

buffer solutions of varying, but known, pH in the vicinity of the  $pK_a$  of the dye. Optical density vs. wave-length curves were recorded for all solutions over a range of wave lengths which included the maximum for the acid and base forms of each compound. The  $pK_a$  values were then evaluated in the several buffer solutions using the method of simultaneous equations required when the base and its conjugate acid have overlapping absorptions.<sup>23</sup> Averaged values for the eight compounds are reported in Table II and are shown plotted against  $\sigma$ -values<sup>24,25</sup> in Figure 4.

**Spectroscopic Studies.** Samples of the various compounds were dissolved in acetonitrile or in acetone-water mixtures of the appropriate compositions, and the position of their visible absorption bands was determined using a Cary Model 14 recording spectrophotometer. Transition energies were calculated from the expression<sup>11</sup>  $E_t = 285,900/\lambda$ . Data for  $E_t$  vs. substituent are listed in Table II. Data for  $E_t$  vs.  $Z$  values for *p*-CH<sub>3</sub>O-I and -II in acetone-water mixtures are recorded in Table III.

**N.m.r. Spectra.** <sup>1</sup>H spectra were recorded at 60 Mc./sec. on a Varian Model A-60 spectrometer with acetonitrile as solvent. Chemical shifts were measured relative to solvent and are listed as p.p.m. relative to tetramethylsilane. The <sup>11</sup>B spectra were obtained at 19.3 Mc./sec. on a Varian Model HR-60 spectrometer with acetonitrile or water as solvent. Chemical shifts were calculated relative to an external boron trifluoride etherate standard.

**General Procedure for the Hydrosulfite Reduction of the Dyes.** Four grams (15 mmoles) of unsubstituted I as its K<sup>+</sup> salt was dissolved in 100 ml. of water and the pH adjusted to about 12 by the addition of KOH pellets. Sufficient base was added to maintain the pH at about 12, along with 5.0 g. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. After

(23) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962.

(24) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 184.

(25) P. W. Wells, *Chem. Rev.*, **63**, 171 (1963).

stirring 30 min. the solution was acidified to pH 0.5, and after an additional 15 min. it was filtered. Aqueous tetramethylammonium chloride was added, whereupon 2.4 g. of (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>9</sub>NH<sub>3</sub> (77%) precipitated and was collected by filtration. Recrystallization from dimethyl sulfoxide-water afforded an analytical sample. *Anal.* Calcd. for B<sub>10</sub>C<sub>4</sub>H<sub>24</sub>N<sub>2</sub>: C, 23.1; H, 11.5; N, 13.5; B, 51.9; equiv. wt., 208. Found: C, 25.4; H, 11.8; N, 13.4; B, 49.9; equiv. wt., 201. The filtrate was made basic and extracted with two 25-ml. portions of ether. The ether was concentrated to about 15 ml. and HCl added. Aniline hydrochloride, 1.1 g. (54%), precipitated and was collected by filtration. Its infrared spectrum was identical with an authentic sample.

**10-NH<sub>3</sub><sup>+</sup>-I.** Acetonitrile (50 ml.) containing 3.7 g. (1.9 mmoles) of benzenediazonium tetrafluoroborate was added to a solution of 4.0 g. (1.9 mmoles) of (CH<sub>3</sub>)<sub>4</sub>NB<sub>10</sub>H<sub>9</sub>NH<sub>3</sub> in 1 l. of acetonitrile and stirred at room temperature overnight. The acetonitrile was removed *in vacuo* and the product taken up in methanol. The product was precipitated by addition of water and recrystallized from aqueous methanol to give 1.5 g. (32%) of 10-NH<sub>3</sub><sup>+</sup>-I. *Anal.* Calcd. for C<sub>6</sub>H<sub>17</sub>N<sub>3</sub>B<sub>10</sub>: B, 45.2. Found: B, 44.1. An aqueous solution of the base form was prepared by extraction of an ethereal solution of the acid with aqueous KOH.

**1,10-(H<sub>3</sub>N)<sub>2</sub>B<sub>10</sub>H<sub>8</sub>.** Reduction of 10-NH<sub>3</sub><sup>+</sup>-I with excess tin in a 30:70 hydrochloric acid-methanol solvent afforded 1,10-(H<sub>3</sub>N)<sub>2</sub>B<sub>10</sub>H<sub>8</sub> in 48% yield. The excess tin was removed by filtration and the solvent removed *in vacuo*. The product was recrystallized from aqueous ethanol and gave, after drying at 100° *in vacuo*, an infrared spectrum which was superimposable with that of an authentic sample.

**Acknowledgments.** The authors wish to thank the Alfred P. Sloan Foundation and the Army Research Office (Durham) for generous support of this work. We also wish to thank Dr. E. L. Muettterties for an infrared spectrum of authentic 1,10-(NH<sub>3</sub>)<sub>2</sub>B<sub>10</sub>H<sub>8</sub>.

