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Carbon-13 and Nitrogen-15 Nuclear Magnetic Resonance Study of 1*H*,3*H*-Pyrimidine-2,4,5,6-tetrone 5-Oximato Complexes and Their 1,3-Dimethyl Derivatives

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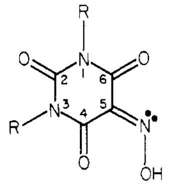
Carbon-13 NMR spectra have been obtained for 1*H*,3*H*-pyrimidine-2,4,5,6-tetrone 5-oxime, H_3vi, the monoanion H_2vi^-, obtained after deprotonation of the oxime function, and the low-spin d^6 complexes $Co(H_2vi)_3$, $Fe(H_2vi)_3^-$, and $Ru(H_2vi)_3^-$, as well as the corresponding 1,3-dimethyl compounds. The ^{13}C- and ^{15}N-labeled compounds were synthesized in order to obtain an unequivocal assignment of the ^{13}C signals. The assignments are based on the following arguments: (1) ^{13}C-labeled carbon 2 in the pyrimidine ring; (2) dependence of the $^{13}C-^{15}N$ coupling constant values on lone-pair orientation of the N_5 atom; (3) the $^{14}N/^{15}N$ isotope effects on ^{13}C chemical shielding. The ^{13}C shift changes from the free ligand positions upon protonation and complexation reflect the current concept of Lewis-acid charge withdrawal (H^+, C_0(III), and π-back-bonding (Fe(II) and Ru(II))) when comparisons are made for methyl carbons at the N_1 and N_3 sites in the *N*-methyl derivatives. The changes in the ^{13}C chemical shift of the C_1 and C_3 atoms are consistent with the ^1H shift changes. The shift changes at the C_2, C_4, C_5, and C_6 atoms of the pyrimidine ring are not explained in this manner. The ^{15}N NMR spectra have been obtained for the ^{15}N-labeled compounds. An observed correlation between the ^{15}N chemical shifts and the energy of the electronic transition suggests that the paramagnetic contribution is dominant.

Ketoximes and their derivatives are interesting ligands because these compounds have low-lying π^* systems which may be available for back-bonding.[2] Several means for obtaining information concerning the nature of metal-to-ligand π bonding have been previously described.[3] More recently, NMR studies demonstrate that chemical shift changes offer a promising means[4] of observing directly π-back-bonding effects. However, the interpretation of NMR data, such as chemical shifts[5] and coupling constants,[6] often depends on theoretical considerations which provide quantitative information about the electron density at the atoms of the molecules of interest. The generally unsatisfactory nature of the theory of NMR shifts in coordination chemistry is well documented,[7] and the nature of the mechanism by which electron density alterations cause chemical shift change in transition-metal complexes is not yet clear.[4d,8]

In this paper we report a ^{13}C and ^{15}N NMR study of 1*H*,3*H*-pyrimidine-2,4,5,6-tetrone 5-oxime, H_3vi, the 1,3-dimethyl derivative, Hdmvi, the monoanions, H_2vi^- and $dmvi^-$, obtained after deprotonation of the oxime function of H_3vi and Hdmvi, and diamagnetic substitution-inert d^6 cobalt(III), iron(II), and ruthenium(II)[2f] complexes. The interpretation of the ^{13}C NMR spectra requires the correct assignment of the signals. For this assignment it was necessary to use ^{13}C-enriched and ^{15}N-labeled molecules. The influence of protonation and coordination to the metal center on chemical shifts of ^1H, ^{13}C, and ^{15}N NMR signals, $^{13}C-^{15}N$ coupling constants, and ^{15}N isotope effects is discussed.



R = H, H_3vi
R = CH_3, Hdmvi

Experimental Section

Materials. $(CD_3)_2SO$ (99.8 atom % D, Merck), $Na^{15}NO_2$ (96 atom % ^{15}N, Merck), urea ($NH_2{}^{13}C(O)NH_2$; 90 atom % ^{13}C, CEA France), and barbituric acid ($C_4H_4N_2O_3$; Merck) were used without further purification. $Na_2[Ru(NO)(NO_2)_4(OH)]\cdot 2H_2O$ was prepared by a previous procedure.[2f]

Syntheses. The unlabeled compounds H_3vi (**1**), NaH_2vi (**2**), $Co(H_2vi)_3$[9] (**3**), $Na[Fe(H_2vi)_3]$[10] (**4**), $Na[Ru(H_2vi)_3]$ (**5**) and their *N*-dimethyl derivatives Hdmvi (**6**), Na(dmvi) (**7**), $Co(dmvi)_3$ (**8**), $Na[Fe(dmvi)_3]$ (**9**), and $Na[Ru(dmvi)_3]$ (**10**) were synthesized by methods outlined previously.[2f]

The following syntheses of the ^{13}C- and ^{15}N-labeled compounds were developed so as to proceed smoothly, be economical in the use of [^{13}C]urea and $Na^{15}NO_2$, and result in high isotopic substitution in the desired products. The labeled compounds were characterized by IR, UV-vis, and ^1H, ^{13}C, and ^{15}N NMR spectroscopy.

