when the last of the $Sb_2F_{11}^-$ salt has decomposed. The conversion of 5.55 mmol of $O_2Sb_2F_{11}$ to 5.54 mmol of O_2SbF_6 required 282 hr at 110°. $O_2Sb_2F_{11}$ may be converted to O_2SbF_6 more rapidly under vacuum at higher temperatures, but the yield is lower; *e.g.*, at 160° the conversion of 0.76 mmol of $O_2Sb_2F_{11}$ to 0.49 mmol of O_2SbF_6 was complete in only 3 hr the loss of material being due to thermal decomposition. X-Ray powder photography and Raman spectroscopy revealed that removal of SbF_5 from $O_2^+Sb_2F_{11}^-$ was associated with the appearance of $O_2^+SbF_6^-$. No phases other than $O_2^+SbF_6^-$ and $O_2^+Sb_2F_{11}^-$ were indicated.

$O_2Sb_2F_{11}$ was also prepared from O_2SbF_6. The 1:1 salt (1.75 mmol) was placed in a Pyrex tube with excess SbF_5 (2–3 ml), under 300 mm of nitrogen pressure. The tube was brought to 125° and shaken. A clear solution was not obtained, but care was taken to break up the clumps of solid by agitating the mixture to a white slurry. The mixture was cooled to room temperature before unreacted SbF_5 was removed under vacuum. The white solid which remained was shown by X-ray and Raman spectra to be $O_2Sb_2F_{11}$ and the weight corresponded to 1.61 mmol.

The preparative technique for X-ray powder diffraction and Raman samples has been previously described, as has the equipment used.[12] Long exposure times were required to obtain a suitable powder pattern for $O_2^+Sb_2F_{11}^-$, but the 26 lines reported in Table II unambiguously fingerprint that compound. The Raman spectra have been intensity corrected for nonlinear sensitivity of the phototube. For the antimony salts the exciting line was the 5145-Å Ar$^+$ line and for the deep red platinum salt the 6741-Å Kr$^+$ line.

Infrared spectra from 4000 to 400 cm^{-1} were recorded on a Perkin-Elmer 237 Infracord spectrophotometer. The powdered solids were pressed between AgCl windows in an all Kel-F cell. O_2SbF_6 shows only one broad band in the region examined, at 660–670 cm^{-1}, characteristic of the ν_3 mode of the SbF_6^- ion. $O_2Sb_2F_{11}$ shows three bands centered at 677, 652, and 470 cm^{-1}.

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Registry No. $O_2^+Sb_2F_{11}^-$, 12592-38-0; $O_2^+SbF_6^-$, 12361-66-9; SbF_5, 7783-70-2; F_2, 7782-41-4; O_2, 7782-44-7.

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Proton Magnetic Resonance Spectra of Nickel(II)- and Cobalt(II)-1,8-Naphthyridine Complexes. A Comparison among the Contact Shift Patterns of Heterocyclic Nitrogen Ligands

Sir:

The enthusiasm of researchers in the proton contact shift field has recently attenuated owing to the lack of a simple model correlating the observed shifts to the nature of the coordinative bond in metal complexes. Theoretical models of increasing sophistication have been proposed[1-5] and laborious calculations have been performed which gained in some cases partial success[4-6] but never found general applicability. In many istances however these partial models have been the origin of lively controversies.[4-8]

The numerous investigations on nickel(II) and cobalt(II) complexes with nitrogen-containing heterocyclic ligands are typical in this connection. First, Happe and Ward[9] suggested that the spin-delocalization mechanism in pyridine complexes occurred *via* σ bonds; Holm, Everett, and Horrocks[10] proposed that also some π ligand orbitals were involved but they were unsuccessful in matching the observed contact shifts through an extended Huckel molecular orbital treatment of the pyridine anion. By mixing the two σ and π mechanisms Cramer and Drago[8] reproduced the pattern of the shifts for para-substituted pyridine ligands but failed to do it for pyridine. Finally INDO calculations reproduced the observed values but pyridine had to be treated either as a phenyl radical or as a mixture of cation and anion.[4,5]

