished viz. π -1, π -2 and Σ . The first two are indirect processes, the last one is a direct one.

a. In the first order process π -1 the unpaired electrons which are primarily concentrated on the metal ion, are delocalized into the carbon $2p_z$ framework of the ligands and a positive spin density on the carbon atoms results.

This spin density is transferred to the protons via the well-known spin polarization process⁴ and results in $A_H < 0$.

b. The second order process π -2 is immaterial to our case and further discussion of it will be omitted.

The magnitude of the hyperfine splitting constant in π processes is related to the unpaired spin density ρ_c by the McConnell relation

$$A_H = \frac{Q}{2S} \rho_c \quad [3]$$

in which Q is approximately - 25 gauss.

¹⁰ D. M. L. Goodgame and L. M. Venanzi, Journ. Chem. Soc. 616 (1963).

¹¹ R. G. Hayter and F. S. Hummer, Inorg. Chem. 4, 1701 (1965).

¹² D. Forster and D. M. L. Goodgame, J. Chem. Soc. 2791 (1964).

¹³ D. R. Eaton, A. D. Josey, W. D. Phillips and A. E. Benson, J. Chem. Phys. 37, 347 (1962).

¹⁴ R. Prins, *ibid.* 50, 4804 (1969).

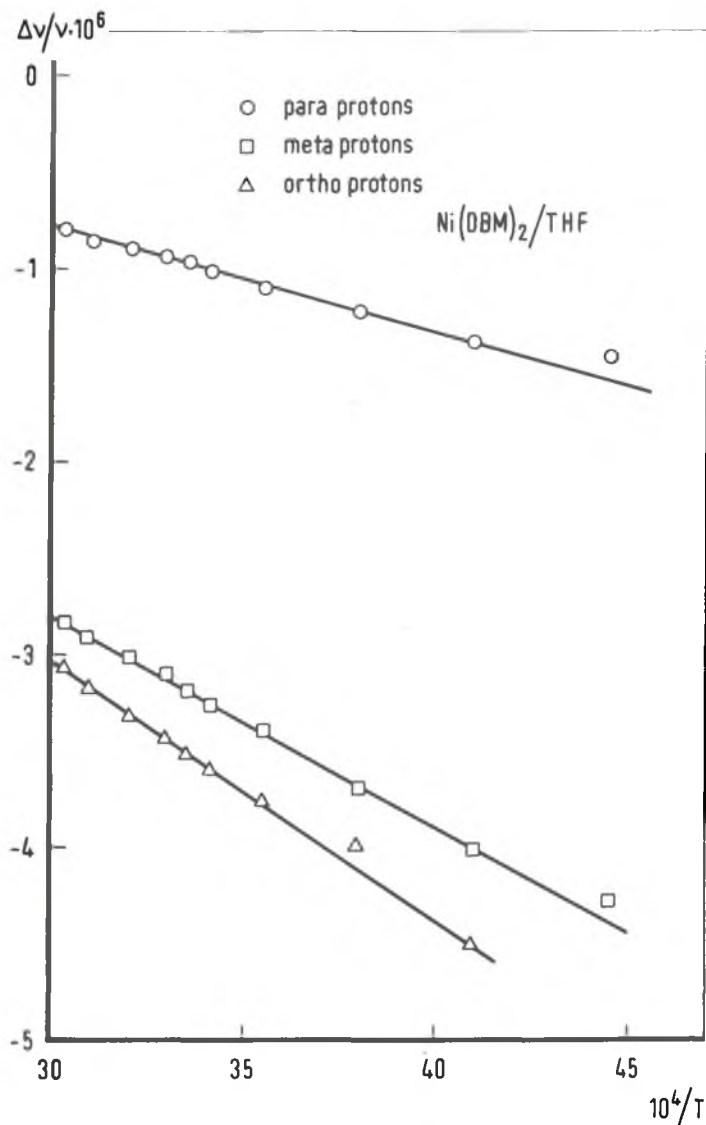


Fig. 2. Contact shifts (p.p.m.) of $\text{Ni}(\text{DBM})_2$ ring protons as a function of T^{-1} .

