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Enthalpies of Ligand Exchange for the Complexes $[(NH_3)_5Co–L]^{3+}$ (L = Water, Dimethyl Sulfoxide, *N*,*N*-Dimethylformamide, and Pyridine)

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The enthalpies of ligand exchange for monosubstituted complexes of pentaamminecobalt(III) have been determined by using solution calorimetry in the solid phase and in aqueous solution. It is found that stabilities toward ligand exchange for the compounds $[(NH_3)_5Co–L]^{3+}$ increase in the following order: L = DMSO < water < *N*,*N*-DMF < pyridine = ammonia. The results obtained are correlated with the rates of aquation of the different complexes and with the position of the visible absorption band in the visible spectrum of each complex. Comparison to the enthalpies of ligand exchange for the monosubstituted pentaammineruthenium(II) system is discussed.

Introduction

Complexes of pentaamminecobalt(III), due to their ease of preparation and their properties toward ligand substitution, have been used extensively in the study of mechanisms of inorganic reactions.[1] These include substitution processes,[2] electron transfer reactions,[3] and coordinated ligand reactions.[4] Although their kinetic inertness is well documented,[1] the relative thermodynamic stabilities of the monosubstituted pentaamminecobalt(III) complexes have never been determined. In order to learn more about a metal's thermochemical influence on a variety of inorganic reactions, and as part of a program of inorganic thermochemistry, the heats of ligand exchange of the complexes $[(NH_3)_5CoL]^{3+}$ have been determined with L = DMSO, DMF, H_2O, and C_5H_5N. The results obtained herein and those for the $[(NH_3)_5Ru]^{2+}$ will be compared.[5] A correlation between the complex's thermodynamic stability and kinetic substitution parameters is attempted.

Experimental Section

Dimethyl sulfoxide, *N*,*N*-dimethylformamide, and pyridine were stored over molecular sieves (4A) for at least 24 h prior to use. Trifluoromethanesulfonic acid (Eastman Kodak) was used as received. All manipulations were carried out with the use of syringe techniques in order to avoid exposure to atmospheric moisture. $Ba(OSO_2CF_3)_2$ was generated in situ by the reaction of $HOSO_2CF_3$ and $BaCO_3$. All other chemicals were reagent grade and were used without further purification. Infrared spectra were obtained on a Perkin-Elmer Model 1800 FT-IR spectrometer. Ultraviolet and visible spectra were obtained with a Shimadzu UV-265, a Perkin-Elmer Lambda-3, or a Varian Cary 2315 spectrophotometer. Elemental analysis was carried out by Galbraith Laboratories, Knoxville, TN.

Preparation of Complexes. **$[(NH_3)_5CoOH_2](OSO_2CF_3)_3$.** $[(NH_3)_5CoOH_2](HSO_4)(SO_4)$ (10 g), prepared as described in ref 6, was dissolved in a minimum of warm water (around 100 mL at 60 °C). A stoichiometric amount of barium trifluoromethanesulfonate was added while the solution was stirred. The resulting mixture was digested at 70 °C for 2 h and cooled to room temperature. The mixture was filtered in order to remove the $BaSO_4$. The solvent was removed from the filtrate with a rotary evaporator, resulting in a red-orange solid residue. This residue was heated, under vacuum, to 80 °C for 2 h in order to remove any excess $HOSO_2CF_3$. The solid was then redissolved in a minimum of warm water (60 °C). $LiOSO_3CF_3$ (1 g) was added, and the solution was *slowly* cooled in a refrigerator at 5 °C overnight, preferably longer. Yellow to light orange needle-shaped crystals were collected by filtration. These crystals have not been fully characterized, but spectral measurements indicate them to be a mixture of $[(NH_3)_6Co](OSO_2CF_3)_3$ and $[(NH_3)_5CoOH_2](OSO_2CF_3)_3$. The visible spectrum of the filtrate was obtained and compared to the visible spectrum of an aqueous solution of the aquo complex (λ_{max} = 492 nm).[7,8] An additional amount of $LiOSO_2CF_3$ was added, and the solution was again refrigerated overnight. The orange-red crystals that formed were removed by filtration. This procedure was repeated until the absorbance maxima of the filtrate matched those of an aqueous solution of $[(NH_3)_5CoOH_2]^{3+}$. When this was achieved, additional $LiOSO_2CF_3$ and $HOSO_2CF_3$ (5 mL) were added and the solution was slowly cooled to 1 °C, usually overnight, sometimes longer. Fine orange-red crystals precipitated, were removed by filtration, and were washed thoroughly with 200 mL of 2-propanol and then ether, and were dried under vacuum overnight. This product was analyzed by comparison to its well-known spectral properties[7,8] including its UV-visible spectrum (λ_{max} = 492 nm (ϵ = 47.5 $M^{-1}\ cm^{-1}$), 346 (ϵ = 44.4)) and infrared spectrum. Yield was between 4 and 6 g of product.

