in Figure 1, are based on the chemical analysis and infrared spectral information. These structures are reminiscent of the macrocycles made by Curtis and coworkers over the past 10 years[10] in which various diamines and carbonyl compounds are condensed about a metal template. In the present work 2,2-dimethoxypropane is used both as a dehydrating agent and as a source of acetone for the acid-catalyzed condensation with dhph. The fact that both taph and daph can be isolated from two different reactions is attributed to the solubility properties of the derived complexes in methanol.

From the infrared spectra of the complexes, Figures 2 and 3, it is clear that the ligands taph and daph are closely related. The bands between 3200 and 3350 cm^{-1} are attributed to the N–H stretching frequencies. The ligand taph has only secondary amine groups and displays only one type of N–H stretch while daph has both primary and secondary amine groups and correspondingly shows two different bands. In the range 1630–1650 cm^{-1} is found the imine stretch which is the normal position for this moiety.[11] A strong band appears at 1510 cm^{-1} in all of the complexes and is associated with the phthalazine ring system since complexes of dhph show a similar band. This information when coupled with the chemical analyses and the methods of preparation places the proposed structures on firm ground.[12]

The availability of these ligands now makes it possible to study the effects that macrocyclic ligands have on two metal ions which are in close proximity to one another.

Acknowledgment.—We wish to thank Dr. Kurt L. Loening, Nomenclature Director, Chemical Abstracts Service, for help in naming the ligands.

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[10] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 33 (1968).

[11] The weak intensity of the imine frequency in taph is attributed to the polymeric nature of the complex.

[12] The disposition of the imine linkages with respect to one another is only speculative in taph.

Correspondence

Spin Delocalization in σ Systems

Sir:

Large isotropic nuclear resonance shifts[1] are often observed in paramagnetic systems owing to an electron–nuclear hyperfine contact interaction (dipolar shifts[2] which arise in magnetically anisotropic systems will be ignored for the present discussion). In transition metal complexes such shifts occur when unpaired electron spin density is transferred, by whatever mechanism, from the central metal to the ligand nucleus in question. It has been customary to describe electron spin delocalization according to the symmetry (σ or π) of the ligand orbitals involved in the process. The early work in this area was devoted almost entirely to proton resonance and the systems most extensively studied such as salicylaldimine and aminotropone imine complexes of nickel(II)[3] exhibit isotropic shift patterns which are generally attributed[4] to spin delocalization in ligand π orbitals. Several features lead to this conclusion: (i) the shifts alternate in sign between adjacent positions on an aromatic fragment, (ii) no particular attenuation in shift magnitude is observed as the protons become further removed from the metal, (iii) the shifts are interpretable in a semiquantitative manner by VB[5] and MO[6] calculations considering the π-electron system alone, and (iv) substitution of a methyl group for a proton results in a methyl proton resonance shift in the direction opposite to that of the replaced proton, as required by the hyperconjugative model for the interaction of a pπ electron with methyl protons.[7] The aforementioned features have generally been taken as diagnostic of π-spin delocalization.

On the other hand, the downfield shifts experienced by pyridine protons, which decrease in magnitude in the order $\alpha > \beta > \gamma$ when this ligand is coordinated to nickel(II) acetylacetonate, $Ni(acac)_2$, were attributed in 1963 by Happe and Ward[8] to spin delocalization in the ligand σ system. This intuitively reasonable conclusion has been cited on numerous occasions as diagnostic of σ-spin delocalization. Furthermore it is usually, though not invariably,[9] observed for saturated aliphatic groups that proton resonance shifts are downfield and attenuate rapidly in magnitude as the number of bonds intervening between the metal and the proton increases. In an early attempt to interpret σ-spin delocalization *via* a theoretical model, Holm, Everett, and Horrocks carried out an extended Hückel (EHMO) calculation on pyridine.[10] This calculation predicted the magnitude of the downfield shifts in the order $\gamma > \alpha > \beta$ for direct spin delocalization in the highest filled σ MO, in poor agreement with experiment. It was noted however that the proton shifts paralleled quite closely the hyperfine interaction constants observed in an epr experiment[11] for the phenyl radical, a σ species.

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[1] For a review see D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance* **1**, 103 (1965).

[2] For a recent discussion see W. DeW. Horrocks, Jr., *Inorg. Chem.* **9**, 690 (1970).

[3] See R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969), for a discussion and leading references.

[4] See, however, D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 4484, 5255 (1970).

