# Nuclear Magnetic Resonance Studies of Lewis Acid–Base Interactions. Part II.[1] A Correlation between Isotropic Contact Shifts and Taft $\sigma^*$ values for some Pyridine Base Adducts of Nickel(II) Bis(*O*-Alkyl Dithiocarbonates) and Bis(β-Diketonates)

By **Yau Y. Lim** * and **Kee L. Chua**, Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

The Lewis acid–base interaction between pyridine bases and various *O*-alkyl dithiocarbonates and β-diketonates of $Ni^{II}$ has been studied by n.m.r. spectroscopy. There is correlation between the isotropic contact shifts of the $H^2$ and $H^3$ protons of pyridine bases and the Taft $\sigma^*$ values of the substituent group R in $[Ni(S_2COR)_2]$. An explanation, based on a detailed study of the change in energy levels of the individual metal *d* orbitals, is proposed for the observed correlation which implies the relative strength of the Lewis acid–base interaction can be inferred from contact-shift studies. The observed trend in relative isotropic shifts of the protons at the 3-Me, 4-Me, and $H^4$ positions and the absolute isotropic shifts of the $H^2$ protons on the spin-delocalization mechanism is also discussed.

THE n.m.r. study of Lewis acid–base adduct formation between diamagnetic square-planar four-co-ordinate nickel(II) complexes of bidentate sulphur ligands, *e.g.* *O*-alkyl dithiocarbonates, $ROCS_2^-$, and aromatic amines has been a subject of recent interest in this laboratory.[1] The chemical shifts of the protons in the acid–base moiety of the paramagnetic adduct exhibit large isotropic shifts compared with their diamagnetic analogues. The isotropic shift is the sum of two terms: the ' Fermi-contact ' shift which reflects delocalization of unpaired metal electron(s) into the ligand orbital; and the through-space ' pseudo-contact ' shift which arises from an anisotropic magnetic interaction between the electronic magnetic moment of the metal and the nuclear magnetic moment of the ligand.[2] Although it is generally agreed that the isotropic shift of pyridine-ring protons in tetragonal nickel complexes is mainly ' Fermi contact ' in nature and the ' pseudo-contact ' or dipolar contribution is considered to be negligible,[3,4] there has been some controversy over the mode of spin delocalization.[5-7]

The present study serves two purposes. The first is to

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[1] Part I, Y. Y. Lim, *Austral. J. Chem.*, 1974, **27**, 213.

[2] For a review see G. A. Webb in 'Annual Reports on N.M.R. Spectroscopy,' ed. E. F. Mooney, Academic Press, New York, 1970, vol. 3, p. 211.

[3] J. A. Happe and L. Ward, *J. Chem. Phys.*, 1963, **39**, 1211.

[4] J. I. Zink and R. S. Drago, *J. Amer. Chem. Soc.*, 1970, **92**, 5339.

[5] R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, 1970, **92**, 66.

[6] W. D. Horrocks, jun., and D. L. Johnston, *Inorg. Chem.*, 1971, **10**, 1835.

[7] M. S. Sun, F. Grein, and D. G. Brewer, *Canad. J. Chem.*, 1972, **50**, 2626.

examine the feasibility of using the n.m.r. isotropic contact shift to measure the strength of the Lewis acid–base interaction. The strength of the acid–base interaction between $Ni^{II}$ complexes and a fixed pyridine-type base can be varied by changing the electron-withdrawing ability of the R group of the co-ordinated *O*-alkyl dithiocarbonate, $RCS_2^-$, or the R and R′ groups of the co-ordinated β-diketonate, $RCOCHCOR'^-$, both of which are used in the present study. The electron-withdrawing ability of the R group can be measured by the Taft $\sigma^*$ values.[8] By attempting to correlate the n.m.r. isotropic contact shifts of the pyridine (py) and methylpyridine protons with Taft $\sigma^*$ values we hope to be able to throw some light on this problem. It should be noted that, although the correlation of n.m.r. chemical shifts with $\sigma^*$ values is well known,[9] and the effect of varying the axial ligand on the isotropic contact shift of the equatorial ligand in tetragonal and square-pyramidal complexes has been the subject of interest recently,[1,4,10,11] we are not aware of any study on the effect of varying the acid strength of a square-planar complex on the isotropic contact shifts of axial pyridine ligands. The second aim of this study is to use the experimental data to verify some aspects of the spin-delocalization mechanism proposed recently[7] on the basis of INDO–MO calculations.