$[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$. Pure $[(NH_3)_5CoOH_2](OSO_2CF_3)_3$ was placed in a heated vacuum desiccator at 110 °C overnight in order to drive off the coordinated H_2O. Anal. Calcd: C, 6.09; H, 2.56; N, 11.84. Found: C, 6.1; H, 2.5; N, 11.6. UV-vis ($HOSO_2CF_3$):[8a] λ_{max} = 525 nm (ϵ = 47 $M^{-1}\ cm^{-1}$), 347 (ϵ = 43). Since this complex is somewhat susceptible to hydration by atmospheric moisture it was stored in a vacuum desiccator over calcium sulfate. Prior to use in a thermochemical experiment, any H_2O that had contaminated the complex was driven off by again placing the complex overnight in a heated vacuum desiccator at 110 °C. A visible spectrum of the complex in trifluoromethanesulfonic acid was obtained and compared to accepted values in order to determine purity.

$[(NH_3)_5CoNC_5H_5](OSO_2CF_3)_3$. To liquid pyridine (35 mL) was added (trifluoromethanesulfonato)pentaamminecobalt(III) trifluoromethanesulfonate (4 g), and the resulting solution was allowed to stir for 2 h. The pyridine was evaporated, leaving a yellow residue, which was dissolved in water and recrystallized by addition of $LiOSO_2CF_3$ and slow cooling. Anal. Calcd: C, 14.33; H, 3.01; N, 12.54. Found: C, 14.6; H, 2.9; N, 12.3. UV-vis (H_2O): λ_{max} = 474 nm (ϵ = 65 $M^{-1}\ cm^{-1}$), 340 (ϵ = 61).

The other complexes used in this study, $[(NH_3)_5CoOS(CH_3)_2](OSO_2CF_3)_3$ and $[(NH_3)_5CoOC(H)N(CH_3)_2](OSO_2CF_3)_3$, were prepared by using procedures analogous to those described for $[(NH_3)_5CoNC_5H_5](OSO_2CF_3)_3$. These complexes were characterized by comparison to accepted literature values.[8-11]

Thermochemical Measurements. An isoperibol calorimeter, built as described in ref 12, was used in all calorimetric measurements. The

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Table I. Enthalpies[a] of Reaction of $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$ with L and Enthalpy of Solution of $[(NH_3)_5CoL](OSO_2CF_3)_3$ in L

L	ΔH^{L}_{reacn} [b]	$\Delta H^{M-L}_{soln(L)}$ [c]	ΔH^{L}_{subs} [d]	ΔH^{*}_{solv} [e]
$(CH_3)_2SO$	−20.7 ± 0.31	−16.92 ± 0.04	−3.8	+18.5
H_2O	+4.3 ± 0.16	+8.45 ± 0.11	−4.2	+18.0
$(CH_3)_2NC(O)H$	−26.2 ± 0.19	−17.58 ± 0.28	−8.6	+17.7
C_5H_5N	−22.6 ± 0.34	−11.78 ± 0.23	−10.8	+17.4

[a] All units in kcal/mol. [b] Enthalpy of the reaction $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2(c) + L(l) \rightarrow [(NH_3)_5CoL]^{3+}(solv) + 3(OSO_2CF_3)^-(solv)$. [c] Enthalpy of the reaction $[(NH_3)_5CoL](OSO_2CF_3)_3(c) \xrightarrow{L} [(NH_3)_5CoL]^{3+}(solv) + 3(OSO_2CF_3)^-(solv)$. [d] Enthalpy of the reaction $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2(c) + L(l) \rightarrow [(NH_3)_5CoL](OSO_2CF_3)_3(c)$. [e] Enthalpy of activation for the reaction $[(NH_3)_5CoOSO_2CF_3]^{2+}(solv) + L \rightarrow [(NH_3)_5CoL]^{3+}(solv) + 3(OSO_2CF_3)^-(solv)$.

calorimeter was electrically calibrated with a 10.00-Ω resistance that is traceable to the National Bureau of Standards. The instrument was tested by measuring the heat of solution of KCl in water and comparing it to literature values.

