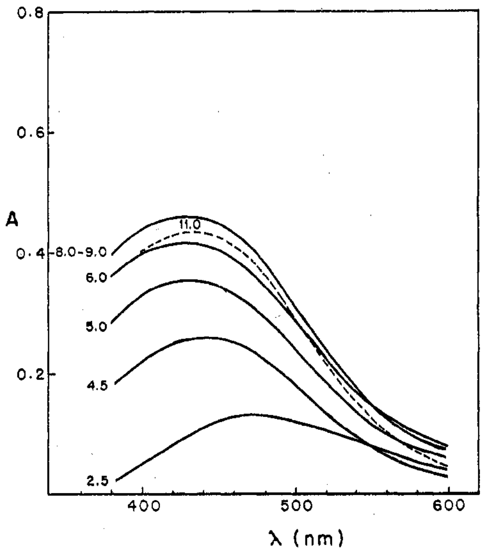

Figure 5. Visible spectra of Fe(III)/GHA as a function of pH. $C_M = 2.00 \times 10^{-3}$ M; $C_A = 2.00 \times 10^{-2}$ M (1-mm cells).

already been shown to possess a high ability to regenerate hemoglobin levels in anemic rats.[1]

In Vitro Absorption. Table IV shows interestingly that 15–20% of the Fe(GHA) chelate is absorbed (in 90 min) by rat intestines, and this result is similar to that of Fe(AHA). Moreover, the appearance of *undissociated* metal chelate in the Ringers solution suggests that the chelate remains stable in the intestine after initial absorption and on migration through cell membrane of the intestine.

Conclusion. The above potentiometric, spectroscopic, and magnetic results show that glycinehydroxamic acid coordinates to Fe(III) via the α-amino nitrogen and the hydroxyl oxygen of the NHOH group and that aqueous solutions contain monomeric species in the pH range 2.0–10.0. The kinetic criteria show effective depolymerization of the ferric citrate polymer by GHA and very rapid donation of iron to apotransferrin by the chelate. We conclude therefore that the Fe(III)/GHA system satisfies all the criteria for biological activity proposed,[1] giving a strong indication for Fe(GHA) as a suitable source of iron as a trace element. Animal studies are presently in progress to test this prediction based on chemical criteria. Finally, it has been suggested that aminohydroxamic acids may be useful in the treatment of iron-overload diseases[16] with emphasis on the surface-active role of an uncoordinated amino group. Our results show clearly that, at least in the Fe/GHA system at physiological pH values, the assumption of an uncoordinated α-amino group is incorrect since the major species in this pH region is MA_2 which involves coordination of the α-amino group and the hydroxamate OH group.

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Registry No. $Fe(GHA)_3$, 74610-16-5; GHA, 5349-80-4; AHA, 546-88-3; FeCit, 28633-45-6.

Contribution from the Department of Chemistry,
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A Tensimetric Titration Study of Adduct Formation Involving the Lewis Acids $Cl_xGa(n\text{-}C_4H_9)_{3-x}$ and the Lewis Bases $(CH_3)_zNH_{3-z}$ Where x and z = 0–3[1]

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Received August 30, 1979

The Lewis acid–base reactions of a series of butylgallium chlorides, $Cl_xGa(n\text{-}C_4H_9)_{3-x}$, and methylamines, $(CH_3)_zNH_{3-z}$, where x and z = 0–3, were studied in toluene by using a tensimetric technique. Adduct formation was found to be dependent on x, z, and the reaction temperature, with acid affinity toward base decreasing in the order $GaCl_3 > Cl_2GaC_4H_9 > ClGa(C_4H_9)_2 > Ga(C_4H_9)_3$ and with base affinity toward acid decreasing in the order $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. These results are explained by steric and/or inductive effects in the acids and steric, back-strain effects in the bases. The general structural model $[Cl_{x-y+1}GaR_{3-x}B_y]^{y-1},(y-1)Cl^-$, where y is the base/acid mole ratio in the adduct and B is base, is proposed for all adducts.

