Table II. Pmr Chemical Shifts of 6-H of Cytosine and 2-H of Imidazole in Solutions Containing 0.1 M $ZnCl_2$, 0.1 M Cytosine, and Varying Concentrations of Imidazole in DMSO, at 36°

Concn of imidazole, M	ν, cps: 6-H of cytosine	ν, cps: 2-H of imidazole
0	449.4	
0.10	448.5	485.5
0.20	443.8	482.6
0.30	441.9	477.7
0.40	441.8	474.3

kept constant at 0.1 M in DMSO, and the imidazole concentration was varied. Table II gives the results obtained. As the imidazole concentration increases from 0.1 to 0.4 M, the imidazole 2-H signal moves upfield from 485.5 to 474.3 cps, and the cytosine 6-H signal also moves upfield, from 448.5 to 441.8 cps. This is qualitative evidence for the reaction

$$\text{imidazole–Zn–cytosine} + 3\text{Im} = \text{Zn(Im)}_4 + \text{cytosine} \qquad (12)$$

since Figure 1 shows that the frequency of imidazole 2-H at (Im)/(Zn) = 4:1 is 473.5 cps, which is upfield from the limiting frequency of 486.5 cps, obtained when the ratio (Im)/(Zn) $\leq$ 1. The upfield shift of cytosine 6-H frequency on increasing imidazole concentration is as expected, since part of the cytosine bound in the ternary complex is becoming free.

The value of K of eq 12 was calculated for a solution of 0.1 M $ZnCl_2$, 0.1 M cytosine, and 0.4 M imidazole in DMSO, as follows: the observed frequency for 6-H in cytosine, ν = 441.8 cps, may be considered to be the weighted average of the free and complexed cytosine

$$\nu = \frac{0.1 - x'}{0.1}\nu_f + \frac{x'}{0.1}\nu_c \qquad (13)$$

where x' = concentration of the ternary complex at equilibrium, and ν_f and ν_c are the characteristic frequencies of free and complexed cytosine (taken to be equal to 439.7 and 459.7 cps, respectively). From eq 13, the value of x' was calculated to be 0.01. The equilibrium constant of eq 12 is then given by

$$K = \frac{(0.1 - 0.01)^2}{0.01(0.4 - 0.01 - 4(0.1 - 0.01))^3} = 3 \times 10^4$$

The large value of K of eq 12 is in line with the expectation that $Zn(Im)_4^{2+}$ is much more stable than Im–Zn–cytosine^{2+}.

Proton Nucear Magnetic Resonance Contact Shifts in the Complexes $Co\{OP[N(CH_3)_2]_3\}_2X_2$ and $Co(C_5H_5N)_2X_2$

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Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois. *Received December 10, 1965*

Abstract: The proton nmr contact shifts for a series of paramagnetic cobalt(II) complexes of general formula CoL_2X_2 (where L = pyridine or $[(CH_3)_2N]_3PO$ and X^- = Cl^-, Br^-, I^-, or NCS^-) are reported. Mechanisms for spin delocalization are proposed. Evidence for both π- and σ-electron-spin-delocalization mechanisms is found for pyridine. The magnitude of electron spin delocalization to the neutral ligand is found to increase in the order $CoL_2Cl_2 \leq CoL_2Br_2 < CoL_2I_2$. A molecular orbital model is invoked to explain the anion effects.

The present status of the theory for nuclear magnetic resonance contact shifts has been discussed in several recent publications.[2–8] This article reports the anion effects on the neutral ligand proton contact shifts for the series of complexes of the general formula

$$CoL_2X_2\ (X^- = Cl^-, Br^-, I^-, NCS^-;\ L = \text{HMPA}\ ([(CH_3)_2N]_3PO),\ \text{py}\ (C_5H_5N))$$

The metal ion and neutral ligand are the same in each series of complexes. Only the coordinated anion is changed. For these series of complexes, it is possible to relate the ligand proton contact shifts directly to the relative unpaired electron density on the neutral ligand.

Experimental Section

Apparatus. The nmr spectra were obtained with Varian Model A-60 and Varian Model DP-60 nmr spectrometers. All nmr spectra were measured relative to tetramethylsilane (TMS) as an internal standard. When very accurate chemical shift measurements were necessary, two internal standards, TMS and cyclohexane or benzene, were used.

