Carbon-13 Nuclear Magnetic Resonance Spectra of μ-Oxo-bis(disalicylideneiminatoiron) Complexes

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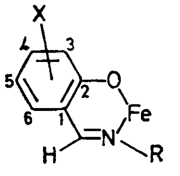
Natural-abundance ^{13}C n.m.r. shifts have been measured for a range of paramagnetic iron salicylideneiminato-complexes of the type $[\{(N\text{-R-}x\text{-Xsal})_2Fe\}_2O]$ (R = Et, Pr^n, or p-MeC_6H_4 and X = H, 3-Me, 4-Me, or 5-Me). In one case the shifts have been determined over the temperature range 320—225 K and carbon hyperfine-coupling and exchange-coupling constants have been obtained. The present results, together with those of a previous ^1H n.m.r. study, are discussed in terms of spin densities. A π-delocalisation mechanism is dominant, though σ paths to certain nuclei are probably involved.

In order to complement a recent study of ^1H isotropic shifts in binuclear oxo-bridged iron(III) complexes,[1] I have carried out ^{13}C n.m.r. studies on the same complexes. The complexes are μ-oxo-bis(disalicylideneiminatoiron) chelates of the type $[\{(N\text{-R-}x\text{-Xsal})_2Fe\}_2O]$, the metal-ligand structure being shown below. It was hoped that ^{13}C n.m.r. studies would give more information on the mechanism of electron delocalisation, and, when carried out over a temperature range, provide a fuller test of the theory previously developed for these exchange-coupled complexes.[2] Further interest derives from the possible application of such studies to ^{13}C n.m.r. shifts in polynuclear iron proteins. The few previous ^{13}C n.m.r. studies on paramagnetic compounds have recently been reviewed by McGarvey and Kurland.[3]



X = H, 3-Me, 4-Me, or 5-Me
R = Et, Pr^n, or p-MeC_6H_4

RESULTS AND DISCUSSION

Diamagnetic ^{13}C n.m.r. shifts were measured for both the free ligands and some of their zinc(II) chelates; the results are given in Table 1 and a typical spectrum is shown in Figure 1. There were appreciable differences in the resonance positions for the free base and zinc(II) chelate, particularly in the case of the carbons contiguous to the donor atoms and in the 4—6 ring carbons. The β-CH_2 and CH_3 of Pr^n and the ring methyl carbon atoms were little affected. These shifts on chelation are much more marked than in the ^1H n.m.r. spectra and, as seen below, can sometimes cause the sign of the isotropic shift to change. The importance of these diamagnetic corrections has also recently been observed in the ^{13}C n.m.r. spectra of lanthanoid shift reagents.[4]

The ^{13}C n.m.r. spectra of the binuclear iron(III) complexes were quite well resolved with half-widths of the lines at room temperature of 20—40 Hz for the sharp lines and *ca.* 200 Hz for the broad lines. The lines retained similar resolution down to −50 °C. The chemical shifts were reproducible to *ca.* ±0·3 p.p.m. A typical spectrum, in the case of $[\{(N\text{-}Pr^n\text{-5-Mesal})_2Fe\}_2O]$, is shown in Figure 2. As in the ^1H n.m.r. study, methyl substitution on the salicylaldehyde ring and R substitution on the N atom were used to try to assign the carbon resonances. Off-resonance decoupling experiments also aided the assignments. In most of the spectra two

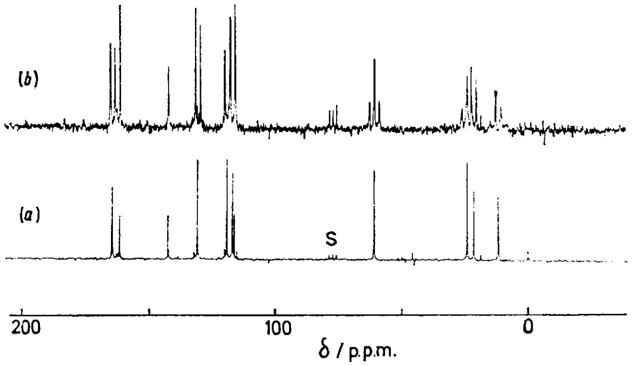


FIGURE 1 ^{13}C N.m.r. spectrum of N-Pr^n-4-Me-Hsal in $CDCl_3$ solution with proton-decoupled (*a*) and off-resonance proton irradiation (*b*) (S = solvent)

