

15 and 16 elements exert a stabilizing inductive effect upon the benzene π^* orbitals. In the P and As compounds, the π_6^* and σ^* orbitals apparently mix to the extent that no distinct π_6^* resonance is observed.

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Electron Spin Resonance of the *N*-Methylpyrazine Radical: A New Spin-Labeled Ligand

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Abstract: The electron spin resonance spectrum of the *N*-methylpyrazine radical, obtained by dithionite reduction of *N*-methylpyrazinium iodide, is reported. It is a long-lived, air-stable species which can be protonated in methanolic solution. It can also act as a ligand with metal ions and it is suggested that it may prove to be a useful probe for studying the details of metal-ligand bonding. To investigate this possibility the complex between the radical and the pentacyanoferrate(II) moiety has been prepared. The ESR spectrum of this molecule demonstrates that there has been a significant redistribution of spin density on complexation. Molecular orbital calculations show that both σ interaction with the complexing N atom and π interactions involving the metal d orbitals are required to interpret the ESR results. The use of spin-labeled ligands of this type allows a rather direct estimation of the molecular orbital parameters describing metal-ligand bonding. The structure of a second radical species produced during the reduction of the *N*-methylpyrazinium pentacyanoferrate(II) ion is discussed. It is concluded that it is probably the hydridotetracyano(*N*-methylpyrazine)ferrate(II) ion radical.

A variety of metal complexes containing free radical ligands have been reported.¹ Such compounds are of potential utility in elucidating the details of bonding in metal complexes by means of electron spin resonance (ESR) studies. The inverse experiment of bonding a suitable paramagnetic metal to a diamagnetic ligand and investigating the distribution of the small amount of spin delocalized to the ligand by measuring the NMR contact shifts has yielded valuable information on the electronic structures of the ligands involved.² Experiments of this type have, however, provided relatively little quantitative information on the details of metal-ligand bonding. The combination of a paramagnetic ligand with a diamagnetic metal ion is potentially more profitable. In this case the spin distribution in the ligand, measured by ESR, is perturbed by interaction with the metal ion and the details of this perturbation provide information regarding the symmetries and relative energies of the interacting metal orbitals. A free radical ligand which acts as a probe for metal-ligand interactions may be described as a "spin-labeled ligand" by analogy with the variety of spin labels developed as probes for biologically important systems.^{3,4}

A good spin-labeled ligand must satisfy a number of criteria. It should form stable complexes with a variety of metal ions in various ligand environments. These complexes should preferably be inert rather than labile, since rapid ligand exchange can complicate the ESR spectroscopy. The radical itself should be thermally stable at least over a period of several hours if direct synthesis of the paramagnetic complexes is envisaged. The ESR spectra should be of modest complexity. The more coupling parameters available for measurement the greater the potential information but ease of spectral analysis places a limit on the desirable complexity. The spin distribution in the ligand should

be sensitive to interaction with the metal ion but this interaction should not be so strong as to lead to complete, or almost complete, transfer of the odd electron to a metal orbital.

Of the various radical ligands reported in the literature none show all the desirable characteristics of a spin-labeled ligand. The earliest work involved *o*-semiquinone radicals.^{5,6} These do not complex well with the later group metals and tend to be chemically unstable. Semidiones have proved useful labels when attached to cyclopentadienyl ligands⁷ but not when attached to pyridine.⁸ Zelewsky and his collaborators⁹⁻¹¹ have used diimine radicals but air sensitivity limits the variety of complexes. Most of the other ligands reported have used the nitroxide group as a spin label. Combination with pyridine was fairly successful⁸ but the complexes tend to be labile. Helbert et al.¹² have reported the ESR spectra of a series of metal complexes in which the nitroxide label is part of a five-membered heterocyclic ring. These are rather poor ligands and the hyperfine coupling constants (other than those involving the metal itself) do not change much from compound to compound. An attempt to obtain a wider range of more stable complexes by attaching the nitroxide label to an acetylacetonate ligand was not successful.¹³ With *tert*-butyl substituents steric restraints prevented complex formation and with trifluoromethyl substituents the ESR spectra were not sensitive to metal complexation unless the nitroxide was directly coordinated. Basters¹⁴ has reported a very interesting series of aromatic pentacyanocobaltate(III) nitroxides but extension to other metal ions

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
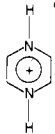
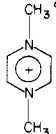
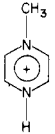



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Table I. ESR of Pyrazine Radicals^a

