Correspondence

On the Nuclear Magnetic Resonance Spectra of Tris(bipridyl)iron(III)

Sir:

The mechanism of spin delocalization in tris-bipyridyl and -phenanthroline complexes of Fe(III) has been the subject of considerable controversy.[1-4] Criticism has been directed toward our interpretation of this problem which we shall answer here. In this correspondence, we correct an error in our earlier work and demonstrate that it is of minor consequence and in no way affects our original conclusions. We also evaluate several other points which have been raised.

We begin first by repeating our original contentions. Based on the data given in Table VI of ref 2 and by comparison with the data for the previously studied nickel(II) complexes,[5] it was concluded that in these d^5 complexes, the proton shifts are dominated by an "extensive amount of π delocalization". We took issue with the statement[1] that the nickel(II) and iron(III) shifts were similar. Finally, we indicated that *some* upfield σ delocalization is required to account for the ruthenium(III) and osmium(III) shifts. We did not propose a mechanism, and contrary to the literature,[1] there is no way of knowing, on the basis of the information presently available, what the most reasonable source of this upfield σ shift is. This is not to say that exchange polarization[3] may not be the correct origin of all or part of the actual σ shift, but we felt and still feel that sufficient evidence has not been offered to support the rather emphatic claim made. We now focus our attention on the various attacks which have been made on our work in an attempt to discredit our conclusions.

We criticized the earlier study[1] for ignoring the dipolar interaction. Clearly, one cannot ascertain the magnitude of the pseudocontact and contact shift at a single proton and deduce anything about the delocalization mechanism that dominates the proton shifts in the entire molecule. A statement[3] like "except at the 4,7 position similar spin delocalizations are operative in these Co(II) and Ni(II) complexes" is misleading. Different mechanisms are operative but the ligand wave functions so work out that certain protons are insensitive to the differences. If one knew the wave functions, the ratio technique could be used with discretion. When pseudocontact contributions are considered at all protons, as we criticized these authors for failing to do, the contact shift order for the various protons becomes different and the ratios still do not resemble the nickel(II) shifts.

We now come to the dipolar shift and the errors made in its evaluation. An analysis of our epr spectra indicated that one of the g-tensor components is required to be negative, and while this is not a common occurrence, signed g values (actually the product $g_xg_yg_z$) do indeed have physical significance[6-9] in terms of the precession of the magnetic moment vector. There are several documented examples of negative g values which are predicted theoretically. The question arises as to whether it is appropriate to use signed g values in the contact shift equations. The Zeeman energy of a state is of course independent of the sign of the g value and the susceptibility anisotropy, of importance in the dipolar shift equation, is likewise independent of the sign of g, since χ for all paramagnetic molecules is necessarily positive. It is therefore incorrect to use signed g values and our data have been corrected to take this into account. Tables VI–VIII of ref 2 are reproduced here in corrected form as Tables I–III. Errors in overestimation of the dipolar shift ranged from a factor of 1.25 to 1.55 for the iron(III) and ruthenium(III) shifts; the osmium shifts are unaffected. These changes, as we explain below, do not invalidate our previous conclusions. Furthermore, there is ambiguity on what form of the pseudocontact shift equation to use.[2] If the alternate form of the equation is required, the pseudocontact contributions are close to those reported in our initial paper. Since the conclusions we wish to draw are independent of these uncertainties, we have not pursued the matter any further.