The *Lewis acid properties* of a main-group organometallic are fundamental to its entire chemistry. Although the literature contains several references to selected gallium compounds[4] and comparison with organometallics of other main-group metals, no systematic study of a homologous series of organogallium compounds has appeared. Therefore, the relative importance of such factors as "*front* strain", "*back*

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(1) Kovar, R. A., paper presented in part at the 6th International Conference on Organometallic Chemistry; see: "Abstracts of Papers", 6th International Conference on Organometallic Chemistry, Amherst, Mass., Aug 1973; ICOMC: 1973; No. 31.

(2) Taken in part from: Johnson, Joy A., Senior Honors Dissertation, University of Northern Colorado, Greeley, Colo., 1974.

(3) Taken in part from: Cook, Ronald L., Senior Research Project Dissertation, Department of Chemistry, University of Northern Colorado, Greeley, Colo., 1977.

(4) (a) Shriver, D. F.; Parry, R. W. *Inorg. Chem.* **1962**, *1*, 835–838. (b) Kochetkora, A. P.; Tronev, V. G. *Zh. Neorg. Khim.* **1957**, *2*, 99–107. (c) Lincoln, S. F. *Aust. J. Chem.* **1972**, *25*, 2705–2709. (d) Schmidbaur, H.; Fuller, H. J. *Chem. Ber.* **1974**, *107*, 3674–3679. (e) Jennings, J. R.; Wade, K. *J. Chem. Soc. A* **1967**, 1222–1226. (f) Kristoff, J. S.; Shriver, D. F. *Inorg. Chem.* **1973**, *12*, 1788–1793. (g) Buddhadev, S.; White, G. L. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2207–2215. (h) Anz, T. T.; Dunell, B. A. *J. Chem. Soc., Faraday Trans. 2* **1974**, 17–29. (i) Hargittai, M.; Hargitta, I. *J. Mol. Struct.* **1976**, *30*, 31–35. (j) Raymond, H.; et al. *Org. Magn. Reson.* **1973**, *5* (10), 463–468. (k) Gusakov, G. M.; et al. *Dokl. Akad. Nauk SSSR* **1974**, *215* (2), 343.

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Table I. Values for the Base/Acid Mole Ratio at the Equivalence Point in Tensimetric Titrations

$$(C_4H_9)_{3-x}GaCl_x + yB \xrightarrow{\text{toluene}} (C_4H_9)_{3-x}GaCl_x(B)_y$$

	y for various cases							
	B = $N(CH_3)_3$		B = $(CH_3)_2NH$		B = $(CH_3)NH_2$		B = NH_3	
x	0 °C	−45 °C	0 °C	−45 °C	0 °C	−45 °C	0 °C	−45 °C
0	1	1	1	1			1	1
1	1	1	1	1–2[a]			1, 2[b]	2
2	1	1	1	2	2	3	2	3
3	1–2[a]	2					4	4

[a] Smooth increase in pressure over the molar ratio indicated.
[b] Two distinct breaks at the ratios indicated (see Figure 1).

strain",[5] inductive effects, reorganization energies,[6] solvation effects, temperature, etc. for Lewis acid behavior of organogallium compounds is not known with certainty. This study was conducted, in part, to address these factors.

Experimental Section

Pyrophoric compounds were handled with use of Schlenk-ware under dry nitrogen, a nitrogen filled drybox, and/or a multipurpose vacuum manifold. Tensimetric titrations were performed by using the apparatus described by Shriver.[7] The apparatus was equipped with a solenoid stirrer and current-interrupting device. Lecture bottles of the gases, trimethylamine, dimethylamine, methylamine, and ammonia, were purchased from Matheson Gas Co. Each gas was introduced into the multipurpose vacuum manifold and fractionated twice at an appropriate, low temperature to remove any impurities of lesser volatility. The vapor pressure of each gas was recorded at an appropriate temperature and found to agree with the literature value.[7] The bases were stored in gas-storage tubes isolated from the manifold with Teflon stopcocks.

