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Amide Contact Shift Studies and the Assignment of the Methyl Peaks in N,N-Dimethylamides

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Abstract: The nmr contact shifts for a series of amides and lactams in six-coordinate nickel(II) complexes are reported. Mechanisms to account for the nonequivalence in the contact shifts of the two N-methyls of the N,N-dimethylamides are considered. Comparison of the contact shifts in the amides and lactams are employed to assign the spectral peaks to methyl groups which are *cis* and *trans* to the carbonyl oxygen.

While engaged in a study of nmr contact shifts in paramagnetic transition metal complexes of various amide and lactam ligands, we were faced with the problem of assigning the various ligand resonances to the appropriate protons of the ligands and then, by a continuous dilution method,² identifying these resonances with the corresponding signal in the contact shift spectra of their paramagnetic complexes. There have been literature assignments for the nmr spectra of such relatively simple amides as N,N-dimethylformamide (DMF),^{3,4} N,N-dimethylacetamide (DMA),^{3,4} and N,N-diethylformamide (DEF).^{5,6} The N-alkyl groups in these amides are magnetically nonequivalent due to a high barrier to rotation about the carbonyl carbon-nitrogen bond⁷ which causes the N-alkyl groups to preferentially occupy sites in the OCN plane which are either *cis* or *trans* with respect to the carbonyl bond. The separate resonances are assigned to the *cis* or *trans* positions on the basis of the relative magnitudes of their coupling constants ($J_{\text{H}_{\text{A,B}}-\text{H}_{\text{C}}}$) with the formyl proton in formamides or the acetyl methyl protons in acetamides.^{3,5} Assignments of the N-methyl resonances of DMA and DMF by this method indicate that the *cis* methyl group is more shielded than the *trans* or more distant methyl group. Yet the magnetic nonequivalence of these two sites is generally attributed to the magnetic anisotropy of the carbonyl group.^{5,8,9} Several studies both theoretical⁹ and experimental⁹⁻¹¹ indicate that the magnetic anisotropy of the carbonyl group should provide a de-

shielding effect throughout the molecular plane. The theoretical and experimental assignments are clearly contradictory. The spectral assignments based on the coupling constant arguments are compelling, but not rigorous and another independent assignment is needed to confirm these results.

Recent studies in this laboratory have provided new information concerning the relative chemical shifts in amide molecules and the question of carbonyl anisotropy. This paper will deal with the results of a contact shift nmr study of Ni(II) amide complexes as a means of identifying *cis* and *trans* resonances in the free amide. This new evidence supports the previous assignments based on coupling constants. In a subsequent article a possible explanation for the observed difference in the chemical shifts of two N-methyl groups of DMA and DMF will be presented.

Experimental Section

Nmr Spectra. The nmr spectra were obtained with a Varian Model A-60 and a Varian Model DP-60 spectrometer. All spectra were obtained at approximately room temperature ($27 \pm 2^\circ$). All nmr spectra were measured relative to tetramethylsilane (TMS) as an internal standard.

Reagents and Solutions. Eastman White Label grade amides were distilled from barium oxide at reduced pressure and a center fraction accepted. Reagent grade nitromethane, nitrobenzene, chloroform, acetone, methylene chloride, and carbon tetrachloride were stored over Linde 3A molecular sieves for use as solvents. All solutions of hygroscopic materials were prepared in a drybox equipped with an automatic continuous air flow drying system. When accurate complex or ligand concentrations were necessary, materials were weighed in stoppered volumetric flasks. All solutions for nmr work which did not include a paramagnetic species were carefully degassed by repeated freezing with liquid N₂ and evacuation at low pressures.