## Trends in Transition Metal Ion-Ligand Covalency from Nuclear Magnetic Resonance Contact Shifts

Bradford B. Wayland<sup>1</sup> and Russell S. Drago

Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois. Received December 7, 1964

*N.m.r. contact shifts are reported for a series of transition metal ion complexes of hexamethylphosphoramide. Evidence is reported to indicate that several of these complexes exist as tetrahedral complexes in the solvent nitrobenzene. The effect of excess ligand on the species in solution is investigated. The contact shifts also*

*indicate that pronounced changes occur when several of the complexes are dissolved in some acidic and basic solvents. The n.m.r. contact shifts of the tetrahedral complexes are interpreted as indicating an increase in covalent bonding ability for the series Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II). The electron spin-nuclear spin coupling constants are found to correlate with the respective metal ion ionization potentials and with the first formation constant for some oxygen donors with the respective metal ions.*

(1) Abstracted in part from the Ph.D. Thesis of B. B. Wayland, University of Illinois, Urbana, Ill.; N.S.F. Graduate Fellow, 1963-1964.

## Introduction

The use of nuclear magnetic resonance (n.m.r.) as a means of studying paramagnetic complexes is yet in its infancy. Until recently it was widely thought that it was impossible to do n.m.r. experiments on compounds possessing unpaired electrons. Unpaired electrons in orbitals which have a finite existence at the magnetic nucleus affect the n.m.r. spectrum of that nucleus through both relaxation broadening and a large shift in the position of resonance.<sup>2-4</sup> The requisite condition for observing the n.m.r. of a paramagnetic compound is that either or both  $1/Te \gg A_n$  and  $1/Tc \gg A_n$  is fulfilled, where  $1/Te$  is the rate of electron spin relaxation,  $1/Tc$  is the rate of chemical exchange, and  $A_n$  is the unpaired electron spin-nuclear spin coupling constant.<sup>5,6</sup> When this condition is fulfilled, the nucleus senses only the time-averaged spin orientation of the unpaired electron. In the absence of a magnetic field there is in general an equal population of the possible electron spin states. In the presence of a magnetic field the degeneracy of the electron spin states is removed, and there is thus a population distribution. The spin state in which the magnetic field of the electron is oriented with the external field is of lowest energy, and thus has the largest population. Contact n.m.r. shifts arise from the effects due to this small population difference in the electron spin states. Fortunately, the electron spin relaxation or ligand-exchange rates of many transition metal ion complexes in solution are sufficiently fast so as to allow observation of the n.m.r. spectra of ligand nuclei. The shifts in the n.m.r. arising from electron spin-nuclear spin coupling are called contact shifts.

The general quantitative relationship between the electron spin-nuclear spin coupling constant and the contact shift is given by eq. 1.<sup>7,8</sup> The quantity  $\Delta\nu$

$$\frac{\Delta\nu}{\nu} = -\frac{4}{9} A_n \frac{\gamma_e g \beta I(I+1) S(S+1)}{\gamma_n kT} \quad (1)$$

is the n.m.r. shift,  $\nu$  the resonant frequency (60 Mc. in our work),  $\beta$  the Bohr magneton,  $I$  the nuclear spin,  $S$  the electron spin,  $\gamma_e/\gamma_n$  the magnetogyric ratio for the electron and the nucleus, and  $A_n$  the electron spin-nuclear spin coupling constant. Equation 3 gives this relationship evaluated for nuclei with nuclear spin ( $I$ ) equal to  $1/2$ . The isotropic contact shift arises principally from the Fermi contact term which is proportional to the electron density at the nucleus.<sup>9-11</sup> The nuclear spin and electron spin may couple due to the finite probability of s-type electrons existing at the nucleus. A through space dipolar shift (pseudo-contact shift) can arise when the complex is not magnetically isotropic.<sup>12,13</sup> This effect is considered in the

Discussion section in relation to the specific complexes studied. The magnitude of the true contact shift for hydrogen nuclei is thus directly related to the unpaired electron density in the hydrogen 1s orbital. The amount of unpaired electron density at the proton is of course directly related to the total odd electron density on the molecule. The amount of unpaired spin density ( $\rho$ ) in the hydrogen 1s orbital can be calculated from

$$A_H = A_H \cdot \rho_H \quad (2)$$

where  $A_H$  is the measured electron proton coupling constant in the molecule,  $\rho_H$  is the spin density in the hydrogen 1s orbital, and  $A_H$  is the electron spin coupling-nuclear spin coupling constant for the hydrogen atom ( $A_H = 1420$  Mc./sec.).<sup>14</sup>

One important and unique feature of the n.m.r. contact shift experiment is the determination of both the magnitude and sign of the electron spin-nuclear spin coupling constant. This technique has been used to demonstrate that the sign of the coupling constant for an electron in a  $p\pi$  orbital of  $sp^2$  carbon with the nucleus of a directly bonded hydrogen is negative and that the coupling constant with the protons of a directly bonded methyl group is positive.<sup>15</sup> From the knowledge of the magnitude of the coupling constant the amount of electron delocalization can be assessed. In some cases the sign of the coupling constant for ligands in transition metal ion complexes helps determine the mechanism of electron delocalization by aiding in determining which metal orbitals are the source of the unpaired electron and which ligand orbitals the unpaired electron occupies.<sup>16-18</sup>

Contact shifts for isotropic complexes arise from covalency in the metal ion-ligand bond, for an ionic interaction cannot give rise to electron delocalization. Measurements of contact shifts can thus offer a direct means of assessing covalency in transition metal ion complexes. The only other method of directly measuring covalency in complexes is electron spin resonance (e.s.r.).<sup>19,20</sup> The principal difficulty in e.s.r. studies is that the magnetic moments of the ligand nuclei make only a small perturbation on the unpaired electron, and in only a few cases can the electron-nuclear coupling be resolved. In contrast, the unpaired electron delocalized onto the ligand makes a very large perturbation on the nuclear magnetic moments. Thus n.m.r. contact shifts offer a generally applicable and sensitive tool for directly observing covalency in metal-ligand bonding.