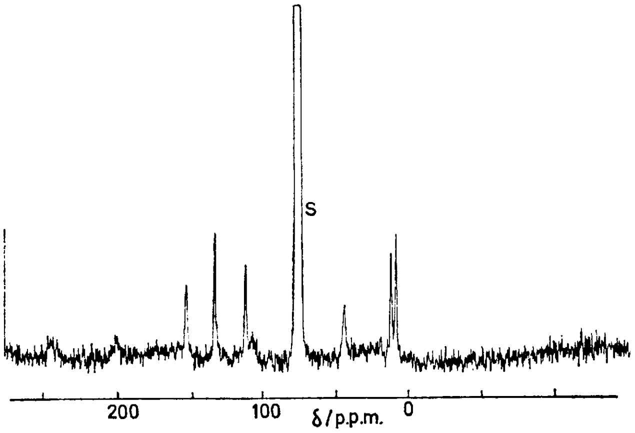


FIGURE 2 Proton-decoupled ^{13}C n.m.r. spectrum of $[\{(N\text{-}Pr^n\text{-5-Mesal})_2Fe\}_2O]$ in $CDCl_3$ solution at 300 K (S = solvent)

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* This work was carried out whilst the author was on study-leave from the Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia.

[1] P. D. W. Boyd and K. S. Murray, *J. Chem. Soc.* (*A*), 1971, 2711.

[2] K. S. Murray, *Co-ordination Chem. Rev.*, 1974, **12**, 1.

[3] B. R. McGarvey and R. J. Kurland, in ' N.M.R. of Paramagnetic Molecules,' eds. G. N. La Mar, W. DeW. Horrocks, and R. H. Holm, Academic Press, 1973.

[4] B. F. G. Johnson, J. Lewis, P. McArdle, and J. R. Norton, *J.C.S. Dalton*, 1974, 1253.

fewer than the total possible number of expected carbon resonances were observed, *e.g.* for [{(*N*-Pr^n-Hsal)$_2$Fe}$_2$O] eight lines were observed compared to a possible 10. It is likely that the CH=N resonance is shifted outside the observed frequency range, the remaining line being shifted off range, or superposition of resonances may occur. A limited number of the carbon atoms have been assigned with certainty. The line positions, together with assignments, are shown in Table 2. The isotropic shifts for ^{13}C and ^{1}H are given in Table 3.

TABLE 1

Diamagnetic ^{13}C n.m.r. chemical shifts [a] (ν_d/ν_0 in p.p.m.) for free ligands and Zn^{II} chelates [CDCl$_3$ solutions measured at *ca.* 300 K, shifts downfield from SiMe$_4$ (ν_0 = 22·62 MHz)]

		Aromatic CH				Quaternary C			R			
Compound	CH=N	4	6	5	3	C–O	C–Me	C–CH=N	CH$_2$	CH$_2$	CH$_3$	Ring CH$_3$
N-Et-Hsal	164·4	132·1	131·4	118·5	117·4	161·5		119·0	53·8		16·3	
N-Pr^n-Hsal	164·8	132·0	131·3	118·4	117·0	161·6		119·0	61·1	24·1	11·6	
N-Pr^n-3-Me-Hsal	165·1	133·2	129·1	118·2		160·0	126·0	118·2	61·4	24·4	11·9	15·0
N-Pr^n-4-Me-Hsal	164·5		131·2	119·5	117·4	161·7	142·7	116·7	61·1	24·2	11·7	21·6
N-Pr^n-5-Me-Hsal	164·7	132·9	131·3		116·8	159·3	127·4	118·6	61·4	24·1	11·7	20·3
[Zn(*N*-Pr^{n}sal)$_2$]	171·8	136·2	135·4	123·7	115·0	171·3		118·5	63·6	24·3	11·8	
[Zn(*N*-Pr^n-4-Mesal)$_2$]	171·2		136·0	123·7	116·7	171·2	146·4	116·3	63·4	24·4	11·8	22·3
[Zn(*N*-Bu^{n}sal)$_2$] [b]	171·7	136·2	135·4	123·7	115·0	171·1		118·5	61·5 33·0	20·5	14·1	