[5] (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); **39**, 3513 (1963); (b) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, **86**, 379 (1964).

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[7] (a) A. D. McLachlan, *ibid.*, **1**, 233 (1958); (b) D. B. Chestnut, *J. ibid.*, **29**, 43 (1958).

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Subsequently Drago and coworkers[12] and others[9b] sought to use EHMO calculations to explain proton contact shifts arising from σ-spin delocalization. While apparent agreement between theory and experiment was achieved in some cases, the modest number of sets of equivalent protons treated by any given calculation and problems of conformational averaging have prevented a really rigorous test of this theory. EHMO theory is, of course, only capable of accounting for direct delocalization; the upfield shifts which are occasionally observed for σ systems have been either ignored or attributed to spin polarization or other spin delocalization mechanisms.

Two developments, one theoretical and one experimental, prompt us to present a reevaluation of the theory of σ-spin delocalization, particularly as it pertains to coordinated pyridine-type ligands.[13] Semiempirical MO calculations at the INDO/2 level have been remarkably successful in predicting the signs and magnitudes of nuclear–electron hyperfine interaction constants, A_i, of organic free radicals both of the σ and π varieties.[14] In addition, the availability of ^{13}C nmr data,[15] for pyridine and derivatives coordinated to Ni(acac)$_2$, allows a more stringent test of theory than was possible when only a small number of proton resonance shift data were at hand.

As a model for σ-spin delocalization in coordinated pyridine derivatives we have chosen the phenyl radical and the *o*-, *m*-, and *p*-tolyl radicals. This choice was prompted by several factors: first, the proton isotropic shift ratios for coordinated pyridine closely parallel those observed[11] for the phenyl radical ($\alpha:\beta:\gamma = 1.00:0.34:0.11$); moreover, they compare well with the ortho, meta, and para proton spin–spin (*J–J*) coupling constant[16a,b] ratios of benzene (1.00:0.18:0.09). The *J–J* coupling constants reported[16c] for toluene provide an even more convincing demonstration of this parallelism in that the methyl proton to aromatic proton coupling constants are *negative* for the ortho and para protons, corresponding to the observed upfield shifts of the α- and γ-methyl group resonances of the coordinated picolines (*vide infra*). The close relationship between the theories of *J–J* coupling and electron–nuclear hyperfine (enh) interactions has been discussed theoretically by Luz[17] and commented on in conjunction with isotropic shifts of aliphatic proton resonances of iminodicarboxylic acid[18] and ethylenediamine complexes[19] of nickel(II). Both phenomena depend primarily on Fermi contact interactions and this parallelism becomes particularly apparent when one considers the finite perturbation theory of Pople, *et al.*,[20] used to describe nuclear *J–J* coupling.[21] In the case of benzene, for instance, the nuclear magnetic moment of one proton is considered as a finite perturbation in the calculation of its coupling to the remaining nuclei. In the limit of infinite magnetic moment, the β electron of the C–H bond is merged with the perturbing nucleus and the problem closely resembles the phenyl radical.[22] The above-mentioned experimental and theoretical analogies suggest that ligand electronic structure may determine the details of spin delocalization and that a calculation performed on a molecular fragment may succeed to a degree in accounting for electron spin delocalization, provided that the perturbation upon complexation is not too great. It is not clear at present whether such calculations should be approached from the *J–J* or enh limits; however, since computer programs for the former are not generally available, we have undertaken open-shell INDO/2 calculations[23] on these neutral doublet species.[13b] The orbital containing the unpaired electron has σ symmetry (no out-of-plane p$_z$ contributions) and a large contribution from the carbon 2s and 2p$_x$ orbitals which correspond to the nitrogen lone pair of pyridine. In Table I are presented the calculated hyperfine coupling constants along with the normalized isotropic ^{1}H and ^{13}C shifts[15a] for coordinated pyridine and γ-, β-, and α-picoline and ratios of these quantities. Very good qualitative agreement is obtained, with the sign of the shift being predicted correctly for 34 out of the 35 sets of nuclei.[24] For the 34 cases of correct sign, the relative magnitudes are correct (considering ^{1}H and ^{13}C nuclei separately) in 31 of them. The ratios R of the shifts to the hyperfine coupling constants ($\Delta\nu_i/A_i$) within the sets of carbon, R_C, and sets of hydrogen nuclei, R_H, show moderate semiquantitative agreement (ideally a single value of R_C and single value of R_H would be obtained for a given ligand). Furthermore the ratio R_C/R_H should equal the ratio of magnetogyric ratios of hydrogen to carbon γ_H/γ_C of 3.977. Taking average values of R_C and R_H (deleting the case of incorrect sign), R_C/R_H ratios of 6.2, 7.2, 5.4, and 7.7 for the species in the order listed in Table I are obtained. This moderate semiquantitative agreement is perhaps all that can be expected considering the crudity of the model and the approximations inherent in the theory. Probably the most serious approximation is the fact that one is attempting to com-

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(22) We are indebted to Professor J. A. Pople for making this point.

