Solvent-exchange Kinetics in Nickel(II) Solutions of Aqueous Tris(dimethylamino)phosphine Oxide studied by Pulsed Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy

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When small quantities of water are progressively added to solutions of nickel(II) perchlorate in anhydrous $P(NMe_2)_3O$ electronic and n.m.r. spectroscopy provide evidence for the presence of the six-co-ordinate mixed complex $[Ni\{P(NMe_2)_3O\}_2(OH_2)_4]^{2+}$ at a $[H_2O]$: $[Ni^{2+}]$ mol ratio of *ca.* 8 : 1. Phosphorus-31 relaxation times of such solutions have been measured at two frequencies (8 and 14 MHz) and five temperatures (8—45 °C). These data yield the ^{31}P hyperfine coupling constant (A) = 17.5 MHz, the electronic relaxation times (T_{1e} and T_{2e}) = 3.91×10^{-12} and 1.86×10^{-12} s (at 25 °C and 14 MHz), the trace of the square of the zero-field splitting tensor (Δ) = 1.96 cm^{-1}, the relevant correlation time (τ_V) = 6.3×10^{-12} s, and the kinetic parameters for the exchange bound $P(NMe_2)_3O \xrightarrow{k_M}$ bulk $P(NMe_2)_3O$, *i.e.* k_M (25 °C) = $(2.8 \pm 0.4) \times 10^6$ s^{-1}, $\Delta H^{\ddagger} = 25.5 \pm 6.3$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -35.5 \pm 16.7$ J K^{-1} mol^{-1}. The mechanism of ligand substitution is dissociative. Rates are higher than for identically substituted nickel(II) complexes by about three orders of magnitude. This result is compared with literature data, and accounted for by a lower activation enthalpy, by *ca.* 25 kJ mol^{-1}, as qualitatively expected from crystal-field theory.

SOLVATION complexes of the nickel(II) ion with water or organic solvents have been the subject of a number of kinetic studies during the past few years.[1] In these experiments the perchlorate salt is generally used so that complete dissociation is obtained in the solvent under investigation. Quantitative studies consist in determining the nuclear relaxation times T_1 and T_2 of such solvents.

The first solvation shell of the cation forms a paramagnetic site S_M which is distinct from the diamagnetic site S_D representing the remainder of the solution; this is because there is a delocalization of the electron spin of the cation over the solvent molecules in direct contact with it. The sites S_M and S_D are characterized by resonance frequencies ν_M and ν_D and by relaxation times T_{1M}, T_{2M} and T_{1D}, T_{2D} respectively. The resonance frequency of the second site differs from that of the first site S_D, which in fact represents the pure solvent, by $\Delta\nu_M/Hz = \nu_M - \nu_D$ or $\Delta\omega_M$/rad s^{-1}. The corresponding peak is also broadened ($T_{2M} \ll T_{2D}$), due to electron–nucleus relaxation interactions. In addition, there is a rapid chemical exchange (1) between the two sites which causes the two peaks to coalesce to a single, usually very broad, peak with a chemical shift of $\Delta\nu$ (or $\Delta\omega$) relative to the pure solvent and apparent relaxation

$$S_M \overset{k_M}{\rightleftharpoons} S_D \qquad (1)$$

times T_1 and T_2. Investigation of these factors as functions of the temperature T and the observation frequency ω allows the determination of the parameters $\Delta\omega_M$, T_{1M}, and T_{2M} of the paramagnetic site as well as the kinetic parameters k_M, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ of the exchange reaction [provided that this is sufficiently slow on the n.m.r. time scale ($k_M \sim \Delta\nu_M$)].