Preparation of Complexes. The octahedral amide complexes of Ni(ClO₄)₂ were prepared by the reaction of anhydrous NiCl₂ with a solution of anhydrous AgClO₄ in the respective amide or in an amide-methylene chloride solution. AgCl was removed by centrifugation and filtration. The complexes were precipitated by addition of diethyl ether or carbon tetrachloride. Complexes were then recrystallized from a methylene chloride solution containing excess amide by slow addition of diethyl ether with stirring. Representative C, H, and N analyses are shown below. *Anal.* Calcd for Ni(DMA)₆(ClO₄)₂: C, 36.9; H, 6.9; N, 10.8. Found: C, 36.3; H, 7.0; N, 10.5. Calcd for Ni(DMF)₆(ClO₄)₂: C,

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Table I. Nmr Contact Shifts for the N-Alkyl Protons in Octahedral Ni(II) Lactam and Amide Complexes Relative to the Uncomplexed Ligand Protons

Complex	$\Delta\nu_{NRcis}^{a,b}$	$\Delta\nu_{NRtrans}^{a,b}$	$\Delta\nu_{C=O}$	Solvent
Ni(NMBL) ₆ (ClO ₄) ₂	-156 (CH ₃)	-144 (CH ₂)		Nitrobenzene
	-123	-393		Methylene chloride
	-145	-386		Chloroform
	-124	-360		Acetone
Ni(NMVL) ₆ (ClO ₄) ₂ ^c	-141 (CH ₃)	-436 (CH ₂)		Nitrobenzene
	-125	-418		Methylene chloride
Ni(NMCL) ₆ (ClO ₄) ₂ ^c	-101 (CH ₃)	... (CH ₂)		Nitrobenzene
	-88	-250		Methylene chloride
Ni(DMA) ₆ (ClO ₄) ₂	-122 (CH ₃)	-261 (CH ₃)	+182 (CH ₃)	Methylene chloride
Ni(DMF) ₆ (ClO ₄) ₂	0 (CH ₃)	-63 (CH ₃)	-548 (H)	Methylene chloride
Ni(DEF) ₆ (ClO ₄) ₂	-43.6 (CH ₂)	-43.6 (CH ₂)	-162 (H)	Methylene chloride
	-27 (CH ₃)	-91 (CH ₃)		
Ni(DMTA) ₆ (ClO ₄) ₂ ^c	-1390 (CH ₃)	-1640 (CH ₃)	-1190 (CH ₃)	Methylene chloride

^a $\Delta\nu_{cis}$ and $\Delta\nu_{trans}$ refer to the positions relative to the carbonyl group that the two alkyl groups may occupy (Figure 1). ^b A negative entry indicates a shift of the complex resonance to lower field. ^c NMVL = N-methylvalerolactam, NMCL = N-methylcaprolactam, NMBL = N-methylbutyrolactam, and DMTA = N,N-dimethylthioacetamide.

Table II. Nmr Spectra of Amides and Lactams (Internal References TMS; in cps)

Compd	$\Delta\nu_{C=O}$	$1/T_2$	$\Delta\nu_{NRcis}$	$1/T_2$	$\Delta\nu_{NRtrans}$	$1/T_2$
DMF	-482 (H)	3.5	-167 (CH ₃)	2.9	-177 (CH ₃)	2.4
DMA	-119 (CH ₃)	3.0	-170 (CH ₃)	1.9	-180 (CH ₃)	1.4
DEF	-484 (H)	...	-64 (CH ₃)	...	-69 (CH ₃)	...
			-201 (CH ₂)	...	-201 (CH ₂)	...
DMTA	-157 (CH ₃)	2.2	-206 (CH ₃)	2.9	-199 (CH ₃)	1.9
NMBL	-130 (CH ₃)	...	-170 (CH ₃)	...	-207 (CH ₂)	...
NMVL	-131 (CH ₃)	...	-168 (CH ₃)	...	-203 (CH ₂)	...
NMCL	-137 (CH ₃)	...	-172 (CH ₃)	...	-198 (CH ₂)	...

31.1; H, 6.1; N, 12.1. Found: C, 31.0; H, 6.1; N, 11.8. Visible, ultraviolet, and infrared spectral data in addition to magnetic susceptibility measurements for these complexes indicate that their structure^{12,13} is essentially octahedral.

Results

Table I presents the nmr contact shift data for the octahedral lactam and amide complexes (also see Figure 1). Values for $\Delta\nu$ are in cps at 60 Mc and are given relative to the corresponding resonance of that ligand in the solvent indicated.

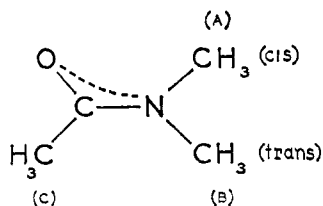


Figure 1. System of labeling employed for the amides.

