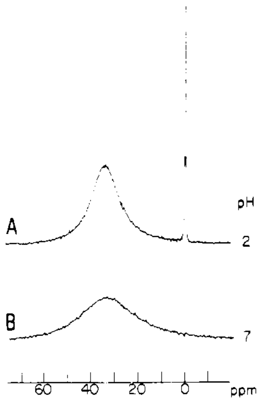

Figure 5. ^{27}Al NMR spectra for a 10 mM equimolar mixture of aluminum chloride and EDTA adjusted to pH 2 (A) and 7 (B).

among species containing different numbers of citrate and water molecules.

Because of the greater complexity of the citrate ligand, ^{27}Al NMR cannot define the structural characteristics of its Al complexes as well as those of the lactate complexes: citrate has three carboxyl groups and one hydroxyl group; numerous coordination possibilities can be generated from this combination. The most likely structure for the most stable complex, i.e., the one corresponding to the peak at 12 ppm, which remains constant between pH 5 and 8, has Al bound to citrate via two carboxyls and one hydroxyl, producing two six-membered rings. Evidence for such a structure has been obtained potentiometrically.[34,35]

Aluminum Complex of EDTA. EDTA contains six electron donor groups—four carboxyls and two nitrogens—that can completely saturate the coordination sphere of an octahedral metal and produce remarkably stable complexes.[21,36,37] As a consequence of the great stability of the complex of Al(III) bound to all six of the coordination positions, the ^{27}Al NMR spectrum exhibits only one bound peak, at ~32 ppm, corresponding to an Al(III)–EDTA complex (Figure 5). This complex is presumably the one in which the electron donor atoms of the ligand are bound to the Al.

At pH 2 the spectrum consists of two peaks corresponding to hydrated and EDTA-bound aluminum in slow exchange (upper limit ~10^4 s^{-1}). As the pH is increased to 4, the former disappears. The Al(III)–EDTA peak remains at the same position throughout the observed pH range but is broadened from 850 Hz at pH 2 to 1400 Hz at pH 7, and at pH 10 the peak is no longer detectable. Thus, EDTA coordination results in the apparently simultaneous displacement of water molecules from $[Al(H_2O)_6]^{3+}$; displacement of EDTA by OH^- at high pH presumably occurs in the same way. Thus no peaks with positions intermediate to those of $[Al(H_2O)_6]^{3+}$ and Al(III)–EDTA can be detected, because no intermediate complexes exist. Therefore the pH profile of the Al(III)–EDTA system is more monotonous than the pH variation of the NMR spectra of the lactate and citrate complexes. The broadening of the complex peak at pH 7 in Figure 5B may perhaps be attributed to changes in the outer coordination sphere.

Conclusions

We have demonstrated the ability of ^{27}Al NMR to identify complexes generated by three chelating ligands in aqueous solution at 10 mM aluminum concentration. pH-stable complexes have been observed in a unique chemical shift position for each ligand. It has been possible to directly observe substitution equilibria in which chelating ligands displace waters of hydration and hydroxides displace the ligands, as a function of increasing solution pH. Metastable reaction products have been observed under altered mixing conditions. These results demonstrate the utility of ^{27}Al NMR in the examination of Al complexes, including those involving biological ligands. ^{27}Al NMR clearly provides a significant tool in the identification and interaction of aluminum complexes in aqueous solution.

Acknowledgment. We wish to thank Dr. R. P. Pillai for his critical reading of this paper.

Registry No. Al, 7429-90-5.

---

(34) Cadariu, I.; Goina, T.; Oniciu, L. *Stud. Univ. Babes-Bolyai, [Ser.] Chem.* **1962**, 81; *Chem. Abstr.* **1965**, 6121.

(35) Aikens, D.; Bahbah, F. *Anal. Chem.* **1967**, *39*, 646. Bhat, T. R.; Das, R. R.; Shankar, J. *Indian J. Chem.* **1967**, *5*, 324. Saito, K.; Terry, H. *J. Chem. Soc.* **1956**, 4701.

(36) Sawyer, D. T.; Tackett, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 2390.

(37) Polynova, T. N.; Bel'skaya, N. P.; Turk de Garcia Banus, D.; Porai-Koshits, M.; Martynenko, L. *Zh. Strukt. Khim.* **1970**, *11*, 164; *Chem. Abstr.* **1970**, *72*, 125981.

