lar conclusions concerning the relative energy levels of these d_{z^2} and d_{xy} orbitals, as is described in papers by Basch and Gray,[3] by Martin and co-workers,[4] and by others.[4]

Gray's proposal was based on the spectral properties of square-planar complexes in which the donor atoms are carbon (in cyanide), sulfur, chlorine, and bromine. Until now, absorption spectra have not been available for square-planar complexes involving donor atoms other than those. This note reports the absorption spectra of square-planar complexes of nickel(II) and palladium(II) with a tetradentate nitrogen-donor ligand, *viz.*, ethylenebisbiguanide (enbbg, $C_6H_{16}N_{10}$).

Preparation of these compounds has been described by Ray.[5] The chloride salt of $Ni^{II}(enbbg)^{2+}$ is a typical square-planar d^8 complex, orange and diamagnetic.

The absorption spectrum of $Ni(enbbg)Cl_2$ in 0.0100 *M* solution (observed in 1-cm cells with a Cary Model 14 spectrophotometer over a range of 300–1600 mμ, *i.e.*, *ca.* 33,000–6200 cm^{-1}) consists of only a single detectable peak, with maximum absorbance at a wavelength of 478 mμ (20,900 cm^{-1}) (see Figure 1). A similar peak for $Pd(enbbg)Cl_2$ in aqueous solution occurs at 307 mμ (32,500 cm^{-1}), which is consistent with the expectation of a substantial increase in the magnitude of ligand field splitting on going from the first transition series to the second. Finding peaks at these wavelengths is also consistent with the expected location of ethylenebisbiguanide in the spectrochemical series, *i.e.*, $Cl^- <$ enbbg $< CN^-$.

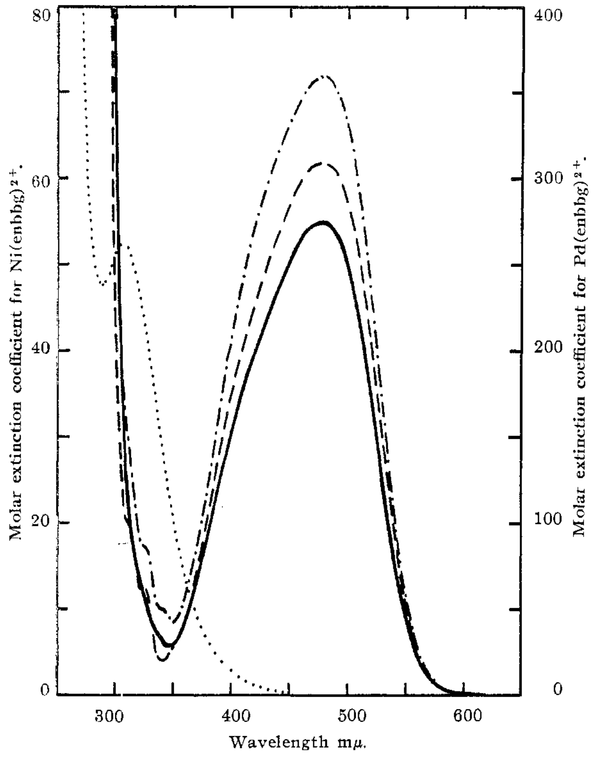

Figure 1.—Absorption spectra (25°): ———, $Ni(enbbg)^{2+}$ in H_2O; - - - -, $Ni(enbbg)^{2+}$ in formamide; — · —, $Ni(enbbg)^{2+}$ in DMSO; · · · ·, $Pd(enbbg)^{2+}$ in H_2O. Note use of different scale for $Pd(enbbg)^{2+}$.

Because no other peaks are found at longer wavelengths (even out to more than 1600 mμ in the case of $Ni(enbbg)Cl_2$ in dimethyl sulfoxide solution) it must be assumed that the one observed peak corresponds to that d–d transition which has the smallest energy. Peaks for two other such d–d transitions, expected to occur at shorter wavelengths, are not observed, presumably because they are obscured by the very intense charge-transfer absorption occurring at wavelengths below about 300 mμ.

Identification of the transition responsible for that lowest energy peak depends on the fact that its wavelength is not shifted by a change of solvent. The only significant difference between the spectra of $Ni(enbbg)Cl_2$ in water and in dimethyl sulfoxide (DMSO) is a difference in molar extinction coefficient; *i.e.*, ϵ_{max} is 55 in H_2O and 72 in DMSO. In formamide solution, ϵ_{max} is 62. There does not seem to be any obvious correlation between absorbance and solvent dielectric constant.