							
<i>b</i>						Fe(CN) ₅ ³⁻	HFe(CN) ₄ ³⁻
N1	7.15	7.42	8.36	7.14	8.28	8.21	9.68
CH2	2.66	3.15	2.85	3.05	4.58	4.77	4.28
CH3				2.95	1.21	1.02	0.90
N4				7.62	7.00	7.18	6.90
CH ₃			8.30	8.53	7.32	7.18	6.90
NH4		7.96		9.06			
ρ_{N1}	0.264	0.258	0.320	0.247	0.244	0.233	0.330
ρ_{C2}	0.116	0.137	0.124	0.133	0.199	0.207	0.186
ρ_{C3}				0.128	0.0526	0.0443	0.0391
ρ_{N4}				0.277	0.316	0.334	0.324
Q_{CH3}			25.9	34.5	30.0	35.2	20.9
Q_{NH}		30.9		32.7			
<i>g</i>	2.0033			2.0032	2.0034	2.0032	2.0032

^a Estimated errors in coupling constants 0.05 G. The ratios of coupling constants in a given spectrum are more accurate. Thus the ratios of the proton coupling constants in the fifth radical (3.79) is unambiguously different from that in the sixth radical (4.68). ^b Calculated from $a_H = Q\rho_c$ where $Q = -23$ G, $a_N = 19.1\rho_N + \sum 9.1\rho_c$. All hyperfine coupling constants in gauss. ^c Reference 17. ^d Reference 21. ^e Reference 22.

would be synthetically difficult.

In the present paper we report the ESR spectrum of the *N*-methylpyrazine radical and show that it has potential utility as a spin-labeled ligand.

Experimental Section

Preparation of Radicals. *N*-Methylpyrazinium iodide was prepared by the method of Bahner and Norton¹⁵ and used to prepare the pentacyanoferrate(II) derivative following the procedure of Toma and Malin.¹⁶

The *N*-methylpyrazine radical was obtained by reducing *N*-methylpyrazinium iodide with sodium dithionite in methanolic solution. A little crown ether was added to the solution to increase the solubility of the sodium dithionite. Upon analysis of the ESR spectra it became apparent that the radical produced by this procedure was protonated at the N4 position. The corresponding deuterated cation radical was obtained by adding D₂O to the mixture prior to reduction. The neutral radical was obtained by adding a pellet of KOH to the methanolic solution of *N*-methylpyrazinium iodide prior to reduction.

The product obtained from the dithionite reduction of *N*-methylpyrazinium pentacyanoferrate(II) depends critically upon the pH. Neutral or slightly acidic solutions give a product showing a seven-line ESR spectrum at $g = 2.035$. This is assigned to an Fe(I) species. The radical ligand species discussed in the present paper can only be obtained at high pH. Typically a pellet of KOH was dissolved in 2.5 mL of an ca. 0.2 M solution of *N*-methylpyrazinium pentacyanoferrate(II) complex in water, methanol, and methylene chloride (1:1:1) and an excess of sodium dithionite (0.4 g) was added. This procedure leads to a brown solution giving the ESR spectrum assigned below to the complexed *N*-methylpyrazine radical. The same spectrum can be obtained by adding KOH to a solution containing the Fe(I) complex. These solutions do not show the single strong line at $g = 2.0058$ characteristic of the SO₂⁻ radical. This line appears if water is added to the solution but rapidly decays if air is also present. The ESR spectrum that remains after the decay of excess SO₂⁻ in solutions richer in water is that assigned below to the radical hydride complex. This spectrum is again only produced at high pH. The ESR spectra obtained from these radicals are of sufficient complexity and reproducibility that they are excellent "fingerprints" for the identification of the radical species. Thus direct comparison of the free and complexed radical spectra readily demonstrates that they arise from different species even though the changes in coupling constants are quite modest.

A Bruker ER-100D spectrometer was used to obtain the ESR spectra. Spectral simulations were carried out on an Aspect 2000 computer associated with a Bruker WP80 NMR spectrometer.

Results

There have been several studies of the ESR spectra obtained by the reduction of pyrazine¹⁷⁻¹⁹ and of its C-methyl derivatives.²⁰

