Carbon-13 Nuclear Magnetic Resonance Studies of Substituted Amino-acid and Ethylenediamine Complexes of Nickel(II) in Aqueous Solutions†

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Summary The contact shifts observed in the ^{13}C n.m.r. spectra of a number of ethylenediamine and α-amino-acid complexes of Ni^{II} are reported, and suggested spin transfer mechanisms are discussed in light of these observations.

THE large contact shifts observed in the ^{1}H n.m.r. spectra of paramagnetic complexes of transition metal ions with organic ligands have been used to elucidate the bonding in these complexes.[1,2] Of particular interest have been the transfer mechanisms whereby unpaired electron spin density is delocalized from the metal ion to the ligands. The enhanced proton-relaxation rates in the paramagnetic systems have also contributed to our knowledge of the dynamic properties of metal ion complexes in solution.[3-6] Considering the large contribution of the carbon orbitals to the electron-spin containing molecular orbitals of these complexes and in view of the difference between the magnetogyric ratios of ^{13}C and ^{1}H, we expect that ^{13}C n.m.r. studies should not only provide unique information about electron-spin delocalization in paramagnetic systems but also allow the study of a wider range of dynamic solution properties of metal-ion complexes.

We report here the results of ^{13}C n.m.r. studies of aqueous solutions containing bidentate chelate complexes of Ni^{II} with substituted α-amino-acids and ethylenediamines. The chemical shift data (Table) were obtained using a Varian DP-60 spectrometer operated at 15·1 MHz in the wide line dispersion mode. The solution compositions were 1·0 M-$NiCl_2$ and 3·0 M-amino-acid or ethylenediamine (natural abundance ^{13}C). Solutions of the amino-acid complexes were adjusted to pH 10. The samples were contained in stationary 15 mm polyethylene tubes. The assignments of the ^{13}C resonances (Table) were made with the aid of the ^{13}C spectrum of the Ni^{II} complex with glycine which had been selectively labelled with ^{13}C (80%) in the carboxyl position.

The large shifts observed here undoubtedly are contact shifts: pseudo-contact interactions should be negligible for these octahedral Ni^{II} complexes which have orbitally non-degenerate ground states.[7,8] As required for a contact interaction, the ^{13}C shifts of the glycine and ethylenediamine complexes exhibit a Curie law temperature-dependence.[9] The upfield shifts of the C_α,C-1, and C-2 atoms suggest that these positions acquire net negative electron (α) spin densities *via* a spin polarization mechanism[10-12] which overwhelms the effect of the direct delocalization of β electron spin from Ni^{II} through the σ-orbitals of the complex. Large upfield shifts have also been observed for the N-H protons in Ni^{II} complexes with NH_2,[13] ethylenediamines, [14] amino-acids, [14,15] and alkylamines.[16]

It has been suggested[13] that the appearance of negative spin density at the proton in the $Ni(NH_3)_6^{2+}$ complex can be taken as good evidence for a negligible hydrogen contribution to the ligand molecular orbital (the nitrogen "lone pair") containing unpaired electron spin. In the absence of such a contribution of course, net spin density at the ^{1}H nucleus could only be induced by polarization effects. However, the observation of net α-spin density at a nucleus in σ-systems such as these cannot be used to exclude direct delocalization to that nucleus of significant amounts of β-spin.

For example, the INDO molecular orbital model of Pople *et al.*[17] which incorporates both spin polarization and direct delocalization effects, predicts net α-spin density at the C′ carbon atoms of the ethyl ($H_3C'CH_2$) and vinyl ($H_2C'CH$) radicals. Although significant amounts of β-spin should be delocalized to the C′ atoms (they make large contributions to the orbital containing unpaired electron spin), exchange polarizaton terms dominate the net unpaired electron spin distribution. Cramer and Drago[18] have also pointed out that, with an MO model which neglects spin polarization, it is not possible to draw conclusions about direct delocalization mechanisms from the contact shifts of atoms which are adjacent to the donor atoms of a complex. The carboxyl carbon atoms, C_0, of the amino-acid complexes also exhibit upfield shifts.

Since spin polarization effects are expected to attenuate rapidly with increasing distance from the metal ion,[19] the large downfield shifts of the remote carbon atoms, C_β, C_γ, and C-3, are probably the result of direct delocalization of β-spin. We have observed a similar pattern of ^{13}C shifts for the Ni^{II} complex of propylamine ($H_2N{\cdot}C_\alpha H_2{\cdot}C_\beta H_2{\cdot}C_\gamma H_3$) C_α *ca.* + 118; C_β *ca.* −460; and C_γ *ca.* −337 p.p.m.‡ The CH_2 and CH_3 *protons* in all these complexes are shifted downfield, consistent with a predominating direct delocalization of β-spin to the hydrogen atoms. It is apparent from the experimental work of Pratt and Smith[15] and Ho and Reilley,[6] and the calculations of Fitzgerald and Drago,[2] that the proton shifts in these systems are extremely sensitive to the conformation of the ligand. Presumably the ^{13}C shifts will exhibit the same sensitivity. (Note the trend in the shifts of the C_β and C-3 carbon atoms.) We defer a detailed comparison of the ^{1}H and ^{13}C shifts until the completion of high resolution ^{13}C studies which are potentially capable of distinguishing the geometrical isomers that these chelate ring systems may form. Preliminary studies indicate that high resolution studies will be possible with ^{13}C-enriched samples now being prepared in this laboratory.

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‡ The shifts reported are for a solution of one part $Ni(ClO_4)_2$ in nine parts propylamine ($PrNH_2$). Extrapolation to the chemical shift for the complex in the slow exchange limit is difficult because chemical exchange of the solvent $PrNH_2$ with $Ni(NH_2Pr)_6^{2+}$ is not completely in the rapid exchange limit where the shift reaches a maximum. The data for the complexes in Table 2 were obtained in the slow chemical exchange limit (ref. 4).

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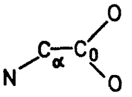
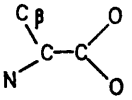
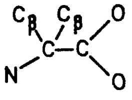
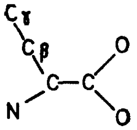
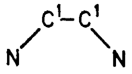
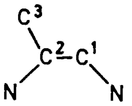
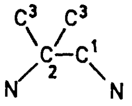
Carbon-13 chemical shifts of aqueous solutions of nickel(II) *complexes with substituted amino-acids and ethylenediamines at* 15·1 *MHz and* 33°[a]

Ligand Amino-acids			^{13}C Shifts (p.p.m. ± 5)		
		C_0	C_α	C_β	C_γ
	Glycine	123	383		
	(±)-Alanine	145	347	−193	
	α-Aminoisobutyric acid	125	312	−131	
	α-Aminobutyric acid	132	345	−173	−24
Ethylenediamines		C-1	C-2	C-3	
		328			
	1,2-Diaminopropane	330	282	−471	
	1,2-Diamino-2-methylpropane ..	325	238	−186	

[a] Chemical shifts are in p.p.m. with respect to the resonance of the appropriate ^{13}C atom in the parent ligand. The ^{13}C shifts of complexes of these ligands with Zn^{II} and/or Co^{III} are negligible within the experimental uncertainty (±5 p.p.m.). A negative sign denotes a *downfield* shift.

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