The d–d transition of lowest energy in a square-planar d^8 complex must be either $d_{xy} \rightarrow d_{x^2-y^2}$ ($^1A_{1g} \rightarrow {}^1A_{2g}$) or $d_{z^2} \rightarrow d_{x^2-y^2}$ ($^1A_{1g} \rightarrow {}^1B_{1g}$). If it were the latter, involving the d_{z^2} orbital, that orbital being the one which is most exposed and therefore most strongly influenced by the solvent, a change of solvent should change the wavelength of the peak. Because the wavelength of the observed peak is found to be independent of the choice of solvent, the transition producing that lowest energy peak must be $d_{xy} \rightarrow d_{x^2-y^2}$ ($^1A_{1g} \rightarrow {}^1A_{2g}$), a conclusion which supports the proposal that the order of energy levels is $d_{xy} > d_{z^2}$.

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[3] H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967).

[4] See footnotes in ref 3.

[5] P. Ray, *Chem. Rev.*, **61**, 313 (1961).

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Ammonia Proton Contact Shift Studies. π Interaction of Ammonia with Metal Ions

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Proton contact shifts for many first transition series hexaaquometal ion complexes have recently been reported.[1,2] These studies suggest that a π-donation

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[1] B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **6**, 54 (1966).

[2] Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).

mechanism using a bonding orbital of water is the dominant spin delocalization mechanism in metal complexes with unpaired electrons in π orbitals. This proposed spin delocalization mechanism is very closely related to hyperconjugation in organic molecules except that electrons from the O–H bonds are delocalized into metal d orbitals. This paper reports direct evidence for a π hyperconjugative interaction between ammonia and the metal ions Co(II) and Mn(II) from proton contact shifts for hexaammine complexes. A brief report of the Ni(II) and Cu(II) hexaammines has previously appeared.[3]

Experimental Section

Preparation of Complexes.—The hydrated perchlorate complexes $M(H_2O)(ClO_4)_2$ [M = Co(II), Ni(III), Cu(II), Zn(II)] were dehydrated by stirring in contact with 2,2-dimethoxypropane for approximately 3 hr. Anhydrous ammonia (Matheson) was then bubbled through the solution and the resulting precipitate filtered and dried under vacuum. For Co(II) and Ni(II) light brown and light blue solids were obtained, respectively. For Cu(II) the initial blue (hexacoordinate) changed to purple upon drying, giving a hydrogen analysis for four ammonias. The white Zn(II) complex gave an analysis for four ammonias.

Representative analysis: Calcd for $Ni(NH_3)_6(ClO_4)_2$: H, 5.05; N, 27.25; Ni, 16.31. Found: H, 5.17; N, 27.27; Ni, 16.05.

The Mn(II) ammonia complex could not be isolated in high purity due to its apparent instability in air.[4] This complex was prepared *in situ* and used without initial isolation (see below).

Nmr Spectra.—The spectra consisted of a single ammonia peak with a downfield benzene peak as standard. The shifts ($\Delta\nu_{obsd}$) were measured relative to a standard solution containing the same concentration by mole fraction of NH_4ClO_4 in ammonia as the sample. Solutions of the diamagnetic Zn(II) complex gave no observable shift throughout the concentration range for the complexes reported here. The resonance position of complexed ammonia relative to uncomplexed ammonia ($\Delta\nu_{com}$) was calculated from the relationship $\Delta\nu_{com}f_{com} = \Delta\nu_{obsd}$ where f_{com} is the mole fraction of ammonia complexed assuming hexacoordination in solution. No concentration dependence was noted either for a wide range of benzene–ammonia concentrations or for the reported range of metal ion concentrations in liquid ammonia. Thus, the changes in ion pairing and anion–solvent interactions, in the range of concentrations studied, caused no significant effects on the nmr shifts. The electron–nuclear coupling constants were calculated by substitution of the contact shift ($\Delta\nu_{com}$) into the equation $A/h = (\Delta\nu/\nu)\gamma_H(3kT)/g_e\beta_eS(S+1)h$ where $\Delta\nu$ is the nmr shift, A the electron–nuclear coupling constant, ν the resonant frequency (60 Mc), g_e the Lande g factor, β_e the electron Bohr magneton, S the electron spin, and γ_H the magnetogyric ratio for the nucleus.