TABLE I

PSEUDOCONTACT SHIFTS[a]

	$\Delta\nu_{6,6'}$	$\Delta\nu_{5,5'}$	$\Delta\nu_{4,4'}$	$\Delta\nu_{3,3'}$	$\Delta\nu_{4\text{-}CH_3}$	$\Delta\nu_{5\text{-}CH_3}$
$Fe(bipy)_3(PF_6)_3$	+827	+115	−53	−262	. . .	. . .
$Fe(4,4'\text{-}dmb)_3(PF_6)_3$	+1026	+142	. . .	−324	−48	. . .
$Fe(5,5'\text{-}dmb)_3(PF_6)_3$	+824	. . .	−52	−261	. . .	+91
$Ru(bipy)_3(PF_6)_3$	+925	+111	−83	−339	. . .	. . .
$Os(bipy)_3(PF_6)_3$	+1053	+127	−95	−386	. . .	. . .
	$\Delta\nu_{2,9}$	$\Delta\nu_{3,8}$	$\Delta\nu_{4,7}$	$\Delta\nu_{5,6}$		
$Fe(phen)_3(PF_6)_3$	+1164	+162	−75	−185		
$Ru(phen)_3(PF_6)_3$	+972	+117	−38	−181		
$Os(phen)_3(Pf_6)_3$	+1001	+120	−91	−187		

[a] In hertz at 60 MHz. Four significant figures are reported but as mentioned earlier[2] these are accurate only to ~10%.

TABLE II

FERMI-CONTACT SHIFTS[a,b]

	$\Delta\nu_{6,6'}$	$\Delta\nu_{5,5'}$	$\Delta\nu_{4,4'}$	$\Delta\nu_{3,3'}$	$\Delta\nu_{4\text{-}CH_3}$	$\Delta\nu_{5\text{-}CH_3}$
$Fe(bipy)_3(PF_6)_3$	+2269	+363	+485	+359	. . .	. . .
$Fe(4,4'\text{-}dmb)_3(PF_6)_3$	+2113	+345	. . .	+378	−756	. . .
$Fe(5,5'\text{-}dmb)_3(PF_6)_3$	+2267	. . .	+510	+301	. . .	+18
$Ru(bipy)_3(PF_6)_3$	+1317	−145	+625	−100	. . .	. . .
$Os(bipy)_3(PF_6)_3$	+1019	−29	+111	−140	. . .	. . .
	$\Delta\nu_{2,9}$	$\Delta\nu_{3,8}$	$\Delta\nu_{4,7}$	$\Delta\nu_{5,6}$		
$Fe(phen)_3(PF_6)_3$	+2129	+492	+550	+322		
$Ru(phen)_3(PF_6)_3$	+1591	+1	+697	+151		
$Os(phen)_3(PF_6)_3$	+1155	−27	+180	+126		

[a] In hertz at 60 MHz. [b] Numbers for Ru and Os are to be regarded as approximate due to restrictions mentioned in the text.

We have also been criticized[4] for neglecting the second-order Zeeman (SOZ) contribution to the susceptibility, and to back up this criticism, figures were given

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(1) G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **91**, 3443 (1969).

(2) R. E. DeSimone and R. S. Drago, *ibid.*, **92**, 2343 (1970).

(3) G. N. La Mar and G. R. Van Hecke, *ibid.*, **92**, 3021 (1970).

(4) G. N. La Mar and G. R. Van Hecke, *Inorg. Chem.*, **9**, 1546 (1970).

(5) M. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6946 (1968).

(6) (a) M. H. L. Pryce, *Phys. Rev. Lett.*, **3**, 375 (1959); (b) A. Abragam and B. Bleany, "Electron Paramagnetic Resonance of Transition Ions," Oxford University Press, London, 1970; (c) J. S. Griffith, *Mol. Phys.*, in press.

(7) M. Blume, S. Geschwind, and Y. Yafet, *Phys. Rev.*, **181**, 478 (1969).

(8) R. S. Rubins, *Phys. Rev. B*, **1**, 139 (1970).

(9) C. A. Hutchison and B. Weinstock, *J. Chem. Phys.*, **32**, 56 (1960).