The recent work on the tetrahedral Ni(II) aminotroponeiminoates has stimulated a general investigation into the contact n.m.r. shifts of ligand nuclei in para-

(2) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **27**, 314 (1957).

(3) D. A. Levy and L. E. Orgel, *Mol. Phys.*, **3**, 583 (1960).

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 207-211.

(5) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

(6) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *ibid.*, **37**, 347 (1962).

(7) N. Bloembergen, *ibid.*, **27**, 595 (1957).

(8) T. W. Swift and R. E. Connick, *ibid.*, **37**, 307 (1962).

(9) S. I. Weissman, *ibid.*, **25**, 890 (1956).

(10) H. M. McConnell, *ibid.*, **24**, 764 (1956).

(11) A. J. Freeman and R. E. Watson, *Phys. Rev. Letters*, **6**, 343 (1961).

(12) N. Bloembergen and W. C. Dickinson, *Phys. Rev.*, **79**, 179 (1950).

(13) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(14) J. A. Brivati, N. Keen, and M. C. R. Symons, *J. Chem. Soc.*, 237 (1962).

(15) A. Foreman, J. N. Murrell, and L. E. Orgel, *J. Chem. Phys.*, **27**, 314 (1957).

(16) R. E. Watson and A. J. Freeman, *Phys. Rev. Letters*, **6**, 277 (1961).

(17) J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

(18) W. D. Phillips and R. E. Benson, *ibid.*, **33**, 607 (1960).

(19) J. Owen, *Discussions Faraday Soc.*, **19**, 127 (1955).

(20) R. E. Robertson, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and N. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962, pp. 617-660.

magnetic complexes.<sup>6, 18, 21, 22</sup> Back  $\pi$ -bonding in transition metal ion complexes of nitriles,<sup>23</sup> phosphines, and isonitriles,<sup>24</sup> and electron delocalization in  $\sigma$ -bonding orbitals of pyridine bonded to Ni(II) and Co(II)<sup>17</sup> acetylacetonate are several very interesting recent studies. This article is the first in a series that will report investigations of the changes in the n.m.r. contact shift as one parameter is systematically varied in a series of transition metal ion complexes. In this paper, the effect of varying the transition metal ion in a series of complexes which are otherwise very similar will be reported. Since a series of transition metal ion complexes of hexamethylphosphoramide (HMPA, [(CH<sub>3</sub>)<sub>2</sub>N]<sub>3</sub>PO) have been reported to have very similar symmetries,<sup>25, 26</sup> they were considered ideal for this study. The data obtained can be interpreted in terms of the effect on the n.m.r. contact shift due to the relative tendencies of the metal ions to undergo covalent interactions with the ligand.

## Experimental

*Apparatus. a. N.m.r. Spectra.* The n.m.r. spectra were obtained with a Varian Model A-60 and a Varian Model DP-60 n.m.r. spectrometer. A Varian temperature control unit was used and temperature measurements were made by utilizing the temperature dependence of the hydroxyl resonance of methanol and ethylene glycol. The temperature was held constant at  $\pm 1.0^\circ$ . All n.m.r. spectra were measured relative to tetramethylsilane (TMS) as an internal standard.

*b. Visible and Ultraviolet Spectra.* All near-infrared, visible, and ultraviolet spectra were determined using a Cary recording spectrophotometer Model 14M. Infrared spectra were recorded using a Perkin-Elmer Model 521.

*c. Magnetic Susceptibility Measurements.* Solid and solution magnetic susceptibilities at  $28^\circ$  were measured using a Guoy magnetic balance. The Guoy tubes were calibrated using Hg(Co(NCS)<sub>4</sub>). The measured susceptibilities were corrected for diamagnetism by use of Pascal's constants. The temperature dependence of the magnetic susceptibilities of the solid complexes of Ni(II) and Fe(II) were measured on a Faraday balance with temperature-controlling apparatus. The calculations involved are described in detail by Figgis and Lewis.<sup>27</sup>

*Reagents and Solutions.* Hexamethylphosphoramide (HMPA) (Fisher) was distilled from barium oxide at reduced pressure. The middle fraction boiling at  $127^\circ$  (20 mm.) was collected. The material 2,2-dimethoxypropane was obtained from Dow Chemical Co. and was used without further purification. Reagent grade CH<sub>3</sub>NO<sub>2</sub> and CDCl<sub>3</sub> were used without further purification. Methylene chloride, nitrobenzene, and acetone were dried over Linde 3A Molecular Sieves.

(21) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).

(22) D. R. Eaton, W. D. Phillips, and P. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963).

(23) R. S. Drago and B. B. Wayland, to be published.

(24) W. D. Horrocks, Jr., R. C. Taylor, and G. N. LaMar, *J. Am. Chem. Soc.*, **86**, 3031 (1964).