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(24) If the ^{13}C data of ref 15b are accepted, the qualitative agreement is perfect for all 35 cases and the quantitative agreement is improved slightly.

TABLE I

NORMALIZED ^{1}H AND ^{13}C ISOTROPIC SHIFTS, $\Delta\nu_1$,[a] FOR PYRIDINE-TYPE BASES COORDINATED TO Ni(acac)$_2$, INDO/2 HYPERFINE CONSTANTS, A_i,[b] CALCULATED FOR THE PHENYL RADICAL ANALOGS,[c] AND RATIOS OF THESE QUANTITIES

	Phenyl			*p*-Tolyl			*m*-Tolyl			*o*-Tolyl		
Nuclei[d]	$\Delta\nu_i$	A_i	$\Delta\nu_i/A_i$	$\Delta\nu_i$	A_i	$\Delta\nu_i/A_i$	$\Delta\nu_i$	A_i	$\Delta\nu_i/A_i$	$\Delta\nu_i$	A_i	$\Delta\nu_i/A_i$
α-H	−943	+18.7	−48.4	−394	+19.2	−20.5	−930	+17.4	−53.4	−293	+17.4	−16.8
α'-H							−930	+19.3	−48.2			
α'-CH$_3$										+48	−1.9	−25.3
β-H	−286	+6.1	−46.9	−71	+6.5	−10.9	−360	+5.7	−63.1	−146	+6.6	−22.1
β'H										−73	+5.3	−13.8
β'-CH$_3$							−72	+1.6	−45.0			
γ-H	−86	+3.9	−17.9				−214	+4.3	−49.8	−24	+4.2	−5.7
γ-CH$_3$				+36	−1.2	−30.0						
α-C	+1000	−4.7	−213	−1000	−5.1	−196	+1000	−4.9	−204	+1000	−4.0	−250
α'-C							+1000	−5.0	−200	−488	−3.2	+153
α'-CH$_3$										−585	+6.2	−94
β-C	−3689	+10.8	−342	−1930	+10.4	−186	−3214	+10.7	−300	−1659	+10.7	−155
β'-C							−3000	+10.4	−288	−1122	+10.8	−104
β'-CH$_3$							−430	+0.82	−524			
γ-C	+371	−2.6	−143	+180	−2.3	−78.2	+430	−2.8	−154	+98	−2.6	−37.7
γ-CH$_3$				−144	+1.4	−103						

[a] Taken from ref 15a with the α-C shift normalized to +1000. [b] Gauss. [c] Standard geometries were assumed with 120° or tetrahedral bond angles and the following bond distances: C–C(aromatic), 1.40 Å; C–CH$_3$, 1.51 Å; C–H(aromatic), 1.08 Å; C–H(methyl), 1.10 Å. [d] The primes refer to nuclei on the same side of the molecule as the methyl group.

pute a property of a complex *via* a calculation on a molecular fragment. Programs for calculations at the INDO/2 level of sophistication which can include transition metal atoms are not yet available.

If one accepts the present INDO/2 results as a reasonably accurate representation of σ-spin delocalization in coordinated pyridine derivatives, the following conclusions may be drawn.

(a) The original postulate of Happe and Ward,[8] that σ-spin delocalization results in downfield shifts which attenuate in magnitude with the number of intervening bonds is justified for directly bonded hydrogens but does not necessarily apply to attached methyl protons.

(b) An alternation in sign of the carbon hyperfine constants as one proceeds around the aromatic ring is predicted for σ-spin delocalization. Such alternative behavior cannot be considered in general as diagnostic of π-spin delocalization. For the carbon atoms with positive A_i's, the magnitudes of these quantities appear to decrease as the distance from the coordinating atom increases.

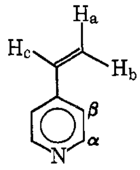
(c) The observed direction of the methyl proton shifts (upfield α and γ, downfield β) is correctly predicted by the σ model and implies that the widely used criterion of opposite shifts for hydrogen and methyl protons at a given position is *not* diagnostic of π-spin delocalization.