Reagents and Solutions. Hexamethylphosphoramide (HMPA) (Fisher) was distilled from barium oxide at reduced pressure. The middle fraction boiling at 127° (20 mm) was collected. The material 2,2-dimethoxypropane was obtained from Dow Chemical Co. and was used without further purification. Reagent grade $CDCl_3$ was used without further purification.

All solutions of hygroscopic materials were prepared in a drybox equipped with an automatic continuous air-flow drying system. When accurate complex or ligand concentrations were necessary, materials were weighed in stoppered volumetric flasks.

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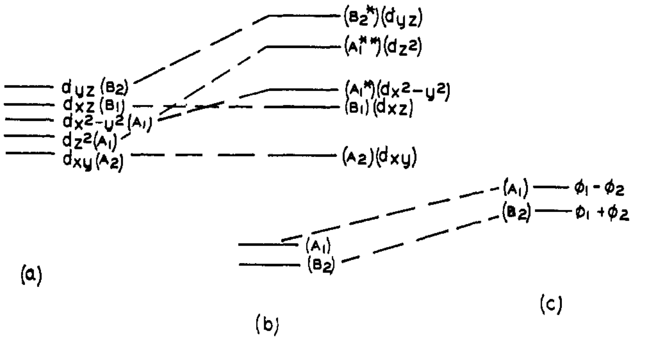

Figure 1. (a) Metal d orbitals; (b) CoX_2 σ molecular orbitals; (c) halide ion (X^-) σ donor orbitals.

Preparation of Complexes. The method of preparation and structural information about the HMPA complexes have been reported previously.[9,10] Some of these complexes were available from these earlier studies. The pyridine complexes were prepared by the method of Nelson.[11]

Results

The results of our nmr studies are reported in Table I.

Table I. Nmr Shifts for Ligand Protons in CoL_2X_2 Complexes[a]

Complex		$\Delta\nu^{b,c}$	$1/T_2$, sec^{-1}
$Co(HMPA)_2Cl_2$		-102	66
$Co(HMPA)_2Br_2$		-152	62
$Co(HMPA)_2I_2$		-180	61
$Co(HMPA)_2(NCS)_2$		-203	94
$Co(HMPA)_2(NO_3)_2$		-191	36
$Co(HMPA)_4(ClO_4)_2$		-176	65
	$\Delta\nu_\alpha{}^{b,c}$	$\Delta\nu_\beta{}^{b,c}$	$\Delta\nu_\gamma{}^{b,c}$
$Co(py)_2Cl_2$	-8820 ± 30	-2220 ± 10	$+208 \pm 3$
$Co(py)_2Br_2$	. . .	-2330 ± 10	$+221 \pm 3$
$Co(py)_2I_2$	-9090 ± 30	-2360 ± 10	$+315 \pm 3$

[a] $\Delta\nu$ is expressed in cps relative to the corresponding free ligand resonance position. [b] $CDCl_3$ solvent. [c] Concentration of complex is 0.2 *M*.

Discussion

The neutral ligand proton nmr contact shifts for several series of complexes CoL_2X_2 have been determined. This study was conducted to help elucidate the anion effects on the metal–neutral ligand bonding. In order to discuss these effects, the spin-delocalization mechanisms that give rise to proton nmr contact shifts and the effects of variations in X on the cobalt–neutal ligand bond must be considered.

In the formation of molecular orbitals from the metal d orbitals having unpaired electrons and ligand orbitals, some unpaired electron spin density is placed at every atom in the complex. The unpaired electron spin couples with the nuclear spin, causing a shift in resonance position. The magnitude of this nmr contact shift is related to the electron spin–proton nuclear spin coupling constant A_H by eq 1,[4,5,8] where A_H is the electron–proton coupling constant and γ_e and γ_H are the magnetogyric ratio for the electron and proton, respectively.

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

The distribution and direction of the ligand contact shifts can provide information about electron spin delocalization arising from π and σ bonding of the neutral ligand L with the paramagnetic metal ion. Cobalt(II) in a C_{2v} or T_d complex (Figure 1) has unpaired electrons in d orbitals that are capable of overlapping both σ and π ligand donor orbitals. Unpaired electron density can thus be placed in either or both the σ and the π electronic system of the ligand, depending upon the ligand orbitals available. In $Ni[(C_6H_5)_3P]_2X_2$ ($X^- = Cl^-, Br^-, I^-$) the principal delocalization mechanism which places unpaired spin density in the phenyl ring is reported to involve the π system.[12] The σ system predominates in cases where the magnetic nuclei are closer to the bonding site or where low-energy π orbitals are not available.[7]

