

Nuclear Magnetic Resonance Studies of Lewis Acid–Base Interactions.

Part III [1]. Effects of the Axial Ligand Strength on the Proton Isotropic Contact Shifts of the Equatorial Ligand in the Acid–Base Adducts of Bis(2,2,6,6-Tetramethyl-3,5-Heptanedionato)nickel(II)

Y. Y. LIM

Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

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Introduction

The effect of varying the axial ligand on the proton isotropic shifts of the equatorial ligand in the tetragonal nickel(II) complexes has been the subject of interest [2, 3]. In one case [2], the effect of varying the axial anionic ligand on the isotropic shifts of stilbenediamine of the bis(stilbenediamine)-nickel(II) complexes was studied and it was found that the observed proton isotropic shift increases as the axial ligand strength increases. In another case [3], where the isotropic shifts for the acetylacetonate protons in bis(acetylacetonato)nickel(II) were observed, no apparent correlation was found. In order to resolve this discrepancy and to provide better understanding of the factor(s) determining the trend, if any, of the isotropic shifts of the equatorial ligand as the axial ligand varies, I have carried out an investigation on the measurement of the proton isotropic shifts of 2,2,6,6-tetramethyl-3,5-heptanedionate (DPM) ligand in Ni(DPM)₂ in the presence of various Lewis bases.

Ni(DPM)₂ is a good Lewis acid and it has advantage over Ni(acac)₂ studied earlier [3] in that the unpaired spin density which is delocalized into the tert-butyl protons originates wholly or predominantly from the σ -orbital so that complication from the π -orbital delocalization and spin-polarisation mechanisms is absent. Furthermore, acetylacetonate ring is plucked whereas the bulky chelated ring is practically not [4]. The ring plucking effect had been invoked as a possible cause for the trend observed in ref. 2 [5].

Experimental

Ni(DPM)₂ was prepared according to a method given in literature [6]. It was purified by vacuum sublimation and stored over anhydrous P₂O₅.

Dimethylsulphoxide (DMSO) and pyridine were spectroscopic grade reagents and were used as received.

Hexamethylphosphoric triamide (HMPA), N,N-dimethylformamide (N,N-DMF), tetrahydrofuran (THF), piperidine and triethylamine were purified according to methods given in ref. 7. Vigreux column was used in all the distillation process. Dimethylsulphide was also fractionately distilled. Carbon tetrachloride and chlorobenzene which were of high quality grade were redistilled once. Deuterated liquid bases were used as received without further purification. All solvents and bases were stored over 3A molecular sieve, for at least 24 hours prior to use.

The PMR spectra were obtained with a Hitachi Perkin-Elmer R-20B spectrometer (60 MHz) at 34 °C and a Jeol JNM-FX100 Fourier Transform NMR spectrometer (99.55 MHz) at 28 °C using TMS as an internal standard. The visible spectra were obtained with a Cary 17D spectrophotometer using 1 cm quartz cells.

The bis-adducts of Ni(DPM)₂ were formed by preparing solution of Ni(DPM)₂ in chlorobenzene and adding excess of the appropriate base. The ratio of base to acid was between 110 and 150. Whenever the solubility allows, the PMR spectra were also obtained in neat base. To check the solvent effect, carbon tetrachloride was also used as a solvent in some cases.

Results and Discussion

The isotropic shifts of the tert-butyl protons which are downfield are slightly dependent on the solvent medium. The largest difference found is in Ni(DPM)₂(HMPA)₂ case where the shift in chlorobenzene is 0.24 ppm larger than in neat HMPA. In other cases, the difference is much smaller, being 0.1 ppm or less.

Chlorobenzene was a solvent of choice in all cases because of its good solubility power and its signals are remote from the signals of interest. The proton isotropic shift values and the visible spectral data of the bis-adducts are summarised in Table I.

Parameter to Measure the Axial Ligand Strength

In literature the strength of a donor is frequently measured either by the donor number [9] or the C and E parameters [10]. Various investigators have reported successful correlations of spectral and reactivity data based on the use of the donor numbers. However, since there are extensive contributions to the donor numbers from solvation effects [11] and they provide only single-scale basicity orders without taken into account differences in hardness and softness, this scale is not suitable in the present

TABLE I. A Summary of Visible Spectral and Proton Isotropic Shift Data.

Axial ligand	ν_1^a (cm^{-1})	ν_2^a (cm^{-1})	$\Delta\nu_{\text{tert}}^b$ (ppm)	$\Delta\nu_{\text{met}}^d$ (ppm)
Triethylamine	10,530	14,580	C	
Pyridine	10,100	17,090	-3.56	18.76
Piperidine	9,880	16,750	-3.26	
THF	9,130	15,750	-4.31	20.12
Me_2S^e	9,110	15,870	-4.34	
N,N-DMF	9,010	15,340	-4.01	19.24
DMSO	8,850	15,100	-4.02	19.64
HMPA	8,580	14,000	-5.13	

^aError is approximately $\pm 100 \text{ cm}^{-1}$ or less. In most cases, a weak shoulder appears between ν_1 and ν_2 . ^b $\Delta\nu_{\text{tert}}$ is the proton isotropic shift of the tert-butyl protons of DMP ligand at 34°C in chlorobenzene as solvent. The negative sign means downfield shift. Error is less than ± 0.03 ppm. ^cIn triethylamine, the tert-butyl protons signal overlaps with that of the donor. The maximum downfield shift is estimated to be 3 ppm. ^d $\Delta\nu_{\text{met}}$ is the proton isotropic shift of the methine proton at 28°C in CCl_4 as solvent using the FT-NMR spectrometer. ^eFrom ref. 8.

correlation study. The C and E parameters provide a good estimate of σ -bond strength. However, without the knowledge of the C and E values for $\text{Ni}(\text{DPM})_2$, prediction of the order of the axial donor strength will run into difficulty if $C_1 > C_2$ and $E_1 < E_2$ (or vice versa) where '1' and '2' refer to bases 1 and 2, respectively. Furthermore, both the DN and C and E parameters give the wrong enthalpy value if there is a steric interaction between acid and base.