The equations for the calculation of these parameters contain, however, an additional unknown: the solvation number n_M (*i.e.* the number of co-ordinated solvent molecules in the first sphere). In the first studies an incorrect value of $n_M = 4$ was assumed on the basis of the separate signals which were observed with certain systems such as Ni^{2+}–MeCN. In actual fact this number was six in the examples which were then studied: solvent = water, MeOH, MeCN, dimethyl sulphoxide (dmso), dimethylformamide (dmf), NH_3, and EtOH. Paramagnetic four-co-ordinate nickel(II) complexes (having a tetrahedral structure) are, in fact, an exception

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[1] For reviews, see (*a*) F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions, Wiley, New York, 1958; (*b*) D. J. Hewkin and R. H. Prince, *Co-ordination Chem. Rev.*, 1970, **5**, 44; (*c*) E. S. Amis, 'Techniques of Chemistry,' Wiley, New York, 1975, part I, vol. **7**, ch. 3.

and it was left to Donoghue and Drago [2] to confirm their existence with the complex $[Ni\{P(NMe_2)_3O\}_4][ClO_4]_2$.

In a previous paper [3] we described the exchange reaction between $P(NMe_2)_3O$ molecules in a solution of this complex in anhydrous $P(NMe_2)_3O$:

$$[Ni\{P(NMe_2)_3O\}_4]^{2+} + P(NMe_2)_3O^* \text{ (free)} \longrightarrow [Ni\{P(NMe_2)_3O\}_3\{P(NMe_2)_3O^*\}]^{2+} + P(NMe_2)_3O \text{ (free)}$$

this was the first known example of a substitution reaction in a tetrahedral nickel(II) complex. This reaction is characterized by a clearly negative activation entropy (revealing an associative mechanism), and by an unusually small activation enthalpy (almost zero) which is in agreement with the qualitative predictions of crystal-field theory.

It was very important in these experiments to rid the $P(NMe_2)_3O$ of its residual water. Indeed, the presence of very small amounts of water appreciably affects the electron spectrum and the relaxation times of the ^{31}P nuclei. The present paper gives a detailed study of this phenomenon centred on the evidence for, and the kinetic study of, the mixed complex $[Ni\{P(NMe_2)_3O\}_2(OH_2)_4]$. In addition to electron spectroscopy, n.m.r. spectroscopy was used. The contact chemical shift for the proton is small (*ca.* 1.7 p.p.m.) and the exchange is too fast to be studied with this nucleus. The difference $\Delta\omega_M$ for the ^{31}P nucleus is, however, large (3 900 p.p.m.) due, first, to chemical shifts which are intrinsically larger than those of the proton and, secondly, to its proximity to the Ni^{2+} cation. This explains the use of pulsed ^{31}P n.m.r. for this system; this nucleus has been utilised relatively little so far for studies of this type.

EXPERIMENTAL

Preparation of the Solutions.—Tris(dimethylamino)phosphine oxide (Pierrefite) was purified by double distillation over barium oxide under reduced pressure and an atmosphere of argon (b.p. = 127 °C). The residual water, determined by the Karl Fischer method, was found to be $< 5 \times 10^{-3}$ mol dm^{-3}. The nickel(II) solutions were prepared from the hydrated salt $[Ni(OH_2)_6][ClO_4]_2$ (Fluka). The water content of the solutions was brought to the desired level either by using a 3-Å Linde molecular sieve or by addition of a calculated quantity of water.

Ultraviolet spectroscopy was carried out with a Unicam SP 1800 spectrophotomer equipped with a temperature control unit.

Physical Measurements.—The electron magnetic moments. This was performed in solution according to the method of Evans.[4] The molecular susceptibility χ_M and the magnetic moment μ_M of the complex ion $[Ni\{P(NMe_2)_3O\}_2(OH_2)_4]^{2+}$ have the following values at 25 °C; $\chi_M = (5.39 \pm 0.15) \times 10^{-3}$ mol^{-1}, $\mu_M = 3.60 \pm 0.05$ B.M.*