The observed shifts for the pyridine protons in $Co(py)_2X_2$ complexes can be interpreted as arising from two competing spin-delocalization mechanisms. The very large downfield shift for the α protons and the attenuated downfield shift for the β protons are consistent with spin delocalization in the ligand σ molecular orbitals.[7,13] The relatively small upfield shift for the pyridine γ protons can best be explained by π molecular orbitals dominating the spin delocalization to the γ position.[3,7] The competition of spin delocalization in the π and σ molecular orbitals has previously been proposed to explain the pyridine proton contact shifts in nickel complexes.[7,13]

It is experimentally observed that the downfield contact shift increases for α and β hydrogens and the upfield contact shift increases for the γ hydrogens of pyridine as the anion is changed from Cl^- to Br^- to I^- (Table I). In keeping with the spin-delocalization mechanisms for complexed pyridine proposed above, both σ and π spin delocalization from the metal to the neutral ligand appear to increase in the order $CoL_2Cl_2 < CoL_2Br_2 < CoL_2I_2$.

The unpaired electrons in these complexes are in antibonding orbitals, where the antibonding orbitals are primarily of metal d-orbital character (Figure 2). The differences in the ligand proton contact shifts reflect differences in the ligand contributions to the antibonding orbitals. An increase in ligand contribution to the antibonding orbitals requires an increase in metal d orbital contribution to the bonding orbitals which are primarily of ligand character. An increase in spin delocalization in both the σ and π ligand orbitals indicates an increased mixing of the ligand σ and π donor orbitals with the partially filled metal d orbitals. The simultaneous increase of spin delocalization in both the σ and π orbitals of the ligand strongly suggests an increase in metal–neutral ligand bond covalency in the order $Co(py)_2Cl_2 < Co(py)_2Br_2 < Co(py)_2I_2$.

In the complexes $Co(HMPA)_2X_2$ where HMPA (hexamethylphosphoramide) is the neutral ligand, it is not apparent whether the σ or π spin-delocalization mechanism predominates. Both mechanisms predict a positive spin density in the methyl hydrogen 1s

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orbital. An increase in either σ or π bonding with the metal d orbitals will cause an increase in the HMPA proton contact shift. It is probable that both the π and σ donor orbitals of HMPA are important in the bonding. The order of HMPA proton contact shifts is the same as that found for pyridine, that is, $CoL_2Cl_2 < CoL_2Br_2 < CoL_2I_2$.

The above interpretation is based on the assumption that the trends in chemical shift are not dominated by the pseudo-contact term. Since Co(II) in near tetrahedral symmetry should be orbitally nondegenerate, only small pseudo-contact shifts are anticipated due to g-value anisotropy. The presence of a small upfield pseudo-contact interaction suggested in $Co[(C_6H_5)_3P]_2Br_2$[14] is reasonable, for there is a large difference in ligand field strength between $(C_6H_5)_3P$ and Br^-. On the other hand, the donor properties of hexamethylphosphoramide (HMPA) have been compared to those of the halides,[9,10] so the metal ion should be in a field which is much closer to tetrahedral symmetry in the complexes employed here. The changes in anisotropy expected on substituting I^- for Cl^- are not expected to be large enough to account for the observed change of −77 cps in the HMPA methyl resonance.

Anisotropy in g can be more rigorously precluded as the principal source of the difference in proton resonance positions for pyridine in $Co(py)_2I_2$ and $Co(py)_2Cl_2$. The sign of the shift due to pseudo-contact interaction, a dipolar effect, is the same for all of the pyridine hydrogens. Contrary to this behavior, it is observed that the α and β protons shift downfield and the γ proton shifts upfield in changing the anion from Cl^- to I^- (Table I). This behavior is consistent only with the dominant effect being one induced in the ligand electronic system by bonding to the metal, *i.e.*, a contact shift. If pseudo-contact interaction effects were dominant, all of the pyridine protons would be shifted in the same direction.

Effect of Variations in X on the Co–L Bond. The proton nmr contact shifts for a series of complexes $Ni[(C_6H_5)_3P]_2X_2$ ($X^- = Cl^-, Br^-, I^-$) have recently been reported.[12] The ligand phenyl proton shifts increased in the order $Cl^- < Br^- < I^-$. These data were explained by invoking "back-donation" of metal d electrons into empty phosphorus d orbitals as the major mechanism for the transfer of unpaired electron effects from the metal to the ligand. The stabilization of dπ–dπ "back-bonding" by anion π donation was considered to increase in the order $Cl^- < Br^- < I^-$. These arguments may be appropriate for ligands with low-lying empty π orbitals like $(C_6H_5)_3P$, but are not adequate to explain the anion effects on the proton contact shift for either pyridine or HMPA. The explanation to be offered here could also be used to account for the contact shifts when triphenylphosphine is the ligand.

