and the hydroxy group of a bulky etolenH complex in the absence of external acids, the proton which activates the carbonyl group of ketene probably comes from the alcoholic OH group. The process must involve a weakening of the O–H bond prior to migration of the proton. As the OH bond is weakened, the oxygen becomes more negative and there is a competition for O^- between the metal ion and the electron-deficient carbon of the carbonyl group in the ketene, resulting in the formation of a mixture of the acetylated complex and the $Co(etolen)_n$ complexes. Tentatively, such a mechanism may be assumed to occur in the reaction of acetone suspensions of etolenH complexes with ketene, as pictured in Scheme II.

The reaction with ketene in dimethyl sulfoxide must operate by attack on the NH group of the etolenH complexes along with the OH, since similar reactions occur with ethylenediamine complexes as well. The mechanism in this case probably involves partial dissociation of a metal–nitrogen bond, or acid dissociation of an NH bond, liberating a proton to further activate the carbonyl group of ketene, or both. Both of the above processes will weaken the metal complex, leading to reduction of incompletely complexed metal. This second process will be favored in highly polar solvents like dimethyl sulfoxide, but may occur to a small extent in reactions in acetone suspension (see Scheme III).

All the etolenH complexes described in this paper are capable of existence in several stereoisomeric forms, but no attempt has been made to identify the structures or to isolate these.

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Contact Shift Studies of Some Octahedral Benzamide Complexes of Iron(II), Cobalt(II), and Nickel(II)

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Abstract: Isotropic shifts are reported for some paramagnetic, six-coordinate complexes of benzamide, with Ni(II), Fe(II), and Co(II). Although it is impossible to draw any conclusions about a π-bonding interaction between the metal "d" orbitals and the ligand π orbitals from the Ni(II) shifts alone, a very convincing case can be made for interaction of metal t_{2g} orbitals and ligand π orbitals by comparing the shifts in the Ni(II) and Fe(II) complexes. These results further support our earlier claim that one cannot necessarily assume similar delocalization mechanisms in octahedral iron(II), cobalt(II), and nickel(II) systems. These interpretations are supported, and a mechanism for spin delocalization in the Ni(II) and Fe(II) complexes is proposed from the results of EHT molecular orbital calculations. It is also shown that a σ-delocalization mechanism does not necessarily lead to attenuation of the shift as one proceeds away from the metal. Pronounced variation in the Co(II) shifts with change in solvent, change in anion, and change in concentration of the complex are attributed to a pseudocontact effect induced by ion pairing. Conditions for observing a pseudocontact contribution to the shift are elucidated for six-coordinate complexes undergoing rapid ligand exchange.

Amides are known to be very good donors toward the first-row transition metal ions, and many coordination compounds involving amides as ligands have been synthesized.[2] In this laboratory we first became interested in coordination compounds of amides such as N,N-dimethylacetamide (DMA) and N,N-dimethylformamide (DMF)[2a] in studies of nonaqueous solvents.[3] Recently, because of our interest in understanding the nmr spectra of paramagnetic transition metal complexes, we investigated the contact shifts of the octahedral nickel(II) complexes of N,N-dimethylacetamide and N,N-dimethylformamide[4] and proposed possible mechanisms for the delocalization of unpaired electron spin density in these complexes. It was not clear, however, whether spin was being transferred *via* a σ or π mechanism or *via* a combination of both. The six-coordinate iron(II)-, cobalt(II)-, and nickel(II)-benzamide complexes, recently reported by Ragsdale, *et al.*,[5] were prepared in this study in order to determine how spin is delocalized in amide complexes of O_h symmetry. Benzamide (BA) and *p*-toluamide (PTA) were chosen as ligands because they contain phenyl groups which possess several nonequivalent protons whose proton contact shifts can be very useful in recognizing σ or π delocalization of unpaired electrons. Furthermore, two solvents (acetone and propylene carbonate) and two anions (ClO_4^- and BF_4^-) were utilized in order to study

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(1) Abstracted in part from the Ph.D. Thesis of M. Wicholas, University of Illinois, Urbana, Ill., 1967.

(2) See, for example, (a) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963); (b) W. E. Bull, S. K. Madan, and J. E. Willis, *ibid.*, **2**, 303 (1963); (c) S. K. Madan, *ibid.*, **6**, 421 (1967).

(3) R. S. Drago and K. F. Purcell, *Progr. Inorg. Chem.*, **6**, 271 (1964).

(4) B. B. Wayland, R. S. Drago, and H. F. Henneike, *J. Am. Chem. Soc.*, **88**, 2455 (1966).

(5) M. B. Welch, R. S. Stephens, and R. O. Ragsdale, *Inorg. Chim. Acta*, **2**, 367 (1968).

Table I. Analytical Data

Compound	$X = ClO_4^-$ Calcd, % C	Calcd, % H	Found, % C	Found, % H	$X = BF_4^-$ Calcd, % H	Calcd, % C	Found, % C	Found, % H
$Ni(BA)_6X_2$	51.24	4.30	51.10	4.31	52.59	4.41	52.34	4.58
$Co(BA)_6X_2$	51.23	4.30	50.94	4.31	52.58	4.41	52.49	4.63
$Fe(BA)_6X_2$	51.39	4.31	51.38	4.22	52.75	4.43	52.51	4.35
$Zn(BA)_6X_2$	50.89	4.33	50.63	4.33	52.23	4.38	52.17	4.52
$Ni(PTA)_6X_2$	53.93	5.09	53.90	5.27				
$Co(PTA)_6X_2$	53.93	5.09	53.82	5.42				
$Fe(PTA)_6X_2$	54.08	5.11	53.77	5.20	55.43	5.23	55.14	5.27
$Zn(PTA)_6X_2$	53.63	5.06	53.84	5.05				

Table II. Electronic Spectra of the Complexes[a]

