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^{13}C Nmr Spectra of Hexakis Pyridine-N-oxide Cobalt(II) and Nickel(II) Complexes

I. BERTINI, C. LUCHINAT and A. SCOZZAFAVA
Cattedra di Chimica Generale ed Inorganica della Facoltà di Farmacia dell'Università and Laboratorio per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, Firenze, Italy
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^{13}C nmr spectra of hexakis pyridine-N-oxide cobalt (II) and nickel(II) complexes have been recorded and the isotropic shifts compared with the ^{1}H isotropic shifts of the same complexes. Whereas the ^{1}H contact shift patterns are the same for the two metal complexes, the ^{13}C contact shift patterns are not the same; neither can be univocally related to the ^{1}H contact shifts. A tentative discussion of these data is presented.

Introduction

The ^{13}C nmr spectra of paramagnetic molecules may furnish a direct method for measuring unpaired spin densities on the carbon atoms of organic ligands in paramagnetic complexes and shed light on the problem of spin density delocalization mechanisms.[1,2] Most of the work in the area up to date available in the literature is based on the analysis of proton isotropic shifts.[3]

It has been shown that γ-CH_3-py-NO (py-NO = pyridine-N-oxide) gives the same proton contact shift pattern in both cobalt(II) and nickel(II) hexakis γ-CH_3-py-NO complexes.[4] The same holds for the unsubstituted pyridine-N-oxide ligand.[5] In other words the contact shift ratios *meta/ortho/para* are the same for the complexes of the two metal ions although the shifts of cobalt are larger than those of nickel (1.3 times larger for the py-NO complex).[5]

In order to better characterize these complexes and to better understand the role of the metal ion in the resulting spin distribution on the ligand, the ^{13}C nmr spectra of $M(py\text{-}NO)_6(BF_4)_2$ complexes (M = Co, Ni) in solution have been recorded.

Experimental

The complexes $M(py\text{-}NO)_6(BF_4)_2$ (M = Co, Ni) were prepared and analyzed as previously reported.[5,6] They were dissolved in acetonitrile, then a large excess of pure ligand was added in order to obtain metal/ligand ratios of 0.001–0.01. The proton decoupled ^{13}C spectra were recorded with a Varian CFT 20 spectrometer locked on deuterium of the deuterated solvent. Isotropic shifts were determined relatively to the free ligand chemical shifts. The isotropic shift ratios were determined from the least-squares slopes of the lines obtained on plotting the ^{13}C isotropic shifts *versus* the molar fraction of bound ligand.

Longitudinal relaxation times, T_1, were measured with the sequence 180° pulse–τ–90° pulse delay with τ varying between 0.2 and 30 s in order to have a satisfactory pattern of the line heights.

Results and Discussion

The measurements were carried out in presence of a large excess of pure ligand in order to avoid solvolysis and to make the signals sharp enough to be detected. In all cases a single resonance for each equivalent set of carbons is obtained showing that the equilibrium between free and bound ligand is fast on the ^{13}C nmr time scale. The measured shifts from the free ligand position are assumed to be essentially contact in origin as the complexes are essentially cubic and the fast exchange should quence any residual dipolar contribution.[7]

The py-NO carbons experience large up- and downfield shifts with *meta/para/ortho* shift ratios of 1/–1.40/–2.58 for nickel and 1/–1.76/–3.57 for the cobalt complex. The difference in these patterns is somewhat surprising since the ^{1}H contact shift ratios are coincident for the two metal complexes within the experimental error. By recalling[5] that the *meta/para/ortho* proton shift ratios are 1/–1.60/–1.20 it appears that the ^{13}C shift patterns are definitely different from the ^{1}H shift pattern (see also Table I), even if spin polarization effects from the contiguous atoms are qualitatively taken into account.[1,8] These experimental data outline the danger of relating the ^{1}H contact shifts with carbon spin densities even in those cases (as the present one) in which the alternancy of ^{1}H contact shifts would suggest a substantial π spin delocalization. It is worth noting that a linear relationship between hydrogen and carbon spin densities was found

TABLE I. ^1H and ^{13}C Contact Shift Data for Nickel(II) and Cobalt(II) Hexakis Pyridine-N-oxide Complexes.[a]

	Ni	Co
C_α	–2.58(0.06)	–3.57(0.20)
C_β	1	1
C_γ	–1.40(0.12)	–1.76(0.10)
H_α	–1.20(0.10)	
H_β	1	
H_γ	–1.60(0.10)	
R_α	–15.0(0.3)	–19.5(1.6)
R_β	–7.0(0.2)	–6.5(0.5)
R_γ	–6.1(0.5)	–7.2(0.3)

[a] Normalized for the β values (standard deviations in brackets). Isotropic shifts for the β positions equal to 1 ppm correspond to the following molar fractions of bound ligand: 1.55 (^{13}C, Ni); 1.35 (^{13}C, Co); 8.3 (^1H, Co d_3-acetonitrile); 10.7 (^1H, Ni d_3-acetonitrile). R gives the ratio between ^{13}C and ^1H isotropic shifts at the same position.

for the CH_3 group attached to several aromatic heterocyclic ligands.[9]

Any attempt of interpretation of the observed ^{13}C and ^1H shift patterns cannot only rely on the idea that the spin delocalization mechanism occurs through the non-orthogonality between σ metal orbitals (in the idealized O_h symmetry) and π orbitals of the ligand.[4,10] Presumably more than one spin delocalization mechanism are operative despite the strict similarity of the ^1H contact shift patterns for the two metal complexes. This apparent contradiction could be accounted for by assuming that only one spin delocalization mechanism gives rise to detectable shifts of the hydrogen nuclei.

Actually Drago *et al.*[4] have suggested that proton contact shifts in γ-CH_3-py-NO complexes are determined only by π spin delocalization. The σ contribution due to the highest energy filled σ molecular orbital is negligible because of the small proton coefficients in that MO. However, if also a σ spin density delocalization mechanism is operative (and it is sizeable on C atoms), different shift ratios between ^{13}C and ^1H shifts are expected. Of course this is just a possible path, not necessarily actual, to overcome the seemingly contradictory data. A further analysis, however, would be meaningful only if adequate theoretical tools[11–13] were available which allowed to compare the experimental results with sophisticated models including spin polarization mechanisms as well as the metal orbitals.

The comparison of the patterns of the ratios, R, between ^{13}C and ^1H shifts of each CH group for the two metal complexes is quite meaningful in understanding the role of the metal ion in determining the overall spin distribution (Table I). From these data it appears that the difference in spin delocalization mechanisms due to the change of the metal ion is relatively small.

The shape of the nmr spectra deserves a further comment. The ^{13}C line broadening pattern qualitatively follows the contact shift pattern[2] ($C_\alpha > C_\gamma > C_\beta$) whereas T_1 values are smaller for C_α than C_β and C_γ. For example the T_1 values for a solution $1.1 \times 10^{-2} M$ of the cobalt complex and $2.9 M$ of the free ligand are 1.75, 4.75, 5.05 s for *ortho, meta* and *para* carbon atoms respectively. Presumably the carbon T_1 values are also affected by a dipolar coupling mechanism with the metal ion.[14] On the contrary the pattern of the proton line broadening is not determined by the magnitude of the contact shifts but from the proton to metal distances. In every case the line width is larger for the nickel than for the cobalt complex, as expected.[15]

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