formation of $(C_6H_5)_3SbFX$ is indicated by the appearance of ^{19}F signals ~20 ppm to low field of the difluoride signal.[2] Comparison of the equilibrium constants for reactions 1(a)–(c) with 2(a)–(c), respectively, indicates that, in the case of the difluoride–dichloride reactions, the deviation from statistical behavior depends on the R group whereas in the cases of the difluoride–dibromide and difluoride–diiodide reactions, the different R groups do not significantly change the value of K. To date we have not been able to obtain reproducible values of equilibrium constants for reactions 2(a)–(c) at additional temperatures, because the ^{19}F signals saturate easily at higher temperatures and solubilities are reduced significantly at lower temperatures.

As shown in Table II, equilibrium constants have also been measured for the reactions between tribenzylarsenic difluoride and tribenzylarsenic dichloride (reaction 5) and for the analogous antimony compounds (reaction 3). A comparison of the equilibrium constants for these reactions with those of reactions 1(a), 2(a), and 4 is further evidence that the deviation from statistical behavior for the difluoride–dichloride reactions is a function of the R group. As shown in Table II the equilibrium constants increase in the manner $CH_3 < C_6H_5CH_2 < C_6H_5$ for reactions of types 1(a), 2(a), and 3. In the case of the analogous arsenic compound reactions, namely, 4 and 5, the equilibrium constant is also larger where R is benzyl.

Likewise, a comparison of reactions 3 with 5 and 1(a) with 4 indicates that the central atom has some effect on the equilibrium constants.

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Water Exchange with the Monoamminepentaaquonickel(II) Ion[1]

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We are concerned here with direct measurements of the effect of substitution on water lability in aquo ions. Previous ^{17}O nmr studies have been made on NCS^- and Cl^- effects, for example.[2,3] In these cases considerable uncertainty about species exists and it was felt that the ammine system of Ni(II) would be easier to interpret. Indirect studies on water lability have been made for some time.[4]

Experimental Section

The nmr techniques and the treatment of the data have been discussed previously.[2a] Signal enhancement was obtained here by using a Fabritek LSH1024 point signal averager.

Solutions were prepared using redistilled water containing 1.19 atom % ^{17}O (*ca.* 17% ^{18}O and normal H content) obtained from Bio-Rad Laboratories. Other reagents used were Mallinckrodt AR grade $Ni(NO_3)_2 \cdot 6H_2O$ and NH_4NO_3 and Baker Analyzed NaOH. The pH was measured to ±0.01 pH unit using a Beckman Research Model pH meter.

The values for the acid dissociation constant of NH_4^+ used were those given by Bates and Pinching.[5] Ionic strength corrections to the pH and ammine complex constant data used were those of Bjerrum.[6]

Results

The experimental data are given in Table I. The symbols have the following meanings:[2] Δ' is the line broadening, in gauss, produced by Ni(II) in $H_2{}^{17}O$, W_0 is the full line width at half-maximum absorption for the reference solution not containing Ni(II) (Δ' is $W_{\mathrm{obsd}} - W_0$), and T'_{2p} is defined as $2M(\mathrm{Ni})_T/\gamma\Delta'$, where $M(\mathrm{Ni})_T$ refers to total nickel molarity and γ is the magnetogyric ratio for ^{17}O (3628 gauss^{-1} sec^{-1}).

As a check on the procedures the solution at pH 6.28 was acidified to *ca.* 0.5 M H^+ with HNO_3, and line broadenings at three temperatures were obtained in good agreement with those of Swift and Connick[7] indicating that no appreciable effects were caused by 2 M NH_4NO_3.

The temperature dependences of the line broadenings at the lower temperatures are consistent with control of broadening by the chemical-exchange rate.[7] In this case $T'_{2p} = M(\mathrm{Ni})_T\tau_L$ where τ_L is the mean life for exchange of a free water molecule with bound water molecules. The total rate of water exchange (M sec^{-1}) is $[H_2O]/\tau_L$ or $55.5/T'_{2p}$ for 1 M Ni(II). At 25° in 1 M Ni(II) solutions the total exchange rate for water in $Ni(H_2O)_6{}^{2+}$ solution[7] is 1.62×10^5 M sec^{-1} (*i.e.*, $6k_1$). In our solutions the comparable rates are: for pH 5.75, 4.11×10^5; pH 6.08, 4.63×10^5; and pH 6.38, 5.84×10^5. Thus labilization of water has occurred.

The ammonia concentration in these solutions is too low to permit nmr studies of the ammonia-exchange rate for comparison. Rorabacher[8] has measured the formation rate for the monoammine species using the temperature-jump–relaxation method and it is clear from his data that the process

$$Ni(H_2O)_6{}^{2+} + NH_3 \rightleftharpoons Ni(H_2O)_5NH_3{}^{2+} + H_2O$$

is much too slow to account for our results. The effect of pH alone on the $Ni(H_2O)_6{}^{2+}$ system seems not to have been studied. Hydrolysis of nickel aquo ion appears to be slight and it seems to us likely that the observed rate increase is due to formation of ammine complexes of greater lability than the aquo ion. The results can be approximately rationalized taking $R_{\mathrm{total}} = R_{\mathrm{aquo}} + R_{\mathrm{monoammine}}$ and assuming that R_{aquo} has

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[1] Supported by USAEC Contract AT(45-1)-2040; Report RLO-2040-2.