TABLE III

FERMI-CONTACT COUPLING CONSTANTS[a,b]

	$A_{6,6'}$	$A_{5,5'}$	$A_{4,4'}$	$A_{3,3'}$	$A_{4\text{-}CH_3}$	$A_{5\text{-}CH_3}$
$Fe(bipy)_3(PF_6)_3$	−0.3841	−0.0614	−0.0821	−0.0608	...	...
$Fe(4,4'\text{-}dmb)_3(PF_6)_3$	−0.3661	−0.0598	...	−0.0655	+0.1310	...
$Fe(5,5'\text{-}dmb)_3(PF_6)_3$	−0.3869	...	−0.0871	−0.0514	...	−0.0030
$Ru(bipy)_3(PF_6)_3$	−0.2372	+0.0261	−0.1125	+0.0180	...	...
$Os(bipy)_3(PF_6)_3$	−0.2133	+0.0061	−0.0232	+0.0293	...	...
	$A_{2,9}$	$A_{3,8}$	$A_{4,7}$	$A_{5,6}$		
$Fe(phen)_3(PF_6)_3$	−0.3681	−0.0850	−0.0951	−0.0557		
$Ru(phen)_3(PF_6)_3$	−0.2947	−0.0002	−0.1291	−0.2729		
$Os(phen)_3(PF_6)_3$	−0.2516	+0.0059	−0.0392	−0.0274		

[a] In gauss, ±0.01 G at 6,6′ and 2,9 positions and ±0.003 G at other protons. [b] Numbers for Ru and Os are to be regarded with less certainty due to restrictions mentioned in the text.

for $Fe(CN)_6^{3-}$ to show how important SOZ could be and to show how badly our results could be in error. We do not deny that the SOZ can be quite important, but the comparison of $Fe(CN)_6^{3-}$ with $Fe(bipy)_3^{3+}$ and $Fe(phen)_3^{3+}$ turns out to be inappropriate. In $K_3Fe(CN)_6$, the distortion from octahedral symmetry is very small[10] (Figgis, Gerloch, and Mason[10] have in fact attributed this mostly to a second-order perturbation due to the adjacent potassium ions in the lattice) since there is no fixed geometry imposed by a chelate ring. In order to show that it is reasonable to expect $Fe(CN)_6^{3-}$ and $Fe(bipy)_3^{3+}$ to behave quite differently, we have carried out susceptibility anisotropy calculations based on the equations given by Golding.[11] These, except for the omission of the orbital reduction factor, are those previously used by Figgis, *et al.*,[10] and are consistent with the analysis employed in interpreting the esr spectra.[2] We may therefore make use of the parameters derived from both esr and susceptibility measurements. As a further improvement, the experimental g values are used to determine the first-order Zeeman effect of the ground doublet. It should be emphasized that these calculations are not expected to be precise.

Using a value[10] of 0.6 for δ/ξ in $Fe(CN)_6^{3-}$, we calculate $\mu_{\parallel}$ to be 2.17 BM near room temperature and $\mu_{\perp}$ to be 2.46 BM. The experimental values are 2.10 and 2.35 BM, respectively, indicating that the calculation overestimates the SOZ slightly. Noting that, in general, orbital reduction is expected to lower the moment, this overestimation might be due to this effect. If this is indeed the case, $Fe(phen)_3^{3+}$ should yield better values of μ_{calcd} since[2] $k = 1.0$. We find, however, that single-crystal susceptibility data are not available, and we must resort to the less desirable alternative of comparison with the powder susceptibility data. Using δ/ξ from the esr experiment, we find that $\mu_{\parallel\text{calcd}} = 1.58$ BM and $\mu_{\perp\text{calcd}} = 2.54$ BM, giving an average μ_{calcd} of 2.28 BM compared with μ_{exptl} of 3.27 BM.[12] This is about the same discrepancy as we find for $Fe(CN)_6^{3-}$. Using the calculated values of $\mu_{\parallel}$ and $\mu_{\perp}$ to obtain the dipolar shift, we find that the use of the g values results in an overestimation of the shift by about 15%, quite different from the 200% overestimation in $Fe(CN)_6^{3-}$. Repeating the same analysis for $Fe(bipy)_3^{3+}$, we find that the calculated moment is a bit lower than for $Fe(phen)_3^{3+}$ and suspect that the error in the calculation is a bit larger. Remember here that difficulty was encountered by Figgis in fitting the susceptibility of this compound to any theoretical curve with $k \cong 1.0$, and that esr indicates $k \cong 1.07$. With the calculated values of μ, we estimate the dipolar shift to be about 10% larger than that calculated from g values. This result is unlikely, but since the axial field is stronger in the bipyridine complex than in the phenanthroline analog, it seems reasonable to say that the overestimation of the dipolar shift is somewhat less, probably between 0 and 15%, again quite different from that for the ferricyanide. We can conclude on the basis of this admittedly rough calculation that the SOZ contribution to the susceptibility is not of such importance as to cause gross errors in this system but is more reasonably no more significant than any of the other errors and approximations originally described[2] as inherent in this work. Thus, we have chosen not to incorporate this uncertain refinement into Tables I–III.

