Observation of Intramolecular Paramagnetic T_1 Spin Decoupling in the ^{13}C NMR Spectra of Triazacyclohexane Complexes of Ni(II)

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Received May 15, 2006; E-mail: r.d.kohn@bath.ac.uk

As part of our ongoing investigation of triazacyclohexane complexes,[1] we became interested in the quantitative interpretation of NMR spectra of paramagnetic transition metal complexes. The relaxation times T_1 and T_2 of an observed nucleus depend on the distance r from the paramagnetic metal center. T_1^{-1} and T_2^{-1} (if contact contributions can be neglected) will be proportional to r^{-6} and can provide valuable structural information on the complex in solution and have a similar origin in dipolar interactions as the NOE enhancement. These structural constraints from NMR data are widely used in solution structure refinement.[2] Yet paramagnetic relaxation enhancement in the immediate vicinity of the metal, in particular, for heteronuclei, such as ^{13}C, has rarely been used for distance measurements due to difficulties of obtaining reliable relaxation times.

While T_1 can be obtained by the relatively time-consuming inversion–recovery method, T_2 can be readily obtained[2] from the line width $\Delta\nu_{1/2}$ according to

$$T_2^{-1} = \pi\Delta\nu_{1/2} \tag{1}$$

However, the ^{13}C NMR spectra of the new benzyl-substituted triazacyclohexane complexes of Ni(II) described below contained unusually broadened aromatic signals for the ortho position with apparently very small vicinal C–F or C–H coupling constants. We found that this observation can be explained by T_1 spin decoupling from much faster relaxing ^{1}H or ^{19}F nuclei in close proximity to the paramagnetic nickel center—in fact, here we demonstrate that quantitative treatment of this effect leads to improved relaxation data for both the ^{13}C and attached ^{1}H or ^{19}F nuclei. This effect has been described theoretically over 30 years ago[3] and was observed in a few occasions as extra broadening due to ligand exchange with paramagnetic metals and for nuclei close to fast-relaxing heteronuclei, such as ^{205}Tl.[4] None of these cases were suitable to confirm this effect quantitatively. The nickel complexes described here present the first instance of this effect with spectra near the "coalescence" point with reduced apparent coupling constants and exchange-broadened signals for doublet cases but also for triplets and quartets. We present approximate solutions to the complex equations for the line shape. This effect should generally be considered for the NMR of heteronuclei strongly coupled to ^{1}H or ^{19}F in proximity to a paramagnetic center.

The nickel complexes can be prepared according to eq 2. The diamagnetic zinc complexes can be prepared analogously.
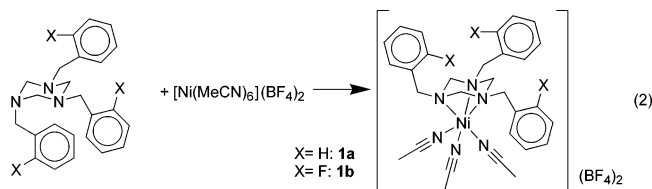
The complexes are highly soluble in acetonitrile. The exchange of nickel coordinated and solvent acetonitrile is slow enough on the NMR time scale to give well separated MeCN signals. Magnetic
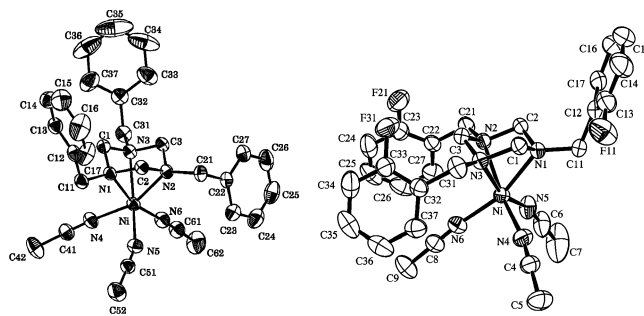
Figure 1. Cation in the crystal structure of **1a** (left) [and **1b** (right)]. Distances (Å): Ni–N1 2.136(2) [2.145(1)] and Ni–N4 2.037(3) [2.026(2)]. Corresponding distances for **1b/Zn**: 2.257(2) and 2.058(2).
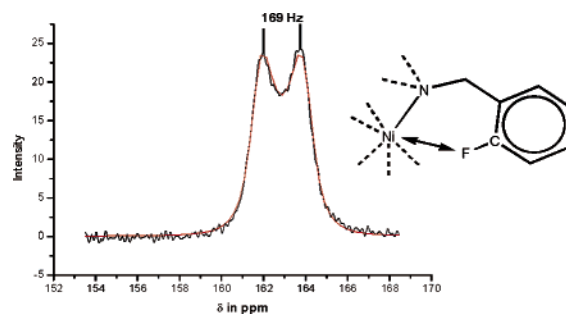
Figure 2. Fast relaxation of F in close proximity to the paramagnetic Ni(II) leads to exchange broadening and decoupling of the attached ^{13}C as shown for the ortho CF in **1b** along with the least-squares fit (red) to the full line shape expression.