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99164

Study by Oxygen-17 Nuclear Magnetic Resonance and Other Methods of the Nickel(II) 1,4,8,11-Tetraazaundecane and 1,4,8,11-Tetraazacyclotetradecane Complexes in Aqueous Solution

RANDALL J. PELL, HAROLD W. DODGEN, and JOHN P. HUNT*

Received June 28, 1982

Oxygen-17 NMR, spectrophotometric, and magnetic susceptibility measurements have been made on the Ni(II)–2,3,2-tet (1,4,8,11-tetraazaundecane) and Ni(II)–cyclam (1,4,8,11-tetraazacyclotetradecane) systems. The high-spin–low-spin equilibria were studied. The high-spin forms contain 2 H_2O/Ni. Water-exchange rate parameters for the high-spin forms are as follows: for Ni(II)–2,3,2 tet $k_1(25\ ^\circ C) = 4 \times 10^6$ s^{-1}, $\Delta H^\ddagger = 9.7$ kcal mol^{-1}, and $\Delta S^\ddagger = 4$ cal mol^{-1} K^{-1}; for Ni(II)–cyclam $k_1(25\ ^\circ C) = 2 \times 10^7$ s^{-1}, $\Delta H^\ddagger = 9$ kcal mol^{-1}, and $\Delta S^\ddagger = 7$ cal mol^{-1} K^{-1}.

Introduction

We have previously reported[1] on the tetraaza system (1,4,7,10-tetraazacyclododecane)nickel(II) (Ni^{II}(cyclen)), where a "high-spin–low-spin" equilibrium exists. This report[2] adds two more examples in which kinetic and equilibrium data are obtained. Water-exchange kinetic data were obtained on the high-spin forms, some independent information on slow cis–trans conversion was obtained, and the positions of the

---

(1) Coates, J. H.; Hadi, D. A.; Lincoln, S. F.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* **1981**, *20*, 707.

(2) Details are in: Pell, R. J. Masters Thesis, Washington State University, 1982.

high-spin–low-spin equilibria were also studied.

A great deal of work has been done on these systems, and the work of Billo[3] and co-workers especially has been of much aid in our studies. We have made additional spectrophotometric and magnetic susceptibility measurements to supplement the oxygen-17 NMR studies.

Experimental Section

The ligands 1,4,8,11-tetraazaundecane (2,3,2-tet) and 1,4,8,11-tetraazacyclotetradecane (cyclam) were obtained from Strem Chemicals, Inc. Gas chromatography showed them to be reasonably pure. Nickel, zinc, and sodium perchlorates were G. Frederick Smith reagent grade. The oxygen-17 water was purchased from Mound Laboratories, Monsanto, Inc. It was purified by repeated distillations. The nickel complexes as perchlorates were prepared by literature methods.[3] Anal. Calcd for $Ni(2,3,2\text{-tet})(ClO_4)_2$: Ni, 14.05; C, 20.11; N, 13.41; H, 4.82. Found: Ni, 14.06; C, 20.08; N, 13.38; H, 4.83. Calcd for $Ni(cyclam)(ClO_4)_2$: Ni, 12.28; C, 26.23; H, 5.28; N, 12.23. Found: Ni, 12.57; C, 26.30; H, 5.47; N, 12.03.

The NMR equipment used was that constructed here and used in our oxygen-17 studies. It and the procedures for obtaining data (line broadenings and shifts) are as described earlier.[1] The reference or blank samples were made from the analogous zinc complexes with conditions matching those of the relevant nickel solutions.

Spectrophotometric studies were made with use of thermostated cells in a Beckman Model DU photometer or Cary 13 or 219 instruments.

Evans' μ_{eff} measurements were made with a Bruker WH90 instrument. Some solid-state μ_{eff} studies were made on a Faraday balance.

Measurements of pH were done with a Beckman Research Model 1019 meter.

For the ^{17}O NMR experiments Ni concentrations were varied from 0.05 to 0.1 M, the pH was varied from 6.5 to 9, and the NMR frequency ν_0 was varied from 5 to 12 MHz. Two to four different sets of chemical conditions were used for each $NaClO_4$ concentration studied. In the spectral and Evans' method studies similar variations were made but Ni concentrations were varied from 0.01 to 0.05 M.