Compound	State (Concn, *M*)	Absorption max, cm^{-1} (ϵ_{molar} for soln)
$Ni(BA)_6(ClO_4)_2$	Nujol mull	24,800; 14,600 (sh); 13,400
	Acetone (0.0545)	24,500 (17); 14,600 (sh), 13,300 (7); 8180 (8)[b]
	Propylene carbonate (0.0541)	24,600 (18); 14,700 (sh); 13,500 (6); 8310 (8)
$Ni(BA)_6(BF_4)_2$	Acetone (0.0547)	24,500 (17); 14,600 (sh); 13,300 (6); 8160 (8)
$Ni(PTA)_6(ClO_4)_2$	Nujol mull	24,800; 14,700 (sh); 13,400
	Acetone (0.0218)	24,700 (17); 14,600 (sh); 13,400 (6); 8290 (7)[b]
$Co(BA)_6(ClO_4)_2$	Nujol mull	19,200
	Acetone (0.0252)	18,900 (20)
	Propylene carbonate (0.0551)	18,900 (26)
$Co(BA)_6(BF_4)_2$	Acetone (0.0262)	18,900 (22)
	Propylene carbonate (0.0276)	18,900 (28)
$Co(PTA)_6(ClO_4)_2$	Nujol mull	19,400
	Acetone (0.0338)	18,900 (23)
$Fe(BA)_6(ClO_4)_2$	Nujol mull	10,000 (broad)
	Acetone (0.0552)	9950 (6); 7800 (sh)
	Propylene carbonate (0.0598)	9920 (5); 7900 (sh)
$Fe(BA)_6(BF_4)_2$	Acetone (0.0544)	9920 (7); 7900 (sh)
	Propylene carbonate (0.0615)	9900 (5); 7900 (sh)
$Fe(PTA)_6(ClO_4)_2$	Nujol mull	10,000 (broad)
	Acetone (0.0474)	10,100 (7); 7900

[a] The solution spectra for the nickel(II) and iron(II) complexes were recorded with an equimolar amount of either $Zn(BA)_6(ClO_4)_2$ or $Zn(PTA)_6(ClO_4)_2$ in the reference solution in order to cancel out ligand absorptions. [b] The equivalent band in the Nujol mull is obscured because of ligand absorptions.

the effects of ion pairing upon the isotropic shifts of benzamide protons in the cations $M(BA)_6^{2+}$. Conditions for observing a pseudocontact shift when rapid ligand exchange is occurring are reviewed and provide information about the geometry of the ion pair.

Experimental Section

Reagents. The hydrated fluoroborate salts of zinc(II), cobalt(II), and nickel(II) were prepared from the metal carbonates and fluoroboric acid. $Fe(H_2O)_6(BF_4)_2$ was prepared from iron powder and fluoroboric acid. All other reagents and solvents were commercially available. Both acetone and propylene carbonate were dried over molecular sieves for a few hours before use.

Preparation of Complexes. All the six-coordinate complexes of benzamide were prepared by the same method. The hydrated metal salt was dehydrated by stirring in 2,2-dimethoxypropane for 2 hr, a stoichiometric amount of ligand was then added, and the stirring was continued. Precipitation of the complex ensued and the solid was then filtered, washed with ether in a drybox, and dried *in vacuo* over P_2O_5 for 24 hr. Analyses, performed under the supervision of Mr. J. Nemeth, University of Illinois, are reported in Table I. The compounds are sparingly soluble in acetone and propylene carbonate but are insoluble in methylene chloride or chloroform.

Spectra. The nmr spectra were obtained with a Varian Model A-60A and a Jeolco Model C60-H spectrometer. All shifts are reported relative to TMS as an internal reference. A Cary Model 14 spectrometer was used for measuring the visible and near-infrared spectra.

Calculations

Extended Hückel molecular orbital calculations[6,7] were carried out on benzamide. The parameters employed were Slater exponents and Hinze and Jaffé VSIP's which were adjusted for charge.[7] A ψ^2 evaluation[8] was carried out to evaluate the total electron density at the protons in the various molecular orbitals.

Results

In Table II, the visible and near-infrared bands of the benzamide and *p*-toluamide complexes in Nujol mulls and in acetone and propylene carbonate solutions are presented. These were compared to show that the complexes remain intact upon solution in both solvents. The proton nmr resonances and contact shifts for the complexes are listed in Table III. The assignments for the *ortho*, *meta*, and *para* protons were made on the basis of area and line width. A nickel(II) complex of $C_6H_5C(O)ND_2$ was prepared to establish that none of these peaks is attributable to the NH protons. We also were not able to detect peaks in the spectrum of the benzamide complexes which could be assigned to the NH protons. For the cobalt(II) and iron(II) complexes, the contact shifts are concentration and solvent dependent, whereas this was not observed for the nickel(II) complexes. Figure 1 presents the nmr spectra for the three benzamide perchlorate complexes in acetone. Note that the frequency of the *ortho*-proton resonance in $Ni(BA)_6(ClO_4)_2$ cannot be accurately reported because of the overlapping of other proton resonances.

Discussion

Characterization of the Benzamide Complexes. Since all nmr spectra were to be run in the solvents acetone and propylene carbonate which are known to possess weak coordinating ability, it was first necessary to determine whether benzamide and *p*-toluamide remain coordinated in both of these solvents. In Table II,

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(6) R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963).

(7) P. C. Van Der Voorn and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 3255 (1966).

(8) R. S. Drago and H. Petersen, *ibid.*, **89**, 3978 (1967).

Table III. Isotropic Shifts of the Complexes

Compound[b,c]	Concn, M	$\Delta\nu$,[a] cps o-H	 m-H	 p-H (CH_3)	Solvent
$Fe(BA)_6(ClO_4)_2$	0.075	+35	−81	+45	Acetone
	0.050	*c*	−80	+48	Propylene carbonate
	0.025	*c*	−57	+46	Propylene carbonate
$Fe(BA)_6(BF_4)_2$	0.20	*c*	−93	+52	Acetone
	0.10	*c*	−95	+50	Acetone
	0.05	*c*	−81	+51	Propylene carbonate
$Fe(PTA)_6(ClO_4)_2$	0.08	+43	−82	−53	Acetone
$Fe(PTA)_6(BF_4)_2$	0.08	*c*	−91	−56	Acetone
$Co(BA)_6(ClO_4)_2$	0.07	−212	−171	−37	Acetone
	0.05	−201	−157	−36	Acetone
	0.05	−158	−145	−23	Propylene carbonate
	0.025	−147	−118	−22	Propylene carbonate
	0.01	−108	−71	−22	Propylene carbonate
$Co(BA)_6(BF_4)_2$	0.10	−144	−145	−19	Acetone
	0.05	−157	−145	−24	Propylene carbonate
$Co(PTA)_6(ClO_4)_2$	0.04	−216	−167	−76	Acetone
$Ni(BA)_6(ClO_4)_2$	0.05	*b*	−81	−1	Acetone
	0.05	*b*	−86	+3	Propylene carbonate
$Ni(BA)_6(BF_4)_2$	0.05	*b*	−94	0	Acetone
	0.05	*b*	−86	+3	Propylene carbonate
$Ni(PTA)_6(ClO_4)_2$	0.03	*b*	−82	−3	Acetone