[a] All lines gave expected splittings and intensity changes in ^{1}H off-resonance irradiation. [b] Kindly provided by Dr. H. A. O. Hill.

TABLE 2

^{13}C N.m.r. chemical shifts of [{(*N*-R-Xsal)$_2$Fe}$_2$O] complexes in CDCl$_3$ solution at *ca.* 300 K (p.p.m. downfield from SiMe$_4$)

N-Etsal	*N*-Pr^{n}sal	*N*-Pr^n-4-Mesal	*N*-Pr^n-5-Mesal	*N*-*p*-MeC$_6$H$_4$-5-Mesal	Assignment
245·3	245·8	247·3	245·7	210·7	(w, br)
201·0	200·6	196·3	201·4	183·7	(w, br)
			154·0 [a]	156·1	5-C (q)
				149·5	*p*-MeC$_6$H$_4$
		145·9			C(4) (q)
142·4	143·8 [b]	143·6			5-CH
133·8	135·3		134·3	133·2	4-CH
				120·0	*p*-MeC$_6$H$_4$
113·9	116·1	115·1	113·3	112·3	(6-CH ?)
99·6	109·5	109·3	109·4 [a]		(w, br)
41·3 (?)	45·1 [c]	45·8	45·5 [c]		CH$_2$ (Pr^n)
		32·0			4-CH$_3$
	13·7 [c]	13·2	13·6 [c]	14·3 (*p*-MeC$_6$H$_4$)	CH$_3$(Pr^n)
			10·2 [c]	8·1	5-CH$_3$

[a] Gains intensity in off-resonance ^{1}H irradiation. [b] Doublet in off-resonance ^{1}H irradiation. [c] Broad multiplet in off-resonance ^{1}H irradiation.

TABLE 3

^{13}C [a] and ^{1}H [b] N.m.r. isotropic shifts (p.p.m.) for [{(*N*-R-Xsal)$_2$Fe}$_2$O] complexes at 300 K

		N-Etsal	*N*-Pr^{n}sal	*N*-Pr^n-4-Mesal	*N*-Pr^n-5-Mesal
Carbon					
C(5)					*ca.* −23 (−26·6)
C(4)				+0·5 (−3·2)	
5-CH		−18·7 (−23·9)	−20·1 (−25·4)	−19·9 (−24·1)	
4-CH		+2·2 (−1·7)	+0·9 (−3·3)		+2·0 (−1·4)
5-CH$_3$					+10·0 (+10·1)
4-CH$_3$				−9·7 (−10·4)	
Pr^{n}CH$_3$			−1·9 (−2·1)	−1·4 (−1·5)	*ca.* −1·9 (−1·9)
Hydrogen (ref. 1)					
6-CH		−3·04	−2·88	−2·84	−2·87
5-CH		+4·44	+4·41	+4·59	
4-CH		−5·88	−5·68		−5·58
5-CH$_3$					−5·14
4-CH$_3$				+1·29	
Pr^n-CH$_3$			*ca.* +1·19		*ca.* +1·11
$\Delta\nu$(C)/$\Delta\nu$(H)					
5-CH	obs.	−4·2 (−5·4)	−4·56 (−5·76)	−4·34 (−5·25)	
	calc. [c]		−10·3	−8·8	
4-CH	obs.	−0·37 (+0·29)	−0·15 (+0·58)		−0·36 (+0·25)
	calc.		−12·0		−12·6
Ring CH$_3$	obs.			−7·5 (−8·1)	−2·0 (−2·0)
	calc.			−3·4	−3·0
Pr^n CH$_3$	obs.		−1·6 (−1·76)		−1·71 (−1·71)

[a] Relative to zinc(II) chelate and free ligand. [b] Relative to free ligand. [c] Using equations (6) and (7).