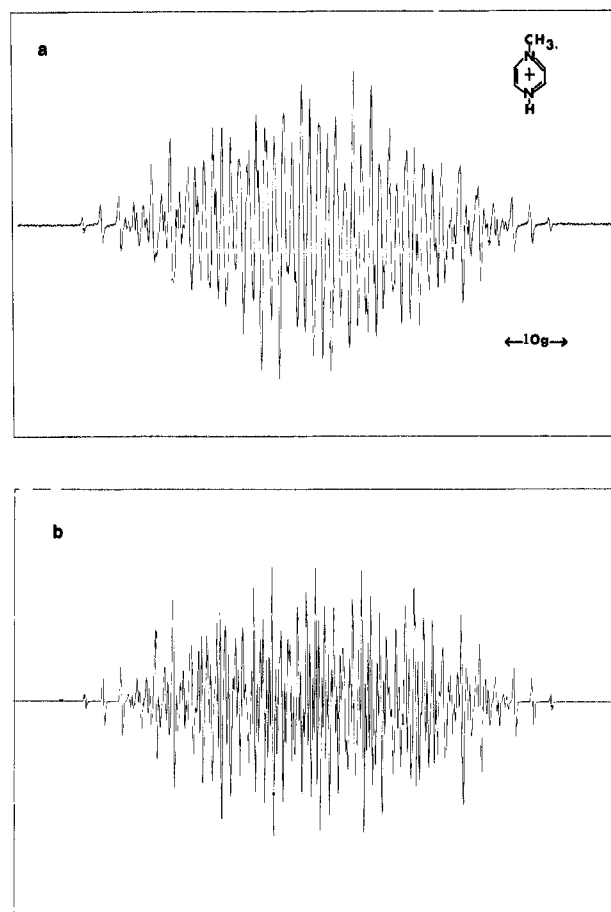


Figure 1. (a) ESR spectrum of the *N*-methylpyrazinium cation radical. (b) Simulation of this spectrum. Gaussian line width 0.45 G.

For pyrazine itself the ESR spectra of both the anion and the diprotonated cation have been reported²¹ and the spectrum of the *N,N'*-dimethylpyrazinium cation radical has also been described.²² The electrochemistry of the reduction of the *N*-methylpyrazinium cation has been discussed²³ but the ESR spectrum of the resulting

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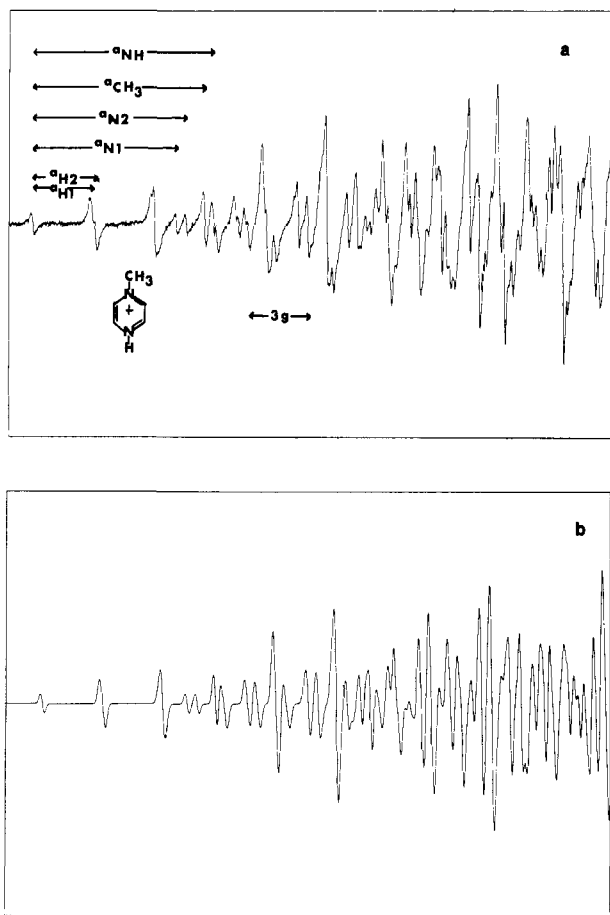


Figure 2. (a) Expansion of wing of Figure 1. (b) Simulation Gaussian line width 0.3 G.

radical does not appear to have been reported. Figure 1a shows the ESR spectrum obtained by dithionite reduction of a methanolic solution of *N*-methylpyrazinium iodide. Splitting by two different nitrogens, two pairs of hydrogens and a methyl group should give 324 lines. The spectrum could not be fitted with this combination of coupling constants. An additional NH coupling is required, giving a total 648 lines. Figure 1b shows a simulation of this spectrum using the hyperfine coupling constants given in Table I and a Gaussian line shape. Figure 2 shows an expanded part of the wing of this spectrum to illustrate the splittings from which the coupling constants were obtained and to demonstrate the quality of the fit. This radical is remarkably stable even in the presence of air. Under these conditions it has a half-life of approximately 5 h which would allow ample time for the preparation of complexes. The presence of an NH coupling was confirmed by carrying out the preparation with the addition of D₂O. A different spectrum was obtained which showed a coupling constant corresponding to that expected for ND. The formation of the protonated radical in methanolic solution is consistent with the report of Castellano et al.²⁴ that the photolysis of pyrazine in methanol yields a protonated radical. The neutral radical was obtained by carrying out the reduction in the presence of excess KOH. The resulting ESR spectrum is shown in Figure 3 together with an appropriate simulation.