Base-free tri-*n*-butylgallium, di-*n*-butylgallium chloride, *n*-butylgallium dichloride, and gallium(III) chloride were prepared according to methods published previously.[8] The purity of these reagents was determined and found to be acceptable by mass spectroscopy.[9] Toluene, which was used as solvent in tensimetric titrations, was rigorously dried by heating at reflux over $LiAlH_4$ for at least 4 h followed by distillation. Ethylenediamine was distilled onto molecular sieve prior to use.

General Tensimetric Titration Procedure. Approximately 1 mmol of a gallium compound, Cl_xGaR_{3-x} where x = 0–3 and R = n-C_4H_9, was accurately weighed and transferred into a tared glass ampule in the dry box. From 1 to 2 mL of toluene was added via a syringe and the ampule connected to the tensimeter under nitrogen purge. The system was thoroughly degassed by repeated freezing with liquid nitrogen and pumping on the frozen sample for a short period, followed by thawing. From 0.10 to 0.33 molar equiv of a volatile amine base, $(CH_3)_zNH_{3-z}$ where z = 0–3, was condensed onto the sample with liquid nitrogen and the tensimeter isolated by closing a small needle-valve stopcock. Molar quantities of all volatile bases were estimated from *PVT* data using the ideal gas equation. The sample was then allowed to warm to the desired temperature maintained by an appropriate slush bath (−45 °C, chlorobenzene; 0 °C, ice water) and a pressure measurement recorded after equilibrium was established while stirring was done magnetically. The next increment of base was introduced after the pressure was measured at all desired temperatures for the previous increment, and this process was continued until at least three points beyond the break point in the titration at a given temperature were recorded. All pressure measurements were made by using a cathetometer which could be read to ±0.01 torr. The base/acid mole ratios at the equivalence points for all such titrations are given in Table I.

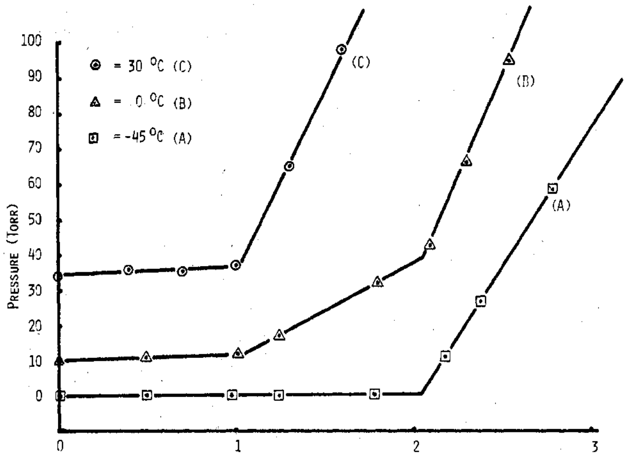

Figure 1. Tensimetric titrations of di-*n*-butylgallium chloride with ammonia at various temperatures: (A) −45 °C; (B) 0 °C; (C) 30 °C.

Table II. Thermodynamic Data for the Equilibrium Involving $(C_4H_9)_2GaClNH_3$, $(C_4H_9)_2GaCl(NH_3)_2$, and NH_3

Temp, °C	*P*, cm	$(1/T) \times 10^3$	log K_P
81	19.98	2.82	1.30
75	18.15	2.87	1.26
68	16.05	2.93	1.20
50	10.52	3.10	1.02
39	7.52	3.21	0.88
32	3.28	5.86	0.77

Temperature Study of the Titration Involving $(n$-$C_4H_9)_2GaCl$ and NH_3. In a manner similar to the above, the tensimetric titration of di-*n*-butylgallium chloride and ammonia was also carried out at 30 °C with use of an oil bath maintained at 30.0 °C by electrical heating. The plots of system pressure vs. base/acid mole ratio for titrations at 30, 0, and −45 °C are shown in Figure 1.

