

Nitrogen-14 Magnetic Resonance Study of Pyridine Exchange in Bis-(pentane-2,4-dionato)dipyridine-cobalt(II) and -nickel(II) Complexes

By **Stephen F. Lincoln**, Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia 5001

A ^{14}N n.m.r. study of the exchange of pyridine in *trans*-[M(acac)₂(py)₂] complexes (M = Co^{II} or Ni^{II}; acac = 2,4-pentanedionato) is reported. When M = Co^{II}, $k_{\text{ex}}(298\text{ K}) = (15 \pm 2) \times 10^5\text{ s}^{-1}$, $\Delta H^\ddagger = 28 \pm 2.5\text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = -33 \pm 17\text{ J K}^{-1}\text{ mol}^{-1}$ and when M = Ni^{II}, $k_{\text{ex}}(298\text{ K}) = (9.8 \pm 1.2) \times 10^4\text{ s}^{-1}$, $\Delta H^\ddagger = 42 \pm 3\text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -9 \pm 10\text{ J K}^{-1}\text{ mol}^{-1}$. Kinetic parameters are discussed in terms of a solvent-exchange model involving solvent interactions outside the first co-ordination sphere in the activation process.

THE mechanism of solvent exchange appears to be a central facet in the process of ligand substitution on many metal ions^{1,2} and consequently much effort has been expended on solvent-exchange studies,³ particularly in aqueous solution.⁴ Recently attention has been drawn to the existence of a single linear relation between ΔH^\ddagger and ΔS^\ddagger for both ligand substitution and solvent exchange on eight bivalent metal ions of similar surface charge density in a range of solvents.⁵ It is apparent from this observation that exchange studies in a wider range of solvents may well further mechanistic interpretation, and accordingly, a ^{14}N n.m.r. study of the exchange of pyridine in the complex bis(pentane-2,4-dionato)dipyridinecobalt(II), [Co(acac)₂(py)₂], and its nickel(II) analogue is reported here.

RESULTS

The relation of bulk-solvent nuclear relaxation, and the associated chemical shift, to solvent exchange processes on paramagnetic metal ions in dilute solution has been

¹ K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107.

² D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 45.

³ T. R. Stengle and C. H. Langford, *Co-ordination Chem. Rev.*, 1967, **2**, 349.

discussed in detail in the literature,^{3,6} and consequently only the salient aspects of this relation applicable to the system under study are considered here. The relaxation of the ^{14}N nucleus of bulk pyridine induced by the complex [Co(acac)₂(py)₂] and its nickel(II) analogue may be expressed as in equation (1), where T_2 and T_{2A} are the observed

$$T_{2p} = [(1/T_2) - (1/T_{2A})]^{-1} \quad (1)$$

transverse relaxation times of bulk pyridine in a paramagnetic solution and of bulk pyridine in a reference solution of the complex [Zn(acac)₂], respectively. The diamagnetic [Zn(acac)₂] species shortens the bulk pyridine transverse relaxation time at temperatures below 283 K, consistent with an increase in solution viscosity. It is assumed that a similar source of relaxation is associated with the paramagnetic species also and that it approximates in magnitude to that observed in the [Zn(acac)₂] reference solutions. The ^{14}N resonance linewidths are related to the appropriate relaxation times by expression (2), where γ

$$T_{2p} \approx 2\gamma^{-1}(W - W_A)^{-1} \quad (2)$$

is the nitrogen-14 gyromagnetic ratio ($1934 \times 10^4\text{ T}^{-1}\text{ s}^{-1}$) and W and W_A are the full linewidths (in T) of the bulk

⁴ J. P. Hunt, *Co-ordination Chem. Rev.*, 1971, **7**, 1.

⁵ H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. (A)*, 1971, 2198.

⁶ T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307; erratum, 1964, **41**, 2553.

pyridine ^{14}N resonance at half maximum amplitude in the paramagnetic and reference solutions respectively.