The relaxation times. The longitudinal (T_1) and transverse (T_2) relaxation times of the ^{31}P nucleus were determined by the inverse-recuperation and the Carr–Purcell–Gill–Meiboom methods respectively.[5,6] In the case of extremely short T_2 times (*ca.* 1 ms) we occasionally utilized the simple free decay after a 90° pulse. The measurements were carried out with six salt concentrations ($10^2c_M = 0$, 3.48, 4.48, 6.00, 6.88, and 7.96 mol dm^{-3}), at two observation frequencies (8 and 14 MHz), and at five temperatures (8, 15, 25, 35, and 45 °C). The relaxation times were determixed with a Bruker B-KR-303-s spectrometer linked to a Texas Instruments 980 A calculator by an Analogic AN 5880 analog–digital converter. In order to increase the signal-to-noise ratio the same sequence was repeated 4—16 times for each determination and the results were accumulated. The numerical processing was then performed entirely automatically both for T_1 and T_2 which were finally calculated by a least-squares method. The reproducibility of each determination of T_1 or T_2 was 2 or 5% respectively. The temperature was controlled by a Bruker BST 100/700 unit.

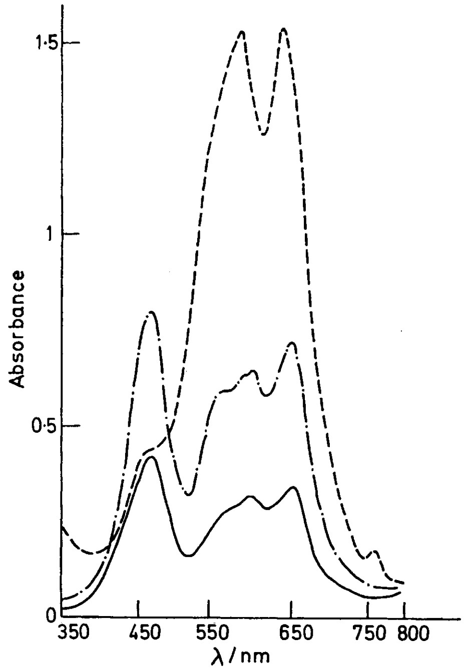

FIGURE 1 Electronic spectra of solutions of $Ni[ClO_4]_2$ in slightly aqueous $P(NMe_2)_3O$ for various $[H_2O] : [Ni^{2+}]$ mol ratios (n): $n \simeq 0$, $[Ni^{2+}] = 0.205$ (— — —); 0.65, $[Ni^{2+}] = 0.025$ (— · — · —); and 7.5, $[Ni^{2+}] = 0.025$ mol dm^{-3} (——)

The contact chemical shifts of ^{31}P. This was performed in the continuous-wave mode with proton decoupling: either at 23.39 MHz with a JEOL C60HL spectrometer using LF frequency scanning an external lock, an external reference of 85% H_3PO_4 contained in a capillary, and an LF frequency counter accurate to within 0.1 Hz; or at 36.43 MHz with a Bruker HX90 spectrometer by using RF frequency scanning, display on a built-in frequency meter accurate to within 0.1 Hz, and an internal deuteriated lock (10-mm diameter tube filled with D_3PO_4 and which contained a concentric 5-mm sample tube).

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

[2] J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, 1962, **1**, 866; 1963, **2**, 572, 1158; M. W. G. De Bolster, and W. L. Groeneveld, *Rec. Trav. chim.*, 1971, **90**, 477; 1972, **91**, 171.

[3] J-C. Boubel, J-J. Delpuech, and A. Peguy, *Mol. Phys.*, 1977, **34**, 1093.

[4] D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

[5] H. V. Carr and E. M. Purcell, *Phys. Rev.*, 1954, **94**, 630.

[6] S. Meiboom and D. Gill, *Rev. Scient. Instrum.*, 1958, **29**, 688.