The *N*-methylpyrazinium cation participates as a ligand in a variety of stable metal complexes as has been recently reported by Darby and Vallarino.²⁵ Radical complexes can therefore be prepared either by the direct reduction of complexed *N*-methylpyrazinium ligands or by complex formation subsequent to reduction to the radical. We have chosen to study initially the reduction of the well-characterized¹⁶ pentacyanoferrate(II) com-

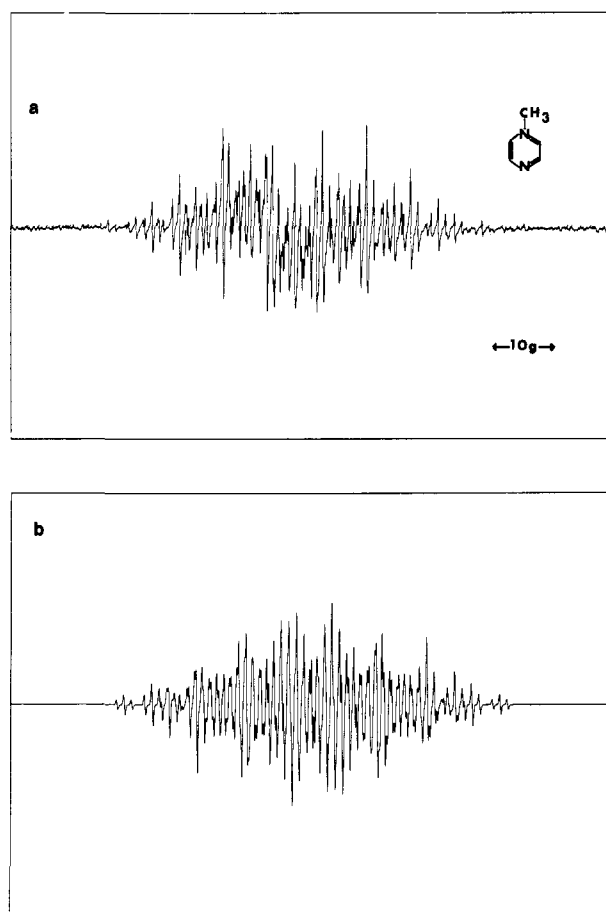


Figure 3. (a) ESR spectrum of the *N*-methylpyrazine radical. (b) Simulation Gaussian line width 0.4 G.

plex containing the *N*-methylpyrazinium ligand. This compound is readily reduced by sodium dithionite. If the reduction is carried out around pH 7 an ESR spectrum ($g = 2.0322$, five or seven lines) corresponding to a square pyramidal Fe(I) complex is obtained. This spectrum is very similar to that described elsewhere²⁶ for the corresponding 4-nitroimidazolate complex and the ESR spectra of this type of Fe(I) complex will be discussed in a subsequent publication. At high pH (around 13) the spectrum of Figure 4a is obtained. The hyperfine coupling constants corresponding to the simulation of Figure 4b are given in table I. This spectrum is different from the spectra of both the neutral and the protonated *N*-methylpyrazine radical. It is therefore reasonable to assume that the *N*-methylpyrazine has remained bonded to the Fe during the reduction and that Figure 4 represents the spectrum of the pentacyanoferrate(II) derivative of the *N*-methylpyrazine radical. This complex resembles the parent radical in being stable for several hours in the presence of air.

If the reduction is carried out in the presence of excess SO₂⁻, as described in the Experimental Section, a rather different spectrum results. This spectrum is shown in Figure 5a. Figure 5b shows an expanded part of the wing of the spectrum and Figure 5c the simulation of this part of the spectrum using the coupling constants of Table I. The assignment of this spectrum will be discussed below. Table I also gives values for the coupling constants of the spectra reported above and for the pyrazine and *N,N'*-dimethylpyrazine radicals described in the literature.

Discussion

The coupling constants for the uncomplexed radicals reported in Table I are consistent with the literature values for the related pyrazine and dimethylpyrazine radicals. Thus the average N hyperfine coupling for the *N*-methylpyrazinium cation radical is 7.38 G which is similar to the N coupling of the corresponding pyrazinium radical (7.42 G) and that of the dimethylpyrazinium radical (8.36 G). Similarly the average proton coupling is 3.00