The recent report on nickel(II) and cobalt(II) complexes with 1,8-naphthyridine (napy)[11] stimulated us to determine the isotropic shift pattern onto this ligand for the following reasons: (i) the complexes are reported to be octacoordinated with an idealized D_{2d} symmetry; (ii) the ligand is structurally similar to pyridine (py), dipyridine (dipy), and phenantroline (phen) and a comparison of the contact shifts among all these ligands may provide useful information on the spin-delocalization mechanisms.

The pmr traces of the $[M(napy)_4](ClO_4)_2$ complexes (M = Ni, Co) are reported in Figure 1 together with the assignment proposed on the basis of line width, the analogy with the spectra of pyridine complexes, and comparison with the spectra of 4-methyl-1,8-naphthyridine. By cooling the solutions the line width drastically increases indicating that there is an interconversion among different species whose rate becomes of the same order of magnitude of the nmr resonance[12] at low temperature. Molecular weight measurements on 10^{-2} *M* solutions of the nickel complex in nitromethane gave an association degree $\bar{n} = 0.36$.[13] In order to evaluate this figure, molecular weight measurements were performed on solutions containing $[Ni(dipy)_3](ClO_4)_2$ (1:2 electrolyte) and $[Ni(dipy)_3](ClO_4)_2$ with dipy added in 1:1 molar ratio. The $\bar{n}$ values obtained are 0.40 and 0.30, respectively. These data suggest that in the case of the napy complexes the following dissociation equilibrium takes place

$$[M(napy)_4]^{2+} \rightleftharpoons [M(napy)_3]^{2+} + napy$$

This equilibrium may be responsible for the observed equivalence of the two rings of napy, while two signals for each ring position would be expected on the basis of the dodecahedral structure of the complexes.[14]

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[13] An experimental molecular weight of 822 has been reported[11] for the $[Cd(napy)_4](ClO_4)_2$ complex, which corresponds to $\bar{n} = 0.33$.

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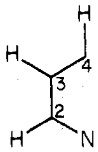
Table I. Proton Contact Shift Ratios for Nickel(II) and Cobalt(II) Complexes of Pyridine, Dipyridine, Phenantroline, and Naphthyridine

M	Proton	$M(py)_2X_2$[d,e]	$M(py)_6$[f]	$M(py)_4X_2$[g]	$M(acac)py_2$[h,i]	$M(bipy)_3$[j,k]	$M(phen)_3$[l,m]	$M(napy)_4$
Ni	2-H	1.00[a]	1.00[a]	1.00[a]	1.00[a]	1.00[a]	1.00[a]	1.00[a]
	3-H	0.30	0.37	0.37	0.29	0.30	0.29	0.38
	4-H	0.07	0.12	0.08	0.08	0.05	0.07	0.19
Co	2-H	1.00[b]			1.00[b]	1.00[b]	1.00[b]	1.00[c]
	3-H	0.25			0.32	0.44	0.48	0.35
	4-H	0.02			0.09	0.09	0.08	0.11

[a] The isotropic shifts are assumed to be essentially contact in origin. [b] Contact shift ratios were estimated through the ratio method [W. D. Horrocks, Jr., *Inorg. Chem.*, 9, 690 (1970)]. [c] These are the isotropic shift ratios; they are presumably close to the contact shift ratios (see text). [d] Reference 10. [e] B. D. Wayland and R. S. Drago, *J. Amer. Chem., Soc.*, 88, 4597 (1966). [f] Reference 8. [g] D. Forster, *Inorg. Chim. Acta*, 5, 465 (1971). [h] Reference 9. [i] R. W. Kluiber and W. D. Horrocks, Jr., *Inorg. Chem.*, 6, 166 (1967). [j] Reference 7. [k] W. D. Horrocks, Jr., *Inorg. Chem.*, 9, 690 (1970). [l] I. Bertini and L. J. Wilson, *J. Chem. Soc. A*, 489 (1971). [m] G. N. La Mar and G. R. Van Hecke, *Inorg. Chem.*, 9, 1546 (1970).

