

SHIFT REAGENT BEHAVIOR OF SOME NICKEL(II) COMPLEXES

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(Received in USA 3 August 1971; received in UK for publication 18 October 1971)

Since Hinckley's paper (1) first reported the use of the pyridine diadduct of

tris(dipivalomethanato)europium(III) as a NMR shift reagent for elucidating the structure of organic compounds, a substantial literature on this subject has developed. Most of this literature has dealt with the use of paramagnetic lanthanide chelates as shift reagents. However, Szarek and Baird (2), as well as other investigators, have examined the shift reagent characteristics of a number of transition metal salts and complexes. For some purposes transition metal complexes may well be found superior to the lanthanide chelates now receiving the greatest attention. In this laboratory bis(O,O'-dialkyldithiophosphato)nickel(II), Ni(R-dtp)₂, complexes have been employed to aid in the interpretation of the pmr spectra of a wide variety of primary and secondary amines. Ni(R-dtp)₂ complexes are readily prepared by straightforward modification of the procedure described by Goldberg, *et. al.*, (3) for the chromium(III) complexes. The complexes are soluble in most organic solvents and the solubilities can be varied by changing the alkyl substituent. Purple, diamagnetic Ni(R-dtp)₂ complexes form yellow-brown, five-co-ordinate, paramagnetic (S=1) adducts with secondary amines and green, six-co-ordinate, paramagnetic (S=1) adducts with primary amines (4). Bis(diphenyldithiophosphinato)nickel(II), Ni(S₂P(C₆H₅)₂)₂ behaves similarly. We now report data illustrating the use of Ni(S₂P(C₆H₅)₂)₂ and Ni(R-dtp)₂ complexes in studying the pmr spectra of primary and secondary amines.

The effect of dissolving bis(di-isobutyldithiophosphato)nickel(II), Ni(iBu-dtp)₂, in neat isopropylamine is shown in Figure 1. The spectra were measured on a Varian T-60 spectrometer with tetramethylsilane as internal standard. Temperature was monitored using the peak separations of absolute methanol (5). Neat amine solutions were chosen so as to maximize the concentration of the most stable adduct. Under these conditions the complexes undergo rapid exchange of adduct molecules and the concentration dependence of the chemical shift obeys the relation (4): $\delta_{\text{obs}} = \delta_{\text{C}}^{\text{M}} + \delta_{\text{L}}$, where δ_{obs} is the observed chemical shift, δ_{C} is the molar paramagnetic

shift for the adduct, M_c , is the molar concentration of the complex in solution, and δ_L is the shift of the neat ligand. The electron spin-nuclear spin coupling constants are calculated using the well-known Bloembergen equation (6). For paramagnetic nickel(II) complexes dipolar shifts can be neglected (7) and an assumed g-value of 2.25 is not unreasonable (4) considering the uncertainty in the determination of the magnetic moments of complexes in solution. In Figure 1 the large upfield paramagnetic shift of the $-NH_2$ protons permits ready identification of the amino group. Where possible, neat amines or highly concentrated solutions of amines in "inert" solvents should be employed since paramagnetic broadening renders detection of amine proton absorption difficult.

In Figure 2 shift differences ($\nu_{obs} - \nu_L$) are given as a function of the molarity of $Ni(iBu-dtp)_2$ in neat isopropylamine. Ordinarily, a plot of ν_{obs} vs. $[M]$ would be employed since extrapolation back to zero molarity would give the chemical shifts from TMS of the uncomplexed amines. Figure 2 emphasizes the shift reagent characteristics of $Ni(iBu-dtp)_2$. Similar results were obtained for the other complexes described in Table I. The magnitude of the shift and concomitant paramagnetic broadening of the regions of the spectra associated with particular sets of equivalent protons attenuate with increasing distance from the paramagnetic nickel(II) ion. Amine protons are strongly shifted upfield while protons bound to carbon are shifted downfield away from TMS according to their proximity to the amine group. Similar results have been obtained for secondary amines. It is noted that the strong upfield shifts of amine protons are diagnostic of amine - nickel(II) bonding. This may be found useful by investigators studying metal ion binding of large molecules.