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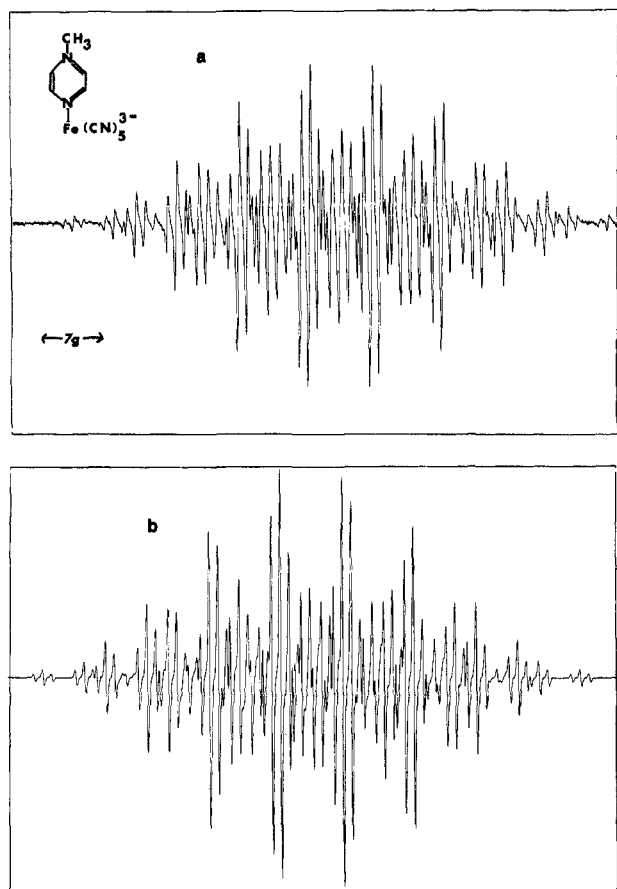


Figure 4. (a) ESR spectrum of the pentacyanoferrate(II) complex of the *N*-methylpyrazine radical. (b) Simulation Gaussian line width 0.4 G.

g compared with values of 3.15 and 2.85 g for the unsubstituted and dimethyl cation radicals, respectively. The neutral radical has slightly lower N and H average coupling constants consistent with the decrease observed on passing from the pyrazine cation radical to the anion radical. These consistencies provide confirmatory evidence for the correctness of the radical assignments.

Complexing of the *N*-methylpyrazine radical to the pentacyanoferrate(II) moiety has substantially modified the hyperfine coupling constants, as is apparent from the data of Table I, but the product is clearly best described as an Fe(II) complex with a radical ligand. Electron counting indicates that the six-coordinated complex is a 19-electron compound and the five-coordinated complex a 17-electron compound. It seems reasonable that the former should revert to $18 + 1$, i.e., an Fe(II) complex with a radical ligand, while the latter remains an Fe(I) complex as demonstrated by its high *g* value and lack of hyperfine coupling from the ligand. Facile loss of a ligand from the 19-electron compound would be anticipated. A reasonable mechanism would be by protonation of the fifth cyanide ligand and an abnormally high pK_a for this ligand would perhaps be expected. The formation of the six-coordinated complex at high pH can be rationalized on this basis. The spectrum of Figure 5 clearly arises from another Fe(II)-radical complex in which one of the cyanides has been replaced by another ligand. The nature of the sixth ligand must remain somewhat speculative but we suggest hydride as a likely possibility. Two consecutive one-electron reduction steps have been demonstrated by stopped-flow spectrophotometry for the dithionite reduction of the pentacyano(4-nitroimidazolato)iron(II) ion²⁶ and the likelihood that the second reduction product is a diamagnetic Fe(II) hydride has been established by the observation of a proton resonance of -20 ppm. A third one-electron reduction would result in an hydridotetracyano(*N*-methylpyrazine)ferrate(II) radical complex. Such a complex would only be formed with

