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Contact and Dipolar NMR Shifts in Nickel and Cobalt Pyridine Complexes

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Proton magnetic resonance data are presented for the paramagnetic complexes $M(ligand)_4X_2$ *where* $M=Co$ *and Ni, ligand = pyridine and γ-picoline and* $X=Cl$, *Br, I, and NCS. The shifts exhibited by the nickel compounds can be interpreted in terms of a contact interaction involving the same electron spin delocalization mechanisms as found previously for other pyridine complexes. In the case of the cobalt complexes, both contact and dipolar effects contribute to the observed shifts. However, the sign of the dipolar effect is found to depend upon the nature of X. The cloroform solvent resonances suffer large shifts in the cobalt systems attributable to a dipolar interaction.*

Introduction

Isotropic nuclear resonance shifts of ligands coordinated to paramagnetic transition metals have been observed in some cases where the electron spin relaxation is sufficiently fast.[1] Pyridine and substituted pyridine complexes of octahedral cobalt(II) and nickel(II) acetylacetonates[2] and tetrahedral cobalt(II)[3] and nickel(II)[4] halides have been studied.

The isotropic resonance shifts in the case of pyridine cordinated to $Ni(acetylacetone)_2$ in which the nickel is approximately octahedrally coordinated were interpreted[2] as rising predominantly from contact shifts[1] due to delocalization of unpaired electron spin. The magnitude and pattern of the shifts indicated[2] that the shifts at the α and β proton positions were due to interaction with unpaired spin in the σ framework of the ligand whereas the shifts at the γ position indicated interaction with unpaired spin in the π system of the ligand.

The isotropic resonance shifts of the corresponding cobalt(II) acetylacetone-pyridine complexes could not be interpreted without invoking[2] the presence of a sizeable dipolar or pseudocontact[1] interaction. This dipolar interaction was most noticeable at the γ position where the contact term was considerably smaller than at the α and β positions. The magnetic anisotropy responsible for the dipolar shift was such that $g_\perp > g_\parallel$.

Evidence for magnetic anisotropy has also been obtained for other [5] octahedral adducts of cobalt(II) acetylacetonate and, in all cases, the dipolar shift indicated that $g_\perp > g_\parallel$. The forces responsible for the sign and magnitude of the magnetic anisotropy appear to be poorly understood. It was of interest to examine a series of compounds in which systematic changes were made and observe the effects, if any, on the magnetic anisotropy.

This study reports nmr shifts of pyridine-type bases coordinated to nickel(II) and cobalt(II) as complexes of the type $metal(ligand)_4X_2$ where $X=I^-$, Br^-, Cl^-, and NCS^-, and ligand = pyridine and γ-picoline. X-ray structural determinations[6] on $Nipy_4Br_2$, $Nipy_4Cl_2$, $Nipy_4(NCS)_2$ (the corresponding cobalt complexes are isomorphous) show the complexes to be *trans* octahedral monomers in the solid state. The electronic spectra of the nickel pyridine complexes in choloroform containing excess pyridine compared with the solid-state spectra indicate[7] that the *trans* octahedral structure is retained in solution.

Experimental Section

The complexes were all prepared by methods described in the literature.[8] The nmr spectra were obtained with a Varian A56/60 spectrometer fitted with a variable temperature probe. The proton resonance peaks were measured relative to an internal TMS reference.

The complexes were examined as solutions in $CDCl_3$ with known concentrations of complex and excess ligand. Electronic spectra were recorded on a Cary Model 14 spectrophotometer.

Results

The isotropic nmr shifts of the cordinated ligands are presented in Tables I and II. The values are all relative to the diamagnetic, uncomplexed ligand resonances. In order to obtain meaningful comparisons, the observed shifts have been extrapolated to the idealized situation of a species $M(ligand)_4X_2$ at 25°. In

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Table I. Magnetic Resonance Data for the Nickel Complexes [a].