The trend in Co–L covalency with trends in halide σ and π donor properties can be rationalized by using a molecular orbital bonding model. In order to analyze the trend in metal d orbital neutral ligand orbital interactions, the metal–anion interaction must first be considered. For the purpose of illustration, the formation of CoL_2X_2 is considered to occur in two steps. The first step illustrated in Figure 1 is the formation of the CoX_2 ($X^- = Cl^-, Br^-, I^-$) fragment of C_{2v} symmetry from Co^{2+} and $2X^-$. The unit CoX_2 may then further react with two neutral ligands as illustrated in Figure 2 to form the complexes CoL_2X_2. The advantage of this approach is that it allows analysis of the effects on the Co^{2+} valence orbitals from interaction with the halide and then analysis of the interaction of these fragments with the neutral ligand L.

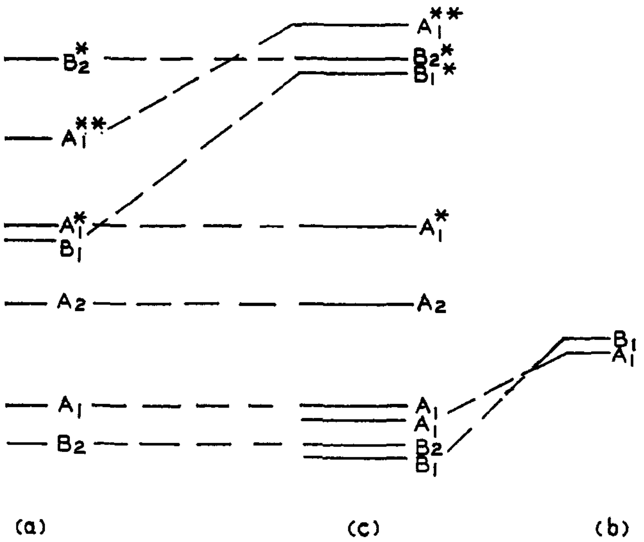

Figure 2. (a) CoX_2 molecular orbitals; (b) neutral ligand (L) σ donor orbitals; (c) CoL_2X_2 molecular orbitals.

For the purpose of simplicity and ease of illustration, only the metal 3d orbitals and the pσ halide donor orbitals are utilized in the molecular orbital diagram in Figure 1. The same conclusions are reached by inclusion of the halide pπ orbitals. The orbitals in Figures 1 and 2 are generated by placing the cobalt and two halogens in the yz plane with the x axis being perpendicular to this plane. The halide ion σ orbitals are pointing directly at two of the lobes of d_{yz}. This corresponds to an arrangement of the d orbitals in a cube such that $d_{z^2-y^2}$ points toward the edges. The main feature of importance in Figure 1 is that, as anticipated, all the empty or partially filled metal acceptor orbitals are raised in energy (destabilized) by interaction with the halide donor orbitals. The relative destabilization of the metal acceptor orbitals increases as the metal–halide bonding increases. Although no thermodynamic data are available for the Co–X bond energy in these complexes, the Co–X bond energy is expected to decrease significantly in passing down the group from Cl^- to I^-.[15] These arguments lead directly to the conclusion that the acceptor orbitals of CoX_2 increase in stability in the order $MCl_2 < MBr_2 < MI_2$. It should also be mentioned that the spherical field will raise the energies of all the d orbitals relative to the gaseous ion. This effect also gives the same order of acceptor orbital stability for the CoX_2 species. The Δ values for the halides toward T_d Co(II) are Cl^-, 3100 cm^{-1}; Br^-, 2850 cm^{-1}; I^-, 2650 cm^{-1}.[16] This order is consistent with the proposed order of stability of the MX_2 valence orbitals.