[2-^{13}C]Barbituric Acid (10 Atom % ^{13}C). Ethyl malonate (7 g, 0.043 mol), unlabeled urea (2.3 g, 0.038 mol), and ^{13}C-labeled urea (0.26 g, 0.0043 mol) were dissolved in dry ethanol (30 mL) containing Na (1 g, 0.043 mol) and refluxed for 7 h. After the mixture cooled, dilute HCl was added and [2-^{13}C]barbituric acid precipitated. ^{13}C NMR spectra showed 10 atom % ^{13}C incorporation at the C_2 position; yield 80%.

[2-^{13}C]H_3vi (10 Atom % ^{13}C). [2-^{13}C]H_3vi was obtained by the standard procedure of C-oximation with [2-^{13}C]barbituric acid and $NaNO_2$ in acidic media; yield 90%.

Na[[2-^{13}C]H_2vi] (10 Atom % ^{13}C). [2-^{13}C]H_3vi was dissolved in water by addition of NaOH (1 equiv). Ethanol was added, and Na[[2-^{13}C]H_2vi] precipitated; yield 95%.

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Table I. ^{13}C Nuclear Magnetic Resonance Chemical Shifts[a] of Free, Deprotonated, and Complexed Ketoximes

	compd no.	C_3	C_1	C_5	C_2	C_4	C_6
H_3vi	**1**			136.1	149.6	155.0	158.9
H_2vi^-	**2**			145.1	150.6	152.7	165.6
$Co(H_2vi)_3$	**3**			133.7	148.0	151.1	175.4
$Fe(H_2vi)_3^-$	**4**			138.6	148.6	150.1	173.5
$Ru(H_2vi)_3^-$	**5**			136.7	148.7	152.2	173.3
Hdmvi	**6**	27.5	28.2	136.0	150.8	153.8	158.4
$dmvi^-$	**7**	26.2	27.3	145.1	150.2	151.4	163.5
$Co(dmvi)_3$	**8**	27.7	28.8	135.6	149.5	150.9	177.5
$Fe(dmvi)_3^-$	**9**	26.9	28.0	138.5	148.8	149.3	171.1
$Ru(dmvi)_3^-$	**10**	26.5	27.7	137.1	149.6	151.2	171.3

[a] In ppm downfield relative to $(CH_3)_4Si$ as internal standard.

$Na[Fe([2\text{-}^{13}C]H_2vi)_3]$ (10 Atom % ^{13}C). The ^{13}C-labeled product was prepared according to the method used for the unlabeled compound,[10] with iron(II) sulfate and $Na[[2\text{-}^{13}C]H_2vi]$; yield 50%.

$Ba_{0.5}[Ru([2\text{-}^{13}C]H_2vi)_3]$ (10 Atom % ^{13}C). The ^{13}C-labeled product was prepared according to the method used for the unlabeled compound,[2f] with $Na_2[Ru(NO)(NO_2)_4OH]$ and $[2\text{-}^{13}C]$barbituric acid; yield 60%.

$[[5\text{-}^{15}N]H_3vi]$ (96 Atom % ^{15}N). $[5\text{-}^{15}N]H_3vi$ was obtained by the standard procedure of C-oximation with barbituric acid and $Na^{15}NO_2$ in acidic media; yield 80%.

$Na[[5\text{-}^{15}N]H_2vi]$ (96 Atom % ^{15}N). The method with $[5\text{-}^{15}N]H_3vi$ was analogous to those reported for the ^{13}C-labeled compound; yield 90%.

$Na[Fe([5\text{-}^{15}N]H_2vi)_3]$ (96 Atom % ^{15}N). The ^{15}N-labeled product was prepared from iron(II) sulfate and $Na[[5\text{-}^{15}N]H_2vi]$ according to a method analogous to that reported for the unlabeled compound;[10] yield 50%.

$Ba_{0.5}[Ru([5\text{-}^{15}N]H_2vi)_3]$ (96 Atom % ^{15}N). A sample of $Na_2[Ru(NO)(NO_2)_4OH]$ (0.4 g, 0.01 mol) was dissolved in an aqueous solution (20 mL) containing $Na[[5\text{-}^{15}N]H_2vi]$ (0.54 g, 0.03 mol). $[NH_3OH]Cl$ (0.35 g, 0.05 mol) was added portionwise to the stirred solution. The solution was warmed at 40 °C for 5 h, and it became deep red. After the mixture cooled to room temperature, a saturated solution of $BaCl_2$ was added. A red product precipitated immediately and was filtered off, washed several times with small portions of water, and dried in vacuo; yield 80%.

NMR Spectroscopy. ^1H NMR spectra were recorded with a multinuclear Bruker WP 80 spectrometer operating in the Fourier transform mode. All the spectra were recorded at 32 ± 1 °C for 0.1 M solutions in $(CD_3)_2SO$ unless otherwise indicated. The proton-noise-decoupled ^{13}C NMR spectra were recorded at 20.15 MHz. Typical parameters were as follows: pulse width 3 μs (i.e. 30° flip angle on spectrometer); no interpulse delay; acquisition time 0.8–1.6 s depending on the sweep width (5000 Hz) and number of data points (8K or 16K). Proton-coupled spectra were obtained by the gated decoupling technique (decoupler off only during acquisition). Chemical shift data of ^1H and ^{13}C NMR spectra are reported in ppm relative to internal $Si(CH_3)_4$.