It is worthwhile making some general comments on the spectra. When R = Pr^n and Et the complexes characteristically showed three broad weak bands at *ca.* 245, 200, and 113 p.p.m. It is tempting to assign these to quaternary carbon atoms on intensity arguments but it is rather risky in paramagnetic systems where the ^{13}C relaxation mechanism will probably not be dominated by ^{13}C–^{1}H interactions. In the absence of other ring-substituted derivatives, only 4- and 5-ring carbon atoms could be assigned with certainty and they showed isotropic-shift values of *ca.* +1 and −20 p.p.m. respectively; it is important to note that the shift for C(4) would show a negative sign if the free ligand were used as diamagnetic reference. The relative magnitude of these (and other) carbon isotropic shifts to the contiguous proton shifts are given in Table 3. The carbon and proton shifts showed opposite signs at each ring position. The ring Me in the 5-Me complex showed an upfield shift (shielded) whilst the carbon to which it is attached exhibited a large downfield shift. Conversely the 4-Me carbon atom in the 4-substituted complex showed a downfield shift whilst the ring carbon to which it is attached exhibited a very small upfield shift. The Me carbon in the saturated Pr^n group generally showed a small isotropic shift, which in turn appears to be smaller than the methylene Pr^n shift. The latter has not been assigned with certainty. The ^1H n.m.r. shifts for the Pr^n methylene and methyl groups were also very small and of opposite sign to the carbon shifts.

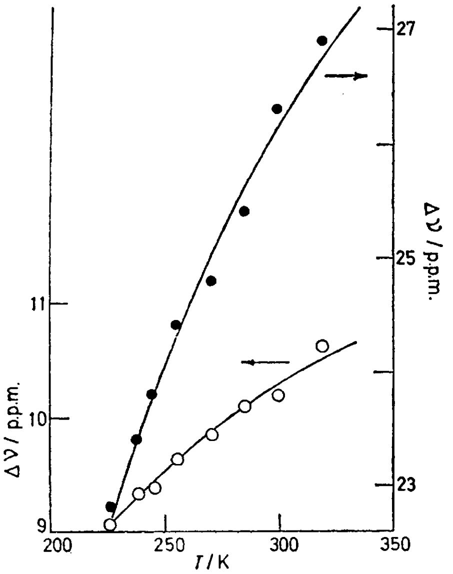

FIGURE 3 Carbon isotropic shifts ($\Delta\nu$) as a function of temperature for [{(*N*-Pr^n-5-Mesal)$_2$Fe}$_2$O]: (——), best-fit calculated from the *J* and *A*(C) parameters in Table 5; (●), C(5); (○), 5-*C*H$_3$

Temperature Dependence of ^{13}C *N.M.R. Shifts in* [{(*N*-Pr^n-5-Mesal)$_2$Fe}$_2$O].—The variable-temperature study was made on this particular complex because of its availability and good solubility in CDCl$_3$. The isotropic shifts over the range 320—226 K for the assigned carbon atoms are given in Table 4 and displayed in Figure 3. It is immediately obvious that large deviations from Curie behaviour are occurring and, for some of the carbon atoms, a decrease in shift with temperature is given in a related manner to that observed for the protons. The decrease in Δν over the 90 K interval was largest for the C(5), 5-Me, and unassigned line at 113 p.p.m., with the decrease for the 5-Me carbon atom being proportionally the same as that for its proton. The Pr^n methyl carbon resonance position was essentially independent of temperature as was the line with chemical shift 45·8 p.p.m.

TABLE 4

Temperature dependence of ^{13}C n.m.r. isotropic shifts [a] in [{(*N*-Pr^n-5-Mesal)$_2$Fe}$_2$O] (ν_0 = 22·63 MHz; $\Delta\nu/\nu_0$ in p.p.m.)