TABLE II

ISOTROPIC SHIFT DATA FOR COORDINATED 4-PHENYLPYRIDINE (L) AND CALCULATED HYPERFINE CONSTANTS FOR THE 4-VINYLPHENYL RADICAL

	Isotropic shifts, $\Delta\nu$, ppm[a]		Hyperfine constants, G[d]	
	Ni(acac)$_2$L$_2$[b]	NiL$_6^{2+}$ [c]	Planar	Perpendicular[e]
H_α	. . .	−43.8	+19.0	+19.1
H_β	−23.8	−20.6	+6.4	+6.5
H_a	−2.8	−3.6[f]	+0.40	+0.07
H_b	−2.9	−4.0[f]	+0.35	+0.16
H_c	+2.7	+1.5[f]	−0.32	−1.50

[a] Computed from $\Delta\nu = \Delta\nu_{\text{obsd}}/P_m$, where P_m is the ratio of moles of coordinated 4-vinylpyridine to total moles of this ligand. [b] Measured at 26° on chloroform-*d* solutions 0.79 *M* in 4-vinylpyridine. [c] From ref 12c. [d] INDO/2 calculations using the program of ref 16 and the vinyl structural parameters of ref 12c. [e] Phenyl and vinyl groups mutually perpendicular. [f] The present reassignment, see text, has been confirmed by Dr. R. E. Cramer in a private communication. He kindly supplied the revised isotropic shifts quoted here, obtained after correction of his inadvertent error.



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In a recent paper[12c] dealing with hexakis complexes of pyridine-type bases with nickel(II), Cramer and Drago concluded, largely on the basis of the observed upfield shifts, that significant π-spin delocalization occurs in these systems. Table I shows that these observations are to be expected on the basis of σ-spin delocalization alone. In order to determine the prediction of the σ model for 4-vinylpyridine, INDO/2 calculations were carried out on the planar form of the 4-vinylphenyl radical[25] and on this radical with the planes of the phenyl and vinyl moieties mutually perpendicular The results are shown in Table II. In both conformations the hyperfine coupling constants for vinyl protons H_a and H_b (see structure 1) are positive, predicting downfield shifts, and that of H_c is negative, corresponding to an upfield shift. Since this assignment differs from that of Cramer and Drago,[12c] who assigned the upfield shifted resonance to H_b, a quantitative study of the system Ni(acac)$_2$–4-vinylpyridine in chloroform-*d* was undertaken. Pmr spectra were recorded on solutions with the Ni(acac)$_2$:4-vinylpyridine ratios, R_p, varying from 1:3 to 1:11. Plots of the chemical shifts *vs.* R_p were linear and, when extrapolated to zero complex concentration, yielded the following diamagnetic reference chemical shifts which are in the same order as those obtained directly from the spectrum of pure 4-vinylpyridine: H_β, −7.50; H_a, −5.87; H_b, −6.23; H_c, −6.53 ppm from TMS. Confirmation of these assignments is provided by the spin–spin coupling structure. The resonances assigned here to H_a and H_b appear as doublets with splittings of 10 and 17 Hz, respectively, while the H_c resonance shows quartet struc-

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(25) The 4-vinylpyridine cation calculates to be a π radical in the INDO approximation; see ref 13a.

TABLE III

COMPARISON OF EXPERIMENTAL AND THEORETICAL ISOTROPIC ^{1}H SHIFT RATIOS FOR PYRIDINE-TYPE BASES, L, OCTAHEDRALLY COORDINATED TO NICKEL(II)

Ligand proton		Experiment			Theory			
		Ni(acac)$_2$L$_2$[a]	Ni(acac)$_2$L$_2$[b]	NiL$_6$$^{2+}$[c]	INDO/2(σ)[d]	EHMO(σ)[e]	EHMO($\sigma + \pi^*$)[e]	EHMO($\sigma + \pi$)[e]
Pyridine	α	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	β	0.294	0.303	0.385	0.326	0.382	0.384	0.398
	γ	0.077	0.091	0.116	0.208	1.01	1.10	1.09
γ-Picoline	α	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	β	0.278	0.180	0.328	0.338	0.394	0.401	0.420
	γ-CH$_3$	−0.090	−0.091	−0.092	−0.063	0.015	−0.092[g]	−0.092[g]
β-Picolineβ	α	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	β	0.296	0.387	0.365	0.310	0.365	0.373	0.390
	γ	0.063	0.230	0.104	0.234	1.02	1.11	1.02
	β-CH$_3$	0.055	0.077	0.072	0.087	0.092	0.074	0.019
4-Vinylpyridine	α			2.13	2.94[h]	2.52	2.46	2.38
	β		1.0[d]	1.0	1.0[h]	1.0	1.0	1.0
	H$_a$		0.118[d]	0.073[f]	0.063[h]	0.241	0.380	0.266
	H$_b$		0.122[d]	0.192[f]	0.055[h]	0.055	−0.009	−0.023
	H$_c$		−0.113[d]	−0.176[f]	−0.050[h]	0.045	0.085	0.100