- c. Σ -delocalization of the unpaired electrons into the σ -framework of the ligands gives a positive spin density ρ_{H} in the hydrogen $1s$ orbital by direct action *via* the relation

$$A_H = \frac{Q^1}{2S} \rho_H$$

where the proportionality constant Q^1 equals + 507 gauss⁷. This process leads to an $A_H > 0$.

In principle, a differentiation among the various delocalization mechanisms follows from measurements of $(A_H)_n$ and of the contact coupling constant of a methyl group substituted at position n , $(A_{CH_3})_n$. The sign of $(A_H)_n$, in combination with the ratio $(A_{CH_3})_n / (A_H)_n$ yields the desired differentiation:

In a pure π -1 process A_H should be < 0 and $A_{CH_3} > 0$, while the ratio A_{CH_3} / A_H equals approximately -1 .

A mere Σ -delocalization process would expectedly yield a value $A_H > 0$ and a value $(A_{CH_3}) > 0$; the value for A_{CH_3} / A_H lies in between 0 and +1. The very low value of the shift of the methyl-protons in $Ni(PMDBM)_2$, renders these criteria inapplicable.

In general, a combination of the various delocalization mechanisms may be expected.

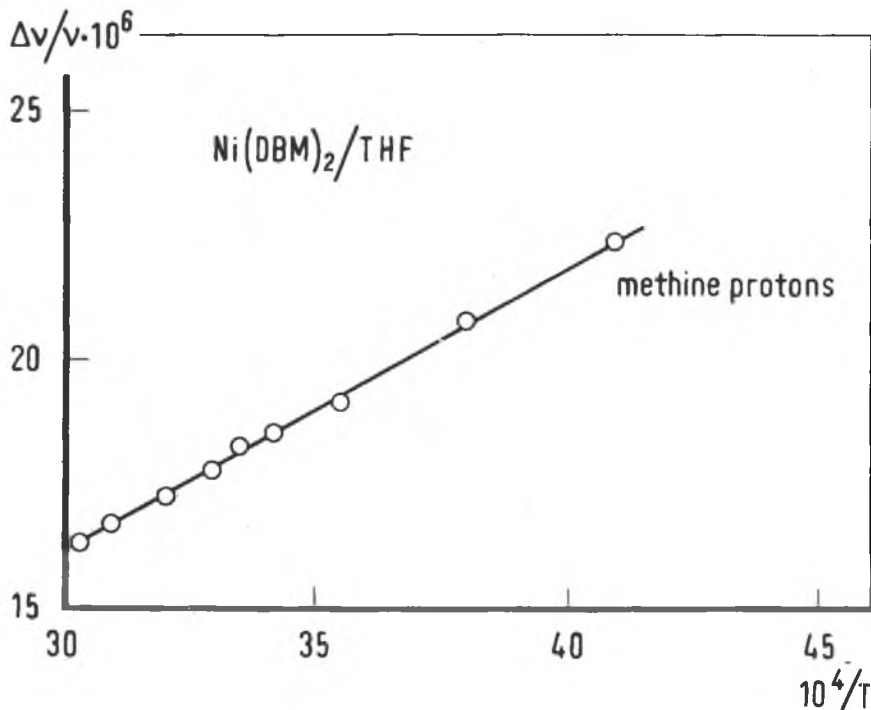


Fig. 3. The contact shift (p.p.m.) of the $Ni(DBM)_2$ methine protons as a function of T^{-1} .

Results and discussion

The value of the hyperfine coupling constants $(A_H)_n$ of the various protons n have been obtained from the slopes of the lines relating the contact shifts $(\Delta H/H_0)_n$ to $(1/T)$ (see equation [1]).

This relationship is illustrated in Fig. 2 for the *para*-, *meta*- and *ortho*-protons of $Ni(DBM)_2$ and in Fig. 3 for the methine protons of this compound. Figs. 4 and 5 show this relationship for the various protons of $Ni(PMDBM)_2$. The figures confirm the linear relation between contact shifts and the inverse temperature. Extrapolation to $(1/T) = 0$ reveals that the lines do not pass through the origin, as suggested by equation [1] (see Table I).