[a] $\Delta\nu$ is reported with respect to the diamagnetic zinc(II) complex resonances. For example, in $Zn(BA)_6(ClO_4)_2$, $\nu_{ortho} = -483$ cps, $\nu_{meta} = -450$ cps, $\nu_{para} = -450$ cps relative to TMS. [b] $\Delta\nu$ for the *ortho* protons is approximately 20 ± 10 cps in the nickel(II) complexes. [c] $\Delta\nu$ for the *ortho* protons is approximately +30 ± 15 cps in the iron(II) complexes.

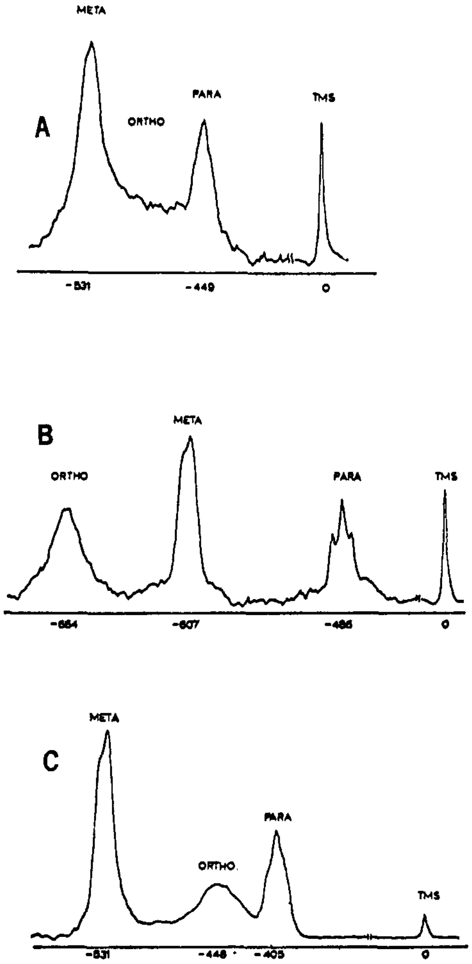

Figure 1. Nmr spectrum of (A) $Ni(BA)_6(ClO_4)_2$, (B) $Co(BA)_6(ClO_4)_2$ in acetone-d_6; (C) $Fe(BA)_6(ClO_4)_2$ in acetone-d_6.

electronic spectra for the complexes are reported. Good agreement was found between the mull and solution spectra, supporting the contention that dissociation or displacement of the amide ligand by solvent does not occur. Furthermore, addition of excess ligand to the solution of the complex did not cause any change in the electronic spectra of the complexes.

For $Ni(BA)_6(ClO_4)_2$ in acetone, the spectrochemical parameters Dq and $\beta(B/B')$ are respectively 818 and 0.859 cm^{-1}. For octahedral amide complexes of nickel(II) such as N-alkylformamide or acetamide complexes,[2a] Dq varies from 820 to 850 cm^{-1} and β is approximately 0.88–0.85. There is very little difference in the spectrochemical parameters of these amide ligands. Good agreement was found between the calculated and experimental frequency for the $\nu_2(^3A_{2g} \rightarrow {}^3T_{1g}(F))$ band of $Ni(BA)_6(ClO_4)_3$ in acetone.

Pseudocontact Shifts. The observed isotropic shifts in these complexes are quite unusual in that no resemblance is found between the cobalt(II), iron(II), and nickel(II) spectra. In what follows, we propose to explain these differences by showing that variations in the mechanism of spin delocalization occur as the metal ion is changed. Furthermore, we investigate the effect of ion pairing by examining the contact shifts in different solvents using both perchlorate and fluoroborate as anions. The concentration dependence, anion dependence, and solvent dependence of the shifts provide insight into pseudocontact contributions.

First consider the problem of estimating the pseudocontact shifts in these complexes. The equation for the pseudocontact shift[9] at the ith proton in complexes having axial symmetry is given by

$$(\Delta\nu/\nu)_i = K\frac{(3\cos^2\theta - 1)(g_{\parallel} - g_{\perp})}{r^3}F(g_{\parallel},g_{\perp}) \qquad (1)$$

where the magnitude of the radius vector between the ith nucleus and the unpaired electron is given by r. The unpaired electron is approximated by a point charge located at the metal nucleus, and θ is the angle between the radius vector r and the molecular symmetry axis. F is a simple linear function of $g_{\parallel}$ and $g_{\perp}$ and its value depends on whether $T_1 \gg \tau_c$ or $T_1 \ll \tau_c$, where T_1 is the electron relaxation time and τ_c is the rotational correlation time for the complex. Since octahedral nickel(II) complexes are generally magnetically isotropic, $g_{\parallel} - g_{\perp} = 0$ and the pseudocontact shift is zero. In both the iron(II) and cobalt(II) complexes the effects of g-tensor anisotropy can be important, but in these complexes in the absence of ion pairing we believe that the pseudocontact shift should be close to zero. Any anisotropy should result from a Jahn–Teller distortion of the complex in solution. The distortion would be of a dynamic nature which is rapid on the nmr time scale, for only at low temperatures in the solid state should a static dis-

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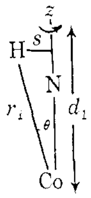
[9] G. N. La Mar, *J. Chem. Phys.*, **43**, 1085 (1965).

tortion be "locked" in.[10,11] In a dynamic distortion, rapid on the nmr time scale, one has an effective octahedron, $g_{\parallel} - g_{\perp} = 0$, and $3\cos^2\theta - 1 = 0$ for any proton, thus giving a zero pseudocontact shift.