Treatment of Data and Results

The Ni–2,3,2-tet system in water presumably contains cis-α, cis-β, trans (octahedral), and planar forms. The cis-α and cis-β forms have not been distinguishable to date. Using the formulation cis $\rightleftharpoons$ trans $\rightleftharpoons$ planar, Billo[3a] has found a slow (ca. 40-min $t_{1/2}$ at 25 °C and pH 7) cis → trans conversion rate while the trans → planar change is rapid. We attempted to repeat his pH-jump experiments on *cis*-Ni(en)(2,3,2-tet) using ca. 1-mL volumes and a stopped-flow apparatus without success, finding only rapid conversions. However, using 10-mL volumes and following his procedure exactly, we confirmed his observations, when the final pHs were 4.68 and 5.87, to ±5%. Another approach was to dissolve the planar crystals and to observe the octahedral forms grow in (the trans at once presumably). Again with use of the larger volumes, our results agreed with Billo's, at a final pH of 7.14, to ±3%. Since the planar form appears to produce no oxygen-17 NMR shift in $H_2{}^{17}O$, we also monitored the growth of the shift due to the equilibration of the species at pH 6.41. Our rate was ca. 15% higher than reported earlier.[3a] We wonder if perhaps the processes going on are more complex than they seem to be. Perhaps surface effects are involved.

In order to interpret the NMR data, we made spectrophotometric and magnetic susceptibility measurements on various solutions and compared them with those of previous studies. The solid $Ni(2,3,2\text{-tet})(ClO_4)_2$ gave a μ_{eff} of 0.35 μ_B at room temperature. The average high-spin form from our solution studies had a μ_{eff} = 3.09 μ_B. Analyses of the solid are not consistent with a 10% high-spin impurity so it appears some residual paramagnetism is present in the solid. The high-spin–low-spin (or octahedral–planar) equilibria were studied by spectrophotometry, Evans' method susceptibilities, and oxygen-17 NMR.

Table I. Results of Spectral High-Spin–Low-Spin Equilibrium Studies of the Aqueous $Ni(2,3,2\text{-tet})^{2+}$ System

$[NaClO_4]$, M	K_{eq}(25 °C)	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} K^{-1}	[Ni], M, pH	ref
0.1	0.30	3.4 ± 0.4	9 ± 2	*e*	4
0.1	0.18 ± 0.02	4.8 ± 0.1	12.8 ± 0.3	0.0499, 8.32	*c*
0.07–0.09	0.21 ± 0.04[a]	4.8 ± 0.2	13.5 ± 1	0.03–0.05, 5.5–8	3a
0.1	0.19 ± 0.08	4.5 ± 0.8	12 ± 2	0.051, 7.34	*c*
0.2[b]	0.17	4.8 ± 0.2	12.5	0.05–2, ~7	7
0.2	0.22 ± 0.03	4.5 ± 0.1	12.1 ± 0.4	0.0335, *d*	*d*
1.5	0.70 ± 0.07	3.2 ± 0.1	10.2 ± 0.5	0.0249, 5.7	*d*
2.0	0.94 ± 0.14	3.4 ± 0.2	11.2 ± 0.8	0.0169, 6.5	*d*
4.0	3.4 ± 0.85	3.1 ± 0.6	12 ± 2	0.0088, 5.9	*d*
4.0	3.5 ± 1.4	3.1 ± 0.6	13 ± 2	0.0104, *d*	*d*

[a] Calculated from data in the reference. [b] Chloride salt of complex used. [c] μ_{eff} data. [d] This work. [e] Not reported.

Table II. Results of High-Spin–Low-Spin Equilibrium Studies of the Aqueous $Ni(cyclam)^{2+}$ System[e]

K_{eq}(25 °C)	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} K^{-1}	[Ni], M, pH	ref
3.3 ± 2.4[a]	5.0 ± 0.3	19 ± 1	0.0513, 7.34	*c*
2.63[a]	2.75	11.2	*d*	8
2.45[b]	5.4 ± 0.4	20 ± 2	*d*	4
2.3 ± 1[b]	5.2 ± 2.1	19 ± 3	0.0084, 6.51	*c*
2.99[b]	5.0 ± 0.2	19 ± 1	0.03–0.05, 5.5–8	3[a]

[a] Evans' method. [b] Spectral method. [c] This work. [d] Not reported. [e] The $NaClO_4$ concentration was 0.1 M for all experiments.