The ^{15}N isotope effect was measured by the following procedure. The ^{13}C NMR spectrum of the ^{15}N-labeled compound (96 atom % ^{15}N) was obtained. A measured quantity of unlabeled (^{14}N) compound was added to the ^{15}N sample, and the ^{13}C NMR spectrum was obtained for the labeled–unlabeled mixture. An additional measured quantity of unlabeled compound was added, and the spectrum was again obtained. In a typical 1000-Hz spectrum, the resolution was approximately 0.12 Hz/data point.

The ^{15}N NMR spectra were recorded at a temperature of 25–30 °C for 0.1 M solutions of ^{15}N-labeled compounds (96 atom % ^{15}N) in $(CD_3)_2SO$ contained in 10 mm o.d. tubes. A Bruker WP 80 operating at 8.12 MHz was used to obtain these spectra. The ^{15}N measurements were made with use of broad-band proton decoupling; the decoupler was turned on only during acquisition of data so the sample remained at the ambient probe temperature. Typical parameters were as follows: pulse width 30 μs (i.e. 27° flip angle on spectrometer); interpulse delay 5 s; acquisition time 1.36 s depending on the sweep width (6000 Hz) and number of data points (16K). Chemical shift data are reported in ppm and are referred to CH_3NO_2 as reference standard. A positive shift corresponds to increasing frequencies.

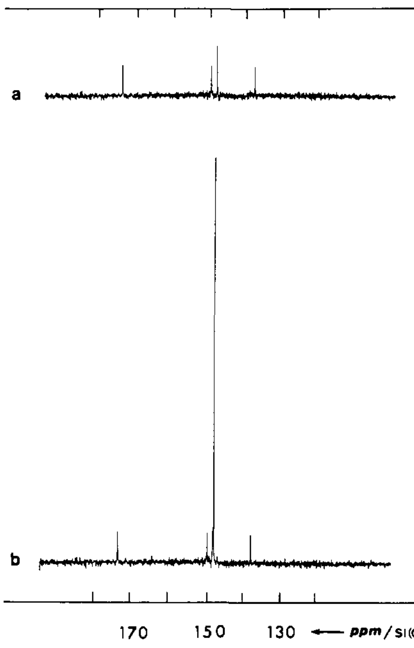

Figure 1. ^{13}C NMR spectra of $Fe(H_2vi)_3^-$ in $(CD_3)_2SO$: (a) natural abundance; (b) ^{13}C enriched at the C_2 atom (10 atom %).

Calculations. CNDO/2 molecular orbital calculations[11] were carried out for H_3vi and H_2vi^-. The molecular dimensions of H_3vi and H_2vi^- were deduced from X-ray structures of H_3vi[12] and NaH_2vi.[13]

Results and Discussion

Assignment of ^{13}C NMR Signals. The chemical shifts from natural-abundance ^{13}C NMR proton-noise-decoupled spectra of the unlabeled compounds are listed in Table I. Each spectrum contains four signals in the 100–200-ppm chemical shift range. For the *N*-methyl derivatives two supplementary resonances appear in the methyl region.

These results indicate, for the tris chelates, the presence of three equivalent ligands. On the basis of the ^1H[2f] and ^{13}C NMR data the facial arrangement is strongly suggested for the tris chelates in solution: no coalescence is observed in the temperature range allowed by the solvent $(CD_3)_2SO$. In view of the known chemistry of low-spin d^6 cobalt and ruthenium complexes the possibility of geometrical changes within the NMR time scale may be ruled out.[2f] Therefore, the molecular structures of all the compounds were assumed to be identical with those reported by X-ray data. The pyrimidine rings are strictly planar,[10,12,14] as are the chelate rings in the tris chelates.[10,14] In order to obtain an unequivocal assignment[15,16] of the ^{13}C NMR signals, ^{13}C- and ^{15}N-labeled **1**, **2**, **4**, and **5** were synthesized. Our assignments are based on the following arguments: (1) ^{13}C labeling of carbon 2 in the pyrimidine ring; (2) dependence of the ^{13}C–^{15}N coupling constant values on lone-pair orientation[17] of the N_5 atom; (3) $^{14}N/^{15}N$ isotope effects on ^{13}C chemical shielding.

Comparison of the ^{13}C spectra of **1**, **2**, **4**, and **5** both at natural abundance and with enrichment at position 2 reveals

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Table II. ${}^nJ({}^{15}N-{}^{13}C)$ Values, ${}^{15}N$ Isotope Effects on ${}^{13}C$ Chemical Shifts, and ${}^{15}N$ Chemical Shifts in Free, Deprotonated, and Complexed Ketoximes

${}^{15}N_5$-labeled species	compd no.	${}^1J(N_5-C_5)$/Hz	C_5 isotopic shifts/ ppm	${}^2J(N_5-C_6)$/Hz	${}^{15}N_5$ chem shifts[a]/ ppm
H_3vi	1	2.55 ± 0.08	−0.025 ± 0.003	10.47 ± 0.08	59.6
H_2vi^-	2	5.51 ± 0.14	−0.028 ± 0.007	9.18 ± 0.14	263.0
$Fe(H_2vi)_3^-$	4	4.39 ± 0.12	−0.029 ± 0.006	5.86 ± 0.12	177.5
$Ru(H_2vi)_3^-$	5	5.13 ± 0.08	−0.030 ± 0.003	5.61 ± 0.08	139.6

[a] Downfield relative to CH_3NO_2 as standard.