Solutions.—Solutions of the Cu(II), Ni(II), and Co(II) ammine complexes in liquid ammonia were prepared by weighing into a thick-walled nmr tube the dried amine complex along with NH_4ClO_4 used to prevent amide precipitation. After introducing a small amount of benzene as internal standard, the nmr tube was placed on the vacuum system, and ammonia was quantitatively distilled into the nmr tube using a standard technique. Solutions of the Mn(II) complex were prepared by repeatedly distilling ammonia into a tube containing a weighed sample of the Mn(II) hydrate and NH_4ClO_4 with subsequent evacuation. The resulting white solid mixture of $Mn(NH_3)_6(ClO_4)$ and NH_4ClO_4 was then redissolved quantitatively in liquid ammonia.

Apparatus.—The nmr spectra were determined on a Varian A60-A spectrometer. The thick-walled nmr tubes were obtained from Ace Glass Co. and NMR Specialties Inc. The thick walled nmr tubes were altered for temperature studies from 50 to 90°. The major problem of solution boiling was overcome by sealing the tubes as close as possible to the ammonia solution allowing sufficient volume to accommodate the expansion of the solution when heated.

Results

The proton contact shift data for the hexaammine complexes of Cu(II), Ni(II), Co(II), and Mn(II) in liquid ammonia are reported in Table I. The proton contact shifts for Cu(II), Ni(II), and Co(II) complexes are upfield relative to the diamagnetic Zn(II) complex and thus have negative election spin–proton spin coupling constants (Table I). The Mn(II) complex exhibits a downfield proton contact shift and has the corresponding positive coupling constant. The temperature dependence of the contact shifts follows Curie law behavior, within experimental error, above 30°. Line-width studies also indicate that 38° is in the region of fast ligand exchange for all ions studied.

TABLE I

PROTON CONTACT SHIFTS AND COUPLING CONSTANTS FOR $M(NH_3)_6(ClO_4)_2$ COMPLEXES IN LIQUID AMMONIA

Metal ion	10^3f[a]	$\Delta\nu_{obsd}$,[b] sec^{-1}	$10^{-3}\Delta\nu_{com}$,[c] sec^{-1}	g_e	$10^{-6}A/h$,[d] sec^{-1}
Cu^{2+}	8.73	42.2	4.83	2.3	−2.6 ± 0.1
	19.0	90.4	4.75		
Ni^{2+}	3.31	23.0	6.95	2.3	−1.5 ± 0.1
	6.49	76.5	7.17		
Co^{2+}	3.15	7.8	2.48	2.6	−0.24 ± 0.02
	4.98	11.7	2.35		
Mn^{2+}	5.92	−58	−9.83	2.0	+0.54 ± 0.06
	12.91	−123	−9.53		

[a] Fraction of total ammonia in the system that is complexed to the metal calculated assuming six coordination. [b] $\Delta\nu_{obsd}$ is the observed average proton resonance position at 38.0° for solutions of hexaammine complex in liquid ammonia. The observed shift is measured relative to benzene as internal standard and then reported relative to the position of pure ammonia at 38.0°. Data are corrected for presence of NH_4ClO_4 added to inhibit amide formation. Estimated error in $\Delta\nu_{obsd}$ is ±0.2 cps except for Mn(II) solutions where the error is approximately ±5 cps. [c] $\Delta\nu_{com}$ is the complexed ammonia proton shift relative to uncomplexed ammonia. $\Delta\nu_{com}$ is calculated from the limit of fast exchange ($\Delta\nu_{obsd} = f\Delta\nu_{com}$). The limit of fast exchange has been demonstrated at 38° from the temperature dependence of the contact shifts and line widths. [d] Electron–proton coupling constants are calculated from the equation: $A/h = (\Delta\nu/\nu)\cdot\gamma_H(3kT)/g_e\beta_eS(S+1)h$.

Discussion

The unpaired electrons in the transition metal ion complexes considered here are in antibonding molecular orbitals which are primarily of metal d-orbital character. Unpaired electron density is transferred to the ligand orbitals by their participation in the antibonding molecular orbitals of the complex. Spin density may reach the ammonia protons by two oppositing mechanisms. (1) Positive spin density reaches the proton by direct electron delocalization which occurs owing to the hydrogen contribution to the molecular orbitals that have unpaired electrons. (2) Negative spin density may reach the proton from spin-polarization effects which cause a small unpairing of the formally paired

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[3] B. B. Wayland and W. L. Rice, *J. Chem. Phys.*, **45**, 3150 (1966).

