infrared data, and suggests an energetic contribution to extraction by preserving the phenol dimer bonds.

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The Kinetics of Exchange of Ammonia with the Hexaamminecobalt(II) Complex in Anhydrous Ammonia[1]

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Kinetic data obtained by n.m.r. line broadening techniques are reported for the $Co^{II}(NH_3)_6-NH_3$ exchange reaction in liquid ammonia. The rate is essentially unaffected by addition of 1.7 m $NaClO_4$, 1.4 m $NaClO_4$ plus 0.25 m NH_4ClO_4, or 1.5 m H_2O. Perchlorate and nitrate salts give similar results. The rate law $R = 6k_1[Co^{II}(NH_3)_6]$ has been used. At $-40.7°$ k_1 is $2.7 \pm 0.3 \times 10^4$ sec.$^{-1}$. The extrapolated value for k_1 at 25° is $7.2 \pm 1.4 \times 10^6$ sec.$^{-1}$. Values for ΔH^* and ΔS^* (calculated from k_1) are 11.2 ± 0.4 kcal./mole and 10.2 ± 2 e.u., respectively. Some comparisons with Ni(II) systems and other Co(II) systems are made. The scalar coupling constant A/h was evaluated from the chemical shift and line broadening data and was found to be $7.5 \pm 0.1 \times 10^6$ c.p.s. for $Co^{II}(NH_3)_6$.

Introduction

The research reported here is in continuation of a general program of study on ammonia exchange rates in transition metal complexes. Previous studies have been published concerning Cr(III),[3] Ni(II),[4] and, less completely, Cu(II)[4] systems.

Experimental

The n.m.r. techniques and equipment previously described in some detail[4,5] have been employed. The ammonia was purified and solutions in ammonia were prepared and handled as described earlier.[4]

Cobalt reagents used were A.R. grade $Co(NO_3)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$ prepared from cobaltous carbonate and perchloric acid, and CoI_2 prepared from cobaltous carbonate and hydriodic acid. The above salts were treated with anhydrous ammonia in the absence of air using a vacuum system. Upon repeated condensation of ammonia on the above salts followed by distillation of excess ammonia, violet anhydrous compounds were obtained which on the basis of Kjeldahl analysis corresponded to the tetraammine salts. The iodide salt was found not soluble enough in ammonia for these studies ($<ca.$ 0.01 M). The perchlorate salt was quite soluble (>0.1 M) over the range -70 to $+30°$, giving pink solutions. The nitrate salt was soluble to the extent of $>ca.$ 0.01 M at temperatures below $-20°$, also giving pink solutions. Anhydrous sodium perchlorate and ammonium perchlorate were prepared as described before.[4]

Treatment of Data and Results

Our NH_3 line broadening results are reported in terms of the quantity T_{2p}'' as in the Ni(II) studies.[4] This quantity is defined as $T_{2p}'' \equiv 2m_{Co}/\gamma\Delta'$ where

(1) This work supported in part by U.S.A.E.C. Contract AT(45-1)-1031·
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(3) H. H. Glaeser and J. P. Hunt, *Inorg. Chem.*, **3**, 1245 (1964).
(4) H. H. Glaeser, G. A. Lo, H. W. Dodgen, and J. P. Hunt, *ibid.*, **4**, 206 (1965).
(5) R. Murray, H. W. Dodgen, and J. P. Hunt, *ibid.*, **3**, 1576 (1964).

m_{Co} refers to the total molality of cobalt present in solution, γ is the magnetogyric ratio for N^{14} (1934 gauss^{-1} sec.$^{-1}$), and Δ' is the line broadening (in gauss) due to Co(II), obtained from the full n.m.r. line widths at half-maximum absorption using recorded absorption curves. The results are given in Table I.