moments in solution (3.15(5) μ_B) and UV/vis absorptions (10 D_q = 10600(100) and B = 860(20) cm^{-1}) are as expected for an octahedral d^8 Ni(II) complex with two unpaired electrons. Layering of the MeCN solution with Et$_2$O or toluene resulted in deep blue crystals of **1a** and **1b** and its isostructural zinc analogue **1b/Zn**. The structures of the cations in **1a** and **1b** are shown in Figure 1 along with some bond distances. The zinc complex has slightly longer metal–nitrogen bond distances.

NMR data of MeCN solutions of **1a/b** and their Zn analogues as diamagnetic references are listed in Supporting Information. T_1 was obtained by the inversion–recovery method and T_2 from the line widths according to eq 1. The ^{13}C data were obtained with and without ^{1}H decoupling.

The ^{13}C NMR signals for the ortho C–F in **1b** are shown in Figure 2. The signal is much broader (135 Hz) than the other (decoupled) ortho carbon signal (29 Hz) and shows a doublet with an apparent ^1J(C–F) coupling constant of only 169 Hz—much smaller than the expected 249 Hz observed for the diamagnetic Zn complex. While all other aromatic C–H positions gave typical ^1J(C–H) coupling constants in both the Ni and Zn complexes and similar line widths in the coupled and decoupled spectra, broad singlets are observed for the coupled ortho C–H positions (100 Hz) that become much narrower on decoupling (30 Hz). However, the broadening is smaller than the expected C–H coupling constant (^1J = 160 Hz).

This observation can be quantitatively rationalized by the theoretical treatment of the T_1 spin decoupling by Navon and Polak.[3] We have extended their approximate solution for the broadening in the fast exchange limit to the slow exchange observed in **1b**. The exact expressions for the line shape in the doublet, triplet, and quartet cases are given in the Supporting Information. It can be shown that coalescence of a doublet signal for nucleus A (with relaxation time T_{2A}) coupling to an $I = \frac{1}{2}$ nucleus X with coupling constant J_X (in hertz) to a single peak due T_1 spin decoupling with the longitudinal relaxation time T_{1X} occurs at

$$\pi^2 J_X^2 = \frac{(T_{1X}^{-1} + T_{2A}^{-1})^3}{3T_{2A}^{-1} + 2T_{1X}^{-1}} \tag{3}$$

An approximate general expression can be derived for the line width W_A (in hertz) of the observed nucleus A coupled to a number n of nuclei X with a coupling constant J_X (in hertz) when the signal has coalesced to a single broadened peak and reduces to the second expression for coupling to n equivalent nuclei:

$$\pi W_A \approx T_{2A}^{-1} + \sum_X \frac{\pi^2 J_X^2}{T_{1X}^{-1} + T_{2A}^{-1}} = T_{2A}^{-1} + n\frac{\pi^2 J_X^2}{T_{1X}^{-1} + T_{2A}^{-1}} \tag{4}$$

This approximation is valid within 5% for $J < (T_{1X}^{-1} + T_{2A}^{-1})/10$.

The corresponding expression for the widths of the peaks in the multiplet before coalescence has been given before by Navon and Polak as

$$\pi W_A \approx T_{2A}^{-1} + \frac{n}{2}T_{1X}^{-1} \tag{5}$$

For the case of a doublet, the following expression for the peak separation Δ (apparent coupling constant) can be derived for the case of $T_{2A}^{-1} \ll \pi J_X, T_{1X}^{-1}$:

$$(\pi\Delta)^2 \approx \pi^2 J_X^2 - (1/2)T_{1X}^{-2} - (1/2)T_{2A}^{-1}T_{1X}^{-1}\left(1 - \frac{T_{1X}^{-2}}{4\pi^2 J_X^2}\right) \approx$$
$$\pi^2 J_X^2 - (1/2)T_{1X}^{-2} \tag{6}$$

For an exact line shape analysis, the full expressions given in the Supporting Information have to be used. The ^{13}C NMR signal for the ortho C–F in **1b** is a good test case, showing a doublet close to coalescence. Least-squares fit to the full expression is shown in Figure 2 and results in $T_{1X}^{-1} = 724(16)$, $T_{2A}^{-1} = 66(10)$, and $J_X = 249(3)$ Hz. These are within experimental error of the values obtained from a direct inversion recovery measurement ($T_{1X}^{-1} = 708(1)$ Hz), CPMG measurement ($T_{2A}^{-1} = 53(4)$ Hz), and from the diamagnetic Zn complex ($J_X = 249$ Hz) and, they confirm the validity of this analysis. Lorentzian fit to a doublet gives an apparent widths of $\pi W_A = 424(10)$ Hz–close to the approximate value of 420 Hz (eq 5). The approximate peak separation Δ is calculated to 191 Hz (1st order) or 186 Hz (2nd order) and close to the observed 169 Hz.