Table II gives the nmr spectral data for the free ligands in CCl₄ solution at 60 Mc and room temperature. All solutions are approximately 5 mole % in ligand. $1/T_2$ is the peak width (or total multiplet width if splitting is unresolved) at half peak height.

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Discussion

Contact Shift Studies. In the lactams employed in this work the position *cis* with respect to the carbonyl oxygen must be occupied by a methyl group while a methylene group is *trans*. As illustrated in Figure 2 this allows an unequivocal assignment of the resonances corresponding to the *cis* and *trans* positions in these systems. For the three lactam complexes studied, the N-methyl or *cis* group exhibits a much smaller downfield shift than does the methylene or *trans* group. In these lactams this difference in shift could be caused by electron delocalization through the bonds and could be due to the fact that the "cis" and "trans" groups are structurally nonequivalent (*i.e.*, one a CH₃ and the other a CH₂). However, in DMA, DMF, DMTA, and DEF the groups are structurally identical and if the downfield shifts of the N-alkyl groups were caused totally by electron delocalization through the bonds, then it would be expected that the two N-alkyl groups would be shifted equally (see discussion of DEF complex below). In fact the data in Table I show that in each case the resonances of the two structurally equivalent, but magnetically nonequivalent N-alkyl groups exhibit very different contact shifts as is shown for Ni(DMA)₆(ClO₄)₂ in Figure 2. The nmr spectrum of this complex consists of three widely separated resonances. When excess ligand is added, rapid exchange of free and complexed amide occurs and a set of averaged line positions is obtained. The resonances in the complex may be traced back to the free ligand resonances by successive addition of free ligand until the addition of more ligand no longer causes a shift in the resonance positions. This

was the method used to support the assignment of the nmr spectra of amide complexes and the results are listed in Table I.

Two methods have been widely used to assign the separate N-alkyl resonances in the nmr spectra of N,N-dialkylamides to the *cis* and *trans* positions. The α protons of these groups are spin-spin coupled to the formyl proton of formamides (DMF, DEF) or the protons of the acetyl methyl group in acetamides (DMA, DMTA). The coupling constants for the two N-alkyl groups are generally not the same. In analogy to ethylene systems the resonance exhibiting the larger coupling constant is assumed to be situated "trans" (across the C-N partial double bond) to the formyl or acetyl protons to which it is coupled.¹⁴ On this basis the high-field methyl resonances in DMF and DMA and the low-field resonance in DMTA are assigned to the methyl groups *cis* with respect to the carbonyl bond.¹⁵ In benzene or other aromatic solvents the two N-alkyl resonances of the N,N-dialkylamides undergo unequal upfield shifts. Hatton and Richards³ suggested that these unequal shifts were due to the formation of an oriented collision complex between the polar amide molecules and the aromatic solvent molecules. Based upon electrostatic considerations and the observed relative shifts of DMF and DMA resonances in benzene, a model for the collision complex places the *trans* N-alkyl group near the center of the aromatic ring and the *cis* N-alkyl group nearer the edge of the ring where it would be less affected by the diamagnetic ring current. On the basis of this model the high-field β -methyl triplet resonance of DEF has been assigned to the "cis" N-ethyl group since it undergoes the smaller relative shift upon dilution with benzene.⁶ This method also substantiates the coupling constant based assignment of the nmr spectrum of DMTA.¹⁵

Although the relative magnitude of "cis" and "trans" couplings across double bonds have been known to vary¹⁶ and the model chosen for the benzene-amide collision complex is largely based on the relative coupling constant assignment of peaks in DMF and DMA and is therefore not an entirely independent method, the assignments based on their use have been widely accepted in the past.