(25) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

(26) J. T. Donoghue and R. S. Drago, *ibid.*, **2**, 572 (1963).

(27) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp. 400-454.

All solutions of hygroscopic materials were prepared in a drybox equipped with an automatic continuous air flow drying system.

*Preparation of Complexes.*  $M(\text{HMPA})_4(\text{ClO}_4)_2$ . The method of preparation of HMPA complexes has been previously reported.<sup>25, 26</sup> The general procedure consists first of dehydrating the hydrated metal perchlorate with excess 2,2-dimethoxypropane for several hours. An excess of HMPA is then added. The complexes are precipitated by addition of excess diethyl ether. The solids are washed several times with ether and dried *in vacuo* over sulfuric acid or P<sub>2</sub>O<sub>5</sub>.

*Treatment of N.m.r. Data.* The HMPA complexes studied here are all sufficiently paramagnetic so that at high temperatures essentially all of the molecules are in the paramagnetic state. For such a system, the temperature dependence of the contact shift is given by

$$\frac{\Delta\nu}{\nu} = -A_n \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{3kT} \quad (3)$$

or

$$\Delta\nu = -A_n \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)\nu}{3kT}$$

where  $\gamma_e/\gamma_H = 6.577 \times 10^2$ ,  $g = \mu_{\text{eff}}/\sqrt{S(S+1)}$ ,  $\beta = 9.273 \times 10^{-21}$  erg gauss<sup>-1</sup>,  $S$  is the sum of the electron spins, and  $A_n$  is determined from the slope of the linear plot of  $\Delta\nu$  (c.p.s.) vs.  $1/T$  ( $^\circ\text{K.}$ ). All of the complexes studied had linear  $\Delta\nu$  (c.p.s.) vs.  $1/T$  ( $^\circ\text{K.}$ ) plots in the high-temperature region, but nonlinearity was observed in the low-temperature region for all metal ions except Co(II). This indicates the presence of a species other than the tetrahedral complex at the lower temperature. The linearity of the plots at temperatures greater than  $50^\circ$  indicates that essentially all of the molecules are in a given paramagnetic state at these temperatures. The measurements above room temperature were carried out in nitrobenzene and those below room temperature in nitromethane.

All of the complexes studied in this work exchange rapidly with excess ligand. Addition of excess ligand leads to a single averaged line position and shape. The line widths and chemical shifts of the complexed HMPA species are calculated from a knowledge of the stoichiometry of the system and the line shape and chemical shift of the free ligand.<sup>28</sup> The chemical shift of the protons in the complex may be calculated from eq. 4.

$$(\text{fraction complexed}) \Delta\nu(\text{complex}) + (\text{fraction free}) \Delta\nu(\text{free}) = \Delta\nu(\text{obsd.}) \quad (4)$$

The line widths of the n.m.r. of ligand nuclei in paramagnetic complexes are generally very large when compared to the diamagnetic complex or free ligand. The n.m.r. line width of nuclei in the complex can be calculated from eq. 5 which assumes the limit of very fast exchange and a large excess of diamagnetic species.<sup>29</sup>  $D$  is the concentration of diamagnetic species,

$$\left(\frac{1}{T_2\rho}\right)_P = \frac{D}{P}Z \quad (5)$$

(28) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(29) M. W. Dietrich and A. C. Wahl, *ibid.*, **38**, 1591 (1963).

**Table I.** Solvent Effects on the N.m.r. Spectra of  $M(\text{HMPA})_4(\text{ClO}_4)_2$ 

$M^{+2}$	Solvent	$-\Delta\nu$ , c.p.s. <sup>a</sup>
Cu <sup>+2</sup>	CH <sub>3</sub> NO <sub>2</sub>	315 ± 5
	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	314 ± 2
	CH <sub>2</sub> Cl <sub>2</sub>	315 ± 5
	CDCl <sub>3</sub>	218 ± 2
	CH <sub>3</sub> C(O)CH <sub>3</sub>	285 ± 2
Ni <sup>+2</sup>	CH <sub>3</sub> C≡N	265 ± 2
	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	365 ± 2
	CH <sub>3</sub> NO <sub>2</sub>	358 ± 3
	CDCl <sub>3</sub>	299 ± 1
	CH <sub>3</sub> C(O)CH <sub>3</sub>	213 ± 1
Co <sup>+2</sup>	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	337 ± 1
	CH <sub>3</sub> NO <sub>2</sub>	332 ± 1
	CH <sub>2</sub> Cl <sub>2</sub>	332 ± 1
Fe <sup>+2</sup>	CH <sub>3</sub> C(O)CH <sub>3</sub>	338 ± 2
	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	350 ± 1
	CH <sub>3</sub> NO <sub>2</sub>	350 ± 1
	CH <sub>3</sub> C(O)CH <sub>3</sub>	345 ± 2

<sup>a</sup> Chemical shifts are relative to TMS as an internal standard; concentrations are about 0.2 M; 32°.

arise from coupling. The proton n.m.r. spectrum of  $\text{Zn}(\text{HMPA})_4(\text{ClO}_4)_2$  consists of a doublet separated by 9.8 c.p.s. This is also good evidence that the doublet arises from coupling, for the nonequivalence of the two methyl groups would not be expected to be identical in the complex and pure HMPA.