A typical enthalpy of reaction experiment was carried out as follows. Pure $[(NH_3)_5CoOH_2](OSO_2CF_3)_3$ (3 g) was converted to $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$ by heating in a vacuum desiccator at 110 °C overnight. UV–vis spectra were obtained in $HOSO_2CF_3$ and extinction coefficients compared with accepted literature values to determine purity. Four glass ampules were evacuated and sealed after they had been loaded with $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$ (0.3–0.5 g). The calorimeter was loaded with reagent grade dimethyl sulfoxide (350 mL), which had been stored over molecular sieves (4A) for at least 24 h. The stirrer and constant-temperature bath were turned on, and the system was allowed to reach thermal equilibrium overnight. An ampule was loaded into the calorimeter, and after 30 min an electrical calibration was performed. The calorimeter was again allowed to equilibrate (30 min) and the glass ampule was broken, introducing the $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$ into the dimethyl sulfoxide reagent. Reaction was complete within 5 min as monitored by following the formation of the $[(NH_3)_5CoOS(CH_3)_2]^{3+}$ using visible spectroscopy. The system was allowed to equilibrate for an additional 30 min, and a second electrical calibration was carried out. The results obtained were as follows: −21.6, −20.0, −20.6, and −21.1 kcal/mol; av = −20.8 ± 0.4 kcal/mol. When a new sample of the $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$ was available, the experiment was repeated with one additional ampule and resulted in an enthalpy of reaction of −20.0 kcal/mol. The average of the 5 values obtained was −20.7 ± 0.31 kcal/mol.

Enthalpies of solution of the complexes $[(NH_3)_5CoL](OSO_2CF_3)_3$ in water (0.1 M H^+) and in L were carried out as follows. $[(NH_3)_5CoDMSO](OSO_2CF_3)_3$ (3 g) was dried in a vacuum desiccator overnight. The purity of the complex was determined by obtaining a UV–vis spectrum and extinction coefficients in aqueous solution just before loading the ampules. The calorimeters were prepared as described except that one was filled with DMSO (350 mL) and the other was filled with water (350 mL) to which $HOSO_2CF_3$ (5 mL) was added. Results for $[(NH_3)CoDMSO](OSO_2CF_3)_3$ in DMSO were as follows: −17.00, −16.86 and −16.92 kcal/mol; av = −16.90 ± 0.04 kcal/mol. Results for dissolution in water (0.1 M H^+): +6.41, +7.63, +7.04, and +6.54 kcal/mol; av = +6.91 ± 0.28 kcal/mol.

Enthalpies of solution of the ligands were measured as follows: Four ampules were loaded with dimethyl sulfoxide (0.2–0.5 g), which had been stored for at least 24 h over molecular sieves. The calorimeter was loaded with distilled deionized water (350 mL). After equilibration and electrical calibration, the ampule was broken, introducing the dimethyl sulfoxide into the water. The system was allowed to equilibrate for 30 min, and a second electrical calibration was performed. Typical results were as follows: 3.57, 3.50, and 3.47 kcal/mol. av = −3.51 ± 0.04 kcal/mol. Literature value[13] = −3.6 kcal/mol.

Table II. Enthalpies[a] of Ligand Exchange, Enthalpies of Aqueous Solution, and Various Properties of Monosubstituted Pentaamminecobalt(III) Complexes

L	$\Delta H^{M-L}_{soln(aq)}$ [b]	$\Delta H^{L}_{soln(aq)}$ [c]	ΔH^{aq}_{exc} [d]	k_{aq} [e]	λ_{max} [f]
OSO_2CF_3				27 000	524
$(CH_3)_2SO$	+6.91 ± 0.28	−3.51 ± 0.04	0	22	518
H_2O	+8.45 ± 0.11	0	−2.4	5.9	492
$(CH_3)_2NC(O)H$	+6.60 ± 0.08	−3.41 ± 0.16	−5.2	1.5	506
C_5H_5N	+5.34 ± 0.22	−2.58 ± 0.2	−9.5		474
NH_3			−9.6[g]	6×10^{-6}	475