Ammonia Balance in Adduct Formation Involving $(n$-$C_4H_9)_2GaCl$ and NH_3. Di-*n*-butylgallium chloride (0.860 g, 3.92 mmol) was transferred into a small glass ampule equipped with a solenoid stirrer and side arm closed with a 2-mm glass stopcock. This was attached to the vacuum system under nitrogen purge with an O-ring connection. Ammonia (8.62 mmol) was allowed to react with the sample at −45 °C. Ammonia uptake was complete after 30 min, and excess ammonia was transferred to a trap cooled with N_2(l) while the sample was maintained at −45 °C. A total of 0.768 mmol of ammonia was recovered under these conditions. The sample was then warmed to room temperature, approximately 25 °C, and evolved ammonia equivalent to 3.72 mmol was transferred to a trap cooled with N_2(l). Neat ethylenediamine (3.0 mL, 72 mmol) was syringed into the ampule while being cooled with N_2(l). The sample was then allowed to warm to room temperature while being stirred magnetically. Displaced ammonia equivalent to 3.78 mmol was transferred to the trap cooled with N_2(l). Excess ethylenediamine was removed under vacuum, leaving a white solid weighing 1.10 g.

Thermodynamic Study of the Equilibrium Involving $(n$-$C_4H_9)_2GaCl{\cdot}NH_3$, $(n$-$C_4H_9)_2GaCl{\cdot}2NH_3$, and NH_3. Di-*n*-butylgallium chloride (0.1739 g, 0.792 mmol) was transferred to an ampule equipped for magnetic stirring. The tube was attached to the multipurpose vacuum-line tensimeter under nitrogen purge and evacuated while being cooled with N_2(l). Ammonia equivalent to 1.58 mmol was then allowed to react with the sample. The equilibrium pressure of ammonia in the sample was then measured with the tensimeter while stirring was done at selected temperatures in the range 32–81 °C. Heating was accomplished by using a constant-temperature water bath. These experimental data are given in Table II. The sample was then heated at 35 °C while evolved ammonia equivalent to 0.76 mmol was transferred to a trap cooled with N_2(l). The hydrogen NMR spectrum of the liquid residue dissolved in benzene consisted of a singlet (δ 2.64, 3 protons) and complex multiplet (δ 2.22–1.56, 18 protons) and was found to be identical with the spectrum of authentic $(n$-$C_4H_9)_2GaCl{\cdot}NH_3$ prepared by the reaction of di-*n*-butylgallium chloride and ammonia on the benchtop.

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Results and Discussion

The series of Lewis acids $Cl_xGa(n\text{-}C_4H_9)_{3-x}$ where $x = 0\text{–}3$ and Lewis bases $(CH_3)_zNH_{3-z}$ where $z = 0\text{–}3$ were chosen as the basis for this study. The degree of association and bonding characteristics for this series of acids are well-known,[8,9] making possible judgments concerning importance of reorganization energies, *front* strain, and inductive effects in their Lewis acid reactions. The bases make it possible to address the relative importance of back strain and inductive effects in their Lewis base reactions. A tensimetric titration method of study was employed because of its relatively direct measure of adduct composition as a function of temperature. Toluene was used as the solvent because of its relatively low basicity, low volatility, and wide liquid range.

Nearly all the titrations gave sharp breaks at an integral (±0.05) mole ratio of base/acid. The ratios for all reactions are given in Table I. The base/acid mole ratio at the equivalence point, y in eq 1, can be seen to be a function of the number of chlorine atoms in the Lewis acid, x, the number of methyl groups in the base, z, and temperature.