	$\Delta\nu/\nu_0$			
T/K	5-CH$_3$	C(5)	4-CH	CH$_3$(Pr^n)
320	+10·62	−26·9 [b]	+2·3 (−1·0) [c]	−1·60
300	10·19	26·3	2·1 (1·2)	1·70
285	10·10	25·4	2·1 (1·2)	1·62
270	9·84	24·8	2·0 (1·3)	1·75
255	9·64	24·4	2·0 (1·3)	1·62
245	9·38	23·8	1·7 (1·6)	1·68
238	9·32	23·4	1·7 (1·6)	1·88
226	9·05	22·8	1·7 (1·6)	1·95

[a] Relative to zinc(II) chelate; + upfield, − downfield.
[b] Relative to free ligand since chelated position uncertain.
[c] Relative to free ligand.

The theory developed previously[1] to interpret the temperature dependence of the proton shifts involved the interaction of two weakly coupled $S = \frac{5}{2}$ iron(III) centres according to the exchange Hamiltonian $-J\bar{S}_1\bar{S}_2$ where *J* is the singlet–triplet separation between *S′* = 0 and 1 of the spin-state multiplet *S′* = 0—5. The resulting expression for the isotropic contact shift is (1)

$$\frac{\Delta\nu}{\nu_0} = -\frac{Ag\beta\boldsymbol{h}}{g_n\beta_n\boldsymbol{k}T}\cdot F \qquad (1)$$

where $F = [\exp(J/\boldsymbol{k}T) + 5\exp(3J/\boldsymbol{k}T) + 14\exp(6J/\boldsymbol{k}T) + 30\exp(10J/\boldsymbol{k}T) + 55\exp(15J/\boldsymbol{k}T)]/[1 + 3\exp(J/\boldsymbol{k}T) + 5\exp(3J/\boldsymbol{k}T) + 7\exp(6J/\boldsymbol{k}T) + 9\exp(10J/\boldsymbol{k}T) + 11\exp(15J/\boldsymbol{k}T)]$. In this model, *A*, the hyperfine coupling constant (in Hz), is the same for each spin state. The nuclear constants for carbon are $g_C = 1{\cdot}405$ and $\beta_n = 2{\cdot}543 \times 10^{-8}$ cm^{-1} G^{-1}, thus $g\beta\boldsymbol{h}/g_n\beta_n\boldsymbol{k} = 2{\cdot}56 \times 10^{-8}$. The dipolar contributions to the shift from both metal and ligand centres are assumed zero, the lack of magnetic anisotropy confirming the former assumption.[2]

The Δν values for the C(5) and 5-Me carbon atoms gave good computed least-squares fits to this expression and the resulting *J* and *A*(C) values are given in Table 5. The *J* values were of the same order as those obtained from the proton fits, *e.g.* *J*(5-C*H*$_3$) — 244 and *J*(5-*C*H$_3$) — 288 cm^{-1}. The *A*(C) value for the 5-Me carbon atom was opposite in sign to the *A*(H) value and smaller in magnitude. The 4-CH carbon shift was small and decreased very little with temperature, the data giving a fair fit to equation (1) with a concomitant small value of *A*(C) and large value of *J*, the latter being almost twice that obtained from the 4-H results.[4] The behaviour in this particular ring position probably indicates that the delocalisation mechanism is not the same as that operating in the 5-position. The temperature independence of the Pr^n carbon shifts most likely reflects the σ-bonded nature of the group. The Pr^n proton resonances behaved in a similar manner.