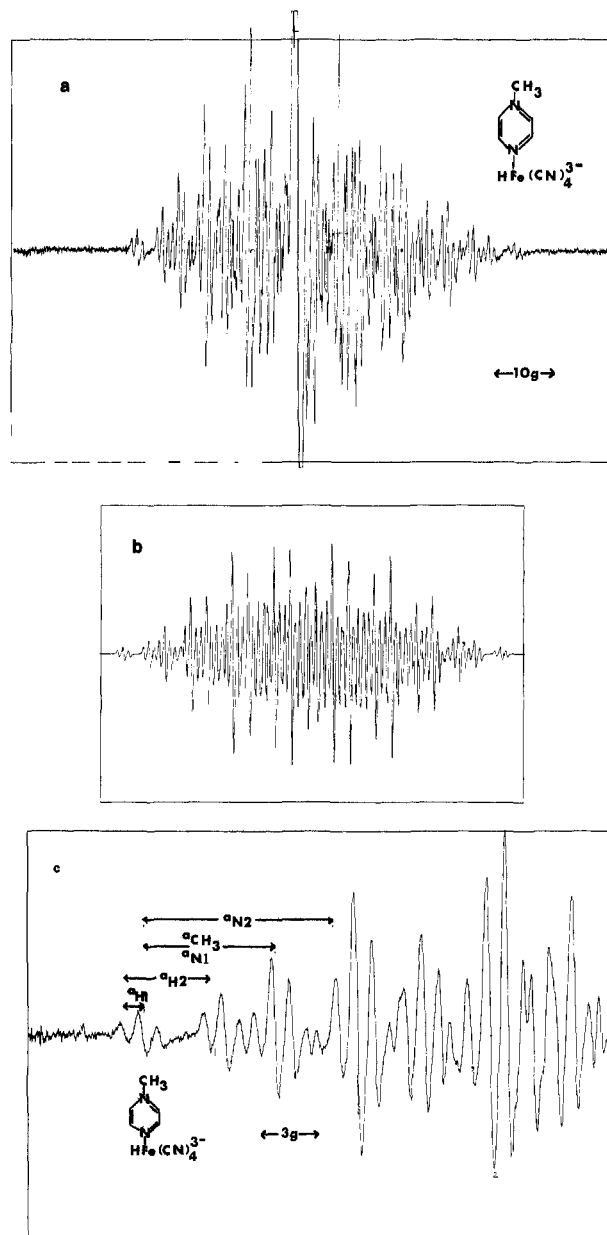


Figure 5. (a) ESR spectrum of the radical assigned to the hydride species. The intense line close to the center of the spectrum is SO_2^- . (b) Simulation Gaussian line width 0.2 G. (c) Wing of spectrum showing analysis.

excess dithionite, at high pH, and in the absence of air, since both the excess dithionite and the Fe(II) hydride are air sensitive. These are the conditions used to obtain the spectrum of Figure 5. We note that no hyperfine coupling to the hydride proton is likely since the spin-containing Fe orbital is orthogonal to the H 1s orbital no matter whether the hydride ligand is cis or trans to the *N*-methylpyrazine radical.

The coupling constants of the complexed radicals change in a manner that can be accounted for with a simple model. Protonation of the neutral radical decreases the difference between the CH coupling constants indicating that the electronic environments of the N atoms have become more similar. Both the proton and the methyl group form predominantly σ bonds with the nitrogens. Attachment to the metal complex increases the difference between the CH couplings. This is consistent with π -bonding interaction between the metal d orbitals and the ligand π orbitals. Without such interaction the radical is even alternant, analogous to the benzene negative ion. With the interaction it is odd alternant analogous to the benzyl radical. In the latter case negative spin densities become possible and large spin density differences between the starred and nonstarred positions are

Table II. Molecular Orbital Calculations^a

α_{N1}	α_{N4}	α_{Fe}	β_{FeN}	ρ_{N1}	ρ_{C2}	ρ_{C3}	ρ_{N4}	ρ_{Fe}
0.4	0.4	0	0	0.372	0.064	0.064	0.372	0
0.4	0.2	0	0	0.367	0.087	0.029	0.400	0
0.6	0.4	0	0	0.338	0.099	0.043	0.377	0
0.6	0.55	0	0	0.343	0.083	0.069	0.353	0
1.0	0.5	0	0	0.271	0.154	0.023	0.375	0
1.0	0.75	0	0	0.280	0.128	0.065	0.334	0
1.0	0.85	0	0	0.284	0.119	0.081	0.316	0
1.0	0.9	0	0	0.286	0.114	0.089	0.307	0
1.3	1.2	0	0	0.246	0.133	0.111	0.266	0
1.3	0.75	0	0	0.230	0.172	0.041	0.344	0
1.3	0.75	-0.1	0.277	0.226	0.185	0.032	0.340	0.001
1.3	0.75	-0.1	0.308	0.226	0.186	0.027	0.346	0.000
1.3	0.75	-0.2	0.171	0.225	0.182	0.036	0.334	0.006
1.3	0.75	-0.3	0.098	0.227	0.179	0.043	0.329	0.000
1.3	0.75	-0.3	0.347	0.226	0.185	0.027	0.349	-0.001
1.3	0.75	-0.5	0.340	0.227	0.182	0.029	0.350	0.0001
1.0	0.75	-0.1	0.265	0.272	0.145	0.052	0.335	-0.004
1.2	0.75	-0.1	0.241	0.240	0.172	0.038	0.337	0.004
1.3	1.3	+0.1	0.3	0.248	0.124	0.109	0.257	0.029
1.3	1.2	-0.1	0.3	0.144	0.104	0.020	0.211	0.398

^aMethod of ref 27. $\lambda = 1.2$ throughout.

predicted. The results for the hydride radical indicate an increased π -bonding interaction compared with the pentacyano radical. This can be rationalized on the basis that a hydride ligand competes less effectively for π donation from the metal than a cyanide ligand.

Molecular Orbital Calculations. Molecular orbital calculations have been carried out to quantify the conclusions of the previous paragraph. Hückel calculations usually prove fairly satisfactory for even-alternant radicals but not for odd-alternant radicals. The extended Hartree-Fock method of McLachlan²⁷ has therefore been used throughout for consistency. Some examples of the results of these calculations are shown in Table II. The results in the top half of this table have been obtained by using a zero resonance integral between the Fe d orbital and the N p orbital and therefore refer to the free radical. Those in the bottom half of the table have included metal orbital parameters. Since the interaction is with a filled metal d orbital for the d^6 complex it is appropriate to select a Coulomb integral for the Fe orbital which is higher in energy than the carbon p orbitals but which is lower in energy than the spin containing π MO. The N Coulomb integrals have been chosen to make the N p orbital lower in energy than the C p orbital by 0.5–1.5 β .