RESULTS

Evidence for the Complex Ion $[Ni\{P(NMe_2)_3O\}(OH_2)_4]^{2+}$.—The addition of small quantities of water to a solution of the complex $[Ni\{P(NMe_2)_3O\}_4][ClO_4]_2$ in anhydrous $P(NMe_2)_3O$ caused a colour change from blue to green when the molar ratio (n) of $[H_2O]:[Ni^{2+}]$ exceeded 4 : 1. The intensity of the absorption peaks also decreased considerably (Figure 1). The spectrum then changed very little and remained almost unchanged when n was varied from 7 to 9 : 1. This suggests that there is a single solvated species MX_nY_{6-n} of O_h symmetry in this region [$X \equiv P(NMe_2)_3O$, $Y \equiv OH_2$]. This was confirmed by the relaxation rates $1/T_1$ and $1/T_2$ of the ^{31}P nucleus (see below) which vary strictly linearly in this region with the concentration c_M of the dissolved Ni^{2+} ion. Other different species whose relative proportions vary with c_M and which have their own separate relaxation times would give weighted relaxation rates varying in some other fashion.

TABLE 1

Absorption spectrum of nickel(II) complexes in anhydrous and aqueous (n = 8.2 : 1) $P(NMe_2)_3O$

Solvate	λ / nm	ν / cm^{-1}	ε / $dm^3\ mol^{-1}\ cm^{-1}$	Transition
Anhydrous $P(NMe_2)_3O$	465	21 505	21	$^3T_1 \rightarrow {}^1T_2$
Tetrahedral $[Ni\{P(NMe_2)_3O\}_4]^{2+}$	580	17 240	74	$^3T_1 \rightarrow {}^3T_1(P)$ or ν_3
	635	15 750	75	
	755	13 245	8	$^3T_1 \rightarrow {}^1E$
Aqueous $P(NMe_2)_3O$	465	21 505	17	$^3A_{2g} \rightarrow {}^3T_1(P)$ or ν_3
Octahedral $[Ni\{P(NMe_2)_3O\}_2(OH_2)_4]^{2+}$	570	17 545	shoulder	
	595	16 805	12.9	
	655	15 265	13.7	

TABLE 2

Computed n.m.r. and kinetic parameters for the system Ni^{2+}–$P(NMe_2)_3O$–water (n = 8.2 : 1)

	θ_c/°C				
	8	15	25	35	45
$T^P{}_{1M}{}^{-1}/s^{-1}$	32 200 ± 250	30 600 ± 250	28 200 ± 250	26 300 ± 260	24 000 ± 260
$T^P{}_{2M}{}^{-1}/s^{-1}$	62 200 ± 7 250	55 600 ± 6 750	45 800 ± 5 650	41 900 ± 5 100	35 400 ± 4 050
$10^{12}T_{1e}$/s (at 14 MHz)	5.68 ± 1.18	4.95 ± 1.02	3.91 ± 0.83	3.53 ± 0.73	2.87 ± 0.60
$10^{12}T_{2e}$/s (at 14 MHz)	2.17 ± 0.17	2.04 ± 0.16	1.86 ± 0.15	1.71 ± 0.14	1.55 ± 0.13
$10^{12}T_{1e}$/s (at 8 MHz)	2.77 ± 0.37	2.51 ± 0.33	2.13 ± 0.28	1.95 ± 0.26	1.68 ± 0.22
$10^{12}T_{2e}$/s(at 8 MHz)	1.64 ± 0.13	1.56 ± 0.13	1.46 ± 0.12	1.35 ± 0.11	1.25 ± 0.10
Δ/cm^{-1}	1.71 ± 0.14	1.79 ± 0.14	1.96 ± 0.16	2.05 ± 0.18	2.24 ± 0.20
$10^{12}\tau$/s	8.20 ± 1.60	7.56 ± 1.55	6.35 ± 1.15	6.21 ± 1.05	5.40 ± 0.98
$\Delta\nu_M$/Hz (at 14 MHz)	57 850 ± 1 750	54 450 ± 1 700	54 550 ± 1 650	52 800 ± 1 600	51 150 ± 1 700
$10^{-6}k_M/s^{-1}$	1.32 ± 0.19	2.01 ± 0.28	3.04 ± 0.43	4.18 ± 0.58	5.43 ± 0.77