If there were a static tetragonal Jahn–Teller distortion locked in by ion pairing, the effect of rapid ligand exchange in such cases is very interesting in that it greatly diminishes the magnitude of the pseudocontact shift contributions to the ligand resonances. As an illustrative example, we consider the proton pseudocontact shifts of a simple complex ion, $Co(NH_3)_6^{2+}$.

For the sake of this discussion let us assume there is a static tetragonal distortion which lengthens the two axial bonds. With no ligand exchange occurring there are two distinct types of ammonia ligands: the four equatorial and two axial ligands. The geometric factors for these two sets of protons can readily be calculated. The geometric factor for the axial protons is called G_1. In this model (shown below), the axial ligands rotate about the z axis. The notation used is consistent with that used previously.[9]



$$\cos\theta = d_1/r_1;\ r_1^2 = s^2 + d_1^2 \tag{2}$$

$$3\cos^2\theta - 1 = \frac{2d_1^2 - s^2}{r_1^2} \tag{3}$$

$$G_1 = \frac{3\cos^2\theta - 1}{r_1^3} = \frac{2}{r_1^3} - \frac{3s^2}{r_1^5} \tag{4}$$

It is also quite simple to calculate the geometric factor G_2 for the equatorial protons. Here, free rotation of the ligand about the metal–ligand bond axis is assumed. Using an ammonia molecule on the x or y axis, one need only consider a rotation of 90° about the axis. Assume that the proton begins to rotate clockwise at point a and sweeps out on angle α; $0° \leq \alpha \leq 90°$. At any point b on the arc of this quadrant of rotation, $(r_2)_z$ is the z component of the proton vector r_2 at point b; s is also the radius of the circle of rotation. Using trigonometric relationships

$$(r_2)_z = s\cos\alpha \text{ and } (r_2)_z = r_2\cos\theta \tag{5}$$

$$\cos^2\theta = \frac{s^2\cos^2\alpha}{r_2^2} \tag{6}$$

The average value of the geometric factor, $\langle G_2\rangle$, is readily obtained by integrating over the limits $0° \leq \alpha \leq 90°$.

$$\langle\cos^2\theta\rangle = \frac{s^2}{r_2^2(\alpha_2 - \alpha_1)}\int_{\alpha_1 = 0°}^{\alpha_2 = 90°}\cos^2\alpha\, d\alpha \tag{7}$$

$$\langle\cos^2\theta\rangle = s^2/2r_2^2 \tag{8}$$

$$\langle G_2\rangle = \frac{3\langle\cos^2\theta\rangle - 1}{r_2^3} = \frac{3s^2}{2r_2^5} - \frac{1}{r_2^3} \tag{9}$$

In the nmr spectrum of $Co(NH_3)_6^{2+}$ with no ligand exchange, one would see two proton resonances, each having different dipolar contributions of opposite sign (eq 4 and 9). In the presence of rapid ligand exchange, however, only one signal would be observed, that being the weighted average of the two previous signals.

The dipolar contribution to the average signal contains the average value of the geometric factor, or

$$\langle G\rangle = {}^1/_3 G_1 + {}^2/_3\langle G_2\rangle \tag{10}$$

The two terms in $\langle G\rangle$ are of opposite sign and lead to a partial cancellation of the pseudocontact shift. The expression for $\langle G\rangle$ in terms of r and s for a tetragonal complex is

$$\langle G\rangle = {}^2/_3\left(\frac{1}{r_1^3} - \frac{1}{r_2^3}\right) + s^2\left(\frac{1}{r_2^5} - \frac{1}{r_1^5}\right)$$

Were all the tetragonal distortion removed, then $r_1 = r_2$, $d_1 = d_2$, $\langle G\rangle = 0$, and the dipolar shift would be zero. Of importance, however, is the fact that rapid ligand exchange will greatly diminish the pseudocontact contribution to the isotropic shift for any given proton in a ligand.

This can be simply demonstrated using as an example the complex $Co(NH_3)_6^{2+}$. Let the HNH bond angle be 109° 28′, the NH bond distance be 1.00 Å, and assume a static tetragonal distortion where the axial Co–N bond length is 2.10 Å and the in-plane Co–N bond length is 2.00 Å. The axial Co–H distance is therefore 2.61 Å, and the axial N–Co–H angle is $\theta = 21° 11'$. The radius of the circle of rotation is $s = 0.9428$ Å for both the axial and in-plane ligands, and the in-plane Co–H distance is 2.52 Å. With these values it is found that $G_1 = 9.05 \times 10^{-2}$ Å^{-3} and $G_2 = -4.94 \times 10^{-2}$ Å^{-3}. Hence

$$\langle G\rangle = {}^1/_3(9.05 \times 10^{-2}) + {}^2/_3(-4.94 \times 10^{-2}) = -2.7 \times 10^{-3}\ \text{Å}^{-3}$$

Thus in this example, the geometric factor in the rapid exchange limit is reduced to 0.03–0.05 of the nonexchange value. It is easy to ascertain whether or not rapid exchange occurs so these considerations can be applied easily. A similar analysis would be applicable to the square-pyramidal complex ion[12] $Cu(NH_3)_5^{2+}$ where $G = {}^4/_5 G_{\text{basal}} + {}^1/_5 G_{\text{apical}}$.

Proceeding in a similar way, multiple integrals are used in the derivation of equations for $\langle G\rangle$ for ligands such as benzamide which possess more than two axes of rotation leading to the prediction that there should be very small pseudocontact shifts in octahedral iron(II) and cobalt(II) complexes that undergo rapid exchange even should extensive ion pairing lock in a tetragonal distortion. If, on the other hand, the anions were located on the face of an octahedron, the resulting trigonal distortion would destroy the geometric relations described above, and a pseudocontact contribution could arise which would not be averaged to near zero by exchange.