The coupling constants of the various protons are related to the unpaired spin densities at the adjacent carbon atoms and at the hydrogen $1s$ orbitals (equations [3] and [4]). Table III lists the measured A_H -values, the unpaired

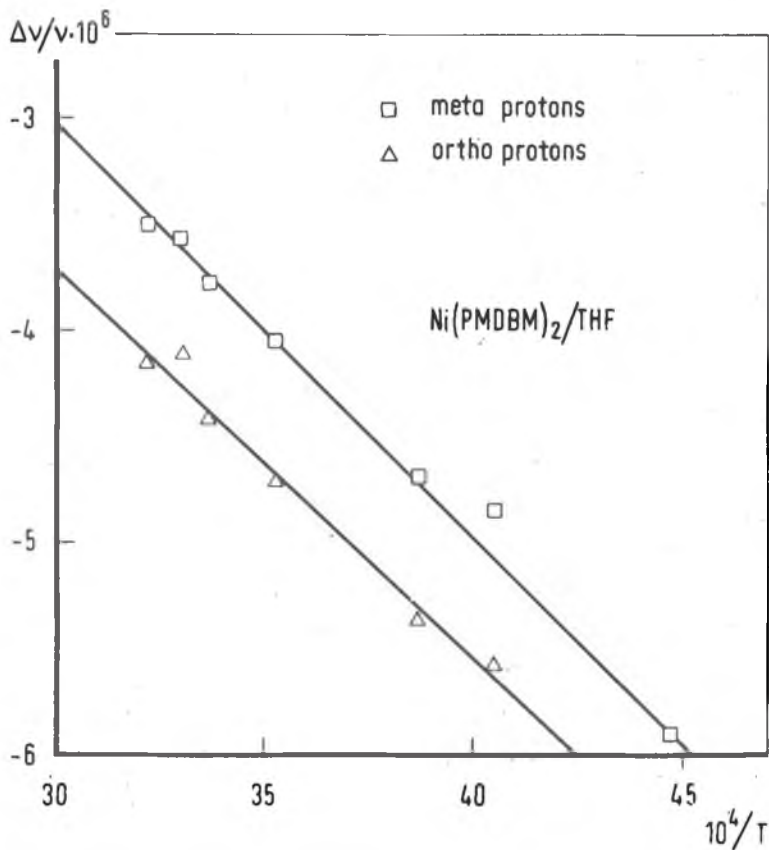


Fig. 4. The contact shift (p.p.m.) of $Ni(PMDBM)_2$ ring protons as a function of T^{-1} .

electron densities c_i^2 calculated by the Hückel method, and the spin densities ρ_i calculated by the McLachlan method on the ligand molecules only.

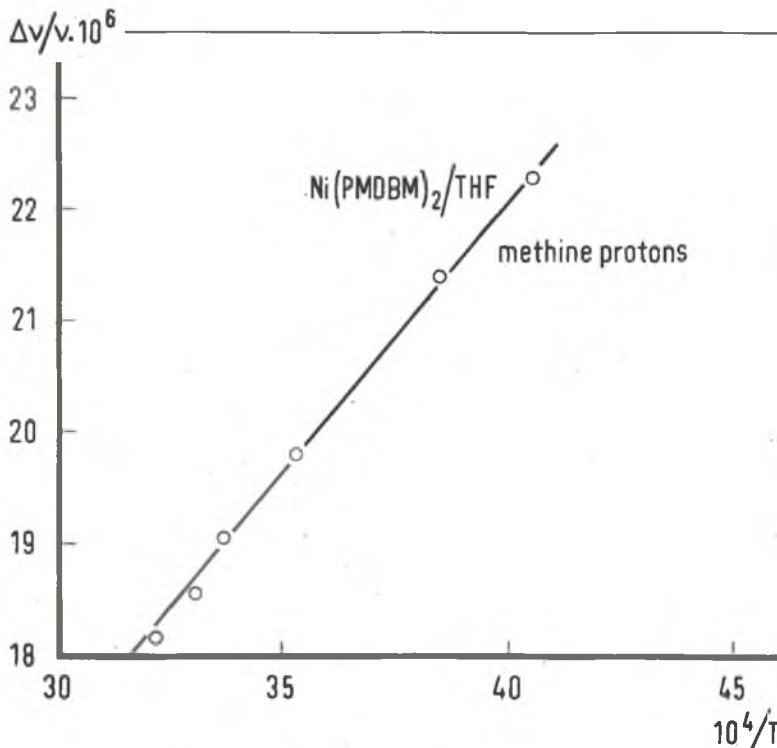


Fig. 5. The contact shift (p.p.m.) of the Ni(PMDBM)₂ methine protons as a function of T^{-1} .