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TABLE I

LINE-BROADENING DATA FOR $^{17}OH_2$ IN THE Ni(II)–NH_3 SYSTEM

$10^3/T$, deg^{-1}	Δ', gauss	$T'_{2p}M$, sec × 10^5	W_0, gauss
(A) pH 5.75,[a] total [Ni] = 0.114 *M*, $[NH_4NO_3]$ = 2.0 *M*			
3.47	0.31	20.0	0.23
3.46	0.38	16.5	0.23
3.38	0.45	14.0	0.23
3.35	0.44	14.4	0.23
3.23	0.55	10.8	0.20
3.22	0.68	9.24	0.18
3.20	0.78	8.06	0.18
3.13	1.15	5.46	0.19
(B) pH 6.08,[b] total [Ni] = 0.199 *M*, $[NH_4NO_3]$ = 2.0 *M*			
3.70	0.20	55.6	0.32
3.62	0.33	33.7	0.22
3.53	0.54	20.6	0.22
3.51	0.45	24.5	0.22
3.37	0.88	12.5	0.22
3.30	1.14	9.62	0.22
3.20	1.48	7.41	0.25
(C) pH 6.37,[c] total [Ni] = 0.116 *M*, $[NH_4NO_3]$ = 2.1 *M*			
3.51	0.40	15.9	0.21
3.40	0.62	10.4	0.23
3.30	0.78	8.20	0.20
3.20	0.99	6.43	0.19
3.11	1.21	5.29	0.20
(D) pH 6.39,[d] total [Ni] = 0.201 *M*, $[NH_4NO_3]$ = 2.0 *M*			
3.56	0.55	20.0	0.28
3.44	0.79	14.0	0.25
3.34	1.20	9.20	0.22

[a] 79.3% $Ni(H_2O)_6^{2+}$, 19.4% $Ni(H_2O)_5NH_3^{2+}$, 1.3% $Ni(H_2O)_4(NH_3)_2^{2+}$, and higher species. [b] 62.7% $Ni(H_2O)_6^{2+}$, 32.4% $Ni(H_2O)_5NH_3^{2+}$, 4.9% $Ni(H_2O)_4(NH_3)_2^{2+}$, and higher species. [c] 41.7% $Ni(H_2O)_6^{2+}$, 44.0% $Ni(H_2O)_5NH_3^{2+}$, 14.3% $Ni(H_2O)_4(NH_3)_2^{2+}$, and higher species. [d] 41.7% $Ni(H_2O)_6^{2+}$, 44.0% $Ni(H_2O)_5NH_3^{2+}$, 14.3% $Ni(H_2O)_4(NH_3)_2^{2+}$, and higher species.

the values measured by Swift and Connick at lower pH (*ca.* 1). At 25° and 1 *M* $Ni(H_2O)_5NH_3^{2+}$ the rates for exchange of water with the monoammine species are then calculated to be: at pH 5.75, 1.49×10^6 *M* sec^{-1}; at pH 6.08, 1.13×10^6; and at pH 6.38, 1.18×10^6, with activation energies of 6.7, 7.5, and 7.5 ± 1 kcal/mole, respectively.

Our calculations show that, over the temperature range used, the composition of the solutions with respect to ammine species remains essentially constant so that no large errors are introduced in the activation energies. The activation energy for exchange of water with $Ni(H_2O)_6^{2+}$ is 12.2 kcal/mole.

One could attempt to include higher species as contributing to the observed rates. We do not feel that the precision of the data warrants this, and the approximate agreement of the data with the simpler assumptions suggests that contributions from higher species are not large enough to require consideration at this time. It will be of interest as improvement in precision and sensitivity can be made to investigate further the higher ammine species. Perhaps it should be pointed out at this stage that independent exchange paths may exist which are not directly connected with measured substitution rates. Our earlier work[2] has given some hint that such may be the case. One cannot say from the present results whether 1 or 5 (or some other number) water molecules are labilized so that the statistical factor is unknown.

Comparison of our results with the treatment given by Margerum,[4] assuming 5 equivalent water molecules per nickel atom to be consistent with his values, suggests that the labilizing effect of ammonia may be similar to that for ethylenediamine which seems not unreasonable.

It would be of interest to have measurements on substitution rates in the monoammine species to see if the results can be compared directly with the water-exchange rate. We plan to continue our studies on water exchange in various complexes of en and EDTA, for example, to provide more direct comparisons.

Correspondence

The Contributions of Ligand Field Stabilization Energies to the Observed Variations with Ligand of Cobalt(II)–Cobalt(III) and Iron(II)–Iron(III) Oxidation Potentials

Sir:

The effects of inner orbital splittings on the thermodynamic properties of transition metal compounds has been the subject of several excellent review articles,[1–3] and the utility of crystal field theory as an interpretive aid in the explanation of observed variations in thermodynamic properties of transition metal ions is well established.

George and McClure[1,3] considered the observed variations in the standard oxidation potentials, $\mathcal{E}°_{ox}$, of aqueous M(II)–M(III) couples and found that $\Delta G° - \Delta H°_{LF}$ (where $\Delta H°_{LF}$ is the difference in crystal field stabilization energies calculated from spectroscopic data) for the reaction

$$M^{2+}(aq) + H^+(aq) = {}^1/_2H_2(g) + M^{3+}(aq) \qquad (1)$$

correlated fairly well with the third ionization potential of M(g). In making this correlation George

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