[a] All enthalpies in kcal/mol. [b] Enthalpy for the process $[(NH_3)_5CoL](OSO_2CF_3)_3(c) \xrightarrow{H_2O} [(NH_3)_5CoL]^{3+}(aq) + 3(OSO_2CF_3)^-(aq)$. [c] Enthalpy for the process $L(l) \xrightarrow{H_2O} L(aq)$. [d] Enthalpy of the reaction (in kcal/mol) $[(NH_3)_5CoDMSO]^{3+}(aq) + L(aq) \rightarrow [(NH_3)_5CoL]^{3+}(aq) + DMSO(aq)$. [e] Rates ($\times 10^{-6}\ s^{-1}$) of aquation of $[(NH_3)_5CoL]^{3+}$, from ref 8a and references therein. [f] Visible absorption maxima (in nm) of the complexes $[(NH_3)_5CoL]^{3+}$ in aqueous solution, from ref 8a and references therein. [g] Calculated as discussed in ref 18.

Results and Discussion

This work takes advantage of the relative lability of the trifluoromethanesulfonate ligand in the complex $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$. Dissolution of this complex in a good coordinating solvent yields the solvent-substituted complex[6,8] (reaction 1), where the products are solvated in L. The enthalpies

$$[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2(c) + L(l) \rightarrow [(NH_3)_5CoL]^{3+}(solv) + 3(OSO_2CF_3)^-(solv) \quad (1)$$

c = crystal; solv = solvated in ligand L; l = liquid

of reaction of $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$ with L (L = water, dimethyl sulfoxide, pyridine, and *N,N*-dimethylformamide) were determined, and these are reported in Table I. These heats vary from decidedly exothermic (−26.2 for *N,N*-DMF) to slightly endothermic (+4.3 kcal/mol for water). The heats of solution of the complexes $[(NH_3)_5CoL](OSO_2CF_3)_3$ in the ligand L (L = H_2O, DMSO, *N,N*-DMF, and C_5H_5N) were also measured and are also given in Table I. These also vary considerably, being endothermic for water and exothermic for the rest of the solvents.

$$[(NH_3)_5CoL](OSO_2CF_3)_3(c) \xrightarrow{L} [(NH_3)_5CoL]^{3+}(solv) + 3(OSO_2CF_3)^-(solv) \quad (2)$$

$$[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2(c) + L(l) \rightarrow [(NH_3)_5CoL](OSO_2CF_3)_3(c) \quad (3)$$

Subtraction of eq 2 from eq 1 yields eq 3, exchange of the ligand L for the ligand $OSO_2CF_3^-$ when the complexes are in the crystal phase. The enthalpies for reaction 3 are calculated by using eq 4, where ΔH^{L}_{reacn} is the enthalpy of reaction of $[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2$ with L (eq 1) and $\Delta H^{M-L}_{soln(L)}$ is the enthalpy of solution of $[(NH_3)_5CoL](OSO_2CF_3)_3$ in L (eq 2), and $\Delta H^{L}_{subs(s)}$ is the enthalpy of substitution of the ligand L for the $OSO_2CF_3^-$ in the solid phase (eq 3). These enthalpies vary from −3.8 kcal/mol to −10.8 kcal/mol (see Table I). In general, nitrogen ligands yield more stable complexes than oxygen donors. The DMSO and the H_2O complexes are of similar stabilities toward ligand exchange. This is somewhat surprising since the DMSO complex is considered more labile than the aquo complex.[11] The most stable complex is $[(NH_3)_5CoNC_5H_5](OSO_2CF_3)_3$. The heats of activation for the solvolysis of $[(NH_3)CoOSO_2CF_3)]^{2+}$ (reaction 5)

$$\Delta H^{L}_{subs(s)} = (\Delta H^{L}_{reacn} - \Delta H^{M-L}_{soln(L)}) \quad (4)$$

$$M{-}L = [(NH_3)_5CoL](OSO_2CF_3)_3$$

$$[(NH_3)_5CoOSO_2CF_3]^{2+}(solv) + L \rightarrow [(NH_3)_5CoL]^{3+}(solv) + 3(OSO_2CF_3)^-(solv) \quad (5)$$

have been reported by another group;[14] see Table I. The enthalpies of activation do not vary as much (from +18.5 to +17.4 kcal/mol); however, the more stable the product complex, the less endothermic

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(12) *Operating Instructions, Solution Calorimeter*; Catalog Number 400; Guild Corp.: Bethel Park, PA 15102; see also references therein.