Spin Delocalisation.—In principle ^{13}C n.m.r. studies should yield more direct information on the transmission of unpaired spin density than analogous ^1H studies, since spin is transmitted to the hydrogen atoms indirectly *via* the carbon skeleton. ^1H N.m.r. shifts can give information on unpaired π-spin density at contiguous carbon atoms by use of proton hyperfine-coupling constants and McConnell's relations.[5] ^{13}C N.m.r. studies, however, are much more sensitive to spin delocalisation *via* σ paths.[6]

In the present complexes, ^1H n.m.r. studies pointed to a predominant contact mechanism, with π-type alternation of the spin density on ring carbon atoms of the type 3(+), 4(−), 5(+), and 6(−). The magnitude of the spin densities (or shifts) at each position varied little within a range of substituted derivatives. A change in sign of proton shift of a substituting ring methyl gave further support for a π-delocalisation path. The present ^{13}C n.m.r. shifts add significant information to the delocalisation mechanism within the ligand–iron moiety. The discussion essentially follows that outlined by Doddrell and Roberts as applied to $Ni(pd)_2 \cdot 2L$ (pd = pentane-2,4-dionate) and Ni(aminotroponeiminate) systems [6,7] and more generally by La Mar [8a] and Horrocks.[8b] Considering first evidence for spin density being transmitted *via* the π framework, within the salicyl ring $\Delta\nu(\mathit{C}\text{-H})$ is of opposite sign to $\Delta\nu(\text{C-}\mathit{H})$, *i.e.* $\Delta\nu(C)/\Delta\nu(H)$ is always negative (Table 3), and $\Delta\nu(\mathit{C}\text{-H})$ appears to alternate in sign around the ring. In the case of a ring methyl, spin density on the carbon atom arrives from the ring through π–σ polarisation, and $\Delta\nu(\mathit{C}H_3)/\Delta\nu(C\mathit{H}_3) \sim -3$ is predicted theoretically (see below). The negative sign was observed in both the X = 5-Me and 4-Me complexes and a value close to that predicted was given by the 5-Me carbon, in good agreement with a π mechanism. However, the ratio for the 4-Me carbon was about twice that predicted and may imply transmission *via* a σ mechanism to this particular methyl group. In the R = Pr^n complexes the shifts for the Pr^n methyl carbon and hydrogen atoms were of opposite sign and were both small in magnitude. Together with the lack of attenuation in proton shifts along the Pr^n chain,[1] the results are qualitatively in accord with a predominantly π mechanism. This is in contrast to tetrahedral (*N*-alkylaminotroponeiminate)nickel(II) complexes where σ delocalisation is important.[7]

TABLE 5

Hyperfine coupling constants (Hz) and π-spin densities for $[\{(N\text{-Pr}^n\text{-Xsal})_2Fe\}_2O]$ complexes in $CDCl_3$

X		Ring C(4)	Ring C(5)	Ring C(6)	Ring Me
4-Me	A(H) [a]		−215 696	+142 488	−52 046
	ρ_π(C) [b]		+0·0034	−0·0023	−0·0012 (Q 44·6)
	A(C) (calc.) [c,d]	−437 000 [e]	+766 000		+44 000
5-Me	A(H)	+219 066		+152 142	+214 656
	ρ_π(C)	−0·0034		−0·0024	+0·0042 (Q 51·1)
	A(C) (calc.) [d]	−687 000	+650 000		−159 600
	A(C) [f]	−49 600	+363 800		−135 438
	J [g]/cm^{-1}	−416	−300		−288
H	A(H)	+223 038	−217 878	+120 099	
	ρ_π(C)	−0·0035	+0·0035	−0·0019	
	A(C) (calc.) [d]	−437 000	+551 000		

[a] From ref. 1 (corrected). [b] From equations (2) and (3). [c] From equations (4) and (5). [d] Error *ca.* ±500 Hz. [e] Estimated from ρ[C(3)] value of $[\{(salen)Fe\}_2O]$ [salen = *NN'*-ethylenebis(salicylideneiminato)] (G. N. La Mar, G. R. Eaton, R. H. Holm, and F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **95**, 63). [f] Best fit of observed $\Delta\nu/\nu_0$ to equation (1). Error *ca.* ±20 cm^{-1}.