## EXPERIMENTAL

*Preparation and Characterization of Compounds.*—All the β-diketones used in this study were purchased from Eastman Kodak Organic Chemicals Co. The nickel(II) β-diketonates were prepared by previously described methods.[12,13] Except for *O*-ethyl dithiocarbonate which was available commercially, the other ligands ($ROCS_2^-$; R = $MeOCH_2CH_2$, $PhCH_2CH_2$, and $Bu^tCH_2$) were prepared in this laboratory by mixing stoicheiometric amounts of the respective alcohol with potassium hydroxide and carbon disulphide. The dark brown $Ni^{II}$ complexes were prepared by a standard procedure.[14] The yield was generally good (>50%). Elemental analyses were by the Australian Microanalytical Service, Melbourne, and the results are summarized in Table 1.

The n.m.r. spectra were obtained with a Hitachi–Perkin-Elmer R-20B spectrometer at 34 °C. Tetramethylsilane was used as the internal reference. The spectra were calibrated with a frequency counter. I.r. spectra were recorded with a Beckman IR-12 spectrophotometer. The samples were prepared in a Nujol mull placed between NaCl plates for the region 650—2 000 cm$^{-1}$ and between Polythene plates for the region 250—650 cm$^{-1}$. The n.m.r. spectra in nitrobenzene and methylene chloride are consistent with those expected from the structural formulae. The i.r. spectrum of $[Ni(S_2COEt)_2]$ has been studied and assigned before,[15] but not those of the other complexes prepared in this work. Although it is not possible to assign all the observed frequencies to the various modes of vibration in the absence of normal-co-ordinate analyses, the band due to the nearly pure asymmetric Ni–S stretching vibration, however, can be assigned without difficulty. This sharp band is shifted to lower frequency on adduct formation.[16] The pertinent frequency values for the complexes prepared are listed in Table 1.

*Purification.*—Pyridine (py) (B.D.H., AnalaR) was purified as previously described.[17] Nitrobenzene (Hopkins and Williams, AnalaR) was fractionally distilled under reduced pressure and stored over 4A molecular sieves. Methylene chloride (Merck, Spectroscopic grade) was distilled once and stored over 4A molecular sieves. Deuteriated chloroform (Stohler isotope chemicals) was used without further purification.

All solutions used in this work were checked with a conductivity meter and found to have negligible conductance.

## RESULTS AND DISCUSSION

Although the β-diketonate complexes are not present as monomers in non-co-ordinating solvents, in the presence of excess of donor they are converted into monomeric bis(adducts)[10] with the two donor molecules occupying *trans* positions of a six-co-ordinate tetragonal structure. Thus both the present systems can be described by equation (1) where L = pyridine base and X = $RCS_2^-$ or $RCOCHCOR'^-$.

$$[NiX_2] + 2L \rightleftharpoons [NiX_2L_2] \qquad (1)$$

TABLE 1

Analytical data

| | | | Analyses/% | | | |
|---|---|---|---|---|---|---|
| | | | Found | | Calc. | |
| Complex | M.p. ($\theta_c$/°C) (uncorrected) | $\tilde{\nu}$(Ni–S) (±2 cm$^{-1}$) | C | H | C | H |
| $[Ni(S_2COCH_2CH_2OMe)_2]$ | 135—136 | 383 | 26.9 | 3.9 | 26.6 | 3.9 |
| $[Ni(S_2COCH_2CH_2Ph)_2]$ | 153—154 | 386 | 47.9 | 4.0 | 47.7 | 4.0 |
| $[Ni(S_2COEt)_2]$ * | 141—142 | 381 | 24.3 | 3.4 | 23.9 | 3.3 |
| $[Ni(S_2COCH_2Bu^t)_2]$ | 209—210 | 390 | 37.5 | 5.7 | 37.4 | 5.7 |

* Data from ref. 1.