[a] Data from ref 8. [b] Data from ref 14. [c] Data from ref 12c. [d] Present work. [e] From ref 12c. [f] See footnote f of Table II. [g] Forced fit, see text. [h] Planar form.

ture which becomes unresolvable at higher R_p values; all are in good agreement with the spectrum of pure 4-vinylpyridine.

Finally, we compare the present INDO/2 results for the pmr shift ratios with an interpretation recently presented[12c] involving EHMO theory. In Table III are presented ratios of isotropic shifts for pyridine and three derivative ligands L in complexes of the types Ni(acac)$_2$L$_2$ and NiL$_6$$^{2+}$. No theoretical model limited to the ligand moiety can be expected to provide better agreement than that found between different systems involving the same ligand or variations observed by different investigators on the same system. Also listed in Table III are the ratios predicted on the basis of INDO/2 hyperfine coupling constant calculations. The sign of the shift is correctly predicted by these calculations in every case and reasonable semiquantitative agreement with the observed ratios is apparent. In the final three columns of Table III are given the results of an EHMO analysis of these systems.[12c] The column labeled EHMO(σ) gives the ratios of hyperfine interactions expected for spin delocalization in the highest filled σ MO. EHMO theory is of course incapable of accounting for upfield shifts and yields particularly poor results for H$_\gamma$, as noted elsewhere.[12] Cramer and Drago[12c] attributed the upfield shifts to a contribution from β-spin delocalization in the ligand π system, involving either the highest filled, π, or lowest vacant, π^*, orbital. By forcing a fit for the H$_\alpha$ and γ-CH$_3$ resonances they analyzed the spin delocalization in terms of a linear combination of σ and π mechanisms as shown in the last two columns of Table III. This procedure does not improve the agreement for H$_\gamma$ and apparently predicts an upfield shift for the H$_b$ resonance rather than for H$_c$ of 4-vinylpyridine, contrary to our observations.

We conclude that INDO/2 theory shows reasonable promise on the semiquantitative level in interpreting contact shifts of both protons and ^{13}C nuclei. The analysis presented here, which involves but a single (σ) spin delocalization mechanism, represents an alternative (to that presented in ref 15c) interpretation of contact shifts in pyridine-type bases coordinated to octahedral nickel(II).

Acknowledgments.—We thank Drs. D. Doddrell and J. D. Roberts for preprints of ref 4 and 15a. We are indebted to Dr. J. P. Lowe and Mr. T. J. Moulson for supplying us with the computer program and to Mr. J. P. Sipe for experimental assistance.

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RECEIVED AUGUST 28, 1970

The Cotton Effect of Tris(1,3-diaminopropane)cobalt(III) Ion, Co(tn)$_3$$^{3+}$

Sir:

Recent assignments of the ligand field circular dichroism (CD) spectra of $\Delta(+)$-Co(tn)$_3$$^{3+}$ are at variance. Those based on a single-crystal study[1] assign the high-energy component as E$_a$ symmetric while solution studies with oxyanions suggest that this is the A$_2$ component.[2-4] Assuming both assignments to be correct we suggest an explanation for these apparently discordant results in terms of Piper's model[5-8] for the sign of the Cotton effect in trigonally symmetric tris-bidentate transition metal complex ions. This electrostatic model determines the sign of the Cotton effect in terms of distortions of the ligand atoms from exact O_h symmetry. The Cotton effect is predicted to change sign as the twist angle, ω of Figure 1, changes from less than 60° to greater than 60° taken in a Λ chiral sense.[5,7] This model predicts no optical activity for $\omega = 60°$ and neglects the chiral distribution of the ligands around the C_3 axis. Alternatively, the sign of the Cotton effect is related to the absolute configuration of the

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