TABLE I

LINE BROADENING DATA FOR $Co^{II}(NH_3)_6-NH_3$ EXCHANGE

t, °C.	Δ', gauss	$T_{2p}'' \times 10^5$, m sec.	t, °C.	Δ', gauss	$T_{2p}'' \times 10^5$, m sec.
(A)	Co =	0.050 m^a	(D)	Co =	0.25 m
−21.5	0.65	7.8	−36.3	1.29	20.1^c
−30.5	0.36	14.2	−36.3	1.24	20.9^d
(B)	Co =	0.083 m	−36.3	1.15	22.7^e
−20.0	1.21	7.1	−48.0	0.31	84^c
−36.3	0.44	19.4	−49.8	0.28	93^d
−36.8	0.33	25.7^b	−50.2	0.21	124^e
−40.0	0.26	32.4^b	(E)	Co =	0.333 m
−45.5	0.13	64^b	14.2	0.66	52
(C)	Co =	0.166 m	11.8	0.90	38
25.8	0.10	172	5.6	1.46	24.2
− 3.1	1.27	13.5	−35.0	1.92	17.9
− 6.8	1.45	11.9	−41.2	0.77	45
−11.8	2.16	7.9	−43.2	0.56	61
−23.8	2.21	7.8	−45.2	0.57	60
−27.8	1.87	9.2	−51.2	0.27	127
−35.0	1.30	13.2			
−41.1	0.27	64			

^{a} $Co(NO_3)_2 \cdot 4NH_3$ used instead of $Co(ClO_4)_2 \cdot 4NH_3$. ^{b} 0.01 m $Co(NH_3)_6(NO_3)_3$ present. ^{c} 1.67 m $NaClO_4$ present. ^{d} 1.42 m $NaClO_4$ plus 0.25 m NH_4ClO_4 present. ^{e} 1.52 m H_2O present.

A chemical shift (S) in the N^{14} absorption frequency in NH_3 due to Co(II) was observed. The shift data relative to pure NH_3 are given in Table II.

TABLE II
CHEMICAL SHIFT DATA; $m_{Co} = 0.166$

$$S = (\omega_{obsd} - \omega_0)/\omega_0,$$

t, °C.	p.p.m.	TSm_{NH_3}/m_{Co}
25.8	259	27.2
-3.2	184	17.5
-6.8	205	19.3
-11.8	173	15.9
-23.8	65	5.8
5.6	507	24.9[a]

[a] Co $= 0.333\ m$.

We have modified our treatment[5] of the data to include the expected temperature variation of the quantity $\Delta\omega_6$ in the equation[5] $T_{2p}'' = m_{Co}p_0/p_6\tau_{60}\Delta\omega_6{}^2 + m_{Co}p_0\tau_{60}/p_6$ (assuming only the species NH_3 and $Co^{II}(NH_3)_6$ where p_0 is the atom fraction of N^{14} in free ammonia, p_6 is the atom fraction of N^{14} in $Co^{II}(NH_3)_6$, τ_{60} is the mean life (for exchange) of an ammonia ligand on the complex, and $\Delta\omega_6$ is the n.m.r. absorption frequency (radians/sec.) for N^{14} in $Co^{II}(NH_3)_6$ *minus* the actual observed frequency in NH_3 in the presence of the cobalt ($\omega_6 - \omega_{obsd}$). In the treatment of the data used here and previously we are also assuming that $p_0 \simeq 1$ or that the solutions are dilute in paramagnetic species as was done by Swift and Connick.[6] For our solutions "dilute" means $p_0 \geq 0.95$. Under these circumstances, $\Delta\omega_6 = (\omega_6 - \omega_{obsd}) \simeq (\omega_6 - \omega_0)$ where ω_0 is the absorption frequency for pure ammonia. For more concentrated solutions or more precise work the difference between ω_{obsd} and ω_0 should be taken into account in the T_{2p}'' equation giving more cumbersome expressions than those which follow. The temperature dependence of T_{2p}'' can then be treated to a reasonable approximation as follows. The mean life, τ_{60}, is $6[Co^{II}(NH_3)_6]/R$, where R is the exchange rate for NH_3. Assuming $R = 6k_1[Co^{II}(NH_3)_6]$, $\tau_{60} = 1/k_1$ where k_1 is the first-order specific rate constant for exchange of *a particular ligand*.