The calculated spin densities of Table II may be compared with the experimental spin densities of Table I. The experimental spin densities have been calculated by assuming $a_H = Q\rho_C$ with $Q = -23$ g for the aromatic H's. For the nitrogens the relationship of Henning²⁸ is assumed: i.e.,

$$a_N = \sum Q_C \rho_C + Q_N \rho_N$$

where the sum is over the neighboring carbons and $Q_C = +9.19$ and $Q_N = +19.19$. This equation allows the N spin densities to be calculated once the neighboring C spin densities are known. The methyl coupling presumably arises from the accepted hyperconjugative mechanism²⁹ and can be related to the spin density on N1 by an equation of the form

$$a_{CH_3} = Q_{CH_3} \rho_{N1}$$

Q values calculated from this equation are included in Table I. Similarly an effective Q value can also be calculated for the NH proton and this information is also included in Table I. The large values of the methyl Q 's, relative to the "normal" +27 G found in aromatic radicals, can be attributed to the positive charge on the quaternary nitrogen. Bolton et al.³⁰ pointed out that the methyl coupling constants of substituted aromatic cations are considerably larger than those of the corresponding anions. They considered

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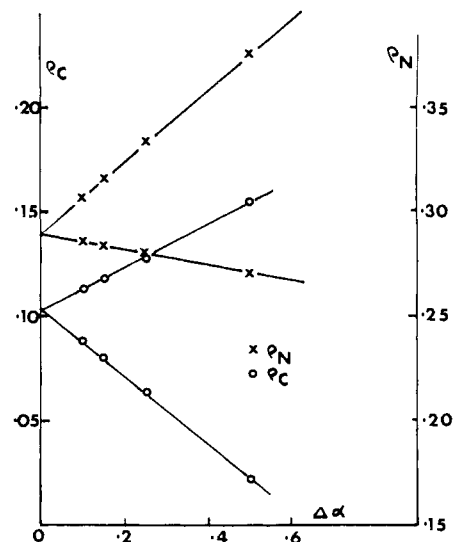


Figure 6. Dependence of carbon (ρ_C) and nitrogen (ρ_N) spin densities on the difference in the nitrogen Coulomb integrals ($\Delta\alpha$). The first nitrogen has $\alpha_N = \alpha + 1.0\beta$ and the second nitrogen $\alpha_N = \alpha + (1 + \Delta\alpha)\beta$.

this to be proof of the hyperconjugative mechanism for methyl coupling since more donation of electrons to a positive center than to a negative center is clearly to be anticipated. Hulme and Symons³¹ correlated the Q_{CH_3} values with the charges on the neighboring carbon. Application of such a relationship to the present data implies that the methyl-bearing N's of all radicals except the hydride complex have a considerable positive charge. The diminished positive charge in the latter case is consistent with the enhanced back-donation from the d orbitals.

Three parameters have been varied to optimize the fit between the observed and calculated spin densities; the N Coulomb integrals, the Fe Coulomb integral, and the Fe–N resonance integral. We find that the results are relatively insensitive to the value of the Fe Coulomb integral and so the discussion will focus on the other two variables. The effect of increasing the difference between the Coulomb integrals of the two nitrogens is illustrated in Figure 6. Increasing this difference reflects the difference between the electron-withdrawing or -donating ability of the group attached to N4 and that of the methyl group attached to N1. As shown in Figure 6 the spin densities on both the C's and the N's become increasingly different with increasing difference in these Coulomb integrals. The results and Table II indicate that the spin densities of the cation free radical can be reasonably fitted with $\alpha_{N1} = \alpha + 1.3\beta$ and $\alpha_{N4} = \alpha + 1.25\beta$. (The assignments N1 and N4 could be reversed in this case.) For the neutral radical $\alpha_{N1} = \alpha + 1.3\beta$ and $\alpha_{N4} = \alpha + 0.75\beta$ is an equally reasonable fit. It is probably not profitable to search for any closer fits since neither the experimental spin densities, depending on the validity of Henning's formula for the N densities, nor the calculated spin densities are entirely reliable. This result is qualitatively reasonable indicating that protonation of the N removes charge to approximately the same extent as quaternization with a methyl group.