The MO-formation between the metal $3d$ functions and the ligand functions can be visualized as follows*: The paramagnetic molecules in the THF solutions contain Ni(II) surrounded by four oxygen atoms in a tetrahedral-like structure. The S_4 symmetry group describes the symmetry of these molecules. The unpaired electrons are found in the d_{xz} and d_{yz} metal functions which in this symmetry group transform according to the E representation. These metal functions must be combined with combinations of ligand functions with suitable symmetry in order to account for the observed delocalization of unpaired electrons into the ligands.

From Fig. 6 it is seen that the d_{xz} metal function fits into a ligand combination which is of σ -character with respect to ligand A and of π -character with respect to ligand B.

* The authors are indebted to Dr. L. L. van Reyen and Mr. P. J. J. M. van der Put (Laboratory for Physical Chemistry, T.H.-Delft) who suggested this description of MO-formation.

Table I

Proton hyperfine coupling constants of Ni(DBM)₂ and of Ni(PMDBM)₂

Position	Ni(DBM) ₂		Ni(PMDBM) ₂	
	A _H (± 1.5%) (gauss)	(ΔH/H ₀) (p.p.m.) (± 0.04 p.p.m.) 1/T = 0	A _H (± 1.5%) (gauss)	(ΔH/H ₀) (p.p.m.) (± 0.05 p.p.m.) 1/T = 0
<i>para</i> -	+ 0.0073	+ 0.87	—	—
<i>meta</i> -	+ 0.0148	+ 0.56	+ 0.0260	+ 2.86
<i>ortho</i> -	+ 0.0172	+ 0.83	+ 0.0238	- 1.61
methine	- 0.0753	- 0.87	- 0.0644	+ 2.59
<i>para</i> -methyl	—	—	< 0.004	≈ 0

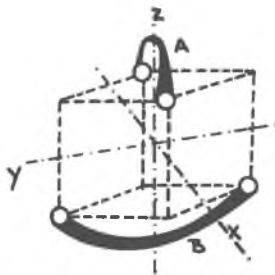


Fig. 6. Schematic representation of the paramagnetic molecules in THF solution. The Ni is located at the origin of the coordinate system; A and B represent the ligand molecules.

The d_{yz} metal function fits into an analogous combination of ligand functions, but now of π -type with respect to the A ligand and of σ -type with respect to the B ligand. The bonding combinations of metal and ligand functions are fully occupied by electrons. The antibonding combinations, belonging to an E representation, contain each an unpaired electron. Part of its spin density is to be found at the ligand nuclei.

The ligand π -functions, which in the S_4 symmetry group transform according to the E representation, are symmetrical with respect to the symmetry plane through the methine carbon atom perpendicular to the plane of the ligand. This corresponds with the symmetry of the HOMO orbitals. For energy reasons the HOMO orbitals are considered to be mainly responsible for the bond formation. MO-formation with the LVMO's of

the ligand can be ruled out as they are anti-symmetrical.

According to the McConnell relation the unpaired electron density in the π -system yields a negative coupling constant for all protons when the Hückel unpaired electron densities are used. Table II demonstrates that at the methine position, where the highest negative coupling constant is expected, it is indeed found.

The σ -type of delocalization raises coupling constants $(A_{H\sigma})_n$, which should be mixed in with the coupling constants obtained from the π -type delocalization according to

$$(A_H)_n = \lambda(A_{H\pi})_n + \mu(A_{H\sigma})_n \quad [5]$$

In principle, the parameters λ and μ could be adjusted to give the best fit with the experimental A_H values provided the $A_{H\pi}$ and $A_{H\sigma}$ values are known. The $A_{H\pi}$ are known indeed (see equation [3] and Table II).