In order to use eq. 4 to calculate the contact shift of the complex, one must demonstrate that the chemical shift of the uncomplexed ligand is concentration independent. The chemical shift of neat HMPA is found to be 157.2 c.p.s. relative to TMS. The same result is obtained for weight fractions of HMPA in CH<sub>3</sub>NO<sub>2</sub> of 0.65, 0.44, and 0.25.

In order to evaluate the effect of solvent on the n.m.r. contact shift and to gain evidence for the stability of the complexes, the contact shifts of the pure complexes in a series of different solvents were studied. The range of solvents employed for the iron(II) complex is limited by solubility properties. The results are contained in Table I.

**Table II.** N.m.r. Contact Shifts and Line Widths of  $M(\text{HMPA})_4(\text{ClO}_4)_2$ 

$D^a$	$-\Delta\nu_{\text{obsd}}^b$	$-\Delta\nu_P^{b,c}$	$Z,^d \text{ sec.}^{-1}$	$(D/P)Z,^e \text{ sec.}^{-1}$	Solvent
$\text{Cu}(\text{HMPA})_4(\text{ClO}_4)_2$					
0	315	315	...	70 <sup>f</sup> ± 5	CH <sub>3</sub> NO <sub>2</sub>
0.7144	203	318	31.6 ± 0.8	79 ± 8	CH <sub>2</sub> Cl <sub>2</sub>
0.8123	187	314	20.3 ± 0.8	88 ± 8	CH <sub>2</sub> Cl <sub>2</sub>
0.8795	...	315	11.7 ± 0.8	86 ± 8	CH <sub>2</sub> Cl <sub>2</sub>
$\text{Co}(\text{HMPA})_4(\text{ClO}_4)_2$					
	333	333	...	64 <sup>f</sup> ± 3	CH <sub>3</sub> NO <sub>2</sub>
0.8517	183	332	10.4 ± 0.5	60 ± 5	CH <sub>2</sub> Cl <sub>2</sub>
0.8415	185	331	11.5 ± 0.5	61 ± 5	CH <sub>2</sub> Cl <sub>2</sub>
0.9269	170	333	5.2 ± 0.5	66 ± 5	CH <sub>2</sub> Cl <sub>2</sub>
0.7873	194	332	16.6 ± 0.5	61 ± 5	CH <sub>3</sub> NO <sub>2</sub>
$\text{Fe}(\text{HMPA})_4(\text{ClO}_4)_2$					
	350	350	...	54 ± 2	CH <sub>3</sub> NO <sub>2</sub>
0.6017	234	350	32.7 ± 0.5	51 ± 2	CH <sub>3</sub> NO <sub>2</sub>
0.7590	202	342	19.2 ± 0.5	60 ± 5	CH <sub>3</sub> NO <sub>2</sub>
0.6672	223	351	26.0 ± 0.5	52 ± 5	CH <sub>3</sub> NO <sub>2</sub>
$\text{Ni}(\text{HMPA})_4(\text{ClO}_4)_2$					
0	358	358	...	6.7 ± 0.3	CH <sub>3</sub> NO <sub>2</sub>
0.7550	199	329	3.9 ± 0.2	12.0 ± 5	CH <sub>3</sub> NO <sub>2</sub>
0.7850	193	324	2.9 ± 0.2	10.6 ± 5	CH <sub>3</sub> NO <sub>2</sub>
0.8717	176	306	...	...	CH <sub>3</sub> NO <sub>2</sub>
0.9063	169	286	3.6 ± 0.2	34.8 ± 5	CH <sub>3</sub> NO <sub>2</sub>
0.9234	166	277	...	...	CH <sub>3</sub> NO <sub>2</sub>
0.9512	162	254	3.7 ± 0.2	72.1 ± 5	CH <sub>3</sub> NO <sub>2</sub>

<sup>a</sup> This is the fraction of the moles of HMPA in the solvent which are not coordinated, (moles free)/(total moles), assuming 4 moles of HMPA are coordinated per mole of metal ion. <sup>b</sup> In units of c.p.s. from tetramethylsilane (TMS). Experimental error is ± 0.5 c.p.s. <sup>c</sup> Proton chemical shift of the complex calculated from eq. 4. The error is ± 4 c.p.s. <sup>d</sup>  $Z = (1/T_2)_{\text{obsd}} - (1/T_2)_H$  (the difference in the observed line width for the peak from complexed and free HMPA,  $(1/T_2)_{\text{obsd}}$ , and that of pure HMPA,  $(1/T_2)_H$ ). The value of  $(1/T_2)_H$  is a constant for these systems equal to 1.3 sec.<sup>-1</sup>. <sup>e</sup> This is the line width for the metal complex in the solution. This is obtained by multiplying  $Z$  by the fraction of free HMPA,  $D$ , divided by the fraction of complexed HMPA. <sup>f</sup> Line width observed for a solution of the pure complex in the solvent indicated.

$P$  is the concentration of paramagnetic species,  $Z = (1/T_2)_{DP} - (1/T_2)_D$ ,  $(1/T_2)_{DP}$  is the observed  $1/T_2$ ,  $(1/T_2)_D$  is the line width of diamagnetic species, and  $(1/T_2)_P$  is the line width of the paramagnetic species.