The spectrum of the solvate MX_nY_{6-n} (Figure 1) shows features (Table 1) which are clearly different from those of tetrahedral $[Ni\{P(NMe_2)_3O\}_4]^{2+}$, denoted by MX_4, in anhydrous $P(NMe_2)_3O$. The latter complex was investigated in the solid state and in nitromethane solution by Donoghue and Drago [2] and then by Lever; [7] these workers were able to identify the principal transitions. In our solutions the positions and weak intensities of the absorption bands are characteristic of an O_h arrangement around the Ni^{II}; the small disturbance to the O_h symmetry brought about by the fact that the ligands can be different, H_2O or $P(NMe_2)_3O$, is neglected.[8] The molar absorption coefficients ε of the most intense peaks are considered to be $<$*ca.* 50 $dm^3\ mol^{-1}\ cm^{-1}$ for an O_h arrangement.[9] Another attempt at verification utilized the measurement of the electron magnetic moment μ_M of the complex; this was found to be 4.06 and 3.60 B.M. for MX_4 and MX_nY_{6-n} respectively, whilst the values usually admissible for tetrahedral Ni^{II} lie between 3.7 and 4.1 B.M. and those for octahedral nickel between 2.8 and 3.5 B.M. The value of 3.6 B.M. lies, unfortunately, on the borderline. However, the important difference of 0.66 B.M. between the two complexes (due to the fact that the tetrahedral complex has a very large moment) indeed suggests the structural change envisaged.

The strongest peak (ε 17 $dm^3\ mol^{-1}\ cm^{-1}$) of the MX_nY_{6-n} complex, which also has the highest frequency (21 500 cm^{-1}), corresponds in its O_h symmetry to the ν_3 or $^3A_{2g} \rightarrow {}^3T_1(P)$ transition. It should be noted that this band is also found in the spectrum of MX_4 with a similar frequency and intensity. This is only a fortuitous coincidence since this peak has already been attributed [2,7] to the $^3T_1(F) \rightarrow T_1(P)$ or ν_1 transition.

Let us now follow the development of this strongest band when small quantities of water are added to the initially anhydrous solution. The increased absorption is shown as a function of n in Figure 2 at the frequency under investigation (21 505 cm^{-1} corresponding to a wavelength of 465 nm). The observed intensity increases sharply at first with very low water contents ($n \leqslant 0.5 : 1$) corresponding to an apparent absorption coefficient of 35.1 $dm^3\ mol^{-1}\ cm^{-1}$. It then decreases more gradually in an approximately linear fashion up to a ratio of $n \simeq 4 : 1$; above this value the curves show a distinct break and then become almost horizontal (ε 17 $dm^3\ mol^{-1}\ cm^{-1}$ when n 7—9 : 1). A similar anomaly was observed by Donoghue and Drago [2] on addition of free $P(NMe_2)_3O$ to a nitromethane solution of $[Ni\{P(NMe_2)_3O\}_4][ClO_4]_2$: this could be explained by the action of trace amounts of water present in the added $P(NMe_2)_3O$ which is very hygroscopic and this could result in a five-co-ordinate complex.

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[7] A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' ed. M. F. Lappert, Elsevier, Amsterdam, 1968, pp. 333—349.

[8] Ref. 7, p. 143.

[9] T. M. Dunn, D. S. McClure, and R. G. Pearson, 'Some Aspects of Crystal Field Theory,' Harper and Row, New York, 1965, p. 39.