Before proceeding to discuss the effects of these alternate data on our interpretations, one last point needs to be made. After much unnecessary confusion regarding the nature of the ground state of these d^5 complexes, we must return to the assignment made in our original paper; *i.e.*, the orbitally degenerate ground doublet arising from the trigonal field perturbation lies lower in energy than the singlet giving rise, for d^5 systems, to a $^2A_2$ ground *term*.[13] This assignment is consistent with recent Mössbauer studies[14] in which the sign of the principal component of the electric field gradient tensor, V_{zz}, is measured in the presence of a large external magnetic field. The original susceptibility studies of Figgis[15] are not really unambiguous, and it is not made especially clear what the results mean. The same ground state is arrived at by La Mar and Van Hecke[3] by a method relying on the temperature dependence of the contact-shifted proton resonances. Their method of analysis, however, which was intended to rationalize their findings, contains the following serious pitfall. The neglect of spin–orbit coupling and its effects on the energy levels cannot be justified since, along with the trigonal field, it *completely* removes the degeneracy of the d orbitals before a further rhombic distortion is added. The simple picture of Figure 4 in ref 3 is not valid since the splitting between d^1 and d^2 is likely to be quite large (depending on λ, of course) even *without* a small rhombic distortion, and the changing populations, if indeed they do change

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(10) B. N. Figgis, M. Gerloch, and R. Mason, *Proc. Roy. Soc., Ser. A*, **309**, 91 (1969).

(11) R. M. Golding, "Applied Wave Mechanics," Van Nostrand, Princeton, N. J., 1969, p 244–252.

(12) This laboratory. Other values have ranged from 2.36 to 2.40 BM.

(13) The portion of the errata in *J. Amer. Chem. Soc.*, **92**, 5291 (1970), concerning this point should be disregarded.

(14) W. M. Reiff, *Chem. Phys. Lett.*, **8**, 297 (1971).

(15) B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198 (1961).

significantly (in $Fe(bipy)_3^{3+}$, the lowest level is 99% populated at room temperature), *could* behave almost identically, with or without the slight reduction in symmetry which the authors claim is so important. Furthermore, in view of the complications which have been discussed[16] in connection with nonzero intercepts, whereby many effects cause the magnitude of the intercept to be different for different protons on the same ligand, a variation in the "apparent spin distribution" with temperature cannot *reliably* be used to infer *anything* about the ground state unless the complications described above can be shown to be insignificant compared to the deviations observed for the nonzero intercepts.