## Results

The proton n.m.r. spectrum of hexamethylphosphoramide is found to consist of two peaks of equal intensity separated by  $9.7 \pm 0.3$  c.p.s. The doublet could be due to phosphorus-hydrogen coupling or to nonequivalent methyl groups. Values for  $J_{P-H}$  of approximately 10 c.p.s. have been reported for similar compounds,<sup>30</sup> suggesting that the two peaks in HMPA

In an attempt to find out information regarding the nature of the species formed when the HMPA complexes are dissolved in nitromethane, the n.m.r. spectra of the complexes in this solvent were investigated as a function of added HMPA. The results are contained in Table II.

The n.m.r. contact shifts,  $\Delta\nu$ , and the electron spin-nuclear spin coupling constants,  $A$ , for the tetrahedral HMPA complexes of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) are reported in Table III. The temperature

(30) N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956).

**Table III.** N.m.r. Contact Shifts and Electron Spin–Nuclear Spin Coupling Constants for  $M(\text{HMPA})_4(\text{ClO}_4)_2$  Complexes in  $\text{C}_6\text{H}_5\text{NO}_2$

Ion	$\Delta\nu$ , c.p.s.		Slope <sup>c</sup>	$A^d$	$A^e$	$1/T_2$ , sec. <sup>-1</sup>	<i>g</i> - value <sup>g</sup>	Total $S(S+1)^h$	$S(S+1)^h$ in $t_{2e}$
	<i>a</i>	<i>b</i>		$\times 10^3$	$\times 10^3$				
Mn <sup>2+</sup>	370 ± 50	204	...	...	4.6	500 ± 50	1.80	35/4	15/4
Fe <sup>2+</sup>	350 ± 3	184	59.2	5.27	4.95	65 ± 5	2.18	6	15/4
Co <sup>2+</sup>	337 ± 3	171	46.2	9.85	9.54	64 ± 3	2.36	15/4	15/4
Ni <sup>2+</sup>	365 ± 3	199	67.7	13.2	12.5	7 ± 1	2.85	2	2
Cu <sup>2+</sup>	314 ± 3	148	49.2	30.9	27.8	85 ± 5	2.40	3/4	3/4
Zn <sup>2+</sup>	166 ± 2	0	...	...	...	1.3	...	...	...

<sup>a</sup> Shift relative to TMS at 33°. <sup>b</sup> Shift relative to the analogous diamagnetic Zn(II) complex at 33°. <sup>c</sup> Slope of  $\Delta\nu$  vs.  $1/T$  (°K.)  $\times 10^3$  at elevated temperatures. <sup>d</sup> The coupling constant *A* in units of gauss; calculated from the slope of  $\Delta\nu$  (c.p.s.) vs.  $1/T$  (°K.) according to eq. 3 using total  $S(S+1)$ . <sup>e</sup> Calculated from  $\Delta\nu$  (c.p.s.) at 33° from use of eq. 3 and the total  $S(S+1)$ . <sup>f</sup> Line width at half intensity. <sup>g</sup> These *g*-values were estimated from magnetic susceptibility data. <sup>h</sup> Total electron spin *S* is evaluated from the sum of the spin quantum numbers of the unpaired electrons. For the calculation in the last column only the unpaired electrons in  $t_{2g}$  were considered.

**Table IV.** Temperature Dependence of the Contact Shifts for  $M(\text{HMPA})_4(\text{ClO}_4)_2$  in  $\text{C}_6\text{H}_5\text{NO}_2$

Temp., °K.	$1/T$ (°K.)	$\Delta\nu$ , c.p.s. <sup>a</sup>			
		Cu <sup>2+</sup>	Ni <sup>2+</sup>	Co <sup>2+</sup>	Fe <sup>2+</sup>
282.0	0.3546		370		362
293.5	0.3407		369		358
306.5	0.3263	314	365	337	350
326.0	0.3067	303	357		
336.7	0.2970	300	352	322	335
363.5	0.2751	288	336	312	319
389.0	0.2571	274	318	304	

<sup>a</sup>  $\Delta\nu$  relative to tetramethylsilane as an internal standard.

dependence of the contact shift for each of these complexes is reported in Table IV.

## Discussion

In this study we are interested in determining the n.m.r. contact shifts of the tetrahedral transition metal ion complexes of hexamethylphosphoramide. The electronic spectra of several of these complexes in solution<sup>25,26</sup> indicate that tetrahedral species are present in solution. However, for this study it is essential to demonstrate that there is no equilibrium in solution involving appreciable concentrations of other species, at least at the temperature at which contact shifts are calculated. The discussion will consist of three parts: (1) evidence for tetrahedral species in nitromethane solution, (2) evidence for reaction of the complexes in certain solvents, and (3) conclusions regarding covalency in the metal–ligand interaction from n.m.r. contact shifts.

(1) *Evidence for Tetrahedral Species in Solution.* The n.m.r. spectra of all the paramagnetic HMPA complexes studied consist of only one peak. The line width of the methyl resonance in the  $\text{Ni}(\text{HMPA})_4(\text{ClO}_4)_2$  complex is 7.0 c.p.s., and the phosphorus–hydrogen coupling constant in HMPA is 9.7 c.p.s. Thus, a doublet resonance in the nickel(II) complex should be resolved. The phosphorus must be decoupled from the hydrogen by some process in the paramagnetic complex. Covalency in the metal–ligand bond places odd electron density from the metal onto the ligand. The unpaired electron in the phosphorus orbitals must be strongly coupled with the phosphorus nucleus causing very rapid relaxation of the nuclear spin, thus effectively decoupling the phosphorus from the methyl protons. The fact that we were unable

to observe the phosphorus nuclear magnetic resonance is consistent with this conclusion.