For both Ni–2,3,2-tet and Ni–cyclam the absorption at 445 nm was used as described by Billo.[3] We find in agreement with Billo an extinction coefficient for the planar form ϵ_0 of 60 ± 1 for Ni–2,3,2-tet independent of temperature and assumed independent of added salt. For Ni–cyclam ϵ_0 was found to be 65 ± 1 in agreement with Paoletti et al.[4] The concentration constant K for high spin $\rightleftharpoons$ low spin is given by $K = A/(C_t\epsilon_0 b - A)$, where A is the measured absorbance at 445 nm, $\epsilon_0 = 60$, b is the path length, and C_t is total nickel molarity corrected for density changes with temperature. The results are shown in Table I.

The magnetic susceptibility data obtained by the Evans method can also be used to find K. Solution data suggested that μ_{eff} for the low-spin form *in solution* was ca. zero, while a value of μ_0 = 3.09 μ_B was used for the octahedral forms (a reasonable average of literature values). Thus, $K = (\mu_0{}^2 - \mu_{obsd}{}^2)/\mu_{obsd}{}^2$. The results are given in Table I.

The oxygen-17 determination of K is less straightforward as it involves fitting the line broadenings and shifts to fairly complex equations. The kinetic and equilibrium parameters are determined together in this fitting procedure, and the treatment will be discussed here for both. We use the quantities $T_{2p}{}^* \equiv [M]/[L]2\pi(\Delta W)$ and $Q \equiv T(\Delta\omega)[L]/[M]\omega_0$, where [M] and [L] are concentrations of total metal ion and solvent water, respectively, ΔW is the increase in line width for the nickel solution compared to that for the zinc blank, line widths are half-widths at half-maximum absorption, and

---

(3) (a) Vitiello, J. D.; Billo, E. J. *Inorg. Chem.* **1980**, *19*, 3477. (b) Billo, E. J. *Ibid.* **1981**, *20*, 4019.

(4) Anichini, A.; Fabbrizzi, L.; Paoletti, P. *Inorg. Chim. Acta* **1977**, *24*, L21.

Table III. Equilibrium Parameters from $^{17}OH_2$ Exchange Studies[b]

$[ClO_4^-]$, M	K_{eq}(25 °C)	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} K^{-1}	Q_0	[Ni], M	pH	ν_0, MHz
0.1	0.35 ± 0.09	3.6 ± 0.5	9.9 ± 1.2	2.3 ± 0.9	0.0507	9.65	5.748
0.1	0.21 ± 0.02	4.8 ± 0.3	13.1 ± 0.9	1.0 ± 0.2	0.0507	9.65	11.497
0.1	0.19 ± 0.01	4.8 ± 0.2	12.9 ± 0.4	0.91 ± 0.16	0.0507	9.65	12.208
0.1	0.25 ± 0.01	4.3 ± 0.1	11.7 ± 0.3	1.2 ± 0.1	0.0525	9.88	12.208
0.2	0.41 ± 0.05	3.6 ± 0.2	10.4 ± 0.5	2.5 ± 0.5	0.1013	9.65	5.748
0.2	0.36 ± 0.01	3.9 ± 0.1	11.0 ± 0.2	1.9 ± 0.1	0.1013	9.65	11.497
0.2	0.31 ± 0.03	4.0 ± 0.2	11.0 ± 0.5	1.4 ± 0.3	0.1013	9.65	12.208
1.5	0.74 ± 0.01	3.5 ± 0.1	11.2 ± 0.3	0.55 ± 0.06	0.0823	6.53	12.208
4.0	3.3 ± 0.03	2.1 ± 0.03	9.5 ± 0.1	−0.07 ± 0.05	0.0791	9.61	12.208
4.0	3.6 ± 0.04	2.1 ± 0.03	9.5 ± 0.1	0.12 ± 0.08	0.0706	8.30	12.208
0.1	2.8 ± 0.03[a]	4.5 ± 0.1	17.1 ± 0.4	fixed at 0.0	0.0502	8.46	12.208

[a] Ni-cyclam system. [b] Conditions: six parameter variations ($Q°_{lim} - Q_0 = 8.2$); $E_a = -3.00$ kcal mol^{-1}.