	α	β	γ	γ-CH_3
$Nipy_4Cl_2$	~ —5600	—2060	—468	
$Nipy_4Br_2$	— [b]	—2030	—450	
$Nipy_4I_2$	~ —5500	—2100	—486	
$Nipy_4(NCS)_2$	~ —5100	—2030	—425	
$Ni(\gamma pic)_4Cl_2$	~ —5650	—1930		+560
$Ni(\gamma pic)_4Br_2$	~ —5400	—1910		+568
$Ni(\gamma pic)_4I_2$	~ —5550	—1960		+560
$Ni(\gamma pic)_4(NCS)_2$	— [b]	—2260		+695

[a] Shifts in Hz at 60 MHz/sec and 25° from resonance positions in diamagnetic ligand; in no case measured directly (see text). [b] Resonance too broad for accurate measurement.

Table II. Magnetic Resonance Data for the Cobalt Complexes [a].

	α	β	γ	γ-CH_3
$Copy_4I_2$	~ —5550	—2550	—475	
$Copy_4Br_2$	~ —5000	—2200	—150	
$Copy_4Cl_2$	~ —4400	—1680	+275	
$Copy_4(NCS)_2$	~ —4960	—1800	+410	
$Co(\gamma pic)_4I_2$	~ —5400	—2540		—175
$Co(\gamma pic)_4Br_2$	~ —5000	—2170		+105
$Co(\gamma pic)_4Cl_2$	~ —4510	—1700		+530
$Co(pic)_4(NCS)_2$	~ —4780	—1720		+630

[a] Shifts in Hz at 60 MHz/sec and 25° from resonance positions in diamagnetic ligand. In no case were these values measured directly (see text).

no case is it possible to measure this value directly. In the case of the nickel compounds, decomposition of the complexes occurs in the absence of excess ligand, and in the presence of excess ligand, exchange between coordinated and uncoordinated ligand is rapid at 25° giving an averaged spectrum. Thus it is necessary to know the relative concentrations of complex and excess ligand in order to determine the 'absolute' shifts of the coordinated ligand. The validity of this procedure can be checked in this instance, since it is possible to 'freeze out' the exchange at temperatures less than —30° and thus observe resonances of coordinated and free ligand. With the instrument used in these studies only the γ-proton of coordinated pyridine could be observed (the shifts at the other positions being too large). However, if the shift of the γ-proton of the coordinated ligand observed at low temperatures is extrapolated back to 25° using an inverse temperature dependence (both the contact and pseudocontact mechanism have a Curie Law dependence), the resulting value agrees well with that calculated from the rapid exchange situation.

In the case of the cobalt complexes, there is also an equilibrium between tetrahedral $Co(ligand)_2X_2$ and octahedral $Co(ligand)_4X_2$. The equilibrium may be forced to the octahedral side by excess ligand and low temperatures;[9] thus these conditions were chosen for measurements. As in the nickel case, ligand exchange is rapid at temperatures above —30°, leading to an averaged spectrum.

Discussion

Examination of the shifts of the series of nickel complexes shows that the dependence upon X for $Ni(ligand)_4X_2$ is small. The ratios of α:β and β:γ shifts are quite similar to those reported by Happe and Ward for pyridine coordinated to Ni^{II} acetylacetonate[2]. Thus there is no evidence for an appreciable dipolar interaction. This is not surprising since esr studies on a variety of distorted six-coordinate nickel compounds have shown[10] that magnetic anisotropy is less than ~5%. Anisotropy of this order of magnitude will give rise to very small pseudocontact shifts.

The shifts observed for hte nickel-picoline complexes at the α and β positions are very similar to those of the pyridine complexes but the γ—CH_3 resonance is found upfield whereas the γ–H resonance of the pyridine complexes occurred downfield from the diamagnetic position. This is expected if the contact shift at the γ-position is dominated by interaction with unpaired electrons in the π system of the ligands. The shifts observed for the coordinated pyridine and γ-picoline in the nickel complexes are very similar in magnitude to those reported for pyridine and picoline in octahedral adducts with *bis*–(salicylaldehydato) nickel[11a] and with *bis*–(benzoylacetonato) nickel(II)[11b] but substantially less than previously observed[4] in tetrahedral nickel(II) complexes.