Returning now to a reinterpretation of the contact shift data, let us first consider the problem of deciding, in a delocalization consisting of σ, π, and dipolar contributions, which, if any, is dominant. It is clear that evidence for both σ and π delocalization can be found, and it is also apparent that several orbitals are likely to be involved, producing shifts which may cancel or add to give a pattern which can get quite complicated and difficult to unravel. For pyridine type ring systems, σ shifts (toward Ni(II)) are found to decrease unchanged in sign as one moves away from the source of unpaired spin. Shifts from π delocalization are not so easily classified as to behavior; we may find π shifts which alternate around an aromatic ring as the standard picture has it, but this is not a requirement. Low-energy π orbitals may or may not have nodes in qualitatively predictable places or they may have no nodes at all. Thus, it is somewhat more difficult to eliminate a π-delocalization than a σ-delocalization mechanism, simply because of the wide variety of behavior exhibited by π orbitals. The presence of alternating signs indicates the presence of π delocalization, but its absence does not disprove its presence. Similarly, if both σ and π effects are operative, methyl groups do not necessarily have to shift opposite in sign to the ring proton they replace. They are often found to shift opposite to the π contribution to the shift at the ring proton. Our criteria for σ or π delocalization must be very carefully examined, and we must not fall into the trap of expecting every case to be described by a few simple rules.

A look at Table II shows that for $Fe(bipy)_3^{3+}$ both the 3- and 5-proton shifts are smaller than the 4-proton shift by about 30%. The 4-proton shift remains virtually unchanged, as does the 4-CH_3 shift, but the 6-proton shift is considerably further upfield. The 5-CH_3 shift now becomes +18 Hz, or essentially zero within experimental error. Making the comparison to nickel(II), once again we find that the Fe(III):Ni(II) shift ratios are as follows, with the iron(III) shifts normalized to 1: $H_{6,6'}$, -1.56; $H_{5,5'}$, -2.92; $H_{4,4'}$, -0.34; $H_{3,3'}$, -4.08. Clearly, the situation is not much changed and no resemblance to the nickel(II) shifts, which are accepted as being dominated by σ delocalization, is yet evident.

We are forced to conclude once again that there appears to be extensive π delocalization in iron(III) which we have no reason to believe is manifested only at the 4-H and 4-CH_3 protons as contended.[5] As mentioned previously,[2] an upfield σ shift could reverse a downfield π shift at the 3 and 5 positions. Furthermore, as mentioned above, the π orbitals involved may indeed have no nodes and give rise to upfield shifts at *all* positions. The large shift at the 4 proton should not be dismissed as anomalous or "secondary π-spin density."[1] Clearly, if one were to look for significant π delocalization, this would be the place to look. Significantly, the nickel(II) shifts at this position relative to the other positions are much smaller. The small upfield shift at 5-CH_3 is too small (zero within experimental error) to be significant, and the directions of the π shifts expected here are unknown until one can ascertain if there are nodes at this position.[17]

The Fermi-contact contribution to the shift in the ruthenium complexes displays no significant changes from those reported previously by us, the required corrections being even less than in the iron complexes; the osmium shifts are completely unaffected.

Summarizing our conclusions, then, it still appears to us that, after correcting for the dipolar shifts, *extensive π delocalization is suggested by comparison with the nickel(II) shifts*, the σ mechanism is not dominant, and π delocalization far outweighs σ delocalization for a general interpretation of the proton shifts in these d^5 complexes. We emphasize that this cannot be "proven" until the spin densities can be confidently fit to a complete molecular orbital calculation, but, at the present time, all available evidence points toward direct π delocalization as opposed to an indirect σ delocalization as the dominant mechanism influencing the proton shifts.

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[16] W. D. Perry and R. S. Drago, *J. Amer. Chem. Soc.*, **93**, 2183 (1971).

[17] Note Added in Proof—Recently, W. D. Horrocks, Jr., and D. L. Johnston [*Inorg. Chem.*, **10**, 1835 (1971)] criticized the use of a change in the sign of the spin density at the proton when a CH_3 group is substituted for a proton as being diagnostic of a π system contribution to the contact shift of pyridine. They carried out INDO calculations on a simulated pyridine σ radical and found negative spin density on the methyl group. We understand that Horrocks and Johnston failed to factor out the spin polarization of the π system in the σ radical in their INDO calculation. When this is done, it is found that spin in the σ framework does not place significant spin density on the methyl protons negating their criticism of one of our earlier papers [R. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 66 (1970)] and permitting us to use this criterion here as evidence for a π contribution to the observed shifts.