Using the absolute reaction rate theory approach, we write $k_1 = (kT/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R}$. It is reasonable to write that $\Delta\omega_6 = \alpha/T$ (Curie's law). Making the substitutions we obtain $T_{2p}'' = (m_{Co}p_0/p_6)(kT^3 \cdot e^{-\Delta H^*/RT}e^{\Delta S^*/R})/\alpha^2 h + (m_{Co}p_0/p_6)e^{\Delta H^*/RT}/(kT/h)e^{\Delta S^*/R}$. The procedure to be followed at this point will depend on whether the T_{2p}'' data lie largely (or are more precise) in the region described by the first or by the second term in T_{2p}''. If one divides T_{2p}'' by T^3 and plots log T_{2p}''/T^3 vs. $10^3/T$ one can obtain $-\Delta H^*$ from the limiting slope due to the first term (left-hand portion of curve) or multiplying T_{2p}'' by T and plotting log $T_{2p}''T$ vs. $10^3/T$ one obtains ΔH^* from the slope due to the second term (right-hand portion of curve). In Figure 1 we have plotted log $T_{2p}''T$ and the quantity TSm_{NH_3}/m_{Co} vs. $10^3/T$. The shift (S) is defined by the relation $S \equiv (\omega_{obsd} - \omega_0)/\omega_0$. The shift data provide an independent criterion for fitting the T_{2p}'' data. The quantity TSm_{NH_3}/m_{Co} falls to one-half its high-temperature limiting value at the intersection point of the limiting T_{2p}'' curves, and the shift curve can be cal-
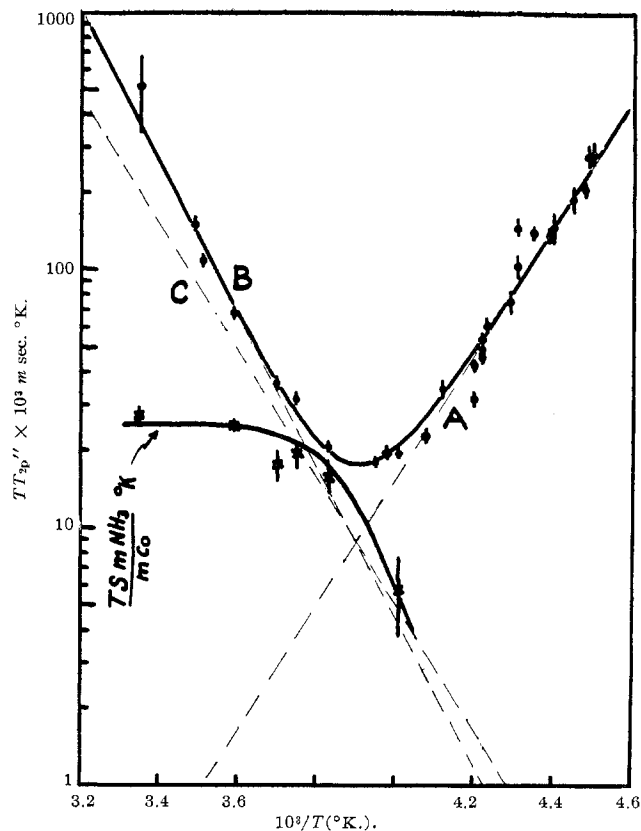
(6) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

Figure 1.—Plot of $T_{2p}''T$ vs. $10^3/T$ and TSm_{NH_3}/m_{Co} vs. $10^3/T$.

culated from the T_{2p}'' data.[5] The straight lines in Figure 1 result from the fitting process. The lower line on the left side (C) is drawn with the same slope as the right-hand line (A). To obtain the curve (B) through the experimental points on the left side the points on C are multiplied by $(T/T_i)^4$ where T_i is the temperature at the intersection point. It may be noted that use of data corresponding to line B only without correction for variation of $\Delta\omega_6$ with temperature leads to an appreciable error in the estimation of the kinetic parameters. The line through the shift points is calculated using lines A and B. The complete curve for $T_{2p}''T$ is obtained from the sum of A and B. Slopes and intersection points were varied to give the best fit for all the data. We calculate k_1 from the relation $k_1 = 58.7/6T_{2p}''$ where 58.7 is the number of moles of ammonia per 1000 g. of ammonia. The value of k_1 at $-40.7°$ is found to be 2.7 $\pm$ 0.3 $\times$ 10^4 sec.$^{-1}$. The extrapolated value for k_1 at 25° is 7.2 $\pm$ 1.4 $\times$ 10^6 sec.$^{-1}$. Using the slope of line A and k_1 we calculate $\Delta H^* = 11.2 \pm 0.4$ kcal./mole and $\Delta S^* = 10.2 \pm 2$ e.u. At the intersection of A and B $\Delta\omega_6 = 1/\tau_{60} = 58.7/6T_{2p}''$. The scalar coupling constant A/h can be obtained from the relation $A/h = (\Delta\omega_6/\omega_0 h)3kT\gamma/S(S + 1)\gamma_e = 7.4 \times 10^6$ c.p.s. at 25°. In this equation, A is the scalar coupling constant, h is Planck's constant, k is Boltzmann's constant, ω_0 the N^{14} resonance frequency in free ammonia, γ the magnetogyric ratio for N^{14}, S the resultant electron spin for spin-free Co(II) (1.5), and γ_e the magnetogyric ratio for the electron.