(13) (a) The literature value was obtained as follows (enthalpy of formation data from ref 13b):

$$\Delta H_{soln(aq)} = \Delta H_f(DMSO(aq)) - \Delta H_f(DMSO(l))$$

$$\Delta H_{soln(aq)} = -52.2\ kcal/mol - -48.6\ kcal/mol$$

$$\Delta H_{soln(aq)} = -3.6\ kcal/mol$$

(b) Wagman, D. D. et al. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data, Suppl.* **1982**, *11* (No. 2).

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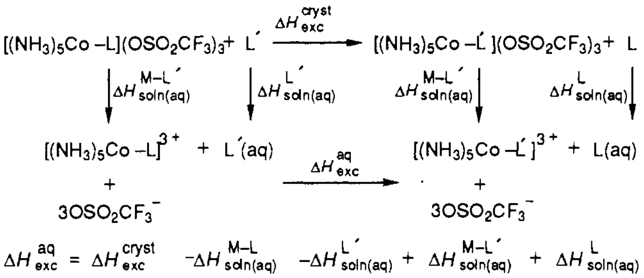
Scheme I



the enthalpy of activation is. This is consistent with a mechanism of substitution that is mostly dependent on the metal–ligand bond strength of the reacting triflato complex. The fact that there is some variation in the enthalpies of activation and the variation is inversely related to the product complex stability is consistent with a mechanism where bond breaking of the cobalt–triflato bond is not complete when the incoming ligand–cobalt bond begins forming.[2,15]

In order to compare the relative enthalpic stabilities of these complexes in aqueous solution,[16] the enthalpies of solution of the complexes $[(NH_3)_5CoL](OSO_2CF_3)_3$ and the ligands L in water were determined (eq 6 and 7). These results are shown in Table II.

$$[(NH_3)_5CoL](OSO_2CF_3)_3(c) \xrightarrow{H_2O} [(NH_3)_5CoL]^{3+}(aq) + 3(OSO_2CF_3)^-(aq) \quad (6)$$

$$L(l) \xrightarrow{H_2O} L(aq) \quad (7)$$

The enthalpies of ligand exchange in aqueous solution (eq 8) is given by eq 9 (see Scheme I), where $\Delta H^{cryst}_{exc} = \Delta H^{L'}_{subs} - \Delta H^{L}_{subs}$ (see ref 17) and $\Delta H_{soln(aq)}$ are the heats of solution in water of the complexes and the ligands.

$$[(NH_3)_5Co{-}L]^{3+}(aq) + L'(aq) \rightarrow [(NH_3)_5Co{-}L']^{3+}(aq) + L(aq) \quad (8)$$

$$\Delta H^{aq}_{exc} = \Delta H^{cryst}_{exc} - \Delta H^{M-L}_{soln(aq)} - \Delta H^{L'}_{soln(aq)} + \Delta H^{M-L'}_{soln(aq)} + \Delta H^{L}_{soln(aq)} \quad (9)$$

These reaction enthalpies are shown in Table II with L = DMSO. The ordering of stabilities is similar to that given before. Again, ligands that bind through nitrogen form more stable complexes than ligands that bind through oxygen. The aquopentaamminecobalt(III) complex is more stable than the DMSO complex in aqueous solution by 2.4 kcal/mol. This is more consistent with kinetic observations. The rates of aquation for these complexes have been measured (see ref 8a and references therein) and the rates decrease as the enthalpies of ligand exchange increase, consistent with dissociative activation (see Table II). Correlation was attempted between the enthalpy of ligand exchange in aqueous solution and the position of the maximum absorption in the visible region. It was found that in general the larger the enthalpy of ligand exchange, the lower the absorption maxima; however, the aquo complex is a notable exception (Table II). There is no real difference in positions of the λ_{max} peaks for $[(NH_3)_5CoNC_5H_5]^{3+}$ and $[(NH_3)_6Co]^{3+}$, and the difference in their stability toward ligand exchange is essentially also zero.[18]

