

^{15}N - ^{13}C Coupling Constants and $^{15}\text{N}/^{14}\text{N}$ Isotope Effects on ^{13}C N.M.R. Chemical Shifts of Pyrimidine-2(1*H*),4(3*H*),5(6*H*),6-tetrone 5-Oximato Complexes

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^{15}N -Labelling of the oxime function of pyrimidine-2(1*H*),4(3*H*),5(6*H*),6-tetrone 5-oximato iron and ruthenium complexes has enabled the measurement of one- and two-bond ^{13}C - ^{15}N coupling constants and upfield isotopic shifts in the ^{13}C n.m.r. spectra.

During the course of the assignment of the ^{13}C n.m.r. resonances for free and co-ordinated oximes it was found necessary to enrich the oxime function in ^{15}N . This labelling has permitted the measurement of ^{15}N - ^{13}C coupling constants and $^{14}\text{N}/^{15}\text{N}$ isotopic effects on ^{13}C resonances. Interesting applications of the isotopic effect on ^{13}C chemical shifts in the case of $^{18}\text{O}/^{16}\text{O}$ substitution have already been reported in studies of metal-carbonyl interactions.^{1,2} Unfortunately few data concerning the $^{14}\text{N}/^{15}\text{N}$ isotopic effect³ and ^{15}N - ^{13}C couplings^{3,4} in co-ordination chemistry are available in the literature.

We report herein the results concerning pyrimidine-2(1*H*),4(3*H*),5(6*H*),6-tetrone-5-oxime, (1) (denoted H_3vi); the anion (2) obtained by deprotonation of the oxime function; the trischelate *fac*- $[\text{Fe}(\text{H}_2\text{vi})_3]^-$ (3); *fac*- $[\text{Ru}(\text{H}_2\text{vi})_3]^-$, (4).

The natural abundance Fourier transform ^{13}C n.m.r. proton noise decoupled spectra† of the unlabelled compounds (1)–(4) dissolved in $(\text{CD}_3)_2\text{SO}$ each contain four signals. Those for (3) and (4) indicate three equivalent ligands and suggest a *facial* configuration for the trischelates with a rigid structure in solution. The possibility of geometrical changes within the n.m.r. time scale may be ruled out. It was not possible to assign the ^{13}C resonances with the help of classical decoupling techniques because the ^{13}C - ^1H coupling constants were found to be less than 0.2 Hz. In order to

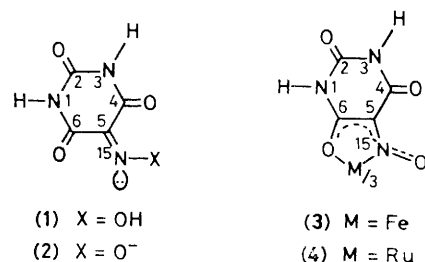


Table 1. nJ (^{15}N - ^{13}C) Values and $^{14}\text{N}/^{15}\text{N}$ isotope effects on ^{13}C chemical shifts in oximato complexes.

Species	1J [N(5)-C(5)] /Hz	C(5) isotopic shift /p.p.m.	2J [N(5)-C(6)] /Hz
(1)	2.55 ± 0.08	-0.025 ± 0.003	10.47 ± 0.08
(2)	5.51 ± 0.14	-0.028 ± 0.007	9.18 ± 0.14
(3)	4.39 ± 0.12	-0.029 ± 0.006	5.86 ± 0.12
(4)	5.13 ± 0.08	-0.030 ± 0.003	5.61 ± 0.08

obtain an unequivocal assignment, ^{15}N -labelled compounds were synthesized. The ^{15}N (5)-enriched (96%) oxime was prepared by the standard procedure of C-oximation using barbituric acid and labelled $\text{Na}^{15}\text{NO}_2$ (96%). The ^{15}N -labelled compounds (2)–(4) were synthesized from (1) as previously described^{5,6} for unlabelled compounds and their natural abundance ^{13}C n.m.r. spectra were obtained, from which absolute values for nJ [^{15}N (5)- ^{13}C] were deduced.

† Spectra were recorded at 20.15 MHz on a Bruker WP 80 spectrometer.