Increasing the Fe–N resonance integral has two principal effects. Initially it induces a negative spin density on the Fe. This is analogous to the negative spin density found on a proton attached to a π spin bearing C or N. As β_{Fe-N} is increased the negative spin density reaches a minimum and then increases rapidly to give positive values. Experimentally the total spin density on the complexed radicals is very similar to that on the free radicals, indicating that there is little spin, either positive or negative, on the Fe. This conclusion is consistent with the observed g values which are very close to the free electron value. A Fe–N resonance integral in the range of 0.1–0.3 β is required to obtain zero spin density on the Fe and values in this range have been used in the

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calculations. The second effect on increasing this resonance integral is to increase the difference between the two carbon spin densities without significantly changing the N spin densities. This can be illustrated by the results of Table II. Comparison of the figures of row 6 with those of row 17 shows that inclusion of Fe-N interaction has changed the ratio of the N spin densities from 1.19 to 1.23 and that of the C spin densities from 1.97 to 2.79. The N spin densities therefore provide a measure of the overall electron-withdrawing or -donating ability of the metal moiety and the C spin densities of the π back-bonding. For the pentacyano complex reasonable agreement is obtained with parameters such as those in row 14 of Table II. These parameters indicate that the pentacyanoferrate group is overall less electron withdrawing than a proton. Presumably this is the result of a balance between σ withdrawal and π donation. The fit for the hydride radical is less satisfactory as illustrated by the final two rows of Table II. Qualitatively, since the N spin densities are very similar, the electron-withdrawing ability of the metal group is quite similar to that of a proton or methyl cation and since the C spin densities are very different the π -donating ability is high. These are reasonable electronic properties for this group.

Conclusion

The *N*-methylpyrazine radical shows considerable promise as a useful spin-labeled ligand. Its ease of preparation and air stability suggest that an extensive coordination chemistry may be developed. It will no doubt reduce metal ions in oxidation states

susceptible to easy reduction but there are prospects for forming complexes with a fairly wide variety of metals. The spin density distribution, and hence the ESR spectrum, has been shown to be sensitive to metal complexation. The calculations show that the effects of σ metal-ligand bonding differ from the effects of π metal-ligand bonding. The former is reflected in the change of nitrogen Coulomb integral and the latter in the resonance integral required for the metal-ligand interaction. The ESR spectra obtained are fairly complex but, now that computers are readily available for the rapid simulation of spectra using a range of coupling constants, this is a less serious disadvantage than it was some years ago. Information on metal-ligand bonding can of course be obtained by using a wide variety of spectroscopic techniques but very few allow direct comparison with molecular orbital calculations in the manner made possible by the use of spin-labeled ligands.

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Registry No. Pyrazine radical anion, 34512-20-4; 1,4-dihydropyrazine radical cation, 35862-59-0; 1,4-dihydro-1,4-dimethylpyrazine radical cation, 78147-93-0; 1,4-dihydro-1-methylpyrazine radical cation, 93638-38-1; *N*-methylpyrazine radical, 97613-77-9; (1,4-dihydro-4-methylpyrazin-1-yl)pentacyanoiron(III) free radical, 97570-81-5; (1,4-dihydro-4-methylpyrazin-1-yl)hydridotetracyanoiron(III) free radical, 97570-82-6.

Surfactant and Hydrophobic Derivatives of *trans*-Stilbenes as Probes of Vesicle and Micelle Solubilization Sites. Studies Using Fluorescence and Photoisomerization as Probes¹

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Abstract: An investigation of the fluorescence and photoisomerization of several surfactant *trans*-stilbene derivatives in aqueous micelles and vesicles is reported. The temperature dependence of ϕ_f was determined for several media over the range 5–70 °C. The results present a picture of similar micellar solubilization sites for the *trans*-stilbene chromophore in every case; the micelle is "seen" by the stilbene as a moderately viscous fluid medium with slightly higher values for ϕ_f and slightly reduced $\phi_{t \rightarrow c}$ compared to nonviscous homogeneous solutions. For vesicles considerably more complex behavior is observed. Generally ϕ_f is considerably higher than in solution and $\phi_{t \rightarrow c}$ is much lower. Several, but not all, of the surfactant and hydrophobic stilbenes show a sharp sensitivity in ϕ_f as a function of *T* when passing through *T_c*, the vesicle phase transition temperature. Arrhenius plots for the process competing with fluorescence as a function of temperature show relatively high values for *E_a* and log *A*, above *T_c*, consistent with the high temperature phase providing a microenvironment for the stilbene chromophore like a viscous solvent. Below *T_c*, the variation of ϕ_f gives much lower values for *E_a* and log *A* which suggest escape from the fluorescence state is "order limited" rather than viscosity dominated. These results suggest that the low-temperature phase of vesicles presents an environment for the stilbene chromophore more like an inclusion complex than a fluid medium. The effect of cholesterol addition on DODAC vesicles containing the stilbenes is to increase fluidity below *T_c* and to effectively increase viscosity above *T_c*.

The structure of assemblies formed by self-assembly of surfactant or amphiphilic molecules, as well as the reactivity of solutes incorporated into these assemblies, has been the subject of extensive investigations.³⁻¹⁵ A great deal of work has focused on the

structure and properties of micelles; although considerable controversy has centered around both theoretical and experimental

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