The enthalpies of ligand exchange have been determined for a related system, $[(NH_3)_5RuL]^{3+}$,[5] with a number of different ligands. From these results, we can compare the enthalpies of the following reactions (M = Ru(II), Co(III)):

$$[(NH_3)_5MOH_2]^{n+}(aq) + C_5H_5N(aq) \rightarrow [(NH_3)_5MNC_5H_5]^{n+}(aq) + H_2O \quad (10)$$

M = Ru(II), $\Delta H = -12.7$ kcal/mol

M = Co(III), $\Delta H = -7.1$ kcal/mol

$$[(NH_3)_5MOH_2]^{n+}(aq) + DMSO(aq) \rightarrow [(NH_3)_5MDMSO]^{n+}(aq) + H_2O \quad (11)$$

M = Ru(II), $\Delta H = -19.2$ kcal/mol

M = Co(III), $\Delta H = +2.4$ kcal/mol

These enthalpies of reaction indicate that the Ru(II) system has a greater preference for the pyridine ligand relative to the aquo ligand than does the pentaamminecobalt(III) system (eq 10). This is not surprising due to the possibility of back-bonding in the Ru–pyridine system. For the DMSO complexes, very large differences in enthalpies of exchange do exist. In the case of the cobalt system, the aquo complex is slightly more stable than the DMSO complex (eq 11). However, in the Ru(II) system, the DMSO complex is 19.2 kcal/mol more stable than the aquo complex. It is not unexpected that the ruthenium and cobalt systems differ in their properties with dimethyl sulfoxide since the donor atom in the Co(III)–DMSO complex is oxygen[19] while in the Ru(II)–DMSO system it is sulfur.[20] However, the magnitude of the difference is impressive and is indicative of the preference of Ru(II) complexes for sulfur ligands.

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(16) Ideally, it would be best to study enthalpies of ligand exchange in the gas phase in order to be able to account for crystal formation effects as well as solvation effects, but although the heats of vaporization of the ligands L are available, the heats of sublimation of the complexes are not. For this reason and the fact that most studies of these reactions were carried out in aqueous solution, we chose to obtain our enthalpies in aqueous solutions.

(17) If the enthalpy of reaction 3 is determined for L and L′

$$[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2(c) + L(l) \rightarrow [(NH_3)_5CoL](OSO_2CF_3)_3(c) \quad (3)$$

$$[(NH_3)_5CoOSO_2CF_3](OSO_2CF_3)_2(c) + L'(l) \rightarrow [(NH_3)_5CoL'](OSO_2CF_3)_3(c) \quad (3')$$

then subtraction of eq 3 from 3′ yields ΔH^{cryst}_{exc}, the enthalpy of ligand exchange in the solid phase.

$$[(NH_3)_5Co{-}L](OSO_2CF_3)_2(c) + L'(l) \rightarrow [(NH_3)_5Co{-}L'](OSO_2CF_3)_2(c) + L(l)$$

(18) The enthalpy of ligand exchange for this reaction was determined by using the data[13b]

compd	ΔH_f
$[(NH_3)_5CoOH_2]^{3+}(aq)$	−181.7 kcal/mol
$NH_3(aq)$	−19.2 kcal/mol
$[(NH_3)_5CoNH_3]^{3+}(aq)$	−139.8 kcal/mol
$H_2O(l)$	−68.3 kcal/mol

and calculating the enthalpy change for

$$[(NH_3)_5CoOH_2]^{3+}(aq) + NH_3(aq) \rightarrow [(NH_3)_5CoNH_3]^{3+}(aq) + H_2O(l)$$

$$\Delta H = 181.7 + 19.2 - 139.8 - 68.3 = -7.2 \text{ kcal/mol}$$

Since we know the enthalpy exchange for

$$[(NH_3)_5CoDMSO]^{3+}(aq) + H_2O(l) \rightarrow [(NH_3)_5CoOH_2]^{3+}(aq) + DMSO(aq)$$

$$\Delta H = -2.4 \text{ kcal/mol}$$

by addition we can determine the enthalpy of the ligand exchange

$$[(NH_3)_5CoDMSO]^{3+}(aq) + NH_3(aq) \rightarrow [(NH_3)_5CoNH_3]^{3+}(aq) + DMSO(aq)$$

$$\Delta H = -7.2 - 2.4 = -9.6 \text{ kcal/mol}$$

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