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[8] J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, Tokyo, 1962, ch. 4.

[9] 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1972, chs. 4 and 7.

[10] G. N. LaMar, *J. Mag. Resonance*, 1969, **1**, 185.

[11] M. M. Dhingra, P. Ganguli, and S. Mitra, *Chem. Phys. Letters*, 1974, **25**, 579.

[12] R. H. Holm and F. A. Cotton, *J. Phys. Chem.*, 1961, **65**, 321.

[13] F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, 1966, **82**, 2979.

[14] D. R. Dakternieks and D. P. Graddon, *Austral. J. Chem.*, 1971, **24**, 2509.

[15] A. Ray, D. N. Sathyanarayana, G. D. Prasad, and C. C. Patel, *Spectrochim. Acta*, 1973, **A29**, 1579 and refs. therein.

[16] M. R. Hunt, A. G. Kruger, L. Smith, and G. Winter, *Austral. J. Chem.*, 1971, **24**, 53.

[17] T. F. Bolles and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 3921.

In order to measure the absolute isotropic shifts of the 1 : 2 adduct in solution the observed isotropic shifts $\Delta\nu_0$ were first measured in solution with a large excess of the pyridine base. The absolute isotropic shifts $\Delta\nu_p$ were calculated from equation (2)[18] where $x_p$ is the mol

$$\Delta\nu_0 = x_p\Delta\nu_p \qquad (2)$$

fraction of the co-ordinated pyridine and there is rapid exchange (on the n.m.r. time scale) between protons in the paramagnetic and diamagnetic environments. The ratios of [L] to [Ni$^{II}$] used for the dithiocarbonate complexes in methylene chloride lay between 30 and 70 : 1. For the β-diketonates in deuteriated chloroform it was slightly greater than 100 : 1.[10] The choice of the ratio was dictated by factors such as the need for complete conversion into the paramagnetic adduct and resolution of overlapping signals, for example, those of the protons of the pyridine molecule at the 3 and 4 positions.

TABLE 2

N.m.r. isotropic shifts (Hz) of pyridine bases (L) in $[Ni(S_2COR)_2L_2]$ [a]

| | | py | | | 4-Mepy | | | 3-Mepy | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| R | σ* [b] | $H^2$ | $H^3$ | $H^4$ (±8%) | $H^2$ | $H^3$ | 4-Me | $H^2$ | $H^3$ | 3-Me | $H^4$ (±5%) |
| $Bu^tCH_2$ | −0.30 | −4 733 | −2 050 | −443 | −3 609 | −1 933 | +586 | −5 008 | −2 245 | −456 | −441 |
| Et | 0 | −4 616 [c] | −2 046 | −439 | −3 552 | −1 924 | +594 | −4 764 | −2 175 | −456 | −421 |
| $PhCH_2CH_2$ | +0.215 | −4 404 | −1 960 | −442 | | | | | | | |
| $MeOCH_2CH_2$ | +0.64 | −4 076 | −2 000 | −421 | −2 992 | −1 827 | +571 | −4 140 | −2 151 | −458 | −440 |

[a] Measured at 60 MHz in methylene chloride; error, except where noted, is ±3%. [b] From ref. 8, p. 97. [c] The results given in ref. 1 were in error and the values reported here are the corrected ones.

TABLE 3

N.m.r. isotropic shifts (Hz) of pyridine bases (L) in $[Ni(RCOCHCOR')_2L_2]$ [a]

| | py | | | 4-Mepy | | |
|---|---|---|---|---|---|---|
| R,R′ | $H^2$ | $H^3$ | $H^4$ | $H^2$ | $H^3$ | 4-Me (±10%) |
| Me, Me | −5 350 | −1 600 | −400 | −5 180 | −1 590 | +590 |
| Ph, Ph | −2 800 | −1 400 | −350 | −2 462 | −1 230 | +560 |
| $CF_3$, Naphthyl | *b* | *b* | *b* | *b* | *b* | *c* |

[a] Measured at 60 MHz in deuteriated chloroform; error, except where noted, lies within ±3%. [b] Very small negative value. [c] Very small positive value.