Under ligand excess conditions the isotropic shifts depend linearly on the metal to ligand ratio. This may be accounted for by the similar pattern of the isotropic shifts for the two $[M(napy)_4]^{2+}$ and $[M(napy)_3]^{2+}$ species (*vide infra*). Under these conditions significant signal broadening occurs.

If the contact shift patterns observed for both Ni- and Co-napy complexes are compared to those of dipy, phen, and py complexes for the common moiety



it must be admitted that such patterns are quite similar (see Table I). All the contact shifts are downfield in the order 2-H > 3-H >> 4-H, the 4-H values being quite small; the 3-H:2-H shift ratios vary in a very narrow range. The variations of the latter value and of the 4-H:2-H ratio are well within the range for which calculated and observed values would be considered to represent an excellent fit. The results suggest that a unique spin-delocalization mechanism is operative for all of these complexes. Models capable of rationalizing the shifts for one complex without being transferable to the others are to be discarded.

The above conclusions are quite surprising in view of (i) the differences among these ligands, *i.e.*, denticity and chelate ring size, and (ii) the large variation of symmetry (O_h, D_{4h}, D_3, D_{2d}) and coordination number (4, 6, 8) of the complexes whose shifts are considered in Table I. The different denticity and chelate ring size would be expected to affect the metal–ligand orbital overlap and the different symmetries should cause different electronic configurations on the metal. For these reasons spin-delocalization mechanisms *via* direct π bonds do not appear consistent with the present experimental results, since π bonds are presumably the most affected by the symmetry and coordination number of the complexes. It should be recalled here that π spin density has often been proposed to be present in dipy and phen complexes,[15-17] although a σ-π intraligand interaction has also been invoked.[16] A σ mechanism on the other hand would presumably be less sensitive to the differences among the ligands and the complexes. This mechanism is also in accord with the shift pattern; *i.e.*, the shifts decrease as the number of bonds between the paramagnetic center and the resonating nucleus increases, closely resembling the pattern of alkylamines,[3] for which the mechanism has to be σ. The fact that the shift patterns for Ni(II) and Co(II) are similar is also consistent with this model.[18] The failure of MO calculations to reproduce the observed pattern might be imputed to the inadequacy of the calculation models. For example it has been reported that almost degenerate σ and π molecular orbitals are the highest filled orbitals in pyridine radicals.[4,5] By shifting to dipy, phen, and napy the type and/or the eigenvectors of the highest filled orbitals will presumably be affected whereas very close patterns of shifts are observed.

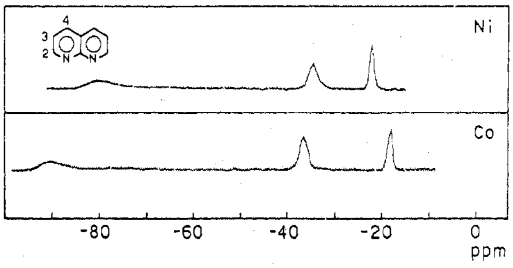


Figure 1. Proton magnetic resonance spectra of nitromethane solutions of $[M(napy)_4](ClO_4)_2$ (M = Ni, Co) recorded with a Varian DA-60 spectrometer operating at 60 MHz in the HR mode. Spectra were calibrated from internal TMS.

It must be concluded therefore that in many instances proton contact shift investigations, although quite useful for structural determinations, do not appear to give much information on the coordinative bond.[19] This is also the case of metal complexes with pyridine *N*-oxide,[20-22] aniline,[23,24] and probably triphenylphosphine,[25] where proton contact shifts are insensitive to the metal probably because spin-density transfer occurs through nonorthogonality of σ and π systems, *i.e.*, without involving the metal-donor bonds.