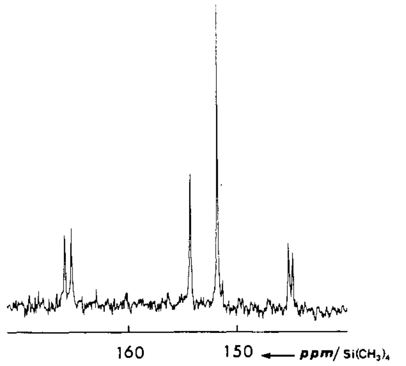

Figure 2. Natural-abundance ${}^{13}C$ NMR spectrum in $(CD_3)_2SO$ of ${}^{15}N_5$-labeled H_2vi^- (96 atom %).

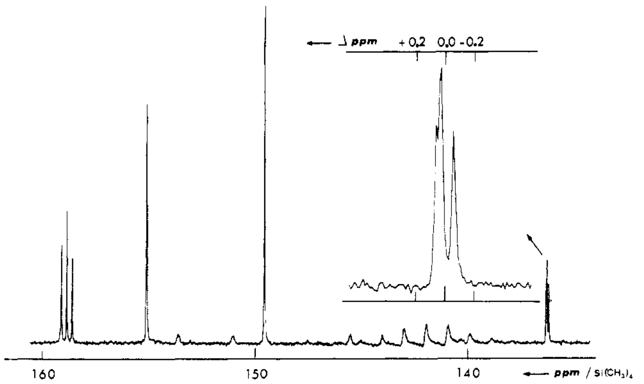

Figure 3. Natural-abundance ${}^{13}C$ NMR spectrum in $(CD_3)_2SO$ of ${}^{15}N_5$-labeled H_3vi (60 atom %).

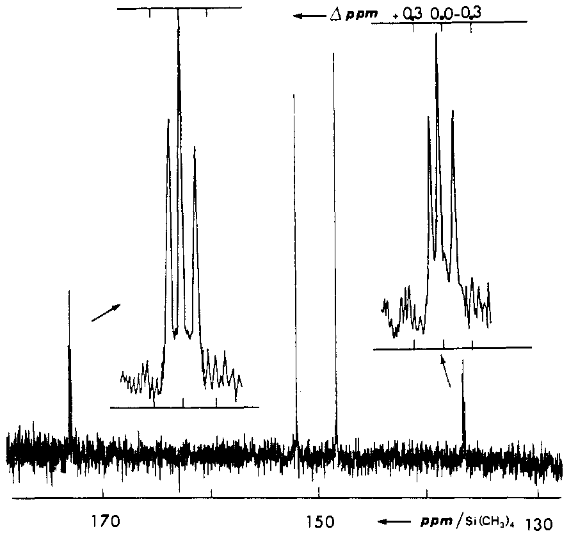

Figure 4. Natural-abundance ${}^{13}C$ NMR spectrum in $(CD_3)_2SO$ of ${}^{15}N_5$-labeled $Ru(H_2vi)_3^-$ (60 atom %).

that only one signal is enhanced approximately 10-fold for the labeled compound (Figure 1). This resonance is assigned to the C_2 of the pyrimidine ring. With the enrichment used, no ${}^{13}C_2-{}^{13}C_{4(6)}$ coupling is detected with the experimental signal:noise ratio.

Assignments for the remaining ${}^{13}C$ resonances of the free and coordinated ketoximes were made by comparison of the natural-abundance ${}^{13}C$ NMR spectra of the ${}^{15}N$-labeled compounds at the N_5 position with the spectra of ${}^{15}N$-unlabeled **1**, **2**, **4**, and **5**.

Replacement of ${}^{14}N$ by ${}^{15}N$ at the C_5 position in the pyrimidine ring gives rise to a doublet for two ${}^{13}C$ resonances of all the ${}^{15}N_5$-labeled compounds (Figure 2). These two doublets may be assigned to the carbon C_5 bound to N_5 and the β carbons, C_4 or C_6, by virtue of their one- and two-bond couplings to the ${}^{15}N_5$. With regard to geminal ${}^{13}C-{}^{15}N$ dependence on lone-pair orientation in oximes[17] it was tempting to assign the doublets to C_6 and C_5 resonances. Indeed the absolute value of ${}^2J({}^{15}N-{}^{13}C)$ is greatly enhanced when the nitrogen 5 lone pair lies cis to the carbon.[17] The marked changes observed upon coordination in the chemical shifts of the two signals differentiated by ${}^{15}N_5$ enrichment are in good agreement with coordination of a metal center through N_5 and O_6 atoms[10,14] directly linked to the C_5 and C_6 atoms, respectively. To assign the C_5 resonance affected by one-bond coupling ${}^{13}C_5-{}^{15}N_5$, the ${}^{14}N/{}^{15}N$ isotope effect on the ${}^{13}C$ NMR spectra was measured.[18] Appreciable upfield shifts (ca. 0.03 ppm) for one signal differentiated by ${}^{13}C-{}^{15}N$ coupling are observed for all of the compounds **1**, **2**, **4**, and **5** (Figures 3 and 4, Table II). This signal is assigned to carbon 5 bearing the ${}^{15}N_5$ atom. Generally, the ${}^{13}C$ resonance of the carbon bearing the labeled atom is shifted substantially and the adjacent carbon atoms are shifted to a smaller extent. The ${}^{13}C$ resonance differentiated by ${}^{15}N-{}^{13}C$ coupling with the less intense isotope effect is assigned to the C_6 atom, and the remaining ${}^{13}C$ resonance is attributed to the C_4 atom.