The shifts of the pyridine and picoline protons in the cobalt complexes show marked differences from their nickel(II) analogues. In particular, there is a considerable dependence upon the halide or pseudohalide coordinated. The shifts for the bromide and iodide complexes fall substantially downfield from those observed for the chloride and thiocyanate complexes. The resonances observed for the chloride and thiocyanate complexes resemble those reported for pyridine and γ-picoline coordinated to *bis*–(salicylaldehydato) cobalt,[11a] where the results were interpreted[11] as arising from the superposition of an upfield dipolar effect on a primarily downfield contact effect. The shifts for bromide complexes are very similar to the nickel analogues and can be interpreted as being due primarily to interaction with unpaired spin in the σ orbital at the α and β positions and interaction with unpaired spin in the π orbital at the γ position, with no good evidence for a dipolar effect operating in these systems. The cobalt iodide complexes display shifts downfield of those observed for the other cobalt species, in particular the methyl resonance for $Co(\gamma\text{–}pic)_4I_2$ is the only methyl resonance found downfield for any of the cobalt or nickel picoline complexes. This could be reasonably interpreted in two ways (a) the shifts are the net effect of contact shifts of a similar magnitude to those found for the other cobalt complexes and a dipolar shift of opposite sign to that observed for the chloride and thiocyanato complexes, or (b) the shifts at all positions are the result of contact shifts caused by interaction with unpaired spin in the σ orbital. Now since in all other pyridine and picoline complexes of nickel(II) and cobalt (II),[2,3,4,11] the contact shift at the γ position has been

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the result of interaction with unpaired spin in the π system, explanation (b) above does not seem very plausible. Thus, the tentative conclusion reached from consideration of the ligand shifts is that the dipolar effect seems to be contributing in an upfield direction for the chloride and thiocyanato complexes but in a downfield direction in the iodide complexes with the bromide complexes displaying little evidence of any dipolar effects. More definite proof for these conclusions comes from a consideration of the solvent shifts observed in these systems.

Table III. Effect of Metal Complexes on Chloroform Proton Resonance Shift (at —60°).

Complex	Shift (Hz) [a]	Complex	Shift (Hz) [a]
$Nipy_4Cl_2$	+26	$Copy_4Cl_2$	—96
$Nipy_4Br_2$	+26	$Copy_4Br_2$	+35
$Nipy_4I_2$ [b]	+11	$Copy_4I_2$	+116
$Nipy_4(NCS)_2$	—2	$Copy_4(NCS)_2$	—80
$Ni(\gamma\text{-pic})_4Cl_2$ [b]	+12	$Co(\gamma\text{-pic})_4Cl_2$	—48
$Ni(\gamma\text{-pic})_4Br_2$ [b]	+9	$Co(\gamma\text{-pic})_4Br_2$	+32
$Ni(\gamma\text{-pic})_4I_2$ [b]	+10	$Co(\gamma\text{-pic})_4I_2$	+151
$Ni(\gamma\text{-pic})_4(NCS)_2$ [b]	0	$Co(\gamma\text{-pic})_4(NCS)_2$	—55

[a] Except as noted the complexes were examined as 0.10 *M* solutions in $CDCl_3$ containing 1% $CHCl_3$, which was also 0.2 *M* with respect to pyridine. [b] Complexes examined as 0.05 *M* solutions because of lower solubility. However, the shifts are linear with respect to concentration variations and thus comparisons are readily made.