The isotropic shifts of the py and Mepy adducts of the nickel(II) dithiocarbonate and β-diketonate systems are summarized in Tables 2 and 3. The values are the average of several determinations at various [L] to [Ni] ratios. The maximum error was estimated to lie within ±3% for the $H^2$ and $H^3$ shifts, with slightly larger error for the 3-methyl, 4-methyl, and $H^4$ shifts. Figure 1 shows a plot of $\Delta\nu_p$ for $H^2$ of various pyridine bases against Taft σ* value (which is a measure of the inductive effect of the aliphatic group, more positive values indicating greater electron withdrawal). Such a plot could not be drawn for the β-diketonate system as the data were rather limited. As can be seen in Figure 1, an approximately linear relation was obtained. A highly electron-withdrawing ligand in the equatorial position (*e.g.* X = $MeOCH_2CH_2OCS_2^-$) gave small isotropic shifts (in absolute magnitude) of the protons of the axial ligand and *vice versa*. The same trend also held for the $H^3$ isotropic shifts in all the systems studied (see Tables 2 and 3). For the $H^4$, 4-Me, and 3-Me shifts, although the experimental error is relatively large, closer examination revealed that the same trend was probably observed. It should be noted that in the interaction between nickel(II) 1,3-bis(trifluoromethyl)propane-1,3-dionate and 4-trifluoromethylbutane-1,3-dionate complexes and py in deuteriated chloroform the $^1H$ n.m.r. signals of py merely broaden with no significant shifts.

The observed trend can be rationalized as follows. It is generally agreed that when a pyridine base co-ordinates to a Ni$^{II}$ complex to form a six-co-ordinate tetragonal adduct the spin-transfer process between Ni$^{II}$ and the base is dominated by a σ-delocalization mechanism.[6,7] On adduct formation the unpaired spin is in the σ* (antibonding) orbital of the nickel–pyridine system which

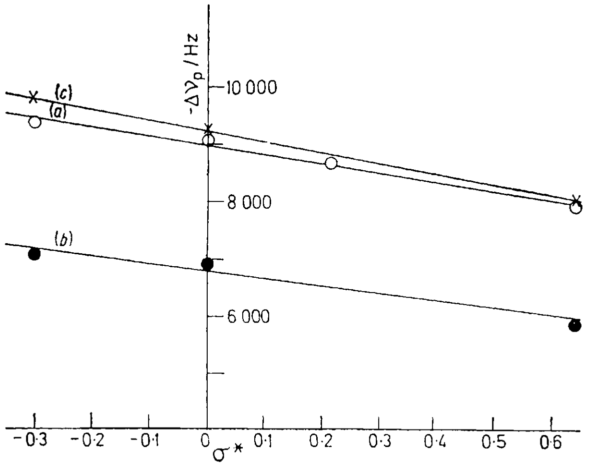

FIGURE 1 Plots of $H^2$ isotropic shift, $-\Delta\nu_p$, against Taft σ* values for py (*a*), 4-Mepy (*b*), and 3-Mepy (*c*)

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[18] J. C. Fanning and R. S. Drago, *J. Amer. Chem. Soc.*, 1968, **90**, 3987.