The ${}^{13}C$ NMR signals of the *N*-methyl derivatives (dmvi) are assigned on the basis of the assignment obtained for the N–H derivatives (H_2vi). Indeed, the chemical shifts of four ${}^{13}C$ signals of dmvi derivatives are observed in the same range as the corresponding signals of the H_2vi^- derivatives (Table I). The two remaining signals are attributed to the C_1 methyl for the more deshielded signal and to the C_3 methyl for the less deshielded signal.

Solvent Effects and Concentration Dependence. The magnitude of solvent effects on chemical shifts has not been investigated systematically. The solubilities of ligands and complexes are poor in several solvents, and ${}^{13}C$ and ${}^{15}N$ NMR measurements were achieved only in dimethyl sulfoxide as solvent. The solvent effects on ${}^1H$ chemical shifts of free and coordinated ketoximato ligands have been previously demonstrated.[2f] Quite different solvent effects will be found for a ketoxime that is complexed to a metal atom as compared to those for the free ligand. The major reason for this effect is likely to be the unavailability of the nitrogen atom lone pair for solvent interaction in the complexes. In dimethyl sulfoxide self-association of oxime molecules should be minimal and intermolecular oxime-to-unshared-pair bondings are substituted by solvent-to-unshared-pair hydrogen bonding. All ${}^1H$

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Table III. Calculated Atomic Populations (Q in Electrons) and Chemical Shifts (σ in ppm) in H_3vi and H_2vi^-

H_3vi	Q	σ	H_2vi^-	Q	σ
N_1	5.248		N_1	5.252	
H_1	0.852		H_1	0.901	
C_2	3.550	149.6	C_2	3.555	150.6
O_2	6.371		O_2	6.428	
N_3	5.242		N_3	5.255	
H_3	0.860		H_3	0.902	
C_4	3.640	155.0	C_4	3.642	152.7
O_4	6.285		O_4	6.415	
C_5	4.062	136.1	C_5	4.249	145.1
N_5	4.924	59.6	N_5	4.924	263.0
O_5	6.162		O_5	6.375	
H_5	0.848				
C_6	3.646	158.9	C_6	3.654	165.6
O_6	6.310		O_6	6.447	

and ^{13}C resonances are significantly shifted upfield as the concentration of ligands is increased. The magnitudes of the shifts observed for the complexes are less than those observed for the free ligands. At high concentration, the free ligands may undergo significant intermolecular interactions such as ring stacking.[19] Unfortunately, in the experimental concentration range (0.1–0.2 M) the shifts are too weak (0.2 ppm) to permit an extensive interpretation. The comparison of the ^{13}C and ^{15}N chemical shifts is done for a 0.1 M concentration of the product dissolved in $(CD_3)_2SO$.

Interpretation of ^{13}C NMR Chemical Shifts. The C-oximation and C-nitrosation at the C_5 position of the pyrimidine ring of barbituric acid induces a dramatic effect on the ^{13}C NMR spectra particularly for the C_5 and C_4 signals: The deshielding of the C_5 signal from 60 ppm (barbituric acid)[20,21] to 136 ppm (H_3vi) is expected. However, the shielding of the C_4 signal from 171 to 155 ppm is unexpected. The C_2 and C_4 atoms appear nearly magnetically equivalent for all the compounds listed in Table I whereas C_4 and C_6 atoms are equivalent in barbituric acid. In addition the replacement of N–H by N-methyl at the N_1 and N_3 sites has only a small effect on the ^{13}C chemical shifts of the atoms of the pyrimidine ring (Table I). An attempt to correlate calculated electron distribution $\sigma + \pi$ of carbon atoms of H_3vi and H_2vi^- with ^{13}C NMR chemical shifts is unsuccessful (Table III). The chemical shifts $\delta = \delta_d + \delta_p + \Sigma\delta$ are likely dominated by local paramagnetic contribution δ_p, as well as by paramagnetic current on neighboring atoms and neighbor anisotropy effects[22] $\Sigma\delta$. The local diamagnetic part δ_d, which is the one that depends only on the unperturbed ground-state wave function,[23] is probably to be less important. The downfield shifts of the C_5 and C_6 signals of H_3vi upon deprotonation of the oxime function (Table I) are apparently caused by a change in the electron distribution about the carbon atoms, rather than by the net electron density (Figure 1). The ^{13}C data (Table I) indicate a much greater sensitivity to the effect of complexation than do the corresponding ^1H data.[2f] The shift changes are comparable in magnitude to those previously reported for other complexes.[4]

Upon chelation of H_2vi^- through N_5 and O_6 atoms[10,14] to a metal center, a marked shielding of the C_5 signal and a marked deshielding of the C_6 signal are found (Table I). It is probable that the net effect is anisotropic with respect to the C_5 and C_6 atoms, irrespective of the total electron density around these centers. However, the C_5 and C_6 signals of the "softer" ruthenium(II) and iron(II) complexes are not as far upfield and downfield as the corresponding signals of the "harder" cobalt(III) complexes. Attenuation of local perturbations caused by protonation and chelation produces smaller shifts at the C_4 and C_2 positions (Table I). The degree of attenuation of perturbations is not sufficiently known to allow unambigous interpretation of the small changes in the C_2 and C_4 chemical shifts.