The comments above can be made more quantitative by considering spin-density values. Assuming only a contact contribution to the shift, π-spin densities on the ring carbon atoms, ρ_π(C), have been calculated from the previously determined proton hyperfine constants * by use of the McConnell relation (2). The calculated values

$$A(\mathrm{H})/\mathrm{MHz} = -63\rho_\pi(\mathrm{C}) \qquad (2)$$

are given in Table 5. In the case of ring carbons bonded to a methyl group the appropriate expression is usually (3), but the proportionality constant can vary from

$$A(\mathrm{C}\mathit{H}_3)/\mathrm{MHz} \approx +75\rho_\pi(\mathrm{C}) \qquad (3)$$

position to position. The calculated values in Table 5 employ the Q constants deduced by Holm [9] for $[Ni(N\text{-R-Xsal})_2]$ complexes. From these ρ_π(C) values it is possible to calculate carbon hyperfine-splitting parameters. ^{13}C Hyperfine splitting is a much more complicated problem [10] than is ^1H; McConnell relations do not apply and

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* The published A values should all be multiplied by a constant factor of 2·08; this computational error does not affect the J values. The theoretical expression for $\Delta\nu/\nu_0$ is correct.

[5] H. M. McConnell, *J. Chem. Phys.*, 1958, **28**, 1188.

[6] D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 6839.

[7] D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 4484, 5256.

[8] 'N.M.R. of Paramagnetic Molecules,' eds. G. N. La Mar, W. DeW. Horrocks, and R. H. Holm, Academic Press, 1973, (*a*) ch. 3; (*b*) ch. 4.

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

[10] A. Carrington and A. D. McLachlan, 'Introduction to Magnetic Resonance,' Harper, 1967, ch. 6, p. 93.

spin-polarisation effects between adjacent ring carbon atoms are important. Expression (4) has been worked out by Karplus and Fraenkel [11] for carbon atoms within the π framework. From the present data only a limited number of A(C) values can be calculated and these are also given in Table 5.

$$A(\mathrm{C}_i)/\mathrm{MHz} = 99{\cdot}7\rho_\pi(\mathrm{C}_i) - 39{\cdot}2[\rho_\pi(\mathrm{C}_{i-1}) + \rho_\pi(\mathrm{C}_{i+1})] \tag{4}$$

The hyperfine parameter for the carbon atom of a ring methyl is approximated by equation (5).

$$A(\mathit{C}\mathrm{H}_3)/\mathrm{MHz} \approx -38\rho_\pi(\mathrm{C}) \tag{5}$$

Equations (2)—(5) can be further combined to yield predicted ratios of the carbon and hydrogen contact shifts, where X is generally *ca.* 2, but using different Q values [9] $X = -3{\cdot}4$ (4-Me) and $-3{\cdot}0$ (5-Me).

$$\Delta\nu(\mathit{C}\mathrm{H})/\Delta\nu(\mathrm{C}\mathit{H}) = -6{\cdot}3 + \{2{\cdot}5[\rho_\pi(\mathrm{C}_{i-1}) + \rho_\pi(\mathrm{C}_{i+1})]/\rho_\pi(\mathrm{C})\} \tag{6}$$

$$\Delta\nu(\mathit{C}\mathrm{H}_3)/\Delta\nu(\mathrm{C}\mathit{H}_3) \approx -X \tag{7}$$

Equations (5) and (6) assume that the exchange mechanism for both carbon and hydrogen is identical, *i.e.* the expression for $\Delta\nu/\nu_0$ given in equation (1) is general for both nuclei; thus $\Delta\nu(\mathrm{C})/\Delta\nu(\mathrm{H}) = A(\mathrm{C})g(\mathrm{H})/A(\mathrm{H})g(\mathrm{C})$. The predicted and observed values of these quantities are given in Table 3; those for the 4-CH nuclei immediately stand out by showing a large disagreement.

Perusal of Table 5 shows that the sign of the A(C) (calc.) parameter is opposite to that of A(H) for both ring carbon atoms and ring methyls; A(C) (calc.) is greater in magnitude than A(H) for ring carbons but smaller for ring methyls. In the case of [{(*N*-Pr^n-5-Mesal)$_2$Fe}$_2$O] the best-fit A(C) value for 5-Me is very close to that calculated using equation (5), whilst for C(5) the calculated value is approximately twice that observed. The agreement therefore between the A(C) values deduced from the exchange-coupled model and the π contribution calculated using Karplus–Fraenkel expressions is reasonable for the carbon nuclei at the 5-position; the reverse is true at the 4-position.