The ^{13}C NMR signals for the ortho CH in **1a** and **1b** are cases for T_1 spin-decoupled broadening just after coalescence to a single broad peak. Unfortunately, the ^{13}C NMR signals for para CH overlap with this signal in both cases. However, ^{1}H decoupling gives narrower, nearly baseline resolved singlets that allow the direct measurement of both T_{2A}^{-1} of 35(4) Hz for para CH (**1a** and **b**) and 79(4) (**1a**) and 90(3) Hz (**1b**) for ortho CH. Simultaneous least-squares fit of the coupled spectrum to two peaks of the full line shape expression gives widths of $\pi W_A = 35(5)/32(9)$ Hz (para **1a/**

1b) and 79(16)/91(20) Hz (ortho **1a/1b**), and the coupling constants of 151(9)/156(12) for ortho **1a/1b** and 160(1)/163(7) Hz for para **1a/1b** are very close to those found in the zinc complexes. T_1^{-1} values of the attached ortho (900(60)/1000(80) and para protons (71(7)/65(12) Hz) for **1a/1b** are close to those observed by inversion–recovery experiments (870(90), 1030(220), 61(7), and 67(7), respectively). Thus, a satisfactory explanation for the observed line shape can be given by the equations for T_1 spin decoupling.

Generally, broadening due to T_1 spin decoupling in very broad peaks in ^{13}C NMR spectra can be detected by a decrease of the line width upon ^{1}H decoupling. Such a case is the "quartet" for CH_3CN observed at just over $+200$ ppm for both **1a** and **1b**. ^{1}H decoupling around -30 ppm (coordinated CH_3CN) results in a decrease of the line width from $\pi W_A = 1486(9)$ to $1059(6)$ Hz (**1a**) and from $\pi W_A = 1301(16)$ to $986(30)$ Hz (**1b**). Fast exchange of MeCN in the zinc complex does not give a separate signal for coordinated MeCN and therefore no "diamagnetic" J value for the complex. However, using the coupling constant for MeCN in $[Pd(MeCN)_4](BF_4)_2$ ($J = 140$ Hz) and the measured T_{1X}^{-1} (327(6) and 330(30) Hz) in eq 4 ($n = 3$) gives $\pi W_A = 1478$ Hz (**1a**) and $\pi W_A = 1390$ Hz (**1b**). The full expression gives $\pi W_A = 1439$ Hz (**1a**) and $\pi W_A = 1340$ Hz (**1b**), in excellent agreement with the experiment.

The compounds also provide a case for a broadened and coalesced T_1 spin-decoupled triplet. The ^{13}C signal of the benzylic CH_2 is observed at about -100 ppm, and the line widths decrease upon ^{1}H decoupling at around $+145$ ppm (CH_2) from $\pi W_A = 1363(16)$ to $1244(16)$ Hz (**1a**) and from $\pi W_A = 1288(31)$ to $1220(30)$ Hz (**1b**). Using $J = 139$ Hz from **1a,b/Zn** and the measured T_{1X}^{-1} (2750(100) and 2760(70) Hz) gives calculated $\pi W_A = 1340$ (**1a**) and 1316 Hz (**1b**). The full expression gives 1354 (**1a**) and 1330 Hz (**1b**). Thus, this smaller but still significant effect is well described by the T_1 spin decoupling.

The results show that T_1 spin decoupling can have a significant effect on the line shapes in NMR spectra of paramagnetic compounds, in particular, in ^{13}C NMR. Expressions have been derived that allow a quantitative analysis of the effect. The use of the expressions will allow a correction of the measured line widths for extra broadening by T_1 spin decoupling and gives an independent method for the determination of T_1 of the attached nuclei X and the coupling constant J_X and may be difficult to determine from other methods. As these relaxation times contain structural information, the inclusion of T_1 spin decoupling effects will give more reliable data for structure determination in solution. A full treatment of the NMR spectra of the nickel complexes for structure determination will be given in a separate publication.

Supporting Information Available: Crystallographic data of **1a**, **1b**, and **1b/Zn**, experimental preparations and analytical data, including NMR spectra and data, deductions for equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA063357X