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Proton Magnetic Resonance Spectra of Six-Coordinate Iron(II), Cobalt(II), and Nickel(II) Complexes with Pyridine-N-oxide and Benzamide

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Pmr spectra of octahedral Ni^{II}, Co^{II}, and Fe^{II} complexes with pyridine-N-oxide and benzamide in solution with excess ligand have been recorded. The contact shift ratios of pyridine-N-oxide protons are identical for the three metals. Also the benzamide complexes, which were reported to show different shift patterns for the three metals,[1] are found to give rise to superimposable spectra of Ni^{II} and Co^{II} and a stricly similar spectrum of Fe^{II} under excess ligand conditions. These data are interpreted as the experimental exidence of the validity of the ratio method.[2]

Introduction

The interpretation of proton magnetic resonance spectra of paramagnetic compounds is often a difficult matter owing to the simultaneous contributions of Fermi contact shifts and dipolar shifts to the total isotropic shifts.[3] Pmr spectra of solutions of paramagnetic ML_6 complexes, in excess of monodentate ligand L, may provide contact shifts alone; in fact if solvation effects are reduced by the excess ligand, it may reasonably be assumed that the effective symmetry of the complex is octahedral. Such symmetry requires isotropic magnetic properties so that the isotropic shifts must arise from contact interations only. A comparison of these shifts for different metal systems can give information on the delocalization mechanisms of spin density.

Recently Drago *et al.* investigated hexakis-4-methylpyridine-N-oxide Ni^{II} and Co^{II} complexes in solution in presence of excess ligand.[4] They found that the ratios of proton contact shifts are identical for the two metal complexes; however they considered the identity of shift ratios purely accidental on the basis of an approximate EHMO calculation. In view of the importance of this result on the current debate[1,2,4-6] on spin density delocalization mechanism and since we believe[6] that spin delocalization mechanisms can be identical for complexes differing only in the metal ion, we have extended the research to pyridine-N-oxide and benzamide ligands with the ions Ni^{II}, Co^{II}, and Fe^{II}. Contact shift data on these complexes are expected to be of particular interest because *i*) the donor and steric properties of pyridine-N-oxide are quite similar to those of the 4-methyl derivative, whereas the spin density distribution onto the aromatic ring may be different: *ii*) different spin delocalization mechanisms have been claimed[1] for hexakis-benzamide complexes of Ni^{II}, Co^{II}, and Fe^{II} by inspecting their pmr spectra recorded without excess ligand.

Experimental Section

Pyridine-N-oxide,[7] benzamide,[8] and the relative complexes were prepared as BF_4^- salts as reported elsewhere.[9,10] Analyses for C, H, N, were in full agreement with the formulae $ML_6(BF_4)_2$.

Physical Measurements. Proton magnetic resonance spectra were recorded with a Varian DA-60 spectrometer operating at 60 MHz. Spectra were calibrated from internal TMS. Iron(II) spectra were recorded under nitrogen in sealed tubes in order to avoid oxidation.

Results

Pyridine-N-oxide Complexes. Pmr spectra shows the usual pattern of *ortho* and *para* peaks upfield and *meta* peak downfield[11,12] (Figure 1). By adding pyridine-N-oxide to the complex solution, the range of shifts narrows indicating a rapid ligand exchange on the nmr time scale, such that the isotropic shifts are a function of the molar fraction bound to the metal

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(N_b).[11,12] However, when N_b is >0.50, shifts are slightly concentration dependent. This suggests that extensive solvolysis occurs under slight excess ligand conditions.