From assignments based on these two procedures, it is generally concluded that the *cis* N-methyl group resonances of DMF and DMA occur at higher field (are more shielded) than the *trans* N-methyl groups. However, an approximate MO calculation of the principal paramagnetic susceptibilities of the carbonyl group in formaldehyde by Pople indicated that the effect of carbonyl group magnetic anisotropy should be deshielding everywhere in the plane of the carbonyl carbon bonds. The acetyl methyl group resonances of acetaldehyde, acetone, DMA, and DMTA all fall between τ 0.7 and 0.4 unit below the line correlating τ_H and J_{C-H} for compounds with only small anisotropies.¹⁷ This is interpreted as meaning that the anisotropy in these carbonyl compounds deshields these

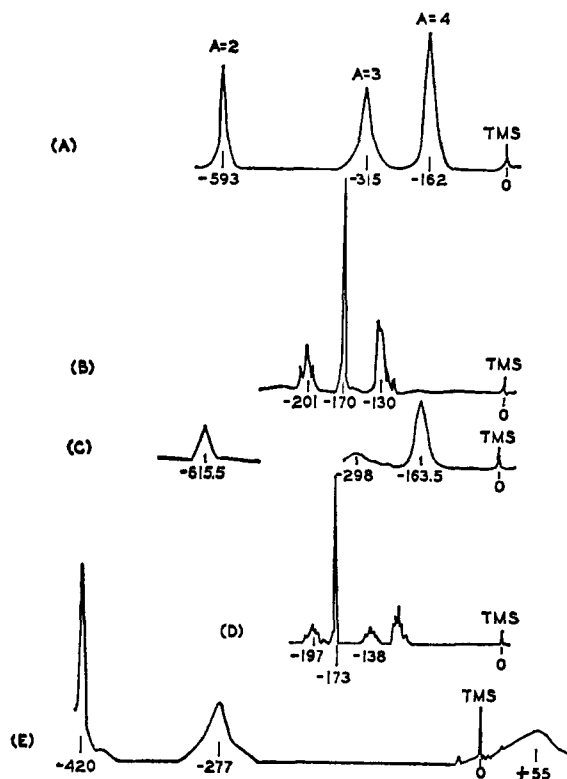


Figure 2. Nmr spectra of several ligands and complexes: (A) Ni(NMBL)₆(ClO₄)₂ in CDCl₃, (B) NMBL in carbon tetrachloride, (C) Ni(NMVL)₆(ClO₄)₂ in methylene chloride, (D) NMVL in methylene chloride, (E) Ni(DMA)₆(ClO₄)₂ in CDCl₃.

protons in agreement with prediction. An empirical calculation of the principle components of the magnetic susceptibility of the carbonyl group in several amides,⁸ undertaken before these assignments were made, favored as the most probable values ones which predict deshielding of the *cis*-N-methyl group of DMA and DMF relative to the *trans* group. The observed relative shielding of the *cis* groups by the carbonyl bond of DMF and DMA would therefore seem to require a carbonyl anisotropy quite different than that calculated for aldehydes. There is obviously an inconsistency in the coupling constant based and anisotropy based assignment of these peaks.

Lactams are cyclic amides and the ring structure requires the N-methyl group to be in the *cis* position with respect to the carbonyl oxygen. The lactams and lactam complexes were chosen as model systems for studying the nmr spectra of the *cis* N-methyl group. The N-methyl resonance in the series of lactams studied all appear within 2 cps of the higher field N-methyl resonance in DMA (Table II). This observation helps to support the assignment of the higher field resonance to the *cis* N-methyl group.

The *cis* and *trans* assignment for amide nmr spectra which are employed in Tables I and II are those we finally decided on and are the same as those based on relative coupling constants and relative shifts in benzene. It will be noted that in each case the *cis* resonance undergoes a much smaller downfield shift in the complex than does the *trans* resonance, behavior very similar to that of the lactams. From the magnitude of the nonequivalence of the *cis* and *trans* resonances in the paramagnetic complexes, it is obvious that it is due

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in some way to the paramagnetic electrons of these complexes. Since the relative order of chemical shifts (and line widths)^{17a} is preserved in going from free amide to the complexes, it appears that there is an effect operative in the complexes which selectively shields the methyl protons pointed toward oxygen.

In the diamagnetic DMTA (N,N-dimethylthioacetamide) the *cis*-N-methyl resonance is assigned to the lower field N-methyl resonances (Table II). In the paramagnetic complex the N-methyl resonances cross over (Table I). The lowest field N-methyl resonance of DMTA in the complex is assigned to the *trans* N-methyl resonance of DMTA in the complex. The order of the protons shifts in the Ni(DMTA)₂(ClO₄)₂ complex is the same as that in the other amide complexes.