The directions of the paramagnetic shifts of aliphatic amines are accounted for in terms of σ -spin polarization and σ -delocalization mechanisms (4). Negative amine proton unpaired electron spin densities (upfield NH proton shifts) in ammonia complexes of nickel(II) have been rationalized (8) in terms of a σ -spin polarization mechanism. Positive spin densities (downfield shifts) for CH protons in ligands bound to nickel(II) have been interpreted (9) in terms of a σ -delocalization mechanism. Both mechanisms attenuate rapidly with increasing distance from the metal ion but attenuation appears to proceed more rapidly with the σ -spin polarization mechanism. Pmr parameters are summarized in Table I.

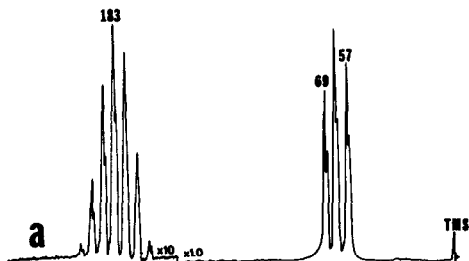


Figure 1. 60 MHz pmr spectra of isopropylamine:

(a) neat, (b) $3.7 \times 10^{-3} M$ in $Ni(iBu-dtp)_2$ and, (c) $14.8 \times 10^{-3} M$ in $Ni(iBu-dtp)_2$.

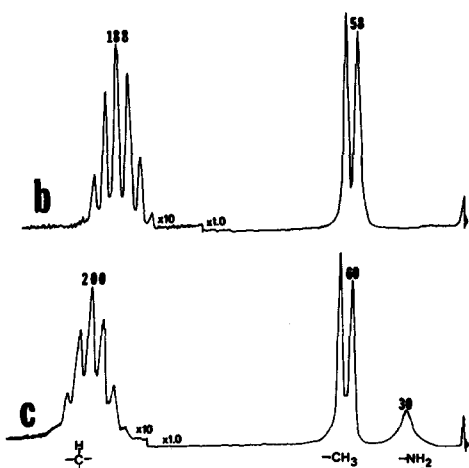


Figure 2. Shift differences (at 60 MHz) vs. molar concentration of $Ni(iBu-dtp)_2$.

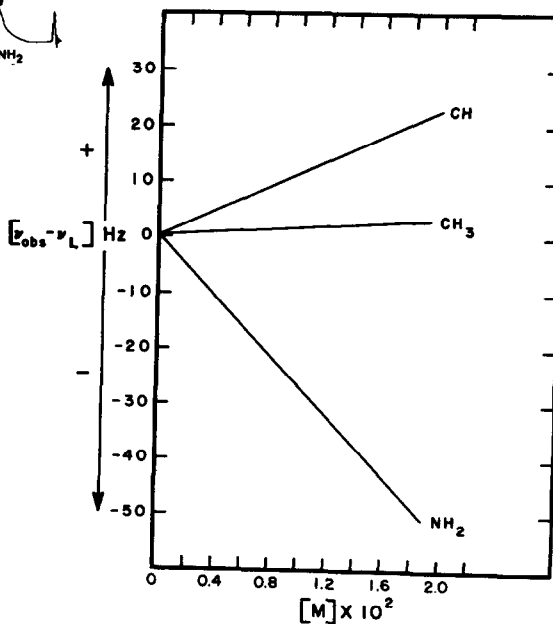


TABLE I: Pmr Parameters for Isopropylamine Diadducts of Nickel(II) Complexes

<u>Complex</u>	<u>Group</u>	<u>S, Ligand</u>	<u>g_c</u>	<u>A₁[*] (gauss)</u>
Ni(isopropyl-dtp) ₂	NH ₂	1.15	+42.0	-0.178
	CH	3.05	-19.0	+0.080
	Temperature = 316°K	CH ₃	1.04	- 4.1
Ni(isobutyl-dtp) ₂	NH ₂	1.15	+44.0	-0.188
	CH	3.05	-19.2	+0.082
	Temperature = 319°K	CH ₃	1.04	- 3.4
Ni(S ₂ P(C ₆ H ₅) ₂) ₂	NH ₂	1.15	+41.8	-0.175
	CH	3.05	-15.3	+0.064
	Temperature = 312°K	CH ₃	1.04	- 2.3

* A₁ = electron spin-nuclear spin hyperfine coupling constant.

ACKNOWLEDGMENT

This work was partially supported by the University of Kentucky Research Foundation and Project Themis.

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