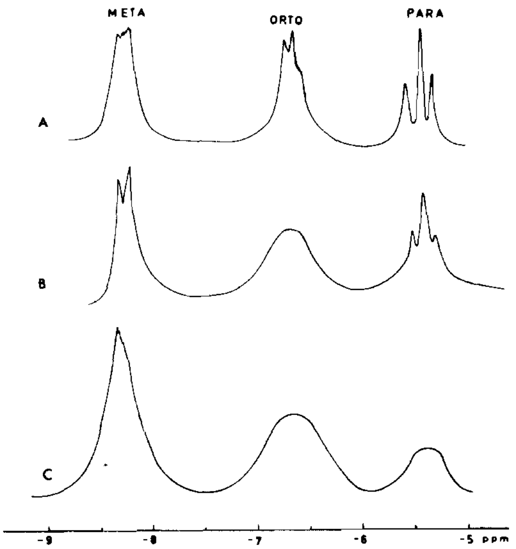

Figure 1. Pmr spectra from TMS of: A) $Co(PyO)_6(BF_4)_2$ in d_5-nitroethane at 90°C ($N_b=9\%$); B) $Ni(PyO)_6(BF)_4)_2$ in d_5-nitroethane at 100°C ($N_b=15\%$); C) Fe $(PyO)_6(BF_4)_2$ in d_3-acetonitrile at 26°C ($N_b=14\%$).

For $N_b<30\%$ the ratios of contact shifts are independent of the concentration and identical for the three metal complexes, the values *meta*: *ortho*: *para* being 1: -1.5 ($\pm.07$): -1.85 ($\pm.04$). These values are independent of the solvent, *e.g.* d_6-acetone, d_5-nitroethane, d_3-acetonitrile, and temperature. In Figure 1 superimposable spectra (under different experimental conditions) of the three complexes are shown.

Although these results, with the extension to Fe^{II} complexes, are quite similar to those obtained with 4-methyl-pyridine-N-oxide, the *meta/ortho* contact shift ratios are different (1: 1.50 against 1: 1.25) indicating that the unpaired spin density distribution onto the aromatic rings is different for the two ligands.

Benzamide Complexes. Pmr spectra of hexakis benzamide complexes of Ni^{II}, Co^{II}, and Fe^{II}, have been already reported although only the aromatic proton signals were observed.[1] Benzamide is a weak ligand and solvolysis of the complexes is likely to occur.[10] In such case the cubic simmetry is lost and some dipolar effects, although reduced by rapid ligand exchange,[1] may become evident. Figure 2 shows the effect of dilution on the isotropic shifts of $Co(bz)_6^{2+}$ in d_6-acetone. While *ortho*-H, *para*-H and NH_2 signals move upfield with increasing concentration, the *meta*-H signal moves down-field. Dipolar contributions of one solvolyzed species, *e.g.* $[$*trans*$-Co(bz)_4(solvent)_2]^{2+}$, cannot account for the observed pattern since the geometric factors, which govern the sign and the magnitude of dipolar shifts,[13] are expected, by simply inspecting a molecular model, to give rise to dipolar contributions in the same direction for all the protons. This behavior could be accounted for by assuming that several solvolyzed species are in equilibrium, as it was suggested by Ragsdale *et al.* who first described these complexes. Therefore the observed isotropic shifts are the average of contact and dipolar shifts of all the present species, weighted according to their relative abundance. On this basis it can be explained that the NH_2 signal of the cobalt complex moves upfield when benzamide is first added to the solution then moving downfield, towards the diamagnetic position, only after further additions. It is interesting to note that the *para*-H resonance, which was reported downfield,[1] goes upfield either with increasing concentration (Figure 2) or by adding excess ligand (Figure 3). This is consistent with a larger abundance of one species, presumably the CoL_6 species, either at higher concentrations or in presence of excess ligand. Therefore the previous claim[1] of different contact shift pattern for the three metal complexes and most of the relative speculations, based on spectra of presumably solvolyzed species, appear to be unsound.