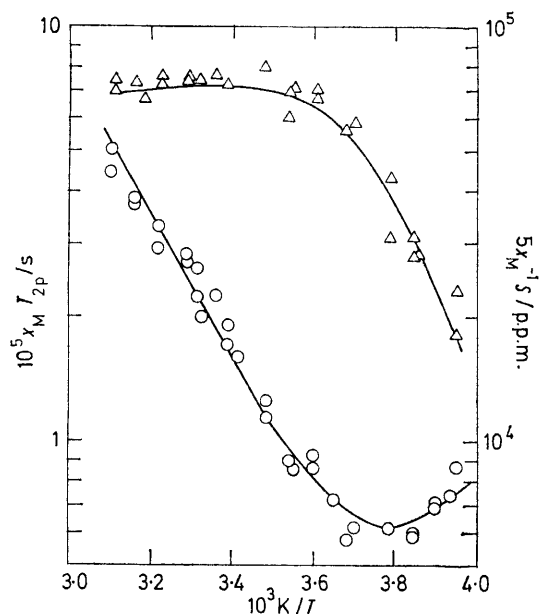


FIGURE 1 Nitrogen-14 relaxation (\circ) ($x_M T_{2p}$) and shift (Δ) ($x_M^{-1}S$) data for the bulk-solvent pyridine resonance in the $[\text{Co}(\text{acac})_2(\text{py})_2]$ system. The computed best fit of equation (3) to the relaxation data is shown as a solid curve. The solid curve passing through the shift data was computed from the best fit $\Delta\omega_M$ and τ_M values derived from the relaxation data.

The ^{14}N relaxation and shift data for both the $[\text{Co}(\text{acac})_2(\text{py})_2]$ and the $[\text{Ni}(\text{acac})_2(\text{py})_2]$ systems are consistent with a ' $\Delta\omega$ ' nuclear relaxation mechanism⁶ such that equation (3) is applicable, where τ_M is the mean life time of

$$T_{2p} = \tau_M x_M^{-1} + (x_M \tau_M \Delta\omega_M^2)^{-1} \quad (3)$$

a single co-ordinated pyridine molecule, x_M the mole fraction of co-ordinated pyridine, and $\Delta\omega_M$ is the difference in the ^{14}N resonance frequencies of co-ordinated and bulk pyridine. In both systems T_{2p} exhibits a linear dependence on $[\text{M}(\text{acac})_2(\text{py})_2]$. In Figures 1 and 2 the best fits of equation (3) to relaxation data for the $[\text{M}(\text{acac})_2(\text{py})_2]$ systems are

constant and rate for pyridine exchange and the other symbols have their usual meaning. The derived exchange parameters, together with those of related studies,⁷⁻⁹ are listed in the Table. It has been shown that the chelate-ring exchange rate is slow compared to the solvent exchange rates reported here.⁸

The bulk-pyridine chemical shift (S) variation may be calculated from the relaxation data using equation (5).

$$S x_M^{-1} = -\Delta\omega_M (1 + \tau_M^2 \Delta\omega_M^2)^{-1} \quad (5)$$

The coincidence of the calculated and observed chemical-shift values shown in Figures 1 and 2 demonstrates the

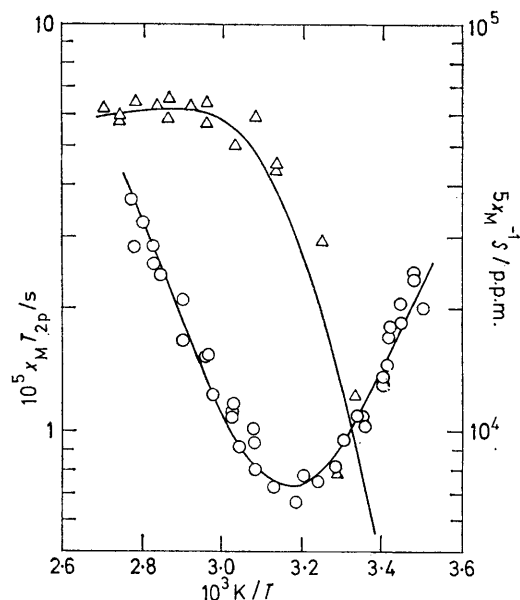


FIGURE 2 Nitrogen-14 relaxation (\circ) ($x_M T_{2p}$) and shift (Δ) ($x_M^{-1}S$) data for the bulk-solvent pyridine resonance in the $[\text{Ni}(\text{acac})_2(\text{py})_2]$ system. The computed best fit of equation (3) to the relaxation data is shown as a solid curve. The solid curve passing through the shift data was computed from the best fit $\Delta\omega_M$ and τ_M values derived from the relaxation data.