The decrease in absorption observed at higher water contents ($n > 0.5 : 1$) indicates a progressive disappearance of this unknown complex (by displacement of the equilibrium) until there is a single octahedral species when $n = 7$—$9 : 1$. {The experiment could be performed at ratios greater than this leading to the formation of other intermediate solvates ending with $[Ni(OH_2)_6]^{2+}$.} The clear change in absorption when $n = 4 : 1$ suggests the formation of a six-co-ordinated species containing four molecules of water around a central nickel(II) ion, $[Ni\{P(NMe_2)_3O\}_2(OH_2)_4]^{2+}$ in accordance with the total substitution:

$$[Ni\{P(NMe_2)_3O\}_4]^{2+} + 4H_2O \rightleftharpoons [Ni\{P(NMe_2)_3O\}_2(OH_2)_4]^{2+} + 2P(NMe_2)_3O$$

In the following we therefore use a solvation number of $n = 2$ for $P(NMe_2)_3O$. This assumption is confirmed by the ^{31}P n.m.r. measurements described below.

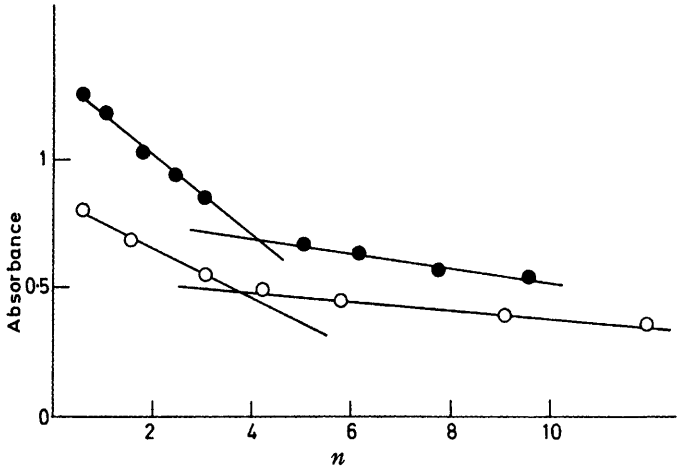

FIGURE 2 Absorption of aqueous $P(NMe_2)_3O$ solutions of Ni^{2+} as a function of the mol ratio $n = [H_2O] : [Ni^{2+}]$, at 25 °C and 465 nm, and for $[Ni^{2+}] = 0.025$ (○) and 0.035 mol dm^{-3} (●)

Phosphorus-31 *N.M.R. Measurements*.—The principle of these measurements has been described previously, and we use the notation defined therein.[3] The parameters under investigation can be derived from the experimental findings by a set of equations [(2)–(12) of ref. 3]. Calculations were performed by successive approximations according to a method described previously.[10]

The scalar contribution to the longitudinal ($1/T_{1P}$) and transverse ($1/T_{2P}$) relaxation rates is once again predominant. The hyperfine coupling constant A is moreover greater for MX_2Y_4 than for the MX_4 complex: 17.5 as compared with 11.9 MHz. The results obtained are summarized in Table 2.

DISCUSSION

The calculations were performed with the assumption that $n = 2$ for $P(NMe_2)_3O$. With a larger value it is not possible to obtain a positive value for τ_V at the end of the calculation; the two equations (8) and (12) of ref. **3** for the two working frequencies cannot be solved under these conditions.