$$Cl_xGa(n\text{-}C_4H_9)_{3-x} + yB = Cl_xGa(n\text{-}C_4H_9)_{3-x}\cdot B_y \quad (1)$$

$$B = (CH_3)_zNH_{3-z};\ z = 0\text{–}3$$

These variables to adduct formation can be evaluated separately. For a given base at constant temperature the acids show increasing affinity for base as the number of chlorine atoms increases (and the number of butyl groups correspondingly decreases). This is seen most dramatically for NH_3 at −45 °C but is evident generally for all other conditions. Clearly, the affinity of these acids for base decreases in the order $GaCl_3 > Cl_2GaC_4H_9 > ClGa(C_4H_9)_2 > Ga(C_4H_9)_3$. This result is consistent with both steric (*front* strain) and inductive effects in the acids. For this study no separation can be made between these effects since they could each independently explain the observed results. On the other hand, the opposite trend in acidity would be predicted were "reorganizational energy" to play a significant role. All of the chlorine-containing acids (where $x = 1\text{–}3$) are known to be dimeric in solution while tri-*n*-butylgallium is definitely monomeric.[8,9] Reorganization would naturally be the greatest for the associated species, tending to reduce their affinity for base, which is contrary to these results. Therefore, a combination of steric and inductive effects outweighs the reorganization effect for these acids.

Differences in basicity are most apparent in reactions involving butylgallium dichloride, the "strongest" butyl-containing acid, at −45 °C (Table I). Clearly, the tendency of these bases to react with acid decreases in the order $NH_3 \geq CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$. This is the order expected if the "*back*-strain effect" outweighs inductive effects in these bases. Thus, steric factors are important for both the acids and the bases.

As expected, lower temperature favors more extensive acid–base reaction. The base/acid mole ratio (y) at −45 °C was found to be greater than or equal to y at 0 °C for every case studied. In many cases y at −45 °C is 1 unit larger than y at 0 °C consistent with the generalized endothermic equilibrium (eq 2) being shifted completely to the left at −45 °C

$$AB_{y+1} + \text{heat} = AB_y + B \quad (2)$$

and to the right at 0 °C. Fortuitously, the system dibutylgallium chloride and ammonia exhibited two breaks at 0 °C indicating an intermediate state of equilibrium[10] involving 1:1 and 1:2 adducts (Figure 1 and eq 3). This equilibrium is

$$ClGa(C_4H_9)_2\cdot 2NH_3(s) = ClGa(C_4H_9)_2\cdot NH_3 + NH_3(g) \quad (3)$$

shifted completely to the left at −45 °C and to the right at 30 °C, as indicated by single breaks in the titrations at these temperatures (Figure 1). The temperature-dependence of this equilibrium (absent of solvent) was studied in an effort to extract appropriate thermodynamic parameters. The pressure of free ammonia in equilibrium with $ClGa(C_4H_9)_2\cdot NH_3(l)$ and $ClGa(C_4H_9)_2\cdot 2NH_3(s)$ was recorded over the temperature range 32–81 °C. The normal thermodynamic treatment[11] of these data (Table II) gave a nearly linear plot of log K_p vs. $1/T$. A least-squares treatment gives $\Delta H° = +5.24$ kcal/mol and $\Delta S° = +20.8$ cal/(K mol) with a correlation coefficient of −0.997. The entropy has the appropriate sign and magnitude when compared with literature values for similar reactions.[12] However, the enthalpy is somewhat less than initially expected. This may be due to the fact that the reaction is complicated by "inner-sphere/outer-sphere" *exchange* of the Lewis bases NH_3 and Cl^- (eq 4) and a solid–liquid phase change (eq 5).

$$[R_2Ga(NH_3)_2]^+,Cl^-(s) = R_2GaCl\cdot NH_3(s) + NH_3(g) \quad (4)$$

$$R_2GaCl\cdot NH_3(s) = R_2GaCl\cdot NH_3(l) \quad (5)$$

A study designed to recover the complexed ammonia in $ClGa(C_4H_9)_2\cdot 2NH_3(s)$ was conducted to test the assumptions implicit in the above equilibrium treatment. Reaction of 3.92 mmol of $ClGa(C_4H_9)_2$ and 8.62 mmol of ammonia at −45 °C was followed by recovery of 0.768 mmol of excess ammonia. This leaves 7.85 mmol of complexed ammonia or a base/acid mole ratio of 2.00. Warming to 25 °C yielded an additional 3.72 mmol of ammonia for a complexed base/acid ratio of 1.05. Reaction with an excess of ethylenediamine yielded an additional 3.78 mmol of ammonia, giving a complexed ammonia/acid mole ratio of 0.09. Removal of excess ethylenediamine under vacuum gave 1.10 g of solid residue. From this it follows that the final product formula is $ClGa(C_4H_9)_2\cdot en$ (en = ethylenediamine). Equations 6–8 are suggested by these data.