close internal consistency of the relaxation and chemical-shift data of the $[\text{M}(\text{acac})_2(\text{py})_2]$ systems. This internal agreement indicates that, for both the cobalt(II) and the

Kinetic parameters for solvent exchange

Complex	$10^4 k_{\text{ex}}(298 \text{ K})$ s^{-1}	ΔH^\ddagger kJ mol^{-1}	ΔS^\ddagger $\text{J K}^{-1} \text{mol}^{-1}$	N.m.r. method
$[\text{Co}(\text{acac})_2(\text{py})_2]^b$	150 ± 20	28 ± 2.5	-33 ± 17	$^{14}\text{N}^a$
$[\text{Co}(\text{acac})_2(4\text{-Mepy})_2]^c$	100	37.7	4.2	^1H
$[\text{Co}(\text{py})_4\text{Cl}_2]^d$	670 ± 110	55.2 ± 2	71 ± 8	^{14}N
$[\text{Ni}(\text{acac})_2(\text{py})_2]^b$	9.8 ± 1.2	42 ± 3	-9 ± 10	$^{14}\text{N}^a$
$[\text{Ni}(\text{acac})_2(4\text{-Mepy})_2]^c$	110	47.7	11.8	^1H
$[\text{Ni}(\text{acac})_2(\text{mpo})_2]^e$	75	46.9	22.6	^1H

4-Mepy = 4-Methylpyridine, mpo = 4-methylpyridine 1-oxide.

^a The complexity of the pyridine signal precludes ^1H studies. ^b This work. ^c Ref. 8. ^d Ref. 7. ^e Ref. 9.

shown. The pyridine-exchange parameters may be derived through equation (4), where k_{ex} and ξ are the rate

$$\tau_M^{-1} = k_{\text{ex}} = (\xi/2)[\text{M}(\text{acac})_2(\text{py})_2]^{-1} = (kT/h)\exp(-\Delta H^\ddagger/RT)\exp(\Delta S^\ddagger/R) \quad (4)$$

⁷ G. D. Howard and R. S. Marianelli, *Inorg. Chem.*, 1970, **9**, 1738.

⁸ R. W. Kluiber, R. Kulka, and W. D. Horrocks, *Inorg. Chem.*, 1970, **9**, 1319.

nickel(II) system, $\Delta\omega_M$ exhibits a Curie temperature dependence [see equation (6)] consistent with the chemical shift being predominantly contact in character. This is not unexpected for the nickel(II) system as ^1H chemical shifts for the pyridine ligands have been shown to be predominantly contact in nature, but such is not the case for

⁹ R. W. Kluiber, F. Thaller, R. A. Low, and W. D. Horrocks, *Inorg. Chem.*, 1970, **9**, 2592.

the analogous cobalt(II) system where large pseudo-contact contributions to the observed shift have been detected.¹⁰ When both contributions to the observed chemical shift are similar in magnitude, a non-Curie temperature dependence is expected¹¹ as reported for ¹H in the [Co(MeCN)₆]²⁺ system.¹² It appears that for the co-ordinating ligand atom (¹⁴N), the contact interaction becomes predominant {as in the case for [Co(MeCN)₆]²⁺ also} and the ¹⁴N chemical shift exhibits a Curie temperature dependence. Nitrogen-14 scalar-coupling constant (A/h) values of 6.49×10^6 and 13.8×10^6 Hz for the cobalt(II) and nickel(II) systems respectively were calculated using equation¹³ (6), where S' is the nett electron spin for

$$\frac{\Delta\omega_M}{\omega} = \frac{-2\pi\mu_{\text{eff}}\beta(A/h)}{3kT\gamma} [S'(S' + 1)]^{\frac{1}{2}} \quad (6)$$

the metal ion, and where μ_{eff} values of 4.82¹⁴ and 3.13 B.M.¹⁵ pertain to the cobalt(II) and nickel(II) systems respectively.