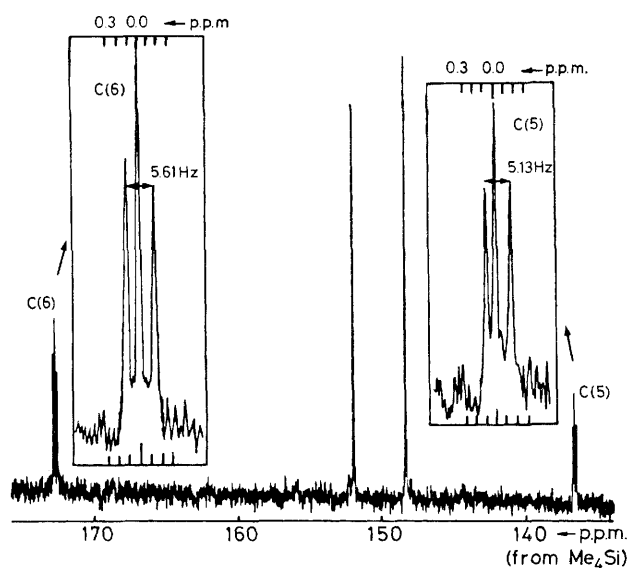


Figure 1. ^{15}N -Labelled (60%) natural abundance ^{13}C carbonyl and oxime n.m.r. signals for (4) in $(\text{CD}_3)_2\text{SO}$. The ^{15}N -labelled $^{13}\text{C}(5)$ oxime signal is shifted upfield by 0.030 p.p.m. from its unlabelled analogue.

The absolute coupling constants, $^1J[\text{N}(5)\text{--C}(5)]$, observed for the free oxime (1) and the oximate (2) (Table 1) are in the same range as those reported for several other oximes. The 1J values for the oximate complexes (3) and (4) are in the same range as those reported for some cyano³ and methylidimethylaminocarbene complexes.⁴ The 1J values listed in Table 1 are less than 6 Hz and are always smaller than the corresponding $^2J[\text{N}(5)\text{--C}(6)]$ values for the α -anti carbon atom C(6) while $^2J[\text{N}(5)\text{--C}(4)]$ values for the α -syn carbon atom C(4) are negligible (less than 0.2 Hz) as are the $^4J[\text{N}(5)\text{--C}(2)]$ values. The present results for (1) and (2) are in good agreement with those previously reported for oxime derivatives such as acetophenone oximes:⁷ the two-bond couplings to nitrogen can be related to lone pair orientation. Upon co-ordination, significant changes are observed in the chemical shifts and the $^{15}\text{N}\text{--}^{13}\text{C}$ coupling constants (Table 1) of the C(5) and C(6) resonances; these observations indicate that co-ordination occurs through the N(5) and O(6) atoms.

The ^{15}N -isotope effect was measured by the following procedure. The ^{13}C n.m.r. spectrum of the ^{15}N -labelled compound was obtained. A measured quantity (40%) of un-

labelled compound was added to the ^{15}N sample and the spectrum was obtained for the labelled-unlabelled mixture (Figure 1). Appreciable upfield shifts (ca. 0.03 p.p.m.) were observed for all the compounds for the carbon bearing the ^{15}N atom, taking the corresponding ^{13}C signal of the unlabelled compound as a standard. The isotopic shifts for the carbon bearing the ^{15}N atom are comparable in magnitude and direction with the recently reported $^{14}\text{N}/^{15}\text{N}$ one-bond isotope effect on ^{13}C chemical shielding in cyano complexes³ and they are also comparable with the $^{16}\text{O}/^{18}\text{O}$ isotope effect observed in metal carbonyl derivatives.¹ It should be noted that a weak second atom shift for the atom adjacent to C(6) can be detected when the solubility of the compound allows a good signal:noise ratio to be obtained. Indeed the $^{13}\text{C}\text{--}^{15}\text{N}$ couplings permit a good determination of the n.m.r. peaks (Figure 1) without the help of the curves resolver set. After several measurements the shift is found to be significant although close to the estimated experimental error: upfield for (1) (-0.006 ± 0.003 p.p.m.) and downfield for (4) ($+0.006 \pm 0.003$ p.p.m.).

The observation of isotopic effects through several bonds appears to be a general phenomenon. Indeed after the introduction of one deuterium atom into cyclic⁸ or aliphatic⁹ compounds, shifts in the α , β , and γ carbon signals are detected. However the magnitudes of such shifts are ten-fold greater than the $^{14}\text{N}/^{15}\text{N}$ effects reported in the present work.

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