is obtained by ' mixing ' the $d_{z^2}$ orbital with the pyridine $\sigma_b$ orbital containing the lone-pair electrons. The smaller the energy difference between the $d_{z^2}$ and the $\sigma_b$ orbitals the greater will be the ' mixing ' effect and this will be manifested in a larger n.m.r. contact shift of the various protons of the axial pyridine. The magnitude of the n.m.r. contact shifts of pyridine protons is thus a function of the energy difference between the $d_{z^2}$ and $\sigma_b$ orbitals. If the equatorial ligand becomes more electron withdrawing two opposing effects on the $d_{z^2}$ orbital can be envisaged. (*i*) The formal charge on the nickel increases thereby increasing the metal–pyridine interaction. This increased interaction raises the energy of the $d_{z^2}$ orbital[19] (Figure 2). (*ii*) The $d_{z^2}$ orbital energy is slightly lowered.[20] Of the two opposing effects, (*i*) will dominate. Hence, for Ni$^{II}$ co-ordinated to a more electronegative equatorial ligand the magnitude of the n.m.r. contact shifts of pyridine protons should be smaller as was observed in this study. Although there may not be a theoretical justification for the linear relation between the two properties because of the various opposing effects involved, the correlation as found indicates that with due care one can infer qualitatively the strength of the acid–base interaction from n.m.r. isotropic-contact-shift studies.

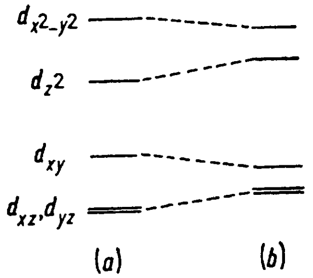

FIGURE 2 Energy-level diagram showing the effect of adding two ligands axially to a square-planar nickel(II) complex.[19] The ordering in (*a*) is for square-planar complexes. The strength of the interaction increases from (*a*) to (*b*)

One of the results of INDO–MO calculations made by Sun *et al.*[7] predicted that the relative isotropic shifts of 3-Me, 4-Me, and H$^4$ (as measured by the ratio, say $\Delta\nu_{H^4} : \Delta\nu_{H^2}$), which are dominated by a $\sigma$–$\pi$ spin-polarization mechanism, should become larger as the amount of $\sigma$ spin delocalized over the ligand becomes smaller. As the total $\sigma$-spin density is linearly related to that on H$^2$ which in turn is linearly related to the isotropic contact shift, we may use the magnitude of the isotropic shift of H$^2$ to measure $\sigma$-spin density and see how it correlates with the relative isotropic shifts of the protons at 3-Me, 4-Me, and H$^4$. As can be seen from Table 4 for all the systems under investigation, the relative isotropic shifts increase with decreasing H$^2$ shifts (*i.e.* with total $\sigma$-spin density in the pyridine bases). The agreement between our experimental observations and the INDO–MO calculations based on a $\sigma$–$\pi$ spin-polarization mechanism is significant for it provides a good indication that the isotropic shifts at 3-Me, 4-Me, and H$^4$ are indeed dominated by the $\sigma$–$\pi$ spin-polarization mechanism.

TABLE 4

Comparison of H$^2$ contact with relative isotropic shifts for pyridine bases co-ordinated to nickel(II)

| py | | 4-Mepy | | 3-Mepy | | |
|---|---|---|---|---|---|---|
| | Relative shift | | Relative shift | | Relative shift | |
| H$^2$ | H$^4$ | H$^2$ | (4-Me proton) | H$^2$ | 3-Me proton | H$^4$ |
| −5 350 | 0.075 * | −5 180 | −0.114 * | −5 008 | 0.091 | 0.088 |
| −4 733 | 0.094 | −3 609 | −0.163 | −4 764 | 0.096 | 0.088 |
| −4 616 | 0.095 | −3 552 | −0.167 | −4 140 | 0.111 | 0.107 |
| −4 404 | 0.100 | −2 992 | −0.191 | | | |
| −4 076 | 0.103 | −2 462 | −0.228 * | | | |
| −2 800 | 0.125 * | | | | | |

* Data are for [Ni(RCOCHCOR')$_2$L$_2$]; shifts in Hz. The relative shift is defined as the ratio of the H$^4$ or 3,4-Me proton shift to the H$^2$ shift.

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[19] Adapted from F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry.', 3rd edn., Wiley–Interscience, New York, 1972, p. 560.

[20] J. I. Zink and R. S. Drago, *J. Amer. Chem. Soc.*, 1972, **94**, 4550.