In the presence of excess HMPA in the solvents  $\text{CH}_3\text{NO}_2$  and  $\text{CH}_2\text{Cl}_2$ , a rapid exchange of free and coordinated ligand occurs, and only a single peak is observed in the n.m.r. spectrum. The average chemical shift is reported as  $\Delta\nu_{\text{obsd}}$  in Table II for the complexes of interest. Since the proton chemical shift of HMPA is found to be independent of concentration, eq. 4 can be used to calculate the chemical shift of the coordinated HMPA. The results are listed under  $\Delta\nu_P$  in Table II. For the purpose of this calculation, it was assumed that the stoichiometry of the complex is not changed by addition of excess HMPA. This assumption appears valid for all of the complexes except that of Ni(II). The calculated  $\Delta\nu_P$  continually decreases with increase in the excess HMPA ligand. A five- or six-coordinate HMPA complex may be formed, or a square-planar tetrahedral equilibrium may exist in solution as has been proposed for some four-coordinate Ni(II) complexes.<sup>6</sup> If this latter type of equilibrium exists in the  $\text{Ni}(\text{HMPA})_4^{2+}$  solutions, then changes in the solvent properties due to excess HMPA may merely have shifted this equilibrium. A change in species on addition of HMPA is consistent with observations of the electronic spectrum.<sup>25,26</sup>

Table II also contains the results of line width studies under the column  $(D/P)Z$ . The line widths for the paramagnetic complexes were calculated from eq. 5 assuming very fast ligand exchange. The line widths calculated for the Cu(II), Fe(II), and Co(II) complexes in the presence of excess HMPA agree well with those observed for the pure complex. This is added proof that these complexes are essentially four coordinate in solution even with large excesses of ligand. The line widths calculated for the Ni(II) complex in the presence of excess ligand increase with an increase in free HMPA. This is in keeping with the formation of a complex in which the Ni(II) ion has a longer electron spin lifetime. Octahedral Ni(II) is expected to have a longer electron spin lifetime than is tetrahedral Ni(II) because of the absence of electron spin degeneracies in the former.<sup>31</sup>

*Evidence for Reaction of the Complexes in Certain Solvents.* The solvent dependence of these HMPA complexes was studied in several weakly basic and weakly acidic solvents (Table I). The n.m.r. of  $(\text{Co}(\text{HMPA})_4)^{2+}$

(31) C. J. Ballhausen, "Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

is essentially the same in  $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CH}_3\text{NO}_2$ . This result reflects the preference of  $\text{Co}(\text{II})$  for four-coordinate tetrahedral symmetry. The complex  $(\text{Cu}(\text{HMPA})_4)^{+2}$  in the solvents  $\text{RNO}_2$  and  $\text{CH}_2\text{Cl}_2$  apparently maintains tetrahedral or distorted tetrahedral symmetry. In either more basic or more acidic solvents the n.m.r. shifts are decreased. Either increased metal-ligand dissociation or Z-axis solvation could be responsible for the decreased HMPA proton n.m.r. shifts. The solvent resonances of  $(\text{Cu}(\text{HMPA})_4)(\text{ClO}_4)_2$  in solutions of  $\text{CH}_3\text{C}\equiv\text{N}$  and  $(\text{CH}_3)_2\text{CO}$  were shifted presumably owing to coordination on the Z-axis of the paramagnetic  $\text{Cu}(\text{II})$  ion. The line width of the HMPA resonance in  $(\text{Cu}(\text{HMPA})_4)_2(\text{ClO}_4)_2$  was not diminished in the basic solvents. This result suggests that HMPA is not appreciably dissociated from the metal ion. The smaller value for the shifts for the  $\text{Cu}(\text{II})$  complex in the more basic solvents may be indicative of the reduced covalency in tetragonal complexes compared to that in tetrahedral complexes.<sup>32</sup> The n.m.r. of the  $\text{Ni}(\text{II})$  complex was found to be strongly concentration dependent in both acidic and basic solvents. These results are to be expected owing to the preference of  $\text{Ni}(\text{II})$  for octahedral or square-planar coordination. It is surprising that  $(\text{Ni}(\text{HMPA})_4)^{+2}$  maintains tetrahedral symmetry in  $\text{CH}_3\text{NO}_2$ .

*Interpretation of the Contact Shifts for the Tetrahedral Complexes.* Contact shifts,  $\Delta\nu$  (c.p.s.), for the methyl protons of the four-coordinate hexamethylphosphoramide complexes of some first transition series divalent metal perchlorates are listed in Table III. The contact shifts are reported relative to the diamagnetic  $\text{Zn}(\text{II})$  complex. Measurement of the solution magnetic moments indicate that these complexes are close to being fully paramagnetic at room temperature. Contact interaction coupling constants were calculated from the high-temperature data and from the slope of the high-temperature  $\Delta\nu$  vs.  $1/T$  ( $^\circ\text{K}.$ ) plot (see eq. 3). Since solvation would be exothermic, it is expected that the tetrahedral nickel complex would be the principal species at elevated temperatures. The coupling constants are also listed in Table III.