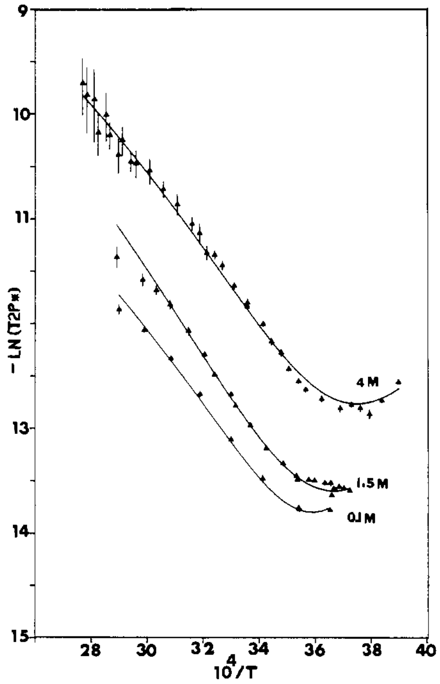

Figure 1. $-\ln T_{2p}^*$ vs. $10^4/T$ for $Ni(2,3,2\text{-tet})^{2+}$ at three perchlorate concentrations.

ω is defined below. The modified Swift–Connick equations used are

$$1/T_{2p}^* = f\left[\frac{n[(1/T_{2M})^2 + 1/T_{2M}\tau_M + \Delta\omega_M^2]}{\tau_M[(1/T_{2M} + 1/\tau_M)^2 + \Delta\omega_M^2]}\right]$$

$$Q = f\left[\frac{nT(\Delta\omega_M)/\omega_0}{\tau_M^2[(1/T_{2M} + 1/\tau_M)^2 + \Delta\omega_M^2]} + Q_0\right]$$

The symbols are as follows: f is the fraction of paramagnetic species present, $1/(1 + K)$ (where K is the equilibrium constant for formation of the low-spin form); n is the number of H_2O's per Ni in the high-spin form; T is the temperature in K; $\Delta\omega_M$ is the difference (rad s^{-1}) in bound water resonance frequency and blank (ω_0); T_{2M} is the transverse relaxation time for bound $H_2{}^{17}O$; τ_M is the mean lifetime for bound water exchange; Q_0 is the outer-sphere shift function. Only $\Delta\omega_M$ is taken as field or frequency dependent. The temperature dependencies were taken to be in the forms $\tau_M = h/kT \exp[(\Delta H/T - \Delta S)/R]$, $T_{2M} = T_{2M}{}^0 \exp[E_a/R(1/T - 1/T^0)]$, and $K = K_{298}\cdot\exp[-(\Delta H°/R)(1/T - 1/298)]$. The T_{2p}^* and Q data were fit together with use of the above equations and a weighted, nonlinear least-squares program. Since a number of the variables are closely correlated, the final fits were done with ($Q_{lim} - Q_0$) = 8.2 and E_a = −3.00 kcal mol^{-1} as fixed values. Q_{lim} is the observed high-temperature shift limit, and the subtraction of Q_0 gives the inner-sphere limiting Q value. A value of E_a = −3.0 kcal mol^{-1} is quite reasonable in such systems. The kinetic parameters are fairly insensitive to the choice made. Values near those fixed were found even when all parameters were varied so that we believe the approach is valid. The equilibrium NMR results are shown in Table III.

Table IV. Kinetic Parameters for $^{17}OH_2$ Exchange Studies[b]

$[ClO_4^-]$, M	$10^6 k_1$-(25 °C), s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	$10^6 T_{2M}$-(25 °C), s
0.1	4.5 ± 0.8	10.7 ± 1.1	7.8 ± 0.4	6.3 ± 0.8
0.1	3.8 ± 0.3	9.3 ± 0.5	2.8 ± 0.2	6.2 ± 0.7
0.1	4.3 ± 0.2	9.5 ± 0.3	2.8 ± 0.1	5.7 ± 0.4
0.1	3.7 ± 0.1	9.1 ± 0.3	2.3 ± 0.1	6.7 ± 0.5
0.2	4.2 ± 0.5	10.5 ± 0.8	7.0 ± 0.2	6.5 ± 0.4
0.2	3.6 ± 0.01	9.6 ± 0.2	3.5 ± 1.9	5.0 ± 0.2
0.2	4.5 ± 0.4	10.4 ± 0.6	6.8 ± 0.2	4.7 ± 0.3
1.5	3.7 ± 0.3	7.4 ± 0.3	−3.7 ± 0.2	9.8 ± 2.3
4.0	4.3 ± 0.2	6.6 ± 0.2	−6.0 ± 0.1	19.5 ± 6.1
4.0	5.3 ± 0.3	7.4 ± 0.2	−2.8 ± 0.1	7.3 ± 0.9
0.1	21 ± 6.9[a]	9.6 ± 1.6	7.3 ± 0.7	2.1 ± 0.1