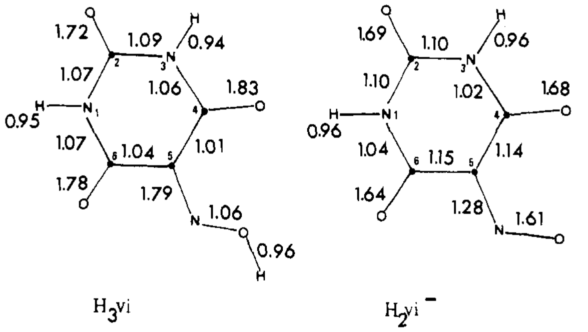

Figure 5. Bond order in H_3vi and H_2vi^-.

Attenuation of local perturbations of the O_6 and N_5 binding sites should produce the smallest shift of the C_1 and C_3 signals of the methyl groups in *N*-methyl derivatives **6–10**. Upon protonation and complexation the downfield shifts of the C_1 and C_3 signals increase from Ru(II) $\approx$ Fe(II) to $H^+ \approx$ Co(III), indicating that inductive charge withdrawal is effectively compensated by π-back-bonding in Ru(II) and Fe(II) complexes. These results are in good agreement with the ^1H NMR data[2f] on the *N*-methyl derivatives, as well as the N–H compounds. Proton chemical shifts have been shown to be related to the electron density of the atom to which the H atom is bound in aromatic molecules.[24] Heterocycles, however, elude such a straightforward interpretation due to the anisotropy introduced by the heteroatoms.[4d,5a,25] Nevertheless, the downfield changes in the chemical shift of the proton signals of N_1–H and N_3–H upon complexation parallel the values of the deprotonation constants[2f] of the N_1 and N_3 sites and increase from Ru(II) to Fe(II) and Co(III). Thus, the dependence of the ^1H chemical shift on charge density of the N_1–H and N_3–H hydrogen atoms centers on the diamagnetic term δ_d,[25] although neighbor anisotropy effects and ring currents may be operative.

Nitrogen-15 Chemical Shifts. The ^{15}N signal of the oxime function of H_3vi falls into the chemical shift range of oxime.[26,27] Upon deprotonation of the oxime function the signal is dramatically shifted downfield into the chemical shift range of nitroso compounds.[27,28] For H_3vi (Figure 5) the bond order of the C_5–N_5 and N_5–O_5 bonds (respectively 1.79 and 1.06) corresponds effectively to an oxime function. For H_2vi^-, the bond order of the C_5–N_5 and N_5–O_5 bonds (1.28 and 1.60, respectively) correspond to a nitroso function.

While it is difficult to evaluate the respective contribution to the chemical shift δ, it is apparent that in nitrogen resonance the range is extended to low field by the presence of lone pairs on nitrogen, with strong deshielding from $n_N \rightarrow \pi^*$ circulations.[5b] The energy of the HOMO and LUMO of H_3vi and H_2vi^- has been evaluated by CNDO/2 molecular orbital calculations: H_3vi, HOMO −0.4766 au, LUMO +0.0502 au; H_2vi^-, HOMO −0.1729 au, LUMO +0.3252 au.

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The low-lying π^* system of H_2vi^- probably contributes significantly to the local paramagnetic term δ_p, which is dominant in magnetic shielding of nitrogen nuclei.[5b,27] An observed correlation between the chemical shifts and the energy of the $n \rightarrow \pi^*$ transition provides experimental support for this interpretation. The $n \rightarrow \pi^*$ transition (540 nm)[2f] observed in the electronic spectrum of H_2vi^- is of much lower energy than that of H_3vi (250 nm). When ΔE, the so-called mean electronic excitation energy, is small, the paramagnetic term, δ_p, is important and low-field resonances are observed (Table II).

The ^{15}N chemical shift changes upon metal complex formation are due to changes in both the paramagnetic term δ_p and the neighboring perturbation term $\Sigma\delta$. However, the ^{15}N chemical shifts (Table II) parallel the charge-transfer transition energies of Ru(II) and Fe(II) complexes at 495 and 605 nm, respectively. This observation is in accordance with an important contribution of δ_p to the chemical shift δ.