Owing to the high symmetry of these complexes, pseudo-contact shifts are not expected to be large. All of the  $\text{M}(\text{HMPA})_4^{+2}$  complexes with the exception of  $\text{Cu}(\text{II})$  are found to give similar powder patterns to that of the  $\text{Zn}(\text{II})$  complex. This result is good evidence for tetrahedral symmetry about the metal ion. The maximum pseudo-contact shift for  $\text{Cu}(\text{HMPA})_4^{+2}$  has been estimated to be about  $-12$  c.p.s. This estimate was made by making the approximation that the HMPA protons sweep out a volume shell that is a portion of a sphere. All angles of  $\theta$  from  $-\pi/3$  to  $\pi/3$  and all metal-proton distances from 4 to 7 Å. are considered to be equally populated. The  $g$ -value anisotropy is taken from known values of square-planar  $\text{Cu}(\text{II})$ .<sup>20</sup> The average value of  $(3 \cos^2 \theta - 1)/r^3$  was evaluated from the above assumptions and substituted into eq. 6.<sup>12,13</sup> The term  $\theta_i$  is the angle between the

$$\frac{\Delta\nu}{\nu} = \frac{-(\beta^2)S(S+1)(g_{\parallel} + 2g_{\perp})(g_{\parallel} - g_{\perp})}{27kT} \times \frac{(3 \cos^2 \theta_i - 1)}{r_i^3} \quad (6)$$

(32) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **2**, 342 (1958).

principle molecular axis and the magnetic nucleus, and  $r_i$  is the distance of the magnetic nucleus from the metal ion.

The temperature dependence of the chemical shift relative to tetramethylsilane (TMS) for the  $\text{Cu}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Co}(\text{II})$ , and  $\text{Fe}(\text{II})$  complexes of HMPA are recorded in Table IV. The measurements above room temperature were performed in nitrobenzene, while those below room temperature were done in nitromethane. A linear plot of  $\Delta\nu$  (c.p.s.) vs.  $1/T$  ( $^\circ\text{K}.$ ) from  $-40$  to  $+120^\circ$  is found for  $(\text{Co}(\text{HMPA})_4)(\text{ClO}_4)_2$ . Extrapolation leads to a chemical shift of  $-180$  c.p.s. relative to TMS at infinite temperature. There is therefore a temperature-independent shift of approximately  $-20$  c.p.s. relative to the free ligand. An approximately linear relationship is found between the chemical shift and  $1/T$  ( $^\circ\text{K}.$ ) above  $50^\circ$  for the  $\text{Cu}(\text{II})$ ,  $\text{Fe}(\text{II})$ , and  $\text{Ni}(\text{II})$  complexes. Extrapolation to infinite temperature (where according to eq. 1 the contact shift goes to zero) yields a chemical shift of  $-(150-160)$  c.p.s. relative to TMS which is close to the free ligand value. The  $\text{Fe}(\text{II})$  complex is rapidly oxidized (apparently by  $\text{ClO}_4^-$ ) above  $80^\circ$ , a situation which prevents study of the contact shifts at high temperature.

The mechanism for placing unpaired electron density onto the HMPA ligand cannot be unambiguously determined by these n.m.r. experiments. Many mechanisms for the transfer of electronic effects are possible and most probably several operate simultaneously. The ligands considered in this work can be involved in both  $\pi$ - and  $\sigma$ -bonding to the metal. The classical interaction of the phosphoryl oxygen lone pairs with the metal d-orbitals is a  $\sigma$ -interaction. Unpaired electron density is placed on the ligand by the interaction of ligand orbitals with metal orbitals containing unpaired electrons. The unpaired electron density on the ligand is distributed in accordance with the ligand  $\pi$ - and  $\sigma$ -molecular orbitals. The scant experimental evidence presently available indicates that the delocalization of the unpaired electron spin through the  $\sigma$ -bonds produces the same orientation of the spin at every position.<sup>17,33</sup> In terms of the proton n.m.r. experiments this means that all of the protons involved in the  $\sigma$ -molecular orbital are deshielded by an electron with a magnetic field oriented with the external field (positive spin density), or shielded by an electron with a magnetic field opposing the external field (negative spin density).

In the presence of an external magnetic field the magnetic dipoles of the unpaired metal d-electrons tend to align with the field. A  $\sigma$ -ligand to metal bond then places positive spin density at all the ligand protons. The methyl hydrogens of HMPA are predicted to be deshielded by this mechanism and this is found experimentally (Table III). The delocalization of electrons in  $\pi$ -type molecular orbitals is more familiar to our experience. Valence bond structures are frequently convenient for the purpose of predicting the unpaired electron spin orientation for  $\pi$ -delocalization at various positions in the molecule (Figure 1).<sup>34</sup> The direction of the arrow ( $\uparrow$ ) in structure I indicates that the lowest energy electron spin orientation occurs when the magnetic field of the unpaired electrons on the metal

(33) R. S. Milner and L. Pratt, *Discussions Faraday Soc.*, **34**, 88 (1962).

(34) A. Carrington, *Quart. Rev. (London)*, **17**, 67 (1963).