[a] Ni-cyclam system. [b] Conditions: $Q°_{lim} - Q_0 = 8.2$; E_a = −3.0 kcal mol^{-1}.

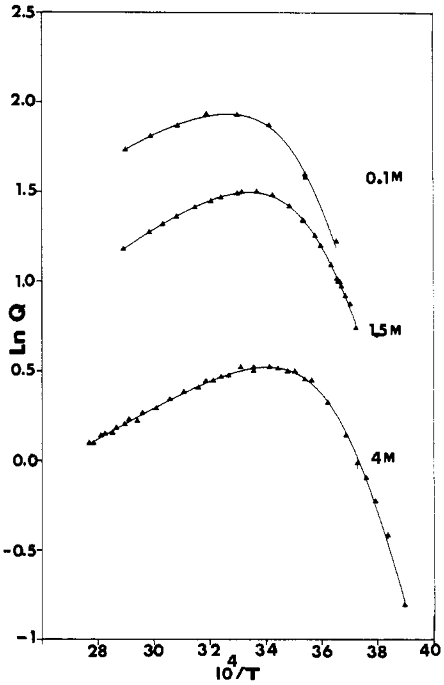

Figure 2. ln Q vs. $10^4/T$ for $Ni(2,3,2\text{-tet})^{2+}$ at three perchlorate concentrations.

The only variable, of those changed within the limits given in the Experimental Section, that affected any of the equilibrium results in Tables I-III within experimental error was the $NaClO_4$ concentration.

The kinetic and other NMR parameters are shown in Table IV. The entries correspond in the order listed to those solution compositions given in Table III in the same order. The last entry is again for Ni-cyclam. Figures 1 and 2 show the typical T_{2p}^* and Q data obtained and the calculated lines based on the fitted parameters.

Discussion

Some four species can be present in the Ni-2,3,2-tet solutions: cis-α, cis-β, trans, and planar. As far as the water-exchange data are concerned, the behavior is consistent with only two forms, NiL and $NiL(H_2O)_2$. The slow cis-trans conversion is not evidenced in the water-exchange rate, and it appears that all $NiL(H_2O)_2$ species exchange with similar rates. It would be difficult to specify the limits of detection for unequal rates, but certainly factors of 10 would easily be seen and perhaps even factors of 2.

The equilibrium parameters are necessarily rather imprecise; thus, the agreement among the various studies and methods is quite reasonable. For the Ni-2,3,2 tet system, where the high-spin-low-spin equilibrium $NiL(H_2O)_x \rightleftharpoons NiL + xH_2O$ is described by the concentration quotient K, the value of x is found to be 2 on the basis of the ^{17}O NMR results. The argument is that the high-temperature limit of Q_{inner} should be ca. 4.0 per H_2O bound to Ni(II).[5] The data found all point to a Q_{obsd} of ca. 8.0, thus 2 H_2O/Ni is consistent with our results. As sodium perchlorate concentration increases, K increases, ΔH becomes a bit less positive, and ΔS remains about the same. The ΔS value is *roughly* what one would expect for the liberation of two water molecules.[3] The activity of H_2O does not decrease enough to account for the results, and one must suppose that ClO_4^- plays some more specific role in favoring the low-spin form. Since water appears to be excluded from this form, one seems forced to conclude that some long "bond" to ClO_4^- in the axial position(s) is involved.

The Ni-cyclam low-spin form has about a 10-fold greater K, than for Ni-2,3,-tet due to a more positive ΔS and in spite of a more positive ΔH. Again the ^{17}O NMR data suggest 2 H_2O/Ni in the high-spin form. The greater stability of cyclic ligand complexes has been discussed by Hinz and Margerum[6] in terms of ligand solvation.