Carbon-13–Nitrogen-15 Coupling Constants. Table II contains the various $^nJ(^{13}C-^{15}N)$ absolute values for ^{15}N-labeled **1**, **2**, **4**, and **5**. There has been a good deal of recent interest[17,29] in the magnitude and sign of coupling constants involving ^{15}N and other magnetic nuclei such as ^{13}C. Some time ago Ramsey[30] discussed the theory appropriate to such coupling in terms of the following electron-coupled mechanisms: (a) interaction between the nuclear moments and the electronic spins in s orbitals, the Fermi contact term J_{FC}; (b) interactions between the spin magnetic moments of the electrons and the nucleus, the dipolar term J_D; (c) interaction between the nuclear moments and the electronic currents produced by the orbiting electrons, the orbital term J_O: $J = J_{FC} + J_D + J_O$. The absolute values of ^1J(N–C) in oxime derivatives are generally less than 5 Hz.[17] Molecular orbital calculations[31] indicate that the Fermi contact contribution J_{FC} to ^1J(N–C) in oximes is small. The same kind of argument can be made for the ^1J(N–C) coupling constants of the free, deprotonated, and coordinated ketoximes listed in Table II. Upon deprotonation the $^1J(N_5-C_5)$ value of H_3vi increases from 2.5 to 5.5 Hz and upon chelation of H_2vi^- the ^1J value lies in the same range. With regard to geminal $^{15}N-^{13}C$ interactions, previous work[17] has demonstrated the sensitivity of the ^2J(N–C) constant values to nitrogen lone-pair orientation. The data reported in Table II demonstrate the dramatic effect of lone-pair orientation of the ^2J(N–C) couplings. When the lone pair is cis to the coupled carbon, the absolute values of ^2J(N–C) are much greater than in the cases where the lone pair is trans. It is striking that, for all of the compounds listed in Table II, the ^2J(N–C) values are greater than the ^1J(N–C) values. Upon coordination and protonation, significant changes are observed in the $^1J(N_5-C_5)$ and $^2J(N_5-C_6)$ values (Table II) whereas the $^2J(N_5-C_4)$ values remain very weak. The ^1J values for the oximato complexes **4** and **5** are in the same range as those reported for some cyano[29a] and methyl(dimethylamino)carbene complexes.[29b] In contrast to the one-bond ^1J constant, ^2J values are usually dominated by the Fermi contact term.[31]

$^{15}N/^{14}N$ Isotope Effects. Numerous examples of the effects of isotopic substitution upon the NMR resonance positions of various nuclei are known.[32] Recently the ^{18}O isotope effect in ^{31}P NMR was reported and has found extensive use as a technique for studying problems of biochemical interest.[33] The broadly applicable ^{18}O shift in ^{13}C and ^{15}N NMR has been described.[34] However, few examples of ^{15}N isotope effects in ^{13}C NMR have been reported previously.[29a]

Appreciable upfield shifts (ca. 0.03 ppm) (Table II) of the carbon 5 resonance are observed upon $^{14}N/^{15}N$ substitution at the N_5 atom of **1**, **2**, **4**, and **5**. It should be noted that a weak second atom shift for the C_6 atom adjacent to C_5 can be detected when the solubility of the compound is sufficient to allow a good signal:noise ratio to be obtained. After several measurements the secondary ^{15}N isotope effect on the C_6 signal is found to be real: upfield for **1** (−0.006 ± 0.003 ppm) and downfield for **5** (+0.006 ± 0.003 ppm). The observation of isotopic effects through several bonds appears to be a general phenomenon. Indeed after the introduction of one deuterium atom into cyclic[35] or aliphatic[36] compounds, shifts in the α-, β-, and γ-carbon signals are detected. However, the magnitude of the β ^2H isotope effect is 10-fold greater than the ^{15}N isotope effects reported in the present work. The β ^2H isotope effect provides an unambiguous tool for probing the mechanism of charge delocalization in carbocations,[37] whereas the α effects are insensitive. Our data show that α-^{15}N chemical shift isotope effects in free, deprotonated, and coordinated ketoximes are rather insensitive both to deprotonation and to coordination with iron(II) and ruthenium(II). The isotope shifts (ca. 0.03 ppm) are comparable in magnitude and direction with the reported ^{15}N one-bond isotope effect on ^{13}C chemical shielding in cyano complexes,[29a] and they are also comparable with the ^{18}O isotope effects observed in metal carbonyl derivatives[38] and in organic chemistry.[34] Several theoretical studies of the chemical shift isotope effect have focused on the way in which vibrational changes due to isotopic substitution affect nuclear shieldings.[39] However, the differentiation and evaluation of the different factors responsible for the observed overall effect are not definitively known.

Conclusions

The weak downfield shifts of the ^1H signals of the H atoms and methyl groups at the N_1 and N_3 sites of the pyrimidine ring are probably the best indicators of charge density changes. The ^1H chemical shift changes show that electron density depletion at N_1 and N_3 sites in the protonated and cobalt(III) species are greatest, with iron(II) and ruthenium(II) markedly lower, indicating that inductive charge withdrawal is effectively compensated by π-back-bonding.

The effect of protonation and complexation on the ^{13}C signals of the carbon atoms of the pyrimidine ring is greater than the ^1H chemical shift changes but is dominated by various perturbations. The dependence of ^{13}C shifts on the charge density may not be of a simple type. However, the ^{13}C shift changes of the methyl groups at the N_1 and N_3 sites parallel the ^1H chemical shift changes and reflect the electronic effect of protonation and chelation.