$\Delta\omega_0$ can also be obtained from the limiting value at

high T of $TSm_{NH_3}/m_{Co} = 6T\Delta\omega_6/\omega_0$. The value of A/h calculated is 7.6×10^3 c.p.s., in good agreement with that obtained at the intersection of lines A and B.

The presence of 1.7 m sodium perchlorate or a mixture of 1.42 m sodium perchlorate and 0.25 m ammonium perchlorate had no appreciable effect on T_{2p}'' in the exchange rate controlled region.

Addition of $Co(NH_3)_6Cl_3$ at 0.01 m produced no change in T_{2p}''.

The effects of adding water to the anhydrous system have been studied in some detail and will be reported in a later publication. The general results are that the presence of 1.5 m H_2O has only a small effect on k_1 and ΔH^* but as more water is added k_1 changes as does ΔH^*.

Use of the cobalt(II) nitrate salt appeared to give the same results as for the perchlorate salt when no additional nitrates were present.

Discussion

Some general features of the Co(II)–ammonia system resemble those for the Ni(II) case. Salt and acidity effects are small. Addition of *small* amounts of water to either anhydrous system produces relatively small effects on the kinetic behavior.

It is of some interest to compare further the kinetic behavior of the Ni(II) and Co(II) ammonia complexes. In anhydrous ammonia we obtain for Ni(II) the values k_1 (25°) $= 1.0 \times 10^5$ sec.$^{-1}$, $\Delta H^* = 11 \pm 1$ kcal./mole, $\Delta S^* = +2 \pm 3$ e.u.; for Co(II) k_1 (25°) $= 7.2 \times 10^6$ sec.$^{-1}$, $\Delta H^* = 11.2 \pm 0.4$ kcal./mole, $\Delta S^* = 10 \pm 2$ e.u. The faster rate for Co(II) is in accord with the predictions of Basolo and Pearson[7] but is not due to a lower activation enthalpy as their crystal-field arguments suggest. We cannot be certain at all that the

(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958.

rate laws are of the same type for Ni(II) and Co(II), so that we may not be comparing similar mechanisms. It is possible, for example, that the cobalt case involves a rate-determining step of the sort

$$Co^{II}(NH_3)_6 \longrightarrow Co^{II}(NH_3)_4 + 2NH_3$$
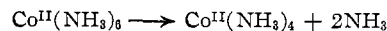
which could give a high activation enthalpy but a positive entropy. Such a decrease in coordination number for Co(II) has been postulated in the aquo complexes.[8] We have not as yet been able to extend our results to high enough (or low enough) temperatures to decide whether a new cobalt species becomes important. Processes involving very rapid equilibria (producing no observable broadening) such as $Co^{II}(NH_3)_6 \rightleftharpoons Co^{II}-(NH_3)_4 + 2NH_3$ followed by observable exchange due to complex species other than the hexa complex can be ruled out as a chemical shift would then be observed over the entire range of temperature studied.

The analogous water exchange reaction $Co(H_2O)_6{}^{2+} + H_2O \rightleftharpoons$ studied by Swift and Connick[6] is described by the values, k_1 (25°) $= 1.13 \times 10^6$ sec.$^{-1}$, $\Delta H^* = 8.0$ kcal./mole, and $\Delta S^* = -4.1$ e.u. These values are rather different from the ammonia results in contrast with the Ni(II) systems where the water and ammonia exchanges have more similar rate parameters. Qualitatively, the results to date are consistent with the notion that for the $Ni(H_2O)_6{}^{2+}$, $Ni^{II}(NH_3)_6$, and $Co(H_2O)_6{}^{2+}$ data reported, these exchanges proceed *via* similar mechanisms, while for the $Co^{II}(NH_3)_6$ a new mechanism may be involved.

The details of the effects of adding water to give aqueous ammonia solutions involve some complications at low ammonia concentrations which may well be due to changes in the major species present. We intend to relate these effects to the results discussed here in a subsequent publication.

(8) T. J. Swift, *Inorg. Chem.*, **3**, 526 (1964).