The effect of ion pairing could be to create a trigonal distortion in the complex or to give rise to g-tensor anisotropy *via* d-orbital perturbation by the anion as was calculated for the cations in $(R_4N^+)_2MX_4^{2-}$ complexes.[13]

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(10) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **3**, 304 (1958).

(11) H. C. Allen, G. F. Kokoszka, and R. G. Inskeep, *J. Am. Chem. Soc.*, **86**, 1023 (1964).

(12) A. A. G. Tomlinson and B. J. Hathaway, *J. Chem. Soc., A*, 1905 (1968).

(13) I. M. Walker and R. S. Drago, *J. Am. Chem. Soc.*, **90**, 6951 (1968).

Those $\Delta\nu$ values in Table III which show pronounced changes with variation in solvent or change in concentration are attributed to this effect.

Nickel(II) Complexes. The observed shifts in the octahedral nickel(II) complexes are believed to be due solely to contact shifts derived from a Fermi contact interaction.[14] The esr spectrum of $Na[Ni(acac)_3]$ (acac = acetylacetonate) perturbed by axial and rhombic fields at 4.2°K was found to be essentially isotropic.[15] A trigonal distortion of the amide ligands *via* ion pairing would also be expected to give rise to an isotropic g-tensor and essentially no pseudocontact shifts.

In both the benzamide and *p*-toluamide complexes the *ortho*-proton resonances are obscured as is shown in Figure 1 for $Ni(BA)_6{}^{2+}$, and the contact shifts for the protons are very small and negative in sign. The *para*-proton and *para*-methyl-proton contact shifts are effectively zero and these protons experience no net spin. Another general observation that may be made is that the contact shifts in both complexes are unusually small. However, in the absence of pseudocontact shift contributions, these observed shifts should be representative of the mechanism of spin delocalization. In octahedral nickel(II), the two unpaired electrons are in the σ-bonding e_g orbitals, and so one expects that the metal–ligand interaction giving rise to the contact shifts will involve a σ-delocalization mechanism. It is generally observed that when a σ-delocalization mechanism is operative, the contact shifts for protons in a ligand are negative and attenuate, the further removed the proton is from the metal ion. It is of interest to inquire if this is valid when the ligand contains a phenyl ring. In the octahedral benzylamine[16] and aniline[17] complexes of nickel(II), the phenyl proton contact shifts are typical of a π distribution even though the metal–ligand bonding interaction involves only σ orbitals. We also find both σ and π spin delocalization in the nickel(II)–benzamide complex discussed herein. For σ delocalization in nickel(II)–benzamide the qualitative prediction for the order of the shifts would be attenuation: $|\Delta\nu_{ortho}| > |\Delta\nu_{meta}| > |\Delta\nu_{para}|$ but instead one finds $|\Delta\nu_{meta}| > |\Delta\nu_{ortho}| > |\Delta\nu_{para}|$. In order to further investigate the mechanism of spin delocalization in $Ni(BA)_6{}^{2+}$, an extended Hückel molecular orbital calculation[5–7] was attempted for benzamide for which the structural parameters of Penfold and White[18] were employed. These investigators found that in the crystalline state benzamide is nonplanar and the phenyl ring is rotated 26° out of the plane containing the amide group. In solutions containing $Ni(BA)_6{}^{2+}$ it is very likely that the phenyl group is freely rotating since the nmr spectra of the nickel(II), cobalt(II), and iron(II) complexes do not show nonequivalent *ortho* or *meta* protons. Furthermore, molecular models show that in $Ni(BA)_6{}^{2+}$, the phenyl groups can freely rotate. Nonplanarity will decrease the amount of conjugation between the phenyl and amide groups, but a small distortion from planarity will not eliminate it. For example, the donor properties of a similar base, N,N-dimethylbenzamide, toward iodine have been studied,[19] and it was concluded that the phenyl ring in N,N-dimethylbenzamide is conjugated with the amide group.

For this calculation the 26° rotamer was chosen to be representative of the benzamide ligand in these complexes. The carbonyl carbon, oxygen, nitrogen, and NH protons of benzamide were placed in the xy plane and the phenyl group was rotated about the x axis.

The nonplanarity of the ligand increases the complexity of the problem since the wave functions do not represent simple σ- or π-molecular orbitals; however, the molecular orbitals and energies of the planar and nonplanar ligand differ only slightly. As an example in the 26° rotamer the highest filled molecular orbital (ψ_5) is very similar to the σ-molecular orbital of the planar configuration; *i.e.*, it is composed primarily of ligand s, p_x, and p_y atomic orbitals with a very small admixture of p_z atomic orbital included. However, an important consequence of this nonplanarity is that the π–σ separation of the molecular orbitals does not occur. The energies of the molecular orbitals for the nonplanar configuration are listed in Table IV.

Table IV. Molecular Orbital Energies of Benzamide (26° Rotamer)

Molecular orbital[a]	E, eV
ψ_9 (π^*)	−4.298
ψ_8 (π^*)	−7.160
ψ_7 (π^*)	−8.231
ψ_6 (π^*)	−9.147
ψ_5 (σ)	−11.159
ψ_4 (π)	−12.152
ψ_3 (σ)	−12.738
ψ_2 (π)	−12.747
ψ_1 (π)	−12.885

[a] The molecular orbitals for the 26° rotamer are not "pure" σ or π orbitals but are of these approximate symmetries.