$$ClGaR_2\cdot 2NH_3(s) \xrightarrow{-45\ °C} \text{no dissociation} \quad (6)$$

$$ClGaR_2\cdot 2NH_3(s) \xrightarrow{25\ °C} ClGaR_2\cdot NH_3(l) + NH_3(g) \quad (7)$$

$$ClGaR_2\cdot NH_3(l) + en \xrightarrow{25\ °C} ClGaR_2\cdot en(s) + NH_3(g) \quad (8)$$

The general structure of these adducts is probably best described by a neutral-covalent model when y equals 1 and by a charged-ionic model when y is greater than 1. The following generalized structural formula which is consistent with these models is proposed: $[Cl_{x-y+1}GaR_{3-x}B_y]^{y-1}, (y-1)Cl^-$ where x equals the number of chlorine atoms present in the original acid, y is the molar ratio of base/acid in the adduct, and B is the base. This formula is based upon the assumption that the coordination number about the gallium atom is 4 in all adducts. It follows that the acids would combine with 1 mol of base to form a four-coordinate gallium adduct but that all subsequent association with base would cause heterolytic dissociation of gallium–chlorine bonds. For cases where y equals 1 the formula simplifies to $Cl_xGaR_{3-x}B$, no Cl^- ions are dissociated, and the adduct is neutral. Like the neutral acids themselves, these adducts are predicted to be mobile liquids at room temperature and soluble in noncomplexing hydro-

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(10) Similar behavior was reported for the tensimetric titration of trimethylamine with boron trifluoride: Mills, Jerry L.; Flukinger, Larry C. *J. Chem. Educ.* **1973**, *50* (9), 636.

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carbon solvents. Both predictions were realized without exception. When y is 2, 3, or 4, the general formula simplifies to $[Cl_{x-1}GaR_{3-x}B_2]^+,Cl^-$, $[Cl_{x-2}GaR_{3-x},B_3]^{2+},2Cl^-$, and $[Cl_{x-3}GaR_{3-x}B_4]^{3+},3Cl^-$, respectively. All such adducts would be expected to precipitate from toluene, which was observed in all cases. Moreover, it is assumed that the strongest base, NH_3, is able to dissociate all Ga–Cl bonds initially present in the acid when the reaction temperature is −45 °C. This would give values of y equal to 1, 2, 3, and 4 when x equals 0, 1, 2, and 3, respectively. These are the observed results (Table I).

Acknowledgment. Support of this research by the University of Northern Colorado Research Committee and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. $Ga(C_4H_9)_3$, 15677-44-8; $ClGa(C_4H_9)_2$, 73873-07-1; $Cl_2Ga(C_4H_9)$, 73873-08-2; $GaCl_3$, 13450-90-3; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; $(CH_3)_2NH$, 124-40-3; $(CH_3)_3N$, 75-50-3.

Contribution from the Department of Chemistry,
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Nitrogen-14 Magnetic Resonance Studies of the Effect of Pressure on the Exchange of Acetonitrile Solvent on Nickel(II) and Cobalt(II)

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The following volumes of activation have been obtained by nitrogen-14 FT NMR at 0–160 MPa for processes occurring in acetonitrile: for diffusion by rotation perpendicular to the C_{3v} molecular axis, +6.3; for solvent exchange with $Ni(CH_3CN)_6^{2+}$, +7.3; and for solvent exchange with $Co(CH_3CN)_6^{2+}$, +6.7 $cm^3\ mol^{-1}$. The mechanistic significance of these results is discussed.