In order to obtain the $A_{H\sigma}$ parameters an extended Hückel calculation should be performed involving all valence electrons of a ligand¹⁵ (84 of DBM and 96 of PMDBM). This type of calculation would put heavy demands on a computer with a very large memory.

Another approach to the problem of subdividing the experimental coupling constant A_H into an $A_{H\sigma}$ and an $A_{H\pi}$ part, is to calculate the $\mu A_{H\sigma}$ terms of seven equations [5] from the experimental coupling constants and the theoretical $A_{H\pi}$ parameters.

Because of two unknown λ parameters and seven $\mu A_{H\sigma}$ terms, the measurements alone do not provide enough equations to solve for all unknowns. However, it is possible to estimate individual contributions of the σ and π delocalization mechanism on the basis of certain assumptions.

The simplifying assumptions are deduced from the results of Cramer and Drago¹⁶, who performed research on complexed pyridine and *para*-methylpyridine. The assumptions are:

1. $\left. \begin{array}{l} \{\rho(\sigma) \text{ PMDBM}/\rho(\sigma) \text{ DBM}\}_{\text{meta}} \\ \{\rho(\sigma) \text{ 4 me py}/\rho(\sigma) \text{ py}\}_{\text{meta}} \end{array} \right\} = 1.03$
2. $\left. \begin{array}{l} \{\rho(\sigma) \text{ PMDBM}/\rho(\sigma) \text{ DBM}\}_{\text{ortho}} \\ \{\rho(\sigma) \text{ 4 me py}/\rho(\sigma) \text{ py}\}_{\text{ortho}} \end{array} \right\} = 1.00$
3. $\lambda_{\text{DBM}}/\lambda_{\text{PMDBM}} = \mu_{\text{DBM}}/\mu_{\text{PMDBM}}$

¹⁵ Russel S. Drago and Harold Peterson, J. Am. Chem. Soc. **89**, 3978 (1967).

¹⁶ Roger E. Cramer and Russel S. Drago, *ibid.* **92**, 66 (1970).

Table II

Comparison of experimental coupling constants A_H with calculated* electron spin distributions

Compound Ni(DBM) ₂		π_z -electron spin distribution in ligand molecule	
Position	A_H (gauss)	HOMO	
		McLachlan ρ	Hückel c^2
1 = <i>para</i> -	+ 0.0073	+ 0.019	+ 0.012
2 = <i>meta</i> -	+ 0.0148	- 0.003	+ 0.001
3 = <i>ortho</i> -	+ 0.0172	+ 0.012	+ 0.009
4 = methine	- 0.0753	+ 1.204	+ 0.530
Compound Ni(PMDBM) ₂		π_z -electron spin distribution in ligand molecule	
Position	A_H (gauss)	HOMO	
		McLachlan ρ	Hückel c^2
<i>para</i> -methyl	0.004	-	-
2 = <i>meta</i> -	+ 0.0260	- 0.046	+ 0.001
3 = <i>ortho</i> -	+ 0.0238	- 0.017	+ 0.009
4 = methine	- 0.0644	+ 1.119	+ 0.0529

The first two assumptions state that the change of the σ -electron distribution caused by *para*-methyl substitution in the phenyl rings of DBM equals that of pyridine, and is 3% or less on the relevant proton positions; the third assumption states that the amount of π and the σ electron delocalization is equally affected by *para*-methyl substitution, as found by *Cramer* on pyridine and substituted pyridine.

The λ parameter represents the fractional amount of unpaired electron spin in the π -bond of the ligand molecule; the μ parameter has a similar meaning with reference to the σ system.

* Parameter values used:

α oxygen = $\alpha + \beta$

β carbon-oxygen = $\beta \sqrt{2}$

α C methyl = $\alpha - 0.10 \beta$

α H₃ methyl = $\alpha - 0.50 \beta$

β C - H₃ = 2.50β

β C - CH₃ = 0.76β

McLachlan constant = 1.00

With coupling constants after Hückel, λ was found to be > 12 , which is an order of magnitude too large. Therefore no meaningful quantitative description was possible in this case.