DISCUSSION

The ¹⁴N n.m.r. data is consistent with pyridine exchange on single species in the cobalt(II) and nickel(II) systems which, on the basis of solid-state X-ray studies^{16,17} and solution spectral studies,^{10,18,19} is considered to be *trans*-[M(acac)₂(py)₂]. The relative magnitudes of ΔH^\ddagger and k_{ex} for the two systems are as expected from crystal-field arguments,²⁰ and also from the greater metal-nitrogen distance in the cobalt(II) system.^{16,17} For the [Co(py)₄Cl₂] system,⁷ for which intermediate species with co-ordination numbers less than six exist, the large positive ΔS^\ddagger observed for pyridine exchange is as expected for a dissociative mechanism if ΔS^\ddagger is considered to arise solely from first-co-ordination-sphere interactions. If, however, ΔS^\ddagger is considered to reflect second-co-ordination-sphere and more-distant interactions in the transition state, then the interpretation of ΔS^\ddagger becomes less facile.

On the basis that ligand substitution on cobalt(II) and nickel(II) complexes appears to be controlled by co-ordinated solvent lability, Bennetto and Caldin⁵ have proposed a model which envisages solvent-exchange processes to be largely dissociative in nature, and which also considers contributions to ΔH^\ddagger and ΔS^\ddagger arising from solvent-rearrangement processes at some distance from the first co-ordination sphere. According to this model, solvent in the immediate vicinity (region B) of a metal complex is in a state of high entropy, whereas the more-distant bulk solvent (region C) is relatively ordered. If nett transfer of solvent from region B to region C is synchronous with bond breaking in the dissociative activation process, a negative ΔS^\ddagger results, whereas a positive ΔS^\ddagger will arise for nett passage of solvent in the opposite direction. The

former case fits the pyridine-exchange data presented here, whereas the latter fits the data for the other systems. If solvent transfer from region B to C is considered analogous to condensation, and transfer from C to B analogous to evaporation, then negative and positive contributions to ΔH^\ddagger (which contains an enthalpy term for the first co-ordination sphere bond-breaking process, the magnitude of which is considered to be almost invariant from system to system⁵) will arise from these respective processes. The ΔH^\ddagger and ΔS^\ddagger values in the Table exhibit trends consistent with the above model, and, after allowance for crystal-field effects,²⁰ lie close to the correlation line of Bennetto and Caldin.⁵

The difference in ΔS^\ddagger for the two pyridine systems reported here probably arises from quite small structural effects. In the solid state the pyridine ligands in the complex *trans*-[Co(acac)₂(py)₂] [Co-N bond length 2.187(5) Å] are staggered, whereas in the nickel analogue [Ni-N bond length 2.112(5) Å] they are eclipsed,^{16,17} and whilst these ligands presumably freely rotate in solution, it is conceivable that the factors producing the solid-state stereochemical differences also produce differing transition-state stereochemistries in solution, which in turn interact differently with pyridine outside the first co-ordination sphere. The rather large differences in ΔS^\ddagger between the pyridine and 4-methylpyridine systems may reflect the presence of large amounts of CDCl₃ diluent in the latter systems (which probably leads to major modifications in 4-methylpyridine solvent characteristics) rather than a difference in ligational characteristics of pyridine and 4-methylpyridine. Ideally, determination of the order of exchange with respect to solvent concentration provides an invaluable aid to mechanistic interpretation, and it is noteworthy that Kluiber *et al.*^{8,9} report a zero-order exchange-rate dependence on 4-methylpyridine and 4-methylpyridine 1-oxide concentrations in the presence of CDCl₃ diluent, for the systems in the Table. The kinetic method employed by Kluiber, and also in the present study, requires that the mole fraction of co-ordinated solvent, x_M , should not exceed *ca.* 0.1, under which conditions preferential solvation in the presence of a diluent may obscure the true kinetic order. Tsiang and Langford²¹ have investigated this aspect for exchange of dimethyl sulphoxide on nickel(II) in the presence of a diluent and conclude from kinetic and solvation studies that kinetically significant preferential solvation does not occur, however.