Figure 2 is the molecular orbital diagram for CoL_2X_2 generated from the CoX_2 molecular orbitals and the σ

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neutral ligand donor orbitals. The relative amount of metal–neutral ligand covalent bonding depends upon the stability of the MX_2 acceptor valence orbitals, *i.e.*, energy match of L and appropriate cobalt(II) orbitals. As the energy of the MX_2 acceptor valence orbitals of the MX_2 group increases, the covalent bonding with the neutral ligand decreases. Application of the MO bonding model leads to the prediction that the energy (destabilization) of the MX_2 acceptor orbitals increases in the order $MCl_2 > MBr_2 > MI_2$ (Figures 1 and 2). The magnitude of the metal–neutral ligand covalent bonding is thus expected to increase in the order $CoL_2Cl_2 < CoL_2Br_2 < CoL_2I_2$. This result agrees with the increase in ligand proton contact shifts when the anion is changed from Cl^- to Br^- to I^-.

The bonding properties of thiocyanate are almost certainly affected by $d\pi$–$p\pi$ back-bonding (from the metal d to the thiocyanate π MO). The very large *Dq* for thiocyanate (N-bonded) toward T_d Co(II) can best be explained in terms of the lowering of the filled metal d orbitals (the e set) due to back-donation into the antibonding π orbitals of thiocyanate. The large neutral ligand contact shift in the thiocyanate complex is consistent with increased effective charge on the metal that would result from back-bonding.

Conclusions from a comparison of $Co(HMPA)_2(NO_3)_2$ with the halide complexes have to be qualified because of the uncertainty in the symmetry of $CoL_2(NO_3)_2$ in solution. Bidentate nitrate has been found[16] in similar complexes in the solid state. If, as previously proposed,[16] the immediate environment about the cobalt has, in a sense, "distorted tetrahedral symmetry," the pseudo-contact term may be small and comparison of the contact shift of the complex with the halide complexes legitimate. According to the data in Table I, nitrate would be located between iodide and thiocyanate. This is reasonable for nitrate would not be expected to form strong covalent bonds. Since back-bonding from metal to nitrate would not be expected to be very large, the large contact shift in this complex is attributed to a lesser degree of covalency in the metal–nitrate bond than in the metal–chloride bond.

Comparison of the contact shifts for $Co(HMPA)_4{}^{2+}$ and $Co(HMPA)_2Cl_2$ indicates that HMPA does not decrease the charge on cobalt as much as chloride or bromide.

The conclusion of the above discussion can be generalized to rationalize some of the halogen effects in other chemical species. The order for the C–H stretching force constants in CH_3X is $F < Cl < Br < I$.[15] The order of C–X bond energies is $I < Br < Cl < F$.[17] The C–H force constants thus decrease as the C–X bond energy increases. These data may reflect the trend in destabilization of the carbon orbitals used in bonding with hydrogen as the C–X bond energy increases. The increase in the enthalpy for formation of $Co(py)_4X_2$ from $Co(py)_2X_2$[18] as the anion is changed from Cl^- to Br^- to I^- is also consistent with these arguments.

Acknowledgment. The authors acknowledge partial support of this research by the Chemistry Branch of the Atomic Energy Commission through Contract No. AT(11-1)-758.

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Investigations of the Cobalt(II) Complexes of N,N-Dimethylacetamide

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Received December 27, 1965

Abstract: Complexes with the formulas $[Co(DMA)_6](ClO_4)_2$ and $[Co(DMA)_4](ClO_4)_2$ have been isolated. Infrared spectral and conductance data are presented to eliminate the possibility of perchlorate coordination in $[Co(DMA)_4](ClO_4)_2$. Parameters obtained from the electronic spectra and magnetic moments indicate approximate tetrahedral and octahedral ligand fields for the four- and six-coordinate complexes, respectively. Vibrational spectra demonstrate coordination through the DMA carbonyl oxygen for both complexes. Simultaneous coordination through both the carbonyl oxygen and amide nitrogen may be present in $[Co(DMA)_4](ClO_4)_2$ or distortion from pure T_d symmetry may result from ion pairing. The crystal-field prediction that *Dq*(tetrahedral)/*Dq*(octahedral) = 0.44 is found not to agree with our experimental results, and possible explanations are offered. The nmr contact shifts of the octahedral and tetrahedral complexes indicate more covalency in the tetrahedral complex.

The preparation and isolation of mixed neutral ligand–anion complexes of a metal ion in two different symmetries is well known. The best known examples of this type of complex are the four-coordinate $Co(py)_2X_2$ and the six coordinate $Co(py)_4X_2$ (py = pyridine, X = halide).[2,3] Tetrahedral and octahedral environments for nickel(II)[4] and cobalt(II)[5] metal ions

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