The $CHCl_3$ solvent shifts in Table III show some dramatic differences between the cobalt and nickel series. The upfield solvent shifts observed in the systems containing $Nipy_4Cl_2$, $Nipy_4Br_2$, and $Nipy_4I_2$ are slightly larger than those observed[12] for $CHCl_3$ solutions containing $[(C_6H_5)_3PCoI_3]^-$ and $[(C_6H_5)_3PNiI_3]^-$ ions where the shift was attributed to a contact shift *via* a hydrogen bond between the $CHCl_3$ and the halide on the metal. Apparently this mechanism does not exist in the case of $Nipy_4(NCS)_2$ which shows essentially no solvent shift. The solvent shifts for the cobalt containing systems are much larger than those observed in the nickel cases. It is apparent that the solvent is experiencing a dipolar shift.[13] Since the solvent shifts in the nickel system indicate an interaction between the solvent and the electron spin *via* a halide chloroform hydrogen bond, it is obvious that metal to chloroform-proton distance will result in a smaller value along the z axis on average than along the x and y axes (where the metal—N_4 grouping defines the xy plane). Thus if the metal is magnetically anisotropic, one would expect dipolar solvent shifts in the opposite direction to those observed for the pyridine protons. This is borne out for the $Copy_4Cl_2$ and $Copy_4(NCS)_2$ systems where the pyridine resonances experience an upfield dipolar shift (*vide supra*) whereas the solvent protons are shifted downfield. Thus the sign and magnitude of the solvent shift can be used as a test for magnetic anisotropy in these systems. In this light, the large upfield solvent shift of the $Copy_4I_2$ system is evidence for considerable magnetic anisotropy of the opposite sign to that found for $Copy_4Cl_2$ and $Copy_4(NCS)_2$. Therefore the pyridine protons in $Copy_4I_2$ should experience a downfield dipolar shift. This agrees with the tentative explanation put forward from consideration of the ligand shifts.

The ligand and solvent shifts in the case of $Copy_4Br_2$ indicate that this system has only slight magnetic anisotropy. The solvent shift is in the same direction as $Copy_4I_2$ but much smaller and only slightly larger than the corresponding nickel complex.

We have so far assumed that the structure of all of the complexes remains *trans*-octahedral in solution, and that the explanation of the observations is a change in sign of the magnetic anisotropy in a series of closely related cobalt complexes. There are some alternative explanations for these observations which will now be considered.

(1) Some of the cobalt complexes change to a *cis* configuration in solution.

(2) Some of the cobalt species become five-coordinate complexes of the type $Copy_3X_2$ or $[Copy_4X]^+X^-$ in solution.

Several pieces of evidence indicate that the explanation based on anisotropy inversion is the best available. Firstly the nmr spectra of these complexes at temperatures low enough to allow observation of both coordinated and free ligand (~—60°) shows that there is only one type of coordinated ligand, and that there are four of these per cobalt. This immediately precludes *cis* Mpy_4X_2 species and five-coordinate species of the type $Copy_3X_2$. The electronic spectra of the cobalt complexes in chloroform containing excess pyridine and cooled to ~—20° are very similar to the reflectance spectra of the solids.[14] Further, the intensities of these transitions are typical of octahedral cobalt(II); *i.e.* $\varepsilon < 20$, militating against five-coordinate structures of the type $[Copy_4X]^+X^-$ where the intensities would be expected to be similar to those reported for tris(2—diphenylphosphinoethyl)amineCoX[15] where ε values of $\geqslant 100$ were found. We thus conclude that all of the complexes examined retain the *trans*-octahedral structure in solution.

It is apparent therefore that the cobalt complexes fall into two groups, with respect to magnetic anisotropy, the chloride and isothiocyanate exhibit $g_{\|} > g_{\perp}$ whereas the iodide and bromide display anisotropy of the same sign as the cobalt(II)acetylacetonate-adducts,[2,5] $g_{\perp} > g_{\|}$.

The effect of a weak field of O_h symmetry on the lowest state (^4F) of the free Co^{2+} ion is to resolve the sevenfold orbital degeneracy into two triplets and a singlet, with the lowest state being a triplet ($^4T_{1g}$). In considering the magnetic anisotropy of the cobalt compounds studied here at least two further perturbations must then be applied, (a) a lower symmetry component (δ) and (b) spin-orbit coupling. This leads to a ground state manifold containing six Kramers doublets. If δ is known to be much larger than λ the spin-orbit coupling constant, the anisotropy results could be interpreted[16] in terms of the sign of δ. Such

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an approach is probably of limited usefulness when δ and λ are of comparable magnitude,[17] which may be the situation in many cobalt compounds.[18] This may explain the difficulty in interpreting the inversion of magnetic anisotropy by use of 'chemical logic'. Gerloch and Slade have recently shown[19] that the anisotropy of distorted tetrahedral nickel(II) complexes can be expected to pass through at least two inversions with respect to variation of a single parameter (in this case an angular distortion parameter). Similar trends might well be expected in octahedral cobalt(II) complexes.[20]

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