EXPERIMENTAL

Anhydrous bis(pentane-2,4-dionato) complexes of cobalt(II), nickel(II), and zinc(II) were prepared by methods

¹⁰ J. A. Happe and R. L. Ward, *J. Chem. Phys.*, 1963, **39**, 1211.
¹¹ R. J. Kurland and B. R. McGarvey, *J. Magnetic Resonance*, 1970, **2**, 286.

¹² R. J. West and S. F. Lincoln, *Inorg. Chem.*, 1972, **11**, 1688.

¹³ N. Bloembergen, *J. Chem. Phys.*, 1957, **27**, 595.

¹⁴ F. A. Cotton and R. H. Holm, *J. Amer. Chem. Soc.*, 1960, **82**, 2979.

¹⁵ R. Nast and H. Ruckemann, *Ber.*, 1960, **93**, 2329.

¹⁶ R. C. Elder, *Inorg. Chem.*, 1968, **7**, 1117.

¹⁷ R. C. Elder, *Inorg. Chem.*, 1968, **7**, 2316.

¹⁸ J. T. Hashagen and J. P. Fackler, *J. Amer. Chem. Soc.*, 1965, **87**, 2821.

¹⁹ R. W. Kluiber and W. D. Horrocks, *Inorg. Chem.*, 1967, **6**, 166.

²⁰ A. L. Companion, *J. Phys. Chem.*, 1969, **73**, 739.

²¹ J. H. G. Tsiang and C. H. Langford, *Inorg. Chem.*, 1970, **9**, 2346.

similar to those reported for the cobalt(II) complex¹⁴ {Found: C, 46.3; H, 5.90; [Co(acac)₂] requires C, 46.35; H, 6.20. Found: C, 46.45; H, 5.80. [Ni(acac)₂] requires C, 46.4; H, 6.25. Found: C, 45.0; H, 6.0. [Zn(acac)₂] requires C, 45.2; H, 6.05%}. I.r. spectra of concentrated Nujol mulls of the complexes exhibited no water peak in the 3500 cm⁻¹ region. AnalaR pyridine was dried over Linde 4A molecular sieves. Solutions for n.m.r. determinations were made up by weight and transferred to 10 mm o.d. n.m.r. tubes under a dry nitrogen atmosphere. The solutions in the n.m.r. tubes were degassed and sealed under vacuum. The cobalt(II) solutions (5) were in the range 0.04339–0.2790 mol kg⁻¹, the nickel(II) solutions (5) 0.03167–0.2050 mol kg⁻¹, and the zinc(II) solutions (4) 0.02711–0.2843 mol kg⁻¹.

N.m.r. measurements were made at 3.07 MHz on previously described modified Varian equipment.²² Absorption mode signals were obtained by both side-band²³ and first-derivative methods, which gave identical results after correction of the first-derivative data for modulation broadening.²⁴ (The latter never exceeded 5% of the total linewidth at half signal amplitude.) Greater signal intensity was obtained using the first-derivative method and consequently linewidths >0.25 mT were determined

by that method only. Linewidth and chemical-shift measurements were made in triplicate, at least, and were reproducible to 0.01 mT. The linewidths of pure pyridine varied from 0.08 mT (360 K) to 0.17 mT (253 K) and wider linewidths were only observed in the Zn^{II} reference solutions below 283 K. The largest reference linewidth employed was 0.19 mT (253 K) for an interpolated 0.04339 mol kg⁻¹ Zn^{II} solution, which compared with a 0.28 mT (253 K) linewidth observed for a 0.04339 mol kg⁻¹ Co^{II} solution. All n.m.r. measurements were made at r.f. levels well below saturation. Sample temperature was measured with a copper–Constantan thermocouple inserted into a 3 mm o.d. well in the sample tube.

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²² R. J. West and S. F. Lincoln, *Austral. J. Chem.*, 1971, **24**, 1169.

²³ J. V. Acrivos, *J. Chem. Phys.*, 1962, **36**, 1097.

²⁴ H. J. Wahlquist, *J. Chem. Phys.*, 1961, **35**, 1708.