In a σ-delocalization mechanism for nonplanar benzamide, one would expect the e_g orbitals on nickel to overlap with ψ_5 and thus transmit positive spin directly onto the phenyl protons which make a contribution to this MO because they are not orthogonal. Negative contact shifts would result. In a σ mechanism one is interested in the electron density at the hydrogen nuclei or, more directly, the value of ψ^2 at the nucleus of concern where ψ is the eigenvector of the molecular orbital in which the electron is delocalized. The value of ψ_j at the point (x,y,z) is given by $\Sigma_i C_{ij}\phi_i(x,y,z)$ where C_{ij} is the coefficient of atomic orbital ϕ_i in molecular orbital ψ_j. The numerical values of C_{ij} are taken from the extended Hückel calculation, and from these $\psi_j{}^2$ is evaluated at the proton by means of a computer.[7] The values of $(\psi_5)^2$ evaluated at the *ortho*, *meta*, and *para* protons are, respectively, 3.071×10^{-4}, 3.265×10^{-4}, and 3.686×10^{-4}. ψ^2 in turn for this σ interaction can be directly converted to the coupling constant A_σ by multiplication by a scaling factor of 1877.[7] Since there is no strict π–σ separability, some spin is placed directly into the nonorthogonal phenyl "π orbitals." A minor correction must be made for spin which reaches the proton indirectly *via* the carbon p_z atomic orbitals of ψ_5. In this case A_π can be calculated knowing the coefficients, C_{ij}, of the carbon $2p_z$ orbitals in ψ_5. This is done by

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Table V. Coupling Constants for ψ_5

Proton	ψ^2	A_σ	A_π	A^a
ortho	3.07×10^{-4}	0.579	−0.01	0.58
meta	3.26×10^{-4}	0.616	0	0.62
para	3.69×10^{-4}	0.696	−0.01	0.69

[a] A positive coupling constant is equivalent to a negative contact shift.

multiplying the respective C_{ij}^2 value by a scaling factor of 28.5.[8] The resulting number is A_π and the total coupling constant A equals $A_\sigma + A_\pi$. The coupling constants for these protons are listed in Table V. Were benzamide planar, A_π would be zero for σ spin delocalization in ψ_5. In this calculation A_π is negligible compared to A_σ since for the *ortho* and *para* protons, $A_\pi = -0.01$ G. A_π cannot be calculated for the *meta* proton because configuration interaction was not incorporated into this extended Hückel calculation, but it also would be expected to be small.

Assuming that spin is delocalized into ψ_5, one would expect the contact shifts at the phenyl protons to be directly proportional to their respective calculated (molecular orbital) coupling constants and $A_{ortho}:A_{meta}:A_{para} = \Delta\nu_{ortho}:\Delta\nu_{meta}:\Delta\nu_{para}$. This is not found, and so the contact shifts observed for $Ni(BA)_6^{2+}$ cannot be accounted for solely by metal–ligand σ delocalization involving ψ_5.

One other remaining possibility is that all benzamide rotamers are equally important in the σ delocalization of spin in ψ_5. However, calculations on both the 90° rotamer and planar benzamide molecule show that the ratio of proton coupling constants ($A_{ortho}:A_{meta}:A_{para}$) is changed only slightly when compared to the 26° rotamer. Thus σ delocalization of positive spin into ψ_5 is considered inadequate in explaining the contact shifts, even if free rotation of the phenyl group were assumed. The MO result is of interest in that it shows one cannot *a priori* expect a σ-delocalization mechanism to be characterized by attenuation in the contact shift as one proceeds away from the donor center. The prediction for a σ-delocalization mechanism in this ligand is $A_{para} > A_{meta} > A_{ortho}$.

It is very probable that a second mechanism is simultaneously occurring in which unpaired spin is being transferred to a π orbital, say ψ_4 or ψ_6. By virtue of the complex symmetry the ligand ring π orbitals are not orthogonal to the metal ion e_g orbitals. Of these two "π-type" orbitals, ψ_4, which is a bonding orbital, has a more favorable energy and we believe that some net positive spin density is residing in ψ_4. Spin is then delocalized within ψ_4 according to the eigenvector coefficients. For this mechanism values of A and A_σ, A_π are calculated for the phenyl protons by the same method used for ψ_5. These coupling constants are listed in Table VI. Although ψ_4 predominantly delocalizes spin indirectly *via* the $2p_z(\pi)$ atomic orbitals, some spin is delocalized directly *via* the s, p_x, and p_y atomic orbitals leading to what we shall call A_σ. Delocalization of spin up into ψ_4, which is predominantly a "π-type" molecular orbital, results in alternation of coupling constants and contact shifts. Positive contact shifts at the *ortho* and *para* protons and negative contact shifts at the *meta* protons are expected. In comparing values of A for both the ψ_4 and ψ_5 mechanisms, it is seen that at the *ortho* proton $A(\psi_4)$ and $A(\psi_5)$ are of opposite sign and tend to cancel the effect of each other. The same is true for the *para*-proton coupling constants. The *meta* coupling constants on the other hand are both positive. This implies that when both mechanisms are operative $\Delta\nu_{ortho}$ and $\Delta\nu_{para}$ should be quite small while $\Delta\nu_{meta}$ is much larger and is negative. However, it is difficult if not impossible to quantitatively predict from the calculations the correct coupling constants for all three protons, because one does not know the importance of the mechanism involving ψ_4 relative to the mechanism involving ψ_5 or the magnitude of the contribution from ψ_6. Furthermore, rotation of the phenyl group creates uncertainties as to the numerical values of the coefficients in the wave functions ψ_4 and ψ_5, since the molecular orbital calculations involved only one rotamer. As a rough estimate, however, twice as much spin could be delocalized *via* ψ_5 as compared to ψ_4. The effect of this would be that $A_{para} \cong 0$, and $A_{meta} > A_{ortho} > 0$.

Table VI. Coupling Constants for ψ_4

Proton	$C_4^{2\,a}$	A_π, G	A_σ	$A = A_\pi + A_\sigma$
ortho	2.35×10^{-2}	−0.669	+0.307	−0.362
meta	. . .	0^b	+0.232	+0.2
para	4.49×10^{-2}	−1.28	+0.115	−1.16

[a] C_4^2 is the square of the value of the carbon $2p_z$ coefficient for the phenyl carbon atoms. [b] A_π is positive because of configuration interaction.

The Iron(II)–Benzamide Complexes. The observed contact shifts of the iron(II) complexes listed in Table III suggest a π mechanism for spin delocalization. However, both a σ mechanism and pseudocontact shift contribution may be of some importance. Because of the alternation of the isotropic shifts of the phenyl protons in $Fe(BA)_6^{2+}$ (that is, $\Delta\nu_{ortho}$, $\Delta\nu_{para} > 0$, and $\Delta\nu_{meta} < 0$), a π mechanism seems likely.