The electron relaxation times T_{1e} and T_{2e} of Ni^{II} can be indirectly derived from our calculations. They are of the order of magnitude (10^{-12} s) to be expected from previous results [11-13] and work in our laboratory [3,10] concerning complexes of the Ni^{2+} ion. These relaxation times depend on the working frequency used [see equations (11) and (12) of ref. 3]; one can attempt to explain this by applying the theoretical treatment of McLachlan.[14] This treatment introduces the terms Δ^2 (the trace of the square of the zero-field splitting tensor) and τ_V (the correlation time characterizing the modulation of Δ with time). The value $\Delta = 1.96$ cm^{-1} (at 25 °C) is in good agreement with that found by e.s.r. spectroscopy of solid octahedral complexes (Tutton salts) such as $Ni[NH_4]_2[SO_4]_2{\cdot}6H_2O$ ($\Delta = 1.91$ cm^{-1}) [15] or by n.m.r. spectroscopy of $[Ni(dmso)_6][ClO_4]_2$ (in dmso solution) previously investigated in this laboratory ($\Delta = 1.82$ cm^{-1}).[10] It should be noted that there is a very clear reduction in Δ compared with the MX_4 complex previously studied [3] ($\Delta = 1.82$ compared with 3.31 cm^{-1}); this seems to indicate that the spin–orbit coupling is larger and that the separation energy of the $^3A_{2g}$ and E_g levels of the Ni^{2+} ion is smaller.[16] The small unexpected changes in Δ with temperature are probably not significant due to errors which are difficult to estimate. The correlation time τ_V is very similar for the two solvates MX_4 and MX_2Y_4 and also for $[Ni(dmso)_6]^{2+}$; this is not surprising if, as is generally admissible, it is assumed that τ_V is equal to the inverse of the frequency of the collisions of the free solvent molecules with the solvated cation.[17]

An important point in this study concerns the kinetic exchange parameters. At 25 °C $\tau_M^{-1} = (2.8 \pm 0.4) \times 10^6$ s^{-1}, $\Delta H^\ddagger = (25.5 \pm 6.3)$ kJ mol^{-1}, and $\Delta S^\ddagger = -35.5 \pm 16.7$ J K^{-1} mol^{-1}. The activation entropy is slightly negative, as is the case with most exchange reactions of six-co-ordinate nickel(II) complexes.[10,18] This value is an indication of a dissociative mechanism,[1] D or I_d, according to the terminology of Langford and Gray.[19] For such a mechanism, the criterion of an entropy whose value is close to zero has also been demonstrated in systems with an inert cosolvent where the molecularity of the substitution reaction has been established by concentration effects.[20]

[10] J-C. Boubel and J-J. Delpuech, *Mol. Phys.*, 1974, **27**, 113.

[11] N. A. Matwiyoff, *Inorg. Chem.*, 1966, **5**, 788.

[12] N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, 1961, **34**, 842.

[13] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, 1969, **8**, 2579.

[14] A. D. McLachlan, *Proc. Roy. Soc.*, 1964, **A280**, 271.

[15] J. H. E. Griffiths and J. Owen, *Proc. Roy. Soc.*, 1952, **A213**, 459; M. Date, *Sci. Reports Res. Inst., Tôhoku Univ.*, 1954, **6**, 390; S. A. Al'tshuler and B. M. Kozyrev, 'Electronic Paramagnetic Resonance in Compounds of Transition Elements,' 2nd edn., Wiley, New York, 1974.

[16] A. D. Liehr and C. J. Ballhausen, *Ann. Phys. New York*, 1959, **2**, 134.

[17] M. Rubinstein, A. Baram, and Z. Luz, *Mol. Phys.*, 1971, **20**, 67.

[18] C. H. Langford and V. S. Sastri, *M.T.P. Internat. Rev. Sci., Inorg. Chem. Ser.*, 1972, **9**, 203.

[19] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965.

[20] J-J. Delpuech, M. R. Khaddar, A. A. Peguy, and P. R. Rubini, *J. Amer. Chem. Soc.*, 1975, **97**, 3373; J-J. Delpuech, A. A. Peguy, P. R. Rubini, and J. Steinmetz, *Nouveau J. Chim.*, 1977, **1**, 133; L. Rodehüser, P. R. Rubini, and J-J. Delpuech, *Inorg. Chem.*, 1977, **16**, 1837; L. S. Frankel, *Chem. Comm.*, 1969, 1254; R. Good and A. F. Merbach, *Inorg. Chem.*, 1975, **14**, 1030.