Unfortunately the measured isotropic shifts are small and are further reduced by the excess ligand. For N_b of the order of 40% the isotropic shift values

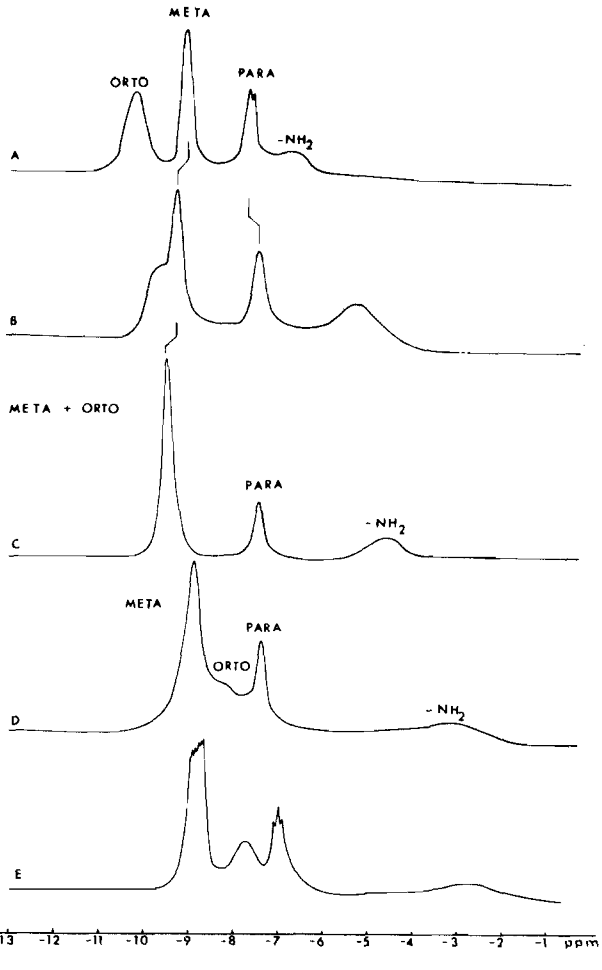

Figure 2. Pmr spectra from TMS in d_6-acetone at 26°C: $Co(bz)_6(BF_4)_2$ $2\cdot10^{-2}M$, $5\cdot10^{-2}M$, $7\cdot10^{-2}M$ (A, B, C respectively); $Ni(bz)_6(BF_4)_2$ $5\cdot10^{-2}M$ (D); $Fe(bz)_6(BF_4)_2$ $3\cdot10^{-2}M$ (E).

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are still appreciable and not substantially affected by concentration. Under these conditions, strictly similar spectra were obtained for the three metal complexes, as shown in Figure 3. In all the cases the *ortho* peak is masked by the *meta* peak (and can be located in the vicinity of its diamagnetic position at *ca.* –8 ppm) and the *para* peak is close to the diamagnetic position (at *ca.* –7.5 ppm), but on the upfield side, whereas the *meta* and the amidic proton resonances are down- and upfield respectively. The spectra of Ni^{II} and Co^{II} can be easily obtained superimposable by varying the value of N_b, whereas the spectrum of Fe^{II} shows a relatively smaller shift of the *meta* proton (in Figure 3 the positions of the *meta*-H resonances for Co^{II}, Ni^{II}, and Fe^{II} are –0.51, –0.53, –0.38 ppm from the diamagnetic position which is taken at –7.5 ppm).