In summary, the ^{13}C and ^{1}H n.m.r. data point to spin delocalisation occurring chiefly *via* carbon π orbitals. The transfer of unpaired spin density between metal and ligand will be of d_π–p_π origin, the high-spin iron(III) centres having π and σ orbitals ($t_{2g}{}^3\ e_g{}^2$) available. The discrepancies between calculated and observed hyperfine parameters, particularly at the 4-position, are perhaps indicative of some σ component in the spin densities though they may reflect limitations in the theory. The behaviour of the shifts within the *N*-alkyl moiety seems to indicate spin transfer within its σ system. The existence of mixed σ- and π-delocalisation mechanisms, together with different mechanisms for ^{13}C and ^{1}H shifts within the same molecule, have recently been emphasised for Ni$^{\mathrm{II}}$ complexes.[6,7] Finally, the pattern of shifts and spin densities in the iron–ligand groups of these binuclear complexes leads one to treat them effectively as mononuclear units, although ^{13}C n.m.r. studies on mononuclear [M(*N*-Rsal)$_n$] complexes (M = Ni, Co, V, *etc.*) have yet to be made to confirm such a treatment. The effect, if any, of the oxo-bridge on ligand spin densities might emerge from such studies.

EXPERIMENTAL

The iron(III) complexes were synthesised as before.[12] The free ligands were prepared by heating together equimolar amounts of the aldehyde and the primary amine until water evolution ceased, the *N*-alkyl products remaining as yellow liquids. The pale yellow zinc(II) chelates were prepared by published methods [13] {Found: C, 61·4; H, 6·1; N, 7·3. Calc. for [Zn(*N*-Pr^{n}sal)$_2$]: C, 61·6; H, 6·2; N, 7·2. Found: C, 63·0; H, 6·7; N, 7·1. Calc. for [Zn(*N*-Pr^n-4-Mesal)$_2$]: C, 63·2; H, 6·7; N, 6·7%}.

^{13}C N.m.r. spectra were measured on a Bruker WH 90 instrument (ν_0 = 22·63 MHz) in conjunction with a Nicolet computer. In the case of the iron complexes solutions (2 cm^3) of 0·1M concentration in CDCl$_3$ were employed, the solvent being used also as calibrant. Checks showed that the shift of CDCl$_3$ relative to Me$_4$Si was not affected by the presence of these paramagnetic complexes. Though adequate proton-decoupled spectra were obtained after *ca.* 5 000 pulses, much better resolution was conveniently obtained during all-night accumulation of *ca.* 100 000 pulses. A typical set of instrumental conditions for the iron(III) spectra were: sweep width 11 904 Hz; offset 14 000 Hz, pulse width 20 μs; repetition rate 0·7 s (or autorecur); and number of scans *ca.* 80 000. In the variable-temperature study the Bruker accessory BST 100/700 was employed with liquid nitrogen or acetone–dry-ice as coolant. The usual Teflon plug was not inserted over the solution surface during this study. At each temperature counts of 4 000 were sufficient to obtain workable resolution. The liquid ligands were measured as 50% solutions in CDCl$_3$ whilst the zinc(II) chelates could be obtained as *ca.* 1M solutions. The former required only *ca.* 500 counts for excellent resolution whilst the latter required 1 000. In general, off-resonance proton-decoupled spectra required twice the number of counts as the analogous broad-band decoupled measurement. Storage of information on a disc (Diablo 30) proved a very valuable asset in this kind of detailed (and often lengthy) study.

I thank Professor J. S. Anderson for facilities, Drs. H. A. O. Hill and P. Day for advice and hospitality, and Mrs. E. Richards for her skilled experimental assistance.

[4/2358 *Received, 11th November, 1974*]

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