A complicating factor in the interpretation of the isotropic shifts arises because of ion pairing. The nmr spectra of $Fe(BA)_6(ClO_4)_2$ and $Fe(BA)_6(BF_4)_2$ have been examined in two solvents: acetone and propylene carbonate. As can be seen in Table III, the isotropic shifts of both complexes are different, and all the shifts are concentration dependent, although not as concentration dependent as the analogous cobalt(II) complexes. This is attributed to an ion-pairing equilibrium with the ion-paired species predominating at higher concentrations. The isotropic shift for a given proton is then an average of the shifts in the solvated cation and the ion-paired cation. As mentioned previously, the isotropic shift of the ion-paired species should contain a pseudocontact contribution. The literature[12,20,21] now contains several examples of this phenomenon. This dipolar shift has a r^{-3} dependence, so on this basis one expects that it is least important at the *para* position and more important at the *ortho* and *meta* positions in $Fe(BA)_6^{2+}$. However, the $3\cos^2\theta - 1$ term could easily dominate invalidating this sort of argument. From the observed concentration dependence of the isotropic shifts it appears that the r^{-3} dependence results in the absence of the pseudocontact shift at the *para* proton of $Fe(BA)_6^{2+}$. The *ortho*- and *meta*-proton shifts are somewhat concentration dependent and may have a minor pseudocontact shift contribution, whereas the *para*-proton shift is not

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concentration dependent. This implies that at the *para* proton the isotropic shift is dominated by the contact term. The *para*-proton contact shift for $Fe(BA)_6{}^{2+}$ and similarly the *para*-methyl-proton contact shift for $Fe(PTA)_6{}^{2+}$ can therefore be used as probes for elucidating the mechanism of spin delocalization in the iron(II) complexes.

The d-electron configuration of iron(II) is $t_{2g}{}^4e_g{}^2$, so there exists the possibility of metal–ligand spin delocalization *via* the σ-bonding e_g orbitals and the π-bonding t_{2g} orbitals. In a π system the spin density, σ_i, at the *i*th carbon atom in a phenyl ring is related to the electron–proton coupling constant A_i for the attached proton by formula 11, proposed by McConnell.[22] Q_H is a proportionality constant and is equal to -22.5 G for a proton and approximately 27 G (Q_{CH_3}) for a *para*-substituted methyl group in a phenyl ring. It follows that if spin is delocalized into ψ_4, the highest filled "π-type" molecular orbital, $\Delta\nu_{p\text{-}CH_3}$ for $Fe(PTA)_6{}^{2+}$ and $\Delta\nu_{p\text{-}H}$ for $Fe(BA)_6{}^{2+}$, should obey eq 12. Very good agreement is found experimentally; for example, in acetone solution comparing $Fe(BA)_6(ClO_4)_2$ and $Fe(PTA)_6(ClO_4)_2$, $\Delta\nu_{p\text{-}CH_3}/\Delta\nu_{p\text{-}H} = -1.16$ and $Q_{CH_3}/Q_H = -1.20$. This suggests that at the *para* position in the iron(II) complexes, the unpaired spin reaches the protons *via* a π mechanism involving only ψ_4. At the *ortho* and *meta* protons, the isotropic shifts are most likely due to a π-contact interaction with possible contributions from a σ delocalization and a pseudocontact interaction.

$$A_i = Q_H\sigma_i \qquad (11)$$

$$\Delta\nu_{p\text{-}CH_3}/\Delta_{p\text{-}H} = Q_{CH_3}/Q_H \qquad (12)$$

The molecular orbital calculations on benzamide also confirm the alternation of contact shifts for the predominance of a π delocalization mechanism in the iron(II) complexes. In nonplanar benzamide, the "π-like" molecular orbital of interest is ψ_4. Of importance are the charge densities of the phenyl carbon $2p_z$ atomic orbitals in this molecular orbital. Listed in Table VII are the charge densities of the $2p_z$ atomic orbitals in ψ_4. As can be seen, ψ_4 is centered predominantly on the amide part of the ligand, explaining the small magnitude of the contact shifts. Were spin delocalized into ψ_4, very little spin would reach the phenyl carbon $2p_z(\pi)$ atomic orbitals. Again, were configuration interaction included, the charge densities in the $2p_z$ atomic orbitals of C_{meta} would be negative thus showing the predicted alternation of charge densities for the phenyl carbon $2p_z$ atomic orbitals. Mixing ψ_4 with metal t_{2g} orbitals would put spin up in ψ_4 resulting in positive contact shifts at the *ortho* and *para* protons. The calculation also correctly predicts that $\Delta\nu_{para} > \Delta\nu_{ortho}$ for the delocalization of spin into ψ_4 from the t_{2g} metal orbitals, requiring, however, that the pseudocontact shift contributions to the *ortho*- and *meta*-proton isotropic shifts are not as significant.

Table VII. Charge Densities in Benzamide

MO	C_1- (C=O)	C_2	C_{ortho}	C_{meta}	C_{para}	O	N
ψ_4	0.1137	0.0663	0.0515	0.0130	0.0997	0.6995	0.3938

As shown in previous studies,[16,17] one cannot infer the existence of metal–ligand π-bonding interactions simply because the contact shifts in a given Ni(II) complex indicate π delocalization. With these findings, one of the earliest and most attractive features of the contact shift experiment was destroyed. However, in this work we have conclusive evidence for a π-bonding interaction in $Fe(BA)_6{}^{2+}$ involving the metal t_{2g} orbitals from a comparison of the iron(II) and nickel(II) shifts. The shift ratio for the nickel(II) complexes is characteristic of an interaction, involving the metal e_g orbitals. The different delocalization mechanism found for iron(II) results from mixing the t_{2g} metal orbitals and the filled π-ligand orbitals. Since there are five electrons in the t_{2g} set, the net effect of this interaction is probably antibonding, unless ψ_6 is involved.