Introduction

Recent articles by Meyer, Newman, and Merbach[2,3] describing the effects of pressure on the rates of exchange of acetonitrile solvent with hexakis(acetonitrile)nickel(II) and -cobalt(II), as measured by proton NMR, prompted us to report our parallel studies of these processes using nitrogen-14 NMR. The advantages of the latter technique in this context have been demonstrated by Lincoln and West;[4–6] in essence, the ^{14}N nucleus, being nearest to the paramagnetic center in the complexes, experiences a much larger chemical shift than do the protons in coordinated CH_3CN, so giving an extended temperature range in which the Swift–Connick equation[7,8] (see below) approximates closely to the Eyring (or Arrhenius) equation governing the temperature dependence of the inner-sphere solvent-exchange process. In any event, the importance of determining NMR kinetic parameters by at least two independent methods is only too well illustrated by the history of sharp disagreement over enthalpies and entropies of activation for acetonitrile exchange at Co(II) and Ni(II).[2,3]

Modern commercial Fourier transform NMR machines offer further advantages over the continuous-wave apparatus used in the pioneering work of Lincoln and West;[4,5] the higher magnetic fields routinely available give greater chemical shifts, lower concentrations of the complex ions can be used (so reducing the risk of ion pairing or anion complexing), and cumulative pulsing permits the use of relatively small samples. Nevertheless, the NMR sensitivity of ^{14}N remains poor, relative to ^1H, and we chose to trade off field homogeneity in the sample and the range of accessible pressures (200 MPa maximum, 160 MPa in practice) against improved sensitivity by using a longer rf coil and greater sample diameter (and hence slightly reduced pressure vessel wall thickness) than in the static high-pressure probe design of Vanni, Earl, and Merbach[9] upon which our device is based.

Experimental Section

Materials. Baker Analyzed acetonitrile was fractionally distilled twice from 3A or 4A molecular sieves before use. The water content of the distillate was undetectable by Karl Fischer titration ($<1 \times 10^{-4}$ M; in this article, M means mol dm^{-3} at 291 K and 0.1 MPa). Subsequent handling of the solvent, preparation of solutions, and the final stages of preparation of the complexes were always done in a glovebag under dry nitrogen.

Hexakis(acetonitrile)cobalt(II) and -nickel(II) perchlorates were made by the method of Matwiyoff and Hooker.[10] The water content of the solids was less than 0.05 mol/mol of metal ion M^{2+}, but the M^{2+} contents of the vacuum-dried solids, as measured by EDTA titration, were somewhat higher than calculated for $M(CH_3CN)_6(ClO_4)_2$, apparently because of loss of some coordinated acetonitrile.[11] Accordingly, the concentrations of $M(CH_3CN)_6^{2+}$ present in solutions made up for the NMR experiments were determined by analysis of each solution by EDTA titration immediately after use. These solutions were made up either from the solid salt directly or by dissolving $Ni(ClO_4)_2{\cdot}nH_2O$ in acetonitrile and removing the water by Soxhlet extraction with a 4A molecular sieve in the thimble;[12] in the latter case, the water content of the final solution (Karl Fischer) was less than 0.01 mol/mol of M^{2+}, and the electronic spectra and NMR line-broadening results were identical with those obtained from solutions made from the solid acetonitrile complexes. The visible spectrum of $Ni(CH_3CN)_6^{2+}$ in solution showed absorbance maxima at [wavelength λ in nm (molar absorbance ϵ in $M^{-1}\ cm^{-1}$)] 715 (1.34), 577 (5.89), and 362 (7.82); the Beer–Lambert law was precisely obeyed up to 0.13 M at least. For $Co(CH_3CN)_6^{2+}$, the single visible-region band had a maximum at 476 nm (ϵ 16.4 $M^{-1}\ cm^{-1}$) and a shoulder at 520 nm. These spectra agree satisfactorily with those in the literature.[11,13]

NMR Measurements. A Bruker WH-90 (90 MHz ^1H, 6.479 MHz ^{14}N) spectrometer with multinuclear-accessory and quadrature de-

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