The water-exchange rate constant at 25 °C (k_1) of 4×10^6 s^{-1} is about 100-fold greater for $Ni(2,3,2\text{-tet})(H_2O)_2^{2+}$ than for $Ni(H_2O)_6^{2+}$, showing the usual labilizing effect of amine ligands.[5] Sodium perchlorate in the concentration range 0.1-4 M has no significant effect on the exchange rate. For $Ni(cyclam)(H_2O)_2^{2+}$, k_1(25 °C) is ca. 2×10^7 s^{-1}, about 5 times larger than for the 2,3,2-tet complex. For $Ni(trien)(H_2O)_2^{2+}$ k_1(25 °C) is 6×10^5 s^{-1}, and for $Ni(cyclen)(H_2O)_2^{2+}$ k_1(25 °C) is 2×10^7 s^{-1}. The cyclic ligands are more labilizing and remarkably similar in effect, considering the considerably greater strain in the cyclen case. Some discussion of these effects is found in our earlier work.[1]

We are planning to study pressure effects on these systems to obtain ΔV^* values, which may provide new clues to the origin of the differences in ligand effects on water exchange.

In our Ni-cyclen paper[1] we also discussed the relations between τ, the mean lifetime for low-spin-high-spin relaxation, and τ_M, the mean lifetime for water exchange. At that time τ_M for Ni-2,3,2-tet was not known. It is ca. 0.25 μs. This leads to a τ of 0.125 μs compared to 0.28 μs and means that, if only $NiL + H_2O \rightleftharpoons NiL(H_2O)$ and $NiL(H_2O) + H_2O \rightleftharpoons NiL(H_2O)_2$ equilibria are involved in determining both τ's, then one probably cannot say which process is rate controlling for low-spin to high-spin interconversion.

Acknowledgment. This work was supported by NSF Grant No. CHE-7915792.

Registry No. ^{17}O, 13968-48-1; $Ni(2,3,2\text{-tet})(H_2O)_2^{2+}$, 36530-71-9; $Ni(cyclam)(H_2O)_2^{2+}$, 78684-35-2.

---

(5) Hunt, J. P. *Coord. Chem. Rev.* **1971**, *7*, 1.

(6) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941.

(7) Ivin, K. J.; Jamison, R.; McGarvey, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 1763.

(8) Vigee, G. S.; Watkins, C. L.; Bowen, H. F. *Inorg. Chim. Acta* **1979**, *35*, 255.

Contribution from Bruker Spectrospin SA, 67160 Wissembourg, France,
and IUT de Rouen, 76130 Mont St. Aignan, France

Ruthenium NMR Spectroscopy: A Promising Structural and Analytical Tool. General Trends and Applicability to Organometallic and Inorganic Chemistry[1]

CHRISTIAN BREVARD* and PIERRE GRANGER

Received March 4, 1982

A comprehensive study of the ruthenium chemical shift scale is presented. The results obtained clearly show the importance of ruthenium NMR for probing the ruthenium environment ($\Delta\delta = 9100$). Moreover, real chemical problems can be tackled via such a technique, for example, aqueous equilibria of ruthenium aqua ions or structural and electronic mapping around the ruthenium liganding site in organometallic ruthenium complexes.

Introduction

Most of the magnetic nuclei of the periodic table have been observed,[2] and only a few transition-metal isotopes resist NMR detection.[3] Very recently[4,5] both isotopes of Ruthenium (^{99}Ru, ^{191}Ru) were detected, a very important step toward structural and dynamical studies on ruthenium compounds via Ru NMR owing to the role played by the ruthenium nucleus in or-

---

* To whom correspondence should be addressed at Bruker Spectrospin SA.

(1) Presented in part at the 5th International Meeting on NMR Spectroscopy, Exeter, England, July 12-17, 1981.

(2) (a) Harris, R. K.; Mann, B. "NMR and the Periodic Table"; Academic Press: New York, 1978. (b) Brevard, C.; Granger, P. "Handbook of High Resolution Multinuclear NMR"; Wiley: New York, 1981.

(3) Kidd, R. G. *Annu. Rep. NMR Spectrosc.* **1980**, *10*, 1.

0020-1669/83/1322-0532$01.50/0 © 1983 American Chemical Society