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Registry No. [Ni(napy)$_4$](ClO$_4$)$_2$, 36202-33-2; [Co(napy)$_4$](ClO$_4$)$_2$, 41202-96-4.

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"Through-Space" Spin Coupling between Phosphorus and Hydrogen in π-C$_5$H$_5$W(CO)$_2$PR$_3$X

Sir:

Nuclear spin-spin coupling in a freely tumbling molecule is normally transmitted by the electrons associated with the chemical bonds.[1] However, it sometimes happens that a pair of nuclei which are physically close but which are separated by a number of bonds will have an abnormally large coupling constant, and in such cases it is believed that a "through-space" coupling mechanism predominates.[2] This phenomenon is not well understood and the criteria for demonstrating its existence are not well established. Reports of the effect must therefore be examined carefully, especially when the number of bonds separating the coupled nuclei is not large and independent evidence (such as abnormal temperature variation of the coupling constant) is not available.[3]

It has recently been suggested[4] that in *trans*-π-C$_5$H$_5$W(CO)$_2$PR$_3$X [R = CH$_3$, C$_6$H$_5$, OCH$_3$, etc.; X = I, Sn(CH$_3$)$_3$] the observed couplings of 1-2 Hz between ^{31}P and the protons of the π-cyclopentadienyl rings [$^3J(^{31}\text{P}\cdot\cdot\text{H})$] are primarily "through-space" in origin. The main evidence for this is that $^2J(^{31}\text{P}\cdot\cdot\cdot^{13}\text{C})$ which involves some of the same bonds as the ^{31}P-H coupling is apparently zero, and the authors of ref 4 believe that this would not be so if there were appreciable electronic interaction between phosphorus and the cyclopentadienyl ring. We wish to offer an alternative interpretation and suggest that the observed coupling constants can be accounted for satisfactorily by a mechanism which involves the normal chemical bonds.

Firstly, $^3J(^{31}\text{P}\cdot\cdot\text{H})$ in these species is *not* abnormally large. It is, in fact, rather small, and this is probably due to the presence of the bulky tungsten atom and to essentially free rotation of the cyclopentadienyl ring which will lead to conformational averaging.[5] This process can also account for the zero value for $^3J(^{31}\text{P}\cdot\cdot\text{H})$ which has been found in *cis*-π-C$_5$H$_5$W(CO)$_2$PR$_3$X.

Secondly, studies of a range of organophosphorus species have shown that $^2J(^{31}\text{P}\cdot\cdot\cdot^{13}\text{C})$ changes sign as the hybridization of phosphorus changes from essentially p^3 to sp^3, whereas $^3J(^{31}\text{P}\cdot\cdot\text{H})$ remains positive throughout and may increase in magnitude somewhat.[6] For example, in (CH$_3$O)$_3$P $^2J(^{31}\text{P}\cdot\cdot\cdot^{13}\text{C})$ and $^3J(^{31}\text{P}\cdot\cdot\text{H})$ are +9.9 and +10.0 Hz, respectively, and in (CH$_3$O)$_3$PS they are −5.6 and +12.9 Hz. Furthermore, metal complexes of phosphines can be regarded as being intermediate between the two above extremes [this is supported especially by measurements of $^1J(^{31}\text{P-H})$ in PH$_3$, (PH$_3$)$_2$W(CO)$_4$, and PH$_4^+$] and so should exhibit values of $^2J(^{31}\text{P}\cdot\cdot\cdot^{13}\text{C})$ which are close to zero since this coupling constant can vary monotonically from positive to negative as the hybridization of phosphorus changes.[5] The lack of coupling between phosphorus and the cyclopentadienyl ring carbons is therefore not abnormal and does not imply an absence of electronic interaction. In the light of this, the observed $^3J(^{31}\text{P}\cdot\cdot\text{H})$ most reasonably arises from a mechanism involving the normal chemical bonds and there is no reason to postulate "through-space" interaction.

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