The parameter τ_M^{-1} can be identified with the rate constant k_M of the unimolar reaction

$$[Ni\{P(NMe_2)_3O\}_2(OH_2)_4]^{2+} \xrightarrow{k_M} [Ni\{P(NMe_2)_3O\}(OH_2)_4]^{2+} + P(NMe_2)_3O$$

which results in a five-co-ordinate transition state. The value found for k_M is relatively high in comparison with corresponding values for other octahedral nickel(II) complexes; it is of the order of 10^6 s^{-1} compared with 10^3—10^4 s^{-1} for common ligands, *e.g.* H_2O, dmso, and dmf.[18] This seems to be a general feature of mixed $[NiX_4Y_2]^{2+}$ complexes if our results are compared with those of Rusnak and Jordan[21] or those compiled by Langford and Sastri.[18] Thus if X_4 denotes the tetradeuteriated ligand 2,12-dimethyl-3,7,11,17-tetra-azabicyclo[11.3.1]-heptadecapenta-1(17),2,11,13,15-ene or its trimethyl homologue, then the rate of exchange of the ligand Y = dmf solvent is *ca.* 10^3 times greater at 25 °C for the mixed complex $[MX_4Y_2]^{2+}$ than for the identically substituted complex $[MY_6]^{2+}$.[21] The situation seems to be the same for a number of mixed complexes where $Y = H_2O$. Finally, the same phenomenon appears to have been observed in identically substituted $[MY_6]^{2+}$ complexes but where the octahedron is deformed by the Jahn–Teller effect; the water molecules of $[Cu(OH_2)_6]^{2+}$ thus exchange 10^4 times faster in the axial position than in the equatorial position.[22] In all the cases this rate increase is due to a decrease of *ca.* 25 kJ mol^{-1} in the activation enthalpy which thus ranges from 50 ± 8 kJ mol^{-1} for identically substituted $[NiY_6]^{2+}$ complexes to 25 ± 4 kJ mol^{-1} for mixed $[NiX_4Y_2]^{2+}$ complexes.

Several reasons could account for this phenomenon. However, its generality leads first to a consideration of the geometry of the solvation complex which has O_h or D_{4h} symmetry in the two cases. As is the case with tetrahedral $[Ni\{P(NMe_2)_3O\}_4]^{2+}$, these observations again suggest that the difference in mobility arises essentially from a smaller stabilization by the crystal-field effect. This stabilization is weaker for a tetragonal arrangement than for perfectly octahedral symmetry.[1a] In the case of a transition state whose geometry is assumed to be fixed (*e.g.* a square-based pyramid having C_{4v} symmetry) this would lead to a decrease in the activation barrier. It should be noted that the transition state is five-co-ordinate as in the associative exchange reaction of tetrahedral $[Ni\{P(NMe_2)_3O\}_4]^{2+}$. If we now compare the activation barriers of the substitution processes of the two complexes $[Ni\{P(NMe_2)_3O\}_4][ClO_4]_2$ and $[Ni\{P(NMe_2)_3O\}_2(OH_2)_4][ClO_4]_2$, the stabilization due to the crystal field will be similar for the transition states. On the other hand, the initial tetrahedral state is not as well stabilized[1a, 3] which results in a still lower activation energy for the complex of T_d symmetry, in agreement with the experimental values of 3.6 as compared with 25.5 kJ mol^{-1}.

In conclusion we can say that the increasing order of the activation enthalpies, which depends on the symmetry of the nickel(II) complexes as T_d (*ca.* 4) < D_{4h} (*ca.* 26) < O_h (50 kJ mol^{-1}), reflects, to a large extent, the order of increasing stability due to the crystal-field effect.

We thank Professor Rivail for the spin-echo Bruker apparatus, and M. Diter for his technical assistance. Continuous-wave n.m.r. spectra were recorded on spectrometers of the Groupement Régional de Mesures Physiques de l'Académie de Nancy-Metz.

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[21] L. L. Rusnak and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 2686.

[22] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 1962, **37**, 307.