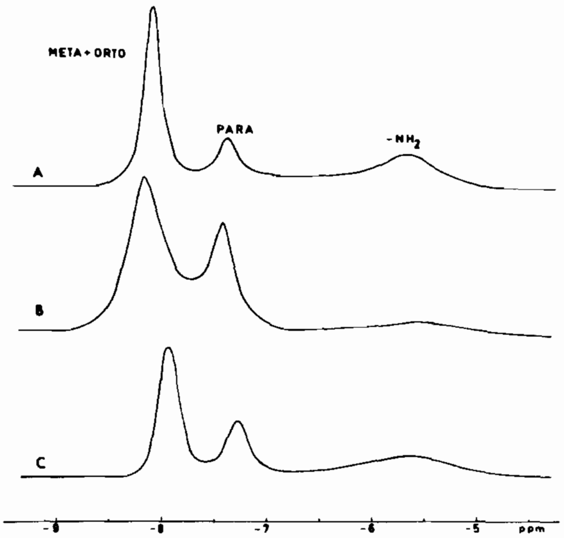

Figure 3. Pmr spectra from TMS in d_6-acetone at 26°C: A) $Co(bz)_6(BF_4)_2$ $N_b=35.8\%$; B) $Ni(bz)_6(BF_4)_2$ $N_b=49.5\%$; C $Fe(bz)_6(BF_4)_2$ $N_b=33.0\%$.

Discussion

The identity of the shift ratios for Ni^{II}, Co^{II}, and Fe^{II} complexes with pyridine-N-oxide and for Ni^{II} and Co^{II} complexes with benzamide and 4-methylpyridine-N-oxide is an experimental evidence of the validity of the equation:

$$\left(\frac{\Delta\nu_i^{\text{contact}}}{\Delta\nu_j^{\text{contact}}}\right)_A = \left(\frac{\Delta\nu_i^{\text{contact}}}{\Delta\nu_j^{\text{contact}}}\right)_B$$

where i and j refer to protons and A and B to a couple of metals.

Such a relationship is the basis of the ratio method[2] which has allowed a successful factorization of the isotropic shifts of the metal (A) complex into their dipolar and contact components when contact shifts of the metal (B) complex are known.[5,6,14] In particular, successful isotropic shift factorizations have been performed for the systems $Ni(acac)_2(PyO)_2$–$Co(acac)_2(PyO)_2$[11] and $Ni(bipyO)_3^{2+}$–$Co(bipyO)_3^{2+}$[15] (where acac is acetyl acetonate and bipyO is α,α'bipyridine-N-N'-dioxide). The success of this method is another proof, although *a posteriori,* of the validity of the above equation. Therefore the previous conclusions that identical spin delocalization mechanisms are not operative is now hardly credible. Such a conclusion was based on extended Hückel MO calculations performed ignoring the metal orbitals. A recent article by Horrocks and Johnston[15] shows these calculations are incapable to provide semiquantitative values of hyperfine coupling constants.

Finally the spin density is not necessarily delocalized into σ or π ligand systems through direct overlap of σ or π metal and ligand orbitals respectively, as it has been proposed.[4] In fact N-substituted anilines have been found to give rise to an isotropic shift pattern qualitatively similar to that of pyridine-N-oxide.[16,17] Such pattern (shift alternation and change in the sign of the coupling constant when a H is substituted by a CH_3) is generally believed typical of a π delocalization mechanism,[3] although the quaternary nitrogen of anilines bound to the metal cannot form direct π bonds. For this reason, σ-π polarization or σ-π non orthogonality has been suggested.[17] Analogously, the Ni–O (of pyridine-N-oxide) bond has to be σ in nature, as the unpaired electrons are in the σ type e_g orbitals, whereas delocalization from oxygen onto the aromatic ring may still occur through several possible mechanisms. As it has been suggested for the aniline system, unpaired spin density may be delocalized into the system through σ-π non orthogonality mechanisms. Alternatively, unpaired spin density might reside in σ molecular orbitals, as it has been recently proposed.[15,18] The hypothesis of non involvement of the Ni–O π bond in the actual spin delocalization mechanism (as the t_{2g} orbitals are filled) is supported by the previous result by Happe and Ward[19] showing that oxygen is an isolating atom, regarding π spin density transfer, comparable to a sp^3 carbon (and then to a sp^3 nitrogen, *e.g.* that of aniline). Consistently with experimental data, the same mechanism is proposed for the other two metal ions.

The benzamide has another carbon atom between the donor oxygen and the aromatic ring. This may explain the shift attenuation of benzamide in comparison to the shifts of pyridine-N-oxide, expecially in view of the conclusion that metal to oxygen spin transfer occurs through σ orbitals.

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