A quite different result was obtained with coupling constants after McLachlan. Here λ for DBM was found to be 0.013 and λ for PMDBM was 0.012 (see Table III). It is interesting to note that from the equations, a value of 0.93 results for $[\rho(\sigma)\text{PMDBM}]/[\rho(\sigma)\text{DBM}]_{\text{methine}}$ which gives further support to our assumptions.

The final results are listed in Table III. From the last column in this table it follows that the amount of $A_{H\sigma}$ decreases with increasing distance from the paramagnetic Ni(II). Unfortunately, due to the circumstance that no $A_{H\sigma}$ value is known, we are unable to calculate μ and hence only the contribution of the σ mechanism to the delocalization can be evaluated from this data. The results are shown in the last column of Table III.

Table III

$A_{H\sigma}$ -values at various proton positions in DBM and in PMDBM
calculated from experimental coupling constants and
 $A_{H\pi}$ -values according to McLachlan spin distributions

Compound: Ni(DBM)₂

Position	A_H (gauss) experimental	$\lambda A_{H\pi}^*$ (HOMO)	$\mu A_{H\sigma}$
1 = <i>para</i> -	+ 0.0073	- 0.0060	+ 0.0133
2 = <i>meta</i> -	+ 0.0148	+ 0.0010	+ 0.0138
3 = <i>ortho</i> -	+ 0.0172	- 0.0038	+ 0.0210
4 = methine	- 0.0753	- 0.3815	+ 0.3062

Compound: Ni(PMDBM)₂

Position	A_H (gauss) experimental	$\lambda' A_{H\pi}^{**}$ (HOMO)	$\mu' A_{H\sigma}$
2 = <i>meta</i> -	+ 0.0260	+ 0.0132	+ 0.0128
3 = <i>ortho</i> -	+ 0.0238	+ 0.0049	+ 0.0189
4 = methine	- 0.0644	- 0.3205	+ 0.2561

* Amount of spin delocalized into the π -system of one DBM ligand according to $\lambda(A_H)_n = -\lambda\{2S/2S\}\rho_n$; $\lambda = 1.3\%$ of one electron.

** *Idem* for PMDBM: $\lambda' = 1.2\%$ of one electron.

Table I lists the value of the coupling constants and intercepts at $1/T = 0$. It is seen that these intercepts are larger for the protons of $\text{Ni}(\text{PMDBM})_2$ than for those of $\text{Ni}(\text{DBM})_2$. Apart from the methine protons of $\text{Ni}(\text{DBM})_2$ all intercepts are positive. In order to test the significance of the value of these intercepts one should bear in mind that they depend on the choice of the diamagnetic reference compounds.

Comparison of the diamagnetic Zn complex and the Na complex reveals that the values of the chemical shifts of corresponding proton-signals display differences ranging between 0.35 and 0.20 p.p.m. The values of the intercepts of the proton signals of $\text{Ni}(\text{DBM})_2$ are of this same order of magnitude, except perhaps those of the methine protons. The intercepts of $\text{Ni}(\text{PMDBM})_2$ protons are considerably larger. Because of the extrapolation involved the size of these intercepts may not be very meaningful.

Nevertheless we have searched for a possible explanation of a significant high field shift of proton resonance signals. It is mentioned that a negative charge of one electron on a particular carbon atom causes an upfield shift of 10 p.p.m. of the resonance signal of a proton bound to that carbon atom¹⁷. An interpretation of the intercepts of $\text{Ni}(\text{PMDBM})_2$ protons as being caused by a surplus negative charge in the ligands of this Ni-complex in comparison with the ligands of the corresponding Zn-complex requires at least 0.9 electrons per aromatic ring.

This value seems unrealistically high. Qualitatively however it corresponds with the electron donating properties of the methyl group which seems to be more effective in the Ni salt than in the corresponding Zn salt.

Acknowledgement

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¹⁷ *T. Schaefer* and *G. W. Schneider*, Can. Journ. Chem. **41**, 966 (1963).