Pseudo-contact shifts arising from anisotropy in the metal ion *g* value are not expected to be significant for Ni(II) in an octahedral field.¹⁸ However it has been suggested that small deviations from octahedral symmetry in these complexes might create a pseudo-contact shift. Since the relative chemical shifts of the N-alkyl groups in these amides show approximately the $(r_{M...H})^{-3}$ dependence expected for a pseudo-contact shift, its presence should not be ruled out in these complexes. A type of pseudo-contact shift that arises within the ligand may contribute to the resonance shifts. If the magnetic field established by the partial unpaired electron on the ligand is not isotropic, then a ligand pseudo-contact shift may contribute. Tumbling of the complex does not average this through-space effect to zero. This effect has not been previously considered. It is customary to treat the ligand as a free radical, and most free radicals have very small *g* value anisotropies. Thus, this effect has been considered insignificantly small and it likely is small here also.

Direct overlap of the proton 1s orbital with the metal ion d orbitals containing unpaired electrons could also cause large isotropic contact shifts due to electron spin-nuclear spin coupling. If the metal ion d orbitals have positive spin density, then the hydrogen 1s orbital should have positive spin density. This mechanism deshields the protons and predicts a downfield shift for these protons. If the nmr assignments are correct, then the fact that a through-space direct overlap mechanism with metal d orbitals deshields the methyl protons precludes this mechanism as the cause of the large difference in N-alkyl resonance positions. The N-alkyl group closer to the metal is also the one closer to the oxygen. This methyl is observed to occur at a higher field than the alkyl group pointed away from

oxygen, which disagrees with the prediction of a through-space direct overlap mechanism involving metal d orbitals.

The contact shift effect is the result of a nuclear spin-electron spin coupling mechanism. Since the two N-alkyl groups are unequally nuclear spin-nuclear spin coupled across the C-N partial double bond to the acetyl or formyl protons, it might be argued that the protons in these two positions are also unequally spin coupled to the paramagnetic electrons delocalized onto the ligands. The unequal contact shifts observed then would be due to this unequal coupling mechanism rather than to a different net unpaired spin density at the *cis* and *trans* sites. However the results with DEF would seem to preclude this. Here the two sets of α protons while unequally coupled with the formyl proton exhibit contact shifts identical within error limits while the β -methyl groups which show no detectable coupling to the formyl proton exhibit unequal contact shifts.

Direct overlap of the N-alkyl group hydrogen 1s orbitals with the carbonyl oxygen orbitals would be expected to deshield these protons in the free amide whether the interaction was considered to be hydrogen bonding or of the van der Waals type. In view of the observed relative shieldings of the N-alkyl groups in the free amides, it is unlikely that this direct overlap mechanism contributes significantly to their chemical shift. However, this would not preclude this effect from being operative in the paramagnetic complexes. In the complex, direct overlap of the hydrogen 1s orbital with oxygen orbitals containing some unpaired spin density could shield the proton by a spin polarization mechanism which places antiparallel spin density at the proton nucleus. The paired oxygen electrons become partially unpaired. The electron closer to oxygen has a favored orientation of spin aligned with the field, while the unpaired electron closer to the methyl protons has an antiparallel electron spin. This process shields the *cis* methyl protons in the complexed ligand in agreement with the observed result. Spin polarization processes have been suggested for systems in which the participating orbitals are nearly (or totally) orthogonal.¹⁹

The similarities in the contact shift behavior of the Ni(II) complexes of the N-methyl lactams and N,N-dialkylamides reported here and the explanation proposed above to account for the unequal contact shifts of the N-alkyl groups of the amides are dependent upon the assignment of *cis* and *trans* resonances in the amides.

We feel that the presence of this marked similarity of the relative contact shifts of the N-alkyl groups in these lactam and amide complexes while somewhat uncertain as the exact origin does provide new and independent support for the correctness of coupling constant based assignment of *cis* and *trans* resonances in the free amides such as DMA, DMF, and DMTA.

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(17a) NOTE ADDED IN PROOF. It has been observed that the resonances of protons nearest the complexed metal ion are often somewhat broadened because of the electron-nucleus dipolar relaxation mechanism which falls off as $1/r^6$.

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