The Cobalt(II)–Benzamide Complexes. Many of the considerations important in the discussion of the iron(II) isotropic shifts apply also to those of the cobalt(II) complexes because in both metal ions there are unpaired t_{2g} and e_g electrons. Again both the σ and π metal–ligand delocalization mechanisms may be operative, and the effects of ion pairing must be considered. The observed shifts of the cobalt(II) complexes are listed in Table III. The isotropic shifts attenuate for both $Co(BA)_6(ClO_4)_2$ and $Co(BA)_6(BF_4)_2$ in both solvents. Were the contact shifts the result of a σ mechanism *via* the metal e_g orbitals and ψ_5, the *para*-methyl-proton contact shift in $Co(PTA)_6{}^{2+}$ would be numerically smaller than the *para*-proton contact shift in $Co(BA)_6{}^{2+}$. To the contrary one finds that in an acetone solution, for example, $\Delta\nu_{p\text{-}H} = -36$ cps for $Co(BA)_6(ClO_4)_2$ and $\Delta\nu_{p\text{-}CH_3} = -76$ cps for $Co(PTA)_6(ClO_4)_2$. This means that both a π-contact shift contribution and a pseudocontact shift contribution are important at the *para* proton—and for that matter, at both the *ortho* and *meta* protons.

Of particular interest is the variation of isotropic shifts upon changing the anion from $ClO_4{}^-$ to $BF_4{}^-$. These changes (Table III) are quite remarkable in acetone but are negligible in propylene carbonate. Since acetone (ϵ 20.7) has a quite lower dielectric constant than propylene carbonate (ϵ 69.0), one would expect that a change in the anion would affect the ion-pairing equilibrium in acetone more than in propylene carbonate.

One difference between the nmr spectra of the iron(II) and cobalt(II) complexes is that the dipolar shift is far more important in the latter complexes. If the r^{-3} term for the dipolar shift is dominant, this shift would be expected to vary in magnitude for the benzamide complexes as follows: $\Delta\nu_{ortho} > \Delta\nu_{meta} > \Delta\nu_{para}$. This is also the trend of the isotropic shifts in $Co(BA)_6{}^{2+}$. The marked concentration dependence of the *ortho*- and *meta*-proton contact shifts is further evidence in support of a large dipolar shift due to ion pairing. Undoubtedly, the dipolar contribution to the isotropic shift is very important for the cobalt(II) complexes. Because of this dominance of the dipolar shift it is impossible to determine the σ and π contributions to the spin delocalization; however, one might expect a mechanism similar to that of the iron(II) complexes.

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Pentamethylcyclopentadienylrhodium and -iridium Halides. I. Synthesis and Properties[1]

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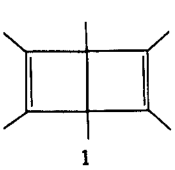
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. *Received April 15, 1969*

Abstract: Details of the reactions of hexamethyl(Dewar benzene), HMDB (hexamethylbicyclo[2.2.0]hexadiene) (**1**), and of 1-(1-chloroethyl)pentamethylcyclopentadiene (**4a**) with $RhCl_3 \cdot 3H_2O$ and $IrCl_3 \cdot 5H_2O$ to give the pentamethylcyclopentadienyl complexes, $(C_5Me_5MCl_2)_2$ (**5**), and proposals for the mechanisms of these reactions are presented. The pentamethylcyclopentadienyl–metal bond in **5** is very strong, but reactions readily proceed at the halogens. Adducts of the type $C_5Me_5RhCl_2L$ (L = *p*-toluidine, pyridine, triphenylphosphine) are described as well as their reactions to form $C_5Me_5RhMe_2PPh_3$ and $C_5Me_5RhMeIPPh_3$. The synthesis of $C_5Me_5Ir(CO)_2$ is also reported.

In 1967 one of us, in connection with some work on the complexes derived from 2-butyne and palladium chloride, began an investigation of the reactions of hexamethyl(Dewar benzene) (HMDB, hexamethylbicyclo[2.2.0]hexadiene) (**1**) toward transition metal halides. This led, in the first instance, to the preparation of hexamethyl(Dewar benzene)palladium chloride (**2**, M = $PdCl_2$),[3] and later to that of the platinum analog (**2**, M = $PtCl_2$).[4] At the same time, a number of other authors reported the synthesis of other HMDB complexes, notably of the group VIb metals (**2**, M = $Cr(CO)_4$, $Mo(CO)_4$, and $W(CO)_4$)[5] and of rhodium(I) (**2**, M = RhCl, dimer).[6] The X-ray crystal structure determination of **2** (M = $Cr(CO)_4$) is in agreement with the proposed structure.[7]



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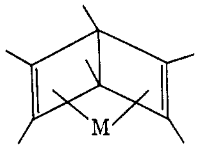

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Our interest in these complexes, especially as possible intermediates in the metal-catalyzed trimerization of 2-butyne,[8] led us to explore the reactions of HMDB toward rhodium and iridium trichloride hydrates.[9]

Results and Discussion

Formation of Dichloro(pentamethylcyclopentadienyl)-rhodium and -iridium Complexes from HMDB and Related Compounds. The Dewar benzene (**1**) reacted readily with $RhCl_3 \cdot 3H_2O$ in methanol at 65° under nitrogen to give a nearly quantitative yield (based on $RhCl_3 \cdot 3H_2O$) of red crystals, together with a substantial amount of hexamethylbenzene (HMB). HMDB is normally quite stable to isomerization under these conditions in the absence of the metal halide;[10] even in the presence of acid only a small degree of isomerization was observed by Criegee and Grüner.[11] The metal must therefore play an important role in this isomerization.

The red crystals were finally identified as dichloro(pentamethylcyclopentadienyl)rhodium dimer (**3**).[12] The methanol and other volatile products were distilled off and analyzed by a combination of vpc and mass spectrometry, and found to contain, apart from methanol, one major component and two minor ones. The major component was isolated and shown to be dimethylacetal ($MeCH(OMe)_2$), and the minor ones were identified as methyl chloride and dimethyl ether. The two latter compounds do not appear to be significant as far as the general ring-contraction reaction is concerned since they were also observed to occur in reactions in which rhodium trichloride was heated in methanol containing sodium carbonate in the absence of HMDB.

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(12) This complex was simultaneously prepared by Booth, Haszeldine, and Hill, who reported it as a hexamethylbenzenerhodium(III) complex $[(C_6Me_6RhCl)_2]Cl_4$.[13] As reported earlier by Kang and Maitlis,[14] this formulation is incorrect; Booth, *et al.*, now concur with our proposed structure.[15]

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