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The ^{15}N chemical shift changes, which are very important, suggest variation in the local paramagnetic contribution to the ^{15}N chemical shifts. An observed correlation between ^{15}N shifts and the wavelength of the electronic transition substantiates this interpretation.

The Fermi contact contribution to the one-bond coupling constants in $J(^{15}N-^{13}C)$ is likely to be small and explains the low values of ^1J compared to the ^2J values of the α-anti carbon atom, which are always dominated by the Fermi contact term.[31] The ^2J values of the α-syn carbon atom remain zero. The ^{15}N isotope effect on the ^{13}C chemical shifts appears rather insensitive to protonation and coordination of H_2vi^-.

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Contribution from the Laboratoire de Physico-Chimie des Composés de Coordination et des Solutions Electrolytiques,
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UV-Visible and Infrared Investigation of Tetrahydrofuran-Copper(II) Chloride Solutions

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The formation of copper(II) chloride complexes in the nondissociating tetrahydrofuran solvent was investigated at 25 °C in the UV-visible range from 220 to 550 nm and in the near-IR range from 600 to 1600 nm with copper(II) perchlorate, lithium chloride, and lithium perchlorate mixtures. A large set of absorbance values, covering the whole UV-visible and near-IR wavelength range, was used in the numerical treatment involving matrix rank and combined least-squares and Marquardt methods for the determination of stability constants and individual electronic spectra of the chloro complexes. The THF-copper(II) chloride solutions are characterized by four molecular complexes $Cu(ClO_4)Cl$, $CuCl_2$, $LiCuCl_3$, and Li_2CuCl_4 for which the overall formation constants are respectively $\log \beta_1 = 11.8$, $\log \beta_2 = 20.3$, $\log \beta_3 = 23.9$, and $\log \beta_4 = 25.7$. The nondissociating solvent properties are reflected in both number and position of the UV and visible absorption maxima of all four molecular species. More specific spectroscopic properties are observed in absorption bands of the tri- and tetrachloro complexes for which significant hypsochromic shifts are obtained compared to analogous complexes characterized in dissociating solvents. In addition, the regular bathochromic shift of the d-d transition bands beyond 800 nm is consistent with a structural change from square-planar to flattened-tetrahedral copper(II) configuration in these complexes.

Introduction

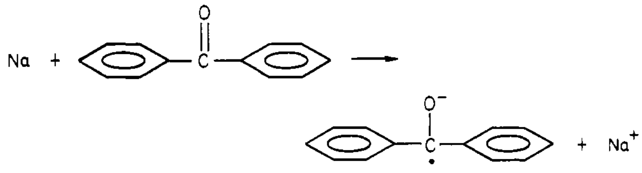
The copper(II) chloride system was recently investigated in several nonaqueous solutions such as DMF,[1] Me_2SO,[2] propylene carbonate,[2] and acetic acid.[3] The emphasis was made upon quantitative conclusions established from accurate analysis of spectrophotometric data. Stability constants and individual electronic spectra of the cooper(II) chloro complexes were calculated for several theoretical models that are taken into account according to the optical densities matrix rank treatment.[4] Statistical, spectroscopic, and chemical criteria were used to improve the best representation of the physical reality.

In this work, our investigation concerns the copper(II) chloride mixtures in tetrahydrofuran (THF). The nature of this solvent must induce significant changes in the stability and the electronic spectra of the individual copper(II) chloro complexes compared to the results obtained in dissociating solvents. The dielectric constant of THF is very low (7.6) as it is for acetic acid (6.1) compared to DMF (36) or propylene carbonate (69); one of the consequences of this low value is that ionic association will occur in the medium. On the other hand, the scale of Gutmann's donor numbers indicates for THF a value of 20, intermediate between the values for propylene carbonate (DN = 15) and DMF (DN = 28). The molecular complexes present in this nondissociating solvent should be characterized by thermodynamic and spectroscopic properties different from those established in DMF or propylene carbonate.

As described in our previous papers,[1,2] the method has its original basis in the numerical treatment of the whole set of spectrophotometric data obtained in the UV-visible and also near-infrared regions. This last wavelength range provides also some structural evidence for the copper(II) configurations. The copper(II) chloride system has to our knowledge never been investigated in THF, and this lack of even qualitative conclusions is certainly due to the difficulty of handling this solvent.

Experimental Section

Reagents. The tetrahydrofuran (Merck, Uvasol) was used after several steps of purification according to the procedure generally used by organic synthesis chemists.[5] THF decomposes easily with traces of water or oxygen into several products such as 4-hydroxybutyric and 4-hydroxyperbutyric acids, butyraldehyde, and essentially peroxides. The solvent was heated with reflux for 48 h in the presence of an excess of solid potassium hydroxide; salt formation from the acids and polymerization of the peroxides, aldehydes, and other secondary decomposition products are produced and recognized from the orange brown coloring of solid KOH. After distillation at 67 °C under reduced pressure (15 mmHg), the procedure continues by a treatment with sodium and benzophenone. The deep blue color of the solution corresponding to the reaction



indicates a stabilization of the benzophenone anion radical and consequently the absence of peroxides in the solvent. This blue solution is distilled with a weak excess pressure of argon and gives an excellent pure solvent containing less than 100 ppm of water (Karl Fisher test)

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