[4] K. Kido and T. Watanabe, *J. Phys. Soc. Japan*, **14**, 1217 (1959).

electrons. Negative proton spin densities are commonly found when the unpaired electrons occupy an orbital with a node at the proton as is the case with $C_6H_6^-$ and NH_3^+.[5,6]

The occupied molecular orbitals of ammonia are $(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2$. In an octahedral metal ion complex the a_1 orbitals are σ-donor levels and the e orbitals are of π symmetry with respect to the metal ion.

The metal ions Ni(II) and Cu(II) in an octahedral ligand field have filled π-type t_{2g} d orbitals and partially filled σ-type e_g d orbitals. The unpaired electrons in octahedral complexes of Ni(II) and Cu(II) are to a good approximation confined to the σ molecular orbitals, and unpaired electron density is placed in the $3a_1$ donor orbital of ammonia by complex formation with these metal ions. The protons in ammonia coordinated to Cu(II) or Ni(II) in liquid ammonia experience a large upfield nmr contact shift relative to uncoordinated ammonia (Table I). The upfield shift corresponds to a negative spin density in the hydrogen 1s orbital of coordinated ammonia. The large negative proton spin densities indicate that spin polarization is the dominant mechanism for transferring unpaired electron density to the proton. The ligand molecular orbital containing the unpaired electrons must have only a small or perhaps negligible hydrogen character. These results are among the best experimental evidence for viewing the highest filled molecular orbital of ammonia as a "lone pair." Negative ammine proton spin densities have also been observed by Fitzgerald and Drago in the octahedral Ni(II) complex of benzylamine[7] and by Kluiber and Horrocks[8] in aniline complexes of Ni(II).

Octahedral complexes of Co(II) and Mn(II) have unpaired electrons in both σ symmetry e_g and π symmetry t_{2g} d orbitals. Molecular orbital formation with donor molecules can potentially place unpaired spin density in both the σ- and π-donor orbitals of ligands. In an octahedral complex, the filled e molecular orbitals of ammonia are potential π-donor levels. The e molecular orbitals are strongly bonding orbitals and thus generally have been overlooked as π-donor orbitals. π interaction of ammonia with a metal containing unpaired electrons in t_{2g} d orbitals places unpaired electron density in the e orbitals of ammonia. Self-consistent field calculations indicate that the e levels are strongly bonding and have a large hydrogen character;[9] thus spin density is expected to reach the protons directly by this mechanism and make a positive contribution to the electron–proton coupling constant. If a π interaction with ammonia occurs, a cancellation of proton spin density is expected by the two opposing mechanisms. Negative spin density reaches the hydrogen 1s by the σ mechanism operative in the Cu(II) and Ni(II) complexes, and positive spin density reaches the ammonia protons by π interaction with the metal ion. The greatly attenuated upfield proton shift and small negative coupling constant in the Co(II) hexaammine complex suggest that opposing mechanisms are operative (Table I). The large downfield proton contact shift and positive coupling constant for the Mn(II) complex indicate the dominance of the π spin delocalization mechanism for this complex. There is only one type of π orbital in ammonia; thus the π interaction of ammonia with the metal ions Co(II) and Mn(II) involves the e molecular orbitals which contribute significantly to the N–H bonds. This mechanism for π spin delocalization in these ammonia complexes is essentially a "hyperconjugative" interaction involving metal t_{2g} π acceptor orbitals. An analogous bonding interaction where electrons from the B–H bonds are delocalized into d orbitals of phosphorus or sulfur has been proposed as making an important contribution to the bonding in compounds such as $(CH_3)_2SBH_3$ and $[(CF_3)_2PBH_2]_3$.[10–12] The direct observation reported here of the very closely related interaction between ammonia and metal ions supports the feasibility of the proposed hyperconjugative bonding mechanism in these boron hydride compounds.

Contact shift studies offer the unusual opportunity to investigate the atomic orbital contributions to the molecular orbitals containing unpaired electrons. Because of this valuable capability, these studies cannot directly indicate the bulk molecular properties such as charge distribution and thermodynamics. Conversely, thermodynamics or charge distribution cannot directly determine the form of molecular orbitals. The ammonia proton contact shift data demonstrate the presence of a π interaction with metal ions having π-acceptor orbitals, but do not directly indicate the extent to which this π interaction contributes to the thermodynamics of complex formation. The results of this investigation and related magnetic resonance studies indicate the need for further theoretical and experimental studies of the importance of hyperconjugation.

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