The best parameter to measure the donor strength of the axial ligand is perhaps the lowest d-d transition energy (ν_1) which arises in the first order approximation from the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ transition in O_h point group [8]. This energy band measures the average ligand field strength in the pseudooctahedral symmetry and since the equatorial ligand is kept constant, the position of this band therefore also measures the axial ligand field strength. One advantage of this experimentally determined parameter is that steric and π -bond effects will show when either one of them is present.

Correlation of Isotropic Shifts with the Axial Ligand Strength

Examination of the data reported in Table I shows that in general there is a correlation between ν_1 and the isotropic shifts of the tert-butyl protons although it is not apparent in the case of the methine proton. The apparently small discrepancies between pyridine and piperidine, between DMSO and THF or Me_2S may be accounted for by the solvent effects on the NMR chemical shift, specifically, the anisotropy effects of the π ring current and the double bond.

They may also be caused by the other effect to be discussed later in this section. Taken as a whole, it can be concluded that the stronger the axial ligand strength, the smaller the isotropic shift of the tert-butyl protons. This conclusion seems to contradict those of Zink and Drago [2] and La Mar [3].

In order to understand the observed trend, the origin of the proton isotropic shifts in the chelated ring should first be looked into. The ground state for tetragonal nickel(II) is orbitally nondegenerate (${}^3\text{B}_{1g}$) and accordingly the dipolar contribution to the proton isotropic shifts will be small and can be neglected for protons in the DPM ligand which are more than at least three bonds away from the metal centre [2]. The shifts arise from contact contribution only.

The unpaired spin delocalization mechanism in the equatorial ligand in $\text{Ni}(\text{acac})_2\text{L}_2$ is believed to involve the highest filled π -orbital with some participation of a σ -orbital [5, 12]. $\text{Ni}(\text{DPM})_2\text{L}_2$ system is closely related to that of $\text{Ni}(\text{acac})_2\text{L}_2$ and therefore, the methine proton isotropic shift originates from a combination of σ and π -delocalization mechanism. Owing to the different signs in these two mechanisms as was shown by the INDO molecular orbital calculation [5] (downfield shift for the σ spin and upfield shift for the π spin mechanism) it is therefore not surprising that a correlation between the axial ligand strength and the proton contact shift of the methine proton does not exist in both the $\text{Ni}(\text{acac})_2\text{L}_2$ and $\text{Ni}(\text{DPM})_2\text{L}_2$ systems. The non-existence of correlation in the methyl protons in $\text{Ni}(\text{acac})_2\text{L}_2$ is also due to the same reason. On the other hand, the unpaired spin density in the tert-butyl protons is expected to originate mainly from the σ -orbital delocalization only. This σ -orbital gains unpaired spin density by mixing of the ligand σ_L orbital with the $d_{x^2-y^2}$ orbital which contains an unpaired electron. The amount of unpaired spin density transferred to the equatorial ligand σ_L orbital depends on the energy difference between σ_L and $d_{x^2-y^2}$ orbital. The larger the difference between them the smaller will be the amount of spin transferred and this will be manifested in a smaller contact shift.

Changes in metal ion d orbital energies in D_{4h} symmetry with increasing axial ligand strength may occur in two ways which have opposite effects on the contact shifts [2]. (i) The energy of the entire d manifold is raised as a result of the lowering of formal charge on the metal (ii) The $d_{x^2-y^2}$ orbital energy is lowered. The former predicts smaller contact shift with increasing axial ligand strength while the latter predicts the opposite. The observed trend in $\text{Ni}(\text{DPM})_2\text{L}_2$ system suggests that the former effect is predominating. This on first glance seems to contradict the conclusion drawn by Zink and Drago [2]. They suggested that the change in the magnitude of the tetragonal splitting of the nickel d orbitals is

greater than the change in energy of the center of gravity of the d orbitals arising from changing the nickel formal charge. This may be true if the variation in the axial ligand donor is not large enough to change the formal charge appreciably. The average Dq value using the average environmental rule in $Ni(stien)_2(anion)_2$ varies from 1110 to 1050 cm^{-1} whereas the corresponding value in $Ni(DPM)_2L_2$ varies from 1050 to 860 cm^{-1} . A much larger variation in the formal charge on nickel is therefore expected in $Ni(DPM)_2L_2$ which therefore shows trend opposite to that of Zink and Drago. It is of interest to note that when the axial ligand varies from DMSO to THF (average Dq from 885 to 913 cm^{-1}) the contact shift increases with increasing axial donor strength within this group of closely related donors. Although the change lies within the range expected from that of the solvent effects, however, we are tempted to speculate that this trend may well be the result of the tetragonal splitting when the formal charge variation is small.

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